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IMS 2004

In April 2004, a new research organization has been established. This organization is named NINS (National Institutes of Natural Sciences) and is formed by the three institutes in Okazaki including IMS and the other two: NAO (national astronomical observatory) and NIFS (national institute for fusion science). The headquarter is in Tokyo. I was appointed as new Director General of IMS and at the same time as a Vice President of NINS. IMS will celebrate its 30-th anniversary next year and is deemed to play an important role for future developments of natural sciences in Japan.

In March this year, quite a few research groups not only of Center for Integrative Bioscience, but also of Research Center for Molecular-Scale Nanoscience and Coordination Chemistry Laboratory moved to the new Yamate



campus, next to which the Yamate lodge is located. New Department of Computational Molecular Science has also been established in the main campus.

This volume of Annual Review contains the research activities of IMS in the period of September 2003–August 2004. As usual, a lot of activities are going on and we are proud of that. Any constructive comments and/or questions are heartily welcome. Naturally, we would like to further promote the advanced researches and international collaborations.

October, 2004

H. Nakamusa

NAKAMURA, Hiroki Director General, Institute for Molecular Science

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Abbreviations

IMS: Institute for Molecular Science GUAS: The Graduate University for Advanced Studies

ORGANIZATION AND STAFF

Organization

The Institute for Molecular Science comprises twenty research laboratories, each staffed by a professor, an associate professor, two research associates and several technical associates, and two research laboratories with foreign visiting professors and five research facilities.

The laboratories are grouped into seven departments and one facility for coordination chemistry:

	Department of Theoretical Studies	Theoretical Studies I Theoretical Studies II Theoretical Studies III Theoretical Studies IVI
	Department of Molecular Structure	Molecular Structure II ¹⁾
	Department of Electronic Structure	Molecular Dynamics Excited State Chemistry Excited State Dynamics Electronic Structure ¹⁾
	Department of Molecular Assemblies	Molecular Energy Conversion ²⁾ Solid State Chemistry Molecular Dynamics Assemblies Molecular Assemblies ¹⁾
	Department of Applied Molecular Science	Applied Molecular Science I
	Department of Vacuum UV Photoscience	Photochemistry Chemical Dynamics
	Department of Computational Molecular Science (April '04–)	Computational Molecular Science I Computational Molecular Science II
	Coordination Chemistry Laboratories	Complex Catalysis Functional Coordination Chemistry Coordination Bond ¹⁾
Tł	e research facilities are:	
	Laser Research Center for Molecular Science	Advanced Lasers for Chemical Reaction Studies Advanced Lasers for Synchrotron Radiation Applications Advanced LIV and IR Tunable Lasers
	Research Center for Molecular-scale Nanoscience	Molecular-scale Electronics Nanocatalysis and Biomolecular Devices Nano-scale Photoscience Interface Molecular Science ³⁾ (–March '04) Molecular Clusters ³⁾ (–March '04) Advanced Molecular Science ³⁾ (April '04–)

- Equipment Development Center
- UVSOR Facility
- Computer Center (–March '04)
- Safety Office (April '04–)

Okazaki research facilities (related to IMS) are:

- Okazaki Institute for Integrative Bioscience
- Research Center for Computational Science
- 1) Professors and associate professors are visiting professors from other universities.
- 2) Research laboratories with foreign visiting professors.
- 3) Professors, associate professors, and research associates, along with their positions, are transferred from other universities.

Scientific Staff

NAKAMURA, Hiroki

NAGAKURA, Saburo HIROTA, Eizi

KIMURA, Katsumi

MOROKUMA, Keiji INOKUCHI, Hiroo

MARUYAMA, Yusei YOSHIHARA, Keitaro

HANAZAKI, Ichiro

IWAMURA, Hiizu SAITO, Shuji IWATA, Suehiro ITO, Mitsuo

KAYA, Koji

Department of Theoretical Studies

Theoretical Studies I NAGASE, Shigeru OKAMOTO, Yuko KOBAYASHI, Kaoru OKUMURA, Hisashi ISHIMURA, Kazuya CHOE, Yoong-Kee NISHINO, Masamichi PULAY, Peter

SLANINA, Zdenek

LU, Jing

TAKAGI, Nozomi RE, Suyong KAWASHIMA, Yukio KATOUDA, Michio KOKUBO, Hironori

MURATA, Katsumi SAKAE, Yoshitake ITO, Satoru ONO, Yuriko

ITO, Satoru MIZOROGI, Naomi

Theoretical Studies II NAKAMURA, Hiroki NOBUSADA, Katsuyuki TAKAMI, Toshiya SUZUKI, Yoko MIL'NIKOV, Gennady V. ZOU, Shiyang

Professor, Director-General

Emeritus Professors

The Japan Academy Professor Emeritus, The Graduate University for Advanced Studies Senior Researcher, Molecular Photonics & Photoelectron Group, Communications Research Laboratory Professor, Emory University, U. S. A. Chief Scientist of Space Utilization Research Program, Japan Aerospace Exploration Agency Professor, Hosei University Professor, Japan Advanced Institute of Science and Technology Professor Emeritus, The Graduate University for Advanced Studies Professor, University of the Air Professor, Fukui University Professor, National Institution for Academic Degree Professor Emeritus, The Graduate University for Advanced Studies, Tohoku University Director, RIKEN Wako Institute, RIKEN Discovery Institute

Professor Associate Professor **Research Associate Research Associate** Technical Associate Post-Doctoral Fellow (-June '04)¹⁾ IMS Fellow (-March '04)²⁾ Visiting Scientist; MONKASHO Invited Fellow (December '03-May '04) Visiting Scientist; JSPS Invited Fellow (-September '03); Post-Doctoral Fellow (October '03-March '04) Visiting Scientist; JSPS Post-Doctoral Fellow (-September '03); Post-Doctoral Fellow (October '03-March '04) JSPS Post-Doctoral Fellow Post-Doctoral Fellow Post-Doctoral Fellow Research Fellow Graduate Student (-September '03); Research Fellow (October '03-) Graduate Student (-September '03)³⁾ Graduate Student (-September '03)⁴⁾ Graduate Student Graduate Student (from Tokyo Institute of Technology)* (-March '04); Post-Doctoral Fellow (April '04-) Graduate Student Graduate Student (April '04-)

Professor Associate Professor (June '04–) Research Associate Research Associate (–March '04)⁵⁾ Research Associate IMS Fellow CHIKAZUMI, Shinpei ISHKHANYAN, Artur

ZHAO,Yi

KONDORSKY, Alexey OLOYEDE, Oluwaponmile

Theoretical Studies III HIRATA, Fumio YONEMITSU, Kenji CHONG, Song-Ho YAMASHITA, Yasufumi OTSUKA, Yuichi KOBRYN, Oleksandr YOSHIDA, Norio IKUTA, Yasuhiro MAESHIMA, Nobuya YAMAZAKI, Takeshi MARUYAMA, Yutaka INOUE, Hitoshi TANIMURA, Ayumi

MATSUGAMI, Masaru ISHIZUKA, Ryosuke

Theoretical Studies IV NAGAOKA, Masataka HADA, Masahiko

TORII, Hajime

NAKAJIMA, Takashi

Department of Molecular Structure

Molecular Structure I OKAMOTO, Hiromi MORITA, Norio IMURA, Kohei NAGAHARA, Tetsuhiko LIM, Jong Kuk

Molecular Structure II OHTA, Toshiaki WADA, Akihide

ISHIMORI, Koichiro

Molecular Dynamics KITAGAWA, Teizo YOKOYAMA, Toshihiko KATO, Tatsuhisa UCHIDA, Takeshi NAKAGAWA, Takeshi FURUKAWA, Ko NAGATOMO, Shigenori

> HAYASHI, Naoki WATANABE, Hirokazu MARUYAMA, Koichi

IMS Fellow Visiting Scientist; MONKASHO Invited Fellow (–December '03) Visiting Scientist; JSPS Post-Doctoral Fellow (November '03–) Visiting Scientist; JSPS Post-Doctoral Fellow Graduate Student

Professor Associate Professor Research Associate (April '04-) Research Associate (June '04–) IMS Fellow IMS Fellow Post-Doctoral Fellow (April '04-) Post-Doctoral Fellow (April '04-) Post-Doctoral Fellow (January '04-) Post-Doctoral Fellow (-March '04)6) Post-Doctoral Fellow Post-Doctoral Fellow Graduate Student (-March '04); Research Fellow (April '04–) Graduate Student Graduate Student (April '04-)

Visiting Professor (from Nagoya University) (-March '04) Visiting Associate Professor (from Tokyo Metropolitan University) (April '04-) Visiting Associate Professor (from Shizuoka University) (-March '04) Visiting Associate Professor (from Kyoto University) (April '04-)

Professor Associate Professor Research Associate IMS Fellow Visiting Graduate Student (from Yonsei University) (April '04–)

Visiting Professor (from The University of Tokyo) Visiting Associate Professor (from Tokyo Institute of Technology) (–March '04) Visiting Associate Professor (from Kyoto University) (April '04–)

Professor (Okazaki Institute for Integrative Bioscience) Professor Associate Professor (–March '04) Research Associate Research Associate (–March '04) Technical Associate (–October '03); Research Associate (October '03–November '03) Technical Associate (–March '04) Technical Associate IMS Fellow PAL, Biswajit

MATSUOKA, Hideto OKUNO, Daichi

MA, Xiaodong

Department of Electronic Structure

Excited State Chemistry NISHI, Nobuyuki BOO, Bong Hyun

> NEGISHI, Yuichi JUDAI, Ken NISHIJO, Junichi KOSUGI, Kentaroh

BUSHIRI, M. Junaid

OKABE, Chie

WATANABE, Michio

Excited State Dynamics OHMORI, Kenji FUJII, Masaaki KATSUKI, Hiroyuki

Electronic Structure IIJIMA, Sumio ICHIMURA, Teijiro

TAKAGI, Noriaki

MISAWA, Kazuhiko

INOKUCHI, Yoshiya

Molecular Energy Conversion KWON, Yong-Seung

PULAY, Peter

COUPRIE, Marie Emmanuelle

Department of Molecular Assemblies

Solid State Chemistry YAKUSHI, Kyuya NAKAMURA, Toshikazu YAMAMOTO, Kaoru FUJIYAMA, Shigeki FURUKAWA, Ko URUICHI, Mikio YAMAMOTO, Takashi HARA, Toshifumi NAKANO, Chikako SUZUKI, Kenji MAEDA, Keisuke DROZDOVA, Olga SIMONYAN, Mkhitar

Molecular Assemblies Dynamics KOBAYASHI, Hayao Visiting Scientist; JSPS Invited Fellow (–November '03); Post-Doctoral Fellow (December '03–) JSPS Post-Doctoral Fellow Graduate Student (–September '03); IMS Fellow (October '03–March '04) Graduate Student (April '04–)

Professor Visiting Professor (from Chungnam National University, South Korea) (July '04–August '04) Research Associate (-March '04) Research Associate (May '04–) Research Associate (April '04–) Research Associate of Research for the Future Program (-March '04)⁷⁾ Research Associate of Research for the Future Program (-March '04)⁸⁾ Graduate Student (from Kyushu University) (-March '04), Post-Doctoral Fellow (April '04–) Research Fellow (April '04–)

Professor (September '03–) Professor (–September '03)⁹⁾ Research Associate (April '04–)

Visiting Professor (from Meijo University) (–March '04) Visiting Professor (from Tokyo Institute of Technology) (April '04–) Visiting Associate Professor (from the Graduate University for Advanced Studies) (April '04–) Visiting Associate Professor (from Tokyo University of Agriculture and Technology) (–March '04) Research Associate (–March '04)

Visiting Professor (from Sungkyunkwan University, South Korea) (October '03–September '04) Visiting Associate Professor (from the University of Arkansas, USA) (January '04–May '04) Visiting Associate Professor (from LURE, France) (June '04–September '04)

Professor Associate Professor Research Associate Research Associate (-March '04) Research Associate (April '04-) Technical Associate IMS Fellow IMS Fellow Research Fellow Graduate Student (-March '04) Graduate Student Research Fellow Research Fellow Research Fellow (Octobar '03-March '04)

Professor

FUJIWARA, Hideki TAKAHASHI, Kazuyuki

OKANO, Yoshinori LEE, Ha-Jin

OTSUKA, Takeo CUI, Heng-Bo OTSUBO, Saika

Molecular Assemblies ENOKI, Toshiaki NAITO, Toshio

Department of Applied Molecular Science

Applied Molecular Science I KINOSHITA, Kazuhiko, Jr. AONO, Shigetoshi INOUE, Katsuya

ADACHI, Kengo

AKITA, Motoko YOSHIOKA, Shiro

OKA, Yoshimi OKUDA, Kazuki NUMATA, Yohei

Applied Molecular Science II AWAZU, Koichi

> IKEDA-SAITO, Masao KIKUCHI, Koichi

NAKAMURA, Kazutaka

Department of Vacuum UV Photoscience

Photochemistry KOSUGI, Nobuhiro HISHIKAWA, Akiyoshi HATSUI, Takaki TAKAHASHI, Eiji HIYAMA, Miyabi SETOYAMA, Hiroyuki MASUDA, Suomi

Chemical Dynamics URISU, Tsuneo MITSUKE, Koichiro MIZUTANI, Masakazu NONOGAKI, Youichi TERO, Ryugo KOU, Junkei MORI, Takanori

> LI, Yanjun WANG, Zhihong YOSHIMURA, Daisuke LEI, Shenbin UNO, Hidetaka SUGA, Yasuhiro

Research Associate (-September '03) JST Post-Doctoral Fellow (-March '04); Research Associate (March '04-) Technical Associate Visiting Scientist; JSPS Post-Doctoral Fellow (-January '04) JSPS Post-Doctoral Fellow JST Post-Doctoral Fellow Graduate Student

Visiting Professor (from Tokyo Institute of Technology) Visiting Associate Professor (from Hokkaido University)

Professor (Okazaki Institute for Integrative Bioscience) Professor (Okazaki Institute for Integrative Bioscience) Associate Professor (-March '04) Professor (April '04-) Research Associate (Okazaki Institute for Integrative Bioscience) Research Associate Research Associate (Okazaki Institute for Integrative Bioscience) (November '03-) Graduate Student (-March '04) Graduate Student Graduate Student (April '04-)

Visiting Professor (from National Institute of Advanced Science and Technology) (–March '04) Visiting Professor (from Tohoku University) (April '04–) Visiting Associate Professor (from Tokyo Metropolitan University) (–March '04) Visiting Associate Professor (from Tokyo Institute of Technology) (April '04–)

Professor Associate Professor Research Associate Research Associate (March '04–) Research Associate (March '04–) IMS Fellow Graduate Student

Professor Associate Professor Research Associate (-March '04) Research Associate Technical Associate IMS Fellow (-March '04) IMS Fellow (September '03-March '04); Post-Doctoral Fellow (April '04-August '04) Post-Doctoral Fellow (-April '04)¹⁰⁾ Post-Doctoral Fellow (-April '04)¹¹⁾ Post-Doctoral Fellow (April '04-) Post-Doctoral Fellow (May '04-) Research Fellow (May '04-) Visiting Scientist (from AISIN COSMOS R&D CO., LTD.) ITO, Masayuki

SUZUKI, Akira

YAMAMURA, Shusaku TAKIZAWA, Morio FUJIKI, Satoshi RAHMAN, Mashiur KIM, Yong-Hoon MISAWA, Nobuo SUZUKI, Masanori

YOGI, Osamu

Synchrotron Radiation Research MORGUNNOV, Roman RUHL, Eckart Gunther Adolf WAN, Lijun DROZDOVA, Olga

Department of Computational Molecular Science

Computational Molecular Science I OKAZAKI, Susumu MORITA, Akihiro

> NANBU, Shinkoh TAKAMI, Toshiya MIURA, Shinichi IWAHASHI, Kensuke

KINJO, Tomoyuki YOSHII, Noriyuki YAMADA, Atsushi MIKAMI, Taiji

KOMATSU, Takahiro SATO, Masahiro TANAKA, Junji

Coordination Chemistry Laboratories TANAKA, Koji

Complex Catalysis MASHIMA, Kazushi YAMASHITA, Masahiro

> CHATANI, Naoto KURIHARA, Masato

Functional Coordination Chemistry TANAKA, Koji KAWAGUCHI, Hiroyuki MATSUO, Tsukasa WADA, Tohru MIZUKAWA, Tetsunori YUKI, Masahiro SHIREN, Kazushi KOIZUMI, Takeaki FUJIHARA, Tetsuaki OHTSU, Hideki YASUE, Takahiro OKAMURA, Rei Visiting Scientist (from AISIN COSMOS R&D CO., LTD.) (July '04–) Visiting Scientist (from AISIN COSMOS R&D CO., LTD.) (July '04–) Graduate Student (–April '04) Graduate Student (–April '04) Graduate Student Graduate Student Graduate Student Graduate Student Graduate Student (from Toyohashi University of Technology)* (April '04–) Graduate Student (from Toyohashi University of Technology)* (April '04–)

Visiting Professor (July '03–March '04) Visiting Professor (April–July '04) Visiting Professor (July '04–) Visiting Associate Professor (–July '04)

Professor (Research Center for Computational Science) Associate Professor (Research Center for Computational Science) (January '04-) **Research Associate Research Associate Research Associate** IMS Fellow (-September '03); Post-Doctoral Fellow (October '03-) IMS Fellow (October '03-March '04) Post-Doctoral Fellow Post-Doctoral Fellow Graduate Student (from Tokyo Institute of Technology)* (-March '04); Post-Doctoral Fellow (April '04-) Graduate Student (from Tokyo Institute of Technology)* Graduate Student (from Tokyo Institute of Technology)* Research Fellow (-March '04)

Director

Visiting Professor (from Osaka University) (April '04–) Visiting Professor (from Tokyo Metropolitan University) (–March '04) Visiting Professor (from Osaka University) (–March '04) Visiting Associate Professor (from Yamagata University)(April '04–)

Professor Associate Professor Research Associate Research Associate IMS Fellow (-March '04)¹²⁾ Post-Doctoral Fellow (-March '04) Post-Doctoral Fellow Post-Doctoral Fellow (-May '04) ¹³⁾ Post-Doctoral Fellow Post-Doctoral Fellow Post-Doctoral Fellow Post-Doctoral Fellow TOMON, Takashi MIYASATO, Yuji KOMURO, Takashi TSUTSUI, Kanako HINO, Takami

Coordination Bond MATSUSAKA, Hiroyuki UENO, Keiji

Research Facilities Laser Research Center for Molecular Science OKAMOTO, Hiromi MATSUMOTO, Yoshiyasu

Advanced Lasers for Chemical Reaction Studies

Advanced Lasers for Synchrotron Radiation Applications SARUKURA, Nobuhiko Associ ONO, Shingo Resear QUEMA, Alex Resear

GOTO, Masahiro OUENZERFI, Riadh MURAKAMI, Hidetoshi TAKAHASHI, Hiroshi DIWA, Girbert KAMEI, Takayuki

Advanced UV and IR Tunable Lasers TAIRA, Takunori SHOJI, Ichiro LUPEI, Voicu

YI, Jong-Hoon

ISHIZUKI, Hideki TSUNEKANE, Masaki DASCALU, Traian SATO, Yoichi SAIKAWA, Jiro PAVEL, Nicolaie

Research Center for Molecular-scale Nanoscience OGAWA, Takuji

Molecular-scale Electronics OGAWA, Takuji TADA, Hirokazu SUZUKI, Toshiyasu TANAKA, Shoji SAKAMOTO, Youichi TANAKA. Hirohumi YAMADA, Ryou TOMURA, Masaaki SHIRASAWA, Nobuhiko FUJIWARA, Eiichi ARAKI. Koiti NAKAO, Satoru ITO, Kaname ARA, Masato TAKADA, Masaki SAKANOUE, Tomo

Post-Doctoral Fellow Post-Doctoral Fellow (April '04–) JSPS Post-Doctoral Fellow (April '04–) Research Fellow Graduate Student

Visiting Professor (from Osaka Prefecture University) Visiting Professor (from Gunma University)

Director (–March '04) Director (April '04–)

Associate Professor Research Associate Research Fellow (–March '04); Visiting Scientist; JSPS Post-Doctoral Fellow (April '04–) IMS Fellow IMS Fellow (September '03–March '04) Research Fellow (July '04–) Graduate Student (–March '04) Graduate Student (May '04–) Graduate Student (April '04–)

Associate Professor Research Associate (-March '04) Visiting Professor (from Institute of Atomic Physics, Romania) Visiting Associate Professor; MONKASHO Invited Fellow (from Yeungnam University, Korea) IMS Fellow Research Fellow Research Fellow Research Fellow Research Fellow Visiting Scientist (from Institute of Atomic Physics, Romania)

Director

Professor Associate Professor Associate Professor **Research Associate Research Associate** Research Associate (October '03-) **Research Associate** Technical Associate (-May '04) IMS Fellow (-April '04) IMS Fellow (-July '04) Post-Doctoral Fellow (-July '04) Post-Doctoral Fellow (April '04-) Post-Doctoral Fellow (-March '04) Graduate Student Graduate Student Graduate Student

ENDO, Hiroaki KAWAO, Masahiro MIZUGUCHI, Eisuke OZAWA, Hiroaki

SATOU, Hirokazu YAJIMA,Takashi TANAKA, Yasuhiko MADANBASHI, Tomokura

MATSUNAGA, Satoshi

NAKATA, Kazuya

KIM, Yong-De

SHIMADA, Kazuhiro

TOMONARI, Yasuhiko

Nanocatalysis and Biomolecular Devices UOZUMI, Yasuhiro FUJII, Hiroshi

> NAGATA, Toshi SAKURAI, Hidehiro KURAHASHI, Takuya NAGASAWA, Takayuki YAMADA, Youich HIGASHIBAYASHI, YOON, Cheol min MORITA, Ryotaro HOSOKAWA, Youichi TAKENAKA, Kazuhiro SUZUKA, Toshimasa GUO, Haiqing MAKI, Suguru HOCKE, Heiko KIKUZAWA, Yoshihiro NAKAI. Yasushi KIMURA, Masahiro TAMAKI, Hirotaka SAKAMAKI, Junichiro MINAKAWA, Maki ARAKAWA, Takayasu BEPPU, Tomohiko

Nano-scale Photoscience MATSUMOTO, Yoshiyasu TSUKUDA, Tatsuya NEGISHI, Yuichi WATANABE, Kazuya NAGAO, Masashi TSUNOYAMA, Hironori FUYUKI, Masanori NARUSHIMA, Takashi SAWADA, Takeshi INO, Daisuke

YAMAGUCHI, Dai

Advanced Molecular Science TAKAHASHI, Masahiko KERA, Satoshi Graduate Student (from Ehime University)* (-March '04) Graduate Student (from Ehime University)* Graduate Student (from Ehime University)* Graduate Student (from Ehime University)* (-March '04), Graduate Student (April '04-) Graduate Student (from Ehime University)* Graduate Student (April '04-) Graduate Student (from Nagasaki University)* (April '04-) Graduate Student (from Tokyo Metropolitan University)* (April '04-) Graduate Student (from Tokyo Metropolitan University)* (April '04-) Graduate Student (from Tokyo Metropolitan University)* (April '04-) Graduate Student (from Japan Advanced Institute of Science and Technology)* (April '04–) Graduate Student (from Japan Advanced Institute of Science and Technology)* (April '04-) Graduate Student (from Kyusyu University)* (April '04-)

Professor Associate Professor (Okazaki Institute for Integrative Bioscience) Associate Professor Associate Professor (October '03-) **Research Associate Research Associate** Research Associate (October '03-) Research Associate (June '04–) Visiting Professor (December '03-Februry '04) Visiting Researcher (-September '03) IMS Fellow (-March '04) IMS Fellow JST Post-Doctoral Fellow (April '04-) JST Post-Doctoral Fellow (April '04-) IMS Fellow (April '04-) JST Post-Doctoral Fellow (-November '03) Graduate Student (-September '04) Graduate Student (-March '04) Graduate Student Graduate Student (-March '04) Graduate Student Graduate Student Graduate Student (April '04-) Graduate Student (April '04-)

Professor Associate Professor Research Associate Research Associate (June '04–) IMS Fellow (April '04–) IMS Fellow (April '04–) Graduate Student (April '04–) Graduate Student (–March '04) Research Fellow (April '04–) Post-Doctoral Fellow (Institute of Research and Innovation) (–March '04) Research Fellow (April '04–)

Associate Professor (from Tohoku University) Research Associate (from Chiba University)

WATANABE, Noboru KHAJURIA, Yugal

Interface Molecular Science MIZUNO, Akira

OKAMOTO, Masayuki

TUN, Lwin

KOMATU, Jun

KINOSHITA, Youhei

SUNG, Bongjo

YOGI, Osamu

SUZUKI, Masanori

Molecular Clusters TANIMOTO, Yoshifumi ISHIDA, Toshimasa

FUJIWARA, Masao

OBA, Toru

DUNIN-BARKOVSKIY, Lev UECHI, Ichiro

Equipment Development Center

YAKUSHI, Kyuya URISU, Tsuneo WATANABE, Michio

UIVSOR Facility KOSUGI, Nobuhiro KATOH, Masahiro

> SHIGEMASA, Eiji KIMURA, Shin-ichi ITO, Kenji KWON, Yong-seung

COUPRIE Marie-Emmanuelle

HOSAKA, Masahito MOCHIHASHI, Akira ITO,Takahiro HIKOSAKA, Yasumasa SAKURAI, Yoko NISHI, Tatsuhiko IM, Hojun

Safety Office

OGAWA, Takuji

TOMURA, Masaaki TANAKA, Shoji Research Associate (from Tohoku University) IMS Fellow (October '03–)

Professor (from Toyohashi University of Technology) (-March'04) Graduate Student (from Toyohashi University of Technology)* (-March'04)

Professor (from Hiroshima University) (-March '04) Associate Professor (from Shizuoka University) (-March '04) Research Associate (from Hiroshima University) (-March '04) Research Associate (from Utsunomiya University) (-March '04) IMS Fellow Graduate Student (from Hiroshima University)* (-March '04)

Director (-March '04) Director (April '04-) Associate Professor (-March '04)

Director Associate Professor (-December '03); Professor (January (04–) Associate Professor Associate Professor Visiting Associate Professor (from Photon Factory) Visiting Professor (from Sungkyunkwan University) (September '03–August '04) Visiting Professor (from Commissariat à l'Énergie Atomique) (June-September '04) Research Associate **Research Associate Research Associate** Research Associate (April '04-) IMS Fellow (April '04–) Graduate Student Graduate Student

Director, Professor (Research Center for Molecular-scale Nanoscience, concurrently) (April '04–) Research Associate (June '04–) Research Associate (Research Center for Molecular-scale Nanoscience, concurrently) (June '04–)

Okazaki Research Facilities (related to IMS) Okazaki Institute for Integrative Bioscience

Department of Strategic Methodology KINOSITA, Kazuhiko, Jr. AONO, Shigetoshi ALI, Md. Yusuf

> FUJII, Hiroshi ADACHI, Kengo YOSHIOKA, Shiro KOBAYASHI, Katsuaki KUJIME, Masato FUJIWARA, Ikuko SHIROGUCHI, Katsuyuki MAKI, Yasushi KON, Rieko FURUIKE, Shou OKAMOTO, Tetsuaki KANDA, Ritsuko YOGO, Katsunori SAKAKI, Naoyoshi ONOUE, Yasuhiro INAGAKI, Sayaka YOSHIMURA, Hideaki OKUYAMA, Kenichi HOSSAIN, Mohammad Delawar

Department of Bio-environmental Science KITAGAWA, Teizo HAYASHIZAKI, Yoshihide

YAMATO, Takehisa

UCHIDA, Takeshi NAGATOMO, Shigenori

TOSHA, Takehiko

KUBO, Minoru WALKER, Gilbert Creighton

KOZLOWSKI, Pawel

MAHINAY, Myrna Sillero GU, Yuzong VAROTSIS, Constantinos

KIM, Younkyoo

EL-MASHTOLY, Samir F. OHTA, Takehiro NAGANO, Yasutomo HIRAMATSU, Hirotsugu PAL, Biswajit GAO, Ying LI, Jiang LV, Ming

Research Center for Computational Science NAGASE, Shigeru OKAZAKI, Susumu MORITA, Akihiro Professor Professor Visiting Professor (from Shahjalal University of Science and Technology, Bangladesh) (October '03–January '04) Associate Professor **Research Associate** Research Associate (November '03-) IMS Fellow IMS Fellow JSPS Post-Doctoral Fellow JSPS Post-Doctoral Fellow Post-Doctoral Fellow (-September '03) Post-Doctoral Fellow Post-Doctoral Fellow Post-Doctoral Fellow (April '04-) Research Fellow Graduate Student (from Waseda University)* Graduate Student Graduate Student Graduate Student Graduate Student Graduate Student Graduate Student

Professor Visiting Professor (from RIKEN Genomic Sciences Center) (April '04–) Visiting Associate Professor (from Nagoya University) (-March '04) **Research Associate** Technical Associate (-September '03); Research Associate (October '03–November '03)¹⁴⁾ Post-Doctral Fellow (-January '04); JSPS Post-Doctoral Fellow (April '04-) IMS Fellow (April '04-) Visiting Scientist; JSPS Invited Fellow (-September '03), Visiting Scientist (from University of Pittsburgh, USA) (October '03–January '04) Visiting Scientist; JSPS Invited Fellow (from University of Louisville, USA) (April-August '04) Visiting Scientist; JSPS Post-Doctoral Fellow Visiting Scientist; JSPS Post-Doctoral Fellow (July '04–) Visiting Scientist; MONKASHO Invited Fellow (from University of Crete, Greece) (-October '03) Visiting Scientist (from Hankuk University of Foreign Studies, Korea) (December '03–February '04) Visiting Scientist (July '04-) JSPS Post-Doctoral Fellow JSPS Post-Doctoral Fellow JSPS Post-Doctoral Fellow Post-Doctoral Fellow (November '03-August '04) Graduate Student Graduate Student Graduate Student

Director (Department of Theoretical Molecular Science) Professor Associate Professor (January '04–) NANBU, Shinkoh

TAKAMI, Toshiya

OONO, Hitoshi MIURA, Shinichi Research Associate (Department of Computational Molecular Science) Research Associate (Department of Computational Molecular Science) Research Associate Research Associate (Department of Computational Molecular Science)

* Carries out graduate research of IMS on Cooperative Education Program of IMS with other graduate schools.

Technical Staff

SAKAI, Kusuo Technical Division Head (-March '04) KATO, Kiyonori Technical Division Head (April '04-) MATSUDO, Osamu Technical Section Chief (-December '03) YAMANAKA, Takaya **Technical Section Chief** HORIGOME, Toshio Technical Section Chief SUZUI, Mitsukazu Technical Section Chief YOSHIDA, Hisashi Molecular Assemblies (Unit Chief) (-May '04) Technical Section Chief (June '04-) Research Center for Computational Science (Unit Chief) MIZUTANI, Fumiyasu (-May '04) Technical Section Chief (June '04-) NAKAMURA, Eiken Electronic Structure (Unit Chief) YAMAZAKI, Jun-ichiro Laser Research Center for Molecular Science (Unit Chief) CHIBA, Hisashi Laser Research Center for Molecular Science (April '04–) UEDA, Tadashi Laser Research Center for Molecular Science NAGATA, Masaaki Research Center for Molecular-scale Nanoscience (Unit Chief) TAKAYAMA, Takashi Research Center for Molecular-scale Nanoscience (Unit Chief) SAKAI, Masahiro Research Center for Molecular-scale Nanoscience Research Center for Molecular-scale Nanoscience MAKITA, Seiji MIZUKAWA, Tetsunori Research Center for Molecular-scale Nanoscience (July '04-) Equipment Development Center (Unit Chief) MIZUTANI, Nobuo Equipment Development Center (Unit Chief) (April '04-) AOYAMA, Masaki UCHIYAMA, Kouichi Equipment Development Center TOYODA, Tomonori Equipment Development Center YANO, Takayuki Equipment Development Center MATSUSHITA, Koji Equipment Development Center (-March '04) KONDOU, Takuhiko Equipment Development Center (April '04–) HASUMOTO, Masami UVSOR facility (Unit Chief) KONDOU, Naonori **UVSOR** facility HAYASHI, Kenji **UVSOR** facility TESHIMA, Fumitsuna Research Center for Computational Science NAITOU, Shigeki Research Center for Computational Science SAWA, Masataka **Research Center for Computational Science** MINAMINO, Satoshi Research Center for Computational Science (April '04–)

List of Present Addresses

- 1) National Institute of Advanced Industrial Science and Technology, Higashi 1-1, Tsukuba, Ibaraki 305-8565
- 2) National Institute for Material Science, Namiki 1-1, Tsukuba, Ibaraki, 305-0044
- 3) Graduate School of Pharmaceutical Science, Kyoto University, Sakyo-ku, Kyoto, 606-8501
- 4) Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshima, Hiroshima, 739-0046
- 5) Department of Physics, Meisei University, 2-1-1 Hodokubo, Hino-shi, Tokyo, 191-8506
- 6) National Institute of Nanotechnology, National Research Council Canada, University of Alberta, 9107-116 Street, Edmonton, AB T6G 2V4, Canada
- Department of Chemistry, Fukuoka University of Education, Akamabunkyo-machi 1-1, Murakara, Fukuoka 811-4192
- 8) Department of Physics, University of Kerala, Kariavattom P.O., Thiruvananthapuram, Trivandrum, Kerala, INDIA-695581
- Chemical Spectroscopy Division, Chemical Resources laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, yokohama, Kanagawa 226-8503
- 10) Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602.
- 11) Department of Applied Physics, Osaka University, Yamada-oka 2-1, Suita 565-0871.
- 12) RIKEN, Wako 351-0198
- 13) Catalysis Research Center, Hokkaido University, Sapporo 001-0021
- 14) Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571

COUNCIL

NAKAMURA, Hiroki

Director-General

Councillors

TSUCHIYA, Soji KATO, Shinichi

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BUILDINGS AND CAMPUS

The IMS campus covering 62,343 m² is located on a low hill in the middle of Okazaki city. The inequality in the surface of the hill and growing trees are preserved as much as possible, and low-storied buildings are adopted for conservation of the environment. The buildings of IMS are separated according to their functions as shown in the map. The Research Office Building and all Research Facilities except for the Computer Center are linked organically to the Main Laboratory Buildings by corridors. Computer Center, Library and Administration Buildings are situated between IMS and neighboring National Institute for Basic Biology and National Institute for Physiological Sciences, because the latter two facilities are common to these three institutes.

The lodging facility of IMS called Yamate Lodge, located within ten minutes' walk, has sleeping accommodations for 15 guests and two families. Mishima Lodge, located within four minutes' walk east of IMS can accommodate 74 guests and 20 families. Scientists who visit IMS as well as the two other institutes can make use of these facilities. Foreign visiting scientists can also live at these lodgings with their families during their stays. The Okazaki Conference Center, which has four conference rooms capable of between 50 and 250 attendance, was built in April, 1997 in Mishima area. Two buildings for Center for Integrative Bioscience, Research Center for Computational Science, and research facilities of ONRI were built in February, 2002 in Yamate Area. Four buildings were built in March, 2004 in Yamate Area.



- 9. Central Administration
- 10. UVSOR Facility
- 11. Power Station
- 12. Waste-Water Disposition Facilities

- 21. Yamate Bldg. 5
- 22. Yamate Lodge
- 23. Waste-Water Disposition Facilities
- 24. Power Station



Okazaki (population 351,000) is 260 km west of Tokyo, and can be reached by train in about 3 hours from Tokyo via Shinkansen and Meitetsu Line.

The nearest large city is Nagoya, about 40 km northwest of Okazaki.



RESEARCH ACTIVITIES I Department of Theoretical Studies

I-A Theoretical Study and Design of Functional Molecular Systems: New Bonding, Structures, and Reactions

It is an important subject to develop functional molecules with novel bonding and structures from theoretical and computational points of view. Thus, novel bonds and structures provided by heavier atoms are investigated, which are expected to serve as new building blocks for the design of functional molecules. In addition, unique spaces and flexible structures provided by large molecules and clusters are highly emphasized to develop functional molecular systems by modulating the electronic properties. Efficient computational methods are also investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1 Spherical Sila- and Germa-Homoaromaticity

CHEN, Zhongfang; HIRSCH, Andreas¹; NAGASE, Shigeru; THIEL, Walter²; SCHLEYER, Paul von Rague³

(¹*Univ. Erlangen-Nürnberg;* ²*Max-Planck Inst.;* ³*Univ. Georgia*)

[J. Am. Chem. Soc. 125, 15507–15511 (2003)]

There has been considerable progress in investigating the effects of silicon and germanium substitution on the aromaticity of arenes with $4n+2\pi$ electrons. However, homoaromaticity, well-established in organic chemistry, has received much less attention in silicon and germanium counterparts. Guided by the $2(N+1)^2$ electron-counting rule, we have designed various spherical sila- and germa-homoaromatic systems rich in group 14 elements. Their significant homoaromaticity is demonstrated by structures and nucleus-independent chemical shifts calculated using density functional theory. The novel homoaromatic systems with welldelocalized electrons in the heavier group 14 elements present new synthetic targets, in particular, the spherical homoaromaticity-stabilized silicon and germanium clusters Si_8M_2 and Ge_8M_2 (M = Li and Na). Besides the formally used endohedral inclusion strategy, spherical homoaromaticity is another way to stabilize silicon and germanium clusters.

I-A-2 Synthesis and Characterization of Tetrakis-Silylated C₆₀ Isomers

MAEDA, Yutaka¹; RAHMAN, G. M. Aminur¹; WAKAHARA, Takatsugu¹; KAKO, Masahiro²; OKAMURA, Mutsuo³; SATO, Soichi¹; AKASAKA, Takeshi¹; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹Univ. Tsukuba; ²Univ. Electron-Communications; ³Niigata Univ.)

[J. Org. Chem. 68, 6791-6794 (2003)]

It is demonstrated that the tetrakis-silulation of C_{60} takes place readily by generating photochemically a silul radical from disilane to afford tetrakis-isomers, (*t*-

BuPh₂Si)₄C₆₀. The relative energies and structures of tetrakis isomers as well as addition positions are revealed by molecular orbital calculations. The redox properties of C₆₀ can be controlled not only by the electronegativity of substituents and regiochemistry of its functionality but also by the number of substituents. Thus, the tetrakis-adducts (*t*-BuPh₂Si)₄C₆₀ has lower oxidation and higher reduction potentials than C₆₀ and the bis-adducts (*t*-BuPh₂Si)₂C₆₀.

I-A-3 Silylation of Fullerenes with Active Species in Photolysis of Polysilane

WAKAHARA, Takatsugu¹; MAEDA, Yutaka¹; KAKO, Masahiro²; AKASAKA, Takeshi¹; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹Univ. Tsukuba; ²Univ. Electron-Communications)

[J. Organomet. Chem. 685, 177–188 (2003)]

Organosilicon compounds represent unique features of materials. A combination of organosilicon compounds and fullerenes forms new classes of organic compounds and open a new field in materials science. Thus, derivatization of fullerenes by the addition of active silicon species generated in the photolysis of polysilanes is developed from the experimental and theoretical points of view, which leads to several new materials. In addition, we summarize recent advance in the chemistry of mono- and bis-silylation of fullerenes with silylenes and silyl radicals to afford new fullerenebased organosilicon materials.

I-A-4 Syntheses and Structures of Silicon Analogues of Cyclopropabenzenes

TAJIMA, Tomoyuki¹; HATANO, Ken²; SASAKI, Takayo¹; SASAMORI, Takahiro¹; TAKEDA, Nobuhiro¹; TOKITOH, Norihiro¹; TAKAGI, Nozomi; NAGASE, Shigeru (¹Kyoto Univ.; ²Kyushu Univ.)

[J. Organomet. Chem. 686, 118–126 (2003)]

The reaction of an overcrowded diaryldilithiosilane, Tbt(Dip)SiLi₂ (Tbt = 2,4,6-tris[bis[trimethylsily]]- methyl]phenyl; Dip = 2,6-diisopropylphenyl), with odibromobenzene and 1,2,4,5-tetrabromobenzene results in the synthesis and isolation of the first stable silacyclopropabenzene and bis(silacyclopropa)benzenes, respectively. The crystallographic analyses and theoretical calculations reveal that the lengths of the juncture carbon-carbon bonds of the mono- and bis(silacyclopropa)benzenes are marginally in the range of carboncarbon bond lengths of usual benzene rings. It is shown that the structural feature is attributable to a decrease in the strain energy of silacyclopropabenzenes relative to the corresponding cyclopropabenzenes, and the strain energy is a simple additive function of the number of the fused three-membered rings involving Si atom.

I-A-5 The Effect of Substituents on the Thermal Decomposition of Diazirines: Experimental and **Computational Studies**

LIU, Michael T. H.¹; CHOE, Yoong-Kee; KIMURA, Masahiro; KOBAYASHI, Kaoru; NAGASE, Shigeru; WAKAHARA, Takatsugu²; NIINO, Yasuyuki³; ISHITSUKA, Midori O.²; MAEDA, Yutaka²; AKASAKA, Takeshi²

(¹Univ. Prince Edward Island; ²Univ. Tsukuba; ³Niigata Univ.)

[J. Org. Chem. 68, 7471–7478 (2003)]

The thermal decomposition of phenylchlorodiazirine (1), phenyl-*n*-butyldiazirine (2), and 2-adamantane-2-3'-[3H]diazirine (3) is studied in solution in the presence of C_{60} . The C_{60} probe technique indicates that in the decomposition diazirine 1 yields exclusively phenylchlorocarbene, diazirine 2 yields mainly a diazo intermediate, and diazirine 3 yields a mixture of carbene and diazo compound. In the case of diazirine 2, 13% of (E)-1-phenyl-1-pentene results from the direct thermal rearrangement of diazirine without the participation of a carbene. As well, the thermal decomposition of these diazirines is theoretically invetigated with ab initio molecular orbital and density functional methods at the CASSCF and B3LYP levels, respectively. The experimental results are broadly in agreement with the theoretical prediction. In addition, the theoretical calculations indicate that the rebound reaction between carbene and molecular nitrogen leading to the formation of a diazo intermediate is an important reaction in the gasphase decomposition of diazirine.

I-A-6 Temperature Development in a Set of C₆₀H₃₆ Isomers

SLANINA, Zdenek¹; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹IMS and Academia Sinica)

[Chem. Phys. Lett. 382, 211-215 (2003)]

Relative stabilities of C₆₀H₃₆ isomers are evaluated using both enthalpy and entropy terms, i.e., the Gibbs free energies. The set consists of eight low energy isomers known from previous calculations and a new C1 species, topologically equivalent to the recently isolated C1 isomer of C60F36. The PM3 and B3LYP/6-31G* methods are applied, and in both treatments the new C₁ species is located 7 kcal/mol below the previous best C1 structure. The treatments differ in the lowest energy isomer but they place the new C1 isomer as the second most populated species at higher temperatures owing to its entropy enhancement.

I-A-7 A Comparison of the Photochemical Reactivity of N@C₆₀ and C₆₀: Photolysis with Disilirane

WAKAHARA, Takatsugu¹; MATSUNAGA, Yoichiro¹; KATAYAMA, Akira²; MAEDA, Yutaka¹; KAKO, Masahiro³; AKASAKA, Takeshi¹; OKAMURA, Mutsuo²; KATO, Tatsuhisa; CHOE, Yoong-Kee; KOBAYASHI, Kaoru; NAGASE, Shigeru; HUANG, Houjin⁴; ATA, Masafumi⁴ (¹Univ. Tsukuba; ²Niigata Univ.; ³Univ. Electro-Communication; ⁴Sony Co.)

[Chem. Commun. 2940–2941 (2003)]

The photochemical bis-silvlation of N@C₆₀ with disilirane is successfully performed. Based on control experiment and laser flash photolysis, it is considered that the bis-silylation reaction proceed by electron transfer from disilirane to ${}^{3}C_{60}*$ via an exciplex. A noticeable finding is that N@C₆₀ has a lower photochemical reactivity toward disilirane than C_{60} , although N@C₆₀ does not differ from C_{60} in its thermal reactivity. This important difference in the photochemical reactivity of N@C60 and C60 may be ascribed to the different excitation energies of N@C60 and C60 or the faster quenching of the triplet N@3C60* state. Theoretical calculations reveal that $N@C_{60}$ and C_{60} have the same orbital energies, suggesting that they have very similar excitation energies. It is likeliest that the three parallel spins on the N atom play an important role in the decay of $N@^{3}C_{60}*$. In fact, preliminary calculations of spin orbit coupling between the excited $\Psi(N@^{3}C_{60}^{*})$ and ground $\Psi(N@C_{60})$ states is larger than the corresponding coupling between $\Psi({}^{3}C_{60}^{*})$ and $\Psi(C_{60})$, suggesting that N@ ${}^{3}C_{60}$ * has a shorter lifetime than ${}^{3}C_{60}$ *.

I-A-8 Strongly Size-Dependent Electronic Properties in C₆₀-Encapsulated Zigzag Nanotubes and Lower Size Limit of Carbon Nanopeapods

LU, Jing¹; NAGASE, Shigeru; ZHANG, Shuang²; PENG, Lianmao² (¹IMS and Peking Univ.; ²Peking Univ.)

[Phys. Rev. B 68, 121402 (4 pages) (2003)]

Encapsulation of fullerenes into single-wall carbon nanotubes leads to the so-called nanopeapod, in which fullerenes self-assemble into a linear chain by weak interactions. By using first-principle calculations, we found that the electronic structures near the Fermi level of the nanotubes rigidly filled by a loose-packed fullerene chain can be approximated by a sum of those of the two constituents that are rigidly relatively shifted. Extending this rigid band shift approximation to the (n,0) nanotubes rigidly filled by a close-packed C₆₀ chain, a dramatic change in electronic properties from semiconductor (n = 17) to metal (n = 18 and 19) is seen, and the recently observed fine double peak structure on the conduction band of the semiconducting nanotube induced by C₆₀ encapsulation is well reproduced. The theoretical smallest diameter of a nanopeapod is 10.64 Å.

I-A-9 A Density Functional Theory Study Applied for Carbon Isotope Effects in the Non-Aqueous [Cu(CO)]⁺/CO System

ONO, Yuriko; FUJII, Yasuhiko¹; NAGASE, Shigeru; ISHIDA, Takanobu²

(¹Tokyo Inst. Tech.; ²State Univ. New York)

[Chem. Phys. Lett. **390**, 71–78 (2004)]

Density functional theory calculations are performed on the carbon isotopomers of CO and CO-complexes $[Cu(NH_2CH_2CH_2OH)_3(CO)]^+$, $[Cu(CH_3OH)_3(CO)]^+$. The results are compared with the experimental results on the carbon isotope exchange equilibrium between CO and CO-copper complexes. The gas-phase model is used even for calculating the isotope effects involving the solutes of solutions. Contributions of the extramolecular motion of the solute molecule to the reduced partition function ratios are responsible for the steep slope of $\ln \alpha vs. -1/T$ plots of the experimental data, where α is the isotope separation which is identical to the equilibrium constant in the present exchange system. The calculated results agree well with the experimental data.

I-A-10 Lanthanum Endohedral Metallofulleropyrrolidines: Synthesis, Isolation, and EPR Characterization

CAO, Baopeng¹; WAKAHARA, Takatsugu¹; MAEDA, Yutaka¹; HAN, Aihong¹; AKASAKA, Takeshi¹; KATO, Tatsuhisa; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹Univ. Tsukuba)

[Chem. Eur. J. 10, 716-720 (2004)]

Two lanthanum endohedral fulleropyrrolidines are produced, isolated, and characterized. Addition of an azomethine ylide to $La@C_{82}$ is very efficient and, to some extent, regioselective. Introduction of pyrrolidines to the endohedral metallofullerene $La@C_{82}$ cannot alter the octet EPR and endohedral character of the encapsulated metal atom but varies the electronic structure of the metallofullerene. The Prato reaction is also a valuable and versatile functinalization methodology for endohedral metallofullerenes, which could afford various endohedral metallofulleropyrrolidines with diversity of functions.

I-A-11 Side-Wall Opening of Single-Walled Carbon Nanotubes (SWCNTs) by Chemical Modification: A Critical Theoretical Study

CHEN, Zhongfang; NAGASE, Shigeru; HIRSCH, Andreas¹; HADDON, Robert C.²; THIEL, Walter³; SCHLEYER, Paul von Rague⁴

(¹Univ. Erlangen-Nürnberg; ²Univ. Calfornia; ³Max-Planck Inst.; ⁴Univ. Georgia)

[Angew. Chem., Int. Ed. 43, 1552–1554 (2004)]

Since single-walled carbon nanotubes (SWCNTs) have unique properties, chemical modifications of the exohedral surfaces is currently of considerable interest for promising applications to functional materials. At present, a vexing problem is ascertaining the detailed structures of nanotube derivatives after their preparation; all experimental attempts to determine the precise location and mode of addition of newly attached groups have failed. Thus, we have performed density functional B3LYP calculations on the O, CH₂, NH₂, and SiH₂ nanotube derivatives for both (5,5) armchair and (8,8)zigzag SWCNTs. The (5,5) and (8,8) SWCNT derivatives have opened structures instead of three-membered rings (3MRs). Since armchair and zigzag tubes are two extremes for SWCNT structures, evidently the side-wall of SWCNTs can be opened by chemical modification. It is pointed out that the often-used ONIOM approach is not appropriate for the systems studied here and has serious limitations to computational nanotube chemistry. The present computational results, that SWCNT derivatives favor opened rather than 3MR structures, may be verified experimentally with new advances in SWCNT solubilization and spectroscopic analysis.

I-A-12 Ca@C₈₂ Isomers: Computed Temperature Dependence of Relative Concentrations

SLANINA, Zdenek¹; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹IMS and Academia Sinica)

[J. Chem. Phys. 120, 3397–3400 (2004)]

Calcium is a relatively common element in formation of endohedral metallofullerenes. Among the calcium endohedrals, Ca@C82 exhibits the richest isomerism. For some cases, it is found that a structure that is not the lowest in potential energy is the most populated at higher temperatures and other higher-energy structures undergo stability interchanges with changing temperatures. Thus, relative concentrations of nine isomers of Ca@C₈₂ derived from the isolated-pentagonrule-satisfying cages of C₈₂ are computed in a wide temperature range. The computations are based on the Gibbs free energies constructed from partition functions supplied with molecular parameters from density functional theory calculations. Five isomers show significant populations at higher temperatures: $C_{2v} > C_s > C_2 > C_{3v}$ $> C_{\rm s}$. These computed relative populations agree well with available observations.

I-A-13 C₇₂ Isomers: The IPR-Satisfying Cage is Disfavored by Both Energy and Entropy

SLANINA, Zdenek¹; ISHIMURA, Kazuya; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹IMS and Academia Sinica)

[Chem. Phys. Lett. 384, 114–118 (2004)]

 C_{72} has been counted as a "missing fullerene." As C_{72} could only be recorded in mass spectroscopic data, its structure is still unknown. Relative concentrations of seven isomeric C_{72} cages (a cage with isolated pentagons, two cages with a pentagon-pentagon junction, a cage with a heptagon, a cage with two heptagons, and two cages with two pentagon-pentagon fusions) are computed using the Gibbs free energies in a broad temperature interval. It is found that the IPR (isolated pentagon rule)-violating C_{2v} cage with one pentagon-pentagon junction prevails at any relevant temperature. Although the IPR-satisfying cage is the second lowest in energy, it is disfavored by entropy so that several cages still higher in energy are in fact more populated at higher temperatures.

I-A-14 How Is the CH/ π Interaction Important for Molecular Recognition ?

RE, Suyong; NAGASE, Shigeru

[Chem. Commun. 658-659 (2004)]

Attractive CH/ π interactions have received considerable attention as a principal factor governing molecular recognition and self-assembly, as accumulated in the database on CH/ π proximate arrangements in crystal structures of host-guest complexes. To address the role of CH/ π interactions in molecular recognition, a resorcinol cyclic tetramer is considered as a typical host and its interactions with alcohols are theoretically investigated with the Hartree-Fock (HF) and secondorder Møller-Plesset perturbation (MP2) methods. The major source of CH/ π attraction is due to the dispersion force (electron correlation). It is pointed out that CH/ π attraction significantly contributes to host-guest complexation, but is not always a direct factor in molecular recognition.

I-A-15 A Bowl-Shaped Fullerene Encapsulates a Water into the Cage

IWAMATU, Sho-ichi¹; UOZAKI, Takashi¹; KOBAYASHI, Kaoru; RE, Suyong; NAGASE, Shigeru; MURATA, Shizuaki¹ (¹Nagoya Univ.)

[J. Am. Chem. Soc. 126, 2668–2669 (2004)]

In recent years, the controlled carbon–carbon cleavage of fullerene cages has attracted much attention, because the resulting open-cage derivatives allow small molecules to enter the internal cavities. Thus, a novel bowl-shaped fullerene cage with a large hole is synthesized by the regioselective multiple cage scissions of C_{60} . It is demonstrated from the observed ¹H NMR chemical shifts and theoretical calculations that one water molecule is encapsulated inside the bowl-shaped cage through the open hole, as the first example of the endohedral water complex of C_{60} .

I-A-16 Ca@C₇₄ Isomers: Relative Concentrations at Higher Temperatures

SLANINA, Zdenek¹; KOBAYASHI, Kaoru; NAGASE, Shigeru (¹IMS and Academia Sinica)

[Chem. Phys. 301, 153-157 (2004)]

Relative concentrations of six isomers of Ca@C₇₄ are evaluated: one species with isolated pentagons, three isomers with a pentagon-pentagon junction, two structures with one pentagon-pentagon pair and one heptagon. In a broad temperature interval, Gibbs energies are calculated using density functional theory. It is shown that the endohedral species derived from the C₇₄ cage with isolated pentagons prevails throughout. Two structures with a pentagon-pentagon junction come as minor isomers at higher temperatures while the remaining three species are always negligible. For the domain species, a kinetic barrier of less than 9 kcal/mol is computed for autoisomerizations mediated by motion of the encapsulated Ca atom.

I-A-17 Computed Temperature Development of the Relative Stabilities of La@C₈₂ Isomers

SLANINA, Zdenek¹; KOBAYASHI, Kaoru; NAGASE, Shigeru

(¹IMS and Academia Sinica)

[Chem. Phys. Lett. 388, 74–78 (2004)]

Relative concentrations of four selected isomers of La@C₈₂ are computed from the Gibbs energy derived from partition functions supplied with parameters from density functional theory calculations. An agreement with experiment can be reached for temperatures roughly from 1000 to 1300 K when the C_{2v} species is the major isomer followed by an isomer that undergoes C_{3v}/C_s symmetry reduction while the intrinsically C_s species comes as a still less populated third product. It is suggested that the C_{3v} isomer can be suppressed in the condense phase because of its higher reactivity.

I-A-18 Characterization of Ce@C₈₂ and Its Anion

WAKAHARA, Takatsugu¹; KOBAYASHI, Junichi¹; YAMADA, Michio¹; MAEDA, Yutaka¹; TSUCHIYA, Takahiro¹; OKAMURA, Mutsuo²; AKASAKA, Takeshi¹; WAELCHLI, Markus³; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa; KAKO, Masahiro⁴; YAMAMOTO, Kazunori⁵; KADISH, Karl M.⁶

(¹Univ. Tsukuba; ²Niigata Univ.; ³Bruker Japan; ⁴Univ. Electro-Communications; ⁵Japan Nuclear Fuel Cycle Development Inst.; ⁶Univ. Houston)

[J. Am. Chem. Soc. 126, 4883–4887 (2004)]

The cage symmetry of Ce@C₈₂ is determined as C_{2v} by measuring the ¹³C NMR spectra of its anion, as theoretically predicted for M@C₈₂ (M = Sc, Y, and La). The ¹³C NMR peaks of [Ce@C₈₂]⁻ show temperature-dependent shifts ascribed to the *f* electron remaining on the Ce atom. This kind of temperature-dependent shifts is the first example for the M@C₈₂ system. Both Ce@C₈₂ and [Ce@C₈₂]⁻ are ESR silent because of the highly anisotopic **g** matrix as well as the fast relaxation process originating from the orbital angular momentum of the *f* electron remaining on the Ce atom. This is the complementary relationship to the observation of the paramagnetic shift in ¹³C NMR. In air, the stability of Ce@C₈₂ is lower than that of La@C₈₂.

I-A-19 Isolation and Characterization of a Carbene Derivative of La@C₈₂

MAEDA, Yutaka¹; MATSUNAGA, Yoichiro²; WAKAHARA, Takatsugu²; TAKAHASHI, Satomi³; TSUCHIYA, Takahiro²; ISHITSUKA, Midori O.²; HASEGAWA, Tadashi¹; AKASAKA, Takeshi²; LIU, Michael T. H.⁴; KOKURA, Kisato⁵; HORN, Ernst⁵; YOZA, Kenji⁶; KATO, Tatsuhisa; OKUBO, Shingo; KOBAYASHI, Kaoru; NAGASE, Shigeru; YAMAMOTO, Kazunori⁷

(¹Tokyo Gakugei Univ.; ²Univ. Tsukuba; ³Niigata Univ.; ⁴Univ. Prince Edward Island; ⁵Rikkyo Univ.; ⁶Bruker AXS K. K; ⁷Japan Nuclear Fuel Cycle Development Inst.)

[J. Am. Chem. Soc. 126, 6858–6859 (2004)]

The addition of 2-admantane-2,3-[3H]-diazirine (Ad) to La@C₈₂ proceeds in a regiospecific way to afford one single isomer that is isolable. As the first example of the crystallographic study of paramagnetic endohedral metallofullerenes derivatives, structural determination of the enantiomeric isomer, La@C₈₂·Ad, is carried out. The bond lengths and angles in the X-ray structure are in good agreement with the values obtained from density functional theory calculations. From the Xray data observed at 90, 213, and 293 K, it is suggested that the La atom in La@C₈·Ad is located at one single site. The selective formation of La@C₈₂·Ad is explained by calculating charge densities and pyramidalization angles (local strain on the C atoms). The redox potentials of La@C₈₂·Ad are cathodically shifted, indicating that the introduction of an Ad group results in decreasing the electron-accepting power, as confirmed by the calculated electron affinity.

I-A-20 Isolation, Characterization, and Theoretical Study of La₂@C₇₈

CAO, Baopeng¹; WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; KONDO, Masahiro²; MAEDA, Yutaka¹; RAHMAN, G. M. Aminur¹; AKASAKA, Takeshi¹; KOBAYASHI, Kaoru; NAGASE, Shigeru; YAMAMOTO, Kazunori³ (¹Univ. Tsukuba; ²Niigata Univ.; ³Japan Nuclear Fuel Cycle Development Inst.)

[J. Am. Chem. Soc. 126, 9164–9165 (2004)]

A new endohedral metallofullerene, La₂@C₇₈, is isolated and characterized. For the C₇₈ fullerene, there are five isomers (D_3 , $C_{2v}(a)$, $C_{2v}(b)$, $D_{3h}(a)$, $D_{3h}(b)$) that satisfy the isolated pentagon rule. The first three isomers ((D_3 , $C_{2v}(a)$, $C_{2v}(b)$) have been isolated up to now for the empty C₇₈. Interestingly, a total of eight lines (five lines with full intensity and three lines with half intensity) is observed in the ¹³C NMR spectrum, which shows that La₂@C₇₈ has D_{3h} symmetry. From theoretical calculations, it is verified that the La atom is encapsulated inside the $D_{3h}(a)$ isomer, as a result of threeelectron transfer from each La to C₇₈.

I-A-21 Energetic, Geometric, and Electronic Evolutions of K-Doped Single-Wall Carbon Nanotube Ropes with K Intercalation Concentration

LU, Jing¹; NAGASE, Shigeru; ZHANG, Shuang²; PENG, Lianmao² (¹IMS and Peking Univ.; ²Peking Univ.)

[Phys. Rev. B 69, 205304 (4 pages) (2004)]

The energetic, geometric, and electronic evolutions of a K-doped single wall (10,10) carbon nanotube rope with K intercalation concentration are systematically investigated by using first principle calculations. The existence of a stable intermediate phase ($K^{exo}C_{13.3}$) before saturation ($K^{exo}C_{6,7}$) for exohedral K-doping is first theoretically confirmed. The optimum K-intercalation density in single-wall carbon nanotube ropes with open ends is predicted to be as high as about $KC_{4,2}$, nearly twice the well-known value in graphite. The simple charge transfer model is applicable only in the low K-doping level regime. The nearly free electron states of the nanotube couple with the 4s orbital on K, and the lower hybridized states do cross the Fermi level as the exohedral and endohedral K-doping densities exceed K^{exo}C₂₀ and K^{endo}C₈₀, respectively. The saturation phase of K-doped open-ended single-wall nanotube ropes is a conductor with three channels: one along the tube wall and the other two along the inside and outside of the tube wall, respectively.

I-B Prediction of Protein Tertiary Structures and Protein Folding Problem

Prediction of the three-dimensional structures of protein molecules by computer simulations is a very challenging problem in theoretical molecular science. The difficulty of the problem lies in two facts: (1) the inclusion of accurate solvent effects is non-trivial and time-consuming (2) there exist a huge number of local minima in the energy function, forcing conventional simulations to get trapped in states of energy local minima. We have been exploring the strategies that allow us to overcome these difficulties and to study the protein folding mechanism by directly folding proteins.

I-B-1 Optimization of Protein Force-Field Parameters with the Protein Data Bank

SAKAE, Yoshitake¹; OKAMOTO, Yuko (¹GUAS)

[Chem. Phys. Lett. 382, 626 (2003)]

We propose a novel method to optimize existing force-field parameters for protein systems. The method consists of minimizing the summation of the square of the force acting on each atom in the proteins with the structures from the Protein Data Bank. We performed this optimization to the partial-charge and torsionenergy parameters of the AMBER parm94 force field, using 100 molecules from the Protein Data Bank. We then performed folding simulations of α -helical and β hairpin peptides. The optimized force-field parameters gave structures more consistent with the experimental implications than the original AMBER force field.

I-B-2 Prediction of Transmembrane Helix Configurations by Replica-Exchange Simulations

KOKUBO, Hironori¹; OKAMOTO, Yuko (¹GUAS)

[Chem. Phys. Lett. 383, 397 (2004)]

We propose a method for predicting helical membrane protein structures by computer simulations. Our method consists of two parts. In the first part, aminoacid sequences of the transmembrane helix regions are obtained from one of existing WWW servers. In the second part, we perform a replica-exchange simulation of these transmembrane helices with some constraints and identify the predicted structure as the global-minimum-energy state. We have tested the second part of the method with the dimeric transmembrane domain of glycophorin A. The structure obtained from the prediction was in close agreement with the experimental data.

I-B-3 Free Energy Calculations for DNA Base Stacking by Replica-Exchange Umbrella Sampling

MURATA, Katsumi¹; SUGITA, Yuji²; OKAMOTO, Yuko (¹GUAS; ²Univ. Tokyo) [Chem. Phys. Lett. 385, 1 (2004)]

We have investigated the free energy change of the stacking process of DNA dimers using molecular dynamics simulations based on replica-exchange umbrella sampling. Pairs of replicas with different umbrella potentials are exchanged in this method, which allows the simulation to sample much wider conformational space and, therefore, to yield more accurate free energy profiles than by the conventional umbrella sampling. From the free energy profiles, we observed good stacking for all DNA dimers and sequence-dependent stacking stability. This sequence dependence of the stacking free energy is in accord with the experimental results.

I-B-4 Comparisons of Force Fields for Proteins by Generalized-Ensemble Simulations

YODA, Takao¹; SUGITA, Yuji²; OKAMOTO, Yuko (¹Nagahama Inst. Bio-Sci. Tech.; ²Univ. Tokyo)

[Chem. Phys. Lett. 386, 460 (2004)]

Secondary structural characteristics of six commonly used force fields for protein systems developed by different research groups have been compared. We performed molecular dynamics simulations of an α -helical polypeptide and a β -hairpin polypeptide with explicit water molecules. Two generalized-ensemble algorithms, replica-exchange multicanonical algorithm and multicanonical replica-exchange method, for efficient sampling of configurational space have been employed. Comparisons of the secondary structure content of polypeptides for different force fields highlighted differences of their structural tendency. The results imply that α helix is favored for AMBER94 and AMBER99 and that β-hairpin is favored for GROMOS96, while CHARMM 22, AMBER96, and OPLS-AA/L have intermediate tendency.

I-B-5 Prediction of Membrane Protein Structures by Replica-Exchange Monte Carlo Simulations: Case of Two Helices

KOKUBO, Hironori¹; OKAMOTO, Yuko (¹GUAS)

[J. Chem. Phys. 120, 10837 (2004)]

We test our prediction method of membrane protein structures with glycophorin A transmembrane dimer and analyze the predicted structures in detail. Our method consists of two parts. In the first part, we obtain the amino-acid sequences of the transmembrane helix regions from one of existing WWW servers and use them as an input for the second part of our method. In the second part, we perform a replica-exchange Monte Carlo simulation of these transmembrane helices with some constraints that indirectly represent surrounding lipid and water effects and identify the predicted structure as the global-minimum-energy state. The structure obtained in the case for the dielectric constant $\varepsilon = 1.0$ is very close to that from the NMR experiments, while that for $\varepsilon = 4.0$ is more packed than the native one. Our results imply that the helix-helix interaction is the main driving force for the native structure formation and that the stability of the native structure is determined by the balance of the electrostatic term, van der Waals term, and torsion term, and the contribution of electrostatic energy is indeed important for correct predictions. The inclusion of atomistic details of side chains is essential for estimating this balance accurately because helices are tightly packed.

I-B-6 Replica-Exchange Extensions of Simulated Tempering Method

MITSUTAKE, Ayori¹; OKAMOTO, Yuko

(¹Keio Univ.)

[J. Chem. Phys. 121, 2491 (2004)]

In this article we consider combinations of two wellknown generalized-ensemble algorithms, namely, simulated tempering and replica-exchange method. We discuss two examples of such combinations. One is the previously developed replica-exchange simulated tempering and the other is the newly developed simulated tempering replica-exchange method. In the former method, a short replica-exchange simulation is first performed and the simulated tempering weight factor is obtained by the multiple-histogram reweighting techniques. This process of simulated tempering weight factor determination is faster and simpler than that in the usual iterative process. A long simulated tempering production run is then performed with this weight factor. The latter method is a further extension of the former in which a simulated tempering replica-exchange simulation is performed with a small number of replicas. These new algorithms are particularly useful for studying frustrated systems with rough energy landscape. We give the formulations of these two methods in detail and demonstrate their effectiveness taking the example of the system of a 17-residue helical peptide.

I-B-7 Self-Assembly of Transmembrane Helices of Bacteriorhodopsin by a Replica-Exchange Monte Carlo Simulation

KOKUBO, Hironori¹; OKAMOTO, Yuko (¹GUAS)

[Chem. Phys. Lett. 392, 168 (2004)]

We examine by a molecular simulation whether or not the transmembrane helices of bacteriorhodopsin have the ability to self-assemble into the native configuration by themselves. Starting from random initial configurations of seven transmembrane helices, the same helix arrangement as the experimental one (PDB code: 1C3W) was obtained by a replica-exchange Monte Carlo simulation. This implies that helix-helix interactions are the main driving force for the native structure formation of bacteriorhodopsin.

I-C Development of Simulation Algorithms for Complex Systems

Developing a powerful simulation algorithm that can alleviate the multiple-minima problem is important in many complex systems. We have been advocating the uses of the so-called generalized-ensemble algorithms such as multicanonical algorithm and replica-exchange method.

I-C-1 New Approach to the First-Order Phase Transition of Lennard-Jones Fluids

MUGURUMA, Chizuru¹; OKAMOTO, Yuko; MIKAMI, Masuhiro² (¹Chukyo Univ.; ²AIST)

[J. Chem. Phys. 120, 7557 (2004)]

The multicanonical Monte Carlo method is applied to a bulk Lennard-Jones fluid system to investigate the liquid-solid phase transition. We take the example of a system of 108 argon particles. The multicanonical weight factor we determined turned out to be reliable for the energy range between 27.0 and 24.0 kJ/mol, which corresponds to the temperature range between 60 and 250 K. The expectation values of the thermo-dynamic quantities obtained from the multicanonical production run by the reweighting techniques exhibit the characteristics of first-order phase transitions between liquid and solid states around 150 K. The present study reveals that the multicanonical algorithm is particularly suitable for analyzing the transition state of the first-order phase transition in detail.

I-C-2 Molecular Dynamics Simulations in the Multibaric-Multithermal Ensemble

OKUMURA, Hisashi; OKAMOTO, Yuko

[Chem. Phys. Lett. 391, 248 (2004)]

We propose a new generalized-ensemble molecular dynamics simulation algorithm, which we refer to as the multibaric-multithermal molecular dynamics. This is the molecular dynamics version of the recently proposed multibaric-multithermal Monte Carlo method. The multibaric-multithermal simulations perform random walks widely both in the potential-energy space and in the volume space. From only one simulation run, therefore, one can calculate isobaric-isothermal-ensemble averages in wide ranges of temperature and pressure. We test the effectiveness of this algorithm by applying it to a Lennard-Jones 12-6 potential system.

I-C-3 Monte Carlo Simulations in Generalized Isobaric-Isothermal Ensembles

OKUMURA, Hisashi; OKAMOTO, Yuko

[Phys. Rev. E 70, 026702 (2004)]

We present three generalized isobaric-isothermal ensemble Monte Carlo algorithms, which we refer to as the multibaric-multithermal, multibaric-isothermal, and isobaric-multithermal algorithms. These Monte Carlo simulations perform random walks widely in volume space and/or in potential energy space. From only one simulation run, one can calculate isobaric-isothermalensemble averages in wide ranges of pressure and temperature. We demonstrate the effectiveness of these algorithms by applying them to the Lennard-Jones 12–6 potential system with 500 particles.

I-D Applications of the Zhu-Nakamura Theory to Electronically Nonadiabatic Chemical Dynamics

I-D-1 Semiclassical Theory of Electronically Nonadiabatic Chemical Dynamics: Incorporation of the Zhu-Nakamura Theory into the Frozen Gaussian Propagation Method

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[J. Chem. Phys. 120, 8937 (2004)]

The title theory is developed by combining the Herman-Kluk semiclassical theory for adiabatic propagation on single potential-energy surface and the semiclassical Zhu-Nakamura theory for nonadiabatic transition. The formulation with use of natural mathematical principles leads to a quite simple expression for the propagator based on classical trajectories and simple formulas are derived for overall adiabatic and nonadiabatic processes. The theory is applied to electronically nonadiabatic photodissociation processes: a one-dimensional problem of H₂⁺ in a cw (continuous wave) laser field and a two-dimensional model problem of H₂O in a cw laser field. The theory is found to work well for the propagation duration of several molecular vibrational periods and wide energy range. Although the formulation is made for the case of laser induced nonadiabatic processes, it is straightforwardly applicable to ordinary electronically nonadiabatic chemical dynamics.

I-D-2 Semiclassical Frozen Gaussian Propagation Method for Electronically Nonadiabatic Chemical Dynamics: Møller Operator Formulation and Incorporation of the Zhu-Nakamura Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[J. Theor. Comput. Chem. in press]

The title theory is developed by combining the Herman-Kluk semiclassical theory for adiabatic propagation on single potential energy surface and the Zhu-Nakamura theory for nonadiabatic transition. A quite simple expression for the propagator based on classical trajectories is derived using the Møller operator formulation of scattering theory. The theory takes into account almost all quantum effects that occur during nonadiabatic transition, especially at low energies and is expected to be applicable to general chemical dynamics of high dimensions. Application to a two-dimensional model system shows that the theory works well for the propagation duration of several molecular vibrational periods and wide wave packet energy range.

I-D-3 Evaluation of Canonical and Microcanonical Nonadiabatic Reaction Rate Constants by Using the Zhu-Nakamura Formulas

ZHAO, Yi¹; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

(¹IMS and Univ. Sci. Tech. China, China)

[J. Chem. Phys. in press]

We consider a problem of calculating both thermal and microcanonical rate constant for nonadiabatic chemical reactions. Instead of using the conventional transition state theory (TST), we use a generalized seam surface and introduce a concept of a coordinate dependent effective nonadiabatic transition probability based on the Zhu-Nakamura (ZN) theory which can treat the nonadiabatic tunneling properly. The present approach can be combined with Monte Carlo method so as to be applicable to chemical reactions in complicated systems. The method is demonstrated to work well in wide energy and temperature range. Numerical tests also show that it is very essential for accurate evaluation of the thermal rate constant to use the generalized seam surface and take into account the nonadiabatic tunneling effect.

I-D-4 Trace Formula of Thermal Rate Constant for Multi-Surface Processes

CHIKAZUMI, Shinpei; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The trace formula for thermal rate constant formulated by W. Miller and co-workers for electronically adiabatic reactions is extended so as to be applicable to multi-potential energy surface processes. A semiclassical theory is formulated with the Zhu-Nakamura theory incorporated to treat the electronically nonadiabatic transition. Adiabatic propagation on the single potential energy surface is treated by the Herman-Kluk type wave packet propagation.

I-D-5 Tragectory Surface Hopping Approach to Electronically Nonadiabatic Chemical Dynamics

OLOYEDE, Ponmile¹; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki (¹GUAS)

With use of the Zhu-Nakamura formulas, the TSH method can be generalized so as to treat both classically allowed and forbidden transitions unformly. This new implementation is applicable to both crossing seam type and conical intersection type processes of high dimension.

I-E Theory of Nonadiabatic Transition

I-E-1 Analytic Solution to Wave Packet Dynamics in a Laser Field: The Case of Linear Chirp

NAKAMURA, Hiroki

[Chem. Phys. 295, 269–273 (2003)]

An analytical expression for the nonadiabatic transition probability is derived for the case that two linear potentials in coordinate space are coupled by a linearly chirped time-dependent laser field. This constitutes a solution to the wave packet dynamics in the high energy approximation. Numerical calculations are carried out to demonstrate the applicability of the formula.

I-E-2 Semiclassical Theory of Nonadiabatic Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir¹; USHAKOV, Vladimir¹; NAKAMURA, Hiroki

(¹Inst. Problems Chem. Phys., Russia)

[Russ. Chem. Phys. 22, 87 (2003)]

The semiclassical analysis is carried out for a twostate model potential system, in which two asymptotically degenerate Morse type potentials are coupled by an exponential diabatic coupling. Both crossing and non-crossing cases are treated and explicit analytical expressions for the full scattering matrix are obtained. The result can be used in a more general problem involving the present type of asymptotic transitions.

I-E-3 Analytical Treatment of S-P Type Collisional Resonant Excitation Transfer

OSHEROV, Vladimir¹; USHAKOV, Vladimir¹; NAKAMURA, Hiroki

(¹Inst. Problems Chem. Phys., Russia)

[Russ. Chem. Phys. 23, 103 (2003)]

The analytical solution developed in the previous paper is applied to the *S-P* type collisional resonant excitation transfer between atoms. The corresponding cross-sections are calculated in the high energy approximation. Good agreement is obtained with the results calculated previously by Watanabe with use of the fully numerical integration of the time-dependent coupled differential equations. This indicates usefulness of the present analytical theory developed in our previous papers.

I-E-4 Rabi Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

ISHKHANYAN, Artur¹; CHERNIKOV, G. P.²; NAKAMURA, Hiroki

(¹Engineering Cent. Armenian Natl. Acad. Sci., Armenia; ²Russian Res. Cent. "Kurchatov institute," Inst. Nuclear Fusion, Russia)

The dynamics of coherent Rabi oscillations in coupled atomic and molecular Bose-Einstein condensates is considered taking into account the atom-atom, atom-molecule and molecule-molecule elastic interactions. The exact solution for the molecule formation probability is derived in terms of the elliptic functions. The 2-dimensional space of the involved parameters is analyzed and divided into two regions where the Rabi oscillations show different characteristics. A resonance curve is found, on which the molecular formation probability monotonically increases as a function of time. The maximum value of the transition probability on this curve is 1 (*i.e.*, total transition to the molecular state) and it is achieved at high field intensities starting from a minimal threshold determined by the inter-species interaction scattering lengths. The explicit form of the resonance curve is determined, and it is shown that the resonance frequency position reveals a nonlinear dependence on the Rabi frequency of the applied field. A singular point is found on the resonance curve, where a power-law time evolution of the system is observed.

I-F Quantum Dynamics of Chemical Reactions

I-F-1 Full Quantum Dynamics of Atom-Diatom Chemical Reactions in Hyperspherical Elliptic Coordinates

KAMISAKA, Hideyuki¹; TOLSTIKHIN, Oleg I.²; NAKAMURA, Hiroki (¹Univ. Tokyo; ²Russian Res. Cent. "Kurchatov

Institute," Russia)

[J. Phys. Chem. in press]

Explicit expressions of the full Hamiltonian of triatomic system in the hyperspherical elliptic (HSE) coordinates are derived. The derivation is made from the expressions in the Delves coordinates. A numerical algorithm is also presented to evaluate the surface eigenfunctions including all the effects of Coriolis coupling terms. The whole formalism is numerically tested by using the Cl + DH and $O(^{1}D)$ + HCl reacton systems. The HSE coordinate system, which is wellknown to be powerful to elucidate reaction mechanisms especially for heavy-light-heavy systems, is now ready to be applied for clarifying full quantum dynamics of such systems.

I-F-2 Quantum Dynamics of O(¹D) + HCI Reactions

ZHAO, Yi¹; NANBU, Shinkoh; NAKAMURA, Hiroki

(¹IMS and Univ. Sci. Tech. China, China)

Quantum dynamics calculations of $O(^{1}D)$ + HCl are carried out with the three potential energy surfaces $(1^{1}A', 2^{1}A', 1^{1}A'')$ taken into account. The three accurate potential energy surfaces are already available (*J. Theor. Comput. Chem.* **1**, 263, 275, 285 (2002)).

I-G Theory of Multi-Dimensional Tunneling

I-G-1 On the Determination of Caustics

OLOYEDE, Ponmile¹; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

 $(^{1}GUAS)$

[J. Theor. Comput. Chem. 3, 91 (2004)]

This paper presents a numerical method which locates caustics of classical trajectories on-the-fly. The method is conceptually simple and is applicable to a system of arbitrary dimensions. The efficiency of the method is demonstrated by determining caustics of trajectories in the 2-D Henon-Heiles potential and of trajectories used to simulate a triatomic reaction process for J (total angular momentum) = 0.

I-G-2 Simple and Accurate Method to Evaluate Tunneling Splitting in Polyatomic Molecules

MIL'NIKOV, Gennady V.; YAGI, Kiyoshi¹; TAKETSUGU, Tetsuya²; NAKAMURA, Hiroki; HIRAO, Kimihiko¹

(¹Univ. Tokyo; ²Ochanomizu Univ.)

[J. Chem. Phys. 120, 5036 (2004)]

A practical and accurate semiclassical method for calculating the tunneling slpitting of the ground state in polyatomic molecules is presented based on a recent version of the instanton theory [J. Chem. Phys. 115, 6881 (2001)]. The method uses ab initio quantum chemical data for the potential energy surface without any concominant extrapolation and requires only a small number of *ab initio* data points to get convergence even for large molecules. This enables one to use an advanced level of electronic structure theory and achieve a high accuracy of the result. The method is applied to the 9-atomic malonaldehyde molecule by making use of the potential energy surface at the level of CCSD(T) with the hybrid basis set of aug-cc-pVTZ (for oxygen atoms and the transferred hydrogen atom) and cc-pVTZ (for other atoms).

I-G-3 Effect of Out-Of Plane Vibration on the Hydrogen Atom Transfer Reaction in Malonaldehyde

YAGI, Kiyoshi¹; MIL'NIKOV, Gennady V.; TAKETSUGU, Tetsuya²; HIRAO, Kimihiko¹; NAKAMURA, Hiroki

(¹Univ. Tokyo; ²Ochanomizu Univ.)

Tunneling splitting of the ground vibrational state is calculated for the planar model of malonaldehyde by the instanton method of Mil'nikov and Nakamura with use of *ab initio* potential energy surface. The planar model gives much larger tunneling splitting than the previous full dimensional calculations, indicating a strong effect of the anharmonic coupling between the in-plane and out-of-plane modes of the hydrogen atom. The anharmonicity is related to the Coriolis coupling between the OH stretching vibration and the pseudo-rotation of the hindered rotor. The present results suggest that the multidimensional effects should be carefully taken into account in the tunneling dynamics of polyatomic molecules.

I-G-4 Tunneling Splitting in Vinyl Radical C₂H₃

MIL'NIKOV, Gennady V.; ISHIDA, Toshimasa¹; NANBU, Shinkoh; NAKAMURA, Hiroki (¹Shizuoka Univ.)

Tunneling splitting of the ground vibrational state in vinyl radical is calculated with use of our theory developed before (*J. Chem. Phys.* **117**, 9588 (2002)). The potential energy surface is calculated accurately by the CCSD(T)/(aug-)cc-pvTZ method. The splitting obtained (= 0.53 cm^{-1}) is in very good agreement with the recent experiment (= 0.54 cm^{-1}) (*J. Chem. Phys.* **120**, 3604 (2004)).

I-G-5 Semiclassical Theory of Tunneling Splitting of Vibrationally Excited State

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The practical implementation of the instanton theory (*J. Chem. Phys.* **117**, 9588 (2002)) is extended so as to be applicable to vibrationally excited states. The effect of multi-dimensionality found before (*J. Chem. Phys.* **102**, 3977 (1995)) can now be nicely interpreted by the analytical expression.

I-H Laser Control of Molecular Processes

I-H-1 Semiclassical Formulation of Optimal Control Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[J. Theor. Comput. Chem. in press]

In the present paper semiclassical formulation of optimal control theory is made by combining the conjugate gradient search method with new approximate semiclassical expressions for correlation function. Two expressions for correlation function are derived. The simpler one requires calculations of coordinates and momenta of classical trajectories only. The second one requires extra calculation of common semiclassical quantities; as a result additional quantum effects can be taken into account. The efficiency of the method is demonstrated by controlling nuclear wave packet motion in a two-dimensional model system.

I-H-2 Control of Electronic Transitions of Wave Packet by Using Quadratically Chirped Pulses

ZOU, Shiyang; KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

We consider an effective scheme for the laser control of the nonadiabatic wave packet dynamics. It is shown that by using specially designed quadratically chirped pulse one can achieve fast and complete excitation of the wave packet without distortion of its shape. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura (ZN) theory regardless of the dimensionality of the system. The efficiency of the laser control scheme is demonstrated by several examples: complete $B^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ excitation in LiH, control of the wave packet dynamics in Nak by using pump-dump mechanism and the bond selective photodissociation of H₂O.

I-H-3 Selective Excitation to Closely-Lying Cs $(7D_{3/2})$ and Cs $(7D_{5/2})$ by Femtosecond Laser Pulses

YAMADA, H.^{1,2}; YOKOYAMA, K.^{1,3}; TERANISHI, Y.¹; SUGITA, A.¹; YAMAKAWA, K.¹; KAWASAKI, M.²; YOKOYAMA, A.³; NAKAMURA, Hiroki

(¹JARI.; ²Kyoto Univ.; ³Japan Atomic Energy Res. Inst.)

Ultrafast selection of closely lying excited states with a broadband light source is reported for a demonstration of precise coherent quantum control based on pulse shaping technique. Transform-limited pulses emitted from a Ti:Sapphire oscillator were shaped to phase-locked pulse pairs by an acousto-optic programmable dispersive filter and focused into cesium vapor to excite the atoms in the ground state to the $Cs(7D_{3/2})$ and $Cs(7D_{5/2})$ states *via* two-photon absorption. The relative excitation probability to each spin-orbit state was measured through the fluorescence to the $Cs(6P_{1/2})$ and Cs(6P_{3/2}) states, and was found to exhibit complete modulation with a period of π as a function of the phase-difference between two pulses. At the destructive phase, the fluorescence vanished below the detection limit. The best contrast of the selection ratio exceeded a thousand within 400-fs delay.

I-I Development of New Molecular Functions

I-I-1 Conversion between Cyclohexadiene and Hexatriene as a Model of Photochromism

TAMURA, Hiroyuki; NANBU, Shinkoh; ISHIDA, Toshimasa¹; NAKAMURA, Hiroki (¹Shizuoka Univ.)

High level of quantum chemical calculations of potential energy surfaces of the title molecules have been carried out. The conical intersection between 2'A and 1'A states, which is expected to play an important role for the photo conversion, has been found and the previously reported results are found to be not necessarily accurate. The corresponding dynamics calculations will be carried out.

I-I-2 Transmission of Atoms through Ring Molecules as a Model of Encapsulation by Carbon Nanotubes

NANBU, Shinkoh; ISHIDA, Toshimasa¹; NAKAMURA, Hiroki (¹Shizuoka Univ.)

The systems composed of ring molecules such as $C_{20}H_{10}$ and atoms such as H, Na, and Li have been studied quantum chemically and dynamically. It is found that in the case that five carbon atoms are replaced by borons nonadiabatic transitions between ground and first excited adiabatic states play a crucial role and hydrogen atom can transmit the ring with high efficiency by appropriately adjusting its translational energy.

I-J Theoretical Studies of Electron Dynamics in Molecular Systems

Electron dynamics in molecular systems is an intrinsic process in a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

I-J-1 High-Order Harmonic Generation from Silver Clusters: Laser-Frequency Dependence and the Screening Effect of *d* Electrons

NOBUSADA, Katsuyuki; YABANA, Kazuhiro¹ (¹Univ. Tsukuba)

[Phys. Rev. A 70, 043411 (7 pages) (2004)]

We present time-dependent density functional studies of harmonic generation from Ag₂ and Ag₈ in pulsed laser fields. The harmonic generation is strongly dependent on the laser frequency. The harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. Such resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence s-electrons are shaken effectively at the tuned laser frequency and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have found that the polarizable core d-electrons significantly screen the valence selectrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The screening effect of the *d* electrons becomes more important in the system of Ag₈ than Ag₂.

I-J-2 Multiple Ionization of a Silver Diatomic Molecule in an Intense Laser Field

SHIRATORI, Kazuya¹; NOBUSADA, Katsuyuki; YABANA, Kazuhiro²

(¹Hokkaido Univ.; ²Univ. Tsukuba)

[Chem. Phys. Lett. to be submitted]

Time-dependent density functional studies of multiple ionization of Ag₂ in an intense laser field 10¹⁴ W/cm² are presented. Special emphasis is placed on elucidating frequency dependence and an effect of the delectrons on the ionization processes. The multiple ionization occurs depending non-monotonically on the laser frequency. The valence s electrons are earlier emitted from the molecules, especially when the applied laser field is in tune with the dipole resonance frequency of the system, and then the *d*-electron emission occurs. Differently from the valence s-electrons, the d electrons are emitted more efficiently with increasing the laser frequency. We have computationally demonstrated that the s and d electrons move reciprocally toward the opposite directions such that the *s*-electron density induced in the laser field is cancelled out. This screening effect of the d electrons suppresses the multiple ionization in comparison with molecular systems without inner-shell electrons such as alkali metal clusters.

I-K Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide significantly different physicochemical properties such as optical response, catalysis, and reactivity from corresponding bare metal clusters or bulk metals. We have investigated electronic structures and photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-K-1 Electronic Structure and Photochemical Properties of a Monolayer-Protected Gold Cluster

NOBUSADA, Katsuyuki

[J. Phys. Chem. B 108, 11904–11908 (2004)]

The electronic structure of a monolayer-protected

gold cluster, $[Au_{13}(SCH_3)_8]^{3+}$, has been investigated by performing density functional calculations. The cluster has a characteristic structure with O_h molecular symmetry and eight (111) facets of a centered cuboctahedral Au_{13} core cluster are fully passivated by eight methanethiolates. The bond distance between two neighboring gold atoms (= 3.673 Å) is much larger than that of the bare Au_{13} cluster (= 2.929 Å), whereas the Au–S bond distance is 2.403 Å. These atomic rearrangement means that the methanethiolates stabilize the enlarged bare Au_{13} cluster by bonding to the (111) hollow sites of the bare cluster. The absorption spectrum of the $[Au_{13} (SCH_3)_8]^{3+}$ cluster is simulated within time-dependent density functional theory. The spectrum shows clear absorption peaks and each peak is assigned to specific excitation processes.

I-L Electronic Structure of a Molecule in Solution

Chemical reaction is undoubtedly the most important issue in the theoretical chemistry, and the electronic structure is a key to solve the problem. As long as molecules in the gas phase are concerned, the theory for the electronic structure has been enjoying its great success. However, when it comes to molecules in solution, the stage of theory is still an infant. We have recently proposed a new method refereed to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the ab initio electronic structure theory (SCF).¹⁾ The integral equation approach replaces the reaction field in the continuum models by a microscopic expression in terms of the site-site radial distribution functions between solute and solvent.

$$V_{\lambda} = \sum_{j} \int 4\pi r^2 \frac{q_j}{r} g_{j\lambda}(r) dr$$

where *j* and λ specify solvent and solute sites, respectively, and *r* denotes the solvent density. The site-site radial distribution functions $g_{\lambda j}(r)$ can be calculated from the extended RISM equation. Using V_{λ} the solvated Fock operator is defined as,

$$F^s = F^g - \sum_{\lambda} V_{\lambda} b_{\lambda}$$

where b_{λ} is a population operator of solute atoms. The statistical solvent distribution around solute is determined by the electronic structure or the partial charges of solute, while the electronic structure of solute is influenced by the solvent distribution. Therefore, the Hartree-Fock equation and the RISM equation should be solved in a selfconsistent manner. It is this self-consistent determination of the solute electronic structure and the solvent distribution around the solute that features the RISM-SCF procedure.

The same Fock operator can be derived from a variation principle.²⁾ Defining the Helmholtz free energy A as follows;

$$A = E_{solute} + \Delta \mu$$

where E_{solute} is the energy of solute under solvent influence, and $\Delta\mu$ is the solvation free energy represented in terms of the Singer-Chandler formula. The Fock operator for a solute molecule in solvent as well as the RISM-HNC equations can be obtained as the first order variations with respect to the wave functions and the pair correlation functions under the constraint of the orthonormality to the molecular orbitals. The latest development along this line are reported below.

References

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I-L-1 A Quantum Solute-Solvent Interaction Using Spectral Representation Technique Applied to the Electronic Structure Theory in Solution

YAMAZAKI, Takeshi; SATO, Hirofumi¹; HIRATA, Fumio

(¹Kyoto Univ.)

[J. Chem. Phys. 119, 6663–6670 (2003)]

In this paper, we present a new approach to treat the electronic structure of a molecule in solution. Unlike the hybrid-type method such as the reference interaction site model self-consistent-field(RISM-SCF) theory, the new approach describes not only the electronic structure of solute but also solute-solvent interactions in terms of the quantum chemistry based on the Hartree-Fock frozen density formulation. In the treatment, the quantum effect due to solvent, including exchange repulsion, is projected on to the solute Hamiltonian using the spectral representation method. The solvent distribution around the solute is handled by the integral equation

theory of liquids. As illustrative applications of the approach, the electronic and solvation structure of noble atoms, neon and argon, in liquid neon are studied. We also investigate the electronic structure of an excess electron in liquid helium. The preliminary results demonstrate that the quantum mechanical effect on the electronic and solvation structure of the solute due to solvent molecules is successfully represented by the new method.

I-L-2 Distortion of Electronic Structure in Solvated Molecules: Tautomeric Equilibrium of 2-Pyridone and 2-Hydroxypridine in Water Studied by the RISM-SCF/MCSCF Method

SATO, Hirofumi¹; HIRATA, Fumio; SAKAKI, Shigeyoshi¹ (¹Kyoto Univ.)

[J. Phys. Chem. A 108, 2097–2102 (2004)]

As well recognized, the electronic structure of a molecule in the solution phase is distorted from that in

the gas phase. We present a new procedure that enables us to partition the electronic distortion energy caused by solvation into the energy contribution of each atom (or each moiety), with which one can evaluate the atomiclevel change of electronic structure. In the present study, we combine the procedure with the RISM-SCF method that can treat solvent molecules explicitly. This method is successfully applied to the tautomerization of 2pyridone in aqueous solution, whose equilibrium is known to show a marked solvation effect, and provides us a new detailed feature of this equilibrium. (1) As expected, electronic structures of oxygen and nitrogen atoms, which are strongly solvated, are distorted significantly. (2) However, the electronic distortion energies of the oxygen and nitrogen atoms are considerably compensated by the microscopic solvation. (3) One of the determining factors of the equilibrium is the carbon atom, with which the oxygen atom is bound, because the electronic distortion cannot be compensated by the microsolvation due to its rather inside position, and (4) the other factor is the distortion energy of the proton that directly relates to the equilibrium probably because the electronic structure changes too much to be compensated by microsolvation. These new findings lead to deep and correct understanding of this equilibrium.

I-L-3 Theoretical Study on Electronic and Solvent Reorganization Associated with a Charging Process of Organic Compounds: II. A New Decomposition Procedure into Electrostatic and Non-Electrostatic Responses

SATO, Hirofumi¹; KOBORI, Yasuhiro²; TERO-KUBOTA, Shozo³; HIRATA, Fumio

(¹Kyoto Univ.; ²Univ. Chicago, USA; ³Tohoku Univ.)

[J. Phys. Chem. B 108, 11709–11715 (2004)]

A new procedure, which enables us to decompose the solvent reorganization energy into electrostatic and nonelectrostatic contributions, is proposed. By using the procedure proposed by us very recently (*J. Phys. Chem. A* **106**, 2300–2304 (2002)), the solvent reorganization process and electronic structures of *N*,*N*-dimethylaniline (DMA) and 1,4-dimethoxybenzene (DMB) associated with a charging process in acetonitrile solution are studied at the molecular level on the basis of the ab initio reference interaction site model-self-consistent field (RISM-SCF) method. Differences as well as similarities between the solvation processes of the two molecules are discussed on the basis of the newly proposed method.

I-L-4 Superexchange Electron Tunneling Mediated by Solvent Molecules: Pulsed Electron Paramagnetic Resonance Study on Electronic Coupling in Solvent-Separated Radical Ion

KOBORI, Yasuhiro¹; YAGO, Tomoaki²; AKIYAMA, Kimio²; TERO-KUBOTA, Shozo²; SATO, Hirofumi³; HIRATA, Fumio; NORRIS, James R. Jr.¹

(¹Univ. Chicago, USA; ²Tohoku Univ.; ³Kyoto Univ.)

[J. Phys. Chem. B 108, 10226–10240 (2004)]

Nanosecond pulsed electron paramagnetic resonance spectroscopy is applied to characterize exponential decay constants (β) of the squared electronic coupling matrix element (V_{DA}^2) in transient, solvent-separated radical ion pairs (RIP) composed of quinone anions and several cation radicals in aprotic liquid solutions of N,N-dimethylformamide, DMSO, and benzonitrile. The distance dependence of singlet-triplet energy splitting (2J) is shown to be described by β in V_{DA} for chargerecombination processes. We show that the radical pair mechanism (RPM) electron spin polarization (P_{RPM}) is quite sensitive to β . The β value is characterized by using the stochastic Liouville equation to fit the experimental P_{RPM} values. The β values (from 0.8 to 1.0 Å⁻¹) manifest that V_{DA} is governed by the superexchange mechanism mediated by the intervening solvent molecules from a result that the β increases with increasing the tunneling energy gap (ΔG_{eff}) for solvent oxidation or reduction in several intermolecular electron-transfer systems. We propose a simple three-dimensional model of V_{DA}, in which the through-solvent tunneling pathways are exponentially increased with the increase in the intermolecular distance in bulk, condensed media. This model explains the ΔG_{eff} dependence of β , including the data previously reported on the charge-transfer reactions both in liquid and frozen (77 K) solutions. Effective solvent-solvent coupling is estimated to be $v_{\rm B}$ $\approx 850 \text{ cm}^{-1}$ at a mean nearest-neighbor distance of 5.7 Å. This relatively large magnitude of $v_{\rm B}$ may agree with dynamical amplifications of the effective coupling by low-frequency motions of the mediators as reported in charge-transfer reactions in biological systems. (Balabin, I. A. and Onuchic, J. Science 290, 114 (2000) and Troisi, A. and Orlandi, G. J. Phys. Chem. B 106, 2093 (2002).)

I-M Solvation Thermodynamics of Protein and Related Molecules

Concerning biomolecules such as protein, it is a final goal for the biochemistry and biophysics to explore the relation between conformations and biological functions. The first important step toward the goal would be to explain the conformational stability of biomolecules in terms of the microscopic structure of the molecules in

solvent. It is an extremely difficult problem by any means due to the overwhelmingly large degrees of freedom to be handled, including protein and solvent. As long as the small and/or short-time fluctuations of protein around the native structure is concerned, a variety of molecular simulation techniques provides a quite powerful tool to explore the microscopic structure of protein and solvent. However, the techniques are not so effective to characterize stability of the macromolecules in solution, to which the thermodynamic limit ($V \rightarrow \infty, N \rightarrow \infty$, with V/N = const.) is concerned. In such a case, methods based on the statistical mechanics of liquids should be natural choice for sampling configurations of solvent interacting biomolecules. The extended RISM theory is the most promising candidate of such methods, which provides not only solvation thermodynamics but also microscopic description at the level of the pair correlation functions.¹) Obvious technical difficulties which one may face in applying the theory to such a large system are not only the computation time but also the stability of the numerical solution.²

Here, we present our recent effort to tackle the problem using the two theoretical tools based on the statistical mechanics of liquids: the extended RISM and the scaled particle theories (SPT).³⁾ The studies for the solvation thermodynamics of small molecules such as ions are also included because it is regarded as elementary processes for the solvation of biomolecules, and because it is prerequisite for studying the more complicated molecules.

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1-M-1 Solvation Thermodynamics of Protein Studied by the 3D-RISM Theory

IMAI, Takashi¹; KOVALENKO, Andriy F.²; HIRATA, Fumio

(¹Ritsumeikan Univ.; ²NRC, Canada)

[Chem. Phys. Lett. 395, 1–6 (2004)]

The partial molar volume and the solvation free energy of five globular proteins in aqueous solutions are calculated by the three-dimensional reference interaction site model (3D-RISM) theory, a modern integral equation theory of molecular liquids.

The partial molar volume calculated by the theory shows quantitative agreement with the corresponding experimental data. Concerning the solvation free energy, the theoretical results are compared with estimations by an empirical method which uses the accessible surface area of atoms, because the corresponding experimental data are not available.

Possible applications of the method to problems related to the solvation thermodynamics of protein are discussed.

I-N Collective Density Fluctuations in Polar Liquids and Their Response to Ion Dynamics

As to the model for molecular diffusion in polar liquids, there are two quite different points of view. One is the conventional rot-translation model, and the other the interaction-site description which sees the diffusion of a molecule as a correlated motion of each atom (site).¹⁾ It is clearly advantageous to use the interaction-site description compared to the rot-translation model to account for chemical characteristics of solvent as well as solute dynamics. However, the interaction-site description has its own disadvantage in interpreting physical meaning of the results, since it does not give an explicit picture for the rotational relaxation of molecules, which can be directly probed by many experimental means including the dielectric and NMR relaxation. We have solved the problem by extracting collective modes of the density fluctuation from the site-site density correlation functions. In our recent study for dynamics of molecular liquids based on the interaction-site model, we have succeeded to abstract the collective excitations in liquids, which can be identified as optical and acoustic modes, by diagonalizing the collective frequency matrix appearing in the generalized Langevin equation. The two modes arise essentially from the rotational and translational motions of molecules.²⁾ We applied the method to the ion dynamics in a dipolar liquid, and could have explained successfully the peculiar size dependence of friction of alkali and halide ions in terms of response of the collective excitations in solvent to the solute displacement.³⁾

In the past year, we have elaborated the memory kernel in our generalized Langevin equation base on the mode coupling theory. We have also extended our treatment to dynamics of water and hydrated ions. Those studies as well as other related topics are reviewed below.

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I-N-1 A Mode-Coupling Analysis of the Translational and Rotational Diffusion of Polar Liquids; Acetonitrile and Water

YAMAGUCHI, Tsuyoshi¹; CHONG, Song-Ho; HIRATA, Fumio (¹Nagoya Univ.)

[J. Mol. Liq. 112/3, 117-124 (2004)]

The translational and rotational motions of two representative polar liquids,water and acetonitrile, are investigated by the mode-coupling theory for molecular liquids based on the interaction-site model. The diffusive motion of acetonitrile agrees fairly well with that from the molecular-dynamics simulation. The pressure dependence of the translational and rotational diffusion coefficients is also in qualitative agreement with experiments. However, the reorientational relaxation of water is predicted to be much faster than that from experiments or simulations. The agreement between the theory and the simulation is partly improved by using the dynamic structure factor determined by the simulation. The effect of three-site correlation in the mode-coupling expression of the memory function is also examined. I-N-2 Pressure Dependence of Diffusion Coefficient and Orientational Relaxation Time for Acetonitrile and Methanol in Water: DRISM/Mode-Coupling Study

KOBRYN, Alexander E.; YAMAGUCHI, Tsuyoshi¹; HIRATA, Fumio (¹Nagoya Univ.)

[J. Mol. Liq. in press]

We present results of theoretical description and numerical calculation of the dynamics of molecular liquids based on the Reference Interaction Site Model/ Mode-Coupling Theory. They include the temperaturepressure (density) dependence of the translational diffusion coefficients and orientational relaxation times for acetonitrile and methanol in water at infinite dilution. Anomalous behavior, i.e. the increase in mobility with density, is observed for the orientational relaxation time of methanol, while acetonitrile does not show any deviations from the usual. This effect is in qualitative agreement with the recent data of MD simulation and with experimental measurements, which tells us that presented theory is a good candidate to explain such kind of anomalies from the microscopical point of view and with the connection to the structure of the molecules.

I-O Statistical Mechanics of Interfacial Fluids

Microscopic structure of fluid interfaces has been drawing a lot of attention due to recent development in the experimental techniques devised particularly to probe the interface. However, there are many open questions remained unanswered. For example, how wide is the interfacial region, how does it depend on the chemical species consisting the solution? Is the interface more or less homogeneous in terms of density or concentration of the two fluids, or is it spatially inhomogeneous? If it is inhomogeneous, what is the spatial extent of the inhomogeneity? Answering those questions is the most difficult and challenging tasks for theoretical physics and chemistry, and not much progress has been made in the past, especially from a molecular view point. We have been developing statistical mechanics for two different types of interfacial fluids: fluid-fluid interface and fluids in porous media. Following are the latest achievement in that direction.

I-O-1 Molecular Description of Electrolyte Solution in a Carbon Aerogel Electrode

KOVALENKO, Andriy F.¹; HIRATA, Fumio (¹NRC, Canada)

[Cond. Matt. Phys. 6, 583-609 (2003)]

We develop a molecular theory of aqueous electrolyte solution sorbed in a nanoporous carbon aerogel electrode, based on the replica reference interaction site model (replica RISM) for realistic molecular quenchedannealed systems. We also briefly review applications of carbon aerogels for supercapacitor and electrochemical separation devices, as well as theoretical and computer modelling of disordered porous materials. The replica RISM integral equation theory yields the microscopic properties of the electrochemical double layer formed at the surface of carbon aerogel nanopores, with due account of chemical specificities of both sorbed electrolyte and carbon aerogel material. The theory allows for spatial disorder of aerogel pores in the range from micro- to macroscopic size scale. We considered ambient aqueous solution of 1 M sodium chloride sorbed in two model nanoporous carbon aerogels with carbon nanoparticles either arranged into branched chains or randomly distributed. The long-range correlations of the carbon aerogel nanostructure substantially affect the properties of the electrochemical double layer formed by the solution sorbed in nanopores.

I-O-2 Microscopic Description of a Liquid-Vapor Interface by an Inhomogeneous Integral Equation Theory

OMELYAN, Ihor¹; KOVALENKO, Andriy F.²; HIRATA, Fumio

(¹Inst. Cond. Matt. Phys., Ukraine; ²NRC, Canada)

[Chem. Phys. Lett. in press]

We developed an inhomogeneous integral equation theory yielding the inhomogeneous pair correlation functions as well as the density profiles of the liquidvapor interface of simple fluid. We analytically derived the long-range asymptotics of the inhomogeneous pair distribution along the interface, related to capillary waves. We showed that their physical nature is the same as long-range fluctuations of critical fluid which are restricted to the two-dimensional interfacial region by the external field shaping the interface.

I-P Photoinduced Phase Transitions in Spin-Crossover and Charge-Transfer Complexes

Now a variety of materials show photoinduced phase transitions. Their characters depend much on the relative importance of the interactions inside the system to those between the system and the heat bath. If the former are dominant, the time evolution is deterministic allowing coherent oscillations for instance. If the latter are dominant, the time evolution is stochastic and the efficiency is generally low. These characters depend also on the time scale. For long-time properties, dissipation generally obscures the deterministic evolution. Thus we need to employ both the deterministic approach with the help of the time-dependent Schrödinger equation and the stochastic approach with the help of the master equation. The macroscopic coherent oscillation of the neutral-ionic domain walls in the TTF-CA complex needs to be described by the former approach. Meanwhile, the photoinduced neutral-to-ionic transition accompanied with ferroelectric ordering in the same material by pump light for intra-molecular excitations would be described by the latter approach. Low-spin-to-high-spin transitions in organometal spin-crossover complexes are well described by the stochastic approach because the evolution is governed by thermal processes.

I-P-1 On Thermo- and Photo-Induced Symmetry-Broken Transformation in Spin-Crossover Complex; Cooperative Activation

LUTY, Tadeusz¹; YONEMITSU, Kenji (¹IMS and Tech. Univ. Wroclaw)

[J. Phys. Soc. Jpn. 73, 1237–1243 (2004)]

We study energetics of a cooperative low-spin (L) to high-spin (H) transformation in a crystal with two sublattices, where thermo- and photo-induced symmetrybroken phases have been recently observed. The model takes into account an intra-dimer antiferroic coupling and inter-dimer couplings. Cooperative activation processes for switching between LH and HL states and that from LL to HH states of a dimer are analyzed. It is shown that locally (within a dimer) preferred symmetrybroken, LH and HL, states compete with inter-dimer couplings, which stimulates dynamical disorder via a decrease in the energy barrier for a flip between asymmetric configurations. On the other hand, a locally nonpreferred symmetric state (HH) is supported by interdimer interaction via a cooperative activation mechanism. We conclude that symmetry-broken states can form an intermediate thermo-induced phase or can be observed as a photo-induced one at low temperatures as a result of local equilibrium. The global equilibrium follows from cooperative interaction and governs the thermo-induced re-entrant phase transition.

I-P-2 Different Stabilities of the Mixed-Spin Phase in Equilibrium from That in Non-Equilibrium in a Two-Sublattice Classical-Spin Model for Spin-Crossover Complexes

OTSUKA, Yuichi; YONEMITSU, Kenji

Some spin-crossover complexes show two-step transitions by changing temperature between high-spin and low-spin phases in equilibrium. In $[Fe(2-pic)_3]$ Cl_2 ·EtOH, high-spin-low-spin ordering is recently observed on the 50% plateau of high-spin fraction at intermediate temperatures. However, the time evolution of this material under continuous photoirradiation does not clearly show the high-spin-low-spin-ordered phase even transiently. We employ a two-sublattice classicalspin model, where an intra-dimer inter-sublattice antiferroic coupling prefers the intermediate phase while an inter-dimer intra-sublattice ferroic coupling the uniformly high-spin or low-spin phase. Although an interdimer inter-sublattice coupling plays the same role with the intra-dimer inter-sublattice coupling at the meanfield level, we find by Monte Carlo simulations that their effects are different especially when the material is under photoirradiation. The inter-dimer coupling so enhances the short-range spin-spin correlation as to give larger deviation from the mean-field results than the intra-dimer coupling. This effect makes the appearance of the high-spin-low-spin-ordered phase difficult in nonequilibrium conditions.

I-P-3 Inter-Chain Electrostriction and Pressure-Induced Multicriticality in Charge-Transfer Organic Complexes

KISHINE, Jun-ichiro¹; LUTY, Tadeusz²; YONEMITSU, Kenji

(¹Kyushu Inst. Tech.; ²IMS and Tech. Univ. Wroclaw)

[Proc. Int. Conf. Sci. Tech. Synth. Met. (2004)]

Pressure-induced multicriticality in the quasi-onedimensional mixed-stack charge-transfer complex TTF-CA is theoretically explained. We show that the interstack electrostriction (Coulomb-lattice coupling) is essential to cause multi-critical phase transitions among the neutral, paraelectric ionic, and ferroelectric ionic phases.

I-P-4 Stochastic Approach to Evolution of Ionicity and Ferroelectricity in Mixed-Stack Organic Charge-Transfer Complexes by the Blume-Emery-Griffiths Model

INOUE, Hitoshi; YONEMITSU, Kenji

Mixed-stack organic charge-transfer complexes show neutral-ionic and dimerization-induced ferroelectric phase transitions. In the most famous TTF-CA complex, they occur simultaneously at ambient pressure but at different temperatures under high pressure. Thus we treat both the ionicity and the dimerization using the Blume-Emery-Griffiths model. Long-time evolution is studied by solving the master equation during and after photoirradiation of the complex. As a first step, we use the mean-field approximation that does not distinguish the intra- and inter-chain couplings. The time evolution of the ionicity and that of the ferroelectricity generally take place on different time scales, allowing the transient appearance of the paraelectric ionic phase. We find photoinduced breaking of the inversion symmetry and spontaneous ordering of electric polarizations leading to the ferroelectric ionic phase after the neutral phase is photoexcited and converted into the paraelectric ionic phase. This would explain the recent experimental findings with intra-molecular excitations.

I-P-5 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: I. Threshold Behavior in Ionic-to-Neutral Transition

YONEMITSU, Kenji

[J. Phys. Soc. Jpn. 73, 2868–2878 (2004)]

Photoinduced dynamics of charge density and lattice displacements is calculated by solving the timedependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials for the mixed-stack organic charge-transfer complex, TTF-CA. A pulse of oscillating electric field is incorporated into the Peierls phase of the transfer integral. The frequency, the amplitude, and the duration of the pulse are varied to study the nonlinear and cooperative character of the photoinduced transition. When the dimerized ionic phase is photoexcited, the threshold behavior is clearly observed by plotting the final ionicity as a function of the increment of the total energy. Above the threshold photoexcitation, the electronic state reaches the neutral one with equidistant molecules after the electric field is turned off. The transition is initiated by nucleation of a metastable neutral domain, for which an electric field with frequency below the linear absorption peak is more effective than that at the peak. When the pulse is strong and short, the charge transfer takes place on the same time scale with the disappearance of dimerization. As the pulse becomes weak and long, the dimerization-induced polarization is disordered to restore the inversion symmetry on average before the charge transfer takes place to bring the system neutral. Thus, a paraelectric ionic phase is transiently realized by a weak electric field. It is shown that infrared light also induces the ionic-toneutral transition, which is characterized by the threshold behavior.

I-P-6 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: II. Linear Behavior in Neutral-to-Ionic Transition

YONEMITSU, Kenji

[J. Phys. Soc. Jpn. 73, 2879–2886 (2004)]

Dynamics of charge density and lattice displacements after the neutral phase is photoexcited is studied by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials. In contrast to the ionic-toneutral transition studied previously, the neutral-to-ionic transition proceeds in an uncooperative manner as far as the one-dimensional system is concerned. The final ionicity is a linear function of the increment of the total energy. After the electric field is turned off, the electronic state does not significantly change, roughly keeping the ionicity, even if the transition is not completed, because the ionic domains never proliferate. As a consequence, an electric field with frequency just at the linear absorption peak causes the neutral-to-ionic transition the most efficiently. These findings are consistent with the recent experiments on the mixed-stack organic chargetransfer complex, TTF-CA. We artificially modify or remove the electron-lattice coupling to discuss the origin of such differences between the two transitions.

I-P-7 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: III. Interference Caused by a Double Pulse

YONEMITSU, Kenji

[J. Phys. Soc. Jpn. 73, 2887–2893 (2004)]

In order to study consequences of the differences between the ionic-to-neutral and neutral-to-ionic transitions in the one-dimensional extended Peierls-Hubbard model with alternating potentials for the TTF-CA complex, we introduce a double pulse of oscillating electric field in the time-dependent Schrödinger equation and vary the interval between the two pulses as well as their strengths. When the dimerized ionic phase is photoexcited, the interference effect is clearly observed owing to the coherence of charge density and lattice displacements. Namely, the two pulses constructively interfere with each other if the interval is a multiple of the period of the optical lattice vibration, while they destructively interfere if the interval is a half-odd integer times the period, in the processes toward the neutral phase. The interference is strong especially when the pulse is strong and short because the coherence is also strong. Meanwhile, when the neutral phase is photoexcited, the interference effect is almost invisible or weakly observed when the pulse is weak. The photoinduced lattice oscillations are incoherent due to random phases. The strength of the interference caused by a double pulse is a key quantity to distinguish the two transitions and to evaluate the coherence of charge density and lattice displacements.

I-P-8 Theory of Optical Phase Control in Charge-Transfer Complexes

YONEMITSU, Kenji

[Proc. Int. Conf. Sci. Tech. Synth. Met. (2004)]

Concerning the paraelectric ionic phase in the

mixed-stacked organic charge-transfer TTF-CA complex, which needs high pressure to realize in thermal equilibrium or some particular photoexcitation to transiently realize at ambient pressure and low temperatures, we theoretically point out that photoexcitations with appropriate strength and duration can generally produce this phase. Photoinduced chargelattice dynamics is calculated in a one-dimensional extended Peierls-Hubbard model with alternating potentials during and after a pulse of oscillating electric field. When the field is so weak and long that the supplied energy does not directly transfer charge in the ionic phase, the dimerization-induced charge polarizations are disordered first to restore the inversion symmetry on average before the neutral phase appears. The interference effect observed after a double pulse due to the charge-lattice coherence is accordingly weakened.

I-P-9 Theory of Photoinduced Phase Dynamics in Organic Charge-Transfer Complexes

YONEMITSU, Kenji

[J. Lumin. in press]

In the quasi-one-dimensional mixed-stack organic charge-transfer complex, TTF-CA, photoirradiation is known to trigger transitions between the neutral and ionic phases. Here we use a one-dimensional extended Peierls-Hubbard model with alternating potentials and calculate the mean-field dynamics of charge density coupled with that of lattice displacements. We show qualitative differences between the photoinduced ionicto-neutral and neutral-to-ionic transitions, which are consistent with recent experimental findings. Namely, the ionic-to-neutral transition proceeds cooperatively, characterized by threshold behavior, while the neutralto-ionic transition proceeds uncooperatively, characterized by linear behavior. The threshold absorption in the former depends on the strength or the duration of the pulse. The coherence during the transition dynamics is also different between the two transitions. In the ionicto-neutral transition, a clear interference effect is observed as a function of the interval when the pulse is spilt into two.

I-Q Theoretical Studies on Chemical Reactions and Molecular Dynamics of Polyatomic Molecules in Condensed Systems

In a lot of chemical, biological and environmental phenomena, the chemical reactions and molecular dynamics *in solution* or *across interface* play a very important role, where the microscopic solvation structures of solute molecules offer essential and inevitable information. In this project, to obtain a stationary point on a multidimensional free energy surface (FES), *e.g.*, stable state (SS) or transition state (TS) in solution chemical reaction, a new optimization method, *i.e.*, the free energy gradient (FEG) method, has been developed and were applied to obtain the hydrated structure and TS in the ionization process of ammonia molecule in aqueous solution.

I-Q-1 Hydrated Structure of Ammonia-Water Molecule Pair *via* Free Energy Gradient Method: Realization of Zero Gradient and Force Balance on Free Energy Surface

NAGAE, Yukihiko¹; OISHI, Yuki¹; NARUSE, Norihiro¹; NAGAOKA, Masataka² (¹Nagoya Univ.; ²IMS and Nagoya Univ.)

[J. Chem. Phys. 119, 7972–7978 (2003)]

The hydrated structure of ammonia molecule in aqueous solution was theoretically optimized as an ammonia-water molecule pair (H₃N···H₂O) by the FEG method [J. Chem. Phys. 113, 3516 (2000)]. The interaction between the pair and a solvent water molecule (TIP3P) [J. Chem. Phys. 79, 926 (1983)] was described by a hybrid quantum mechanical and molecular mechanical (QM/MM) method combined with a semiempirical molecular orbital (MO) method at the PM3 level of theory. It is concluded that the present FEG method works quite well in spite of a simple steepest descent optimization scheme equipped with the adaptive displacement vector. The free energy stabilization was estimated -0.3 kcal/mol from the free energy for the same structure as that of the cluster in gas phase. The optimized structure was found to be almost the same as that in the gas phase except a longer OH bond length of the water molecule. However, its realization in aqueous solution is accomplished by virtue of fulfillment of both "zero gradient" and "force balance" conditions. Finally, we discussed also the effect of microscopic "solvation entropy," compared with the result by the conductorlike screening model (COSMO) method.

I-Q-2 Structure Optimization of Solute Molecules *via* Free Energy Gradient Method

NAGAOKA, Masataka

(IMS and Nagoya Univ.)

[Bull. Korean Chem. Soc. 24, 805–808 (2004)]

Fundamental ideas of the free energy gradient method are briefly reviewed with three applications: the stable structures of glycine and ammonia-water molecule pair in aqueous solution and the transition state (TS) structure of a Menshutkin reaction $NH_3 + CH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$ in aqueous solution, which is

the first example of full TS optimization of all internal degrees of freedom.

I-Q-3 Slowdown of Water Diffusion around Protein in Aqueous Solution with Ectoine

YU, Isseki¹; NAGAOKA, Masataka² (¹Nagoya Univ.; ²IMS and Nagoya Univ.)

[Chem. Phys. Lett. 388, 316-321 (2004)]

Ectoine is one of the most common compatible solutes found in halophilic bacteria, and has an effect to introduce a tolerance to high salt concentration or high temperature. By analyzing 1 ns molecular dynamics simulations at 370 K, we have shown that, in the ectoine aqueous solution, the water diffusion slows down around a protein (chymotrypsin inhibitor 2 (CI2)), keeping the protein hydration structure essentially unchanged. It is concluded that the slowdown of water diffusion around the backbone amide protons must be one of the decisive factors in reducing the exchange rate of the backbone amide protons, whose reduction is experimentally believed closely related to the tolerance effect.

I-R Theory and Applications of Relativistic Quantum-Chemical Methods to Molecular Properties of Compounds Containing Heavy Elements

Accurate quantum-chemical calculations of molecular properties which are concerned with a magnetic field and/or an electron spin distribution are required well-correlated and relativistic quantum-chemical theories, especially when the molecules contain heavy elements. Paramagnetic NMR chemical shifts of Fe-complexes, heavy-element NMR of halogen compounds, and magnetic circular dichroism (MCD) of halogen compounds are listed below. The 2nd-order Douglas-Kroll quantum-chemical theory including a magnetic field is also presented.

I-R-1 Quantum-Chemical Calculations for Para-Magnetic ¹³C NMR Chemical Shifts of Iron-Bound Cyanide Ions of Iron Porphyrins in Ground and Low-Lying Excited States Containing Ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1$ $(d_{xz,yz})^4$ Configurations

HADA, Masahiko

(IMS and Tokyo Metropolitan Univ.)

[J. Am. Chem. Soc. 126, 486-487 (2004)]

The objectives of this brief communication are as follows. (i) Using an accurate quantum-chemical method, SAC/SAC-CI, we present accurate energy-levels for ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ in bis (cyanide) porphyrinato Iron(III) [FeP(CN)₂], bis (cyanide)(*meso*-tetraethyl) por-phyrinatoIron(III) [FeTEP(CN)₂], and (cyanide) (imidazole) porphyrinatoIron(III) [FeTEP(CN)₂], and (cyanide) (imidazole) porphyrinatoIron(III) [FeTEP(CN)₂], and (cyanide) (imidazole) porphyrinatoIron(III) [FeTEP(CN-Im)]. (ii) We calculate the paramagnetic ¹³C NMR chemical shifts of iron-bound ¹³CN of the above three complexes, both in the ground and low-lying excited states including the ferric $(d_{xy})^2$ $(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ configurations. Then we show the relations between the calculated ¹³C chemical shifts, the electronic configurations, and the ruffling of the porphyrin rings.

The trans-ligand effect on the paramagnetic ¹³C NMR chemical shifts of the iron-bound ¹³CN⁻ was well reproduced by the present calculations. Further, in [FeP(CN)₂], which has a ruffled porphyrin ring, the $(d_{xy})^1(d_{xz,yz})^4$ configuration is included in the ground state, and the alternative $(d_{xy})^2(d_{xz,yz})^3$ configuration is located closely in energy to the ground state. Ruffling of porphyrin rings extremely affects the ¹³C chemical shift of iron-bound CN in the $(d_{xy})^1(d_{xz,yz})^4$ configuration but not in the $(d_{xy})^2(d_{xz,yz})^3$ configuration.

I-R-2 Nuclear Magnetic Shielding Constants of Halogens in X⁻ and XO₄⁻ (X = F, Cl, Br, I) —Relativistic and Electron-Correlation Effects—

TANIMURA, Hirotaka¹; HADA, Masahiko² (¹Tokyo Metropolitan Univ.; ²IMS and Tokyo Metropolitan Univ.)

[J. Comput. Chem., Jpn. in press]

A series of calculations of halogen nuclear magnetic

shielding constants and chemical shifts in X⁻ and XO₄⁻ (X = F, Cl, Br, I) was carried out to discuss the relativistic and electron-correlation effects and, in special, the non-additivity of both the effects. The second-order Douglas-Kroll-Hess (DKH2) method was used as a relativistic hamiltonian, and the Møller-Plesset method was applied to the generalized UHF wave function. The calculated chemical shifts in ClO₄⁻ and IO₄⁻ agree reasonably well with the observed ones, though there are no experimental values in FO₄⁻ and BrO₄⁻. The relativistic effect was quite large especially in IO₄⁻ as reported previously, while the electron-correlation effect is significant in both FO_4^- and IO_4^- . The non-additivity of the relativistic and the electron-correlation effects in magnetic shielding constants is unexpectedly large in IO₄⁻, and therefore a relativistic electron-correlated method is crucial for describing accurate heavy-element nuclear magnetic shielding constants and chemical shifts.

I-R-3 Quasi-Relativistic Theory for Magnetic Shielding Constant. I. Formulation of the Douglas-Kroll Transformation with Magnetic Field and Applications to Atomic Systems

FUKUDA, Ryoichi¹; HADA, Masahiko²; NAKATSUJI, Hiroshi¹ (¹Kyoto Univ.; ²IMS and Tokyo Metropolitan Univ.)

[J. Chem. Phys. 118, 1015–1026 (2003)]

A two-component quasi-relativistic theory based on the Douglas-Kroll-Hess transformation is developed in order to study a magnetic shielding constant. The Hamiltonian that is proposed in this study is considering the relativistic effect on magnetic vector potential with the Douglas-Kroll theory. The present Hamiltonian can be applied to calculation of magnetic shielding constants, without further expansion in powers of c^{-1} . By applying the finite-perturbation theory and generalized-UHF wavefunction to this study, we calculate the magnetic shielding constants of two-electron ions, tenelectron ions, and noble gas atoms. The calculation results with the present theory are compared with the result of the Dirac-Hartree-Fock calculation. The numerical difference of the present theory from the DHF is 3% or less. However, a quasi-relativistic theory that handled the magnetic vector potential at the nonrelativistic level largely underestimates the relativistic effect. The picture change effect is quite important for the magnetic shielding constant of heavy elements. The change of orbital picture is significant in the valence orbital magnetic response as well as the core orbital response. The effect of finite distribution of nucleus is also studied with using Gaussian nucleus model. The present theory is able to reproduce the correct behavior of the finite nucleus effect that has been reported in the Dirac theory. However, the non-relativistic theory and quasi-relativistic theory with non-relativistic vector potential underestimate the finite nucleus effect.

I-R-4 Quasi-Relativistic Theory for Magnetic Shielding Constant. II. Gauge Including Atomic Orbital and Applications to Molecules

FUKUDA, Ryoichi¹; HADA, Masahiko²; NAKATSUJI, Hiroshi¹

(¹Kyoto Univ.; ²IMS and Tokyo Metropolitan Univ.)

[J. Chem. Phys. 118, 1027–1035 (2003)]

We present a relativistic theory of the magnetic shielding constants and the chemical shifts for molecules include heavy elements. The present theory is based on the Douglas-Kroll-Hess quasi-relativistic approximation. The gauge-including atomic orbital method is adapted to the quasi-relativistic Hamiltonian to allow the origin independent calculations. The present theory is applied to the hydrogen and halogen magnetic shielding constants of hydrogen halides and mercury magnetic shielding constants and ¹⁹⁹Hg chemical shifts of mercury dihalides and methyl mercury halides. The relativistic correction to the magnetic interaction term little affects the magnetic shielding constant of hydrogen; however, the correction is the dominant origin of the heavy atom shifts of the magnetic shielding constant of the heavy halogens. The basis set dependence of mercury shielding constants is quite large in the relativistic calculation; using the basis function which is optimized by the relativistic method is important to describe the relativistic effect properly. The relativistic correction to the magnetic interaction term is quite important for mercury dihalides in which relativistic effects from mercury and halogen are strongly coupled. Without this correction we obtain quite incorrect results. The origin of the 199Hg chemical shifts in mercury dihalides is the spin-orbit interaction from the heavy halogens. In methyl mercury halides the paramagnetic shielding term as well as the spin-orbit interaction from the heavy halogens dominates the 199Hg chemical shifts.

I-R-5 Theoretical Studies on MCD with Finite Perturbation Method and Relativistic Corrections

HONDA, Yasusi¹; HADA, Masahiko²; EHARA, Masahiro¹; NAKATSUJI, Hiroshi¹; MICHL, Josef³ (¹Kyoto Univ.; ²IMS and Tokyo Metropolitan Univ.; ³Colorado Univ.)

[J. Chem. Phys. submitted]

The generalized UHF (GUHF)/SECI method for the

MCD Faraday terms with the finite magnetic-field perturbation were presented and compared the results for ethylene, p-benzoquinone (BQ), and o-BQ with those by the conventional sum-over-states method. Their difference was not negligible, and even the signs were contrary for the lowest π - π * state of ethylene. Quasi-relativistic treatments in the calculations of the Faraday terms were also discussed. The method was applied to the three $n-\pi^*$ states $({}^{3}\Pi_{1u}, {}^{3}\Pi_{0u}, \text{ and } {}^{1}\Pi_{u})$ of I₂, Br₂, Cl₂, and F₂. The relativistic effects become more important as molecule is heavier. The Faraday terms for I₂ and Br₂ were dramatically changed by the relativistic correction from the non-relativistic results, whereas the effects were negligible for Cl₂ and F₂ in contrast. This indicates that the relativistic corrections are essential to the theoretical treatments of MCD for molecules containing heavy atoms.

I-S Molecular Vibrations and Intermolecular Interactions in Condensed Phases

In this project, intermolecular interactions and their effects on molecular vibrations in condensed phases are analyzed theoretically to clarify the relation between the structures and dynamics of the systems and the frequencyand time-domain spectroscopic features. Specifically, (1) the resonant transfer of vibrational excitations, vibrational dephasing, and their competition in liquids and biomolecules and (2) the relation between electronic structural features of molecules and intermolecular interactions are analyzed with great emphasis.

I-S-1 Vibrational Interactions in the Amide I Subspace of the Oligomers and Hydration Clusters of *N*-Methylacetamide

TORII, Hajime

(IMS and Shizuoka Univ.)

[J. Phys. Chem. A 108, 7272–7280 (2004)]

The diagonal and off-diagonal vibrational interactions in the amide I subspace are examined for the oligomers and hydration clusters of N-methylacetamide (NMA). A method called the average partial vector method is developed for constructing the force constant matrix (F matrix) in the amide I subspace from that in the full Cartesian space. It is shown that the F matrix thus constructed can reproduce quantitatively the vibrational frequencies and vibrational patterns of the amide I modes calculated in the full Cartesian space. For the NMA oligomers consisting of three or more NMA molecules, the cooperative effect on the C=O bond length (and on the diagonal force constant of the amide I mode as well) is seen. Including the values for those oligomers, the shifts in the diagonal terms in the amide I subspace (δk_{I}) and in the C=O bond length ($\delta S_{C=O}$) of the NMA oligomers and NMA-water clusters from the values of an isolated NMA molecule are approximately proportional to each other. In addition, $\delta S_{C=O}$ is shown to be approximately proportional to the electric field (originating from the other molecules in the NMA oligomer or NMA-water cluster) evaluated at a specified point on the C=O bond, indicating that the origin of the cooperative effect is the enhancement of the electric field operating among the molecules. The effect of mechanical anharmonicity on $\delta k_{\rm I}$ is examined by introducing the internal-normal mixed coordinate system representation for the cubic force constants, and is shown to overestimate the variation of $\delta k_{\rm I}$. The partial cancellation by the effect of electrical anharmonicity (dipole second derivative) is also important. For the offdiagonal terms, it is shown that the TDC model provides a good approximation. However, for the (small) coupling constants between distant peptide groups, the effect of the polarization of the intervening peptide group(s) (also called the third-body mediation and may be regarded as a dipole-induced dipole effect) is also recognized.

I-S-2 Atomic Quadrupolar Effect in the Methanol-CCl₄ and Water-CCl₄ Intermolecular Interactions

TORII, Hajime (*IMS and Shizuoka Univ.*)

[Chem. Phys. Lett. 393, 153–158 (2004)]

The intermolecular interactions in the methanol-CCl₄ and water-CCl₄ systems are examined by carrying out *ab initio* molecular orbital calculations on the 1:1 molecular clusters. It is found that, for both systems, the molecular configuration with the C–Cl…O interaction is the most stable. The two-body electrostatic part, especially the effect of the atomic quadrupoles of the Cl atoms of CCl₄, dominates the interaction energy of this configuration. This result suggests that the atomic quadrupolar effect is significant in the structural formation and energetics in the methanol-CCl₄ and water-CCl₄ systems as well as in other related systems.

I-S-3 Atomic Quadrupolar Effect in Intermolecular Electrostatic Interactions of Chloroalkanes: The Cases of Chloroform and Dichloromethane

TORII, Hajime

(IMS and Shizuoka Univ.)

[J. Mol. Liq. in press]

The atomic quadrupolar effect in intermolecular electrostatic interactions is studied for chloroform and dichloromethane. From the fitting to the electrostatic potentials around these molecules obtained by ab initio molecular orbital (MO) calculations, atomic quadrupoles of the magnitude as large as $\Theta \approx 1.5 \ ea_0^2$ are obtained for the chlorine atoms in these molecules. It is shown that a reasonably good fit to the electric field around the molecules can be obtained only by including those atomic quadrupoles, indicating that atomic quadrupoles are essential for correct representation of the intermolecular electrostatic interactions of these molecules. From the calculations of the radial distribution functions (rdfs) of liquid chloroform and dichloromethane by the Monte Carlo and molecular dynamics methods, it is shown that a significant atomic quadrupolar effect is seen in the rdfs of the C…C, C…H, and H…H pairs. The intermolecular distances in the optimized structures of the dimers of chloroform and dichloromethane calculated by the ab initio MO method support the new features in the rdfs of the liquids that are seen upon including the effect of atomic quadrupoles. It is suggested that an atomic quadrupole has a significant effect on the angular (rather than radial) component of the location of the atoms of neighboring molecules.

I-T Nonlinear Processes Induced by Ultrafast and Intense Extreme Ultraviolet (XUV) Pulses

Recent technological progress on the generation of intense XUV pulses has opened up a new field on ultrafast and nonlinear optics. At such short wavelength only a gas can be a nonlinear medium. Nonlinear optics in XUV regions is interesting for two reasons. The first one is that the attosecond pulse generation is possible only in the XUV region, simply because an optical cycle of the visible-UV photon is in the time scale of femtosecond. The second one is that nonlinear response of the medium is not yet known at the XUV region. In this project, we have carried out investigation from those two aspects.

I-T-1 Time-Frequency Analysis of High-Order Harmonic Generation

NAKAJIMA, Takashi¹; WATANABE, Shuntaro²

(¹IMS and Kyoto Univ.; ²Univ. Tokyo)

Recently it has been demonstrated by the group of Krausz (Austria) that it is possible to generate a single attosecond XUV pulse through high-order harmonic generation. Still, there are many things to be understood and clarified on the mechanism and conditions for the attosecond pulse generation. By solving time-dependent Schrödinger equations, we carry out the time-frequency analysis to obtain the temporal profile for each order of harmonic pulses for hydrogen (with a single-active electron) and also for helium (with two-active electrons) at various conditions. When the intensity is low, the temporal peak of harmonics has been found to coincide with the peak of the fundamental pulses. At higher intensity, however, we have found that the peak of the harmonic temporally shifts toward the leading edge of the pulse, and the amount of the shift is smaller for higher order harmonics.

I-T-2 Two-Photon Above-Threshold Ionization Cross Sections of Rare Gases by XUV Photons

NAKAJIMA, Takashi¹; WATANABE, Shuntaro² (¹*IMS and Kyoto Univ.;* ²*Univ. Tokyo*)

[*Phys. Rev. Lett.* **93**, 083903 (2004)] [*Phys. Rev. A* **70**, 043412 (2004)] Above-threshold ionization (ATI) is the successive absorption of an additional number of photons more than the minimum required to ionize an atom. For rare gas atoms, ATI by infrared ~ visible photons has been very well studied theoretically as well as experimentally. Due to the recent technological progress in highorder harmonic generation and free-electron lasers, a bright light source is becoming available in the extreme ultraviolet (XUV) wavelength region. Provided with such progress, the time is matured to investigate, theoretically as well as experimentally, ATI in the XUV regime. Furthermore, two-photon ATI has a practical importance since it can be used for the pulse characterization (*i.e.*, autocorrelation) of XUV pulses.

In this work we have developed a theory to calculate two-photon above-threshold ionization cross sections of rare gases by XUV photons in the extended framework of multichannel quantum defect theory (MQDT). The advantage of the use of MQDT is that it automatically incorporates not only the spin-orbit interactions but also configuration mixing to some extent. On the other hand, the limitation of the present approach is that we have included only two lowest core states (two-core model), $p^{5}[^{2}P_{3/2}]$ and $p^{5}[^{2}P_{1/2}]$. Since free-free dipole moments do not converge in the length gauge, we have made the combined use of the length gauge for small r and the acceleration gauge for large r. The two-photon ATI cross sections for Xe and Ar associated with the $p^{5}[^{2}P_{3/2}]$ and $p^{5}[^{2}P_{1/2}]$ ionic core states are found to be 1.0×10^{-51} cm⁴ s and 2.0×10^{-51} cm⁴ s, respectively, for 25 eV photons.

I-U Control of Photoionization Processes Using Lasers

Optical control of various photoabsorption processes are of great interest in recent years. In this project, we have theoretically explored the possibility to control spin degree of freedom of photoelectrons and ejection angle of photoelectrons.

I-U-1 Control of the Spin-Polarization of Photoelectrons/photoions Using Short Laser Pulses

NAKAJIMA, Takashi (IMS and Kyoto Univ.) [Appl. Phys. Lett. 84, 3786–3788 (2004)]

To establish a method for the control of spin degree of freedom is one of the most important issues in modern technology and science, since highly spinpolarized species such as electrons, ions, and nucleus, *etc.*, are very useful not only to develop a new technology using semiconductors but also to study various spin-dependent dynamics. We theoretically propose a generic pump-probe scheme to control spin-polarization of photoelectrons/photoions by short laser pulses. By coherently exciting fine structure manifolds of a multivalence-electron system by the pump laser, a superposition of fine structure states is created. Since each fine structure state can be further decomposed into a superposition of various spin states of valence electrons, each spin component evolves differently in time. This means that varying the time delay between the pump and probe lasers leads to the control of spin states. Specific theoretical results are presented for twovalence-electron atoms, in particular for Mg, which demonstrate that not only the degree of spin-polarization but also its sign can be manipulated through time delay. Since the underline physics is rather general and transparent, the presented idea may be potentially applied to nanostructures such as quantum wells and quantum dots.

I-U-2 Control of Photoelectron Angular Distributions Using a Dressing Laser

NAKAJIMA, Takashi¹; BUICA, Gabriela²

(¹IMS and Kyoto Univ.; ²Kyoto Univ. and Inst. Space Sci., Romania)

[Phys. Rev. A in press]

Strong dressing laser field can induce various interesting modification in laser-matter interactions. Among them, an interesting modification is observed in the photoionization spectra in the wavelength region at which two-photon near-resonance is satisfied for the initially occupied state by a probe laser and initially unoccupied state by a dressing laser. This is known as laser-induced continuum structure. Related to this, if the ionization processes consists of several channels, it should be possible, in principle, to alter the branching ratio of photoionization into several channels, and if the branching ratio is successfully altered, we may also see the alteration of photoelectron angular distribution. In this work we have theoretically studied the modification of photoelectron angular distributions using a dressing laser. We have found a significant change of photoelectron angular distributions for the K atom, as the probe laser frequency is scanned across two-photon resonance under the presence of dressing laser.

RESEARCH ACTIVITIES II Department of Molecular Structure

II-A Development of Near-Field Dynamic Spectroscopy and Application to Nanometric Systems

There is much demand for the study of local optical properties of molecular assemblies and materials, to understand mesoscopic phenomena and/or to construct optoelectronic devices in nanometric scale. Scanning nearfield optical microscopy (SNOM), which enables spatial resolution beyond the diffraction limit of light, shows remarkable progress in technology in these days. Combination of this advanced optical technology with ultrafast spectroscopic methods may offer a direct probe of molecular dynamical processes in mesoscopic systems. It may bring essential and basic knowledge for analyzing origins of characteristic features and functionalities of mesoscopic systems. We are constructing apparatus for near-field dynamic spectroscopy with femtosecond temporal resolution and nanometer spatial resolution. Using the apparatus developed, we have observed characteristic spatiotemporal behavior of various organic molecular systems and metal nanoparticles, for the purpose of understanding spatial coherence and dissipation of excitations and their dynamics. Outlines of the construction and experimental results obtained are summarized here.

II-A-1 Scanning Near-Field Optical Microscopy with Supercontinuum Light Pulses Generated in Microstructure Fiber

NAGAHARA, Tetsuhiko; IMURA, Kohei; OKAMOTO, Hiromi

[Rev. Sci. Instrum. 75, 4528-4533 (2004)]

We have utilized supercontinuum (SC) pulses as a light source for SNOM experiments with high spatial-resolution (~ 100 nm) determined by the aperture size of the near-field probe. The SC ranging from 560 nm to > 1 μ m is generated by focusing mode-locked Ti: sapphire laser pulses into a microstructure fiber. The continuum can be used as a wavelength-tunable light source for fluorescence excitation as well as for probing absorption of excited states.

To examine performance and versatility of the apparatus, fluorescence image of pseudoisocyanine J-aggregate was measured. The sample was illuminated through the apertured tip by spectrally-sliced SC at 560 nm. Fluorescence from the sample (at 590 nm) was detected by an avalanche photodiode. Fluorescence (Figure 1A) and topographic (not shown) images correlate very well. The images show that the J-aggregates have fibrous structures, in agreement with earlier works. The fluorescence image is in some parts noisy and smeared. The noisy signal is coming from fluctuation of the SC, and quality of the fluorescence image would be much improved by stabilizing the incident Ti:sapphire laser.

Next we describe two-color pump-probe measurements using SC. Time resolution in the near-field with near-IR probe pulse was in 1–2 ps range, while that with 570 nm pulse was 5 ps without pre-compensation of group delay dispersion. As an example, we have measured a thin film of porphyrin J-aggregates. Signals from spectrally sliced SC at 810 nm after excitations at 780 nm are shown in Figure 1C, together with the topography (Figure 1B) of the sample. The lifetimes at positions specified in the topograph $(112 \pm 6 \text{ ps and } 79 \pm 6 \text{ ps})$ show clear site dependence. The site-specificities in excited-state dynamics have been revealed in the present *two-color* experiment much more clearly compared to our previous *one-color* result,¹⁾ since the baselines are directly determined from intensities at negative delay times.

Reference

1) T. Nagahara, K. Imura and H. Okamoto, *Chem. Phys. Lett.* **381**, 368–375 (2003).



Figure 1. (A) Fluorescence image of PIC J-aggregate detected at 590 nm. Scan range: $10 \ \mu m \times 10 \ \mu m$. (B) Topography of tetrakis(4-methoxyphenyl)porphyrin J-aggregate. Scan range: $5 \ \mu m \times 5 \ \mu m$. (C) Signals obtained by 780-nm pump / 810-nm probe experiments and their fit to exponential function.

II-A-2 Near-Field Spectroscopy of Water-Soluble and Water-Insoluble Porphyrin J-Aggregates

NAGAHARA, Tetsuhiko; IMURA, Kohei; OKAMOTO, Hiromi

[Scanning 26 (Suppl. I), 10-15 (2004)]

Recently, we examined the mesoscopic structures and spatial inhomogeneities of J-aggregate of waterinsoluble tetrakis(4-methoxyphenyl)porphyrin (TMe OPP) in thin film by SNOM. The results obtained were as follows: (a) thin film consists of bundles of long and planer microcrystalline structures; (b) site-specific transmittance spectra might reflect spatial inhomogeneity of the sample, which may be a major origin of the broad Jbands in the far-field spectrum. However, influence of substituent groups on the spatial inhomogeneities and morphologies was not investigated. In the present study, we have studied mesoscopic structures and optical properties of J-aggregates of tetraphenylporphyrins with different substituent groups [unsubstituted (TPP) and 4sulfonated (TSPP)].

From topographic images, TSPP sample is composed of needle-like planar microcrystals (~1 μ m-L, ~100 nm-W and 5–10 nm-H), while that of TPP (Figure 1B) shows stacks of planer (300 ~ 600 nm × 300 ~ 600 nm, ~ 20 nm-H) microcrystalline structures. From polarized transmittance images of TSPP (Figure 1A), it was found that a large transition moment is parallel to the long crystalline axis. Individual microcrystallines in TPP sample have been found to be planer rhomboid structures by SEM observations. Such morphological differences are probably due to microscopic differences in aggregate structures.

In the far-field absorption and fluorescence spectra, the bandwidths of the water-insoluble samples (TPP and TMeOPP) were much broader than that of water-soluble sample (TSPP), suggesting serious contributions of inhomogeneous broadening. The near-field transmittance spectra of the water-insoluble samples show strong site-dependence (Figure 1C), while those of the water-soluble ones do not. The origin of the broad absorption band observed in water-insoluble samples can be ascribed to spatial inhomogeneities.

Reference

1) T. Nagahara, K. Imura and H. Okamoto, *Chem. Phys. Lett.* **381**, 368–375 (2003).



Figure 1. (A) Polarized transmittance image of TSPP Jaggregate. Arrows indicate polarization directions. Scan range: $2 \ \mu m \times 2 \ \mu m$. (B) Surface topography of TPP Jaggregate. Scan range: $5 \ \mu m \times 5 \ \mu m$. (C) Transmittance difference spectra at positions indicated in (B).

II-A-3 Near-Field Optical Observation of Gold Nanoparticles

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

[Chem. Phys. Lett. 400, 500-505 (2004)]

Optical properties of noble metal particles have been widely investigated because of fundamental importance in science and in industry. Not only the local field enhancement but also the SP mode behaviors in nearfield arouse fundamental interests and various applications. Wavelength-dependent characteristics of SP modes on metal nanoparticles are essential for utilizing them as novel optical and electronic materials, and also for constructing molecular systems for nanophotonic applications as well.

We investigated interaction between evanescent wave and a single gold nanoparticle in near-field by utilizing an aperture-probe SNOM. A characteristic spectral feature, consisting of transmission enhancement and absorptive parts, was found. Observed spectra were successfully simulated by a model calculation based on extended Mie scattering theory of the near- and far-field scatterings as well as by a Green dyadic treatment of electromagnetic field.

II-A-4 Two-Photon Induced Photoluminescence Imaging of Single Gold Particles

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

[J. Am. Chem. Soc. 126, 12730–12731 (2004)]

Strong field confinement near and/or adjacent particles is important in surface enhanced Raman scattering (SERS). However, knowledge about spatial distribution of electric field near the particle and how plasmon modes play roles in the particle are still not fully understood. We have found that two-photon induced photoluminescence (TPI-PL) of single nanoparticles can be excited in the near-field, and this has been used to reveal spatial distribution of electric field near the particle as well as spatial characteristics of plasmon modes.

Gold nanoparticles were synthesized chemically in solutions by seed-mediated method. Morphology of the sample was verified by topography measurements by the apertured SNOM and/or by a scanning electron microscope. Samples were spin-coated on a cover-slip. A Ti:sapphire laser ($\lambda = 780$ nm, < 100 fs) was used to excite TPI-PL. Laser power dependence measurement of the PL intensity confirmed that PL was due to a two-photon induced process.

Figure 1 (a,b) shows the TPI-PL image of single gold nanorods. Figure 1(a) shows electric field enhancement near the ends of the rod, while Figure 1(b) shows a characteristic spatial oscillation. This oscillatory behavior is well reproduced by an electromagnetic calculation and is ascribed to electromagnetic local density of states which reflect the eigenfunction of certain surface plasmon mode. The origin of the difference between Figures 1(a) and (b) is possibly related to microscopic edge structures of the rod and/or the resonance condition of the plasmon mode at the excitation wavelength.



Figure 1. (a,b) Two-photon induced PL images for two typical single gold nanorods. Scale bars are 100 nm.

II-A-5 Ultrafast Near-Field Imaging of Single Gold Nanorods

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

[J. Phys. Chem. B 108, 16344–16347 (2004)]

We deal with ultrafast dynamics of collective oscillation of electrons, known as surface plasmon (SP), for gold nanorods. The SP modes of nanoparticles give rise to strong interaction with photons. It is of fundamental importance to know how the electron-electron and electron-phonon scattering processes after photoexcitation depend upon size and shape of nanoparticles and how they proceed inside the particle. Dynamical spectroscopy of a single particle with high temporal and spatial resolution must be informative for this purpose. We have performed experiments of ultrafast near-field pump-probe imaging, and investigated the dynamic behavior of the excited particle in a space- and timeresolved manner.

Figure 1 shows transient transmission images of a gold nanorod taken at various pump-probe delay times. As it is clearly seen in the figure, temporal response of central part of the particle is different from those of the both ends. A fast rise and a slow decay are seen for the ends parts, while only a fast rise component is observed for the central part. The time constant for the faster component was found 0.6 ± 0.1 ps and the slower one 2.8–1.5 ps depending on the position inside the particle. The faster and slower components are assigned to electron-electron and electron-phonon scattering, respectively. It is found that the electron-phonon relaxation becomes faster towards the end edge of the nanorod.



Figure 1. (a-f) Transient transmission images of a gold nanorod taken at various pump-probe delay times (indicated in each image). Scan range: 600 nm × 600 nm.

II-B Spectroscopic Studies on Atoms and Ions in Liquid Helium

Atoms and ions in liquid helium are known to reside in bubble-like cavities due to the Pauli repulsive force between electrons. Physical properties of these exotic surroundings are determined by the potential energy of the impurity- He_n system, the surface tension energy of the liquid helium, and the pressure-volume work. Spectroscopic studies of such impurity atoms and ions in liquid helium are expected not only to give interesting information on the structure and dynamics of the bubbles but also to contribute to the study on physical properties of superfluid liquid helium.

II-B-1 Laser Spectroscopic Studies of Mg Atoms in Cold Helium Gas

MORIWAKI, Yoshiki¹; MORITA, Norio

(¹Toyama Univ.)

In our previous laser spectroscopic study¹⁾ on Mg atoms in liquid helium, since both the peak shift and width of the emission spectrum of the $3s3p \ ^{1}P \rightarrow 3s^{2} \ ^{1}S$ transition were significantly larger than those expected from a simple bubble model, we inferred that a Mg(3s3p)¹P)He₁₀ exciplex was formed in a bubble, just similar to the case of excited alkaline atoms in liquid helium. Such exciplexes are known to have a characteristic structure in which helium atoms form a ring in the nodal plane of the excited *p*-electron of an impurity atom, and our theoretical spectrum calculated based on a similar exciplex model showed better agreement with the experimental spectrum in comparison with the one calculated with a simple bubble model. In the case of Mg, however, unlike alkaline atoms, the 3s electron lies around the nodal plane of the 3p electron, and so there is a possibility that the 3s electron prevents helium atoms from forming the ring structure due to the Pauli repulsive force. This means that the formation of the $Mg(3s3p \ ^{1}P)He_{10}$ exciplex is still ambiguous. In the present study, therefore, we have investigated the emission spectrum of Mg atoms in cold helium gas, and have compared it with the calculated spectrum as well as the experimental spectrum obtained for liquid helium. Consequently, as seen in Figure 1, we have found that the spectrum for gaseous helium is in very good agreement with the one calculated based on the model of the $Mg(3s3p \ ^{1}P)He_{10}$ exciplex formation. This result strongly supports our inference that Mg atoms in liquid helium can form $Mg(3s3p \ ^{1}P)He_{10}$ exciplexes in spite of the presence of the 3s electron.

Reference

1) Y. Moriwaki and N. Morita, Eur. Phys. J. D 5, 53 (1999).



Figure 1. Emission Spectra of Mg atoms in gaseous and liquid helium at 1.4 K. A calculated spectrum is also plotted.

II-B-2 Observation of Remarkable Difference between Mobilities of Impurity Eu atoms in Solid Helium-3 and Helium-4

MORIWAKI, Yoshiki¹; MORITA, Norio (¹Toyama Univ.)

We have measured emission spectra of Eu atoms in liquid and solid helium at 1.4 K over a wide pressure range across the solidification pressure. Consequently, as seen in Figure 1, we have found that the behavior of the spectral intensity across the solidification pressure remarkably differs between ³He and ⁴He; while for ⁴He the intensity drastically increases above the solidification pressure, no significant change is seen for ³He across the solidification pressure. This difference can be interpreted as a manifestation of the difference in mobility of Eu atoms. Since the helium atom is so light that even its zero-point vibration has a quite large amplitude, the position exchange between neighboring helium atoms frequently occurs even in solid due to the tunnel effect. Therefore, each helium atom in solid helium always moves around, and impurity atoms can also move and diffuse following the motion of helium atoms. No significant change seen for ³He across the solidification pressure means that impurity Eu atoms in solid ³He can diffuse with almost the same mobility as in liquid. On the other hand, the drastic intensity increase seen for ⁴He shows that the mobility of Eu atoms in solid ⁴He is significantly small in comparison with the one in solid
³He. A possible reason may be the larger mass of ⁴He atom, which results in a smaller amplitude of the zeropoint vibration. Another possible reason might be that solid ⁴He is (partly) a Bose condensate at 1.4 K, while there is no condensate in solid ³He. In a Bose condensate many helium atoms coherently vibrate, and this might cause the less position exchange between neighboring atoms.



Figure 1. Pressure dependences of emission spectra of Eu atoms in liquid ³He and ⁴He at 1.4 K; liquid ⁴He and ³He at this temperature solidify at about 2.5 and 5.0 MPa, respectively.

II-C Surface Chemical Reactions Studied by NEXAFS Spectroscopy

Recently, we have developed an energy dispersive NEXAFS (Near Edge X-ray Absorption Sine Structure) method, which is a technique to measure a NEXAFS spectrum in a certain range simultaneously. This method shortens the measuring time by 1/100 compared with the conventional energy scanning method and enables us to apply the NEXAPS spectroscopy to surface chemical reactions related to fundamental catalytic reactions. Since the time scale is comparable with STM measurement, combined information of NEXAFS and STM as well as dynamic Monte-Carlo simulations provides deep insight to fundamental chemical reactions which have not been clarified yet. So far, we have applied it to the reactions of water formation reaction/Pt(111) and ammonia formation on Rh(111).

II-C-1 Reaction-Path Switching Induced by Spatial-Distribution Change of Reactants: CO Oxidation on Pt(111)

NAKAI, Ikuyo¹; KONDOH, Hiroshi¹; AMEMIYA, Kenta¹; NAGASAKA, Masanari¹; NAMBU, Akira¹; SHIMADA, Tohru¹; OHTA, Toshiaki² (¹Univ. Tokyo; ²Univ. Tokyo and IMS)

[J. Chem. Phys. 121, 5035 (2004)]

CO oxidation on Pt(111) surfaces is one of the most prototypical catalytic reactions. We studied the mechanism of CO oxidation on O-covered Pt(111) surfaces during CO exposure by means of time-resolved NEXAFS spectroscopy. Recent STM study proposed that the oxidation reaction takes place exclusively at island peripheries after an "induction period" where the reaction does not proceed. However, we found that the whole reaction process is composed of two distinct processes; (1) a reaction of isolated oxygen atoms with adsorbed CO, and (2) a reaction of island-periphery oxygen atoms after the CO saturation. If CO pressure is lowered, these two processes are separated by an induction period, in which CO saturates the O-covered surface. A drastic switching of reaction path in CO oxidation reaction is caused by the CO adsorption induced 2D condensation of the O atoms. These results demonstrate that the effects of long-range interactions and consequent dynamic spatial-distribution changes of the reactants are of fundamental importance for understanding the kinetics in the reaction systems deviated from the conventional Langmuir-Hinshelwood kinetics.



Figure 1. (a) Time evolution of θ_0 and θ_{CO} under a low pressure of CO (5 × 10⁻¹⁰ Torr). The annealing temperature and the reaction temperature were 260 K and 252 K, respectively. The gray line shows the saturation coverage of CO. The areas (i) and (ii) correspond to the former and latter processes, respectively.

(b) Variation of θ_{O} and θ_{CO} from Monte Carlo simulation under the same condition as for the experiment shown in (a). The solid and dashed lines represent θ_{O} and θ_{CO} , respectively. Inset: Simulated curves without taking account of CO adsorption-induced condensation of O atoms.

II-D Ultrafast Dynamics of Surface Adsorbed Species

Understanding of reaction dynamics at surfaces using ultra-short laser techniques is an important issue to clarify the mechanism of the reactions. Real-time observation of temporal change of surface species induced by UV, visible, and (Near-) infrared pump pulses is carried out using mid-IR pump-probe vibrational spectroscopy and Sum-frequency generation (SFG) spectroscopy which is one of the non-linear spectroscopies using ultra-short laser has high sensitivity for detection of molecular vibrations of adsorbed species on surface in the first layer. The aim of this study is the identification of molecular structures of the intermediates generated by electronic, vibrational, or thermal excitation and understanding of the reaction kinetics including potential energies, activation barriers, and entropies. Typical systems of our recent studies are formate (DCOO) adsorbed on Ni(111) surface, olefins on OH group of zeolite. In addition to the ultrafast observation of surface events, controls of excited states of molecules and chemical reaction are tried using optimized pulse shaping technique. In the study, we succeeded in controlling the two-photon excitation efficiency and selective excitation of excited states of an α -perylene crystal.

II-D-1 Dynamic Processes of Olefins Adsorbed on Hydroxyl Groups of DM20 Zeolite Excited by Picosecond Infrared Pulses

ONDA, Ken¹; TANABE, Kinuka¹; NOGUCHI, Hidenori¹; DOMEN, Kazunari¹; WADA, Akihide² (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[J. Phys. Chem. B 107, 11391–11396 (2003)]

We have investigated olefins adsorbed on Brønsted acidic hydroxyl groups (OD) of DM20 zeolite by transient infrared absorption spectra after excitation of the OD stretching mode using picosecond infrared lasers. The olefins studied were ethylene, deuterated ethylene, propylene, and isobutene, and only isobutene was adsorbed on OD at its methyl group while the other olefins were adsorbed at their double bonds. For all the olefins except isobutene, simple vibrational relaxation of the v = 1 state was observed and the lifetimes were 2-4 ps. These lifetimes are an order faster than that of isolated OD. For isobutene, a long lifetime component lasting more than 500 ps was observed in addition to vibrational relaxation of 2 ps. The transient absorption spectra for isobutene-adsorbed zeolite at various time delays and frequencies indicated the existence of a short-lived species and a slow desorption process compared with vibrational relaxation.

II-D-2 Dynamical Response of Formate/Ni(111) System to Picosecond Near Infrared Pulses

NOGUCHI, Hidenori¹; ONDA, Ken¹; OKADA, Takuya¹; KUBOTA, Jun¹; KOBAYASHI, Hisayoshi²; KANO, Satoru S.³; DOMEN, Kazunari¹; WADA, Akihide⁴

(¹Tokyo Inst. Tech.; ²Kurashiki Univ. Sci. Arts; ³Hosei Univ.; ⁴IMS and Tokyo Inst. Tech.)

Time-resolved sum-frequency generation (TR-SFG) spectroscopy was carried out on a deuterated formate (DCOO) adsorbed on Ni(111) surface to investigate the surface reaction dynamics induced by irradiation of picosecond near-infrared laser pulses. The irradiation of pump pulse (800 nm) caused rapid intensity decreases of both CD and OCO stretching modes of bridged formate on Ni(111). Different temporal behaviors of intensity recovery between these two vibrational modes

were observed, *i.e.*, the intensity of CD stretching mode recovered significantly faster than that of OCO symmetric stretching mode. From the results of transient measurements, we concluded that the observed intensity change was mainly due to a transient structural change of formate and we discussed about the mechanisms of the change.

II-D-3 Optical Control of Excited States of α-Perylene Crystal Using Optimized Pulse Shaping Method

MIZOGUCHI, Ryuuichi¹; KANO, Satoru S.²; WADA, Akihide³

(¹Tokyo Inst. Tech.; ²Hosei Univ.; ³IMS and Tokyo Inst. Tech.)

[Chem. Phys. Lett. 379, 319-324 (2003)]

Optical control of excited states of α -perylene crystal was realized by a femtosecond optimized pulse shaping method using Genetic Algorithm (GA). We succeeded in controlling the emission spectral feature of an α -perylene crystal; the intensity of E-emission was increased by a factor of 1.4 without the change of Y-emission intensity. Furthermore, we found a near-infrared pulse shape whose multi-photon excitation efficiency is larger than that of a single femtosecond pulse by a factor of two. On the auto-correlation traces of these shaped pulses, the several satellite peaks appeared beside the main peak. The origin and mechanism of the attained change were discussed.

II-D-4 Optical Control of Two-Photon Excitation Efficiency of α -Perylene Crystal by Pulse Shaping

OKADA, Takuya¹; OTAKE, Ikuya¹; MIZOGUCHI, Ryuuichi¹; ONDA, Ken¹; KANO, Satoru S.²; WADA, Akihide³

(¹Tokyo Inst. Tech.; ²Hosei Univ.; ³IMS and Tokyo Inst. Tech.)

[J. Chem. Phys. to be published]

Optimized pulse shaping experiments were carried out on the control of two-photon excitation efficiency of an α -perylene crystal in the temperature region from 30 K to 290 K. It was found that a pulse train with a pulse interval of 90 fs and an alternately reversing phase relation increased the excitation efficiency by a factor of 2 for the whole temperature region. The pulse shape characteristic for effective efficiency increase was educed by double pulse experiments in which the dependence of the emission intensity on the pulse interval and relative phase between pulses were measured. The mechanism of the efficiency increase is briefly discussed using a sliding-window Fourier transform of the pulse shape.

II-E Structure and Function of Metalloproteins and Its Molecular Design

Metal ion is a common cofactor that is crucial for active centers of proteins involved in many biologically important processes in cells, and a relatively small number of metal-based prosthetic groups are utilized to serve numerous and diverse chemical functions. A typical metal-based prosthetic group, which represents a fascinating example in this respect, is heme. Heme promotes a variety of functions, such as dioxygen storage, activation of small molecules, electron transfer reactions, and sensing gaseous molecule. In the field of protein design and engineering, hemoproteins also make particularly attractive targets. There are many reasons for this, including the exciting possibility of engineering protein-based molecules with useful catalytic, electronic or optoelectronic properties. Based on various kinds of spectroscopies, we have functionally and structurally characterized some hemoproteins including newly identified heme-regulated proteins, and designed hemoproteins showing improved activities and new functions.

II-E-1 Structural and Functional Characterization of "Laboratory Evolved" Cytochrome P450cam Mutants Showing Enhanced Naphthalene Oxygenation Activity

MATSUURA, Koji¹; TOSHA, Takehiko¹; YOSHIOKA, Shiro¹; TAKAHASHI, Satoshi¹; ISHIMORI, Koichiro²; MORISHIMA, Isao¹ (¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[Biophys. Biochem. Res. Commun. 324, 1095 (2004)]

To elucidate molecular mechanisms for the enhanced oxygenation activity in the three mutants of cytochrome P450cam screened by 'laboratory evolution' (H. Joo, Z. Lin and Z. F. H. Arnold, Nature 399, 670-673 (1999)), we purified the mutants and characterized their functional and structural properties. The electronic absorption and resonance Raman spectra revealed that the structures of heme binding site of all purified mutants were quite similar to that of the wildtype enzyme, although the fraction of the inactivated form, called "P420", was increased. In the reaction with H₂O₂, only trace amounts of the naphthalene hydroxylation product were detected by gas chromatography. We, therefore, conclude that the three mutants do not exhibit the significant changes in the structural and functional properties from those of wild-type P450cam except for the stability of the axial ligand in the reduced form. The enhanced fluorescence in the whole-cell assay would reflect the enhancement in the oxygenation activity below the detectable limit of the gas chromatography and/or contributions of other reactions catalyzed by the heme iron.

II-E-2 Spectroscopic Characterization of Heme Binding to the Heme Regulatory Motif (HRM) in the Bacterial Iron Response Regulator Protein

ISHIKAWA, Haruto¹; TAKAHASHI, Satoshi¹; HORI, Hiroshi²; O'BRIAN, Mark R.³; MORISHIMA, Isao¹; ISHIMORI, Koichiro⁴ (¹Kyoto Univ.; ²Osaka Univ.; ³New York State Univ.; ⁴IMS and Kyoto Univ.)

The heme regulatory motif (HRM) is a common and crucial amino acid sequence for the heme binding in heme-regulated proteins, but the structural characterization of the heme binding to HRM has not yet been extensively accomplished. The bacterial iron response regulator (Irr), controlling the heme biosynthesis by degrading itself in the presence of iron, has one HRM in the sequence. Although the absorption spectrum of Irr in the presence of ferric heme was quite unusual in that the Soret peak was broad with highly blue-shifted and suggestive of the dissociation of the axial ligand from protein, the EPR signals (g = 2.52, 2.29, 1.90, g = 4 to 8) and the v_3 line at 1491 cm⁻¹ in the resonance Raman spectrum were characteristic of Cys-ligated hemes. By the mutation of ²⁹Cys to Ala, the EPR signals and the v_3 line from the Cys-ligated heme diminished, confirming that ²⁹Cys is the axial ligand for ferric heme bound Irr. In sharp contrast to the ferric heme bound Irr, the spectroscopic features of the ferrous heme bound ²⁹Cvs \rightarrow Ala mutant are quite similar to those of wild-type Irr. In addition, the correlation of the stretching modes of v(Fe-CO) and v(FeC-O) for ferrous CO heme bound Irr indicates that the axial ligand trans to CO is histidine. The reduction of the heme iron, therefore, replaces axial ²⁹Cys with histidine. These results provide the first detailed spectroscopic characterization for the heme binding to HRM and provide evidence for redoxdependent axial ligand exchange in Irr.

[J. Biol. Chem. Submitted]

II-F Controllable Magnetic Anisotropy of Ultrathin Magnetic Films and Nanowires Using Surface Chemical Techniques

In recent years noble properties of magnetic thin films have extremely attracted scientific and technological interests. Magnetic anisotropy is one of the most important subjects in this field since the origin of perpendicular magnetization is not well understood but is useful for high-density recording media. We are investigating the microscopic mechanism of perpendicular magnetic anisotropy that is stabilized by gaseous adsorption on magnetic film surfaces by means of the synchrotron radiation x-ray magnetic circular dichroism (XMCD) and the visible-light magneto-optical Kerr effect (MOKE) techniques. A goal of these works is spin engineering by which the magnetization of ultrathin metal films and nanowires can be controlled artificially.

II-F-1 X-Ray Magnetic Circular Dichroism Study on NO Adsorbed Co and Ni Ultrathin Films on Cu(001)

NAKAGAWA, Takeshi; WATANABE, Hirokazu; YOKOYAMA, Toshihiko

NO is well known as an effective magnetic killer since NO interacts with magnetic metal surfaces very strongly and the unpaired electron couples with the metal spins antiferromagnetically. In this work, we have investigated the effect of NO adsorption on ultrathin Co and Ni/Cu(001) films from the view point of magnetic anisotropy.

Figure 1 depicts the Ni *L*-edge x-ray magnetic circular dichroism (XMCD) of 5.5 and 9 monolayer (ML) Ni on Cu(001), taken at Beamline 4B in UVSOR. In the case of in-plane magnetized 5.5 ML Ni/Cu(001), both $\theta = 30^{\circ}$ (close to the in-plane easy axis) and $\theta = 90^{\circ}$ (along surface normal, hard axis) spectra were taken at a magnetic field of 1000 G and at a temperature of ~100 K. The $\theta = 30^{\circ}$ spectra show noticeable reduction of the magnetization on NO adsorption, while less prominent suppression is found in the $\theta = 90^{\circ}$ spectra. This finding is similar to the NO/Co/Cu(001) case (not shown). The 9 ML spectra (perpendicular magnetization both before and after NO adsorption) show much less change between clean and NO-adsorbed Ni along the easy axis, being different from the 5.5 ML case.

From the quantitative analysis, it is found that in the in-plane magnetized films of 5.5 ML Ni and 3 ML Co (not shown), the in-plane orbital moments are significantly suppressed on NO adsorption, while perpendicular orbital moments show much less change. The Ni 9 ML films give again almost no change in perpendicular orbital moments. These results imply that NO suppress the in-plane orbital moment drastically, while the perpendicular orbital moment is much less influenced. Consequently, NO relatively stabilizes perpendicular magnetization effectively.



Figure 1. Ni *L*-edge XMCD of 5.5 and 9 ML Ni/Cu(001) before and after NO adsorption. The x-ray incidence angles were $\theta = 30^{\circ}$ and 90° for 5.5 ML Ni and $\theta = 90^{\circ}$ for 9 ML Ni.

II-F-2 Is the Perpendicular Magnetic Anisotropy in Ni/Cu(001) Stablized by the Cu Capping ?

NAKAGAWA, Takeshi; WATANABE, Hirokazu; YOKOYAMA, Toshihiko

The effect of the Cu capping on Ni/Cu(001) films has been investigated by different research groups, and essentially contradictory results were reported. In this work, we have examined the Ni films grown on clean and preoxidized Cu(001) surfaces by means of the MOKE and XMCD. These films consequently show completely different properties concerning the spin reorientation transition, leading to a consequent definite answer for the previous contradictions.

For the Cu-capped Ni films grown on clean Cu(001), the MOKE measurement shows that the critical thickness for the spin reorientation transition of ~ 9 ML before Cu capping is significantly reduced to ~ 6.5 ML after > 0.4 ML Cu capping. The XMCD results clarifies that the in-plane orbital magnetic moment is correspondingly suppressed after Cu deposition, while the perpendicular orbital magnetic moment does not vary irrespective of the presence or absence of the Cu overlayer. On the contrary, for the Cu-capped Ni films grown on preoxidized Cu(001), the opposite trends were basically concluded. MOKE shows that the critical thickness of ~ 5 ML before Cu capping is significantly enlarged to ~ 6.5 ML after Cu capping. The XMCD results clarifies that the in-plane orbital magnetic moment is correspondingly enhanced after Cu deposition. Figure 1 shows the orbital magnetic moments from XMCD and the relative hysteresis loss from MOKE, which are in good acoordance with each other.

Such different nature originates from the behavior of adsorbed oxygen. Although Ni was deposited onto oxidized Cu(001) in the latter case, the oxygen atoms act as a surfactant and comes up to the surface of the Ni films. Adsorption of oxygen suppresses surface magnetic anisotropy that favors in-plane magnetization much more effectively than clean Ni and even than the Cu/Ni interface. Furthermore, when depositing Cu, oxygen again comes up to the Cu overlayer and locates at the surface, in spite that the O–Ni bond is much stronger than the O–Cu bond. Since no O–Ni interaction remains any more, the Cu-capped Ni films shows similar magnetic properties. The present finding clearly concludes that the modification of the in-plane orbital moment drives the spin reorientation transition.



Figure 1. Comparison between the hysteresis losses (open symbols) from MOKE and the orbital magnetic moment (filled symbols) from XMCD for (a) Cu/Ni(5.5 ML)/Cu(001) and (b) Cu/Ni(4.8 ML)/O/Cu(001). The plots demonstrate a one-to-one correspondence between the hysteresis loss and orbital magnetic moment.

II-F-3 Switching of the Magnetic Easy Axis in Pseudo-Nanowire Co on Vicinal Cu(1 1 41) Surface *via* Ag and NO Adsorption

NAKAGAWA, Takeshi; WATANABE, Hirokazu; YOKOYAMA, Toshihiko

It is well known that rod magnets are likely to be magnetized along its axis due to shape anisotropy. Metal thin films grown on stepped surfaces can be regarded as pseudo-nanowires, which are connected at the step edges with each other. These films are found to exhibit strong uniaxial magnetic anisotropy along the step direction. Weber *et al.* [*Phys. Rev. B* **52**, R14400 (1995)] reported surprising results whereby Ag capping induces the switching of the easy axis of Co on a vicinal Cu surface. In this work, we have tried to confirm the findings on 10 ML Co on Cu(1 1 41) and moreover have investigated the effect of NO adsorption on 7 ML Co on the same substrate by means of the MOKE experiments.

Figure 1 depicts the hysteresis loops recorded by the longitudinal MOKE measurements of 10 ML Co on Cu(1 1 41) (a) before and (b) after 0.2 ML Ag deposition. On clean Co, a normal hysteresis loop was observed along the step, while a double hysteresis with a shift filed can be found in the direction perpendicular to the step. This implies that the magnetic easy axis, which was along the step as in the usual case, rotates by 90° and is perpendicular to the step direction within the surface plane. The previous experiments were confirmed and more detailed information was derived.

Figure 1(c) shows the hysteresis loops of 7 ML Co before and after NO adsorption. Before NO adsorption, clear uniaxial anisotropy is again seen, implying that the easy axis is along the step. After NO adsorption, the hysteresis loop is dramatically changed. There can be found no angular dependence and both the loops taken parallel and perpendicular to the step are identical. Correspondingly, the coercive field is drastically reduced. This implies that the easy axis disappears and the pseudo-nanowire behaves as if it had a fourfold symmetry. The XMCD measurements are in progress.



Figure 1. (a,b) Hysteresis loops of 10 ML pseudo-nanowire Co on Cu(11 41) (a) before and (b) after Ag deposition with the magnetic field parallel (black) and perpendicular (gray) to the step; (c) Hysteresis loops of 7 ML pseudo-nanowire Co on Cu(11 41) before and after NO adsorption with the magnetic field parallel (solid) and perpendicular (dashed) to the step.

II-G Molecular and Electronic Structures of Metallofullerenes

The continued interest in radical ions of fullerenes and metallofullerenes has resulted from the discovery of superconductivity in the CT complexes of alkali metals with fullerenes. Spectroscopic information concerning the electronic and spin states of the metallofullerene has been of great interest and obtained by ESR measurements.

II-G-1 Characterization of Ce@C₈₂ and Its Anion

WAKAHARA, Takatsugu¹; KOBAYASHI, Junichi²; YAMADA, Michio¹; MAEDA, Yutaka¹; TSUCHIYA, Takahiro¹; OKAMURA, Mutsuo²; AKASAKA, Takeshi¹; WAECHLICH, Markus³; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa; KAKO, Masahiro⁴; YAMAMOTO, Kazunori⁵; KADISH, Karl M.⁶

(¹Univ. Tsukuba; ²Niigata Univ.; ³Bryker Japan; ⁴Univ. Electro-Communication; ⁵Japan Nuclear Fuel Cycle Development Inst.; ⁶Univ. Huston)

[J. Am. Chem. Soc. 126, 4883–4887 (2004)]

Ce@C₈₂ is isolated by HPLC and the cage symmetry is determined as $C_{2\nu}$ by measuring the ¹³C NMR spectra of its anion. The ¹³C NMR peaks of [Ce@C₈₂]⁻ show temperature-dependent shifts ascribed to the *f* electron remaining on the Ce atom. Both Ce@C₈₂ and [Ce@C₈₂]⁻ are ESR silent because of the highly anisotropic *g* matrix as well as of the fast relaxation process originating from the orbital angular momentum of the *f* electron. This is the complementary relationship to the observation of the paramagnetic shift in ¹³C NMR. [Ce@C₈₂]⁻ has a lower stability in air than [La@C₈₂]⁻.

II-G-2 Isolation and Crystallographic Characterization of the La@C₈₂ Derivative

MAEDA, Yutaka¹; MATSUNAGA, Yoichiro²;

WAKAHARA, Takatsugu²; TAKAHASHI, Satomi³; TSUCHIYA, Takahiro²; ISHITSUKA, Midori O.²; HASEGAWA, Tadashi¹; AKASAKA, Takeshi²: LIU, Michael T. H.⁴; KOKURA, Kisato⁵; HORN, Ernst⁵; YOZA, Kenji⁶; KATO, Tatsuhisa; OKUBO, Shingo; KOBAYASHI, Kaoru; NAGASE, Shigeru; YAMAMOTO, Kazunori⁷

(¹Tokyo Gakugei Univ.; ²Univ. Tukuba; ³Niigata Univ.; ⁴Univ. Prince Edward Island; ⁵Rikkyo Univ.; ⁶Bruker AXS K. K.; ⁷Japan Nuclear Cycle Development Inst.)

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The photochemical reaction of La@C₈₂ with 2adamantane-2,3-[3H]-diazirine affords adduct 2, La@ $C_{82}(Ad)$, in a quantitative and highly selective manner. The structure of compound **2** is confirmed by ESR, MS, and UV-Vis-NIR spectroscopies, and the first X-ray crystallographic characterization of an endohedral monometallofullerene derivative is reported. We have reported that the relatively higher reactivity of endohedral metallofullerenes is due to their electronic properties. The reaction EPR spectra reveal the formation of several regioisomers with different La isotopic splittings. In contrast, the regiospecific addition reaction of La@C₈₂ with 2-adamantane-2,3-[3H]-diazirine (1) affords the first single isomer which has been successfully isolated. Reported here is the first isolation and crystallographic characterization of a paramagnetic endohedral monometallofullerene derivative of the selective La@C₈₂ reaction.

II-H High Field and Pulsed Electron Spin Resonance Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of EPR spectroscopy enables us to investigate the heterogeneous and disordered system in detail. Especially the high frequency and pulsed EPR methods achieve the substantial resolution enhancement of spectrum. The advanced EPR spectroscopy is applied to study on the spin state in the heterogeneous system.

II-H-1 W-Band EPR Detection of the Manganese Multiline in the S₂ State of Cyanobacterial Photosystem II Single Crystal

KAWAMORI, Asako¹; SHEN, Jian-Ren²; MINO, Hiroyuki³; FURUKAWA, Ko; MATSUOKA, Hideto; KATO, Tatsuhisa (¹Kwansei Gakuin Univ.; ²Okayama Univ.; ³Nagoya Univ.)

The multiline signal of the manganese cluster in oxygen evolving complex of photosystem II in the S_2 -state was detected in the single crystal form of *thermo-synechococcus vulcanus* by W-band EPR measurement.

The distinct 21 lines with irregular spacing were identified, which is due to the hyper fine coupling (hfc) with manganese (I = 5/2) nuclear spins. The combination of the orientation of hfc- and g-tensors among the multisites of manganese cluster strongly affected the appearance of spectrum, and the overlapped hfc structure was smeared out in some orientation of the single crystal. The peculiar spectral patterns in various orientations of the single crystal were well simulated under the assumption of the trimer-monomer structure for the manganese cluster, and the principal values and the direction of the principal axis of an effective g-tensor were determined. The g_z component of the g-tensor was deduced as to be perpendicular to the two-hold axis relating the dimer structure in one subunit of the protein crystal.

RESEARCH ACTIVITIES III Department of Electronic Structure

III-A Synthesis and Characterization of Exotic Molecule Based Nano-Crystals of Metal Acetylides: Toward Carbon Encapsulated Metal Dot Array, Metal Nano-Fibers and Hydrogen Storage

An anhydrous and oxygen-free condition has made us possible to obtain various transition metal-acetylides, where M = Fe, Co, Ni and so on. These acetylide compounds exhibit high potentiality for magnetic, catalytic, electronic, and gas adsorption functions. In contrast to explosive property of M_2C_2 type acetylides such as Ag_2C_2 and Cu_2C_2 , CoC_2 and NiC_2 are rather stable in atmospheric condition. Thus, one can make the transition metal acetylides efficiently through the ion exchange reaction of metal chloride with CaC_2 in dehydrated acetonitrile solution. The MC₂ type compounds are expected to show CaC_2 type or MgC_2 type structure where metal cations and $C=C^{2-}$ are alternatively stacked like a rock salt crystal, although the relative orientation of the anion molecule may depend on the synthetic condition. Annealing or heating above 300 °C induces the reduction of cations by anions, $C=C^{2-}$ (charge neutralization), and resulting in the segregation of metal atoms by locating C_2 radicals outer and connecting C_2 bi-radicals as graphite-like or pyrolytic carbon shells. The relatively low segregation temperatures for FeC₂ and NiC₂ make it possible to draw metallic dots or wire circuits in MC₂ thin layers by scanning electron or VUV laser beams. The small size matrix MC₂ crystals prevent the strong dipole-dipole interaction between the metallic dots, while one can also wash out the matrix salt crystals by acid solution leaving the carbon encapsulated nano-metals on the base plate.

III-A-1 Manifestations of Ferromagnetism in CoC₂ by Water Coordination

NISHIJO, Junichi; OKABE, Chie; NISHI, Nobuyuki; SAWA, Hiroshi¹ (¹KEK)

 (^{I}KEK) Due to the high absorbency of CoC₂, water molecules are coordinated to the Co^{2+} dication when CoC_2 is exposed to air or water. XRD pattern of the asprepared anhydrous CoC₂, which is mostly originated from the scattering at the Co²⁺ dications, suggests the *fcc*-lattice of Co²⁺ with the lattice constants a = b = 3.41Å and c = 4.82 Å. Judging from the crystal structures of CaC_2 and MgC₂, we expect that the Co^{2+} and C_2^{2-} ions form NaCl-like alternate stack, where the *fcc* arrangement of the Co²⁺ dications indicates the (static) orientation disorder of the C₂²⁻ dianions as shown in Figure 1. The cubic structure involving the orientation disorder of C_2^{2-} ions is also observed in CaC_2 at high temperature. Although CoC₂ is water-stable material unlike CaC₂ and MgC₂, absorbed water changes the crystal structure of CoC₂ drastically. After air-exposure, the XRD peaks become broad and the positions change as Co^{2+} cations form the body-centered-tetragonal sublattice with the lattice constants a = b = 3.88 Å, and c = 3.40 Å. In this phase, the a- and b-axes are expanded due to the absorbed waters coordinated to the Co²⁺. The orientation of the C_2^{2-} dianions is also affected by the lattice expansion and/or steric hindrance of the water, resulting in the structural change from the isotropic disordered orientation (upper case in Figure 1) to anisotropic ordered orientation (lower case in Figure 1). Because the structural change is too drastic to be done in concert,

a CoC₂ particle is divided into many small domains. Inter-molecular magnetic interaction is sensitive to the arrangement of the molecules. Therefore, it is expected that the magnetism of the hydrous and anhydrous CoC₂ are largely different. Figure 1 also shows the temperature dependence of the field-cooled magnetic susceptibilities χ of CoC₂ before and after the airexposure,(a and b, respectively). χ of the anhydrous CoC₂ obeys the Curie-Weiss law in the high temperature range above *ca.* 70 K with Curie constant C = 1.1emu·K/mol and anti-ferromagnetic (AF) Weiss temperature $\Theta = -10$ K, the former of which is obviously larger than the value of Co^{2+} cation (C = 0.375), suggesting the short-range strong ferromagnetic (FM) interaction. Although χ of the hydrous CoC₂ also obeys the Curie-Weiss law above 100 K, $C = 1.5 \text{ emu} \cdot \text{K/mol}$ is significantly larger than that of anhydrous CoC_2 suggesting the expansion of the FM domain, while AF $\Theta = -3$ K indicates the weakening of the AF interaction between FM domains. The difference of the magnetism between hydrous and anhydrous CoC₂ is evidently caused by the water-induced structural changes; that is, the orientation ordering of C_2^{2-} and the expansion of the inter-chain distance. Judging from the fact that the interaction is weakened by lengthening the inter-molecular distance, it is concluded that the AF and FM interactions are attributed to the inter- and intra-chain interaction. In hydrous phase, where the FM interactions are connected each other and form the FM chain elongated parallel to the *c*-axis, resulting in the large FM domains.



Figure 1. Temperature dependence of the field-cooled (10 Oe) magnetic susceptibilities χ of CoC₂ before and after the air-exposure,(a and b, respectively). Inserted are the structures that reproduce the XRD patterns of hydrous and anhydrous CoC₂ nano-crystals.

III-A-2 Molecule-Based Room Temperature Magnet: (CoC₂)₂(H₂O) Nano-Rods

KOSUGI, Kentaroh; NISHIJO, Junichi; OKABE, Chie; BUSHIRI, Junaid M.; NISHI, Nobuyuki

As revealed in the previous study, CoC₂ crystals become ferromagnetic with coordinating water molecules to Co²⁺ ions. Elongation of the Co²⁺–Co²⁺ distance makes the four-center interaction positive with the C_2^{2-} molecular axis perpendicular to the Co–Co axis. $(CoC_2)_2(H_2O)$ was synthesized from acetonitrile solution of CoCl₂ and suspended CaC₂ powder at 100 °C. The black product was washed by methanol with 5% of water. Figure 1 shows TEM images of the nanorods. Figure 1-a indicates the presence of small particles with several nm radii in addition to the rod-like particles. Expanded in Figure 1-b is the lattice pattern of a rod exhibiting the long distances of the lattice stripes and wavy or somewhat disordered orientation of the atoms in the lattice sites. This kind of disorder is hardly seen in metal oxides or metallic particles with similar sizes. This is probably due to gradual hydration after the salt type crystals were formed, and thought to be characteristic of hydrophilic acetylide compounds. Figure 1-c shows the magnetic hysteresis curves of the particles at 300 K and 1.8 K. As seen from the curves, cohesive forces are as large as 780 Oe at 1.8 K and 650 Oe at 300 K. The magnetic saturation curve at 1.8 K suggests that the small spherical particles are superparamagnetic at 300K and only the rod-type crystals behave as room temperature magnets.



Figure 1. a: Transmission Electron Microscope image of the $(CoC_2)_2(H_2O)$ nano-rods that coexist with small spherical particles with several nm radii. b: Expanded view of a lattice image of a nano-rod. c: Magnetic hysteresis curves of CoC_2 synthesized at 100 °C.

III-A-3 Self-Assembled Nano-Wire Formation of Copper Acetylide (C₂Cu₂)

JUDAI, Ken; NISHIJO, Junichi; OKABE, Chie; NISHI, Nobuyuki

Copper acetylide (Cu−C=C−Cu) was synthesized firstly for a long time ago, however, because of its explosive nature, the revealed properties are limited. From the view point of nano-science, the extreme small amount of explosive compound cannot achieve critical point of explosion, and is regarded as good candidate for source of copper or carbon in the dimension of nanoscale. The other side, recent progress of electron microscopy makes it possible to uncover geometric structure of various compounds in atomic scale. We have examined synthesized copper acetylide by transmission electron microscopy (TEM), and its self-assembled nano-rod shape was discovered.

The copper acetylide was synthesized by the following recipe. First, 1 g of copper chloride (I), CuCl, was dissolved into 100 ml of 6% ammonia water. After 30 minutes of Ar gas bubbling in order to remove dissolved oxygen molecules, acetylene (C_2H_2) gas was bubbled in the solution.

 $2 \operatorname{Cu}^{+} + \operatorname{C}_2\operatorname{H}_2 \twoheadrightarrow \operatorname{C}_2\operatorname{Cu}_2 + 2\operatorname{H}^+$

The color of the solution turned from blue (copper

ammine complex) into dark brown, and the product of C_2Cu_2 was precipitated. After 30 minutes reaction, the product was filtered and washed by water and methanol. Since this product contained excess solvent molecules, the estimation of the reaction yield was difficult. Very roughly, 50 ~ 100% of yield was guessed. For the measurement of TEM, small amount of the product was grinded and suspended in methanol. The methanol suspension was dropped onto a micro grid. After dry up, that grid was used as a specimen for TEM observation.

Figure 1 displays the TEM images of copper acetylide. Even if the copper acetylide synthesized in water solution was measured directly by TEM, nano-wires shaped with 5-20 nm of diameter and 200-800 nm in length were observed. This means that C_2Cu_2 in water solution is self-assembled into nano-sized rod structure. Due to the minimization of the electronic circuit on computer, production of nano-wires is one of the hottest topics in nano-technology. The various methods have been suggested for production ways of nano-wires, for example, nano-single crystal wire growth on nano-sized catalysis, deposition of metal on a template with nanoholes, and so on. The self-assembled method for nanowire production is easily applied to mass-production and low-cost compared to the other method. The way of synthesis for nano-wire C₂Cu₂ is so simple that this is regarded as a remarkable way. Its crystal structure, aggregation mechanism, and physical properties (conductivity and so on) are still unclear in the present stage. In our group the theoretical calculation and various analysis techniques are in progress to reveal nature of copper acetylide nano-wire in detail.

Figure 1. (a): Transmission Electron Microscope (TEM) image of copper acetylide (C_2Cu_2). 20 nm of rod diameter is one of the thickest wires. (b): . Typical TEM image of copper acetylide (C_2Cu_2). The bundle of nano-wires with 5 nm of diameter was observed.

III-A-4 Formation of Air Stable Carbon-Skinned Iron Nanocrystals from FeC_2

KOSUGI, Kentaroh; BUSHIRI, Junaid M.; NISHI, Nobuyuki

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Charge neutralization reaction in ionic salt of $Fe^{2+}C_2^{2-}$ is found to produce carbon-skinned Fe nanocrystals. FeC₂ is formed as an intermediate product in the reaction of FeCl₂ solved in acetonitrile with CaC₂ fine powder and also able to be isolated as black nanocrystals. Heating of FeC₂ at temperature higher than 250 °C induces segregation of metallic iron. The segregated carbons grow as graphitic sheets parallel to the growing Fe lattice plane. This direct bonding is due to an accidental matching of the Fe-Fe distance (2.866 Å) with that of the C_1 – C_4 distance (2.842 Å) of the hexagonal rings in graphite. The X-ray diffraction pattern indicates that the particles are composed of α -Fe and graphitic carbon. The thickness of the skin is almost constant as thick as 3.5 nm independent of the body size. The particles with an average size of 30 nm exhibit temperature dependence of the magnetic cohesive force as function of $\hat{T}^{-0.275}$.



III-B States of Neutral and Ionic Molecular Associates in Solutions

States of molecular associates particularly in aqueous solutions are of great importance in understanding the role of molecules in living organisms. We found that any ideally mixed state cannot be seen in protic-protic mixtures such as water-alcohol, water-acetic acid, and alcohol-acetic acid systems on the molecular level at solute molar fractions (χ_A) higher than 0.001. In such a system, solute-solute asociation is highly favored resulting in microscopic phase separation. In this year, we studied the aqueous mixture of hexafluoro-2-propanol (HFIP), and have shown that that structural transition of solvent clusters takes place at $x_{HFIP} \sim 0.1$ from the tetrahedral-like hydrogen bonded network of water at $x_{HFIP} \leq 0.15$.

III-B-1 Structure and Dynamics of Hexafluoroisopropanol-Water Mixtures by X-Ray Diffraction, Small-Angle Neutron Scattering, NMR Spectroscopy, and Mass Spectrometry

YOSHIDA, Koji¹; YAMAGUCHI, Toshio¹; ADACHI, Tomohiro²; OTOMO, Toshiya²; MATSUO, Daisuke³; TAKAMUKU, Toshiyuki³; NISHI, Nobuyuki

(¹Fukuoka Univ.; ²KEK; ³Saga Univ.)

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The structure and dynamic properties of aqueous mixtures of 1,1,1,3,3,3-hexafluoro- 2-propanol (HFIP) have been investigated over the whole range of HFIP mole fraction ($x_{\rm HFIP}$) by large-angle x-ray scattering (LAXS), small-angle reutron scattering (SANS), ¹⁹F-, ¹³C-, and ¹⁷O-NMR chemical shifts, ¹⁷O-NMR relaxation, and mass spectrometry. The LAXS data have shown that structural transition of solvent clusters takes place at $x_{\rm HFIP} \sim 0.1$ from the tetrahedral-like hydrogen bonded network of water at $x_{\rm HFIP} \leq -0.1$ to the structure of near HFIP gradually formed with increasing HFIP

concentration in the range of $x_{\text{HFIP}} \ge 0.15$. The Ornstein- Zernike plots of the SANS data have revealed a mesoscopic structural feature that the concentration fluctuations become largest at $x_{\text{HFIP}} \sim 0.06$ with a correlation length of ~ 9 Å, *i.e.*, maximum in clustering and microhetrogeneities. The ¹⁹F and ¹³C chemical shifts of both CF_3 and CH groups of HFIP against x_{HFIP} have shown an inflection point at $x_{\text{HFIP}} \sim 0.08$, implying that the environment of HFIP molecules changes due to the structural transition of HFIP clusters. The ¹⁷O relaxation data of water have shown that the rotational motion of water molecules is retarded rapidly upon addition of HFIP into water up to $x_{\text{HFIP}} \sim 0.1$, moderately in the range of ~ $0.1 < x_{\text{HFIP}} \le 0.3$, and almost constant at $x_{\text{HFIP}} \ge 0.3$, reflecting the structural change in the solvent clusters at $x_{\text{HFIP}} \sim 0.1$. The mass spectra of cluster fragments generated in vacuum from HFIPwater mixtures have shown that the predominant clusters are A_1W_n (n < 12, A = HFIP, W = water) and water clusters W_n (n = 5-8) at $x_{HFIP} = 0.09$ and 0.20 and only HFIP oligomers in a water-rich region $x_{\text{HFIP}} =$ $0.005 \sim 0.01$. From all the information obtained in the present study, the models are proposed for the aggregation of HFIP and water molecules in HFIPwater mixtures.

III-C Ultrafast Dynamics and Scanning Tunneling Microscopy

For the study of molecules on metallic or crystalline surface, very low temperature Scanning Tunneling Microscope (LT STM) system are now in use for collaboration with users in universities. Ultrafast laser systems with pico and femtosecond time resolutions are also available.

III-C-1 Orientation of Adsorbed Nitrous Oxide on Palladium(110) by STM

MATSUSHIMA, Tatsuo¹; RZEZNICKA, Izabela¹; WATANABE, Kazuo²; INOKUCHI, Yoshiya²; NISHI, Nobuyuki (¹Hokkaido Univ.; ²Univ. Tokyo)

Adsorbed N_2O on Pd(110) was confirmed to be oriented along the [001] direction at around 8 K by using a low temperature scanning-tunneling microscope, confirming the prediction from angular distributions of desorbing product N₂ in thermal N₂O decomposition and through structure analysis of adsorbed N₂O by density functional theory with generalized gradient approximations. Figure 1 shows a STM image of N₂Ocovered Pd(110) at 8 K. Furthermore, the formation of small clusters extended along the [110] direction was first found at low temperatures. These measurements support the reaction mechanism through the N₂O intermediate in catalytic NO_x decomposition.



Figure 1. A STM image of N_2O -covered Pd(110) at 8 K. N_2O was dosed at 90–80 K.

III-C-2 Observation of Ultrafast Dynamics of Jet-Cooled *N*-Salicylideneaniline by Femtosecond Time-Resolved REMPI Spectroscopy

OKABE, Chie; NAKABAYASHI, Takakazu¹; INOKUCHI, Yoshiya²; SEKIYA, Hiroshi³; NISHI, Nobuyuki

(¹Hokkaido Univ.; ²Univ. Tokyo; ³Kyushu Univ.)

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N-salicylideneaniline (SA) is well-known photochromic aromatic anil. The excited-state intramolecular proton transfer (ESIPT) followed by photoexcitation of the enol form to its first ${}^{1}(\pi,\pi^{*})$ state produces the $^{1}(\pi,\pi^{*})$ state of the *cis*-keto form, leading to a metastable trans-keto form as the final photoproducts. To investigate ultrafast processes in photoexcited SA, we have applied the femtosecond time-resolved resonanceenhanced multiphoton ionization (REMPI) spectroscopy under the isolated conditions. The decay profile of SA excited at 320 nm is well reproduced by a convolution of the response function with a bi-exponential decay, giving time constants of $\tau_1 < 300$ fs and $\tau_2 = 3.3$ ps. The decay profile of SA measured by varying the pump wavelength from 360 to 373 nm is well fitted using a triexponential decay function with time constants of τ_1 < 300 fs, $\tau_3 = 1.5$ ps, and $\tau_4 > 100$ ps. The difference is attributable to the difference in the ionization efficiency for the enol and keto forms. A very fast decay component ($\tau_1 < 300$ fs) is assigned to a decay of the $1(\pi,\pi^*)$ state of the enol form. A component $\tau_3 = 1.5$ ps arises from the cis-keto form produced via the excited-state intramolecular proton transfer (ESIPT) reaction, because the probe wavelength at ~ 400 nm is in resonance with the S_n - S_1 transition of the *cis*-keto form. A component $\tau_2 = 3.3$ ps is attributed to the decay of an excited state of the enol form. The ion signals via the (n,π^*) state of the enol form as well as the protontransferred cis-keto form emerge within a few hundred femtoseonds after photo-excitation to the first $^{1}(\pi,\pi^{*})$ state of the enol form. This state must be populated *via* the ${}^{1}(n,\pi^{*})$ state of the enol form, suggesting that an ultrafast non-radiative process occurs in addition to the ESIPT reaction.

Figure 1 shows the deactivation processes following the photoexcitation of the enol form on the basis of the results of the femtosecond time-resolved REMPI measurement together with the theoretical studies. Two ultrafast processes, the ESIPT reaction and an internal conversion (IC) to the ${}^{1}(n,\pi^{*})$ state, occur on a time scale less than a few hundred femtoseconds from the $^{1}(\pi,\pi^{*})$ state of the enol form. The decay time of the $^{1}(\pi,\pi^{*})$ state of the *cis*-keto form largely changes when the enol form is excited at between 370 and 365 nm. The remarkable change in the decay time is reasonably explained by the existence of a threshold for the ultrafast non-radiative process from the (π,π^*) state of the cis-keto form. The opening of an efficient nonradiative channel; an IC from ${}^{1}(\pi,\pi^{*})$ to ${}^{1}(n,\pi^{*})$ of the cis-keto form promotes the production of the trans-keto form as the final photochromic products. The two IC processes provide opposite effect on the quantum yield of photochromic products: IC in the enol form may substantially reduce the quantum yield, but IC in the cisketo form increases it.



Figure 1. Photoexcited processes of SA drawn on the basis of the femtosecond time-resolved REMPI spectroscopy in gas phase. Two ultrafast processes ESIPT and IC occur by photoexcitation of a high vibronic state of the enol form. When the pump wavelength is shrorter than ~ 365 nm, an IC occurs from the ${}^{1}(\pi,\pi^{*})$ to the ${}^{1}(n,\pi^{*})$ state of the protontransferred cis-keto form in addition to the radiative ($hv_{\rm F}$) and non-radiative decay to the S_0 state. The IC efficiently produces the *trans*-keto form as the final photochromic products. The *trans*-keto form may be produced as a minor channel when the enol form is excited at wavelength longer than 370 nm. *TS* indicates a transition state.

III-C-3 Picosecond Time-Resolved Stokes and Anti-Stokes Raman Studies on the Photochromic Reactions of Diarylethene Derivatives

OKABE, Chie; NAKABAYASHI, Takakazu¹; NISHI, Nobuyuki; FUKAMINATO, Tuyoshi²; KAWAI, Tsuyoshi²; IRIE, Masahiro²; SEKIYA, Hiroshi²

(¹Hokkaido Univ.; ²Kyushu Univ.)

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The cyclization and cycloreversion reactions of diarylethene derivatives have been studied with picosecond time-resolved Stokes and anti-Stokes Raman spectroscopies. The cyclization reaction of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (DMTF) is found to occur within 4 ps to produce the vibrationally excited closed forms in the ground electronic (S_0) state. The time constant of the vibrational relaxation toward a thermal equilibrium with solvent molecules is estimated to be about 10 ps. The cycloreversion reaction of 1,2-bis(3,4-dimethyl-5-phenyl-2-thienyl)perfluorocyclopentene (DMPTF) also generates the vibrationally excited open forms in the S_0 state within 4 ps, which

decay on a picosecond time scale. The picosecond timeresolved anti-Stokes Raman spectra of DMPTF show two vibrational bands assignable to the C=C stretching modes of the cyclopentene and thiophene moieties of the generated open forms. The Raman intensity arising from the cyclopentene moiety relative to that from the thiophene moiety becomes smaller with the delay time, indicating that part of the excess energy generated *via* the cycloreversion reaction is localized on the C=C stretching mode of the cyclopentene moiety. This result suggests that the C=C stretching mode of the cyclopentene moiety is one of the promoting or the accepting modes in the cycloreversion reaction.

III-D Spectroscopic and Dynamical Studies of Molecular Cluster lons

Electron deficiency of molecular cluster cations can attract electron rich groups or atoms exhibiting charge transfer or charge resonance interaction in the clusters. This causes dynamical structural change such as proton transfer or ion-core switching in hot cluster ions or clusters in solution.

III-D-1 Structures of $[Mg \cdot (H_2O)_{1,2}]^+$ and [AI \cdot (H_2O)_{1,2}]^+ lons Studied by Infrared Photodissociation Spectroscopy: Evidence of [HO-AI-H]^+ Ion Core Structure in [AI \cdot (H_2O)_2]^+

INOKUCHI, Yoshiya¹; OHSHIMO, Keijiro²; MISAIZU, Fuminori³; NISHI, Nobuyuki (¹IMS and Univ. Tokyo; ²RIKEN; ³Tohoku Univ.)

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Infrared spectra of $[Mg \cdot (H_2O)_{1,2}]^+$ and $[Al \cdot (H_2O)_{1,2}]^+$ are measured in the OH stretching region (3200–3800 cm⁻¹). The spectra show the symmetric and asymmetric OH stretching bands of water molecules that are directly bound to the metal ions thorough metal-oxygen intermolecular bonds. In addition to these bands, the $[Al \cdot (H_2O)_2]^+$ ion has another band at 3714 cm⁻¹. This band is assigned to the free OH stretching vibration of the $[HO-Al-H]^+$ ion; the aluminum ion is inserted into the O–H bond of one water molecule in $[Al \cdot (H_2O)_2]^+$.

III-D-2 Infrared Photodissociation Spectroscopy of $[Mg \cdot (H_2O)_{1-4}]^+$ and $[Mg \cdot (H_2O)_{1-4} \cdot Ar]^+$

INOKUCHI, Yoshiya; OHSHIMO, Keijiro; MISAIZU, Fuminori¹; NISHI, Nobuyuki (¹Tohoku Univ.)

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Infrared photodissociation spectra of $[Mg \cdot (H_2O)_{1-4}]^+$ and $[Mg \cdot (H_2O)_{1-4} \cdot Ar]^+$ are measured in the 3000–3800 cm⁻¹ region. For $[Mg \cdot (H_2O)_{1-4}]^+$, cluster geometries are optimized and vibrational frequencies

are evaluated by density functional theory calculation. We determine cluster structures of $[Mg \cdot (H_2O)_{1-4}]^+$ by comparison of the infrared photodissociation spectra with infrared spectra calculated for optimized structures of $[Mg \cdot (H_2O)_{1-4}]^+$. In the $[Mg \cdot (H_2O)_{1-3}]^+$ ions, all the water molecules are directly bonded to the Mg⁺ ion. The infrared photodissociation spectra of $[Mg \cdot (H_2O)_4]^+$ and $[Mg \cdot (H_2O)_4 \cdot Ar]^+$ show bands due to hydrogen-bonded OH stretching vibrations in the 3000–3450 cm⁻¹ region. In the $[Mg \cdot (H_2O)_4]^+$ ion, three water molecules are attached to the Mg⁺ ion, forming the first solvation shell; the fourth molecule is bonded to the first solvation shell. As a result, the most stable isomer of $[Mg \cdot (H_2O)_4]^+$ has a six-membered ring composed of the Mg⁺ ion, two of the three water molecules in the first solvation shell, and a termination water molecule.

III-E Spectroscopy and Dynamics of Vibrationally Excited Molecules and Clusters

This research group is studying structure and dynamics of molecules and clusters by two-color double resonance spectroscopy. New spectroscopic methods will also be developed to observe the higher vibrational state under collision-free condition.

A molecular cluster is a microscopic system of solution and/or crystal, and is thought to provide detailed information on relaxation and reaction dynamics in condensed phase. However the previous studies are concentrated to stable clusters which has no reaction pathway after photo-excitation. Consequently, spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopies to the reactive clusters to reveal detailed mechanism of intracluster reaction.

For the study of the ground state, the structure of the cluster can be determined by the combination of the IR dip spectroscopy and *ab initio* MO calculations.¹⁾ The IR dip spectroscopy is a kind of IR-UV double resonance spectroscopy which provides the spectrum which corresponds to the infrared absorption spectrum of the cluster (see Figure 1). A tunable IR laser is introduced to the clusters and is scanned its frequency over the fundamental vibrational region (typically 2400 ~ 4000 cm⁻¹). Then a tunable UV laser, of which the frequency is fixed to the S_1 origin of a specific cluster, is introduced and resonant enhanced multiphoton ionization signal *via* S_1 is monitored. When the IR laser is resonant to a vibrational level of the cluster, the ion signal decreases much because of loss of the population in the vibrational ground state. Thus, the IR absorption spectrum of the cluster can be measured by this depletion spectroscopy. The same spectrum can be obtained when the fluorescence intensity from S_1 is monitored instead of the ion current.

The IR spectrum in the excited state S_1 can also be measured by the depletion spectroscopy, when the UV laser is introduced before the IR laser (the UV-IR fluorescence dip spectroscopy; see Figure 2). The molecule is excited to S_1 by the UV laser, and the fluorescence intensity is monitored as well as the IR dip spectroscopy for S_0 . Then the S_1 molecules are further excited to the vibrationally excited level in S_1 by the IR laser. In general, the fluorescence quantum yield decreases in the higher vibronic level. Thus, the total fluorescence intensity decreases when the IR laser frequency is resonant to the vibrational level in S_1 .

Similarly, the IR spectrum of the ionic cluster can be measured by the depletion spectroscopy (mass-selected ion dip spectroscopy; see Figure 3). The ionic cluster can be prepared by the multiphoton ionization *via* S_1 , and the ion current due to the cation cluster of the specific size can be measured through a mass-filter. When the ionic cluster is vibrationally excited by the IR laser, the cluster is dissociated by the vibrational predissociation. Therefore, the IR transition can be measured by the decrease of the parent cluster. The same spectrum can be obtained by monitoring the enhancement of fragments (mass-selected multiphoton dissociation spectroscopy). In addition to these "dip" spectroscopies, the nonresonant ionization detected IR spectroscopy²⁾ and the PFI-ZEKE photoelectron spectroscopy³⁾ are also important tool to obtain the spectral information in the cation and the overtone states. Based on these spectroscopic techniques, we have measured the IR spectra of solvated clusters,⁴⁾ such as phenol/ammonia,⁵⁾ naphthol/alcohol,⁶⁾ carbazole/water⁷⁾ and 7-azaindole dimers,⁸⁾ and have discussed the relation among geometrical structure, electronic state and intracluster reactions.

From 2001, we have been developing the new ultrafast time-resolved IR spectroscopy for the reactive clusters. The pico second time-resolved vibrational spectroscopy is one of the ideal way to reveal the reaction mechanism directly. Here, we will demonstrate its usefulness by applying the hydrogen transfer reaction in photoexcited PhOH-





Figure 1. Principle of the IR Dip Spectroscopy. The IR transition in the ground state cluster can be measured.

Figure 2. Principle of the UV-IR Fluorescence Dip Spectroscopy. The IR transition of the cluster in the S_1 state can be obtained.

 $(NH_3)_n$ cluster.⁹⁾ Figure 4 shows the principle of the picosecond time-resolved UV-IR-UV ion dip spectroscopy. The reactive cluster (PhOH-(NH₃)_n in present case) is excited to S_1 by a picosecond UV laser v_{UV} and the photochemical reaction (hydrogen transfer) is triggered. The final reaction product, *i. e.* $(NH_3)_{n-1}NH_4$, is ionized by a nanosecond UV laser v_{ION} which is irradiated after 100 ns from v_{UV} and the population of the reaction product is monitored as a mass peak of $(NH_3)_{n-1}NH_4^+$. A picosecond tunable IR laser v_{IR} is irradiated after *t* ps from v_{UV} and is scanned over vibrational region. If v_{IR} is resonant to vibrational levels of the transient species, the population of the final reaction product decreases due to the vibrational predissociation of the transient species. Therefore, the vibrational transitions of the transient species at t ps can be observed as decrease of ion current of the final reaction product.

Time resolved UV-IR-UV ion dip spectra of phenol- $(NH_3)_3$ are shown in Figure 5. The numbers in the left hand sides of each spectrum indicate the delay time from v_{UV} to v_{IR} . Here the spectrum at -20 ns corresponds to the IR spectrum of PhOH- $(NH_3)_3$ in S_0 , in which the sharp bands around 3400 cm⁻¹, the broad bands at ~ 3200 cm⁻¹ and the very broad background are assigned to the degenerated antisymmetric stretch vibration v_3 in NH₃, the totally symmetric stretch vibration v_1 in NH₃ and the OH stretch vibration v_{OH} in phenol, respectively. The spectrum at + 180 ns shows the vibrational transitions of the final reaction product *via* S_1 , *i.e.* (NH₃)₂NH₄, and 1) two intense bands at 3180 cm⁻¹ and 3250 cm⁻¹ and 2) a broad band at 2700 ~ 3100 cm⁻¹ which have been assigned to





Figure 3. Principle of the mass-selected IR Ion Dip Spectroscopy. The IR transition of the cluster cation can be measured by the depletion of the parent cluster cation. The same spectrum can be measure by monitoring the enhancement of the fragments produced by the IR predissociation.



Figure 4. Principle of picosecond time-roselved UV-IR-UV ion dip spectroscopy. Potential curves of S_0 and S_1 are schematically drawn along O–H stretch coordinate. Potential curves in different sections on the S_1 O–H stretch coordinate are drawn along arbitrary N–H stretch coordinates.

Figure 5. Picosecond time-resolved UV-IR-UV ion dip spectra of the transient species from the electronically excited PhOH-(NH₃)₃ which was observed by fixing v_{UV} to the low vibronic band in the *S*₁ state of PhOH-(NH₃)₃ (281.49 nm) and monitoring (NH₃)₂NH₄⁺ due to $v_{ION}(355 \text{ nm})$. Times indicated at the left side of each spectrum mean the delay times between v_{UV} and v_{IR} . The spectra whose delay times are -20 ns and +180 ns (indicated by *) are obtained by nanosecond laser system, which have been reported in the previous paper.⁵)

vibrational transitions concerned with NH₄.

One can see that the vibrational bands rise with increasing delay time. The spectral feature at +100 ps is already similar to that of the final reaction product (+180 ns). Here, the intense band at 3250 cm⁻¹ rises slower than the band at 3180 cm⁻¹. The relative intensities of the two bands become comparable at 40 ps, thereafter, the higher band at 3250 cm⁻¹ clearly grows further. Thus, the rising time constant of the band at 3250 cm⁻¹ is apparently different from that of the 3180 cm⁻¹-band. This remarkable difference between the two intense bands suggests that each vibrational transition is derived from different species. The existence of two transient species are naturally interpreted by considering the isomers of (NH₃)₂NH₄; the most stable NH₃–NH₄–NH₃ and the meta-stable NH₄–NH₃–NH₃. The co-existence of isomers is strongly supported by *ab initio* calculations.

As described above, we have successfully measured the picosecond time resolved IR spectra of the transient species for the ESHT of PhOH- $(NH_3)_3$ for the first time. It proves that the picosecond UV-IR-UV ion dip spectroscopy is a powerful tool to explore the dynamics of the intracluster reaction.

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III-E-1 Photochemistry of Phenol-(NH₃)_n Clusters: Solvent Effect on a Radical Cleavage of an OH Bond in an Electronically Excited State and Intracluster Reactions in the Product NH₄(NH₃)_{n-1} (n < 5)

DAIGOKU, Kota¹; ISHIUCHI, Shun-ichi²; SAKAI, Makoto³; FUJII, Masaaki⁴; HASHIMOTO, Kenro⁵ (¹Tokyo Metropolitan Univ.; ²Tokyo Inst. Tech./JST-PRESTO; ³Tokyo Inst. Tech.; ⁴IMS and Tokyo Inst. Tech.; ⁵Tokyo Metropolitan Univ./ACT-JST)

[J. Chem. Phys. 119, 5149–5157 (2003)]

The potential energy surfaces of PhOH-(NH₃)_{0,1} and NH₄(NH₃)₁₋₄ have been investigated theoretically by *ab initio* methods. Intermolecular stretching in PhOH-NH₃ assists in the radical cleavage of an OH bond occurring through a $\pi\pi^*/\pi\sigma^*$ potential crossing. Thus, excited state hydrogen transfer (ESHT) is expected to take place by a solvent-assisted mechanism even in the larger PhOH-(NH₃)_n. Because sufficient energy is obtained by ESHT from PhOH-(NH₃)_n ($\pi\pi^*$) to PhO-NH₄(NH₃)_{n-1} ($\pi\sigma^*$) ($n \le 5$), hydrogen relocation and/or ammonia migration in the product NH₄(NH₃)_{n-1} can readily follow ESHT, which is responsible for observing isomer bands in the absorption spectra of the photoinduced reaction products of PhOH-(NH₃)_n.

III-E-2 Four-Color Hole Burning Spectra of Phenol/ammonia 1:3 and 1:4 Clusters

ISHIUCHI, Shun-ichi¹; DAIGOKU, Kota²;

HASHIMOTO, Kenro³; FUJII, Masaaki⁴

(¹Tokyo Inst. Tech./JST-PRESTO; ²Tokyo Metropolitan Univ.; ³Tokyo Metropolitan Univ./ACT-JST; ⁴IMS and Tokyo Inst. Tech.)

[J. Chem. Phys. 120, 3215–3220 (2004)]

The hole burning spectra of phenol/ammonia (1:3 and 1:4) clusters were measured by a newly developed four-color (UV-near-IR-UV-UV) hole burning spectroscopy, which is a kind of population labeling spectroscopy. From the hole burning spectra, it was found that single species is observed in an n = 3 cluster, while three isomers are observed simultaneously for n = 4. A possibility was suggested that the reaction efficiency of the hydrogen transfer from the electronically excited phenol/ammonia clusters, which was measured by a comparison with the action spectra of the corresponding cluster, depends on the initial vibronic levels.

III-E-3 S_1 - S_0 Electronic Spectrum of Jet-Cooled *m*-Aminophenol

SHINOZAKI, Minako¹; SAKAI, Makoto²; YAMAGUCHI, Shigeru¹; FUJIOKA, Tomoo¹; FUJII, Masaaki³

(¹*Tokai Univ.;* ²*Tokyo Inst. Tech.;* ³*IMS and Tokyo Inst. Tech.*)

[Phys. Chem. Chem. Phys. 5, 5044–5050 (2003)]

The S_1 and S_0 states of *m*-aminophenol have been investigated using laser induced fluorescence and

dispersed fluorescence spectroscopy in a supersonic jet. The dispersed fluorescence spectra, obtained by exciting the bands at 34 109 and 34 469 cm⁻¹, show the same vibronic structure, which suggests the coexistence of rotational isomers in *m*-aminophenol. A quantum chemical calculation also supports the coexistence of rotational isomers. From the relative intensities in the spectrum and the calculated stabilization energies of isomers, the bands are assigned to the origin of the cisand trans-isomers, respectively. The dispersed fluorescence spectra obtained by exciting the S_1 vibronic bands were analyzed by comparing with the calculated vibrational frequencies and IR and Raman spectra. From the analysis, the S_1 vibronic bands have been assigned. It was found that a one-to-one correspondence between the S_1 and S_0 vibrations is broken, and vibrational mixing due to Fermi resonance or the Duschinsky effect is suggested.

III-E-4 Predicted Spatial Resolution of Super-Resolving Fluorescence Microscopy Using Two-Color Fluorescence Dip Spectroscopy

IKETAKI, Yoshinori¹; WATANABE, Takeshi²; ISHIUCHI, Shun-ichi³; SAKAI, Makoto²; OMATSU, Takashige⁴; YAMAMOTO, Kimihisa⁵; FUJII, Masaaki⁶

(¹Olympus Optical Co. Ltd.; ²Tokyo Inst. Tech.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴Chiba Univ.; ⁵Keio Univ.; ⁶IMS and Tokyo Inst. Tech.)

[Appl. Spectrosc. 57, 1312–1316 (2003)]

The theoretical spatial resolution of the novel superresolution fluorescence microscopy was investigated. This microscopy is based on the fluorescence depletion process observed by two-color fluorescence dip spectroscopy. For the investigation, we measured the optical properties of Rhodamine 6G concerning the fluorescence depletion process. Using the obtained data, the spatial resolution of the microscopy is theoretically forecast when a first order of the Bessel beam is used for the erase beam. It is found that the resolution overcomes the diffraction limit in the nanometer scale region. The investigation shows that the microscopy gives a spatial resolution better than 100 nm using a nanosecond laser with a pulse energy of ~ nJ/pulse. The microscopy is expected to be an appropriate novel tool for observing samples with nanometer scale structures.

III-E-5 Vibrational Energy Relaxation of the 7-Azaindole Dimer in CCl₄ Solution Studied by Picosecond Time-Resolved Transient Fluorescence Detected IR Spectroscopy

SAKAI, Makoto¹; FUJII, Masaaki²

(¹Tokyo Inst. Tech; ²IMS and Tokyo Inst. Tech.)

[Chem. Phys. Lett. in press]

The picosecond time-resolved IR spectra of the 7azaindole dimer in a carbontetrachloride solution was measured by using picosecond time-resolved IR/UV double resonance spectroscopy. This spectroscopy selectively detects the IRtransition by transient fluorescence due to an electronic transition from avibrationally excited level. The time-evolution of the IR spectrum is asingle exponential with a 19 ps lifetime, which does not correspond to fastnonstatistical decay due to the intramolecular vibrational redistributionfound in a gasphase cluster. From a comparison with the timeresolved IRspectrum of a jet-cooled dimer, this decay is assigned to vibrationalcooling from the dimer to the solvent.

III-E-6 Pulsed Field Ionization—ZEKE Photoelectron Spectrum of *o*,*m*,*p*-Tolunitrile

SUZUKI, Kazunari¹; ISHIUCHI, Shun-ichi²; SAKAI, Makoto³; FUJII, Masaaki⁴

(¹Waseda Univ.; ²Tokyo Inst. Tech./JST-PRESTO; ³Tokyo Inst. Tech; ⁴IMS and Tokyo Inst. Tech.)

[J. Electron Spectrosc. in press]

Pulsed field ionization-ZEKE photoelectron spectroscopy has been applied to o-, m- and p-tolunitrile in a supersonic jet. The PFI-ZEKE photoelectron spectra of *m*- and *p*-tolunitrile show well-resolved anharmonic structures in the low frequency region, which are assigned to bands due to internal rotational motion of the methyl group in the cation. Level energies and relative transition intensities are reproduced well by a one-dimensional rotor model with a three-fold axis potential. Potential curves for the internal rotation have been determined. For o-tolunitrile, no band due to internal rotation was found in PFI-ZEKE spectrum. It is suggested that the *o*-tolunitrile cation has the high barrier for internal rotation and the stable conformation that is the same as that in S_1 and S_0 . The barrier height and the conformation are compared with other toluene derivatives, and the relation between the electronic character of -CN and the internal rotational motion has been discussed.

III-E-7 Two-Point-Separation in Super-Resolution Fluorescence Microscope Based on Up-Conversion Fluorescence Depletion Technique

WATANABE, Takeshi¹; IKETAKI, Yoshinori²; OMATSU, Takashige³; YAMAMOTO, Kimihisa⁴; SAKAI, Makoto¹; FUJII, Masaaki⁵

(¹Tokyo Inst. Tech.; ²Olympus Optical Co. Ltd.; ³Chiba Univ.; ⁴Keio Univ.; ⁵IMS and Tokyo Inst. Tech.)

[Opt. Express 11, 3271–3276 (2003)]

We have demonstrated a realistic super-resolution scanning fluorescence microscope using conventional nanosecond lasers. This super-resolution microscope is based on the combination of two-color fluorescence dip spectroscopy and shape modulation to a doughnut beam. Only by introducing a doughnut erase beam, the resolution of the laser fluorescence microscope breaks the diffraction limit by two times without using any mechanical probe.

III-E-8 Super-Resolution Fluorescence Microscopy in Nano-Meter Scale Region Using Two-Color Laser Beams

IKETAKI, Yoshinori¹; WATANABE, Takeshi²; SAKAI, Makoto²; ISHIUCHI, Shun-ichi³; OMATSU, Takashige⁴; YAMAMOTO, Kimihisa⁵; FUJII, Masaaki⁶

(¹Olympus Optical Co. Ltd.; ²Tokyo Inst. Tech.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴Chiba Univ.; ⁵Keio Univ.: ⁶IMS and Tokyo Inst. Tech.)

[J. Surf. Sci. Soc. Jpn. 24, 392–399 (2003)]

A super-resolution florescence microscopy using two-color laser beams was proposed. The microscopy is based on the combination of two-color fluorescence dip spectroscopy and a phase modulation technique for the laser beam. By applying the proposed technique to a laser-scanning microscope, a fluorescence image of a sample can be observed with a spatial resolution overcoming the optical diffraction limit. To demonstrate validity of the microscopy, we constructed a scanning microscope system using commercial nano-second pulse lasers. An image of micro beads containing dye molecules was observed by the microscopy. We succeeded in obtaining the image with a resolution overcoming the diffraction limit in nano-meter scale region. The experimental data showed that the resolution was improved three times at least. The microscopy is expected to be an appropriate analysis method for samples with nano-meter scale structure.

III-E-9 Formation of Doughnut Laser Beam for Super-Resolving Microscopy Using a Phase Spatial Light Modulator

WATANABE, Takeshi¹; IGASAKI, Yasumori²; FUKUCHI, Norihiro²; SAKAI, Makoto¹; ISHIUCHI, Shun-ichi³; FUJII, Masaaki⁴; OMATSU, Takashige⁵; YAMAMOTO, Kimihisa⁶; IKETAKI, Yoshinori⁷

(¹Tokyo Inst. Tech.; ²Hamamatsu Photonics K. K.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴IMS and Tokyo Inst. Tech.; ⁵Chiba Univ.; ⁶Keio Univ.; ⁷Olympus Optical Co. Ltd.)

[Opt. Eng. 43, 1136–1143 (2004)]

The formation of a doughnut-shaped laser beam is presented. To generate the beam, we used an optically addressed parallel-aligned nematic liquid-crystal phase spatial light modulator (PAL-SLM), and observed the shape of the focused beam. By using a compensating technique for wave aberration, the beam had a symmetric doughnut shape with a hole size of $1\mu m \phi$ on the focal plane. The experimental result shows that the generated beam can be expected to be applicable to super-resolving microscopy based on the fluorescence depletion process.

III-F Development of High-Precision Coherent Control and Its **Application**

Coherent control is based on manipulation of quantum phases of wave functions. It is a basic scheme of controlling a variety of quantum systems from simple atoms to nanostructures with possible applications to novel quantum technologies such as bond-selective chemistry and quantum computation. Coherent control is thus currently one of the principal subjects of various fields of science and technology such as atomic and molecular physics, solid-state physics, quantum electronics, and information science and technology. One promising strategy to carry out coherent control is to use coherent light to modulate a matter wave with its optical phase. We have so far developed a high-precision wave-packet interferometry by stabilizing the relative quantum phase of the two molecular wave packets generated by a pair of fs laser pulses in attosecond time scale. We will apply our highprecision quantum interferometry to gas, liquid, solid, and surface systems to explore and control various quantum phenomena.

III-F-1 Molecular Wave-Packet Interferometry with Attosecond Quantum Phase Manipulation

OHMORI, Kenji¹; SATO, Yukinori²; NIKITIN, **Evgueni E.³; RİCE, Stuart A.⁴** (¹IMS, CREST, JST; ²Tohoku Univ.; ³Technion-Israel

Inst. Tech.; ⁴Univ. Chicago)

[Phys. Rev. Lett. 91, 243003 (4 pages) (2003)]

Wave packet (WP) interferometry is a clear manifestation of wave nature of matter, and is a basic scheme of controlling a variety of quantum systems from simple atoms to nano structures with possible applications to novel quantum technologies such as bond-selective chemistry and quantum computation. The key technique in the WP interferometry is fine tuning of the delay between two light pulses that produce a pair of WP's with a precision far better than the quantum oscillation cycle of the WP's, say few femtoseconds (fs) to attoseconds (as). The WP's are then phase-locked and produce stable interference. We have constructed an 'attosecond phase modulator (APM)": a device for tuning the delay τ between two UV fs pulses with attosecond stability and resolution. We have utilized this APM to create an unprecedented high-precision WP interferometer with a dilute ensemble of the HgAr van der Waals complex; our interferometer displayed almost 100% fringe contrast as a function of the delay τ between two UV fs pulses at 254 nm (\rightarrow Figure 1). Moreover we have demonstrated the dephasing and rephasing of the interferograms of consecutive vibrational eigenstates within WP's, which arise from a subtle difference in the quantum oscillation cycles of each eigenstates, different from the well-known collapse and revival of the electron WP's in atoms.¹⁾ Our high precision interferometer makes it possible to create virtually arbitrary relative superpositions of the three vibrational eigenstates within a WP only by tuning a single parameter τ . It is pointed out that the interference structure can be retrieved from the population information stored in the thermal ensemble of molecules even after the coherence is wiped out (\rightarrow Figure 2). All these features are quite general in WP interference and therefore provide basis for opening new perspective of coherent control in a wide variety of quantum systems.

Reference





Figure 1. An example of the quantum interferograms of two molecular wave packets moving on the $A(^{3}0^{+})$ -state potential curve of the Hg-Ar vdW complex. The interferogram displays almost 100% fringe contrast as a function of the inter-pulse delay τ tuned with attosecond stability and resolution. Its top and bottom represent amplification and annihilation of the wave packet.



Figure 2. Population codes written in a Hg-Ar vdW complex by using wave-packet interference. Particular information can be encoded as a relative superposition of the vibritonal eigenstates within a wave packet, and that information can be retrieved as a population code stored in the ensemble of molecules even after the coherence is wiped out.

III-G Structure and Properties of Carbon Nanotubes and Nanohorns

Our research on single-wall carbon nanotubes (SWNTs) and single-wall carbon nanhorns (SWNHs) have been extending toward two directions, the analysis of nanometer-scaled structures and the application. Developing new types of transmission electron microscopes (TEM), we could, for the first time, clearly observed holes opened on the tube walls. Also Gd atoms attached at the open end of the tubes and single-carbon-atom defects on the tube walls became observable. Even the determination of chiralities of SWNTs was possible. With aids of these TEM techniques, several methods of encapsulation and de-encapsulation of various molecules and clusters in liquid phase at room temperature have been developed, which assure the future application of SWNTs and SWNHs particularly in biological use.

Application of SWNTs was greatly enhanced by the progress of growth method, that is, site-selective growth by chemical vapor deposition. A top-gate transistor was fabricated and its performances has been ranked at the world top record for some time. For practical realization of SWNT-devices, we need to develop highly refined growth-methods, which we are currently engaging in.

III-G-1 Direct Evidence for Atomic Defects in Graphene Layers

HASHIMOTO, Ayako¹; SUENAGA, Kazutomo¹; GLOTER, Alexandre¹; URITA, Koki^{1,2}; IIJIMA, Sumio^{1,3,4,5,6}

(¹AIST; ²Chiba Univ.; ³JST; ⁴NEC; ⁵Meijo Univ. ⁶IMS)

[Nature 430, 870-873 (2004)]

Atomic-scale defects in graphene layers alter the physical and chemical properties of carbon nanostructures. Theoretical predictions have recently shown that energetic particles such as electrons and ions can induce polymorphic atomic defects in graphene layers as a result of knock-on atom displacements. However, the number of experimental reports on these defects is limited. The graphite network in single-walled carbon nanotubes has been visualized by transmission electron microscopy (TEM) and their chiral indices have been determined. But the methods used require a long image acquisition time and intensive numerical treatments after observations to find an 'average' image, which prevents the accurate detection and investigation of defect structures. Here we report observations in situ of defect formation in single graphene layers by highresolution TEM. The observed structures are expected to be of use when engineering the properties of carbon nanostructures for specific device applications.

III-G-2 Selective Deposition of a Gadolinium (III) Cluster in a Hole Opening of Single-Wall Carbon Nanohorn

HASHIMOTO, Ayako¹; YORIMITSU, Hideki²; AJIMA, Kumiko³; SUENAGA, Kazutomo¹; ISOBE, Hiroyuki²; MIYAWAKI, Jin³; YUDASAKA, Masako³; IIJIMA, Sumio^{1,3,4,5,6}; NAKAMURA, Eiichi²

(¹AIST; ²Univ. Tokyo; ³JST; ⁴NEC; ⁵Meijo Univ.; ⁶IMS)

[Proc. Natl. Acad. Sci. 101, 8527-8530 (2004)]

As has been amply demonstrated in chemistry by way of metal-catalysis, metal-complexation should immensely widen the scope of carbon cluster science. Thus, metal-containing hollow carbon clusters such as endohedral metallofullerenes and carbon nanotube filled with metal atoms have been suggested as promising materials. However, the methodology to rationally control the size and the location of the metal clusters as well as to ensure high yield production of the material on a large scale has been lacking. Herein we report a method for forming a one- to multi-atom metal cluster specifically at the hydrophilic hole opening of a carbon nanotube as demonstrated by deposition of Gd(OAc)₃ in single-wall carbon nanohorns. The hole-selective deposition of the Gd atoms allows atomic scale detection of the structural defect in the graphitic materials, and, on a bulk scale, controls the permeability of molecules through the holes. The result would find use for modulation of the electronic properties of carbon nanotubes.

III-G-3 Material Storage Mechanism in Porous Nanocarbon

AJIMA, Kumiko¹; YUDASAKA, Masako²; SUENAGA, Kazutomo³; KASUYA, Daisuke²; AZAMI, Takeshi²; ILJIMA, Sumio^{1,2,3,4,5} (¹JST; ²NEC; ³AIST; ⁴Meijo Univ.; ⁵IMS)

[Adv. Mater. 16, 397-401 (2004)]

Carbonaceous materials, such as activated carbon and charcoal, have long been known to possess "nanospaces," where a variety of materials can be accommodated. Their structures and chemical properties, however, have never been optimized for any specific purpose, because their mechanism of storing objects is not yet fully understood. We have therefore attempted to visualize how materials is stored in the inner spaces of nanocarbon materials in order to verify the storage mechanism. We used "single-walled carbon nanohorns" (SWNHs) for this purpose. This porous nanocarbon material, composed of single layer/crystal/ atom graphite walls, is known to possess completely enclosed nanoscale spaces, and is therefore quite suitable for these experiments.

III-G-4 Structural Evolutions of Carbon Nano-Peapods under Electron Microscopic Observation

GLOTER, Alexandre¹; SUENAGA, Kazutomo¹; KATAURA, Hiromichi²; FUJII, Ryosuke²; KODAMA, Takeshi²; NISHIKAWA, Hiroyuki²; IKEMOTO, Isao²; KIKUCHI, Koichi²; SUZUKI, Shinzo²; ACHIBA, Yohji²; IIJIMA, Sumio^{1,3,4,5,6} (¹AIST; ²Tokyo Metropolitan Univ.; ³Meijo Univ.; ⁴JST; ⁵NEC; ⁶IMS)

[Chem. Phys. Lett. 390, 462–466 (2004)]

Supramolecular assemblages made of single wall carbon nanotubes (SWNT) filled with fullerenes or metal doped fullerenes exhibit promising electronic structure variations at a nanometer scale. Nevertheless, the knowledge about the structural defects of these systems is still very limited. Here, we report structural evolutions under high-resolution electron microscopic observation at the sensitivity of a single atom detection for Ca@C₈₂ molecules encapsulated within SWNT.

III-G-5 Nano-Extraction and Nano-Condensation for C_{60} Incorporation into Single-Wall Carbon Nanotubes in Liquid Phases

YUDASAKA, Masako¹; AJIMA, Kumiko²; SUENAGA, Kazutomo³; ICHIHASHI, Toshinari¹; HASHIMOTO, Ayako³; IIJIMA, Sumio^{1,2,3,4,5} (¹NEC; ²JST; ³AIST; ⁴Meijo Univ.; ⁵IMS)

[Chem. Phys. Lett. 380, 42-46 (2003)]

We have established two new methods that enable incorporation of guest molecules into single-wall carbon nanotubes in liquid phases; nano-extraction and nanocondensation methods. To make SWNTs that have incorporated C_{60} ((C_{60})_n@SWNT) through nano-extraction, we put C_{60} and SWNTs in ethanol for 1 day during which the C₆₀ molecules deposited themselves inside the SWNTs. The incorporation mechanism appears to be that the C_{60} molecules dissolved slightly in the ethanol, diffused toward the SWNTs, and eventually deposited themselves at the most stable sites-that is, inside the SWNTs. In the case of nano-condensation, we formed thin layers of C₆₀-toluene saturated solution on SWNT surfaces, and then obtained $(C_{60})_n$ @SWNT within a few seconds. A reasonable explanation is that the C_{60} molecules migrated through the thin layers of the toluene-C₆₀ mixtures on the SWNT surfaces and finally deposited themselves inside the SWNTs.

III-G-6 Preferential Deposition of Pt Nanoparticles inside Single-Wall Carbon Nanohorns

YUGE, Ryota¹; ICHIHASHI, Toshinari¹; SHIMAKAWA, Yuichi¹; KUBO, Yoshimi¹; YUDASAKA, Masako¹; IIJIMA, Sumio^{1,2,3,4,5} (¹NEC; ²JST; ³AIST; ⁴Meijo Univ.; ⁵IMS)

[*Adv. Mater.* **16**, 1420–1423 (2004)]

Many types of materials can be incorporated into one-dimensional (1D) spaces of carbon nanotubes (CNTs). CNTs having fullerenes in their insides, "peapods," are well known, and ionic salts, Ga, and organic molecules are also successfully incorporated. This 1D ordering is unique and fascinating but it is too simple to cope with a variety of application demands. Therefore we propose to use three-dimensional nanospaces of single-wall carbon nanohorns (SWNHs. Here, we report that our strategy is promising, that is, Pt nanoparticles could be placed inside this space. Furthermore, a curious size-mismatch is noticed, that is, the Pt particle diameters are large, but no holes with such diameters can be seen, which remind us ships-in-bottles. The formation mechanism of the Pt particle reveals that the starting materials are first incorporated into the SWNHs perhaps through the small wall-holes, and they construct the Pt-particles inside the SWNHs.

III-G-7 Support Materials Based on Converted Aluminum Films for Chemical Vapor Deposition Growth of Single-Wall Carbon Nanotubes

HONGO, Hiroo¹; NIHEY, Fumiyuki¹; ICHIHASHI, Toshinari¹; OCHIAI, Yukinori¹; YUDASAKA, Masako¹; IIJIMA, Sumio^{1,2,3,4} (¹NEC; ²JST; ³Meijo Univ.; ⁴IMS)

[Chem. Phys. Lett. 380, 158–164 (2003)]

We systematically studied the support materials for chemical vapor deposition of single-wall carbon nanotubes (SWNTs). Four support materials with iron catalysts were investigated: silicon dioxide, aluminum film, boehmite, and g-alumina. The boehmite and the γ alumina were progressively converted from evaporated aluminum film. The iron catalysts on the aluminum film, the boehmite, and the γ -alumina produced a good SWNT yield in the growth temperature range of 650– 800 °C, while the catalysts on silicon dioxide produced a poor SWNT yield. The X-ray diffraction patterns suggested that the catalyst particle sizes were kept small on these aluminum-based support materials.

III-G-8 Fe-Sapphire and C-Fe-Sapphire Interactions and Their Effect on the Growth of Single-Walled Carbon Nanotubes by Chemical Vapor Deposition

YUDASAKA, Masako¹; KASUYA, Yohko²; JING, Fan¹; ZHANG, Minfang¹; IIJIMA, Sumio^{1,2,3,4,5} (¹NEC; ²JST; ³Meijo Univ.; ⁴AIST; ⁵IMS)

[J. Nanosci. Nanotechnol. 4, 1–5 (2004)]

We previously reported that the quantity of singlewalled carbon nanotubes grown on Fe-coated sapphire by chemical vapor deposition depended on the crystallographic faces of sapphires. In this report, we show that the interaction of Fe, sapphire, and carbon depended on the sapphire faces. We deduce that the quantity of Fe available to catalyze the growth of single-walled carbon nano-tubes was suppressed by the formation of Fe-Al alloys and whether the Fe-Al alloys were formed on Fecoated sapphire or not depended on the sapphire-surface structure.

III-G-9 Carbon-Nanotubes Field-Effect **Transistors with Very High Intrinsic** Transconductance

NIHEY, Fumiyuki¹; HONGO, Hiroo¹; OCHIAI, Yukinori¹; YUDASAKA, Masako¹; IIJIMA, Sumio^{1,2,3,4}

(¹NEC; ²JST; ³Meijo Univ.; ⁴IMS)

[Jpn. J. Appl. Phys. 42, L1288-L1291 (2003)]

We investigated intrinsic transconductance of carbon-nanotube field-effect transistors (CNT-FETs) with carbon nanotubes (CNTs) grown by chemical vapor deposition. The measured transconductance at a drain voltage of -1 V was 8.7 μ S for a CNT with a diameter of 1.5 nm. Very high intrinsic transconductance of 20 µS was estimated by considering the contribution of parasitic resistance. Apparent and intrinsic transconductance per unit channel width were 5800 μ S/ μ m and 13000 μ S/ μ m, respectively, which are enormously larger than those for the state-of-the-art Si-MOSFETs. The parasitic resistance is dominated by the resistance of CNT in the region between the gate and contact. We expect the performance of CNTFETs will further advance by improving CNT quality and by optimizing device structures.

III-G-10 Raman Scattering Study on Fullerene **Derived Intermediates Formed within Single-**Wall Carbon Nanotube: From Peapod to **Double-Wall Carbon Nanotube**

BANDOW, Shunji¹; HIRAOKA, Tatsuki¹; YUMURA, Takashi¹; HIRAHARA, Kaori¹; SHINOHARA, Hisanori²; IIJIMA, Sumio^{1,3,4,5} (¹Meijo Univ.; ²Nagoya Univ.; ³NEC; ⁴JST; ⁵IMS)

[Chem. Phys. Lett. 384, 320-325 (2004)]

By heating of C₆₀ peapods at 900 °C in vacuum, eight or more Raman peaks associated with the inner tubes were observed in the frequency range of the radial breathing mode vibration. An analysis of time traces of the peak intensities led to the growing mechanism of double-wall nanotubes: inner tubes with ≈ 0.7 nm diameters are first formed and then increase their diameters. To explain these phenomena, we propose a model based on formation of short achiral zig-zag nanotubes in the beginning of C₆₀ coalescence.

III-G-11 Evidence for Substantial Interaction between Gd Ion and SWNT in (Gd@C₈₂)@SWNT Peapods Revealed by STM Studies

KIMURA, K.¹; IKEDA, N.¹; MARUYAMA, Yusei¹; OKAZAKI, Toshiya²; SHINOHARA, Hisanori²; **BANDOW, Shunji³; IIJIMA, Sumio^{3,4,5,6}** (¹Hosei Univ.; ²Nagoya Univ.; ³Meijo Univ.; ⁴NEC; ⁵JST; ⁶IMS)

[Chem. Phys. Lett. 379, 340-344 (2003)]

A metallofullerene, Gd@C₈₂, encapsulated in the inside of single walled carbon nanotube (SWNT) has been identified as an STM image of a carbon cage and a Gd atom by a measurement of the tunnel currents onto the SWNT surface. This fact indicates that there is a substantial local interaction between the wall of SWNT and the Gd ions close to the wall. The origin of this interaction is not yet clear, but its existence has also been supported by the results of axially- and peripherally-resolved STS measurements around the Gd ion sites in the peapod.

III-G-12 Structure Changes of Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns Cued by Heat Treatment

YUDASAKA, Masako¹; ICHIHASHI, Toshinari¹; **KASUYA, Daisuke¹; KATAURA, Hiromichi²; IIJIMA, Sumio^{1,3,4,5}** (¹NEC; ²Tokyo Metropolitan Univ.; ³JST; ⁴Meijo Univ.;

⁵IMS)

[*Carbon* **41**, 1273–1280 (2003)]

Raman spectra and transmission electron microscope images showed that diameter enlargement of HiPco, a kind of single-wall carbon nanotubes, accompanied by tube-wall corrugation was caused by heat treatment (HT) at 1000 to 1700 °C. Further enlargement accompanied by straightening of the tube walls and incorporation of carbon fragments within the tubes became obvious after HT at 1800 to 1900 °C. The transformation of some single-wall carbon nanotubes into multi-wall nanotubes was observed after HT at 2000 °C, and most single-wall tubes were transformed into multi-wall ones by HT at 2400 °C. What influence the Fe contained in the HiPco tubes had on these structure changes was unclear; similar changes were observed in single-wall carbon nanohorns that did not contain any metal. This indicates that thermally induced changes in the structure of single-wall carbon nanotubes can occur without a metal catalyst. Heat treatment increased the intengrity of the nanotube-papers, and this increase may have been due to tube-tube interconnections created by HT.

III-G-13 Diameter Enlargement of Single-Wall **Carbon Nanotubes by Oxidation**

ZHANG, Minfang¹; YUDASAKA, Masako²; IIJIMA, Sumio^{1,2,3,4,5} (¹JST; ²NEC; ³AIST; ⁴Meijo Univ.; ⁵IMS)

[J. Phys. Chem. B 108, 149–153 (2004)]

The diameter of high-pressure CO (HiPco) singlewall carbon nanotubes (SWNTs) has been enlarged by treating them with nitric acid and oxygen, and the diameter enlargement is related to the nitric acid refluxing time. Raman spectra (exciting wavelength 488 nm) and transmission electron microscopy showed that the 0.8-1.2 nm diameter distribution of HiPco SWNTs could be narrowed to one centered around 1.2 nm when the nitric acid treatment time was 1 h. Significantly, SWNTs of 1.37–2.4 nm in diameter were discovered when the nitric acid treatment lasted more than 2 h.

III-G-14 A Theoretical Study on the Geometrical Features on Finite-Length Carbon Nanotubes Capped with Fullerenes Hemisphere

YUMURA, Takashi¹; HIRAHARA, Kaori¹; BANDOW, Shunji¹; YOSHIZAWA, Kazunari²; ILJIMA, Sumio^{1,3,4,5,6}

(¹Meijo Univ.; ²Kyushu Univ.; ³NEC; ⁴JST; ⁵AIST; ⁶IMS)

[Chem. Phys. Lett. 386, 38–43 (2004)]

The structures of the finite-length (5,5) and (9,0) carbon nanotubes capped with fullerene hemisphere are analyzed by quantum chemical calculations at the B3LYP DFT level of theory. DFT calculations demonstrate that the geometries of the armchair tubes depend on the number of cyclic *cis*-polyene chains lined up along the tube axis, whereas the zigzag tubes consist of Kekulé-type networks in the cylinder, the geometries being independent of the number of cyclic *trans*-polyene chains.

III-G-15 The Role of Fullerene Hemisphere in Determining the Geometrical Features of Finite-Length Carbon Nanotubes

YUMURA, Takashi¹; BANDOW, Shunji¹; YOSHIZAWA, Kazunari²; IIJIMA, Sumio^{1,3,4,5,6} (¹Meijo Univ.; ²Kyushu Univ.; ³NEC; ⁴JST; ⁵AIST; ⁶IMS)

[J. Phys. Chem. B 108, 11426–11434 (2004)]

Geometrical and electronic features of the armchair C_{40+20n} and zigzag C_{42+18n} nanotubes, in which n is the number of cyclic *cis*- and *trans*-polyene chains involved in the nanotubes, are analyzed from density functional theory (DFT) calculations. To illuminate the role of the fullerene hemispheres in their structures, $C_{20n}H_{20}$, and $C_{18n}H_{18}$, are also studied in terms of orbital interactions. Although there are various bond-deformation patterns within the *cis*-polyene chains in the $C_{20n}H_{20}$ series, the C_{40+20n} series always have similar bond-length alternate patterns. The geometrical change in the capped nanotubes is a consequence of orbital interactions in the cylindrical segments with the fullerene hemispheres. Accordingly, the fullerene hemispheres play a dominant role in determining the geometrical and electronic properties of the capped nanotubes. DFT calculations also demonstrate that the geometries of the armchair series exhibit an oscillatory behavior as the chain width with a periodicity of 3.

III-G-16 A Catalytic Chemical Vapor Deposition Synthesis of Double-Walled Carbon Nanotubes over Metal Catalysts Supported on a Mesoporous Material

ZHU, Jin¹; YUDASAKA, Masako²; IIJIMA,

Sumio^{1,2,3,4,5}

(¹JST; ²NEC; ³AIST; ⁴Meijo Univ.; ⁵IMS)

[Chem. Phys. Lett. 380, 496–502 (2003)]

Double-walled carbon nanotubes (DWNTs) have been synthesized by catalytic chemical vapor deposition (CCVD) over supported metal catalysts decomposed from Fe(CH₃COO)₂ and Co(CH₃COO)₂ on mesoporous silica. Bundles of tubes with relatively high percentage of DWNTs, in areas where tubular layered structures could be clearly resolved, have been observed by transmission electron microscopy (TEM). In other areas, crystal-like alignment of very uniform DWNTs was observed for the first time, suggesting that mesoporous silica might play a templating role in guiding the initial nanotube growth. In addition, compatible with nanoelectronics research, bridging of catalytic islands by DWNTs has also been demonstrated.

III-G-17 Controlled Opening of Single-Wall Carbon Nanohorns by Heat Treatment in Carbon Dioxide

BEKYAROVA, Elena¹; KANEKO, Katsumi¹; YUDASAKA, Masako²; KASUYA, Daisuke²; IIJIMA, Sumio^{2,3,4,5}; HUIDOBRO, Ana⁶; RODRIGUEZ-REINOSO, Francisco⁶ (¹Chiba Univ.; ²NEC; ³JST; ⁴Meijo Univ.; ⁵IMS; ⁶Univ.

Alicante)

[J. Phys. Chem. B 107, 4479–4484 (2003)]

The opening of *bud*-type single-wall carbon nanohorns (SWNHs) by heat treatment in CO_2 was studied by TEM and nitrogen adsorption (77 K). The adsorption isotherms indicate that oxidation by CO_2 at 1273 K provides a sufficient nanohorn opening. The pore parameters of the open nanohorns can be controlled by varying the treatment conditions; the size of the generated nanopores increases with the temperature and time of treatment. In addition, TPD experiments indicate a significant decrease of the oxygen content in SWNHs opened by heat treatment in CO_2 . This is in contrast to the procedures reported in the literature for opening of carbon nanotubular structures, typically introducing oxygen functional groups.

III-G-18 Interstitial Nanopore Change of Single Wall Carbon Nanohorn Assemblies with High Temperature Treatment

OHBA, Tomonori¹; OMORI, Takumi¹; KANOH, Hirofumi¹; YUDASAKA, Masako²; IIJIMA, Sumio^{2,3,4,5}; KANEKO, Katsumi¹ (¹Chiba Univ.; ²NEC; ³Meijo Univ.; ⁴JST; ⁵IMS)

[Chem. Phys. Lett. 389, 332-336 (2004)]

Single-wall carbon nanohorns (SWNHs) were treated in vacuum at different temperatures of 473 to 1073 K. The nanostructural change due to the heat-treatment was studied by adsorption of N_2 at 77 K and H_2O at 303 K. The determined particle density showed that gas is not adsorbed in internal pores, but in interstitial pores. The high temperature treatment (HTT) in vacuo changed water adsorption, but it gave almost no influence on N_2 adsorption. The maximum nanopore volume from H_2O adsorption was observed at 673 K, indicating the interstitial nanopore change due to a local orientational change of SWNH particles.

III-G-19 Direct Thermal Fluorination of Single Wall Carbon Nanohorns

HATTORI, Yoshiyuki¹; KANOH, Hirofumi¹; OKINO, Fujio²; TOUHARA, Hidekazu²; KASUYA, Daisuke³; YUDASAKA, Masako³; IIJIMA, Sumio^{3,4,} ^{5,6,7}; KANEKO, Katsumi¹

(¹Chiba Univ.; ²Shinshu Univ.; ³NEC; ⁴JST; ⁵Meijo Univ.; ⁶AIST; ⁷IMS)

[J. Phys. Chem. B 108, 9614–9618 (2004)]

Single wall carbon nanohorns (SWNHs) were fluorinated to form more attractive nanohorns that have the characteristic structural and adsorptive properties. Nitrogen adsorption, XPS, TEM studies elucidated the surface states and the morphologies of fluorinated SWNHs (F-SWNHs). The XPS results of F-SWNHs showed that the nature of C-F bonds changed from semi-ionic to covalent with increase of the fluorination temperature. The N₂ adsorption isotherm indicated that the total amounts of N2 adsorption on SWNHs fluorinated at 303 and 373 K was smaller than that of pristine SWNHs. After fluorination at 473 K, nanoorder windows were produced on the sidewalls of SWNHs without change in the shape of each horn and aggregate. Therefore, the SWNHs fluorinated at 473 K can adsorb N₂ molecules on the internal surfaces of nanohorns through the nanowindows.

III-G-20 Synthesis of Carbon Nanohorn Particles by Simple Pulsed Arc Discharge Ignited between Pre-Heated Carbon Rods

YAMAGUCHI, Takashi¹; BANDOW, Shunji¹; IIJIMA, Sumio^{1,2,3,4,5}

(¹Meijo Univ.; ²NEC; ³AIST; ⁴JST; ⁵IMS)

[Chem. Phys. Lett. 389, 181–185 (2004)]

Single-wall carbon nanohorn (SWNH) particles were generated by simple pulsed arc discharge between pure carbon rods in the atmospheric pressure of air. Purity of SWNHs was reached higher than 90%, and the heating in dry air at 500 °C was useful for removal of amorphous carbon. The mean size of SWNH particles was \approx 50 nm, which is smaller than those prepared by the CO₂ laser method. Pre-heating of the carbon rod up to 1000 °C, conducted just before ignition of arc, improved the quality of SWNHs. Transmission electron microscopy, scanning electron microscopy and Raman spectroscopy were used to characterize these SWNH particles.

III-G-21 Solvent Effects on Hole-Edge Structure for Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns

MIYAWAKI, Jin¹; YUDASAKA, Masako²; IIJIMA, Sumio^{1,2,3,4,5}

(¹JST; ²NEC; ³AIST; ⁴Meijo Univ.: ⁵IMS)

[J. Phys. Chem. B 108, 10732–10735 (2004)]

To extend the application fields of single-wall carbon nanotubes (SWNTs) and single-wall carbon nanohorns (SWNHs), their chemical modification is essential. Since their graphene-sheet-based structures are chemically robust, only the edges of the graphene sheets, more specifically the oxygen-containing functional groups at hole edges, are useful sites for chemical modification. However, not much is known about the hole-edges, so the phenomenon reported here, that the hole edges easily react with conventional reagents, was previously unknown. We observed a lowering of the combustion temperature of SWNTs and SWNHs immersed in water; this lowering was induced as a result of the hydrolysis of oxygen-containing functional groups (anhydrides and/or lactones) at the hole edges. We also found that the reactivity of hole edges can be easily controlled through an appropriate choice of solvents. We believe that this study is helpful to our understanding of hole-edge chemistry and will help to enable the production of well-designed carbonaceous materials with high functionality.

III-G-22 Evidence for the Intermolecular Motion of Gd Atoms in a $Gd_2@C_{92}$ Nanopeapod

SUENAGA, Kazutomo¹; TANIGUCHI, Risa²; SHIMADA, Takashi²; OKAZAKI, Toshiya²; SHINOHARA, Hisanori²; IJJIMA, Sumio^{1,3,4,5} (¹AIST; ²Nagoya Univ.; ³NEC; ⁴Meijo Univ.; ⁵IMS)

[Nano Lett. 3, 1395–1398 (2003)]

Atoms in a confined space can be regarded to represent a completely new phase because it should behave differently than the atoms in a solid or in a freespace. The metallofullerene provides an ideal case of the confined atoms since a number of metal atoms are imprisoned in a subnanometer void of the carbon cage. Here we give direct evidence of the dynamic behavior for the confined atoms in metallofullerenes by observing individual atoms using the high-resolution transmission electron microscopy. Rapid movement of Gd atoms in $Gd_2@C_{92}$ peapod is identified for the first time. By comparison with simulation, the amplitude of the motion is roughly quantified as 0.2 nm at room temperature and is reduced to almost half at 100 K.

III-G-23 Laser Vaporization Synthesis of Polyhedral Graphite

KOKAI, Fumio¹; TAKAHASHI, Kunimitsu²; KASUYA, Daisuke³; NAKAYAMA, Atsuko⁴; KOGA, Yoshinori⁴; YUDASAKA, Masako³; IIJIMA, Sumio^{3,4,5,6} (¹Mie Univ.; ²IRI; ³NEC; ⁴AIST; ⁵Meijo Univ.; ⁶IMS)

[Appl. Phys. A: Mater. Sci. Process. 77, 69-71 (2003)]

Polyhedral graphite (PG) particles have been synthesized by CO₂ laser vaporization of graphite in highpressure Ar gas (8×10^5 Pa). Faceted PG particles, ranging in size from 110 to 150 nm, have a turbostratic structure. The yield of PG is more than 90%. This synthesis is based on the condensation of hot carbon species confined by an Ar-gas atmosphere.

III-G-24 Direct Observation of 3D Mesoporous Structure by Scanning Electron Microscopy (SEM): SBA-15 Silica and CMK-5 Carbon

CHE, Shunai¹; LUND, Kristina²; TATSUMI, Takashi¹; IIJIMA, Sumio^{3,4,5,6}; JOO, Sang Hoon⁷; RYOO, Ryong⁷; TERASAKI, Osamu⁸ (¹Yokohama Natl. Univ.; ²Stockholm Univ.; ³JST; ⁴NEC: ⁵Maiia Univ.; ⁶IMS: ⁷Korag Adv. Inst. Soi

⁴NEC; ⁵Meijo Univ.; ⁶IMS; ⁷Korea Adv. Inst. Sci. Tech.; ⁸Tohoku Univ.)

[Angew. Chem., Int. Ed. 42, 2182–2185 (2003)]

Mesoporous silica has attracted much attention in recent years, due to new possibilities for advanced applications in catalysis, separation technologies, electronic engineering, and manufacturing of optic devices. The highly nanoporous structures with good thermochemical stability are suitable for synthesis of new materials such as nano-particles, wires and networks of plantinum and carbon within the pore system. In the case of the carbon synthesis, the fabrication technique has been fully developed so that ordered mesoporous carbons exhibiting Bragg X-ray diffraction (XRD) lines similar to those of the MCM-41-type mesoporous silica can be obtained after the complete removal of silica template.

III-G-25 Study of the Growth of Boron Nanowires Synthesized by Laser Ablation

ZHANG, Yingjiu¹; AGO, Hiroki¹; YUMURA, Motoo¹; OHSHIMA, Satoshi¹; UCHIDA, Kunio¹; KOMATSU, Toshiki¹; IIJIMA, Sumio^{1,2,3,4,5} (¹AIST; ²NEC; ³JST; ⁴Meijo Univ.; ⁵IMS)

[Chem. Phys. Lett. 385, 177–183 (2004)]

Boron nanowires with different morphologies and diameters have been fabricated by laser ablation. The effects of the synthesis temperatures, intensities of the laser beams, the types of the metal catalysts and the addition of H_3BO_3 on the growth of the boron nanowires are studied. The systematic analyses show that the vapor-liquid-solid (VLS) model may play important roles in the growth of the boron nanowires.

III-G-26 Structure and Electronic Properties of a Nongraphitic Disordered Carbon System and Its Heat-Treatment Effects

TAKAI, Kazuyuki¹; OGA, Meigo¹; SATO,

Hirohiko¹; ENOKI, Toshiaki¹; OHKI, Yoshimasa²; TAOMOTO, Akira²; SUENAGA, Kazutomo³; IIJIMA, Sumio^{3,4,5,6}

(¹Tokyo Inst. Tech.; ²Matsushita Indust. Co.; ³AIST; ⁴Meijo Univ.; ⁵NEC; ⁶IMS)

[Phys. Rev. B 67, 214202 (11 pages) (2003)]

The heat-treatment effect on electronic properties is investigated in relation to structural change for pulsedlaser-deposited amorphous carbon thin films having sp^2/sp^3 ratio ≈ 9 . The heat treatment at temperatures 200-400 °C increases conductivity and modifies the hopping conduction mechanism at low temperatures, resulting in the generation of a Coulomb gap at $E_{\rm F}$. In the heat-treatment temperature region above 600 °C, considerably small positive thermoelectric power is suggestive of carrier compensation by the competition of hole and electron carriers that originate from the inhomogeneous charge. In the high-heat-treatmenttemperature region 800-1100 °C, the formation of an infinite percolation path network of the graphitic sp^2 domains induces an insulator-to-metal transition, where the electron transport in the sp^2 -rich metallic state is featured by weakly temperature-dependent conductivity.

III-G-27 Compression of Polyhedral Graphite up to 43 GPa and X-Ray Diffraction Study on Elasticity and Stability of the Graphite Phase

NAKAYAMA, Atsuko¹; IIJIMA, Sumio^{1,2,3,4,5}; KOGA, Yoshinori¹; SHIMIZU, Katsuya⁶; HIRAHARA, Kaori²; KOKAI, Fumio⁷ (¹AIST; ²Meijo Univ.; ³NEC; ⁴JST; ⁵IMS; ⁶Osaka Univ.; ⁷Mie Univ.)

[Appl. Phys. Lett. 84, 5112–5114 (2004)]

The crystal structure of polyhedral graphite particles ("*G balls*") has been investigated under pressure up to 43 GPa and at room temperature by x-ray powder diffraction measurements. The polyhedra maintain the graphite phase under pressure higher than 40 GPa. A 29% compression in volume at 43 GPa involves an unusual decrease in the interlayer distance of 25%. The polyhedra recover their original crystal structure by releasing the pressure. A closed and solid structure of the polyhedra, suppressing a transition into another phase, causes them to become metallic under pressures higher than 20 GPa.

III-H Spectroscopy and Photochemical Dynamics of the Methyl or the Methoxy Internal Rotation in Jet-Cooled Toluene Derivatives and Methylanisoles

The phenomena of energy relaxation in isolated molecules have been central in chemical kinetics over many decades. An extensive subject has been followed by the application of supersonic jet techniques, which enabled the study of well isolated ultra-cold molecules in jets. The jet-cooled molecules are isolated in gas phase, thus, the experiments are not subjected to interactions between molecules and solvents or to vibrational relaxation in condensed phases.

The large transition energy is reserved in optically electronic exited molecules where the idea of temperature for molecular internal energy is replaced by the excess energy, by which photodissociation is induced. Investigation of nonradiative electronic relaxation processes, *i.e.* internal conversion (IC) or intersystem crossing (ISC) between two electronic states of the same or different electron spin multiplicity of photoexcited molecules, respectively, has long been interest of the photochemical dynamics because of the important role of these processes in photochemical reaction system.

A triplet state serves as an important intermediate in nonradiative processes of excited molecules. The dynamics of the triplet state generation, *i.e.* ISC, plays an important role in photochemical processes. For instance, chlorinated benzene derivatives in the first excited singlet (S_1) state have small values (10^{-2}) of the fluorescence quantum yields, suggesting that the ISC process to excited triplet states takes place due to the large spin-orbit coupling induced by the heavy Cl atom effect. The excited triplet state molecules undergo the C–Cl dissociation whose quantum yield is almost unity. Accordingly, the investigation of the ISC process assists to understand the photochemical reactions.

The substituent of the CH₃ or OCH₃ group on the benzene ring should play an important role in their photoexcited states. When these molecules are excited to the singlet excited state, internal rotational bands of these groups are observed for lower frequency regions than 200 cm^{-1} in the LIF excitation spectra. Measurements of these internal band intensities and their fluorescence lifetimes should give information on the relaxation dynamics of these molecules.

III-H-1 Conformational Isomerism and Excited State Dynamics of Fluoroanisole in a Supersonic Jet

ISOZAKI, Tasuku¹; SAKEDA, Kosaku¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

It is known that substituted phenol and anisole derivatives have some stable conformers of internal rotation around the $C(sp^2)$ –O bond both in the ground and excited states. In many cases, their stable structures corresponding to the energy minimum are *planar* conformers such as the cis and trans conformers. But recently, in addition to the existence of most stable planar conformer, it is suggested that the second stable non-planar conformer should exist for o-substituted anisole derivatives. However, a little information on such a non-planar conformer is reported so far. It is expected that the electronic excitation of the non-planar conformer should induce the geometrical change of the methoxy group related to the benzene ring, and alter the excited state dynamics compared to the planar conformer

From these points of view, it is interesting to investigate how halogenation on the benzene ring of anisole affects on the excited state dynamics. In this study on o-, m- and p-fluoroanisole, in order to clarify the electronic transitions of rotational isomers, substituent effect on conformational structure and vibronic structure, and differences of excited state dynamics between the rotational isomers, the LIF excitation and SVL dispersed fluorescence spectra were measured in a supersonic jet. Figure 1 shows the LIF excitation spectra of o-, m- and p-fluoroanisole. The SVL dispersed fluorescence spectra were also measured by pumping each vibronic band observed in the LIF excitation spectra. The vibronic and vibrational bands observed in the spectra were assigned with the aid of quantum chemical calculations on the B3LYP/cc-pVTZ level. The SVL dispersed fluorescence spectra indicated that the vibronic mixing should take place in the S_1 state, and the IVR process becomes more dominant with the higher excess energy.



Figure 1. LIF excitation spectra of *o*-, *m*- and *p*-fluoroanisole.

III-H-2 Spectroscopy and Relaxation Dynamics of Photoexcited Anisole and Anisole-Methyl-d₃ Molecules in a Supersonic Jet

MATSUMOTO, Ryu¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

In this work we measured the LIF and DF spectra of the S_1 - S_0 electronic transition for jet-cooled anisole and anisole-methyl-d₃ molecules. This is the first time measurement of the fluorescence of the deuterated anisole species. The molecular orbital calculations on the molecular and vibrational structures on the electronic ground and excited state were also performed.

For anisole molecule, 3 vibrational modes in the S_0 state and 11 vibrational modes in the S_1 state were reassigned on the basis of experiments and calculations. For deuterated molecule, we assigned 13 and 12 vibrational modes in the S_0 and S_1 states, respectively. Dispersed fluorescence (DF) measurement clarified the anharmonic coupling between several vibrational modes. The Duschinsky rotation between the 10b and 16a, and 6a and 6b modes are significantly observed for

both molecules.

In order to investigate the relaxation dynamics we measured fluorescence lifetimes of the single vibrational levels for the first time and calculated the nonradiative decay rate constant. Among the nonradiative processes, intersystem crossing to the triplet manifolds would be dominant for both species, as in the case of the condensed phase. It was found that the character of the SVL is deeply related to the ISC process; the excess energy dependence of the $k_{\rm nr}$ becomes larger for the out-ofplane bands than for the in-plane bands. Especially the methyl internal rotation in the anisole molecule and vibrational mode of 16a in the anisole-methyl-d₃ molecule exhibited fast nonradiative decay process, revealing accepting modes of the ISC processes. The IVR process was affected by the methyl deuteration but the results were against the expectation; the broadening of DF spectra below 940 cm⁻¹ was depressed by deuteration. On the SVLs with in-plane component the broadening of DF spectra by the IVR and k_{nr} values are well correlated. Therefore we conclude the energy flow to the out-of-plane mode should be responsible for the nonradiative process.

III-I Photophysics and Photochemistry of Aromatic Molecules in the Condensed Phase

Excited aromatic compounds generally release energy by various pathways such as photophysical processes and photochemical reactions. Electronically excited molecules are relaxed into a stable or metastable state through radiative and/or nonradiative processes as photophysical processes. It is well known that photochemical reactions occurring from excited state are bond dissociation, cyclization, isomerization, hydrogen abstraction, electron transfer, and so on. In addition, there exist relaxation processes and their quantum yields characteristic to each compound. It is very important to investigate photodynamics of excited molecules.

Intermediates such as excited states and radicals, which can be generated with laser irradiation, have been detected by laser flash photolysis as described. The shorter pulse width of a light source becomes, the shorter-lived intermediates can be detected. Furthermore, the properties of intermediates would be clarified. These informations should obtained photophysical and photochemical dynamics of the intermediate that are interested.

On the other hand, it becomes difficult to elucidate nonradiative processes, such as internal conversion and intersystem crossing from the excited state, by laser flash photolysis. Time-resolved photothermal techniques, however are powerful to study nonradiative processes because they can detect the released heat from excited molecules directly with high sensibility. They should be described in detail. Combination of photoexcited and photothermal methods will give us detailed information on photophysical and photochemical dynamics of intermediates, as well as excited states.

III-I-1 Photochemical Dynamics of Phenoxy Alkanes

SUZUKI, Tadashi¹; ANDO, Mayaka¹; ICHIMURA, Teijiro²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

Phenoxy radical is one of the fundamental chemical intermediates on the photochemistry. It is known to take an important role on combustion, lignin UV reaction in the plant, biochemical reactions, and so on. Photolysis of phenol and phenoxy alkanes is also known to produce phenoxy radical.¹⁾ In the gas phase phenoxy methane (anisole, methoxy benzene) was reported to produce phenoxy radical with the 193 nm laser excitation.²⁾ We measured transient absorption spectra of several phenoxy-substituted alkanes in solution, however, not only phenoxy radical but also another transient were found. In this study, we made an assignment of the transient and discussed the reaction dynamics in detail. Furthermore, reaction pathway for excited methoxysubstituted toluenes (*o*-, *m*-, *p*-methylanisoles) was also discussed.

The transient absorption spectrum of phenol in solution obtained with the UV irradiation shows a structured band at around 400 nm. It is known as a typical absorption spectrum of phenoxy radical. However, the transient absorption spectrum of anisole was not the same spectrum of phenoxy radical; a broad absorption band appeared around 440 nm in addition to the structured band of phenoxy radical. The broad band was observed in the spectra of the polar and non-polar solutions. The lifetime of the transient was several μ s. To make an assignment of the transient and to clarify the reaction mechanism, photosensitization experiment with acetone was carried out. The broad band appeared at around 440 nm, which is exactly the same one obtained with the photolysis of anisole. We could safely assign the new transient to a radical, which should be produced through hydrogen atom elimination by the UV irradiation.

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III-I-2 Relaxation Processes of Naphthalene in Highly Excited State in Condensed Phase

WATANABE, Sadayuki¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

Relaxation dynamics in highly excited singlet state of naphthalene (NP) in condensed phase is studied by time-resolved thermal lensing (TRTL) technique coupled with nanosecond laser photolysis. The results of TRTL measurements with the 248 nm excitation give heat conversion efficiency of NP, and lead to information on relaxation process, that is, rapid nonradiative process is found to take place from the highly excited singlet state (S_2) into the S_0 state, not through the S_1 (v =0) state. The quantum yield is successfully estimated to be 0.31 ± 0.01 . The occurrence of the rapid nonradiative process is also found in deuterated NP and 1-methylnaphthalene. The mechanism of the relaxation process from the highly excited state is discussed in detail.

III-I-3 Calorimetric Standards for Photothermal Methods at the 248 nm Excitation

WATANABE, Sadayuki¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[Chem. Phys. Lett. 374, 41-44 (2003)]

The time-resolved thermal lensing measurements were carried out on 2-hydroxybenzophenone, pyridazine and benzene in acetonitrile at the 248 nm excitation in order to investigate the feasibility for the calorimetric standards on photothermal methods. The heat conversion efficiency values of 2-hydroxybenzophenone and pyridazine were estimated to be unity compared with that of benzene, revealing that 2-hydroxybenzophenone and pyridazine should show no fluorescence and no photochemical reactions. Therefore, these molecules should be good calorimetric standards at the 248 nm excitation.

III-I-4 Production and Excited State Dynamics of Photo-Rearranged Isomer of Benzyl Chloride and Its Methyl Derivatives Studied by Transient Absorption and Time-Resolved Thermal Lensing Techniques

NAGANO, Mika¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro²; OKUTSU, Tetsuo³; HIRATSUKA, Hiroshi³; KAWAUCHI, Susumu¹

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Gunma Univ.)

[J. Phys. Chem. A submitted]

Production and photoexcited dynamics of reaction intermediates with photolyses of benzyl chloride (BzCl) and methyl-substituted benzyl chlorides (MeBzCls) were studied by using stepwise two-color laser excitation transient absorption (TC-TA) and two-color laser excitation time-resolved thermal lensing (TC-TRTL) measurements. With photoexcitation of BzCl the formation of transient photo-rearranged isomer was suggested in the previous paper [Res. Chem. Intermed. 27, 137 (2001)]. Such an isomer formation for MeBzCls was also observed in a 248 nm excitation. It was found that further photoexcitation of the isomers with the 308 nm light caused photodissociation to yield the corresponding benzyl radicals. The reaction quantum yield and the molar absorptivity of the photo-rearranged isomer of BzCl were estimated. The heat of reaction for the photodissociation of the isomer was successfully determined with the TC-TRTL measurement. These experimental results were excellently consistent with ab initio and DFT calculations.

III-J Excited State Dynamics of Organic Molecules in Cyclodextrin Nanocavities

III-J-1 The Cavity Size Effect on the Excited State Dynamics of Dimethylaniline Derivatives Complexed with Cyclodextrins

MATSUSHITA, Yoshihisa¹; SAKEDA, Kosaku¹; SUZUKI, Tadashi¹; ICHIMURA, Teijiro² (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[*Chem. Phys.* **286**, 399–407(2003)] [*J. Phys. Chem. A* **108**, 7490–7495 (2004)]

The effect of cyclodextrin (CD) complexation on the excited state dynamics of some dimethylaniline derivatives, 4'-dimethylaminoacetophenone (DMAAP), methyl 4-(dimethylamino)benzoate (MDMAB), and ethyl 4-(dimethylamino)benzoate (EDMAB) in bulk solution was studied by means of steady state and timeresolved laser spectroscopy. The dimethylaniline derivatives complexed with CDs exhibited twisted intramolecular charge transfer (TICT) fluorescence whereas only the emission from the locally excited state was observed in aqueous solution without CD (Figure 1). In the case of α -CD complexes of MDMAB and EDMAB, dual TICT emission from different microenvironments was observed. The dependence of TICT emission intensity on pH and α -CD concentration suggested that the dual TICT emission can be attributed to the guest molecule in the 1:1 and 1:2 guest- α -CD complexes (Figure 2). Time-resolved emission spectra also indicate the formation of 1:2 complex with α -CD and faster backward electron transfer from TICT state for 1:1 complexes.

Though the effect of CD complexation on TICT photochemistry has been interpreted in terms of the restriction on molecular motion and the reduced polarity effect introduced by CD cavities, these effects tend to have opposite effects on the TICT emission yield. Thus the overall effect of CD encapsulation is probably complicated and the problem is still in controversy. Our results indicate that polarity effect introduced by the hydrophobic cavity is the dominant factor in the controlling the photochemistry of dimethylaniline derivatives in CD complexes.



Figure 1. Dispersed emission spectra and emission decay profiles of MDMAB (2.5×10^{-5} M) in aqueous solutions (a) without CD, and in the presence of (b) 5.0×10^{-4} and (c) 5.0×10^{-2} M of α -CD excited at 315 nm.



Figure 2. Possible structures of MDMAB- α -CD complex.

III-K Wave Packet Engineering Using a Phase-Programmable Femtosecond Optical Source

We proposed "wave packet engineering" which realizes mutual conversion between phase information of photonic and quantum wave packets by means of light-matter interaction. A phase-programmable femtosecond optical source is indispensable for such interactive control of photonic and quantum wave packets. We demonstrate control of quantum wave packets in organic molecules and semiconductors using phase-programmed pulses.

III-K-1 Molecular Phase-To-Amplitude Converter Using Femtosecond Wave Packet Engineering

MISAWA, Kazuhiko; MATSUDA, Isao¹; LANG, Roy¹

(¹Tokyo Univ. Agric. Tech., CREST(JST))

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The intensity of the spontaneous emission from a cyanine dye molecule (IR-140) is measured to evaluate the remaining excited-state population after photoexcitation with femtosecond chirped pulses. The chirped pulses are prepared by using the chirp variable device with a chirped mirror pair. The center wavelength, pulse energy, and duration of the output from the chirp device are 790 nm, 2 mJ, and 40 fs, respectively. The spectral profile does not change irrespective of the chirp condition. The ethanol solution of IR-140 at a concentration of 2×10^{-4} M is circulated in a 0.5-mm thick quartz cell. The fluorescence intensity is increased and decreased in case of positively chirped (PC) and negatively chirped (NC) excitations, respectively, with respect to the Fourier transform limited (TL) excitation. This chirp dependent fluorescence (CDF) results from the coherent interaction between the chirped pulses and the quantum wave packet in the material. The stimulated emission efficiency is different between the NC and PC excitation. At low excitation the stimulated emission is not efficient and CDF is negligible. As excitation is increased, CDF becomes remarkable. The intensity change is up to about 25 percent of the total intensity. To explain the dependence on the excitationintensity, we perform a quantum mechanical calculation based on a three-level model. Theoretically, an oscillatory dependence like Rabi oscillationis expected in case of NC excitation. However, such strong stimulated emission pumping is not experimentally remarkable. This is due to not only low excitation, but also dephasing in dye molecules.

III-K-2 Wave Packet Engineering Using a Phase-Programmable Femtosecond Optical Source

MISAWA, Kazuhiko; MATSUDA, Isao¹; HASHIMOTO, Naoyuki T.¹; LANG, Roy¹ (¹Tokyo Univ. Agric. Tech., CREST(JST))

[J. Mod. Opt. in press]

A new optical telecommunication method combin-

ing time and frequency domain multiplexing is proposed by using phase-controlled femtosecond pulses. Each pulse in a pulse train can be used as data packet with data bits in the frequency domain. We name the new principle as "wave-packet engineering" to adjust amplitude and phase of the wave function in device materials arbitrarily by controlling spectral phase of femtosecond pulses. The optical phase-to-amplitude converter is demonstrated with organic dye molecules, in which the phase information in the phase-modulated pulses can be demodulated into the luminescence intensity. Luminescence intensity from cyanine dye molecules observed to be chirp dependent, and is explained quantum mechanically in terms of coherent population transfer. According the wave-packet engineering, a design principle of the device using semiconductor coupled quantum nanostructures is also discussed.

III-L In-Situ Observation of Surface Reactions by Variable Temperature Scanning Tunneling Microscopy

Chemical reaction at a well-defined single crystal surface has been intensively investigated as a prototype for heterogeneous catalytic reaction, electrochemical reaction and corrosion. The surface chemical reactions are heterogeneous in nature reflecting the structural and electronic imperfections relevant to steps, vacancies and impurities. In addition, the surface reactions are significantly influenced by the presence of reactants and products which often form ordered arrays. Therefore, in order to get better understanding of the surface reactions, it is vital to unravel the nature of these local properties which are closely linked to chemical reactivity of the surfaces reactions. Advent of scanning tunneling microscopy (STM) has enabled us to tackle the challenge with the ability to image the surface reactions in both real-time and real-space with atomic resolution. We investigate the reactivity of novel one-dimensional (1D) -Ag-O-Ag-O- compounds formed upon the dissociative adsorption of oxygen molecule on Ag(110) by the use of variable temperature scanning tunneling microscopy (VT-STM). The 1D compounds are arranged periodically to form ($n \times 1$)–O (n = 2-7) reconstructed structures in which their mutual distance changes in self-organized manner depending on the O coverage. In addition, 1D compounds show structural fluctuation in the low O coverage regime reflecting the low dimensionality. These intriguing characteristics make them promising as a model system to explore physical and chemical properties of nano-structured materials.

III-L-1 In-Situ Observation of Chemical Reaction of the 1D Compounds with CO on Ag(110)

NAKAGOE, Osamu¹; WATANABE, Kazuya²; MATSUMOTO, Yoshiyasu²; TAKAGI, Noriaki² (¹GUAS; ²IMS and GUAS)

The reduction of O adatoms of the 1D compounds with CO was investigated by using VT-STM. STM measurements were performed as titration measurements by first preparing the (6×1)-O surface and then reacting O adatom with CO to form CO₂ that desorbs immediately after the reaction at constant temperatures at 180-208 K. STM images of the same region were sequentially taken in the constant current mode using an electrochemically etched W tip under the CO pressure of 3×10^{-8} mbar. In order to reduce tip-surface interactions, a high tunneling resistance of $> 1 \text{ G}\Omega$ was used. From sequential images, it is found that the reactivity of O adatoms at the ends of 1D compounds is so high that the reaction occurs only at the ends. Reflecting the specific reactivity of O adatoms at the ends of 1D compounds, the O coverage is decreased linearly with the progress of the reaction. From the temperature dependence of the slopes of the titration curves together with the reaction model, the activation barrier was estimated to be 39.2 kJ/mol.

III-L-2 Real-Time Observation of the Spatial Propagation of Reaction Front with Atomic Resolution: $H_2O + O \rightarrow 2OH$ on Ag(110)(6x1)–O

NAKAGOE, Osamu¹; WATANABE, Kazuya²; MATSUMOTO, Yoshiyasu²; TAKAGI, Noriaki² (¹GUAS; ²IMS and GUAS)

Interaction of H₂O with solid surfaces is important in broad spectrum of scientific fields ranging from meteorology to heterogeneous catalysis. The adsorption of H₂O on $(n\times 1)$ –O has been studied extensively, and various adsorbed states are reported such as chemisorbed H₂O, multilayers, (OH)(H₂O)_n, (OH)₂H₂O and

OH species. However, the reaction kinetics and the influence of these species on the kinetics are unknown. STM measurements were made for the structural variation occurring over the course of the reaction of O adatoms in the 1D compounds with H₂O at 175 K. While chemisorbed H₂O molecules and hydrogenbonded H₂O clusters exist transiently at 175 K, formed OH species remain on the surface stably and form $(OH)(H_2O)_n$ and $(OH)_2H_2O$ clusters as a nucleation center. STM images of the same regions were sequentially acquired in the constant current mode using an electrochemically etched W tip under the H₂O pressure of 1×10^{-9} mbar. Sequential STM images revealed that the reaction is highly nonlinear such that the reaction proceeds explosively with propagating reaction front after an induction period. In the induction period the reaction occurs only at the ends of 1D compounds similar to the reaction with CO. The reaction front propagates on the surface like a tidal wave irrespective of surface steps and impurity islands with the velocity of 1 nm/sec. The reaction model is proposed that the formed OH species play a role of catalyst as follows: OH species act as a nucleation center to form H_2O clusters. Clustering of H₂O increases the local coverage of H₂O by extending the residence time and enhances the reactivity of H₂O located at the periphery of the cluster as a proton donor.
RESEARCH ACTIVITIES IV Department of Molecular Assemblies

IV-A Spectroscopic Study of Charge Carriers in Organic Conductors

The low-frequency reflectivity of an organic conductor provides us with a wealth of information on the nature of charge carriers. For instance, the anisotropy of a band structure, bandwidth, effect of electron-electron correlation, and electron-molecular vibration (e-mv) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. We are investigating the polarized reflection spectra of various organic conductors in the spectral region of 50–33000 cm⁻¹ and in the temperature range of 6–300 K. Usually the molecular vibrations (local phonons) are screened by strong electronic transition by charge carriers. Therefore, few local phonon bands are detected in the reflection spectrum. In this sense, the Raman spectroscopy is a complementary method to reflection spectroscopy for understanding molecular vibrations in a metallic state. Since some molecules have charge-sensitive vibrational modes, the Raman spectroscopic method is a powerful tool to detect the site-charge distribution (oxidation state of molecule). We are investigating the charge ordering (CO) phenomena in organic conductors using the technique of infrared and Raman spectroscopy. In the organic charge-transfer salts, CO is originated from the localization of the charge carriers. Since the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, CO will be widely found through the phase transition. The charge ordering was first found in inorganic narrow-band systems such as copper, manganese, and vanadium oxides. Recently, CO has been found in several organic conductors, and the electronic phase diagrams of typical organic conductors are re-examined taking CO into account. The CO state is drawing attention, since CO is theoretically considered as being related to the pairing mechanism in superconductivity. The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by an inhomogeneous charge distribution. Our goal is the complete understanding of the CO phase transition through the interpretation of the vibrational spectra, and the drawing of a *P*-*T* phase diagram.

IV-A-1 Infrared and Raman Evidence for the Charge Ordering in β "-(BEDT-TTF)₃(ReO₄)₂ Studied by Vibrational Spectroscopy

YAMAMOTO, Takashi; URUICHI, Mikio; YAKUSHI, Kyuya; YAMAURA, Jun-ichi¹; TAJIMA, Hiroyuki¹ (¹Univ. Tokyo)

[Phys. Rev. B in press]

The charge-ordering (CO) state is drawing attention as a new electronic ground state in narrow-band organic charge-transfer salts which do not have a strong dimer unit. The mechanism of the metal-insulator transition of β "-type ET salts (ET = bis-ethylenedithio-tetrathiafulvalene) has not been understood well. As the first step to investigate the ground state of β "-type ET salts, we started from the 3:2 salts, where the carrier density is higher than those of the 2:1 salts. The infrared and Raman spectra of β "-(ET)₃(ReO₄)₂ were measured at various temperatures below 300 K. We investigated the three C=C stretching modes, v_2 , v_{27} and v_3 . The infrared and Raman spectra discontinuously changed at 80 K. Below 80 K, for example, the doublet v_2 bands split into three peaks, the doublet ν_{27} also split into three, and a mutual exclusion rule for the vibronic v_3 modes in the infrared and Raman spectra is broken. This symmetry lowering is consistent with the result of x-ray crystal structure analyses conducted at 100 K and 22 K. The site charges in the unit cell estimated from the splitting of v_2 are +0.7₃, +0.7₃, and +0.5₃ in the metallic phase above 81 K, and they are changed into +0.2, $+0.8_5$, and $+0.9_5$ in the insulating phase below 80 K. The pattern of the site charge distributions exhibits the re-distribution at 80 K, which is shown in the figures. The frequencies of the vibronic v_3 modes are reproduced from the numerical calculation by assuming of the patterns in the figures. From these experimental results, the metal-insulator transition of this compound is characterized as the CO transition originated from the localization of charge due to Coulomb interactions.



Figure 1. The site charge distributions above 81 K (left) and below 80 K (right). The symbols, \bigcirc and \bigcirc in the left denote the site charges of 0.7₃ and 0.5₃, and the symbols \bigcirc , \bigcirc , and \bigcirc denote the site charges of 0.9₅, 0.8₅, and 0.2. The lines represent the magnitude of transfer integrals, which is schematically shown as follows: double > single > dashed > dotted.

IV-A-2 Charge Ordering State of β "-(ET)₃(HSO₄)₂ and β "-(ET)₃(CIO₄)₂

YAMAMOTO, Takashi; URUICHI, Mikio;

YAKUSHI, Kyuya; KAWAMOTO, Atsushi¹

(¹Hokkaido Univ.)

In the previous study, we have demonstrated the charge-ordering (CO) phase transition of β "-(ET)₃ (ReO₄)₂ at 80 K. However, this CO phase transition is accompanied by a drastic structural change. On the other hand, no remarkable structural change is observed in the metal-insulator transition of β "-(ET)₃(HSO₄) and β "-(ET)₃(ClO₄) salts. This enables us to discuss purely the role of the inter-site Coulomb repulsion, V, in the CO state. The Raman and IR spectra of β "-(ET)₃X₂ (X = HSO₄ and ClO₄) were measured at various temperatures below 300 K. We investigated three C=C stretching modes, namely v_2 , v_3 and v_{27} . The spectral patterns of both compounds in the low temperature phases are ascribed to the CO state, where the site charges at charge-poor and charge-rich sites are $\sim+0.3_3$ and ~+0.8₃. The pattern of the CO state in $X = HSO_4$ salt is identical to that in $X = ClO_4$ salt but differs from that of $X = ReO_4$ salt. We have found that the patterns of the CO states are correlated with the inter-molecular distances between the centers of adjacent molecules along the stacking direction. Since the intermolecular distance at the non-slipping point is shorter than that at the slipping point, V at the non-slipping point is larger than that at the slipping point. The unit cells of $X = HSO_4$ and ClO₄ salts contain two non-slipping points whereas an organic layer of the unit cell of $X = \text{ReO}_4$ salt contains one non-slipping point. This structural difference explains the difference in the CO pattern. Through the analyses of the experimental results, we have demonstrated direct evidence for the role of the inter-site Coulomb repulsion in the CO state.

IV-A-3 Inhomogeneous Charge Distributions in β "-(ET)₄Ga(C₂O₄)₃sol (sol = PhNO₂, Py and Ch₂Cl₂)

YAMAMOTO, Takashi; URUICHI, Mikio; YAKUSHI, Kyuya; AKUTSU, Hiroki¹; SATO-AKUTSU, Akane¹; DAY, Peter² (¹Himeji Inst. Tech.; ²Royal Inst. GB)

The reason for the strong attention to the charge ordering (CO) is the theoretical prediction that the superconducting (SC) state neighbored on the CO state has a new paring mechanism. Among various nondimerized ET salts, the β "-type ET salts have attracted attention, because the superconductivity has been found in various β "-type ET salts under hydrostatic pressure. The most interesting point of the title compounds is that they demonstrate superconductivity at ambient pressure. According to the resistivity measurements of the title compounds, the metal-insulator transitions are observed at around 100 K. The electrical resistivity of solvent = Py (pyridine) and CH₂Cl₂ salts keep the insulating behavior down to the liquid-helium temperature. On the other hand, the insulator-superconductor transition is observed at 7.5 K in the electrical resistivity of solvent = $PhNO_2$ (nitrobenzene) salt. The conducting behavior of the title compounds is unique since the SC phase appears with increasing the volume of the unit cell. We have tentatively measured the Raman and IR spectra of

these compounds down to 13 K. The v_{27} and v_2 modes have the broad line-widths around 300 K. With decreasing temperature, these modes show the peak splitting, suggesting the CO state. The difference in the site charge distributions, $\Delta \rho$, has the large value with increasing the size of the solvent molecule in the crystal. The reflectivity in the infrared region decreases as the size of the solvent molecule increases. Our observations suggest the view that that the SC phase is neighbored on the CO phase.

IV-A-4 Infrared and Raman Study of the Charge-Ordered State of θ -(ET)₂Cu₂CN [N(CN)₂]₂

YAMAMOTO, Takashi; YAKUSHI, Kyuya; SHIMIZU, Hiroyasu¹; SAITO, Gunzi¹ (¹Kyoto Univ.)

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According to the resistivity measurements of the θ type ET salts, the conducting behavior can be mapped with the structural parameter, namely the dihedral angle, ϕ , which is defined from the adjacent molecules along the highly conducting direction. The title compound has the largest ϕ among the θ -type ET salts, and the electrical resistivity exhibits an insulating behavior even at 300 K. In order to clarify the electronic state of θ -type ET salts, the polarized Raman and infrared spectra of θ -(ET)₂Cu₂CN[N(CN)₂]₂ were measured at various temperatures below 300 K. We investigated the three C=C stretching modes, v_2 , v_3 and v_{27} . The spectral pattern below the phase transition temperature, ~220 K, is compatible with the horizontally charge-ordered state, where the site-charge distributions are $+0.1_7$ and $+0.8_3$. We have found that the vibronic v_3 bands correlate to the dihedral angles, ϕ . This relation is well reproduced from the numerical calculation based on the cluster model with C_2 symmetry. Among four independent v_3 bands, the lowest-frequency vibronic band is the most sensitive to ϕ . With increasing ϕ , the frequency of the vibronic band is elevated due to the decrease of the transfer integral (and increasing the magnitude of the Coulomb repulsions).

The spectral features above the phase transition temperature, ~220 K, also exhibit the peak splitting due to the precursory effect of the CO state. The charges are nearly localized, and perhaps the short-range ordered horizontal CO stripe is dynamically fluctuating in the high-temperature phase above 220 K.

IV-A-5 Re-Examination of the Charge Sensitive Vibrational Modes in ET Molecule

YAMAMOTO, Takashi; YAKUSHI, Kyuya; URUICHI, Mikio; YAMAMOTO, Kaoru; KAWAMOTO, Atsushi¹; TANIGUCHI, Hiromi² (¹Hokkaido Univ.; ²Saitama Univ.)

The phase transition from charge-ordering (CO) phase to superconducting (SC) phase has not been experimentally observed. Such an experiment will be able to be conducted in the β "-type ET salts using

vibrational spectroscopic method. However, the Raman technique is inappropriate, because the control of the sample temperature is difficult owing to the heating effect by the excitation lasers. On the other hand, the infrared reflectance technique enables us to measure the vibrational mode around the liquid helium temperature. Among the IR-active modes of the ET molecule, the v_{27} mode is the candidate of the charge sensitive probe. We can expect that the frequency decreases with increasing the site charges. However, the relation between the frequency and the degree of the charge transfer is not well established. We detected the frequency of the v_{27} mode of ET⁺ through the measurement of the IR reflectance spectra of (ET)(ClO₄), (ET)(AuBr₂Cl₂) and the isotope analogues of (ET)(AuBr₂Cl₂). The decided frequency is ~ 1400 cm^{-1} , which is remarkably different from 1445 cm⁻¹ in the previous reports.

The frequency of the v_{27} mode in the neutral ET crystal is lower than that of the charge-poor site of θ -(ET)₂Cu₂CN[N(CN)₂]₂ in the CO state. This contradictory result seems to be ascribed to the fact that the ET molecule in the neutral crystal has a boat structure and those of the charge transfer (CT) salts have a flat structure regardless of the degree of the charge transfer, ρ . This conjecture was verified from the normal mode analysis using the DFT method: the frequency of v_{27} in boat ET⁰ is lower than that of flat ET⁰. On the basis of our experimental results and calculations, we deduced the frequency shift of v_{27} as $\Delta v \sim 135$ cm⁻¹/e. The v_{27} mode is the efficient probe to the site charges in the ET salts. Finally, we should emphasize that v_{27} is free from *emv* effect and thus the frequency shift is directly related to the site charge.

IV-A-6 Suppression of the Charge Disproportionation by Hydrostatic Pressure in β "-(ET)(TCNQ)

URUICHI, Mikio; YAKUSHI, Kyuya; YAMAMOTO, Hiroshi^{1,2}; KATO, Reizo^{1,2} (¹*RIKEN*; ²*JST-CREST*)

Charge disproportionation (CD) and charge ordering (CO) in organic conductors originate from the localization of charge carriers. CO has been investigated in the insulating states of several charge-transfer salts. Last year, we presented dynamically fluctuating CD in the metal-like state of the title compound. We measured the polarized Raman and infrared spectra. First we estimated the charge-transfer degree from ET to TCNQ as 0.5 using the C=C stretching mode (v_4) of TCNQ. All of the Raman bands of TCNQ are independent of temperature. However, the C=C stretching modes (v_2 and v_3) of BEDT-TTF show clear splitting, and the low-frequency component of v_3 exhibits a broad vibronic feature. This finding indicates that the holes of BEDT-TTF are nearly localized, and thus CD arises near the room temperature. Very interestingly, the split bands of v_2 merge into a single broad band, and the broad band is sharpened on lowering temperature. The same phenomenon is found in the infrared-active C=C stretching mode v_{27} . This temperature dependence is well reproduced by motional narrowing model. We interpreted this phenomenon as follows: The lowering the temperature contracts the crystal lattice and increases the transfer integral between the adjacent ET molecules. The slight enhancement of the transfer integral accelerates the hopping speed and causes the merge of the split band.

This compound consists of a segregated stack structure, where BEDT-TTF and TCNQ separately form uniform chains. We found week satellite reflections of $0.5a^* + 0.5c^*$ on X-ray diffraction patterns exposed for 8 hours. This result and the vibronic band of infrared spectra polarized to TCNQ stack direction are consistent with dimerization of TCNQ. This year, we applied the hydrostatic pressure to contract the crystal lattice. The split bands of v_2 again merge into a single broad band, and the broad band is sharpened on increasing pressure. All of the Raman bands of TCNQ are independent of pressure. The same phenomenon is found in the temperature dependence of Raman spectra.¹

Reference

1) K. Yakushi, M. Uruichi, H. M. Yamamoto and R. Kato, *J. Phys. IV France* **114**, 149–151 (2004).



Figure 1. Pressure dependence of the Raman spectra of β "-(ET)(TCNQ) at room temperature.

IV-A-7 Electron-Molecular Vibration Coupling Effect on the Raman Spectrum of Organic Charge Transfer Salts

YAMAMOTO, Kaoru; YAKUSHI, Kyuya

[J. Phys. IV France 114, 153 (2004)]

Vibrational spectra of dimerized and tetramerized radical clusters have been calculated to understand the features of electron-molecular vibration (EMV) coupling effects for the charge ordered (CO) system. The calculated spectra show that the totally in-phase Raman band, which is usually used as a measure of the molecular ionicity, approaches to the frequency corresponding to the average molecular ionicity in the cluster, as we increase the EMV coupling constant. When the charge disproportionation (CD) ratio is not large, the frequency of this mode is independent of the molecular ionicity. On the other hand, when large CD presents, the in-phase Raman bands show steep shift for small variation of the CD ratio. These results suggest that concerning to the normal modes with a large EMV coupling constant, we should not use the Raman-active band to estimate the molecular ionicity. We should use the Raman-active mode with small EMV coupling constant or infraredactive mode for the estimation of the molecular ionicity.

IV-A-8 Activation of Strong Overtone in the Infrared Spectrum of a Charge Ordered Organic Conductor

YAMAMOTO, Kaoru; YAKUSHI, Kyuya

Activation of overtones (OT) (asterisk in Figure 1) in the IR spectrum of θ -(BEDT-TTF)₂RbZn(SCN)₄ has been investigated using a diatomic molecular dimer model. When the two molecules are in the charge disproportionation for some reason, deformation of the two molecules along the anti-phase mode ($Q_{-} = Q_{1} - Q_{2}$; $Q_{1,2}$: normal coordinates of molecule 1 and 2) stabilizes the disproportionation *via* electron-molecular vibration (EMV) coupling effect. This stabilization turns the electronic wavefunction (Ψ) to be dependent on Q_{-} and induces an unharmonicity in the vibronic energy,

$$\int \Psi^*(n_1 - n_2)Q_-\Psi dr$$

 $(n_{1,2}:$ electron density on the molecule 1 and 2). Taking the Q_- dependence into account, we have calculated the optical conductivity spectrum including one totally symmetric C=C stretching mode (v₃) using several fitting parameters, such as the vibronic coupling constants and the phenomenological site-energy difference. As shown by the dashed curve in Figure 1, the calculated spectrum reproduces the characteristics of the experimental data including the fundamental and overtone of v₃. According to the model developed here, the overtone is only visible when the degree of charge disproportionation is large, and thus the emergence of overtone can be referred as evidence for the large charge disproportionation.



Figure 1. Solid curve shows the optical conductivity spectrum $(E_{\rm ph}//c\text{-}axis)$ of θ -(BEDT-TTF)₂RbZn(SCN)₄ measured at 50 K. Arrows and an asterisk indicate the fundamental and overtone of v_3 , respectively. The dashed curve shows the calculation results.

IV-A-9 Bond and Charge Density Waves in the Charge Localized Phase of (DI-DCNQI)₂Ag Studied by Single-Crystal Infrared and Raman Spectroscopy

YAMAMOTO, Kaoru; YAMAMOTO, Takashi; YAKUSHI, Kyuya; PECILE, Cesare¹; MENEGHETTI, Moreno¹ (¹Univ. Padova)

[Phys. Rev. B submitted]

The charge distribution and molecular arrangement of a 1/4-filled quasi-1D system (DI-DCNQI)₂Ag (DI-DCNQI = 2,5-diiodo-dicyanoquinediimine) have been studied by IR and Raman spectroscopy. The charge localization of this material was believed to be a 1D generalization of a Wigner crystal driven by inter-site Coulomb repulsion. While charge disproportionation (CD) is confirmed *via* the splitting of b_u modes in the infrared (IR) spectrum, the appearance of intense IR vibronic bands of a_g modes strongly suggests the presence of the dimerization that is not expected from the proposed 1010 charge ordering (CO) model (Wigner crystal). In addition, the selection rules for the IR and Raman signals cannot be explained without a further symmetry reduction of the unit cell. To explain the vibrational behavior observed for a single crystal, we show that a more appropriate model for the charge ordering is 0110 ($2k_F$ CDW + $4k_F$ BOW).

IV-A-10 Infrared and Raman Studies of TTM-TTP and TSM-TTP Charge-Transfer Salts

SWIETLIK, Roman¹; YAKUSHI, Kyuya; YAMAMOTO, Kaoru; KAWAMOTO, Tadashi²; MORI, Takehiko²

(¹IMS and Inst. Molecular Phys.; ²Tokyo Inst. Tech.)

The bis-fused TTF (tetrathiafulvalene) molecule and its derivatives are good electron donors for synthesis of new conducting ion-radical salts. One of these derivatives, TTM-TTF (see Figure 1) yields mostly quasi-onedimensional semiconductors, because four S-CH₃ groups attached to the bis-fused TTF skeleton separate efficiently neighboring TTM-TTP stacks. Nevertheless, some TTM-TTP salts exhibit metallic properties. The charge-transfer salt, (TTM-TTP)I₃ was reported as the first organic metal with 1:1 stoichiometry and a highly one-dimensional half-filled band. To investigate the relation between the molecular ionicity and the frequency of characteristic vibrational modes of TTM-TTP molecule, we measured room-temperature infrared and Raman spectra of neutral TTM-TTP molecule and four conducting charge-transfer salts with different molecular ionicity: (TTM-TTP)I₃, (TTM-TTP)AuI₃, (TTM-TTP)(I₃)_{5/3}, and (TSM-TTP)(I₃)_{5/3}. The vibrational bands related to the C=C stretching modes were analyzed. The frequencies of C=C stretching modes observed both in infrared and Raman spectra depend linearly upon the charge on TTM-TTP (or TSM-TTP) molecules.



Figure 1. Structural formula of TTM-TTP.

IV-B Magnetic Resonance Studies for Molecular-Based Conductors

Magnetic resonance measurements are powerful investigations to understand the fundamental electronic properties, because they are microscopic and also dynamical measurements. Molecular based conductors are one of the extensively studied materials. The development of the understanding of the electronic phases of these materials enables us systematic investigations of low-dimensional highly correlated electrons systems. Competition of the electronic phases in molecular based conductors has attracted much attention. The investigations of such electronic phases by means of magnetic resonance measurements are important to understand the unsolved fundamental problems in the field of solid state physics.

In this project, we performed the multi-frequency ESR (X-, Q- and W-bands), and broad-line NMR measurements for molecular based conductors to understand the electron spin dynamics in the low temperature electronic phases.

IV-B-1 Competition Electronic States of (TMTTF)₂MF₆: ESR Investigations

NAKAMURA, Toshikazu; MAEDA, Keisuke¹ (¹GUAS)

ESR measurements were performed to investigate the low-temperature electronic states of $(TMTTF)_2MF_6$ (M = P, As, Sb and their mixed alloys). The temperature dependence of the ESR linewidth, ΔH_{pp} , of AsF₆ does not change its anisotropy at around T_{sp} . On the other hand, PF₆ and some P-AsF₆ alloys show changes of the ΔH_{pp} anisotropy at around T_{sp} , suggesting reconstruction of electronic charges. We propose the possible charge ordering configuration in the vicinity of the low temperature ground states from the ESR point of view.



Figure 1. (a)–(b) Temperature dependence of the linewidth, $\Delta H_{\rm pp}$, for (a) PF₆ and (b) AsF₆ in the vicinity of the sP transitions.



Figure 2. Schematic diagram of the possible electronic phases with the compositions (chemical pressures) for the MF_6 and their alloys deduced by the ESR results; (i)SbF₆, (ii) (AsF₆)_{0.2}(SbF₆)_{0.8}, (iii) (AsF₆)_{0.5}(SbF₆)_{0.5}, (ix) AsF₆, (x) (PF₆)_{0.3}(AsF₆)_{0.7} (xi) (PF₆)_{0.6}(AsF₆)_{0.4} and (xii) PF₆.

IV-B-2 ESR Study on Low-Dimensional Antiferromagnet α -(BEDT-TTF)₂PF₆ and ζ -(BEDT-TTF)₂PF₆(THF)

MAEDA, Keisuke¹; HARA, Toshifumi; NAKAMURA, Toshikazu (¹GUAS)

ESR measurements were carried out for α -(BEDT-TTF)₂PF₆ and ζ -(BEDT-TTF)₂PF₆(THF). The temperature dependences of the spin susceptibility of the two salts are very similar to each other and seem to behave as typical paramagnetic insulators with low-dimensional antiferromagnetic interaction. The absolute values of the macroscopic antiferromagnetic interaction, $J/k_{\rm B}$, are also very close. However, there are obvious differences in their ground states and microscopic behaviours. ζ -(BEDT-TTF)₂PF₆(THF) undergoes an antiferromagnetic transition at around 5 K, while α -(BEDT-TTF)₂PF₆ shows no long-range magnetic ordering down to 2 K. The temperature dependent behaviours of the ESR linewidth, ΔH_{pp} , are quite different: The ΔH_{pp} of ζ -(BEDT-TTF)₂PF₆(THF) is almost temperature independent in the paramagnetic region and shows an abrupt increase below about 30 K, while the ΔH_{pp} of α -(BEDT -TTF)₂PF₆ gradually decreases as the temperature decreases. The low temperature electronic states of these salts are discussed from the microscopic point of view.



Figure 1. Temperature dependence of the spin susceptibility of α -(BEDT-TTF)₂PF₆. The exchange interaction, J/k_B , is about 27 K evaluated from the Bonner-Fisher model. This behavior is in good agreement with the static susceptibility measured by SQUID.



Figure 2. Temperature dependences of the spin susceptibility of ζ -(BEDT-TTF)₂PF₆(THF). The exchange interaction, J/k_B , is about 25 K.

IV-B-3 Multi-Frequency ESR Measurements for (TMTTF)₂X

HARA, Toshifumi; FURUKAWA, Ko; NAKAMURA, Toshikazu

TMTTF family salts are now attracted attention by the recent progress of the charge ordering (CO) investigations. Recently, we proposed the possible charge ordering configurations for each of $(TMTTF)_2X$ salts according to the difference of the ESR linewidth anisotropy at low temperatures. The CO configurations of $(TMTTF)_2X$ are roughly divided into three groups, and this classification is consistent with the results determined by other measurements. However the origin of the charge ordering phenomena is not clarified, and the quantitative understanding of the ESR linewidth is not succeeded so far. So we performed multi-frequency (X-[10 GHz], Q- [30 GHz], and W-bands [100 GHz]) ESR measurements for one of typical TMTTF salts, $(TMTTF)_2SbF_6$, which shows the charge ordering transition at 154 K. The ESR linewidth determined by the W-band measurement is obviously larger than that by X-band below the charge ordering transition. We discuss the low temperature electron spin dynamics from the ESR point of view.



Figure 1. Temperature dependence of the ESR width, ΔH_{pp} , of (TMTTF)₂SbF₆ determined by X- (open symbols) and W-bands (solid symbols).

IV-B-4 Correlation between Molecular and Spin Structures of $(TMTTF)_2 X$

FURUKAWA, Ko; HARA, Toshifumi; NAKAMURA, Toshikazu

The g-values of organic conductors are determined by the *g*-tensor of the radicals and their configuration. So the g-values of the crystal generally do not change with temperature. According our recent detailed ESR measurement, the g-values of the several TMTTF salts shows significant change with temperature, although these salts do not indicate structural changes. In order to understand the anomalous g-shift, we performed molecular orbital calculation with the Gaussian03, and estimated the g-values by the GIAO method. According to the calculation results, we found that the deformation of the TMTTF molecules along the molecular long axis cause a g-shift toward to an uni-axial symmetry. We can explain the anomalous g-shift observed if we assume the shrink of the TMTTF molecules along the molecular long-axis as the temperature decreases. Further structural investigation such as low-temperature X-ray measurements are now going on.

IV-B-5 Dynamical Charge Disproportionation in Metallic State in θ -(BEDT-TTF)₂RbZn(SCN)₄

TAKAHASHI, Toshihiro¹; CHIBA, Ryo¹; HIRAKI, Ko-ichi¹; YAMAMOTO, M. Hiroshi²; NAKAMURA, Toshikazu (¹Gakushuin Univ.; ²Inst. Phys. Chem. Res.)

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[J. Phys. IV France 114, 269–272 (2004)]

Results of ¹³C-NMR experiments on charge ordering in non-dimerized BEDT-TTF salts are discussed. It has been experimentally confirmed in θ -(ET)₂RbZn(SCN)₄ that charge disproportionation already develops well above the metal-insulator transition temperature while no long-range charge order is stabilized. Dynamics of the charge fluctuations has been determined in this salt and compared with the situations in α -(ET)₂I₃. This result seems to require a serious reconsideration of the transport properties in the metallic state.

IV-B-6 Charge Disproportionation in the Metallic States of α -(BEDT-TTF)₂I₃

MOROTO, Shiori¹; HIRAKI, Ko-ichi¹; TAKANO, Yoshiki¹; TAKAHASHI, Toshihiro¹; YAMAMOTO, M. Hiroshi²; NAKAMURA, Toshikazu (¹Gakushuin Univ.; ²Inst. Phys. Chem. Res.)

[J. Phys. IV France 114, 399–400 (2004)]

¹³C-NMR measurements have been carried out on the quasi two-dimensional organic conductor, α-(BEDT-TTF)₂I₃. We measured the angular dependence of ¹³C-NMR spectrum at several temperatures above metal-insulator transition temperature, 135 K (= $T_{\rm MI}$). We found that charge (spin) disproportionation already exists in the metallic state and gradually develops as temperature approaches to $T_{\rm MI}$.

IV-C Development of Multi-Functional Molecular Systems

The molecules are usually assembled by weak intermolecular interactions and tend to retain their isolated electronic states even in the crystalline state. Consequently, the multi-functional systems can be constructed by assembling various molecules with different characters. Thus, the molecules are regarded as suitable building blocks for the bottom-up construction of the systems where various functions coexist.

Recently, "dual-action system" such as magnetic molecular conductors has attracted a considerable interest. We have discovered many molecular conducting systems exhibiting various dual-active electromagnetic properties such as the organic superconductor exhibiting a "superconductor \rightarrow insulator transition" at low temperature (λ -(BETS)₂Fe_xGa_{1-x}Cl₄ (0.35 < x < 0.5) (1997)), the first antiferromagnetic organic superconductor exhibiting "antiferromagnetic superconductor \rightarrow ferromagnetic metal transition" associated with meta-magnetic transition of magnetic anion layers around 1.6 T (κ -(BETS)₂FeBr₄ (1999–2002)), the first field-induced organic superconductor (λ -(BETS)₂FeCl₄ (2001)). The intriguing field-induced superconductivity was also observed in λ -(BETS)₂Fe_xGa_{1-x}Cl₄ and κ -(BETS)₂FeBr₄. Except these conductors, any hitherto-developed organic conductors scarcely show clear interplay between magnetic building blocks and conducting parts.

We have tried to prepare new TTF-type π donors with stable organic radical parts with the aim of developing new type of magnetic conductors. We are now trying to prepare new molecular conductors exhibiting spin-crossover behavior.

The large designability is another important feature of the molecular system. We have recently developed the single-component molecular metal based on the transition metal dithiolate complex with extended-TTF ligands. The fundamental idea of the molecular design of the single-component molecular metals is based on the development of multi-chalcogen π molecule with TTF-like skeleton and very small HOMO-LUMO gap. Recently the existence of the Fermi surface in the first single-component molecular metal, [Ni(tmdt)₂] (tmdt = trimethylenetetrathiafulvalene) was confirmed by the observation of de Haas-van Alphen oscillation at high magnetic field.

The host-guest molecular system is a good example showing the molecular assembly by weak interactions. By utilizing weak host-guest interaction of porous materials, we are now trying to obtain new functional molecular systems.

IV-C-1 Organic Metals and Superconductors Based on BETS (BETS = Bis(ethylenedithio) tetraselenafulvalene)

KOBAYASHI, Hayao; CUI, HengBo; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

[Chem. Rev. 104, 5265 (2004)]

Since the discovery of the first organic superconductors $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene; $X = PF_6$, ClO_4 , ...) about a quarter century ago, an extremely large progress has been achieved in the field of physics and chemistry of molecular conductors. When the metallic states of TMTSF conductors were found to be stable down to about 10 K, many chemists noticed the possibility of the existence of two-dimensional (2D) organic conductors with intermolecular 2D networks of peripheral chalcogen atoms of π molecules. In fact, by the observations of Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) oscillations in the subsequently developed BEDT-TTF (= bis(ethylenedithio)tetrathiafulvalene) superconductors with β - and κ -type molecular arrangements, the existence of ideally 2D organic π metal systems with stable metallic states was proved. However, in the midst of these rapid progress, an extraordinarily large impact was brought about by the discovery of high temperature cupper oxide superconductors. It became very serious for the chemists in this field to find new ways by making the best use of the merit of molecule-based systems. More than a decade ago, we started to try to prepare magnetic organic conductors

based on BETS molecules and tetrahalide Fe^{3+} ions. Fortunately, the π -*d* interaction in BETS conductors was discovered to be fairly strong and we could obtain very unique magnetic organic superconductors. In this review, we have summarized our recent works on magnetic organic superconductors based on BETS and magnetic and non-magnetic anions MX_4^- (M = Fe, Ga; X = Cl, Br). Many topics such as field-induced superconductivity of λ -(BETS)₂FeCl₄, λ -(BETS)₂FeBr_xCl_{4-x} and κ -(BETS)₂FeBr₄, superconductor-to-insulator transition of λ -(BETS)₂Fe_xGa_{1-x}Cl₄, antiferromagnetic organic superconductors, κ -(BETS)₂FeX₄ and switching behavior of electrical properties of magnetic organic superconductors are described.

IV-C-2 Single-Component Molecular Metals with Extended-TTF Dithiolate Ligands

KOBAYASHI, Akiko¹; FUJIWARA, Emiko¹; KOBAYASHI, Hayao (¹Univ. Tokyo)

[Chem. Rev. 104, 5243 (2004)]

It has been believed for a long time that the formation of electronic bands and the generation of charge carriers by the intermolecular charge transfer between the molecules constituting the band (designated by A) and other chemical species (designated by B) are two essential requirements to design molecular metals. In some cases, both molecules A and B form conduction bands where the electron and the hole carriers are generated on both A and B molecules. This is the reason why the design of metals composed of single-component molecules is difficult. However, we have recently noticed the possibility of carrier generation even in the single-component molecular crystal and prepared the first example of the crystal of a neutral transition metal complex with extended-TTF ligands, [Ni(tmdt)₂] (tmdt = trimethylenetetrathiafulvalenedithiolate) exhibiting metallic behavior down to very low temperature. More recently, a direct experimental evidence for the Fermi surface in [Ni(tmdt)₂] was obtained by detecting the quantum oscillations in magnetization at very high magnetic field (or de Haas-van Alphen (dHvA) effect). Torque magnetometry measurements of single crystals of [Ni(tmdt)₂] using a sensitive microcantilever at low temperature revealed dHvA oscillatory signals for all directions of magnetic field, showing the presence of three-dimensional (3D) electron and hole Fermi surfaces. Thus the existence of single-component molecular metal has been definitely confirmed.

This review describes the frontier orbital engineering for the design of single-component molecular metal and present some examples of recently developed single-component molecular conductors with various extended-TTF ligands such as [Ni(dmdt)₂], [Au(tmdt)₂] exhibiting magnetic transition around 85 K without loss of its high conductivity and [Co(dt)₂] with unique dimeric conformation and high conductivity down to 0.6 K. Experimental evidences showing the validity of our idea on the molecular design of single-component molecular metals are also presented.

IV-C-3 Observation of Three-Dimensional Fermi Surfaces of Single-Component Molecular Metal, Ni(tmdt)₂

TANAKA, Hisashi¹; TOKUMOTO, Madoka¹; ISHIBASHI, Shouji¹; GRAF, D.²; CHOI, E. S.²; BROOKS, J. S.²; YASUZUKA, Shyuma³; OKANO, Yoshinori; KOBAYASHI, Hayao; KOBAYASHI, Akiko⁴

(¹AIST; ²Florida State Univ.; ³Natl. Inst. Mater. Sci.; ⁴Univ. Tokyo)

[J. Am. Chem. Soc. 126, 10518 (2004)]

We have recently reported that the metal electrons can be spontaneously produced by self-assembling of the well-designed π complex molecules with TTF-like ligands and very small HOMO-LUMO gap. We have also reported that the first single-component molecular metal, [Ni(tmdt)₂] and analogous compounds show the very broad low-energy electronic excitation spectra in IR region, which undoubtedly shows the validity of our molecular design of the single-component molecular metals. However, considering that there has been no example of the molecular metal composed of single molecules before our discovery, unambiguous evidence will be desired to establish completely the existence of the metal electrons in the single-component molecular crystal. One of the most rigorous evidence may be the observation of de Haas-van Alphen oscillation. Since the crystals of [Ni(tmdt)₂] were very small, a new micro-cantilever technique of magnetization measurement was adopted using the hybrid magnet at the National High Magnetic Field Laboratory at Florida.

The quantum oscillation observed for all the direction of the magnetic field suggested the existence of the threedimensional Fermi surfaces.



Figure 1. (a) Hole (black) and electron (gray) Fermi surfaces and the first Brillouin zone of $[Ni(tmdt)_2]$. The extremal hole orbits for the field applied parallel to c^* axis are also shown. (b) S1 and S2 are the corresponding extremal cross section sizes calculated by slicing Fermi surfaces.

IV-C-4 Syntheses, Structures and Physical Properties of New Nickel Bis(dithiolene) Complexes Containing TTF (Tetrathiafulvalene) Units

FUJIWARA, Emiko¹; KOBAYASHI, Akiko¹; FUJIWARA, Hideki; KOBAYASHI, Hayao (¹Univ. Tokyo)

[Inorg. Chem. 43, 1122 (2004)]

To contribute to the development of single-component molecular metals, several nickel complexes with cyclohexeno-condensed or ethylenedioxy-substituted TTF (tetrathiafulvalene) dithiolate ligands, $(R_4N)_n$ [Ni(chdt)₂] [R = Me, n = 2: (1); R = ⁿBu, n = 1: (2); n =0: (3)] and $(R_4N)_n[Ni(eodt)_2]$ [R = Me, n = 2: (4); R = ^{*n*}Bu, n = 1: (5); n = 0: (6)], were prepared. X-Ray structures were determined on the monoanionic species (2) and (5). The tetra-*n*-butylammonium complexes of the monoanionic $[Ni(chdt)_2]$ (2) with a 1:1 composition revealed that its magnetic susceptibility gave good agreement with the Bonner-Fisher model $(J/k_B = -28)$ K), which was derived from the one-dimensional chains of anions with regular intervals. On the other hand, the magnetic susceptibility of tetra-n-butylammonium complexes of monoanionic [Ni(eodt)₂] (5) showed Curie-Weiss behavior ($C = 0.376 \text{ K} \cdot \text{emu} \cdot \text{mol}^{-1}$ and $\theta = -4.6$ K). Both of the monoanionic species (2) and (5) indicate that they belong to the s = 1/2 magnetic systems and have relatively large and anisotropic g-values, suggesting the contribution of the nickel 3d orbital. The electrical resistivity measurements were performed on the compressed pellets of the neutral species (3) and (6). The fairly large conductivities were obtained ($\sigma_{rt} = 1-10$) $S \cdot cm^{-1}$). In addition, in spite of the compressed powder pellet sample, the neutral species (6) showed metallic behavior down to ca. 120 K and retained high conductivity even at 0.6 K [$\sigma(0.6 \text{ K})/\sigma_{rt} \approx 1/30$], suggesting the crystal to be essentially metallic down to very low temperature. These electrical behavior and Pauli paramagnetism of (6) indicate the system to be a new singlecomponent metal.



Figure 1. Temperature dependence of electrical resistivities of the neutral nickel complexes measured by use of the compressed pellets. (a)[Ni(chdt)₂] (**3**) and (b) [Ni(eodt)₂] (**6**).

IV-C-5 The Pressure Effect on the Antiferromagnetic and Superconducting Transitions of κ -(BETS)₂FeBr₄

OTSUKA, Takeo; CUI, HengBo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko¹; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

[J. Mater. Chem. 14, 1682 (2004)]

Among a wide variety of highly conducting molecular solids, a special group of conducting salts, so-called π -d system has attracted much concern in recent years, where π -d system is a class of complexes comprising π conducting electrons and localized magnetic moments of transition metal ions together in a crystal. The main interests in these systems are concentrated on the possible multi-functional properties originating from the interplay between localized magnetic moments and π metal electrons because the development of the multifunctional molecular conductors is considered to be an important step for realising molecular devices. However, up to now only a very limited number of systems are known to exhibit physical properties clearly reflecting π -d coupling. The first antiferromagnetic organic superconductor, κ -(BETS)₂FeBr₄ shows a unique successive phase transition from paramagnetic metal to antiferromagnetic metal to antiferromagnetic superconductor with lowering temperature. In order to examine the pressure effect on the antiferromagnetic and superconducting transition (T_N, T_c) , the resistivity was measured up to 6 k bar along two directions. One direction is perpendicular to the conduction plane (I//b)axis), and another is parallel to the conduction plane (I//a). These resistivities along the *a* and *b* axes gave almost the same temperature dependencies though the anisotropy of the resistivity is fairly large $(\rho_{//b}/\rho_{//a} \approx 200)$ at room temperature). The pressure dependencies of $T_{\rm N}$ and $T_{\rm c}$ were obtained from the anomalies in the temperature dependencies of the resistivities. The value of $T_{\rm c}$ decreased with pressure and became less than 0.5 K around 4 kbar. While, T_N was enhanced at high pressure. The high-pressure resistivity measurements under magnetic field showed the critical magnetic field of metamagnetic transition increased gradually with pressure.



Figure 1. Temperature dependence of the resistivity of κ -(BETS)₂FeBr₄ at high pressure (< 5 kbar): a, 1 bar(ambient); b, 2 kbar; c, 3 kbar; d, 3.5 kbar; e, 4 kbar; f, 5 kbar. (b) The temperature dependencies of the resistivities of κ -(BETS)₂ FeBr₄ for *I*//*a* and *I*//*b* at ambient pressure.

IV-C-6 Crystal Structure of [(C₂H₅)₂(CH₃)₂N][Pd(dmit)₂]₂ at High Pressure

OKANO, Yoshinori; ADACHI, Takafumi¹;NARYMBETOV, Bakhyt²; KOBAYASHI, Hayao; ZHOU, Biau³; KOBAYASHI, Akiko³ (¹SPring8, JASRI; ²Uzbek Acad. Sci.; ³Univ. Tokyo)

[Chem. Lett. 938 (2004)]

We have recently reported the crystal structure of high-pressure molecular superconductor, $[(C_2H_5)_2]$ (CH₃)₂N][Pd(dmit)₂]₂ based on the high-pressure X-ray data obtained more than several years ago. The crystal of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ belongs to the triclinic system. Since the $(C_2H_5)_2(CH_3)_2N^+$ cation is on the inversion center, the cation is disordered with taking two possible positions randomly at ambient pressure. The Pd(dmit)₂ molecules are stacked face-to-face to form dimeric columns along the *a* direction. Despite of the high room-temperature conductivity, the crystal becomes semiconducting at low temperature. But as mentioned above, the system shows a superconducting transition at high pressure at 2-7 kbar. However, in contrast to most of the molecular superconductors with stable metallic states above the critical pressures where the superconducting phases are suppressed, the insulating state appears above 7 kbar. The high-pressure X-ray experiments were made by using a specially designed diamond anvil cell. The crystals with typical dimensions of about $0.3 \times 0.2 \times 0.04 \text{ mm}^3$ were used.

The X-ray diffraction spots were detected by X-ray imaging plate system equipped with a rotating anode Xray generator (MoKa). The crystal structure determination at 10 kbar was made using the 815 reflections (I > $3\sigma(I)$). The correction for X-ray absorption by diamond anvil was not made. Due to the limited number of the observed reflections and the relatively large number of crystallographically independent atoms (41 non-hydrogen atoms of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2)$, the anisotropic temperature factors were used only for two Pd atoms. The structure refinements gave the final Rvalue of 0.105. The band structure at high-pressure was calculated based on the high-pressure structure. The calculated orbital levels of HOMO and LUMO at ambient pressure were significantly smaller than those at 10 kbar, which is considered to be related to the increase of planarity of Pd(dmit)₂ molecule (or π conjugation of the molecule) at high pressure.



Figure 1. The crystal structure of $[(C_2H_5)_2(CH_3)_2N]$ [Pd(dmit)₂]₂ at 10 kbar.

IV-C-7 Synthesis, Structures and Physical Properties of a New Organic Conductor Containing a Stable PROXYL Radical

FUJIWARA, Hideki; LEE, Ha-Jin; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Emiko¹; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

[Adv. Mater. 16, 1765 (2004)]

By the recent intensive studies on the moleculebased materials consisting of conducting organic layers and inorganic anion layers with localized magnetic moments, ferromagnetic metals, para- or antiferromagnetic superconductors and organic conductors exhibiting superconductor-to-insulator transition and field-induced superconductivity have been discovered. On the other hand, the development of organic ferromagnetic metals had been stimulated by the theoretical report that pointed out the possibility of the realization of ferromagnets employing the charge transfer complexes with stable organic radical substituents, and several research groups have investigated on the synthesis of donor or acceptor units bearing a stable radical part and reported cation radical salts based on such component molecules so far. However, it was quite difficult to obtain highly conducting cation radical salts because of so large steric hindrance of stable radical parts to construct the conduction pathway by stacking the conducting units such as the TTF (tetrathiafulvalene) skeleton. Recently, we have tried to overcome such problems by introducing π -extended donor skeletons which are regarded as being effective to establish sufficient intermolecular overlap integrals and π conduction bands which are indispensable for realizing the highly conducting complexes. We have discovered highly conducting cation radical salts by use of the bis-fused TTF skeleton called as TTP containing a PROXYL radical substituent and succeeded in the structure analysis of the AsF₆⁻ salt of cyclopentenofused TTP derivative carrying a stable PROXYL radical part having a 4:1 stoichiometry of D:A. Though the size of the crystal was very small (maximum dimension is about 0.15 mm) and the crystal quality was poor, we performed successfully a four-probe resistivity measurement. The crystal was semiconducting with the room temperature conductivity of about 1 S cm⁻¹ and a small activation energy of 0.05 eV. The SQUID susceptibility measurements and ESR experiments suggested the coexistence of the localized PROXYL radical spins and π conduction electrons at high temperature (T > 100 K).



Figure 1. Temperature dependence of the χT values of (TTP-PROXYL)₄AsF₆ measured by SQUID (open square) and normalized ESR intensities.

IV-C-8 Anionic NaCI-Type Frameworks of [Mn^{II}(HCOO)₃⁻], Templated by Alkylammonium, Exhibit Weak Ferromagnetism

WANG, Zheming¹; ZHANG, Bin²;OTSUKA, Takeo; INOUE, Katsuya; KOBAYASHI, Hayao; KURMOO, Mohamedally³

(¹Peiking Univ; ²Chinese Acad. Sci.; ³Inst. Phys. Chim. Matériaux Strasbourg)

[Dalton Trans. 2209–2216 (2004)]

We present the synthesis, characterization by IR, TGA, single crystal X-ray structure and magnetic properties of a novel series of NaCl-type frameworks of [AmineH⁺][Mn(HCOO)₃⁻], templated by alkylammonium. The anionic NaCl-framework of [Mn (HCOO)₃⁻] is counter-balanced by the alkylammonium cations located in the cavities of the framework to which they are hydrogen-bonded. The divalent manganese ions have octahedral geometry and are bridged by the formate in an anti-anti mode of coordination. All the compounds exhibit long-range antiferromagnetism below 9 K with a slight non-collinear arrangement of the moments. The canting, likely due to second-order spin-orbit coupling, is via a Dzyaloshinski-Moriya antisymmetric exchange mechanism. A spin-flop is observed in each case at fairly low fields. An orthorhombic to monoclinic transformation was observed for the protonated cyclotrimethyleneamine that is accompanied by localization of the cations into two positions below 240 K from the rapid dynamic flipping of the ring observed at room temperature.



Figure 1. NaCl-type framework of $[Mn^{II}(HCOO)_3^-]$ including annmonium cations $(CH_3CH_2NH_3^+)$ in the cavity.

IV-C-9 Preparation and Properties of Novel Fe(III) Spin-Crossover Complexes with [Ni(dmit)₂] Anion

TAKAHASHI, Kazuyuki; KOBAYASHI, Hayao; EINAGA, Yasuaki¹; SATO, Osamu² (¹Keio Univ.; ²KAST)

Spin-crossover phenomena are observed in transition metal complexes with d^4 to d^7 configuration under an appropriate octahedral ligand field. The spin conversion is induced by external perturbation such as temperature, pressure, light, and so on. Thus, the spin-crossover complexes are considered as a promising candidate for molecular switching materials. Recently, great attention has been attracted to development of novel multifunctional materials. We have explored possibility to control electrical conductivity by external perturbation. Since molecular-based conductors consist of relatively weak intermolecular interactions, bandwidth and bandfilling can be controlled by substitution with similar size and shape of constituents. The spin conversion between the low-spin and the high-spin states accompanies a remarkable structural change in coordination bond

length. Therefore, electrical conductivity is expected to be controlled by embedding of the spin-crossover ion in molecular-based conductors. We have focused our attention upon the Fe(III) spin crossover complex, [Fe(qsal)₂]X, and the molecular-based conducting salt, $M[Ni(dmit)_2]$ [qsalH = N-(8-quinolyl)-salicylaldimine, dmit = 4,5-dithiolato-1,3-dithiole-2-thione]. We have prepared and characterized novel Fe(III) spin crossover complexes with [Ni(dmit)₂] anion. The syntheses of [Fe(qsal)₂]₂[Ni(dmit)₂] and [Fe(qsal)₂][Ni(dmit)₂]. CH₃CN could be achieved by metathesis between [Fe(qsal)₂]Cl and (Bu₄N)₂[Ni(dmit)₂], and between [Fe(qsal)₂]Cl and (Bu₄N)[Ni(dmit)₂], respectively, in acetonitrile. The composition ratios of them were determined by microanalysis. Temperature dependence of $\chi_{\rm M}T$ in [Fe(qsal)₂]₂[Ni(dmit)₂] revealed that a gradual spin transition from the low-spin to high-spin states occurred above 150 K. However, a complete spin conversion to the high-spin state could not be observed. On the other hand, temperature dependence of $\chi_M T$ in [Fe(qsal)₂][Ni(dmit)₂]·CH₃CN showed a wide hysteresis with about 35 K (Figure 1). These results suggested that there was no intermolecular interaction between [Fe(qsal)₂] ions in the 2:1 complex, whereas a strong cooperative interaction between them existed in the 1:1 complex. The crystal structure analyses were performed on a single crystal of both [Fe(qsal)₂]₂[Ni(dmit)₂] and [Fe(qsal)₂][Ni(dmit)₂]·CH₃CN. In [Fe(qsal)₂]₂[Ni (dmit)₂], crystallographical independent molecules were one [Fe(qsal)₂] ion and a half [Ni(dmit)₂] ion. No interaction was observed between neither $[Fe(qsal)_2]$ nor [Ni(dmit)₂] ions. On the other hand, in [Fe(qsal)₂] [Ni(dmit)₂]·CH₃CN, two-dimensional network was formed by π - π interactions between the π -ligands in [Fe(qsal)₂] ion. These results were consistent to temperature dependence of magnetic behaviors. The LIESST (Light-induced excited spin state trapping) experiment and an attempt to obtain conducting complexes by electrocrystallization of [Fe(qsal)₂] [Ni(dmit)₂]·CH₃CN are now in progress.



Figure 1. $\chi_M T vs. T$ plot of [Fe(qsal)₂][Ni(dmit)₂]·CH₃CN. Scan speed = 2 K min⁻¹, magnetic field = 5000 G.

IV-C-10 Preparation and Characterization of Novel TTP Derivatives Connected with a Stable Organic Radical by a Long Covalent Bond Spacer

TAKAHASHI, Kazuyuki; CUI, HengBo;

FUJIWARA, Hideki¹; KOBAYASHI, Hayao; FUJIWARA, Emiko²; KOBAYASHI, Akiko²

(¹Osaka Prefecture Univ.; ²Univ. Tokyo)

Recently, great attention has been attracted to interplay between conducting electrons and localized spins to develop novel magneto-electronic materials. We have reported synthesis and properties of several π -donor molecules with stable organic radicals and their conducting complexes. However, since the radical part is usually bulky, we often encountered difficulties in the formation of the conduction path based on the overlap of π -donor parts. A moderate distance between the π donor and organic radical parts is considered to decrease a hindrance to the formation of conduction path. Therefore, we have designed novel tetrathiapentalene (TTP) derivatives attached to a stable organic radical by a long covalent bond.

New TTP derivatives with stable TEMPO radicals (3) were synthesized by the reaction between Sprotected TTPTM (1) and iodoalkyl-substitued TEMPO (2). These donors were isolated as a fine powder or filmlike solid, and were unstable in air. Characterization of new donor molecules was carried out by MALDI-TOF mass spectroscopy, ESR spectra, and cyclic voltammetry. On the MALDI-TOF measurement, [M+H]⁺ ions were observed in all new donors. ESR spectra showed triplet signals, indicating that there is a TEMPO radical in each molecule. Cyclic voltammogram of them revealed that the redox behavior of the donor part was independent of that of the TEMPO one. Preparation of the conducting complexes of these donors is now in progress.



Scheme 1. Synthesis of TTP donors with a stable TEMPO radical.

IV-C-11 Crystal Structures and Physical Properties of Novel Molecular Conductors Based on BETS and MX_4^- (M = In, TI; X = CI, Br) Anions

CUI, HengBo; OKANO, Yoshinori; OTSUBO, Saika; TAKAHASHI, Kazuyuki; KOBAYASHI, Hayao; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

So far we have reported many molecular conductors based on BETS and MX_4^- (M = Fe, Ga; X = Cl, Br) anions with various structure types (α , θ , κ , λ , λ '). Among them, κ -(BETS)₂FeBr₄ and κ -(BETS)₂FeCl₄ are the first and second antiferromagnetic superconductors and λ -(BETS)₂FeCl₄ is the first organic conductor exhibiting a field-induced superconductivity. In λ -(BETS)₂FeCl₄, BETS molecules are stacked to form a tetradic column along the *a* axis. There exist many shortest distance between S(Se)...Cl and therefore the strong π -*d* interaction through Cl 3*p* orbitals is expected in λ -(BETS)₂FeCl₄. λ '-(BETS)₂GaBr₄ also has triclinic lattice and tetradic columns. But unlike superconducting λ -(BETS)₂GaCl₄, this salt seems to have a non-magnetic insulating ground state. Recently, we have found the salts with another modified λ -type structure, λ "-(BETS)₂TlBr₄. Similar to the λ -type structure, λ "-type has a triclinic unit cell. BETS molecules are staked to form 8-fold column, and tetrahedral TlBr₄⁻ anions are arranged to take the orientation of "up-up-down-down" along the 8-fold BETS column. The crystal has a fairly high conductivity but slightly semiconducting. (BETS)₃ InCl₅(PhCl)_{0.5} has a unique three-dimensional donor arrangement, and retains its metallic state down to 120 K with high room-temperature conductivity (250 Scm⁻¹). Two-dimensional Fermi surface was obtained by tight-binding band calculation.



Figure 1. Crystal structure of (BETS)₃InCl₅(PhCl)_{0.5}.

IV-C-12 Structural and Physical Properties of Molecular Conductors Based on BEST and MX_4^- (M = Fe, Ga, In; X = CI, Br)

CUI, HengBo; OTSUBO, Saika; OKANO, Yoshinori; TAKAHASHI, Kazuyuki; KOBAYASHI, Hayao; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

We have reported novel λ and κ -type salts based on BETS (bis(ethylenedithio)tetraselenafulvalene) and MX_4^- (M = Fe; X = Cl, Br). These salts exhibit many unprecedented electro-magnetic properties originated from the interplay between π conduction electrons and localized 3d magnetic moments. Recently, we have prepared BEST (bis(ethylenediseleno)tetrathia fulvalene), and grew the crystals of molecular conductors using MX_4^- (M = Fe, Ga, In; X = Cl, Br) anions. We obtained λ -BEST₂MCl₄ (M = Fe, Ga) and another triclinic modification, BEST₂MBr₄ (M = Fe, In). λ -BEST₂MCl₄ (M = Fe, Ga) is isostructural to λ -BEST₂ MCl_4 (M = Fe, Ga) but is semiconducting. In the crystal of $BEST_2MBr_4$ (M = Fe, In), BEST molecules form two kind of diadic columns along b axis. There exist many short S(Se)...Br contacts between BEST molecules and FeBr₄⁻. Thus, it seems possible that intermolecular interaction through the intermolecular overlapping between π orbitals of BEST and d-like orbitals of the anion. The resistivity of $BEST_2FeBr_4$ takes minimum around 180 K (Fe salt).



Figure 1. The crystal structure of BEST₂FeBr₄.

IV-C-13 Unsymmetrical Donors Fused with Pyridazine and Pyrazine Rings

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Hideki¹; FUJIWARA, Emiko²; KOBAYASHI, Akiko²

(¹Osaka Prefecture Univ.; ²Univ. Tokyo)

We have reported the crystal structures and physical properties of a series of organic conductors consisting of Se-containing π donors, bis(ethylenedithio)tetraselenafulvalene (BETS) and metal tetrahalide monoanions such as κ -and λ -(BETS)₂MX₄ (M = Ga, Fe, In, Tl,...; X = Br, Cl). In order to enhance the interaction between donor and anion layers, we have synthesized unsymmetrical donors fused with a pyridazine ring and a pyrazine ring 2-4 and prepared several cation radical salts of 3 and PEDTTSeF (2) by electrochemical oxidation. The ReO₄⁻ salt of **3** has 1:1 donor-to-anion composition, which exhibited a semiconducting behavior (σ_{rt} = 0.45 S/cm, $E_a = 0.094 \text{ eV}$). Whereas (PEDTTSeF)₂FeX₄ (X = Br, Cl) showed a metallic behavior down to 60 K (X = Cl) or 120 K (X = Br). The temperature dependence of magnetic susceptibility suggested very weak magnetic interactions between donors and anions.



Figure 1. Molecular structures of organic donors.

IV-C-14 A Novel TTP Donor Containing a Stable Organic Radical

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; LEE, Ha-Jin; KOBAYASHI, Hayao; FUJIWARA, Hideki¹; FUJIWARA, Emiko²; KOBAYASHI, Akiko² (¹Osaka Prefecture Univ.; ²Univ. Tokyo)

Development of magnetic conductors bearing both conductivity and magnetism has recently played a important role in the research of the multifunctionality of organic molecular materials. Recently, we have synthesized several organic donors containing a TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) radical or a PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxyl) radical. Among them, TTPPROXYL was found to produce interesting conductors exhibiting the coexistence of the conduction electrons and the localized spins. However, TTPPROXYL gives racemic compounds. So, a new TTP donor containing 2,2,5,5-tetramethyl-3pyrrolin-1-yloxyl was synthesized as orange powder in 0.43% yield (14 steps from 2,2,6,6-tetramethyl-4piperidinone). The preparation of cation radical salts by electrochemical oxidation is now in progress.



Scheme 1. Synthetic route of a new organic donor.

IV-C-15 Organic Conductors Containing a TEMPO Radical

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Hideki¹; FUJIWARA, Emiko²; KOBAYASHI, Akiko²

(¹Osaka Prefecture Univ.; ²Univ. Tokyo)

We have reported many intriguing electro-magnetic properties discovered in the magnetic organic superconductors based on Se-containing π donors BETS and magnetic transition metal anions FeX_4^- (X = Cl, Br). Besides BETS conductors, an attempt to obtain new type of magnetic organic conductors has been also performed by using donors containing a TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) radical or NN (4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide). TEMPOET (2), which is constituted of ET part and TEMPO radical part, has been synthesized several years ago but no highly conducting salts has not been prepared yet. We have recently tried to prepare similar TEMPOET-type organic donors (1, 3-5), which were synthesized by cross-coupling reaction and Horner-Wittig reaction (10-20% yield, 2 steps). Several cation radical salts with tetrahedral anions (FeCl₄⁻, BF₄⁻,...) were prepared by electrochemical oxidation. However, up to now, highly conducting salt could not be obtained.



Figure 1. Organic donors with TEMPO radical parts.

IV-D Electronic and Magnetic Properties of π-Electron-Based Molecular Systems

 π -electrons are an interesting building block in architecting functionalized electronic and magnetic molecular systems. We have focused on nano-sized graphite and TTF-based organic charge transfer complexes, in which π -electrons play an important role, in developing new types of molecular electronic systems. In nanographene, single layer nanographite, which is defined as flat open π -electron system have edges and contrasted to closed π -electron systems of fullerenes and carbon nanotubes, non-bonding π -electronic state appearing around the Fermi level generates unconventional nanomagnetism. We have found an interesting electronic wave interference effect in finite-sized graphite with distortion-network structures and anisotropy of the Raman spectra of nanographite ribbons. A combination of TTF-based π -electron donor and counteranion having localized spins is a useful way in producing molecular magnetic conductors, which are expected to have properties different from traditional metal magnets featured with *s*-*d* interaction. Under this scheme, we have developed a new class of TTF-based organic magnetic conductors. The interaction between the conducting π -electrons of donors and the localized *d*-electrons of magnetic anions are found to show interesting interplay between magnetism and electron transport.

IV-D-1 Weak-Ferromagnetism in Molecular Magnets Based on Transition Metal Complexes of Crown Thioether

NISHIJO, Junichi¹; NIYAZAKI, Akira¹; ENOKI, Toshiaki²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[Polyhedron 22, 1755–1758 (2003)]

A new class of molecular based magnets M(9S3)₂ $[Ni(bdt)_2]_2$ (M = Ni, Co) consisting of transition metal complex of crown thioether show weak-ferromagnetic transitions at $T_{\rm N}$ = 6.2 and 2.6 K for M = Ni and Co, respectively, accompanied by remanent magnetizations $0.2\mu_B$ and $0.01\mu_B$ with coercive forces 200 and 10 Oe. $M(9S3)_2^{2+}$ cations (S = 1 and 1/2 for M = Ni and Co, respectively), and a half of Ni(bdt)₂⁻ (S = 1/2) anions form alternate antiferromagnetic (AF) chains (#1), while the other half of Ni(bdt)₂⁻ anions form uniform AF chains (#2). These two type of chains are connected to each other by two weak AF interactions; interaction between Ni(bdt)₂⁻ in #1 and Ni(bdt)₂⁻ in #2, and interaction between $M(9S3)_2^{2+}$ in #1 and $Ni(bdt)_2^{-}$ in the adjacent chain #1. A competition between these two AF interactions causes canted spin configuration, giving rise to weak-ferromagnetism.

IV-D-2 New Bulk Weak Ferromagnet in Ferrimagnetic Chains of Molecular Material Based on DTDH-TTP and Paramagnetic Thiocyanato Complex Anion: (DTDH-TTP)[Cr(isoq)₂(NCS)₄]

SETIFI, Fatima¹; OUAHAB, Lahcène¹; GOLHEN, Stéphane¹; MIYAZAKI, Akira²; ENOKI, Toshiaki³; YAMADA, Jun-ichi⁴

(¹CNRS; ²Tokyo Inst. Tech.; ³IMS and Tokyo Inst. Tech.; ⁴Univ. Hyogo)

[C. R. Chim. 6, 309–316 (2003)]

The preparation, X-ray crystal structure and magnetic properties of a new charge transfer salt, $(DTDH-TTP)Cr(isoq)_2(NCS)_4$, DTDH-TTP = 2-(1',3'-dithiol2'-ylidene)-5-(1",3"-dithiolan-2"-ylidene)-1,3,4,6tetrathiapentalene, ISOQ = isoquinoline) are reported. Crystal data: monoclinic, space group *C*2/*c* (#15), *a* = 16.0836(5), *b* = 19.2488(6), *c* = 12.6829(6) Å, β = 95.669(1), *V* = 3906.5(2) Å³, *Z* = 4, *R* = 0.0515 for 2899 reflections with *I* > 2 σ (*I*). The crystal structure consists of mixed organic and inorganic layers in the *ac*-plane, each layer being formed by mixed columns of DTDH– TTP⁺⁺ radical cations and paramagnetic metal complex anions. Short intermolecular atomic contacts between donor and anion are observed in the column in the *c* direction. Ferrimagnetic interactions are observed between the non-equivalent donor and anion spins. This material exhibits bulk canted weak ferromagnetism below *T*_C = 8.7 K.

IV-D-3 Anomalous Metallic State of One-Dimensional Molecular Conductor (EDO-TTFBr₂)₃I₃

MIYAZAKI, Akira¹; KATO, Takehiko¹; YAMAZAKI, Hisashi¹; ENOKI, Toshiaki²; OGURA, Eiji³; KUWATANI, Yoshiyuki³; IYODA, Masahiko³; YAMAURA, Jun-ichi⁴ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Tokyo Metr. Univ.; ⁴Univ. Tokyo)

[Phys. Rev. B 68, 085108 (6 pages) (2003)]

The structure and physical properties of the onedimensional (1D) molecular conductor (EDO-TTF Br_2 ₃ I_3 are reported. This salt is composed of quasi-1D uniform stacks of the donor molecules and counter anions which are translationally disordered at room temperature. The temperature dependence of the lattice constants shows that, as the temperature decreases, the thermal contraction takes place along the donor columns, leading to the enhancement of the one-dimensionality of the π -electron system. The electrical conductivity and thermoelectric power show a metallic conductivity down to circa 140 K, where a metal-insulator transition takes place. The transition temperature decreases to circa 60 K as the hydrostatic pressure is applied up to 1.1 GPa. Although the transport properties give the itinerant feature of the pelectrons, the static susceptibility behaves as a 1D Heisenberg antiferromagnet-like behavior of localized spins from room temperature down to 15 K, which is consistent with the ESR linewidth governed by the 1D diffusion mechanism of localized spins. The coexistence of the itinerant character of the transport properties and the localized character of the magnetic properties of the π -electron system is attributed to the strongly correlated nature of the quasi-1D electron system.



Figure 1. The diagram of the resistivities *vs.* susceptibilities at room temperature for various TTF-based salts. Filled circle: $(EDO-TTFBr_2)_3I_3$; filled squares: $(TMTTF)_2X$; squares: Mott insulators; open circles: metallic compounds; diamond: band insulator.

IV-D-4 Property of Self-Assembled Monolayers of Long-Alkyl-Chain-Substituted TTF Derivative

YOKOTA, Yasuyuki¹; YUGE, Ryota¹; MIYAZAKI, Akira¹; ENOKI, Toshiaki²; HARA, Masahiko³ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³RIKEN)

> [Mol. Cryst. Liq. Cryst. 407, 121/[517]–127/[523] (2003)]

Self-assembled monolayers (SAMs) of an electron donor TTF derivative with long alkyl chains ($-C_{11}H_{22}-$) are formed on Au(111). STM, surface plasmon resonance, and FTIR reflection absorption spectroscopy measurements suggest that TTF backbone is isolated from the gold substrate by long alkyl chains. Cyclic voltammograms reveal two redox peaks ($E_1^{1/2} = 263$ mV, $E_2^{1/2} = 508$ mV vs. Ag/Ag⁺) corresponding to TTF/TTF⁺ and TTF⁺/TTF²⁺. These peak currents are proportional to the scan rates, indicating that the TTF backbone maintains its electrochemical activity in the SAMs. In addition, the peak-to-peak separations between oxidation and reduction are roughly proportional to the scan rates, which indicates that a potential drop takes place at the long alkyl chains, which work as resistance in the electron transport.

IV-D-5 Magnetic Anisotropy of Cerium Endhedral Metallofullerene

INAKUMA, Masayasu¹; TANIHARA, Atsushi²; KATO, Haruhito²; SHINOHARA, Hisanori²; ENOKI, Toshiaki³

(¹Tokyo Inst. Tech.; ²Nagoya Univ.; ³IMS and Tokyo Inst. Tech.)

[J. Phys. Chem. B 107, 6965–6973 (2003)]

Cerium endohedral metallofullerene ($Ce@C_{82}$) is a π -*f* composite nanomagnet, where anisotropic *f*-electron spin is expected to couple with the rotational motion of the fullerene cage that has π -electron spin. The field cooling effect on the susceptibility of Ce@C₈₂ in organic solutions suggests that the application of a magnetic field forces the molecular orientations to be aligned, in cooperation with the magnetic anisotropy of the felectron spin coupled with the molecular orientation. The role of crystal field in the magnetic anisotropy, which is associated with the off-center geometry of the Ce ion in the cage, is clarified by the crystal field analysis. The crystal field effect in the metallofullerene cage is considerably reduced, in contrast to that of ordinary rare-earth compounds. This is consistent with the findings of a small electronic coupling between the fand π -electrons and a shallow potential of the surrounding cage to the Ce ion. As a consequence, the crystal field effect is emphasized in the low-temperature range (below $\sim 100 \text{ K}$).

IV-D-6 Resonance Raman Scattering in Carbon Nanotubes and Nanographites

PIMENTA, M. A.¹; JORIO, A.¹; DANTAS, M. S.¹; FANTINI, C.¹; DE SOUZA, M.¹; CANÇADO, L. G.¹; SAMSONIDZE, Ge. G.²; DRESSELHAUS, G.²; DRESSELHAUS, M. S.²; GRÜNEIS, A.³; SAITO, Riichiro³; SOUZA FILHO, A. G.⁴; KOBAYASHI, Yousuke⁵; TAKAI, Kazuyuki⁵; FUKUI, Ken-ichi⁵; ENOKI, Toshiaki⁶

(¹Univ. Federal Minas Gerais; ²MIT; ³Tohoku Univ., CREST JST; ⁴Univ. Federal Ceará; ⁵Tokyo Inst. Tech.; ⁶IMS and Tokyo Inst. Tech.)

[Molecular Nanostructures: Proceedings XVII International Winterschool on Electronic Properties of Novel Materials, H. Kuzmany, J. Fink, M. Mehring and S. Roth, Eds., AIP Conference Proceeding **685**, page 219–224 (2003)]

In this work, we discuss the resonant Raman process in nanographites and carbon nanotubes, relating the most important Raman features to a first-order (single resonance) or a second-order (double resonance) process. We also show that, in the case of 1D systems, the term "resonance" has a more strict meaning and occurs when the energy of the photon does not simply coincide with the energy of a possible electron-hole pair, but rather matches the separation between van Hove singularities in the valence and conduction bands.

IV-D-7 Interface Effect on the Electronic Structure of Alkanethiol-Coated Platimum Nanoparticles

TU, Weixia¹; TAKAI, Kazuyuki¹; FUKUI, Kenichi¹; MIYAZAKI, Akira¹; ENOKI, Toshiaki² (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[J. Phys. Chem. B 107, 10134–10140 (2003)]

The structure and electronic properties are investigated for Pt nanoparticles coated with octadecanethiol self-assembled monolayer. The increase in the octa decanethiol/Pt ratio from 0 to full coverage reduces the average particle size from 2.2 to 0.9 nm. The temperature-independent spin susceptibility rises upon the increase in the particle size, quantum size effect being suggested to govern the magnetism. The low-temperature susceptibility shows a large Curie-type divergence, which cannot be explained simply by the even electron state of Pt. XPS spectra suggest an electron deficiency in the interior Pt nanoparticles, which is brought about by charge transfer from nanoparticle to coating thiol monolayer. The ESR line width and the g-value deviation increase as the octadecanethiol/Pt ratio is elevated, which are associated with the enhancement of spin-orbit interaction at the interface between the interior nanoparticle and coating thiol monolayer. This change at the interface works to make first spin-lattice relaxation centers in the carrier scattering process.



Figure 1. The thiol/Pt ratio dependence of Δg^2 and ΔH measured at room temperature for the thiol-coated Pt nanoparticles. The data for the naked Pt particle (thiol/Pt) 0) is obtained from ref 15.

IV-D-8 Tuning Magnetism and Novel Electronic Wave Interference Patterns in Nanographite Materials

HARIGAYA, Kikuo¹; KOBAYASHI, Yousuke²; KAWATSU, Naoki²; TAKAI, Kazuyuki²; SATO, Hirohiko³; RAVIER, Jérôme²; ENOKI, Toshiaki⁴; ENDO, Morinobu⁵

(¹Synthetic Nano-Function Mater. Project, AIST; ²Tokyo Inst. Tech.; ³Chuo Univ.; ⁴IMS and Tokyo Inst. Tech.; ⁵Shinshu Univ.)

[Physica E 22, 708–711 (2004)]

Antiferromagnetism in stacked nanographite is investigated with using the Hubbard-type models. The A–B stacking or the stacking near to that of A–B type is favorable for the hexagonal nanographite with zigzag edges, in order that magnetism appears. We also find that the open shell electronic structure can be an origin of the decreasing magnetic moment with the decrease of the inter-graphene distance, as experiments on adsorption of molecules suggest. Next, superperiodic patterns with a long distance in a nanographene sheet observed by STM are discussed in terms of the interference of electronic wave functions. The period and the amplitude of the oscillations decrease spatially in one direction. We explain the superperiodic patterns with a static linear potential theoretically. In the $k \cdot p$ model, the oscillation period decreases, and agrees with experiments. The spatial difference of the static potential is estimated as 1:3 eV for 200 nm in distance, and this value seems to be reasonable in order that the potential difference remains against perturbations, for example, by phonon fluctuations and impurity scatterings. It turns out that the long-distance oscillations come from the electronic structure of the two-dimensional graphene sheet.

IV-D-9 Magnetic Phase Diagram of Three-Dimensional Diluted Ising Antiferromagnet Ni_{0.8}Mg_{0.2}(OH)₂

SUZUKI, Masatsugu¹; SUZUKI, Itsuko¹; ONYANGO, Tedamann M.¹; ENOKI, Toshiaki² (¹State Univ. New York Binghamton; ²IMS and Tokyo Inst. Tech.)

[J. Phys. Soc. Jpn. 73, 206–215 (2004)]

H-T diagram of 3D diluted Ising antiferromagnet Ni_cMg_{1-c}(OH)₂ with c = 0.8 has been determined from measurements of SQUID DC magnetization and AC magnetic susceptibility. At H = 0, this compound undergoes two magnetic phase transitions: an antiferromagnetic (AF) transition at the Néel temperature T_N (= 20.7 K) and a reentrant spin glass (RSG) transition at T_{RSG} (≈ 6 K). The *H-T* diagram consists of the RSG, spin glass (SG), and AF phases. These phases meet a multicritical point P_m ($H_m = 42$ kOe, $T_m = 5.6$ K). The irreversibility of susceptibility defined by δ (= $\chi_{FC} - \chi_{ZFC}$) shows a negative local minimum for $10 \le H \le 35$ kOe, suggesting the existence of possible glassy phase in the AF phase. A broad peak in δ and χ " at $H \ge 20$ kOe for T_N (c = 0.8, H) $\le T \le T_N$ (c = 1, H = 0) (= 26.4 K) suggests the existence of the Griffiths phase.

IV-D-10 STM Observation of Electronic Wave Interference Effect in Finite-Sized Graphite with Distortion-Network Structures

KOBAYASHI, Yousuke¹; TAKAI, Kazuyuki¹; FUKUI, Ken-ichi¹; ENOKI, Toshiaki²; HARIGAYA, Kikuo³; KABURAGI, Yutaka⁴; HISHIYAMA, Yoshihiro⁴

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Synthetic Nano-Function Mater. Project, AIST;

[Phys. Rev. B 69, 035418 (7 pages) (2004)]

Superperiodic patterns near a step edge were observed by scanning tunneling microscopy on severallayer-thick graphite sheets on a highly oriented pyrolitic graphite substrate, where a dislocation network is generated at the interface between the graphite overlayer and the substrate. Triangular- and rhombic-shaped periodic patterns whose periodicities are around 100 nm were observed on the upper terrace near the step edge. In contrast, only outlines of the patterns similar to those on the upper terrace were observed on the lower terrace. On the upper terrace, their geometrical patterns gradually disappeared and became similar to those on the lower terrace without any changes of their periodicity in increasing a bias voltage. By assuming a periodic scattering potential at the interface due to dislocations, the varying corrugation amplitudes of the patterns can be under-stood as changes in the local density of states as a result of the beat of perturbed and unperturbed waves, *i.e.*, the interference in an overlayer. The observed changes in the image depending on an overlayer height and a bias voltage can be explained by the electronic wave interference in the ultrathin overlayer distorted under the influence of dislocation-network structures.



Figure 1. STM images $(500 \times 500 \text{ nm}^2)$ of superperiodic patterns at higher sample bias voltages; (a) $V_s = 0.3 \text{ V}$, (b) $V_s = 0.4 \text{ V}$, and (c) $V_s = 0.5 \text{ V}$. By increasing the bias voltage, the corrugation am-plitude of superperiodic patterns on the upper terrace decreased gradually [(a) and (b)] and changed into a net pattern (c). In con-trast, no significant change was observed for the pattern on the lower terrace. The net pattern appearing on the upper terrace of (c) is similar to that on the lower terrace. Height differences between two points depicted in (a) are shown in (d) for clarifying the bias-dependent contrast. Solid and blank circles are the height differences of the upper and lower terrace, respectively. (Circles at the sample bias of around 0 V are the height differences at $V_s = 0.02 \text{ V}$.)

IV-D-11 STM Observation of the Quantum Interference Effect in Finite-Sized Graphite

KOBAYASHI, Yousuke¹; TAKAI, Kazuki¹; FUKUI, Ken-ichi¹; ENOKI, Toshiaki²; HARIGAYA, Kikuo³; KABURAGI, Yutaka⁴;HISHIYAMA, Yukihiro⁴ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Synthetic Nano-Function Mater. Project, AIST; ⁴Musashi Inst. Tech.)

[J. Phys. Chem. Solids 65, 199–203 (2004)]

Superperiodic patterns were observed by STM on two kinds of finite-sized graphene sheets. One is nanographene sheets inclined from a highly oriented pyrolitic graphite (HOPG) substrate and the other is a several-layer-thick graphene sheets with dislocationnetwork structures against a HOPG substrate. As for the former, the in-plane periodicity increased gradually in the direction of inclination, and it is easily changed by attachment of a nanographite flake on the nanographene sheets. The oscillation pattern can be explained by the interference of electron waves confined in the inclined nanographene sheets. As for the latter, patterns and their corrugation amplitudes depended on the bias voltage and on the terrace height from the HOPG substrate. The interference effect by the perturbed and unperturbed waves in the overlayer is responsible for the patterns whose local density of states varies in space.

IV-D-12 Theoretical Study on Novel Electronic Properties in Nanographite Materials

HARIGAYA, Kikuo¹; YAMASHIRO, Atsushi²; SHIOMI, Yukihiko¹; WAKABAYASHI, Katsunoi³; KOBAYASHI, Yousuke⁴; KAWATSU, Naoki⁴; SATO, Hirohiko⁵; RAVIER, Jérôme⁴; ENOKI, Toshiaki⁶; ENDO, Morinobu⁷

(¹Synthetic Nano-Function Mater. Project, AIST; ²AIST; ³Hiroshima Univ.; ⁴Tokyo Inst. Tech.; ⁵Chuo Univ.; ⁶IMS and Tokyo Inst. Tech.; ⁷Shinshu Univ.)

[J. Phys. Chem. Solids 65, 123–126 (2004)]

Antiferromagnetism in stacked nanographite is investigated with using the Hubbard-type model. We find that the open shell electronic structure can be an origin of the decreasing magnetic moment with the decrease of the inter-layer distance, as experiments on adsorption of molecules suggest. Next, possible chargeseparated states are considered using the extended Hubbard model with nearest-neighbor repulsive interactions. The charge-polarized state could appear, when a static electric field is present in the graphene plane for example. Finally, superperiodic patterns with a long distance in a nanographene sheet observed by STM are discussed in terms of the interference of electronic wave functions with a static linear potential theoretically. In the analysis by the $k \cdot p$ model, the oscillation period decreases spatially in agreement with experiments.

IV-D-13 Structure and Physical Properties of Molecular Magnets Based on Trasition Metal Complexes of Crown Thioether

NISHIJO, Junichi¹; MIYAZAKI, Akira¹; ENOKI, Toshiaki²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[Bull. Chem. Soc. Jpn. 77, 715–727 (2004)]

A new series of molecule-based magnets, including crown thioether (9S3 = 1, 4, 7-trithiacyclononane) complexes of transition metals (Ni, Co, Cu), are presented. TCNQ salts $[M(9S3)_2](TCNQ)_2$ (M = Ni, Co) are onedimensional (1D), antiferromagnetic (AF) complexes with an intra-chain interaction J = -3.9 K and -1.3 K for M = Ni and Co, respectively, despite its long intermolecular distance, for which the large spin density on the sulfur atom in the magnetic $[M(9S3)_2]^{2+}$ cation is responsible. The mixed valence salt $[M(9S3)_2](TCNQ)_3$ (M = Ni, Co) is a paramagnetic semiconductor. 1D AF magnet [Cu(9S3)Br₂] does not undergo any magnetic transition because of the weak inter-chain interaction. Substituting a very small amount (~ 5%) of Cu with Ni causes a structural change. The change decreases the distances of inter-chain S-S contacts, resulting in the generation of an AF transition at $T_N = 4.5$ K. [M(9S3)₂] [Ni(bdt)₂]₂ (M = Ni, Co; bdt = 1,2-benzenedithiolato) are weak-ferromagnets with $T_{\rm N} = 6.2$ K and 2.6 K for M = Ni and Co, respectively. In the crystals, $[M(9S3)_2]^{2+}$ -[Ni(bdt)₂]⁻ alternate chains and [Ni(bdt)₂]⁻ uniform chains coexist. The appearance of weak-ferromagnetism is associated with a competition between two kinds of inter-chain AF interactions between [M(9S3)₂]²⁺-[Ni(bdt)₂]⁻ alternate chains, where the stronger one is an indirect inter-chain interaction through [Ni(bdt)₂]⁻ uniform chains, while the weaker is a direct inter-chain interaction.

IV-D-14 Effect of Heat-Treatment on Magnetic Properties of Non-Graphitic Disordered Carbon

TAKAI, Kazuyuki¹; OGA, Meigo¹; ENOKI, Toshiaki²; TAOMOTO, Akira³ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Matsushita Electric Industrial Co., Ltd.)

[Diamnod Rel. Mater. 13, 1469–1473 (2004)]

Heat-treatment effect on the electronic properties is investigated by magnetic susceptibility and ESR measurements in elation to structural change for nongraphitic but sp-rich disordered carbon thin-film prepared by pulsed laser deposition. X-ray 2 diffraction reveals that the sp y sp -jumbling "non-graphitic" structure of non-heat-treated sample with atomic-scale disorder is 23 easily relaxed into the nano-sized "graphitic" island-network by heat-treatment at approximately 600 °C, preserving the sp^2/sp^3 ratio in the sample at ;90%. According to the temperature dependence of magnetic susceptibility, non-heat-treated sample shows the Curie-Weiss behavior with the large Pauli paramagnetic temperature-independent term and antiferromagnetic interaction whose strength is significantly larger than that simply expected from the average spin -spin distance. The temperature dependence of ESR signal intensity confirms the large contribution of the Pauli paramagnetism in the non-heat-treated sample.

IV-D-15 Development of TTF-Based Self-Assembled Monolayer Systems and Their Electronic Properties

ENOKI, Toshiaki¹; YOKOTA, Yasuyuki²; YUGE, Ryota²; TU, Weixia²; MIYAZAKI, Akira²; TAKAI, Kazuyuki²; FUKUI, Ken-ichi² (¹IMS and Tokyo Inst. Tech.; ²Tokyo Inst. Tech.)

[J. Phys. IV France 114, 667–671 (2004)]

Self-assembled monolayer (SAM) systems of alkanethiol and TTF-substituted alkanethiol molecules on Au substrate and metal nanoparticles are investigated. TTF-substituted alkanethiol molecules form charge transfer complex SAM with TCNQ molecules, where charge transfer (CT) rate becomes similar to that in bulk TTF·TCNQ crystal. TTF-substituted alkanethiol SAMs with long alkyl chains shows Coulomb-blockade-type electron transport owing to the resistance of the long alkyl chain bridge. In Pt nanoparticles with alkanethiol SAMs on their surface, CT takes place from core Pt nanoparticle to surface SAMs, producing an electron deficient state in Pt core nanoparticle. Pd nanoparticles with SAMs of mixtures of alkanethiol and TTF-substituted alkanethiol molecules take a large reduction of the Pauli paramagnetic susceptibility, which is brought about by CT.

IV-D-16 Crystal Structure and Physical Properties of (EDO-TTFBr₂)₂FeX₄ (X = CI, Br)

MIYAZAKI, Akira¹; AIMATSU, Masashi¹; YAMAZAKI, Hisashi¹; ENOKI, Toshiaki²; UGAWA, Kouhei³; OGURA, Eiji³; KUWATANI, Yoshiyuki³; IYODA, Masahiko³

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Tokyo Metropolitan Univ.)

[J. Phys. IV France 114, 545–547 (2004)]

The crystal structure and physical properties of radical ion salts (EDO-TTFBr₂)₂FeX₄ (X = Cl, Br) composed of halogen-substituted organic donor and magnetic halide anions are investigated. The salts consist of uniformly stacked donor molecules, whose Br substituents are connected to halide ligands of anions with remarkably short intermolecular contacts. Both salts show metallic behavior above ca. 30 K. The FeCl₄ salt shows an antiferromagnetic (AF) transition at $T_{\rm N}$ = 4.2 K despite the absence of anion---anion contacts, thus the magnetic interaction between the localized spins on the anions is mediated by the π -*d* interaction through the Br…Cl contacts. For the FeBr₄ salt the AF transition temperature is elevated to $T_{\rm N} = 13.5$ K, accompanied with another anomaly at $T_{C2} = 8.5$ K. This behavior can be qualitatively explained by a magnetic structure model where the π -*d* interaction between donor and anion is taken into account.

IV-D-17 Strong π-d Interaction Based on Brominated TTF-Type Donor EDT-TTFBr₂

NISHIJO, Junichi¹; MIYAZAKI, Akira¹; ENOKI,

Toshiaki²; WATANABE, Ryoji²; KUWATANI, Yoshiyuki³; IYODA, Masahiko³

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³Tokyo Metropolitan Univ.)

[J. Phys. IV France 114, 561–563 (2004)]

New π -*d* interacting system based on brominated TTF-type donor EDT-TTFBr₂ (= 4,5-dibromo-4',5'ethylenedithiotetrathiafulvalene) was investigated. Magnetic (EDT-TTFBr₂)₂FeBr₄ and non-magnetic (EDT-TTFBr₂)₂GaBr₄ are isostructural salts, which have strong anion-donor interaction through Br–Br atomic contacts with weak direct anion-anion interaction. The iron salt takes an antiferromagnetic transition at $T_N = 11$ K owing to strong π -*d* interaction, which originates from the strong anion-donor interaction. The strong π -*d* interaction also plays an important role in the electron transport phenomenon in the variation of temperature and applied magnetic field.

IV-D-18 Anisotropy of the Raman Spectra of Nanographite Ribbons

CANÇADO, L. G.¹; PIMENTA, M. A.¹; NEVES, B. R. A.¹; MEDEIROS-RIBEIRO, G.²; ENOKI, Toshiaki³; KOBAYASHI, Yousuke⁴; TAKAI, Kazuyuki⁴; FUKUI, Ken-ichi⁴; DRESSELHAUS, M. S.⁵; SAITO, Riichiro⁶; JORIO, A.¹

(¹Univ. Federal Minas Gerais; ²Laboratório Nacinal Luz Síncrontro ; ³IMS and Tokyo Inst. Tech.; ⁴Tokyo Inst. Tech.; ⁵MIT; ⁶Tohoku Univ. and CREST JST)

[Phys. Rev. Lett. 93, 047403 (4 pages) (2004)]

A polarized Raman study of nanographite ribbons on a highly oriented pyrolytic graphite substrate is reported. The Raman peak of the nanographite ribbons exhibits an intensity dependence on the light polarization direction relative to the nanographite ribbon axis. This result is due to the quantum confinement of the electrons in the 1D band structure of the nanographite ribbons, combined with the anisotropy of the light absorption in 2D graphite, in agreement with theoretical predictions.



Figure 1. (a) Raman spectra obtained for light incident with different polarization angles (θ) with respect to the ribbon direction. The inset shows a schematic figure of the sample (horizontal gray line) showing the direction between the ribbon axis and the light polarization vector (\vec{P}). (b) Intensity of the G_1 peak versus . The dotted line is a cos2 θ theoretical curve. The error bars are associated with baseline corrections. (c) Raman frequencies of the G_2 (triangles) and G_1 (squares) peaks as a function of the laser power density.

IV-E Molecular Crystals toward Nano-Devices by Use of *d*-π Interaction, Crystal Designing and Optical Doping

After some 30 years' intensive research on molecular charge transfer (CT) salts as potential functional materials, the research field has now gotten ready to examine how to make them into actual devices. Such efforts are concentrated on the developments of organic thin films for field effect transistors and light-emitting devices, both of which are carried out in a number of laboratories and groups with worldwide competitions. In order to examine the potential applicability of molecular materials from a different point of view, we are carrying out basic studies on development and physical properties of molecular CT single crystals. Major part of our study can be classified into three categories; the physical properties of the CT salts including localized spins, crystal designing using polycarboxylate anions, and device formation by optical doping method.

IV-E-1 Light-Induced Transformation of Molecular Materials into Devices

NAITO, Toshio; INABE, Tamotsu¹; NIIMI, Hironobu¹; ASAKURA, Kiyotaka¹ (¹Hokkaido Univ.)

[Adv. Mater. in press]

Many kinds of molecular solids are now attracting a worldwide interest as promising candidates for advanced materials such as electronic/magnetic/optical devices and energy converters. In particular, semiconductor diodes based on photovoltaic effect appear one of the most effective ways to utilize molecular materials, if there is an appropriate doping method available. This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the desired part of material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photo-excited states reported thus far have typical lifetimes of some hundreds of micro-seconds at longest in general, the doped state survived even several months after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a spaceresolved doping method under a mild condition.



Figure 1. Current-Voltage property curve of the single crystal of $Ag(DM)_2$ after UV-VIS illumination upon only half of it for ~ 21 days.

IV-E-2 Molecular Conductors Containing Photoreactive Species

NAITO, Toshio; INABE, Tamotsu¹ (¹Hokkaido Univ.)

[J. Phys. IV France 114, 553–555 (2004)]

In order to examine the possibility of (persistent) carrier doping to molecular crystals by light exposure, some different types of molecular crystals containing photoreactive species are synthesized and characterized. The $[Ru(bpy)_3]^{2+}$ cation (bpy = 2,2'-bipyridyl) yielded two different new complexes with [Ni(dmit)₂]⁻ radical species, both of which were structurally characterized and turned out to be band insulators. Methy viologen (MV) has been found to yield a new phase of the complex with [Ni(dmit)₂]⁻, MV[Ni(dmit)₂]₂. The temperature dependences of electrical resistivity (decreasing with lowering temperature down to 1.0 K) and magnetic susceptibility (Pauli paramagnetism from 300 K to 1.8 K with a hysteresis below ~ 100 K) clearly indicate that this phase is metallic. The thermoelectric power exhibited ~ 0 $\mu V K^{-1}$ from 300 K-4.2 K. This phase turned out to be metastable, and the crystals gradually turned into insulating ones. The effects of UV-VIS light exposure to the conducting and magnetic properties of Ag(DMe-DCNQI)₂ have been studied, and clear differences between the exposed and the pristine crystals were observed. The ESR signal at 3.7 K suggested that the exposed sample should include the Ag(0) species.



Figure 1. Temperature-dependent electrical resistivity of MV[Ni(dmit)₂]₂.

IV-E-3 Molecular Unit Based on Metal Phthalocyanine Designed for Molecular Electronics

MATSUDA, Masaki¹; HANASAKI, Noriaki¹;

IKEDA, Shingo¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu²

(¹Univ. Tokyo; ²Hokkaido Univ.)

[J. Phys. IV France 114, 541–543 (2004)]

We obtained three conducting crystals based on a $[Fe^{III}(Pc)(CN)_2]$ molecular unit. All crystals showed a large anisotropic negative magnetoresistance arising from the π -*d* interaction self-contained in the $[Fe^{III}(Pc)(CN)_2]$ unit. The anisotropy is attributable to the anisotropic *g*-tensor in the $[Fe^{III}(Pc)(CN)_2]$ unit. We also obtained a thin film containing $[Fe^{II}(Pc)(CN)_2]$. The film exhibits photocurrent response for the UV irradiation. These features suggest $[M(Pc)(CN)_2]$ molecular unit is a well-designed one for a building block of molecular devices.

IV-E-4 Anisotropic Giant Magnetoresistance Originating from the π -*d* Interaction in a Molecule

MATSUDA, Masaki¹; HANASAKI, Noriaki¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu²

(¹Univ. Tokyo; ²Hokkaido Univ.)

[J. Phys. Chem. Solids 65, 749–752 (2004)]

We synthesized TPP[Fe^{III}(Pc)(CN)₂]₂, PTMA_x [Fe^{III} (Pc)(CN)₂]·y(MeCN), and PXX[Fe^{III}(Pc)(CN)₂], a new series of charge-transfer salts containing the axiallysubstituted phthalocyanine (Pc), [Fe^{III}(Pc) (CN)₂]⁻. In this molecular unit, the π conduction electron derived from the Pc-ring coexists with the d electron which is a potential source of a local magnetic moment. Therefore various phenomena associated with the interplay between local magnetic moments and conduction electrons are expected. We observed the giant negative magnetoresistance (GNMR) in all the three salts. The GNMR is highly anisotropic for the magnetic-field direction, and reflects the g-tensor anisotropy of the local magnetic moment in the $[Fe^{III}(Pc) (CN)_2]^-$ unit. This indicates that the GNMR in these salts originates from the strong π -*d* interaction in the [Fe^{III}(Pc)(\breve{CN})₂]⁻ unit.

IV-E-5 Novel Phthalocyanine Conductor Containing Two-dimensional Pc Stacks, [PXX]₂[Co(Pc)(CN)₂] (PXX = *peri*-Xanthenoxanthene, Co(Pc)(CN)₂ = Dicyano(phthalocyaninato)cobalt(III))

ASARI, Takehiro¹; NAITO, Toshio; INABE, Tamotsu¹; MATSUDA, Masaki²; TAJIMA, Hiroyuki² (¹Hokkaido Univ.; ²Univ. Tokyo)

[Chem. Lett. 33, 128–129 (2004)]

A novel phthalocyanine conductor containing 2-D–stacks of the partially oxidized $Co(Pc)(CN)_2$ units has been obtained by the electrochemical oxidation method with PXX. The crystal is highly conductive (> 10^3 Scm⁻¹) at all the temperatures measured (5 K < *T* < 300 K). Though the metallic character becomes clearer compared with the single chain or ladder chain conductors, the 2-D sheet has been found to be still anisotropic.

IV-E-6 Contribution of Degenerate Molecular Orbitals to Molecular Orbital Angular Momentum in Molecular Magnet Fe(Pc)(CN)₂

HANASAKI, Noriaki¹; MATSUDA, Masaki¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu²

(¹Univ. Tokyo; ²Hokkaido Univ.)

[J. Phys. Soc. Jpn. 72, 3226–3230 (2003)]

We measured the static magnetic susceptibility and the electron spin resonance of the $Fe(Pc)(CN)_2$ complexes, and investigated the molecular magnetism of the unit Fe(Pc)(CN)₂. The magnetic susceptibility shows a highly anisotropic Curie behavior. Based on the electron spin resonance, we found a highly anisotropic g-value $(g_1 = 3.62, g_2 = 1.11, and g_3 = 0.52)$ in the molecular unit Fe(Pc)(CN)₂. This anisotropy is caused by the molecular orbital angular momentum in the degenerate next highest occupied molecular orbitals of the molecular unit Fe(Pc)(CN)₂. Since the molecular unit $Fe(Pc)(CN)_2$ has a unique structure with fourfold symmetry, the molecular orbital angular momentum has a finite value of $l_z \sim +1$ and -1. The anisotropic molecular magnetism of the unit $Fe(Pc)(CN)_2$ contributes the highly anisotropic Curie behavior. The molecular unit Fe(Pc)(CN)₂ is a good candidate for a molecular magnet having high magnetic anisotropy.

IV-E-7 Angle-Resolved Mapping of the Fermi Velocity in a Quasi-Two-Dimensional Organic Conductor

KOVALEV, A. E.¹; HILL, S.¹; KAWANO, Koichi²; TAMURA, Masafumi²; NAITO, Toshio; KOBAYASHI, Hayao (¹Univ. Florida; ²Toho Univ.)

[Phys. Rev. Lett. 91, 216402 (2003)]

We demonstrate a new method for determining the Fermi velocity in quasi-two-dimensional (Q2D) conductors. Application of a magnetic field parallel to the conducting layers results in periodic open orbit quasiparticle trajectories along the Q2D Fermi surface. Averaging of this motion over the Fermi surface leads to a resonance in the interlayer microwave conductivity. The resonance frequency is simply related to the extremal value of the Fermi velocity perpendicular to the applied field. Thus, angle dependent microwave studies enable a complete mapping of the in-plane Fermi velocity. We illustrate the applicability of this method for the highly 2D organic conductor κ -(BEDT-TTF)₂I₃.

IV-E-8 Molecular Hexagonal Perovskite: A New Type of Organic-Inorganic Hybrid Conductor

NAITO, Toshio; INABE, Tamotsu¹

(¹Hokkaido Univ.)

[J. Solid State Chem. 176, 243–249 (2003)]

An organic charge-transfer (CT) salt (BEDT-TTF)₃ (MnCl₃)₂(C₂H₅OH)₂ has been synthesized by a standard electrochemical method. The crystal data are monoclinic, C2/c (#15), a = 38.863(4) Å, b = 6.716(1) Å, c =23.608(3) Å, $\beta = 115.007(3)^\circ$, V = 5584(1) Å³, and Z =4. The structure consists of one-dimensional (1D) infinite ${[MnCl_3]^-}_{\infty}$ magnetic chains and two-dimensional (2D) organic conduction pathways. The former consists of face-sharing octahedra of manganese chloride complex ions, and dominates the magnetic properties of this compound. Such a feature of the crystal structure closely relates to transition metal hexagonal perovskite compounds, all of which are known for frustrated triangular lattices comprised of weakly interacting 1D magnetic chains. The new compound exhibits a high conductivity down to 4 K.



Figure 1. (a) Unit cell viewed down along the *c*-axis and (b) viewed down along the *b*-axis. (c) Two molecular overlapping modes of ET. Hydrogen atoms are omitted for clarity except in (c).

IV-E-9 Structure and Physical Properties of Low-Dimensional Molecular Conductors, [PXX][Fe^{III}(Pc)(CN)₂] and [PXX][Co^{III}(Pc)(CN)₂] (PXX = *peri*-Xanthenoxanthene, Pc = Phthalocyaninato)

MATSUDA, Masaki¹; ASARI, Takehiro²; NAITO, Toshio; INABE, Tamotsu²; HANASAKI, Noriaki¹; TAJIMA, Hiroyuki¹ (¹Univ. Tokyo; ²Hokkaido Univ.)

[Bull. Chem. Soc. Jpn. 76, 1935–1940 (2003)]

A novel low-dimensional molecular conductor, [PXX][Fe^{III}(Pc)(CN)₂], has been synthesized. This salt contains the magnetic Fe^{III} ion (S = 1/2), and is isomorphous with [PXX][Co^{III}(Pc)(CN)₂] which includes the non-magnetic Co^{III} ion. In both salts, the [Mc(Pc) (CN)₂] (M = Fe or Co) units form a two-leg ladder chain. The two salts exhibit a similar temperature dependence of the thermoelectric power and a similar reflectance spectrum. The Fe^{III} salt shows semiconducting behavior in its electrical resistivity over the temperature range measured, while the isomorphous Co^{III} salt exhibits metallic behavior in its resistivity above 100 K. The difference in the transport properties between the two salts suggests that the conduction electrons in the Fe^{III} salt are seriously scattered by the local magnetic moment. Spontaneous magnetization is observed below 8 K in the Fe^{III} salt. Upon applying a magnetic field, the resistivity of the Fe^{III} salt drastically decreases below 50 K. The decrease in the resistivity is highly anisotropic to the field orientation. The field orientation dependence is highly consistent with the gtensor anisotropy in the [Fe^{III}(Pc)(CN)₂] unit, suggesting that the negative magnetoresistance originates from the large π -d interaction self-contained in the [Fe^{III} $(Pc)(CN)_2$] unit.

IV-E-10 Torque Study of TPP[Fe(Pc)(CN)₂]₂ (TPP = Tetraphenyl Phosphonium and Pc = Phthalocyanine)

HANASAKI, Noriaki¹; MATSUDA, Masaki¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu²

(¹Univ. Tokyo; ²Hokkaido Univ.)

[Synth. Met. 137, 1227–1228 (2003)]

The magnetic torque shows the anomaly around 20 K. The torque curve suggests the antiferromagnetic state in the one-dimensional $Fe(Pc)(CN)_2$ chain. The magnetic easy axis is directed along the CN-ligand in the $Fe(Pc)(CN)_2$ unit. Because of the strong spin-orbit coupling, the next highest occupied molecular orbital is also ordered so that the molecular orbital angular momentum of the neighboring $Fe(Pc)(CN)_2$ unit is antiparallel. We observed the weak ferromagnetism below 6 K. This is ascribed to the canting of the antiparallel moments.



Figure 1. Temperature dependence of the torque. Inset: Torque curve measured under the magnetic field rotated within the *ac* plane.

IV-E-11 Physical Properties of (ET)₃(MnCl₄)(TCE) and the Related Salts

NAITO, Toshio; INABE, Tamotsu¹;

AKUTAGAWA, Tomoyuki¹; HASEGAWA, Tatsuo¹; NAKAMURA, Takayoshi¹; HOSOKOSHI, Yuko; INOUE, Katsuya (¹Hokkaido Univ.)

[Synth. Met. 135-136, 613-614 (2003)]

The ET salt with a magnetic counter ion $(ET)_3$ (MnCl₄)(TCE) (TCE = 1,1,2-trichloroethane) exhibits pressure-sensitive, complicated electrical behavior due to its semimetallic electronic structure. On the other hand, stronger d- π coupling is suggested in $(ET)_3$ (MnCl₃)₂(C₂H₅OH)₂, which has infinite magnetic chains with semimetallic conducting behavior.

IV-E-12 Magnetic Properties of $d-\pi$ Conducting System, TPP[Fe^{III}_xCo^{III}_{1-x}(Pc)(CN)₂]₂

MATSUDA, Masaki¹; HANASAKI, Noriaki¹; TAJIMA, Hiroyuki¹; SAKAI, Fumiko¹; NAITO, Toshio; INABE, Tamotsu² (¹Univ. Tokyo; ²Hokkaido Univ.)

[Synth. Met. 135-136, 635-636 (2003)]

We have studied the magnetic susceptibility for onedimensional system, TPP[Fe^{III}_xCo^{III}_{1-x}(Pc)(CN)₂]₂ (0.07 $\le x \le 1$). At x = 1, the system shows anisotropic Curie-Weiss behavior and spontaneous magnetization below 6 K. The temperature below which spontaneous magnetization occurs (T_c) shifts downward with a decrease in Fe^{III} concentration, but is still above 2 K at x= 0.07. The anisotropic Curie-Weiss behavior in the susceptibility was observed for all the alloys measured. This magnetic anisotropy was associated with the gtensor anisotropy in the [Fe^{III}(Pc)(CN)₂] unit.



Figure 1. Temperature dependence of the magnetic susceptibility for aligned crystals of TPP[Fe^{III}_xCo^{III}_{1-x}(Pc)(CN)₂]₂ (x = 1 and 0.07). The magnetic field was applied perpendicular and parallel to the *c*-axis. Note the 1×10^{-3} emu mol⁻¹ offset for x = 0.07.

IV-E-13 Magnetic and Optical Properties of One-Dimensional π -*d* System with Axially Substituted Iron(III) Phthalocyanine

MATSUDA, Masaki¹; HANASAKI, Noriaki¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu² (¹Univ.Tokyo; ²Hokkaido Univ.)

[Synth. Met. 133-134, 547-548 (2003)]

We have measured the angular dependence of the ESR spectra on DMDP[Fe^{III}_{0.01}Co^{III}_{0.99}(Pc)(CN)₂] (DMDP = dimethyldiphenylphosphonium, Pc = phthalocyanine), which is the alloy system of magnetic Fe^{III} and non-magnetic Co^{III}. The spectra exhibit giant anisotropic shift in *g*-value of iron(III). We also report the temperature dependence of the polarized reflectance spectra of one-dimensional conductors, TPP[Fe^{III}(Pc) (CN)₂]₂ and TPP[Co^{III}(Pc)(CN)₂]₂ (TPP = tetraphenyl-phosphonium). With lowering the temperature, the plasma edge drastically shifts to a higher wavenumber, and additional dispersion appears around 1600 cm⁻¹ and around 3600 cm⁻¹ in both salts.



Figure 1. Temperature dependence of the reflectance spectra of TPP[Fe^{III}(Pc)(CN)₂]₂ (a) and TPP[Co^{III}(Pc)(CN)₂]₂ (b) for the polarized light parallel to the *c*-axis. In TPP[$M^{III}(Pc)$ (CN)₂]₂, [$M^{III}(Pc)(CN)_2$] units form a one-dimensional regular chain along the *c*-axis. The 0% level is successively shifted by 10% for clarity.

IV-E-14 One-Dimensional π -d Electron System inTPP[Fe(Pc)(CN)₂]₂, [PXX][Fe(Pc)(CN)₂], and (PTMA)_x[Fe(Pc)(CN)₂]_y(CH₃CN): Electron Spin Resonance and Negative Magnetoresistance

HANASAKI, Noriaki¹; MATSUDA, Masaki¹; TAJIMA, Hiroyuki¹; NAITO, Toshio; INABE, Tamotsu²

(¹Univ. Tokyo; ²Hokkaido Univ.)

[Synth. Met. 133-134, 519-521 (2003)]

We measured the electron spin resonance and the magnetoresistance in the iron(III) phthalocyanine complexes. The electron spin resonance in PNP[Fe(Pc) (CN)₂] reveals the large anisotropy of the *g*-value. This is due to the strong spin-orbit coupling in the second HOMO (the third HOMO) hybridizing the d_{yz} (d_{zx}) orbital in the central Fe atom. This anisotropic *g*-value is consistent with the anisotropy of the magnetic susceptibility and the negative magnetoresistance in TPP[Fe (Pc)(CN)₂]₂. We also measured the large negative magnetoresistance in [PXX][Fe(Pc)(CN)₂] and (PTMA)_x[Fe(Pc)(CN)₂]_y(CH₃CN). The iron(III) phthalocyanine complexes are the good materials for the research of the one-dimensional π -*d* electron system.



Figure 1. Angular dependence of electron spin resonance in PNP[Fe(Pc)(CN)₂].

IV-E-15 Phthalocyanine-Based Multi-Dimensional Conductors

INABE, Tamotsu¹; ASARI, Takehiro¹; HASEGAWA, Hiroyuki¹; MATSUDA, Masaki¹; GACHO, Eduardo H.¹; MATSUMURA, Naoko¹; TAKEDA, Sayaka¹; TAKEDA, Keiji¹; NAITO, Toshio

(¹Hokkaido Univ.)

[Synth. Met. 133-134, 515-518 (2003)]

Electrochemical oxidation of $[Co^{III}(Pc)X_2]^-$ yields highly conducting partially oxidized salt crystals. Their crystal structures and dimensionality of the π - π interaction (electronic system) vary by the cationic species in the salts; one-dimensional for TPP (tetraphenylphosphonium) or PTMA (phenyltrimethylammonium) cations, and ladder and two-dimensional for the PXX (*peri*-xanthenoxanthene) radical cation. Substitution of the axial group (X) or extension of the π -conjugated macrocycle (Pc) has been found to influence the magnitude of the π - π stacking interactions. Their electrical properties characterized by the conductivity and thermoelectric power measurements are found to be dependent on the dimensionality and the magnitude of π - π stacking interactions.

IV-E-16 ET₃(MnCl₃)₂(EtOH)₂: A New Organic Conductor with A Perovskite Structure

NAITO, Toshio; INABE, Tamotsu¹; AKUTAGAWA, Tomoyuki¹; HASEGAWA, Tatsuo¹; NAKAMURA, Takayoshi¹ (¹Hokkaido Univ.)

[Synth. Met. 133-134, 445-447 (2003)]

The title salt was obtained as fine black needles from the electrolysis of ET (ET: bis(ethylenedithio)tetrathiafulvalene) with a Mn cluster in 1,1,2-trichloroethane containing 10% of ethanol. The conductivity at room temperature was 25 S cm⁻¹ with weakly semiconducting behavior, yet the salt kept a high conductivity down to 4 K (~ 0.1 S cm⁻¹). The manganese(II) chloride anion formed an infinite chain made of face-shared MnCl₆ octahedrons, and these chains formed insulating sheets with ethanol molecules between the chains. The ET cation radicals formed α -type conducting sheets between the insulating sheets. Such crystal structure was characterized as that of a typical hexagonal perovskite ABX₃, where A equals to a bulky monocation. The magnetic behavior was reproduced by the Curie-Weiss law, which might be attributable to the face-shared $MnCl_6$ octahedron chains.



Figure 1. Temperature dependence of the magnetic susceptibility of $(ET)_3(MnCl_3)_2(C_2H_5OH)_2$.

IV-E-17 Hydrogen-Bond Networks of Mellitate Anions ($[C_6(COO)_6H_{6-n}]^{n-}$) in Salts with Pyridine Derivatives

KOBAYASHI, Norihito¹; NAITO, Toshio; INABE, Tamotsu¹ (¹Hokkaido Univ.)

[Bull. Chem. Soc. Jpn. 76, 1351–1362 (2003)]

Single crystals of mellitate anion ($[C_6(COO)_6]$ H_{6-n} ^{*n*-}) salts with 3-aminopyridinium, [3-NH₂C₅H₄ $NH^{+}]_{3}[C_{6}(COO)_{6}H_{3}^{3-}]$ (1), 4-methylpyridinium, [4- $CH_3C_5H_4NH^+_2[CH_3C_5H_4N_2]C_6(COO)_6H_4^{2-}]$ (2), [4- $CH_{3}C_{5}H_{4}NH^{+}]_{2}[C_{6}(COO)_{6}H_{4}^{2-}]\cdot 2CH_{3}OH$ (3), pyridinium, $[C_5H_5NH^+]_2[C_6(COO)_6H_4^{2-}]\cdot 2H_2O(4)$, 3methylpyridinium, $[3-CH_3C_5H_4NH^+]_2[C_6(COO)_6H_4^{2-}]$ (5), $[3-CH_3C_5H_4NH^+]_5[C_6(COO)_6H_3^{3-}][C_6(COO)_6]$ H_4^{2-}]·CH₃OH (**6**), and isoquinolinium, [C₉H₇NH⁺]₂ $[C_6(COO)_6H_4^{2-}] \cdot CH_3OH$ (7), $[C_9H_7NH^+]_2[C_9H_7NH_{0:5}^{0.5+}][C_6(COO)_6H_{3.5}^{2.5-}] \cdot CH_3OH$ (8) have been structurally characterized. In these crystals, strong hydrogen-bonds between the mellitate anions are formed. Various arrangements that depend on the deprotonation number, n, have been found. All hydrogenbonds found between the anions are combinations of a carboxy and a carboxylato group. The "triangular hydrogen-bond" unit between the anions, in which three anions are connected by the three hydrogen-bonds to form a triangle, in the salt with n = 3, induces the two dimensional (2-D) sheet self-organizing structure in this crystal. "Dual hydrogen-bond" units between the anions, in which two pairs of the hydrogen-bonds connect the neighboring anions, have been found in the salts with n = 2 or 2.5. The repetition of the co-planer "dual hydrogen-bond" induces the anion one-dimensional (1-D) belt structure, while the combination of the standing and co-planer "dual hydrogen-bond" units induces the 2-D grid structure. These 2-D grids are further linked by hydrogen-bonds to form a channel. In all the salts (n = 3, 2, 2.5), the counter cation molecules are arranged in the space defined by the anion network.

IV-E-18 Crystal Design of Cation-Radical Salts Based on the Supramolecular Self-Organizing Arrangement of Mellitate Anions

INABE, Tamotsu¹; KOBAYASHI, Norihito¹; NAITO, Toshio (¹Hokkaido Univ.)

[J. Phys. IV France 114, 449-453 (2004)]

Mellitate anions form hydrogen-bonding infinite networks in the salts with pyridinium cations. The network pattern depends on the number of deprotonation (n) from the mellitic acid; for n = 3, triangular hydrogen-bond units form a two-dimensional sheet, while for n = 2, dual hydrogen-bond units induce onedimensional belts or two-dimensional grids. These selforganizing properties have been utilized for the crystal design of the TTF-type radical cation salts. Crystallization with TMTTF gave two kinds of crystals. One of the radical cation salt crystals consists of channel network of the anions and one-dimensional columns of TMTTF in the channels. In the other TMTTF salt, the anions with n = 1 form a two-dimensional sheet with methanol molecules. The TMTTF radicals are packed between the sheets with their molecular planes parallel to the anion planes.

IV-E-19 Network Formation of Mellitate Anions $([C_6(COO)_6H_{6-n}]^{n-})$ in the Salts with Piperidinium Derivatives and o-Phenylenediammonium

KOBAYASHI, Norihito¹; INABE, Tamotsu¹;

NAITO, Toshio (¹Hokkaido Univ.)

[CrystEngComm 6, 189–196 (2004)]

Single crystals of mellitate anion ($[C_6(COO)_6]$ H_{6-n} ^{*n*}) with piperidinium [C₅H₁₀NH₂⁺]₃[C₆(COO)₆ H_3^{3-}] (1) and $[C_5H_{10}NH_2^+]_2[C_6(COO)_6H_4^{2-}]$. CH₃OH·3H₂O (**2**), with 1-methylpiperidinium $[C_5H_{10}$ NHCH₃⁺]₂[C₆(COO)₆H₄²⁻]·2H₂O (**3**), and with *o*-phenylenediammonium $[C_6H_4(NH_3)_2^{2+}]_2[C_6(COO)_6$ H_2^{4+}]·2CH₃OH (4) have been prepared and structurally characterized. In all of the salts, two-dimensional (2D) networks of mellitate anions were formed due to the strong self-organization of the anion. In 1, a 2D hexagon-type network of hydrogen-bond has been observed to form among the anions. This is characteristic of the mellitate anions with n = 3 (n: deprotonation number from the acid). In other salts, a 2D anion network containing either water molecules or -NH3 groups commonly formed. Since the network pattern occurs with different cation species, this hydrogen-bonding unit was determined to be dominant in the n = 2 anion with water and the n = 4 anion with $-NH_3$ species.

IV-E-20 Physical Properties of Electrically Conducting and Stable Molecular Neutral Radical Solid [Co(2,3-Nc)(CN)₂]CH₃CN (2,3-Nc = 2,3-Naphthalocyanine)

NAITO, Toshio; MATSUMURA, Naoko¹; INABE, Tamotsu¹; MATSUDA, Masaki²; TAJIMA, Hiroyuki²

(¹Hokkaido Univ.; ²Univ. Tokyo)

[J. Porphyrins. Phthalocyanines. in press]

Solid state properties of dicyano(2,3-naphthalo-

cyaninato)cobalt(III) neutral radical crystal, [Co(2,3-Nc)(CN)₂]CH₃CN, were characterized by the measurements of the resistivity under high pressure and under uniaxial strain, thermoelectric power, magnetic susceptibility, ESR and polarized reflectance spectra. The title compound exhibited thermally activated-type electrical conductivity along the *c*-axis. The room temperature (RT) resistivity ρ_{RT} along the *c*-axis and activation energy E_a rapidly decreased with increasing pressure. The temperature-dependent thermoelectric power S was that of a typical one-dimensional (1D) semiconductor. However the high absolute value of S suggested that this electronic system should be strongly correlated. Although the electrical resistivity exhibited monotonical temeperature-dependence, the magnetic susceptibility clearly indicated a Peierls-type transition and marked fluctuation from RT. Both of Peierls-type transitions and fluctuations are characteristic phenomena to 1D conductors. Furthermore ESR spectra manifested that the Peierls-type transition occurred at 100 K. The inconsistency between the electrical behaviour (without a phasetransition) and magnetic behaviour (with a phasetransition) indicates the separation of the degrees of freedom in spin and charge (spin-charge separation) of this material. Spin-charge separation is a theoretically predicted phenomenon peculiar to the 1D conductors with strong correlation. The reflectance spectra were quantitatively explained by a 1D Hubbard model, and manifested the existence of a structural fluctuation of this material from RT. Based on these observed physical properties it is concluded that $[Co(2,3-Nc)(CN)_2]$ CH₃CN is a strongly correlated 1D semiconductor with a Mott-Hubbard type energy gap and characterised with a fluctuation and spin-charge separation.

IV-E-21 Structural, Electrical and Magnetic Properties of α -(ET)₇[MnCl₄]₂·(1,1,2-C₂H₃Cl₃)₂ (ET = bis(ethylenedithio)tetrathiafulvalene)

NAITO, Toshio; INABE, Tamotsu¹ (¹Hokkaido Univ.)

[Bull. Chem. Soc. Jpn. in press]

A new charge-transfer salt of ET with a chloromanganate(II) complex anion has been synthesized and characterized by X-ray structural analysis, resistivity measurements, magnetic susceptibility, electron spin resonance (ESR) and extended Hückel tight biding band calculation. The crystal has a sheet structure comprised of α -type two-dimensional (2D) donor arrangement in the *bc*-plane and insulating sheets of discrete $[MnCl_4]^{2-}$ anions and 1,1,2-C₂H₃Cl₃ (TCE) molecules. Its conducting property exhibits considerable anisotropy, which is of effectively metallic along the *b*-axis down to 1.2 K under 2.9 kbar and higher pressure. The magnetic susceptibility is approximately reproduced by the Curie-Weiss law with the Weiss temperature $\theta = -(1.35 \pm$ 0.07) K from 2-300 K. ESR measurements revealed that the π -electron system in this salt exhibits Pauli paramagnetism at least at 3.6- ~ 50 K. The band calculation suggests that the HOMO (the highest occupied molecular orbital) band has extremely small dispersion almost solely along the b^* -axis with a simple onedimensional (1D) Fermi surface. Considering all the data above, it is concluded that this salt has unusually stable and narrow 1D metallic band structure, which is a rare example even in a great number of molecular conducting salts reported to date.

IV-E-22 New Binuclear Copper Complexes [(9S3)Cu(CN)Cu(9S3)]X_n (X = BF₄, n = 1; X = TCNQ, n = 2) (9S3 = 1,4,7-trithiacyclononane): Syntheses, Crystal Structures and Magnetic Properties

NAITO, Toshio; NISHIBE, Kunimasa¹; INABE, Tamotsu¹

(¹Hokkaido Univ.)

[Bull. Chem. Soc. Jpn. in press]

The binuclear Cu complexes of 1,4,7-trithiacyclononane (9S3) with an inorganic anion (BF4-) and with an organic radical anion TCNQ- (7,7',8,8'-tetracyanoquinodimethanide) were synthesized and their molecular and crystal structures were examined in connection with each magnetic property. A new complex cation [Cu(9S3)CN(9S3)Cu] varied its charges and magnetic properties depending on the counter anions; [Cu(9S3) $CN(9S3)Cu](BF_4)$ (1) was obtained as diamagnetic colorless crystals, while [Cu(9S3)CN(9S3) Cu](TCNQ)₂ (2) was obtained as dark blue crystals with antiferromagnetic property. Complex 1 crystallized in the monoclinic space group C2/c with a = 26.863(2), b =7.0878(5), c = 13.4864(8) Å, $\beta = 116.318(2)^{\circ}$. Complex **2** crystallized in the triclinic space group $P\overline{1}$ with a =12.521(1), b = 20.2698(8), c = 8.0205(4) Å, $\alpha =$ 100.688(4), $\beta = 93.846(5)$, $\gamma = 94.953(4)^{\circ}$. Both complexes were comprised of cyano-bridged two Cu(9S3) ions with tetrahedral coordination geometry. The X-ray structural study revealed that 1 had two crystallographically equivalent Cu(I) centers, while 2 had two crystallographically independent Cu(I/II) sites. The two Cu(I/II) sites could not be distinguished from the X-ray structural study. As for 2 the IR spectra showed that both crystallographically independent TCNQ species were monoanions and were strongly dimerized due to pstacking, which well explained their diamagnetic contribution to the magnetic susceptibility and the highly insulating property of this salt. The temperaturedependent magnetic susceptibility of 2 showed a deviation from the Curie-Weiss behavior around 60 K, which indicated a strong antiferromagnetic intermolecular interaction between the copper complexes and that such intermolecular interaction should partly occur via the TCNQ radical anion dimer.

IV-E-23 Charge Disproportionation and Anomalous Giant Magnetoresistance in a One-Dimensional Conductor, TPP[Co(Pc)(CN)₂]₂

TAJIMA, Hiroyuki¹; HANASAKI, Noriaki¹; MASUDA, Kouki¹; MATSUDA, Masaki¹; KODAMA, Katsuaki¹; TAKIGAWA, Masashi¹; OHMICHI, Eiji¹; OSADA, Toshihito¹; NAITO, Toshio; INABE, Tamotsu²; HASEGAWA, Hiroyuki³ (¹Univ. Tokyo; ²Hokkaido Univ.; ³NICT) [Synth. Met. in press]

Magnetoresistance study on the charge transfer salts of [Fe(Pc)(CN)₂] revealed various interesting phenomena, such as anisotropic giant negative magnetoresistance, weak ferromagnetism, and anisotropic Curie-Weiss magnetic susceptivility.¹⁾ These interesting phenomena originate from the orbital magnetic moment remaining in the [Fe(Pc)(CN)₂] unit, and the d- π interaction inherently existing in this unit. Contrary to the [Fe(Pc)(CN)₂] salts, physical properties of the [Co(Pc) (CN)₂] salts have not been investigated in detail. In this paper, we report the magnetotransport and NQR studies on TPP[Co(Pc)(CN)₂]₂ salts. This salt is a one-dimensional conductor, where the partially oxidized [Co(Pc) $(CN)_2$ units stack uniformly along the *c*-axis. The salt exhibits Pauli-paramagnetic susceptibility. The electrical resistivity is semiconducting with a very small activation energy less than 0.01 eV. Interestingly, this salt exhibits very large positive magnetoresistance at low-temperature ($\Delta R(8 \text{ T})/R(0 \text{ T}) \sim 6$). Moreover, the field orientation dependence is guite small below 10 T. These facts indicate that the magnetoresistance in this salt is not an ordinary orbital effect. In order to examine the mechanism of the anomalous magnetoresistance, we have measured ⁵⁹Co NQR spectra. We found a sign of charge disproportionation at 1.8 K. On the basis of magnetotransport (B < 38 T), NQR and NMR (B < 16T) measurements, we will discuss the anomalous electronic state of this salt.

Reference

1)For example see, N. Hanasaki *et al.*, *Phys. Rev. B* **62**, 5839–5842 (2000).

IV-E-24 A New Optical Doping Method toward Molecular Electronics

NAITO, Toshio; INABE, Tamotsu¹; NIIMI, Hironobu¹; ASAKURA, Kiyotaka¹ (¹Hokkaido Univ.)

[Synth. Met. in press]

This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photo-excited states reported thus far have typical lifetimes of some hundreds of microseconds at longest in general, the doped state survived even a week after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a space-resolved doping method.

RESEARCH ACTIVITIES V Department of Applied Molecular Science

V-A Synthesis of Chiral Molecule-Based Magnets

Construction of molecule-based multifunctional materials is now becoming a challenging target. Especially, magnetic materials which have additional optical and electronic properties in the same crystals are increasing interests. Specific goals aimed for these molecule-based magnets include: i) the ability to design the molecular building blocks and to organize them in the solid for desired dimensionality, ii) the optical transparency. The physical characteristic of current interest involves optical properties, particularly with respect to natural optical activity. When a magnet has optical transparency and chiral structure, the magnetic structure of crystal expects to be a chiral spin structure. These magnets will show an asymmetric magnetic anisotropy and magneto-chiral dichroism. This category of materials don't only have scientific interest but also have the possibility for use in new devices. When we construct chiral molecule-based magnets, chirality must be controlled not only in the molecular structure, but in the entire crystal structure. As a consequence of this difficulty, only few examples of this type of magnet exist. Up to the present reported chiral magnets have low dimensional magnetic structure must be extended in two or three dimension. When we introduce magnetic bricks, which have more than three connections for the construction of magnets, we can expect to make two or three-dimensional magnets. To make high dimensionality molecule-based magnets, we can be brick to make two or three-dimensional magnets.

V-A-1 Synthesis of a Novel Three-Dimensional Chiral Molecule-Based Ferrimagnet with Triple-Helical Strand Structure

IMAI, Hiroyuki; INOUE, Katsuya; KIKUCHI, Koichi¹; YOSHIDA, Yusuke¹; ITO, Mitsuhiro²; SUNAHARA, Tetsuya²; ONAKA, Satoru² (¹IMS and Tokyo Metropolitan Univ.; ²Nagoya Inst. Tech.)

[Angew. Chem., Int. Ed. 43, 5618 (2004)]

Dark orange, hexagonal prism crystals of $[Cr(CN)_6]$ [Mn D- or L-NH₂ala]₃·(3H₂O) were obtained by slow diffusion of MnCl₂·4H₂O (1.7 mmol), D- or L-aminoalanine hydrochloride (D- or L-NH2alaH·HCl, 2.6 mmol), and KOH (5.2 mmol) in H₂O into $K_3[Cr(CN)_6]$ (1.5 mmol) in H₂O/iso-propanol (1:1) mixture under argon atmosphere after several weeks. X-ray crystal structure analyses of D- and L-isomers at 100 K reveal that compounds (1) crystallize in the chiral space group, hexagonal P63, and consist of left- and right-handed helical structures of Mn^{II} ions, respectively (Figure 1). Each aminoalanine ion employs two types of functional groups to bridge between two adjacent MnII ions (Mn-Mn separation is 5.923 Å.). Two amino moieties and one carboxyl group within the aminoalanine ion are coordinated to two Mn^{II} ions in monodentate and bidentate coordination mode, respectively. This unique coordination leads to the construction of two differing chelating rings around the Mn^{II} ion: five- and six-membered rings. These rings align alternately resulting in the generation of extended helical chains along the *c*-axis. As expected, self-assemblies are formed between helical chains to aggregate three helical chains (Figure 2), in which the shortest Mn-Mn separation between chains is 6.517 Å. The channel structure is generated and disordered water molecules exist in the center of the triple helical strand structure (on the screw axis).

On the other hand, each $[Cr(CN)_6]^{3-}$ ion utilizes all cyanide moieties to connect between adjacent strands *via* cyanide bridges to Mn^{II} ions; as a result, a threedimensional cyanide network is formed. The shortest and longest adjacent Cr–Mn distances through cyanide bridges are 5.490 and 5.508 Å, respectively, which are slightly longer than those in the previous crystals. The cyanide bridged network also displays basic units comprised of a helical strand structure. Each cyanide bridged helical strand, which is composed of four metal centers (two Mn^{II} and two Cr^{III} ions) and four cyanide groups as a repeating unit characterized by a reverse turn within the helical strand of Mn^{II} and NH₂ala ions along the *c*-axis, shares the apex of the helical strand (Cr^{III} ion) between three adjacent helical strands (Figure 1).

This compound exhibits ferrimagnetic behavior essentially below 35 K. The magnetic transition temperature of this compound is relatively low despite formation of a three-dimensional cyanide network. This phenomenon is probably attributable to the comparatively long cyanide-bridged distance in this crystal. In addition, it may result consequent to the occurrence of spin frustration between manganese ions within the triple helical strand at high temperature. Below 35 K, the spin on manganese alone survives due to the ferrimagnetic coupling between manganese and chromium ions. From a physical standpoint, this phenomenon is the focus of interesting research, as the spin structure of this compound is also expected to possess triple helical nature. Some chiral molecule-based magnets have been prepared previously; however, at present, a chiral helical spin structure has not been documented. It is one of the reasons affording an explanation as to why a crystal forming a helical structure has never been synthesized. Thus, it is certain that this molecule is a suitable candidate for this endeavor. Magnetization measurements, µSR (muon spin resonance) spectroscopy and neutron diffraction of a single crystal will lead

to characterization of the details of magnetic structure in this compound.



Figure 1. a) Coordination geometry of the heptanuclear unit of $[Cr^{III}(CN)_6][Mn^{II} L-NH_2ala]_3\cdot(3H_2O)$ (1). b) Overall view of crystal structure of $[Cr^{III}(CN)_6][Mn^{II} L-NH_2ala]_3\cdot(3H_2O)$ (1) along the *c*-axis. Cr atoms are shown in yellow brown, Mn in purple, C in gray N in blue and O in red. The hydrogen atoms are omitted for simplicity.



Figure 2. Capped sticks models of a left-handed and a righthanded triple strands in $[Cr^{III}(CN)_6][Mn^{II} D \text{ or } L-NH_2ala]_3$. (3H₂O) (1). Mn atoms are shown in purple, C in gray N in blue and O in red.



Figure 3. $\chi_{mol}T$ versus *T* plot at 5000 G of $[Cr^{III}(CN)_6][Mn^{II} D or L-NH_2ala]_3 (3H_2O)$ (1). Inset: Plot of effective magnetic moment versus 1/T.



Figure 4. Temperature dependence of magnetization of $[Cr^{III}(CN)_6][Mn^{II} D$ - or L-NH₂ala]₃·(3H₂O) (1). The FC (triangle) and ZFC (circle) magnetizations at 5 G are shown. Inset: Field dependence of magnetization of $[Cr^{III}(CN)_6][Mn^{II} D$ - or L-NH₂ala]₃·(3H₂O) (1) at 2 K.

V-A-2 TOF Neutron Powder Diffraction Studies on a Chiral Two-Dimensional Molecule-Based Magnet

HOSHIKAWA, Akinori¹; KAMIYAMA, Takashi¹; PURWANTO, Agus^{1,2}; OHISHI, Kazuki¹; HIGEMOTO, Wataru¹; ISHIGAKI, Toru³; IMAI, Hiroyuki; INOUE, Katsuya

(¹KEK; ²Natl. Nuclear Energy Agency, Indonesia; ³Muroran Inst. Tech.)

[J. Phys. Soc. Jpn. 73, 2597 (2004)]

The magnetic structure of a chiral molecule-based magnet, $[Cr(CN)_6][Mn(S)-pnH(H_2O)](H_2O)$ (Space group = $P2_12_12_1$, Figure 1), has been studied by neutron powder diffraction as a function of temperature from 4 K to 300 K. The 020 and 022 magnetic reflections were clearly observed below $T_C = 38$ K (Figure 2). From the intensity analysis of magnetic reflections, it was concluded that the magnetic structure is non-collinear ferrimagnetic with the magnetic (Shubnikov) space

group $P2_12_1'2_1'$, and magnetic moments of Cr and Mn atoms are mutually antiparallel along a direction near the *a*-axis. Our result implies that the long-period magnetic structure, if exists, is not a helical structure but a conical one.



Figure 1. Crystal structure of [Cr(CN)₆][Mn(*S*)-pnH(H₂O)] (H₂O). Magnetic atoms Cr and Mn are marked with the Arabic and Roman numerals, respectively.



Figure 2. The neutron diffraction patterns at 4 K (below $T_{\rm C}$) and 50 K (above $T_{\rm C}$), and their difference pattern of [Cr(CN)₆] [Mn(*S*)-pnH(H₂O)](H₂O) obtained by the 30 degree bank of the Vega diffractometer. The difference pattern shows the magnetic contribution only. Intensities are normalized by the incident spectrum. The inset shows the temperature dependence of the intensity ratio of the 020 magnetic Bragg reflection to the 002 nuclear Bragg one, I020/I002.

V-B Nano-Structure in Metal Oxides Prepared by Synchrotron Radiation and Swift Heavy Ions

In the project, micro-nano fabrication technique for metal oxide has been examined. The first one is the deep xray lithography and the liquid phase deposition method. Periodic arrangements of titanium dioxide (TiO₂) micro structure projections were fabricated in a supersaturated aqueous solution using ordered microcavities of poly (methylmethacrylate) as a template. The shape and periodicity of the TiO₂ projections were strictly controlled with the depth and arrangement of the cavities because crystalline TiO₂ was uniformly grown on the organic surface through heterogeneous nucleation. This biomimetic route is applicable to designed synthesis of three-dimensional architectures for photonic structures of various metal oxides. The other method is by using of the latent tracks introduced by the swift heavy ion. Micro structure having nano-order flatness was achieved after chemical etching. This method can be applied to create photonic crystal structure of titanium dioxide.

V-B-1 Photoinduced Hydroxylation at ZnO Surface

ASAKUMA, Naoko¹; FUKUI, Toshimi²; TOKI, Motoyuki²; AWAZU, Koichi³; IMAI, Hiroaki¹ (¹Keio Univ.; ²KRI.; ³IMS and AIST)

[Thin Solid Films 445, 284–287 (2003)]

We observed UV-stimulated hydroxylation at the surface of ZnO crystals. Reactive defective sites were initially formed in the surface layer via photoreduction induced with energetic photons above the band gap of ZnO. Hydroxyl groups were produced by a chemical reaction of the photoinduced defective sites with water molecules in the atmosphere. Two types of hydroxyl groups were found at the irradiated surface because two kinds of defective sites were induced with the UV illumination.

V-B-2 Ablation and Compaction of Amorphous SiO₂ Irradiated with ArF Excimer Laser

AWAZU, Koichi¹

(¹IMS and AIST)

[J. Non-Cryst. Solids 337, 241-253 (2004)]

The structure of amorphous SiO₂ exposed to ArF excimer laser irradiation was examined. Threshold fluence for causing ablation with a single pulse depended on sample preparation: more specifically, 1 J/cm² for thermally grown SiO₂ films on silicon and 2.5 J/cm² for bulk SiO₂. It was found that the bond angle of Si-O-Si was reduced by irradiation near the interface of thermally grown SiO₂ films. In contrast, evolution of the bond angle by irradiation was absent in both the bulk SiO₂ and SiO₂ film-near the top surface, even though the concentration of puckered four-menmered rings deduced from Raman spectra dramatically increased. It is assumed that planar three-membered rings were generated in the SiO₂ thin layer near the interface, and puckered four-membered rings were generated in the bulk SiO₂. The concentration of both the Si³⁺ and Si²⁺ structure was increased at a fluence of 800 mJ/cm² with an increasing number of pulses, although generation of both was absent at higher fluence for a single pulse. The author proposes that the structure of SiO₂ is created by

flash heating and quenching by pulse laser irradiation. Structural similarities were found between the irradiated SiO_2 and SiO_2 at high temperatures.

V-C Bioinorganic Chemistry and Structural Biology of Heme Proteins

One of research activities of my group is directed toward developing a rigorous, quantitative understanding of the biochemical function of heme proteins such as oxygenases, peroxidases and oxidases by characterization of their structural and functional properties. We use different experimental strategies including protein engineering, spectroscopic characterization of the molecular structure of the active centers, measurements of dynamics of substrates and inhibitor binding, and X-ray crystallography.

My current heme protein projects include (1) elucidation of the catalytic mechanism of heme oxygenase, one of the essential components of the heme catabolism and biosynthesis of carbon monoxide, a versatile physiological messenger molecule, (2) elucidation of the mechanism of controlling reactivity of hemoglobin and myoglobin, and (3) determination of heme sensing mechanism of Bach1, a heme-dependent transcription factor which regulates heme oxygenase gene expression. Effective clues to delineate the detailed active site structure have been obtained by X-ray crystallography, resonance Raman and magnetic resonance studies. The synergy of site-directed mutagenesis, structural biology, and spectroscopic techniques has revealed the specific roles of amino acids located in the active centers of heme proteins. Ligands and substrates binding measurements complement the structural data for our understanding functional properties displayed by heme proteins at the molecular level.

V-C-1 Kinetic Isotope Effects on the Rate-Limiting Step of Heme Oxygenase Catalysis Indicate Concerted Proton Transfer/Heme Hydroxylation

DAVYDOV, Roman¹; MATSUI, Toshitaka²; FUJII, Hiroshi; IKEDA-SAITO, Masao³; HOFFMAN, Brian M.¹

(¹Northwestern Univ.; ²Tohoku Univ.; ³IMS and Tohoku Univ.)

[J. Am. Chem. Soc. 125, 16208–16209 (2003)]

Heme oxygenase (HO) catalyzes the O_2 and NADPH/cytochrome P450 reductase-dependent conversion of heme to biliverdin, free iron ion, and CO through a process in which the heme participates both as dioxygen-activating prosthetic group and substrate. We earlier confirmed that the first step of HO catalysis is a monooxygenation in which the addition of one electron and two protons to the HO oxy-ferroheme produces ferric- α -meso-hydroxyheme (h). Cryoreduction/EPR and ENDOR measurements further showed that hydroperoxo-ferri-HO converts directly to h, in a single kinetic step without formation of a Compound I. We here report details of that rate-limiting step. Oneelectron 77 K cryoreduction of human oxy-HO and annealing at 200 K generates a structurally relaxed hydroperoxo-ferri-HO species, denoted R. We here report the cryoreduction/annealing experiments that directly measure solvent and secondary kinetic isotope effects (KIEs) of the rate-limiting **R** to **h** conversion, using enzyme prepared in H₂O/D₂O buffers to measure the solvent KIE (solv-KIE), and the secondary KIE (sec-KIE) associated with deuteration of the heme mesocarbons. This approach is unique in that KIEs measured by monitoring the rate-limiting step are not susceptible to masking by KIE's of other processes, and these results represent the first direct measurement of the KIE's of product formation by a kinetically competent reaction intermediate in any dioxygen-activating heme enzyme. The observation of *both solv*-KIE(298) = 1.8and sec-KIE(298) = 0.8 (inverse) indicates that the ratelimiting step for formation of **h** by HO is a concerted process: proton transfer to the hydroperoxo-ferri-heme through the distal-pocket H-bond network, likely from a carboxyl group acting as a general acid catalyst, occurring in synchrony with attack of 'OH⁺' on the α -*meso* carbon to form a tetrahedral hydroxylated-heme intermediate. Subsequent rearrangement and loss of H₂O then generates **h**.

V-C-2 FeNO Structure in Distal Pocket Mutants of Myoglobin Based on Resonance Raman Spectroscopy

COYLE, Candace M.¹; VOGEL, Kathleen M.¹; RUSH, Thomas S. III¹; KOZLOWSKI, Pawel M.¹; WILLIAMS, Robert¹; SPIRO, Thomas, G.¹; DOU, Yi²; IKEDA-SAITO, Masao³; OLSON, John S.⁴; ZGIERSKI, Marek Z.⁵

(¹Princenton Univ.; ²Case Western Reserve Univ.; ³IMS and Tohoku Univ.; ⁴Rice Univ.; ⁵Natl. Res. Council Canada)

[Biochemistry 42, 4896–4903 (2003)]

FeNO vibrational frequencies were investigated for a series of myoglobin mutants using isotopeedited resonance Raman spectra of $^{15/14}$ NO adducts, which reveal the FeNO and NO stretching modes. The latter give rise to doublet bands, as a result of Fermi resonances with coincident porphyrin vibrations; these doublets were analyzed by curve-fitting to obtain the vNO frequencies. Variations in vNO among the mutants correlate with the reported vCO variations for the CO adducts of the same mutants. The correlation has a slope near unity, indicating equal sensitivity of the NO and CO bonds to polar influences in the heme pocket. A few mutants deviate from the correlation, indicating that distal interactions differ for the NO and CO adducts, probably because of the differing distal residue geometries. In contrast to the strong and consistent vFeC/ vCO correlation found for the CO adducts, vFeN correlates only weakly with vNO, and the slope of the correlation depends on which residue is being mutated.

This variability is suggested to arise from steric interactions, which change the FeNO angle and therefore alter the Fe–NO and N–O bond orders. This effect is modeled with Density Functional Theory (DFT) and is rationalized on the basis of a valence isomer bonding model. The FeNO unit, which is naturally bent, is a more sensitive reporter of steric interactions than the FeCO unit, which is naturally linear. An important additional factor is the strength of the bond to the proximal ligand, which modulates the valence isomer equilibrium. The FeNO unit is bent more strongly in MbNO than in protein-free heme-NO complexes because of a combination of a strengthened proximal bond and distal interactions.

V-C-3 The Crystal Structures of the Ferric and Ferrous Forms of the Heme Complex of HmuO, a Heme Oxygenase of *Corynebacterium diphtheriae*

HIROTSU, Shoko¹; CHU, Grace C.²; UNNO, Masaki¹; LEE, Dong-Sun³; YOSHIDA, Tadashi⁴; PARK, Sam-Yong³; SHIRO, Yoshitsugu³; IKEDA-SAITO, Masao⁵

(¹Tohoku Univ.; ²Case Western Reserve Univ.; ³RIKEN Harima Inst./SPring-8; ⁴Yamagata Univ.; ⁵IMS and Tohoku Univ.)

[J. Biol. Chem. 279, 1197–11947 (2004)]

Crystal structures of the ferric and ferrous heme complexes of HmuO, a 24 kDa heme oxygenase of Corynebacterium diphtheriae, have been refined to 1.4 and 1.5 Å resolution, respectively. The HmuO structures show that the heme group is closely sandwiched between the proximal and distal helices. The imidazole group of His20 is the proximal heme ligand, which closely eclipses the β and δ meso axis of the porphyrin ring. A long range hydrogen bonding network is present, connecting the iron-bound water ligand to the solvent water molecule. This enables proton transfer from the solvent to the catalytic site, where the oxygen activation occurs. In comparison to the ferric complex, the proximal and distal helixes move closer to the heme plane in the ferrous complex. Together with the kinked distal helix, this movement leaves only the α -meso carbon atom accessible to the iron-bound dioxygen. The heme pocket architecture is responsible for stabilization of the ferric hydroperoxo active intermediate by preventing premature heterolytic O–O bond cleavage. This allows the enzyme to oxygenate selectively at the α meso carbon in HmuO catalysis.

V-C-4 Crystal Structure of the Dioxygen-Bound Heme Oxygenase from *Corynebacterium diphtheriae*: Implications for Heme Oxygenase Function

UNNO, Masaki¹; MATSUI, Toshitaka¹; CHU, Grace C.²; COUTURE, Manon³; YOSHIDA, Tadashi⁴; ROUSSEAU, Denis L.³; OLSON, John S.⁵; IKEDA-SAITO, Masao⁶

(¹Tohoku Univ.; ²Case Western Reserve Univ.; ³Albert Einstein College Med.; ⁴Yamagata Univ.; ⁵Rice Univ.; ⁶IMS and Tohoku Univ.)

[J. Biol. Chem. 279, 21055–21061 (2004)]

HmuO, a heme oxygenase of Corynebacterium diphtheriae, catalyzes degradation of heme using the same mechanism as the mammalian enzyme. The oxy form of HmuO, the precursor of the catalytically active ferric hydroperoxo species, has been characterized by ligand binding kinetics, resonance Raman spectroscopy, and X-ray crystallography. The oxygen association and dissociation rate constants are 5 μ M⁻¹ s⁻¹ and 0.22 s⁻¹, respectively, yielding an O_2 affinity of 21 μM^{-1} that is ~20 times greater than that of mammalian myoglobins. However, the affinity of HmuO for CO is only 3 to 4fold greater than that for mammalian myoglobins, implying the presence of strong hydrogen bonding interactions in the distal pocket of HmuO that preferentially favor O₂ binding. Resonance Raman spectra show that the Fe–O₂ vibrations are tightly coupled to porphyrin vibrations, indicating a highly bent Fe-O-O geometry that is characteristic of the oxy forms of heme oxygenases. In the crystal structure of the oxy form, the Fe-O-O angle is 110°; the O–O bond is pointed toward the heme α -meso-carbon by direct steric interactions with Gly135 and Gly139; and hydrogen bonds occur between the bound O_2 and the amide nitrogen of Gly139 and a distal pocket water molecule, which is a part of an extended hydrogen bonding network that provides the solvent protons required for oxygen activation. In addition the O-O bond is orthogonal to the plane of the proximal imidazole side chain, which facilitates hydroxylation of the porphyrin α -meso-carbon by preventing premature O-O bond cleavage.

V-C-5 Heme Regulates Gene Expression by Triggering Crm1-Dependent Nuclear Export of Bach1

SUZUKI, Hiroshi¹; TASHIRO, Satoshi¹; HIRA, Shusuke²; SUN, Jiying¹; YAMAZAKI, Chikara¹; ZENKE, Yukari¹; IKEDA-SAITO, Masao³; YOSHIDA, Minoru⁴; IGARASHI, Kazuhiko¹ (¹Hiroshima Univ.; ²Tohoku Univ.; ³IMS and Tohoku Univ.; ⁴RIKEN)

[EMBO J. 23, 2544–2553 (2004)]

Bach1 is a transcriptional repressor of heme oxygenase-1 and β -globin genes, both of which are known to be transcriptionally induced by heme. To test the hypothesis that heme regulates the activity of Bach1, we expressed wild-type and mutated versions of Bach1 together with or without its heterodimer partner MafK in human 293T and GM02063 cells and examined their subcellular localization. Inhibition of heme synthesis enhanced the nuclear accumulation of Bach1 whereas treating cells with hemin resulted in nuclear exclusion of Bach1. While the cadmium-inducible nuclear export signal of Bach1 was dispensable for the heme response, a region containing two of the heme-binding motifs were found to be critical for the heme-induced nuclear exclusion. This region functioned as a heme-regulated nuclear export signal dependent on the exporter Crm1. These results extend the regulatory roles for heme in protein sorting, and suggest that Bach1 transduces metabolic activity into gene expression.

V-D Pro-Oxidants-Induced Iron Release from the Fe-S Cluster of Mitochondrial Aconitase and Its Prevention by Flataxin

Pro-oxidants, such as hydrogen peroxide and superoxide anion, are highly toxic for many living organisms. One of the adverse effects of pro-oxidants is modulation of mitochondrial respiration. Using EPR spectroscopy, we have identified that pro-oxidants deactivates mitochondrial aconitase, the key enzyme in citrate cycle, by releasing one of Fe from the 4Fe-4S cluster, and that mitochondria is surprisingly equipped a recovery mechanism to restore the active 4Fe-4S cluster. We have recently discovered that this restoration is achieved by an iron insertion from frataxin, an iron storage protein in mitochondria, which functions as an iron chaperon protein. We are in the process of elucidation of the inter protein iron transfer mechanism from frataxin to aconitase at molecular level.

V-D-1 Redox-Dependent Modulation of Aconitase Activity in Intact Mitochondria

BULTEAU, Anne-Laure¹; IKEDA-SAITO, Masao²; SZWEDA, Luke I.¹

(¹Case Western Reserve Univ.; ²IMS and Tohoku Univ.)

[Biochemistry 42, 14846–14855 (2003)]

It has previously been reported that exposure of purified mitochondrial or cytoplasmic aconitase to superoxide (O_2^{\bullet}) or hydrogen peroxide (H_2O_2) leads to release of the Fe- α from the enzyme's [4Fe-4S]²⁺ cluster and to inactivation. Nevertheless, little is known regarding the response of aconitase to pro-oxidants within intact mitochondria. In the present study, we provide evidence that aconitase is rapidly inactivated and subsequently reactivated when isolated cardiac mitochondria are treated with H₂O₂. Reactivation of the enzyme is dependent on the presence of the enzyme's substrate, citrate. EPR spectroscopic analysis indicates that enzyme inactivation precedes release of the labile Fe-a from the enzyme's $[4Fe-4S]^{2+}$ cluster. In addition, as judged by isoelectric focusing gel electrophoresis, the relative level of Fe- α release and cluster disassembly does not reflect the magnitude of enzyme inactivation. These observations suggest that some form of posttranslational modification of aconitase other than release of iron is responsible for enzyme inactivation. In support of this conclusion, H₂O₂ does not exert its inhibitory effects by acting directly on the enzyme, rather inactivation appears to result from interaction (s) between aconitase and a mitochondrial membrane component responsive to H₂O₂. Nevertheless, prolonged exposure of mitochondria to steady-state levels of H_2O_2 or (O_2^{\bullet}) results in disassembly of the [4Fe-4S]²⁺ cluster, carbonylation, and protein degradation. Thus, depending on the pro-oxidant species, the level and duration of the oxidative stress, and the metabolic state of the mitochondria, aconitase may undergo reversible modulation in activity or progress to [4Fe-4S]²⁺ cluster disassembly and proteolytic degradation.

V-D-2 Frataxin Acts as an Iron Chaperone Protein To Modulate Mitochondrial Aconitase Activity

BULTEAU, Anne-Laure¹; O'NEILL, Heather A.²;

KENNEDY, Mary Claire³; IKEDA-SAITO, Masao⁴; ISAYA, Grazia²; SZWEDA, Luke I.¹

(¹Case Western Reserve Univ.; ²Mayo Clinic College Med.; ³Gannon Univ.; ⁴IMS and Tohoku Univ.)

[Science 305, 242–245 (2004)]

Friedreich's ataxia is a genetic disorder characterized by a deficiency in frataxin, the mitochondrial ironbinding protein. We have identified a role for frataxin as an iron chaperone protein that is required for the reversible modulation of mitochondrial aconitase activity in response to pro-oxidants. By protecting Fe-S clusters from disassembly, frataxin can prevent iron accumulation and production of the highly reactive and toxic hydroxyl radical. Alterations in the level, structure, and chaperone function of frataxin may participate in the progression of degenerative disorders associated with declines in aconitase and mitochondrial activity.

V-E Quantum Emissions from Solid in Femtosecond Intense Laser Field

Quantum emissions, which are high-energy electron, ion and photon beams, generated by interaction of ultrashort intense laser field with matter has recently been attracting considerable attention because of interest in fundamental photosciences and its potential applications in compact accelerator, proton therapy and materials sciences. We have studied a mechanism of quantum emissions (especially on hard X-ray and fast protons) form metal target in intense laser field.

V-E-1 Hard X-Ray Emission from a Cooper Target by Focusing a Picosecond Laser Beam at 3×10^{13} W/cm²

NAGAO, Hirofumi¹; HIRONAKA, Yoichiro¹; NAKAMURA, Kazutaka²; KONDO, Ken-ichi¹ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[Jpn. J. Appl. Phys. 43, 1207–1208 (2004)]

Hard X-ray pulses are generated by focusing a picosecond laser beam (25-ps, 1064 nm) on a copper target in air at an intensity of 3×10^{13} W/cm². X-ray energy is measured using an X-ray charge-coupled device. The obtained spectrum consists of strong K_a and K_β emissions and a weak continuum at an energy range of 4–10 keV. The photon numbers of the hard X-rays (4–10 keV) were estimated to be approximately 4000 photons/4 π sr/pulse.

V-E-2 Enhanced Generation of Fast Protons from a Polymer-Coated Metal Foil by a Femtosecond Intense Laser Field

KISHIMURA, Hiroaki¹; MORISHITA, Hiroto¹; OKANO, Yasuhisa¹; OKANO, Yasuaki¹; HIRONAKA, Yoichiro¹; KONDO, Ken-ichi¹; NAKAMURA, Kazutaka²; OISHI, Yuji³; NEMOTO, Koshichi³ (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.;

(¹ Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.; ³CREIPT)

[Appl. Phys. Lett. 85, 2736–2738 (2004)]

The results of generation of fast protons from 5- μ m thick copper foil targets by 60 fs laser irradiation at 1.5 $\times 10^{17}$ W/cm² are presented. Both poly-vinyl-methylether (PVME)-coated and uncoated copper foil targets are examined. Fast protons are measured using a Thomson mass spectrometer and maximum proton energies are 570 keV and 280 keV for the PVME-coated and the uncoated target, respectively. The intensity of fast protons with energy of 160 keV from the PVME-coated target is approximately 80-fold higher than that from the uncoated target.
RESEARCH ACTIVITIES VI Department of Vacuum UV Photoscience

VI-A Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules and Clusters

In this project, we have two major subjects: (a) resonant photoelectron spectroscopy and (b) resonant inelastic soft X-ray emission spectroscopy following inner-shell excitations of simple molecules and clusters. We have found some spin-forbidden ionized and excited states in (a) and (b). In the spectral assignments, angle(symmetry)-resolved photoion yield techniques and R-matrix/MQDT theoretical approaches are essential.

VI-A-1 Rydberg-Valence Mixing in Core Excitations of C₂H₂. Angle-Resolved Photoion Yield Spectroscopic Study

MASUDA, Suomi¹; GEJO, Tatsuo²; HIYAMA, Miyabi; KOSUGI, Nobuhiro (¹GUAS; ²Univ. Hyogo)

[J. Electron Spectrosc. in press]

High-resolution angle-resolved ion-yield spectra (ARPIS) are reported for the C1s \rightarrow Rydberg excitations of acetylene. Vibronic coupling features are found in the energy regions of $3s\sigma_g$ and $3\sigma_u^*$ excitation, $3p\sigma_u$ excitation, and near threshold. Figure 1 shows ARPIS of C₂H₂ measured at the C1s \rightarrow 3s and 3p Rydberg excitation region. To select the fragmentation channels, we varied the retarding potentials for ion detectors. The contributions of the $3s\sigma_g$ Rydberg state and $3\sigma_u^*$ valence state were successfully resolved. Consequently, the feature observed in the perpendicular direction is assigned to the C1s \rightarrow $3\sigma_u^*$ valence state coupled with the C1s $\rightarrow \pi^*$ state *via cis* bending vibrational mode.



Figure 1. ARPIS of C_2H_2 measured at the $C_{1s} \rightarrow 3s$ and 3p Rydberg region. Spectra shown on the upper side and lower side correspond to the ion yields measured in the parallel and perpendicular directions, respectively. Spectra shown on the middle are the subtraction spectra measured in the parallel direction with different retarding potentials. : for example, "1.5–3.0 V" means [1.5 V spectra]–[3.0 V spectra].

VI-A-2 Ab Initio R-Matrix/Multi-Channel Quantum Defect Theory Approach to Study Molecular Core Excitation and Ionization: GSCF4R

HIYAMA, Miyabi; KOSUGI, Nobuhiro

[J. Theor. Comput. Chem. in press]

Ab initio R-matrix/MQDT approach, which is a combination of *ab initio* R-matrix techniques and the multi channel quantum defect theory (MQDT), has recently been developed by one of the present authors (MH) and Child,¹⁾ to successfully obtain the potential energy curves of Rydberg states converging to not only the lowest but also the higher ionized states. This approach is also applied to analyze changes in the MQDT scattering matrix arising from the valence state interaction with Rydberg states, the UK molecular R-matrix package developed by Morgan, Tennyson, and Gillan²⁾ has been used.

At IMS we extensively study core excitation and ionization of molecules theoretically as well as experimentally. For this purpose we have developed an original *ab initio* polyatomic R-matrix/MQDT code using Gaussian type basis functions (GTFs) for the bound and continuum states with a core hole. Our new program package named GSCF4R is an extension from the conventional *ab initio* SCF-CI (self-consistent field, configuration interaction) package, GSCF3 by one of the present authors (NK), which can be used for both valence and core excitation.³⁾

References

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VI-A-3 Ab Initio R-Matrix/Multi-Channel Quantum Defect Theory Applied to Molecular Core Excitation and Ionization

HIYAMA, Miyabi; KOSUGI, Nobuhiro

[J. Electron Spectrosc. in press]

Very recently we have completed an original ab initio polyatomic R-matrix/MQDT program package, GSCF4R¹) based on Gaussian type basis functions (GTFs) for the bound and continuum states, to extensively study molecular excitation and ionization in the X-ray region as well as in the VUV region. Calculated results for core excitation and ionization of NO show that the R-matrix/MQDT method is indispensable to describe the core-to-Rydberg states with the higher quantum number and the continuum states which cannot be described by using GTFs in the outer region of an appropriate boundary. In the inner region the closecoupling approximation augmented with the correlation term in GSCF4R is proved to be powerful to obtain the potential energies of valence and Rydberg-valence mixed states and the interchannel couplings between several core-ionized states.

Reference

1)M. Hiyama and N. Kosugi, J. Theor. Comput. Chem. in press.

VI-A-4 Valence in the Rydberg/Continuum Region in Molecular Inner-Shell Spectroscopy

KOSUGI, Nobuhiro

[J. Electron Spectrosc. in press]

Using schematic potential energy curves and molecular orbitals, we have discussed where the 1s \rightarrow σ^* excited state is located in the 1s excitation of N₂, O₂, CH₃F, and C₂H₂, and how we know evidence for the 1s $\rightarrow \sigma^*$ excited state in photoabsorption spectra of CH₄, CO₂, and N₂O. In the former molecules, the σ^* state is identified in the Franck-Condon region from the ground state; in the latter molecules, the σ^* state is not clearly identified but its evidence is observed through the Rydberg-valence mixing in the Franck-Condon region. In N₂, the σ^* state is located above the ionization threshold and is autoionizing. In O_2 , the σ^* state is mainly mixed with the $3p\sigma^*$ Rydberg state converging to the ${}^{4}\Sigma$ ionized state. In CH₃F, the σ^{*} state is observed below the 3s Rydberg state. In C_2H_2 , the σ^* state and the 3s Rydberg state are observed in the same energy region and the σ^* state has an effect of the conical intersection with the lowest π^* state, where the σ^* state

is lower than the π^* state for a longer HCC–H distance. On the other hand, in CH₄, the Jahn-Teller distortion of the 3p Rydberg transition induces contribution from the σ^* state. In the 1s excitations from the terminal atoms in CO₂ and N₂O, some lower s-type Rydberg states get intensities from the σ^* state. In the 1s excitations from the central atoms, the σ^* state is a dark state (not exactly in N₂O). In the C1s excitation of CO₂, the 3s Rydberg states are vibronically enhanced through mixing with the π^* state.

VI-A-5 Spin-Orbit and Exchange Interactions in Molecular Inner-Shell Spectroscopy

KOSUGI, Nobuhiro

[J. Electron Spectrosc. 137-140, 335 (2004)]

In recent high-resolution and sophisticated soft Xray molecular spectroscopies, small exchange interaction (EX) involving the core electron has been revealed. Interatomic core-core EX is generally small; therefore, it is considered that even the core electron described as $1s\sigma_g$ and $1s\sigma_u$ in homonuclear systems is localized on an atom. However, small but appreciable interatomic core-valence EX in N_2 and C_2H_2 results in observable g-u splittings in the core ionization, which are experimentally evaluated from extrapolation of the $1s\sigma_g^{local} \rightarrow np\sigma_u$, $np\pi_u$ and $1s\sigma_u^{local} \rightarrow nsd\sigma_g$, $nd\pi_g$ Rydberg series. Due to intermolecular Rydberg-valence EX, blue shifts in low-lying core-to-Rydberg excitations in N₂ and Ar are experimentally identified from gas phase to surface, from surface to bulk, and from large to small cage size of rare gas matrixes. EX involving the 2p core electron is anisotropic, depending on the relation between the 2p orbital direction and molecular structure. In some sulfur containing molecules, it is experimentally revealed that the S2p and excited electrons have EX compatible to the 2p spin-orbit interaction (SO) for parallel $2p\pi \rightarrow \pi^*$ transitions and EX smaller than SO for perpendicular $2p\sigma \rightarrow \pi^*$ transitions. In other words, the *jj* coupling scheme is not applicable to the parallel transitions. Furthermore, it is revealed that, in resonant photoelectron and soft X-ray emissions on the S2p excitation of CS₂ and SF₆, spinforbidden shake-up valence ionizations with quartet spin couplings and spin-forbidden valence excitations with triplet spin couplings are observable via triplet components mixed in intermediate core-excited states.

VI-B Soft X-Ray Photoelectron-Photoabsorption Spectroscopy and Electronic Structure of Molecular Solids and Clusters

This project has been carried out in collaboration with Würzburg University and RIKEN. We have two subprojects: (a) molecules and radicals in condensed phase and in rare gas matrix, and (b) ionic fragmentations of atomic and molecular clusters following the inner-shell resonance excitation. In (a), we have measured excitation spectra of some matrix phases and of some bases in DNA duplexes at the bending-magnet beamline BL4B of the

UVSOR facility. In (b), we have developed a new cluster source for photoelectron measurements on a newly constructed undulator beamline BL3U.

VI-B-1 Temperature Dependence of the Bulk Ar 2p_{3/2}-4s Excited State of Argon Solid

HATSUI, Takaki; SETOYAMA, Hiroyuki; KOSUGI, Nobuhiro

[J. Electron Spectrosc. in press]

Core excitons of rare gas solid have been studied extensively in order to elucidate their character. In the present study, the Ar 2p_{3/2}-4s excited state for bulk argon solid has been investigated at 8 and 16 K (Figure 1). Careful energy calibration of the monochromater has demonstrated that the peak position at 16 K shows a red shift of 4.2 ± 0.9 meV compared with that at 8 K. The increase of the temperature from 8 to 16 K results in the elongation of the lattice constant of the argon solid from 5.290 to 5.294 Å. The larger lattice constant is expected to cause a blue shift in ionization threshold caused by the weaker stabilization through polarization interaction (PL) of the surrounding atoms/molecules, and a red shift by the weaker exchange interaction (EX) between the excited electron and the electrons of neighboring atoms/ molecules. In order to quantitatively examine the observed temperature dependence, ab initio theoretical calculations has been carried out for Ar₁₉ cluster. The calculations predict the red shift to be 2.7 meV as a sum of the blue shift of 1.1 meV through PL and the red shift of 3.8 meV through EX. The agreement of the theory with the experiment implies the reliability of the calculations. The mean radius of the 4s excited orbital is predicted to be 5.80 Å.

VI-B-2 Sulfur 2p Excited States of OCS in Rare Gas Matrices

SETOYAMA, Hiroyuki; HATSUI, Takaki; KOSUGI, Nobuhiro

[J. Electron Spectrosc. in press]

Sulfur 2p x-ray absorption spectra have been measured for OCS solid and for the mixture of OCS and Ar, Kr or Xe in order to study effects of surrounding molecules on the S 2p excited states of OCS. Figure 1 shows S 2p photoabsorption spectra of OCS solid and Xe matrices for different concentration ratios, OCS:Xe = 1:0, 1:1, and 1:7/3. Bands 1 and 2 are assigned to the S $2p_{3/2}\text{-}$ and S $2p_{1/2}\text{-}4\pi^*$ core-to-valence transitions, respectively. Bands 3, 4, 5 and 6 are assigned to the $2p_{3/2}$ -4s, $2p_{1/2}$ -4s, $2p_{3/2}$ -"d", and $2p_{1/2}$ -"d" transitions with Rydberg character, respectively. The core-tovalence excited states (bands 1 and 2) do not change their positions upon the mixing, whereas the excited states originating from Rydberg 4s and "d" states show energy shifts. The observed dependence of the shifts on the mixing concentration and on the rare gas element were explained in terms of the polarization stabilization of the ionization threshold and the exchange repulsion of the excited electron by the electrons of the neighboring atoms/molecules. At the same mixing ratio, the polarization stabilization was found to be independent of the rare gas element.



Figure 1. Photoabsorption spectra for argon solid around the Ar $2p_{3/2}$ -4s bands at 8 and 16 K. Enlarged spectra around the peak of the bulk Ar $2p_{3/2}$ -4s band are shown in inset.



Figure 1. Soft X-ray absorption spectra for OCS and OCS/Xe matrices with different ratios, 1:1 and 1:7/3.

VI-B-3 Cluster Size Effects in Core Excitons of 1s-Excited Nitrogen

FLESCH, Roman¹; KOSUGI, Nobuhiro;

BRADEANU, Ioana¹; NEVILLE, John²; RÜHL, Eckart¹

(¹Würzburg Univ.; ²Univ. New Brunswick)

[J. Chem. Phys. 121, 8343 (2004)]

Cluster size effects in core excitons below the N 1s ionization energy of nitrogen clusters are reported in the energy regime 405-410 eV. These results are compared to the molecular Rydberg states as well as the corresponding bulk excitons of condensed nitrogen. The experimental results are assigned using ab initio calculations. It is found that the lowest excitons (N 1s \rightarrow 3s σ and N 1s \rightarrow 3p π) are blueshifted relative to the molecular Rydberg transitions, whereas others (N 1s $\rightarrow 3d\pi$ and N 1s \rightarrow 4p π) show a redshift. Results from *ab initio* calculations on $(N_2)_{13}$ clearly indicate that the molecular orientation within a cluster is critical to the spectral shift, where bulk sites as well as inner- and outersurface sites are characterized by different inner-shell absorption energies. These results are compared to the experimental spectra as well as previous work on siteselectively excited atomic van der Waals clusters, providing an improved spectral assignment of core exciton states in weakly bound molecular clusters and the corresponding condensed phase.

VI-B-4 Metal-to-Ligand Charge Transfer in Polarized Metal L-Edge X-Ray Absorption of Ni and Cu Complexes

HATSUI, Takaki; KOSUGI, Nobuhiro

[J. Electron Spectrosc. 136, 67 (2004)]

Metal L-edge X-ray absorption spectra for Ni and Cu complexes are discussed by investigating their linear polarization dependence. The origin of the characteristic bands is revealed to be one-electron transitions to ligand-centered molecular orbitals carrying metal-toligand charge transfer (MLCT). We have shown that the strong bands B and C in K₂[Ni(CN)₄]·H₂O and Ni (Hdmg)₂ are definitely assigned to the MLCT transitions by examining the linear polarization dependence and by carrying out ab initio molecular orbital calculations. The MLCT transitions are also found in metal L_{2,3}-edge Xray absorption spectra of [(n-C₄H₉)₄N]₂[Ni(mnt)₂], (Me₂-DCNQI)₂Cu, K₃Cu(CN)₄, and [(C₂H₅)₄N][Ni (mnt)₂]. It is shown that the intensity of the MLCT transitions is directly correlated to the strength of the back-donation, in which the excited orbital is involved. The linear polarization dependence is also useful to reveal the symmetry of the holes in doped systems and to characterize the Ni-Ni chemical bonding.

VI-B-5 Electronic Structure of Bases in DNA Duplexes Characterized by Resonant Photoemission Spectroscopy near the Fermi Level

KATO, Hiroyuki S.¹; FURUKAWA, Masashi¹; KAWAI, Maki^{1,2}; TANIGUCHI, Masaki³; KAWAI, Tomoji³; HATSUI, Takaki; KOSUGI, Nobuhiro (¹RIKEN; ²Univ. Tokyo; ³Osaka Univ.)

[Phys. Rev. Lett. 93, 086403 (2004)]

The electronic structure of bases in DNA duplexes was investigated by resonant photoemission spectroscopy near the Fermi level, in order to specify charge migration mechanisms. Figure 1(A) shows an N K-edge XA spectrum of poly(dG)·poly(dC) and DNA. In the XA spectrum, two 1s $\rightarrow \pi^*$ resonant peaks at 399.7 eV and 401.9 eV and a broad 1s $\rightarrow \sigma^*$ resonant peak at 407 eV were observed. This spectrum is in good agreement with the previously reported XA spectra of poly(dG). poly(dC) DNA,¹⁾ in which the first (energetically lower) and the second (higher) $1s \rightarrow \pi^*$ resonant peaks have been assigned to resonance at imine (-N) and amine (-NH-) site orbitals, respectively. The off-and-on-RPE spectra near the Fermi level of poly(dG)·poly(dC) DNA are shown in Figure 1(B) as a function of kinetic energy. The Auger signals can be extracted from the on-RPE spectra by subtracting the off-RPE spectra, as indicated by the dotted lines. A kinetic energy shift of N-KLL Auger electrons and an intensity enhancement of valence electrons on the resonant photoemission spectra are clearly observed. Similar behaviors are also found for poly(dA)·poly(dT) DNA. These directly show the localized unoccupied states of the bases. We conclude that the charge hopping model is suitable for electric conduction in DNA duplexes rather than the charge transfer model via delocalized states when electrons pass through the π^* states of DNA bases.

Reference

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Figure 1. N K-edge XA spectrum of poly(dG)·poly(dC) DNA (A), and its off- and on-RPE spectra as functions of kinetic energy (B). Excitation energies are shown as arrows a–d in Figure 1(A). The differential spectra based on the off-RPE spectrum in binding energy show resonant Auger signals.

VI-C Ultrafast Dynamics of Molecules in Intense Laser Fields

The interaction between molecules and an intense laser field $(10^{12}-10^{18} \text{ W/cm}^2)$, whose electric field component comparable with the intramolecular Coulombic field, has been an attractive target of research to elucidate fundamental physical properties underlying in the unique features that do not appear in the weak interaction regime. In the present study, the characteristic dynamics occurring in intense laser fields, such as structural deformation and multiple breaking of chemical bonds, is studied by a newly developed experimental method, called *coincidence momentum imaging*, which allows us to determine the momentum vectors of all the fragment ions ejected from a single parent molecule in an intense laser field. Based on the correlation among the fragment momentum vectors, the evolution of nuclear motion on the light dressed potential energy surfaces and the hydrogen migration process have been clarified. A new coincidence momentum imaging system is constructed to detect the ions and electrons produced from a molecule placed in an intense laser field.

VI-C-1 Nuclear Dynamics on the Light-Dressed Potential Energy Surface of CS₂ by Coincidence Momentum Imaging

HISHIKAWA, Akiyoshi; HASEGAWA, Hirokazu¹; YAMANOUCHI, Kaoru¹ (¹Univ. Tokyo)

[Chem. Phys. Lett. 388, 1-6 (2004)]

The non-sequential three-body Coulomb explosion, $CS_2^{3+} \rightarrow S^+ + C^+ + S^+$, in an intense laser field (0.2) PW/cm², 60 fs) is studied by the coincidence momentum imaging of the fragment ions. The observed angle distribution of the momentum vectors of the two S⁺ ions, $p_1(S^+)$ and $p_2(S^+)$, exhibited a peak at the small angle $\theta_{12} \sim 140^\circ$, showing that the nuclear motion is induced along the bending coordinate to a large extent prior to the explosion. On the other hand, the difference between their absolute values, $\Delta p_{12} = |\mathbf{p}_1(S^+)| - |\mathbf{p}_2(S^+)|$, has a sharp distribution peaked at $\Delta p_{12} = 0$, suggesting that the symmetric stretching motion dominates over the anti-symmetric stretching motion in the laser field. Based on the energy dependence of the momentum vector correlation, the characteristic nuclear dynamics of CS₂ on the light-dressed potential energy surfaces in the intense laser field is discussed.

VI-C-2 Hydrogen Migration in Acetonitrile in Intense Laser Fields Studied by Coincidence Momentum Imaging

HISHIKAWA, Akiyoshi; HASEGAWA, Hirokazu¹; YAMANOUCHI, Kaoru¹ (¹Univ. Tokyo)

[Phys. Scr. T108, 108–111 (2004)]

The two-body Coulomb explosion of acetonitrile, $CH_3CN^{2+} \rightarrow CH_{3-n}^+ + H_nCN^+$ (n = 0-2), in intense laser fields (0.15 PW/cm², 70 fs) is studied by the coincidence momentum imaging technique. It is found that the fragment ions for n = 0 are ejected mostly to the direction of the laser polarization vector with $\langle \cos^2\theta \rangle =$ 0.68, where θ is the angle between the fragment recoil direction and the laser polarization vector, while the angle distribution becomes more isotropic as n increases, *i.e.*, $\langle \cos^2\theta \rangle = 0.49$ for n = 1 and $\langle \cos^2\theta \rangle = 0.37$ for n = 2. From this characteristic correlation between the anisotropy in the fragment ejection and the hydrogen migration, the Coulomb explosion dynamics competing with the hydrogen atom transfer from the methyl group to the nitrile group is investigated.

VI-C-3 Hydrogen Migration in Acetonitrile in Intense Laser Fields in Competition with Two-Body Coulomb Explosion

HISHIKAWA, Akiyoshi; HASEGAWA, Hirokazu¹; YAMANOUCHI, Kaoru¹

(¹Univ. Tokyo)

[J. Electron. Spectrosc. Relat. Phenom. 141, 195–200 (2004)]

Two-body Coulomb explosion processes of acetonitrile (CH₃CN) and deuterated acetonitrile (CD₃CN), CH₃CN²⁺ → CH_{3-n}⁺ + H_nCN⁺ and CD₃CN²⁺ → CD_{3-n}⁺ + D_nCN⁺ (n = 0, 1, 2), in an intense laser field (0.15) PW/cm^2 , 70 fs) are investigated by the coincidence momentum imaging method. The comparable yields derived for the three pathways (n = 0, 1, 2) shows that the hydrogen atom migration proceeds in competition with the Coulomb explosion. The angular distributions of the fragment ions for n = 0 exhibits a sharp peak along the laser polarization direction, while the angular distribution becomes more isotropic as *n* increases. Based on a least-squares analysis of the fragment anisotropy, the dissociation lifetimes of the doubly charged acetonitrile were determined, from which the time scale of the hydrogen migration as well as the deformation of the C-C-N skeleton prior to the explosion were discussed.

VI-C-4 Design and Development of an Ion-Electron Coincidence Momentum Imaging System

HISHIKAWA, Akiyoshi; TAKAHASHI, Eiji J.

A new coincidence momentum imaging system has been developed to study the behavior of molecules exposed to an intense laser field (~ 10^{15} W/cm²) based on the momentum vectors of fragment ions and electrons ejected from a single parent molecule. The electrons and ions are guided by electrodes in the velocity mapping configuration and detected by a pair of position sensitive detectors with delay line anodes, which are placed face by face in an ultrahigh vacuum chamber with a base pressure $< 10^{-8}$ Pa. The performance of the electron detection has been studied with Xe and CS₂ in an intense laser field (~ 10^{13} W/cm², 35 fs, 800 nm). The concentric ring patterns visible in the electron image (Figure 1), separated by the photon energy (~ 1.5 eV) in the energy scale, represent the above-threshold ionization (ATI) process.



Figure 1. Electron image obtained for CS₂ in an intense laser field $(1.5 \times 10^{13} \text{ W/cm}^2, 35 \text{ fs}, 800 \text{ nm})$. In order to to emphasize weak features, a logarithmic intensity scale is adopted. The concentric ring patterns represent the ATI process.

VI-D Synchrotron Radiation Stimulated Surface Reaction and Nanoscience

Synchrotron radiation (SR) stimulated process (etching, CVD) has excellent characteristics of unique material selectivity, low damage, low contamination, high spatial resolution, and high precision etc. In this project, nano-level controlled structures are created by using synchrotron radiation stimulated process, and the reaction mechanisms are investigated by using STM and AFM. Concerning the SR etching, we are considering to apply this technique to the microfabrication of integrated protein transistor circuits.

VI-D-1 Construction of Undulator Beamline for STM Observations of Surface Reaction Stimulated by Synchrotron Irradiation

NONOGAKI, Youichi; URISU, Tsuneo

[J. Electron Spectrosc. Relat. Phenom. submitted]

To investigate excitation energy dependence of SRstimulated reactions, we have designed and constructed an undulator beamline equipped with an UHV-STM system at the UVSOR facility. Since 1st harmonic emission from the undulator is changed from 50 eV to 120 eV, it is possible that the emission is tuned to Si 2p (~100 eV) core-level. The undulator emission is focused by two cylindrical mirrors. The spot size is 1.0 mm × 0.4 mm and photon flux density is estimated to 10^{18} cm⁻²sec⁻¹ on a sample surface in the UHV-STM chamber set at the end station.

Although ESD of H-Si(111) surfaces have been studied extensively, there is no report of photonstimulated reaction on the H-Si(111) surfaces observed by STM. We have successfully observed morphological changes of H-Si(111) after undulator irradiation by STM. Figure 1(a) shows an STM image of a H-Si(111) prepared by 1000L H-exposure to a clean Si(111)-7×7 surface at 400 °C. A 7×7 rest-atom monohydride surface appeared with adatom islands (A) and small protrusions (B). This surface was exposed to undulator irradiation (~ 100 eV) at an irradiation dose of 4900 mAsec. Figure 1(b) shows an STM image of the surface after irradiation. It is found that density of the small protrusions drastically increased on the 7×7 rest-atom monohydride surface. Creation of the small protrusions would be related to H-desorption stimulated by undulator irradiation.

a) ____A ___B

Figure 1. 11 nm \times 11 nm STM images of a) H-Si(111) surface and b) surface after undulator irradiation.

VI-D-2 Shrinking of Spin-On-Glass Films Induced by Synchrotron Radiation and Its Application to Three-Dimensional Microfabrications

RAHMAN, Md. Mashiur; TERO, Ryugo; URISU, Tsuneo

[Jpn. J. Appl. Phys. 43, 4591-4594 (2004)]

Photoinduced etching of siloxane-type spin-on-glass (SOG) by synchrotron radiation (SR) using a SF₆/O₂ etching gas and a Co contact mask has been investigated. The SOG film was etched by direct SR irradiation similarly to the case of thermally oxidized SiO₂. We found that the indirect exposure to SR caused shrinkage of SOG under the Co mask. The shrinkage depth of SOG was attenuated by the thickness of the Co mask, but not eliminated even by a Co mask 350 nm thick, due to the highenergy photons (230 eV) being transmitted through the mask. The shrinkage phenomenon was successfully applied in the fabrication of a threedimensional structure of the SOG thin film on Si(100). Atomic force microscopy observations showed that the surfaces were very smooth both on the completely etched Si area and on the shrunken SOG area. We investigated the mechanism of the shrinkage of SOG by Fourier-transform infrared spectroscopy.



Figure 1. Step profiles of the Co/SOG/Si surface (a) before and (b) after SR etching. The step profile of SOG/Si after removal of the Co layer is superimposed in (b).

VI-E Noble Semiconductor Surface Vibration Spectroscopy

As a new high sensitive and high resolution surface vibration spectroscopy technique, we are developing an infrared reflection absorption spectroscopy using buried metal layer substrate (BML-IRRAS), which have unique characteristics of high resolution and high sensitivity at finger print regions. Several Si surface chemical reactions are investigated using this BML-IRRAS. As a new fabrication technique of BML substrate, we have almost succeeded in developing the wafer bonding technique. It is considered that BML-IRRAS is also extremely useful in the research of bio-material integration on Si substrates.

VI-E-1 Three-Pairs of Doublet Bands Assigned to SiH₂ Scissoring Modes Observed in H₂O-Induced Oxidation of Si(100) Surfaces

WANG, Zhi-Hong; URISU, Tsuneo; NANBU, Shinkoh; MAKI, Jun; GANGAVARAPU, Ranga Rao; AOYAGI, Mutsumi¹; WATANABE, Hidekazu¹; OOI, Kenta² (¹Kyushu Univ.; ²AIST Shikoku)

[Phys. Rev. B 69, 045309 (5 pages) (2004)]

Oxidation of Si(100) surfaces by H₂O has been investigated on 2H+H2O/Si(100)-(2×1), H2O Si(100)- (2×1) , as well as H₂O+H/Si(100)-(2×1) systems by infrared reflection absorption spectroscopy using CoSi₂ buried metal layer substrates BML-IRRAS. Three pairs of doublet bands assigned to the scissoring modes of adjacent and isolated SiH₂ with zero, one, and two inserted back-bond oxygen atoms, respectively, have been reported. This report also has clearly shown the unique high sensitivity of BML-IRRAS for the perpendicular components in the fingerprint region, compared to the multiple internal reflection and the external transmission arrangements. Oxidation mechanisms have been proposed. In the $2H+H_2O/Si(100)-(2\times1)$ system, oxygen insertion into the back bond occurs easily. In the $H_2O+H/Si(100)$ system, however, the tunneling effect is important to reach the oxygen inserted state.



Figure 1. Observed BML-IRRAS spectrum (circles, in the lower panel) of the reaction system $2H+H_2O(5\times1)/Si(100)-(2\times1)$ at $T_m = 373$ K for D = 1000 l. The curve resolutions assuming a Lorenzian form (solid and dotted lines) are also shown. Compared in the upper part is the reported IR spectrum by ET for the similar reaction system. The three pairs of doublet bands are observed at 982, 963, 938, 926, 916, and 901 cm⁻¹, respectively. The 926-cm⁻¹ band, which is not clear in this spectrum, is observed clearly at the lower H doses.

VI-E-2 A Comparative Infrared Study of H_2O Reactivity on Si(100)-(2x1), (2x1)-H, (1x1)-H and (3x1)-H Surfaces

GANGAVARAPU, Ranga Rao; WANG, Zhi-Hong; WATANABE, Hidekazu¹; AOYAGI, Mutsumi¹; URISU, Tsuneo (¹Kyushu Univ.)

[Surf. Sci. in press]

The water adsorption on the bare and H-terminated Si(100) surfaces has been studied by the BML-IRRAS technique. It is found that H-terminated surfaces are much less reactive compared to the bare silicon surfaces. The (1×1) -H and (3×1) -H surfaces show similar and less reactivity pattern compared to the (2×1)-H surface. At higher exposures, the water reaction with coupled monohydride species provides an effective channel for oxygen insertion into the back bonds of dihydride species. It is not attributed to the H-Si-Si-H + $H_2O \rightarrow H$ -Si-Si-OH + H_2 , which could give rise to the characteristic Si-H and Si-OH modes, respectively at 2081 and 921 cm⁻¹. A more suitable reaction mechanism involving a metastable species, $H-Si-Si-H + H_2O$ \rightarrow H₂Si···HO–Si–H (metastable) explains well the bending modes of oxygen inserted silicon dihydride species which are observed relatively strongly in the reaction of water with H-terminated Si(100) surfaces.



Figure 1. BML-IRRAS spectra of the Si(100)- (3×1) -H surface exposed to (a) 20 L atomic H, (b) 500 L atomic H, (c) 2000 L atomic H, (d) 200 L H₂O, (e) 2000 L H₂O, (f) 5000 L H₂O at 400 K. The spectra (a)–(c) are the ratios of absorption spectra of the H exposed Si(100)- (2×1) -D surfaces to the Si (100)- (2×1) -D surface, and the spectra (d)–(f) are the ratios of the absorption spectra of the water exposed Si(100)- (3×1) -H surfaces to the Si (100)- (3×1) -H surfaces to the Si(100)- (3×1) -H surfaces t

VI-E-3 Theoretical Analysis of the Oxygen Insertion Process in the Oxidation Reactions of H₂O+H/Si(100) and 2H+H₂O/Si(100): a Molecular Orbital Calculation and an Analysis of Tunneling Reaction

WATANABE, Hidekazu¹; NANBU, Shinkoh; WANG, Zhi-Hong; MAKI, Jun; URISU, Tsuneo; AOYAGI, Mutsumi¹; OOI, Kenta² (¹Kyushu Univ.; ²AIST Shikoku)

[Chem. Phys. Lett. 383, 523-527 (2004)]

The reaction paths are analyzed, by an ab initio molecular orbital method, for the surface reaction systems $2H+H_2O/Si(100)-(2\times1)$ and $H_2O+H/Si(100)-(2\times1)$, in which SiH₂ species with one or two oxygen atom-inserted back bonds have been observed as stable reaction products. The following results are obtained: The initial energy for the former system is 87.97 kJ/mol higher than the highest transition state energies with the $HF/6-31+G^*$ level. In the latter system, the highest transition state is located 175.66 kJ/ mol higher than the initial energy, and tunneling effect plays an important role.

VI-E-4 Fabrication of CoSi₂-Buried-Metal-Layer Si Substrates for Infrared Reflection Absorption Spectroscopy by Wafer-Bonding

YAMAMURA, Shusaku; YAMAGUCHI, Shouichi¹; WATANABE, Satoru²; TABE, Michiharu³; KASAI, Toshio⁴; NONOGAKI, Youichi; URISU, Tsuneo (¹DENSO Res. Laboratories; ²FUJITSU Laboratories Ltd.; ³Shizuoka Univ.; ⁴Saitama Univ.)

[Jpn. J. Appl. Phys. 42, 3942–3945 (2003)]

Infrared reflection absorption spectroscopy (IRRAS) using buried metal layer substrates (BML) is one of the high resolution and high sensitive surface vibration spectroscopy techniques. A unique characteristic is the wide frequency range including the so-called finger print region. The CoSi₂ Si(100) BML substrates fabricated by Co ion implantation have been used to date. However, the technique has several problems such as the resultant surface roughness due to the ion implantation damage. To solve these problems, in this work, we have examined the fabrication of BML substrates with atomic-level flat surfaces by the wafer-bonding between a Co deposited Si(100) wafer and a Si on insulator (SOI) wafer. Self-assembled alkyl monolayers (SAMs) of octadecyltrichlorosilane and octenyltrichlorosilane were deposited on the fabricated BML substrate surface. Good BML-IRRAS spectra were observed in the wide frequency range from stretching to bending regions. It was also found that well-ordered SAMs were deposited.

VI-E-5 Design of the Sample Holder System for BML-IRRAS in-Liquid

UNO, Hidetaka; URISU, Tsuneo

We have performed BML-IRRAS in a ultra-high

vacuum condition, and investigated hydrogen adsorption on Si clean surfaces. In this report, we present a new project in which the BML-IRRAS is adopted to the bio-material spectroscopy in liquid conditions.

Figure 1 shows a schematic drawing of the sample holder for BML-IRRAS in liquid. The liquid is filled between the BML substrate and the BaF₂ prism. In order to estimate the influence of H₂O to the IR spectrum, we performed calculations with a model in which H₂O was used as a buffer solution. In this model, proteins were substituted by SiC to illustrate the influence of H₂O clearly in the region of Amide I and Amide II bands, because SiC has no spectral features in this region.

The reflectance of the model system was calculated by using the complex refractive indexes of each layer. Figure 2 shows the observed spectrum of the sample with proteins on the BML substrate in a dry condition and the calculated spectrum of the model system described above. Absorption peaks of Amide I and II are clearly seen in the experimental spectrum. In the calculated spectrum, on the other hand, the absorption peak is also seen at 1640 cm⁻¹ which is assigned to the absorption peak of H₂O. It will be very difficult to find Amide I and II peaks from the background of H₂O absorption. This problem should be avoided by using D₂O instead of H₂O. The influence of D₂O should be estimated in the near future.



Figure 1. Schematic drawing of the sample holder for BML-IRRAS in liquid.



Figure 2. Experimental spectrum of the sample with proteins on the BML substrate in the dry condition and the calculated spectrum of the BaF₂/H₂O/SiC/SiO₂/Co model.

VI-F Integration of Bio-Functional Materials on Silicon

Integration of bio-functional materials such as lipids and proteins are expected to find important applications in biosensors, development of new medicines, and diagnosis of intractable diseases *etc*. In this project, we are investigating the area selective modification of Si surfaces by depositing the self-assembled alkyl monolayers, and the integration of lipid bilayers supporting channel proteins keeping their bio-activities. Our specialinterests are developing "protein transistors" and co-integrating them together with the Si MOS FETs on the same Si chip.

VI-F-1 Deposition of Phospholipid Layers on SiO₂ Surface Modified by AlkyI-SAM Islands

TERO, Ryugo; LI, Yanjun; YAMAZAKI, Masahito¹; URISU, Tsuneo (¹Shizuoka Univ.)

[Appl. Surf. Sci. in press]

Formation of the supported planar bilayer of dipalmitoylphosphatidylcholine (DPPC) on SiO₂ surfaces modified with the selfassembled monolayer (SAM) of octadecyltrichlorosilane (OTS) has been investigated by atomic force microscopy (AFM). DPPC was deposited by the fusion of vesicles on SiO₂ surfaces with OTS-SAM islands of different sizes and densities. The DPPC bilayer membrane formed self-organizingly on the SiO₂ surface with small and sparse OTS islands, while did not when the OTS islands were larger and denser. The relative size between the vesicles and the SiO₂ regions is the critical factor for the formation of the DPPC bilayer membrane.

Figure 1. AFM images $(3.0 \times 3.0 \ \mu\text{m}^2)$ of the OTS-modified SiO₂ surface ($\theta_{OTS} = 0.21$) obtained in the buffer solution (a) before and (b) after the deposition of DPPC. (c) The magnified image of the square area in (b) (800 × 800 nm²). (d) The profile of the line drawn in (b). (e) Schematic illustration for the line profile in (d).

VI-F-2 Deposition of 10-Undecenoic Acid Self-Assembled Layers on H-Si(111) Surfaces Studied with AFM and FT-IR

LI, Yanjun; TERO, Ryugo; NAGASAWA, Takayuki; NAGATA, Toshi; URISU, Tsuneo

[Appl. Surf. Sci. in press]

Self-assembling layers of 10-undecenoic acid (UA) were deposited on H-terminated Si(111) surfaces and

characterized with atomic force microscopy (AFM) and Fourier-transform infrared (FT-IR) spectroscopy measurements for the first time. The unique island structures are deposited by layer-by-layer growth mechanism. The IR spectra suggest that the multilayers grown over the first monolayer are deposited by weak intermolecular interactions such as Van der Waals force and hydrogen bonding.

VI-F-3 Structure and Deposition Mechanism of 10-Undecenoic Acid Self-Assembled Layers on H-Si(111) Surfaces Studied by Atomic Force Microscopy and Fourier-Transform Infrared Spectroscopy

LI, Yanjun; TERO, Ryugo; NAGASAWA, Takayuki; NAGATA, Toshi; HARUYAMA, Yuichi¹; URISU, Tsuneo (¹Univ. Hyogo)

[Jpn. J. Appl. Phys. 43, 4591–4594 (2004)]

Ten-undecenoic acid self-assembled multilayers were deposited on H-Si(111) surfaces and the surface morphology was investigated by atomic force microscopy (AFM). Namely, we studied the H-Si(111) surface modification of –COOH terminal functional groups. Characteristic islands of almost the same height are observed. From AFM images and transmission IR spectra, it was confirmed that multilayer deposition easily occurs through weak intermolecular interactions such as the Van der Waals force and hydrogen bond interactions. The growth mechanism and film structure were discussed.

VI-F-4 Deposition of DPPC Monolayers by the Langmuir-Blodgett Method on SiO₂ Surfaces Covered by Octadecyltrichlorosilane Self-Assembled Monolayer Islands

TAKIZAWA, Morio; KIM, Yong-Hoon; URISU, Tsuneo

[Chem. Phys. Lett. 385, 220-224 (2004)]

The morphology of self-assembled monolayer (SAM) islands of *n*-octadecyltrichlorosilane (OTS) deposited on chemically and thermally oxidized SiO₂ surfaces was studied by dynamic force microscopy (DFM). The shape and size of the islands were found to depend significantly on the hydrophilicity of the SiO₂ surface. Langmuir-Blodgett (LB) monolayers of a lipid, dipalmitoylphosphatidylcholine (DPPC), deposited on these SiO₂ surfaces covered by OTS-SAM islands have

shown that the DPPC monolayer is supported firmly on the SiO_2 surface by the hydrophobic islands acting as anchor molecules.

VI-F-5 Characterization of Dipalmitoylphosphatidylcholine/Cholesterol Langmuir-Blodgett Monolayers Investigated by Atomic Force Microscopy and Fourier Transform Infrared Spectroscopy

KIM, Yong-Hoon; TERO, Ryugo; TAKIZAWA, Morio; URISU, Tsuneo

[Jpn. J. Appl. Phys. 43, 3860-3864 (2004)]

The addition effects of cholesterol on the dipalmitoylphosphatidylcholine (DPPC) Langmuir-Blodgett (LB) monolayer have been investigated by atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRRAS). The phase transfor-mation from pure DPPC to the DPPC/cholesterol phase proceeds through two stages: initial drastic changes in the surface morphology and the conformation of the DPPC acyl chains below 10% cholesterol, and the gradual homogenization of the morphology towards the liquid-order phase up to 35% cholesterol. The IRRAS peak position indicates that the conformational disorder of the acyl chain becomes almost that of the liquid level at 10% cholesterol addition. In the homogeneous liquidorder phase at 35% cholesterol, the terminal methyl groups of the DPPC are aligned in good order similarly to the solidlike gel phase, whereas the acyl chains have a liquid-level disordered conformation.



Figure 1. AFM images $(5.0 \times 5.0 \ \mu\text{m}^2)$ of DPPC/cholesterol LB monolayers transferred onto the mica surface at the surface pressure of 10 mNm⁻¹. The concentrations of cholesterol are a) 0% (pure DPPC), b) 5%, c) 10%, d) 20%, e) 30% and f) 35% in molar ratio. g) The profile of the line drawn in d). The scale of the insets in (c) and (d) is $1.34 \times 1.34 \ \mu\text{m}^2$.

VI-F-6 An AFM Characterization of Gramicidin A in Tethered Lipid Membrane on Silicon Surface

LEI, Shenbin; TERO, Ryugo; MISAWA, Nobuo; WAN, Lijun; URISU, Tsuneo

Recently there has been growing interest in supported bilayer lipid membranes (sBLMs). The supported lipid membrane is much more stable in comparison with the unsupported lipid membrane, extending their life from hours to a period of days withstanding mechanical distortion and repeated washes. This stability of sBLMs enables its research applications such as use in developing biosensors and surface coatings.¹⁾

Here we use the avidin-biotin interaction, which is known to be one of the strongest bindings between a protein and a ligand and is a key example of the biological specificity and the biological adaptation,²⁾ to form a tethered phospholipid membrane on oxidized Si(100) surfaces. The procedure for our strategy is schematically shown in Scheme 1. AFM characterizations show avidin molecules are well dispersed and the surface density is estimated to be about 40 molecule/ μ m². When sonicated unilamellae vesicles (SUVs) (0.3 mM DPPC in 0.1 M HEPES buffer) containing 2% mol gramicidin A was deposited on this surface, single lipid bilayers formed in the large area, but with high density of defects as compared with that on the mica surface. The thickness of this bilayer is measured to be 5.8 to 6.1 nm, in consistent with previous reports. In the tethered membrane, gramicidin A appear as depressions, which is the same as reported for gramicidin in supported membrane on mica. However, the topography is significantly different. On mica surface, gramicidin A aggregates into linear structures. However, in the tethered membrane on the silicon surface, both linear and spot like gramicidin aggregations appear. The width and height of these depressions are also different in the tethered membrane as compared with that in the supported membrane on mica. Also, in the tethered membrane, gramicidin appears with higher density than expected. These results seem to indicate that gramicidin A aggregates into larger aggregations in the supported membrane than in the tethered membrane. Certainly the current conclusion needs further characterizations to make it more solid.

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Figure 1. Scheme 1.

VI-F-7 Immobilization of Avidin on COOH-Modified SiO₂/Si(100) Surface and Characterization by AFM and BML-IRRAS

MISAWA, Nobuo; YAMAMURA, Shusaku; URISU, Tsuneo

Nowadays bio-mimetic sensing techniques, using immobilization of intact biomolecules on solid surfaces, attract significant attentions. For solid substrates, silicon is a suitable material since precise micro-fabrication has been established. New biosensors can be combined with electronics devices on the same chip. Characterizations by IR spectroscopy and AFM observation are useful tools to investigate biomolecules immobilized on silicon surface. It is known that BML-IRRAS (Infrared Reflection Absorption Spectroscopy using Buried Metal Layer substrate¹⁾) is a high-resolution surface vibration spectroscopy on the semiconductor or insulator materials, which has sub-monolayer sensitivity for the wide frequency range including fingerprint regions. In this study we have immobilized avidin, which has high versatility for conjugation of biomolecules with solid surfaces, on the SiO₂/Si(100) surface modified with carboxyl groups, and characterized the surface by AFM and BML-IRRAS for the first time. The -COOH modification was produced by the deposition of 2-(carbomethoxy)ethyltrichlorosilane and sequential hydrolysis by HCl. Immobilization of avidin was performed after condensation reaction by N-hydroxysucciniimide and EDC, which enhanced the reactivity of carboxyl group with amino group of avidin.

AFM images (Figure 1) showed that the roughness of the –COOH modified surface was less than 0.5 nm, and protrusions with about 15 nm diameter and 2 nm height appeared after the avidin immobilization. The BML-IRRAS measurements showed clear peaks at 1650 cm⁻¹ and 1550 cm⁻¹, which were assigned to Amide I and Amide II bands of avidin. These bands also consisted of several fine structures which might be assigned to secondary structures such as α -helix and β -sheet *etc*. The detailed shape analysis of these bands could give the information with orientations of these immobilized proteins.

Reference

1) S. Yamamura. et al., Jpn. J. Appl. Phys. 42, 3942 (2003).



Figure 1. AFM images $(1.0 \ \mu\text{m} \times 1.0 \ \mu\text{m})$ and line profiles of COOH-modified surfaces (A) before and (B) after immobilization of avidin.

VI-G Photoionization and Photodissociation Dynamics Studied by Electron and Fluorescence Spectroscopy

Molecular photoionization is a major phenomenon in vacuum UV excitation and provides a large amount of information on fundamental electron-core interactions in molecules. Especially, neutral resonance states become of main interest, since they often dominate photoabsorption cross sections and lead to various vibronic states which are inaccessible in direct ionization. We have developed a versatile machine for two-dimensional photoelectron spectroscopy in order to elucidate dynamical aspects of superexcited states such as autoionization, resonance Auger decay, predissociation, vibronic couplings, and internal conversion. In a two-dimensional photoelectron spectrum (2D-PES), the photoelectron yield is measured as a function of both photon energy E_{hv} and electron kinetic energy E_k (binding energy). The spectrum, usually represented as a contour plot, contains rich information on photoionization dynamics.

Photofragmentation into ionic and/or neutral species is also one of the most important phenomena in the vacuum UV excitation. In some cases, the fragments possess sufficient internal energy to de-excite radiatively by emitting UV or visible fluorescence. It is widely accepted that fluorescence spectroscopy is an important tool to determine the fragments and to clarify the mechanisms governing the dissociation processes of diatomic and polyatomic molecules. For several years we have concentrated our energies on fluorescence spectroscopy of H_2O in the photon energy region of 15–55 eV.

VI-G-1 Photofragmentaion Mechanisms of H₂O Studied by Ultraviolet Dispersed Spectroscopy

MITSUKE, Koichiro

[J. Electron Spectrosc. Relat. Phenom. submitted]

Fragmentation of H₂O has been studied by dispersed fluorescence spectroscopy at excitation photon energies above 20 eV. Figure 1 shows expanded dispersed spectra in the wavelength range from 280 to 420 nm. With appearance energies of $hv \sim 30$ eV several vibrational bands, marked with diamond symbols, begin to emerge below 320 nm. We have assigned these peaks to $OH(\tilde{A}^2\Sigma^+ \rightarrow X^2\Pi)$ transition, judging from characteristic peaks due to the R_1 band heads for the $\Delta v = v' - v'' =$ 0 sequence at 306.4, 312.6, and 318.8 nm. The counter fragment of $OH(A^2\Sigma^+)$ must be $H^*(n)$ in the Rydberg state with $n \ge 2$. The above appearance energies are much higher than the dissociation limits for the OH $(A^2\Sigma^+) + H^*(n \ge 2)$ channels, but in good agreement with the vertical transition energies²⁾ for the associated Rydberg states of H₂O.

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Figure 1. Dispersed fluorescence spectra of H₂O. The symbols \bullet and \bullet designate the vibrational bands due to the OH⁺($A^{3}\Pi \rightarrow X^{3}\Sigma^{-}$) and OH($A^{2}\Sigma^{+} \rightarrow X^{2}\Pi$) transitions, respectively.

VI-G-2 Autoionization and Neutral Dissociation of Superexcited HI Studied by Two-Dimensional Photoelectron Spectroscopy

HIKOSAKA, Yasumasa; MITSUKE, Koichiro

[J. Chem. Phys. 121, 792–799 (2004)]

Two-dimensional photoelectron spectroscopy of

hydrogen iodide HI has been performed in the photon energy region of 11.10–14.85 eV, in order to investigate dynamical properties on autoionization and neutral dissociation of Rydberg states HI*(R_A) converging to HI⁺($\tilde{A}^2\Sigma^+_{1/2}$). A two-dimensional photoelectron spectrum exhibits strong vibrational excitation of HI⁺($\tilde{X}^2\Pi$) over a photon energy region from ~ 12 to 13.7 eV, which is attributable to autoionizing feature of the $5d\pi$ HI*(R_A) state. A noticeable set of stripes in the photon energy region of 13.5–14.5 eV are assigned as resulting from autoionization of the atomic Rydberg states of I* converging to I⁺(${}^{3}P_{0}$ or ${}^{3}P_{1}$). The formation of I* is understood in terms of predissociation of multiple HI*(R_A) states by way of the repulsive Rydberg potential curves converging to HI⁺(${}^{4}\Pi_{1/2}$).

VI-H Development of the Laser-SR Combination System for Photodissociation Studies of Highly Vibrationally Excited Molecules

Initial vibrational excitation in molecules might influence the chemical branching in photodissociation, if two or more different dissociation pathways are accessible from an electronically excited state. Much attention has been focused on the pioneering work of Crim and his collaborators [*J. Chem. Phys.* **92**, 803–805 (1990)], who could accomplish the selective bond-breaking of heavy water, HOD. Very recently Yokoyama, Akagi and coworkers reported that deuterized ammonia NHD₂ in the fourth N–H stretching overtone preferentially photodissociates into the ND₂ + H channel [*J. Chem. Phys.* **118**, 3600–3611 (2003)]. In these two studies UV lasers are employed for vibrationally mediated photodissociation.

Instead, we are planning to use synchrotron radiation (SR) to promote vibrationally excited molecules to electronically excited states in the vacuum UV region. The main objectives are as follows: (1) Elucidating the properties of dissociative states by sampling a wide range of their potential energy surfaces, such as dynamics determining the final-state distributions of the products, nonadiabatic transitions on dissociation, and assignments and characterization of unknown multiply-excited states produced by Auger decay from core-excited states. (2) Aiming at more universal "vibrational state-specific" rupture of chemical bonds, which could be realized by changing the overlap between the wavefuctions of the upper-state continuum and that of the ground state.

VI-H-1 Apparatus for Probing Dissociative Photoionization of Vibrationally Excited H₂O into OH⁺($X^{3}\Sigma^{-}$) + H(*n* = 1)

MITSUKE, Koichiro; MORI, Takanori; KOU, Junkei; ADACHI, Junichi¹; YAGISHITA, Akira¹; AKAGI, Hiroshi²; YOYAMA, Atsushi² (¹KEK-PF; ²JAERI, Tokai)

We have developed an experimental system for laser-SR two photon ionization the crux of which are an ultrahigh resolution continuous titanium-sapphire laser (a bandwidth of 4×10^{-4} cm⁻¹) and in-vacuum beam alignment devices for strict overlapping of the counterpropagating two photon beams. The apparatus was connected to the beam line 28A of the Photon Factory synchrotron radiation facility in Tsukuba. Figure 1 shows a schematic diagram of the experimental setup. The wavenumber of the laser was determined precisely in the range of from 13814 to 13819 cm⁻¹ by observing photoacoustic signal from laser excited H₂O measured with a lock-in modulation technique. The photon beam alignment devices are situated upstream and downstream of a central photoionization chamber. Each device is comprised of two stainless steel plates fitted on two-dimensional motion feedthroughs individually adjustable: one plate has an aperture of 0.8 mm and the other plate is coated with a fluorescing substance. These plates can be inserted across the photon beam axis without breaking the system vacuum, which permits us to easily attain good spatial overlap of the two beams. The OH⁺ ions produced via dissociation of $H_2O^*(4v_{O-H}) + hv \rightarrow OH^+(X^3\Sigma^-) + H(n = 1) + e^-$ were detected by time-of-flight mass spectrometry at SR photon energies near the dissociation threshold of 18.05 eV with respect to the neutral ground state of water.



Figure 1. Schematic diagram of the setup for laser-SR two photon ionization experiments.

VI-I Extreme UV Photoionization Studies of Polyatomic Molecules and Fullerenes by Employing a Grazing-Incidence Monochromator

On the beam line BL2B2 in UVSOR a grazing incidence monochromator has been constructed which supplies photons in the energy region from 20 to 200 eV [M. Ono, H. Yoshida, H. Hattori and K. Mitsuke, *Nucl. Instrum. Methods Phys. Res., Sect. A* **467-468**, 577–580 (2001)]. This monochromator has bridged the energy gap between the beam lines BL3B and BL4B, thus providing for an accelerating demand for the high-resolution and high-flux photon beam from the research fields of photoexcitation of inner-valence electrons, *L*-shell electrons in the third-row atom, and 4*d* electrons of the lanthanides. Since 2001 we have measured photoion yield curves of fullerenes. Geometrical structures and electronic properties of fullerenes have attracted widespread attention because of their novel structures, novel reactivity, and novel catalytic behaviors as typical nanometer-size materials. Moreover, it has been emphasized that the potential for the development of fullerenes to superconductors ($T_c \sim 50$ K) and strong ferromagnetic substances is extremely high. In spite of such important species spectroscopic information is very limited in the extreme UV region, which has been probably due to difficulties in obtaining enough number density of the sample. The situation has been rapidly changed in these few years, since the techniques of syntheses, isolation, and purification have been advanced so rapidly that appreciable amount of fullerenes is obtainable from several distributors in Japan.

VI-I-1 Kinetic Energy Distribution and Anisotropy of Fragment lons from SF₆ by Photoexcitation of a Sulfur 2p-Electron

ONO, Masaki¹; MITSUKE, Koichiro (¹*Chiba Univ.*)

[Chem. Phys. Lett. 379, 248–254 (2003)]

The kinetic energy (KE) distribution and asymmetry parameter β have been studied for photofragmentation of SF_6 near the sulfur 2p ionization edges at 170–208 eV by using synchrotron radiation. The relative yield of fast ions with KE > 5 eV is larger in the post-edge than in the pre-edge region, whereas β of such ions is lower in the post-edge region. The β curve shows a sudden drop from 0.06-0.07 to zero near the edges and remains constant thereafter. These results are ascribed to LVV Auger decay occurring above the edges leading to SF_6^{2+} and SF_6^{3+} transiently. At KE > 2 eV the distribution curve for core excitation to the $(2t_{1u})^{-1}(6a_{1g})^1$ state resembles that for valence-electron ionization at 170 eV. This agreement, together with a similarity in β , suggests that the S $2p \rightarrow 6a_{1g}$ resonance transition and valenceelectron ionization undergo similar formation pathways leading to fast F^+ ions (*i.e.* participation of shake-up satellite states).

VI-I-2 Production of Doubly Charged lons in Valence Photoionization of C₆₀ and C₇₀ at hv = 25-150 eV

KOU, Junkei; MORI, Takanori; S. V. K. Kumar¹; HARUYAMA, Yusuke²; KUBOZONO, Yoshihiro³; MITSUKE, Koichiro

(¹IMS and Tata Inst. Fund. Res.; ²Okayama Univ.; ³IMS and Okayama Univ.)

[J. Chem. Phys. 120, 6005–6009 (2004)]

Photoion yields from gaseous fullerenes, C₆₀ and

C₇₀, for production of singly and doubly charged ions are measured by mass spectrometry combined with tunable synchrotron radiation at hv = 25-150 eV. Since the signal of triply or highly charged ions is very weak, the total photoionization yield curve can be estimated from the sum of the yields of the singly and doubly charged ions. There is distinct disagreement between the resultant curve of C₆₀ and the calculated total photoabsorption cross section previously reported. This difference is understood by the assumption that C_{60}^{2+} ions are chiefly produced by spectator Auger ionization of the shape resonance states followed by tunneling of the trapped electron or by cascade Auger ionization. For C₆₀ and C₇₀ the ratios between the yields of doubly and singly charged ions are larger than unity at hv > 50 eV. These ratios are quite different from those reported in the experiments using electron impact ionization.

VI-I-3 Absolute Photoabsorption Cross Section of C₆₀ in the Extreme Ultraviolet

MORI, Takanori; KOU, Junkei; HARUYAMA, Yusuke¹; KUBOZONO, Yoshihiro¹; MITSUKE, Koichiro (¹Okayama Univ.)

[J. Electron Spectrosc. Relat. Phenom. submitted]

The absolute photoabsorption cross section curve of C_{60} has been determined by means of mass spectrometry with the photon source of monochromatized synchrotron radiation of hv = 24.5-150 eV. Experiments are carried out using a high-temperature source of gaseous fullerenes and an efficient time-of-flight mass spectrometer. The absolute cross section curve is shown in Figure 1. The cross sections are 762, 241 and 195 Mb at hv = 24.5, 90, and 110 eV, respectively with about 10% errors. Our results may suffer from some deviation from the real cross section curve. This deviation chiefly arises from uncertainties in the number density *n* of C_{60} in the ionization region, because we derive *n* from the mass deposition rate at the thickness monitor by assuming effusive flow conditions for the properties of the C₆₀ beam. The present cross section curve was then normalized at hv = 25 eV to the absolute cross section reported by Jaensch and Kamke,¹⁾ the most reliable data so far available in the valence region of C₆₀. Eventually, the present cross section data were reduced to 407, 144 and 114 Mb at hv = 25, 90, and 110 eV, respectively.

References

- 1)R. Jaensch and W. Kamke, *Mol. Materials* **13**, 143–150 (2000).
- 2) J. Berkowitz, J. Chem. Phys. 111, 1446-1453 (1999).



Figure 1. Absolute absorption cross section of C_{60} at hv = 24.5-150 eV (solid line). The closed circles and triangles designate the data measured by Jaensch and Kamke¹⁾ and those compiled by Berkowitz,²⁾ respectively. The open circles indicate the cross section of sixty carbon atoms.

VI-I-4 Photofragmentation of C₆₀ in Valence Ionization

KOU, Junkei; MORI, Takanori; KUBOZONO, Yoshihiro¹; MITSUKE, Koichiro (¹Okayama Univ.)

(Chayania Chivi)

[J. Electron Spectrosc. Relat. Phenom. submitted]

The yield curves for C_{60-2n}^+ (n = 1-3) produced by photoionization of C_{60} were measured in the hv range of 25–150 eV. The appearance energies increase with increasing n, as evidenced from Figure 1. Evaluation was made on the upper limits of the internal energies of the primary C_{60}^+ above which $C_{60-2n+2}^+$ fragments ($n \ge$ 1) cannot escape from further dissociating into C_{60-2n}^+ + C_2 . These limits agree well with the theoretical internal energies of C_{60}^+ corresponding to the formation threshold for $C_{60-2n+2}^+$, assuming that the binding energies of $C_{60-2n+2}^+$ are equal to those proposed by Foltin *et al.*¹

Reference

 M. Foltin, M. Lezius, P. Scheier and T. D. Märk, J. Chem. Phys. 98, 9624–9634 (1993).



Figure 1. Yield curves for C_{60-2n}^+ ions (n = 1-3) obtained from time-of-flight mass spectra.

VI-I-5 Remarkably Large Shifts of the Appearance Energies of C_{60-2n}^{z+} ($n \ge 1$) from Their Thermochemical Thresholds

KOU, Junkei; MORI, Takanori; KUBOZONO, Yoshihiro¹; MITSUKE, Koichiro (¹Okayama Univ.)

[Phys. Chem. Chem. Phys. submitted]

The ion yield curves for C_{60-2n}^{z+} (*n* = 1–5, *z* = 1–3) produced by photoionizaiotion of C₆₀ have been measured in the hv range of 25–150 eV. The appearance photon energies are higher by 30-33 eV than the thermochemical thresholds for dissociative ionization of C_{60} leading to $C_{60-2n}^{z+} + C_2$. With increasing *n* the appearance energies shift to higher hv positions for a given z. Evaluation is made on the upper limits of the internal energies of the primary C_{60}^{z+} above which $C_{60-2n+2}^{z+}$ fragments $(n \ge 1)$ cannot escape from further dissociating into $C_{60-2n^{z+}} + C_2$. These upper limits agree well with the theoretical internal energies of C_{60}^{z+} corresponding to the threshold for the formation of C_{60-2n}^{z+} . The photofragmentation of C_{60}^{z+} is considered to be governed by the mechanism of internal conversion of the electronically excited states of C_{60}^{z+} , statistical redistribution of the excess energy among a number of vibrational modes, and successive ejection of the C_2 units.



Figure 1. Yield curves of C_{60-2n}^{2+} ions (n = 1-5) obtained from time-of-flight mass spectra.

VI-I-6 Photoion Yields from Ce@C₈₂ near the 4*d* Edge of Ce

MITSUKE, Koichiro; MORI, Takanori; KOU, Junkei; HARUYAMA, Yusuke¹; KUBOZONO, Yoshihiro¹

(¹Okayama Univ.)

The yield curves for photoions from Ce@C₈₂ are measured by using synchrotron radiation in the photon energy range from 90 to 160 eV. Parent Ce@C₈₂^{z+} and fragment ions C₆₀^{z+} and C₇₀^{z+} are observed in a mass spectrum (z = 1 and 2). The yield curves for principal ionic species exhibit broad resonance in the region hv=120–140 eV which is ascribed to the $4d \rightarrow \varepsilon f$ giant dipole resonance of the encapsulated Ce atom. The total photoabsotpion cross section of Ce@C₈₂ was determined from partial photofragmentation cross sections for respective ions to be 19.6^{+6.5}_{-3.9} and 5.3^{+1.8}_{-1.1} Mb at hv =110 and 130 eV, respectively.



Figure 1. Time-of-flight mass spectrum of the parent and fragment ions produced by photoionization of $\text{Ce}@C_{82}$ at hv = 125 eV.

RESEARCH ACTIVITIES VII Department of Computational Molecular Science

VII-A Computer Simulation

VII-A-1 Path Integral Influence Functional Theory of Dynamics of Coherence between Vibrational States of Solute in Condensed Phase

MIKAMI, Taiji; OKAZAKI, Susumu

[J. Chem. Phys. 121, 10052 (2004)]

Path integral influence functional theory has been applied to the dynamics of coherence between vibrational states of solute in condensed phase. First, time evolution of the off-diagonal term of the reduced density matrix $\rho_{mn}(t)$ was algebraically described by the cumulant expansion of the perturbative influence functional. Then, the theory is compared with the Redfield theory, rearranging the present description in a familiar way to that found in the Redfield theory. A numerical example of the theory is presented for the vibrational dynamics of cvanide ion in water assuming a coherent state $(1+\sqrt{2})(|0\rangle+|1\rangle)$ at t=0. We find that $\operatorname{Rep}_{10}(t)$ oscillates with high frequency and shows a fast damping. Relaxation time of the oscillation amplitude is estimated to be 5.1 ps for a certain configuration of the solution. Then, secular approximation often used in the Redfield theory is found to work well, at least, in the present system. Population relaxation time for the first excited state and pure dephasing time may also be calculated from the component of $\text{Rep}_{10}(t)$ to be 7.9 ps and 7.5 ps, respectively. Further, many-particle measurement for $\operatorname{Rep}_{10}(t)$ gives the relaxation rate about three times faster than the single-measurement above. This comes from the inhomogeneity of the solute environment. We also calculated $\operatorname{Rep}_{11}(t)$ and found the fast oscillation in the diagonal part of the density matrix $\operatorname{Rep}_{11}(t)$. This oscillation is generated only when the initial density matrix includes the coherence.

VII-A-2 Mixed Quantum-Classical Molecular Dynamics Study of Vibrational Relaxation of CN^{-} Ion in Water: An Analysis of Coupling as a Function of Time

SATO, Masahiro; OKAZAKI, Susumu

[J. Mol. Liq. in press]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water, where coulombic force is predominant in the interaction. The calculation demonstrated that timedependent interaction between the solute vibrational degree of freedom and the solvent water shows randomnoise-like behavior, no collisional or stationary coupling observed in gas or solid, respectively, being found. This is in contrast to short-ranged-force system where the collision plays a dominant role in the relaxation. The interaction has been analyzed in detail as a function of time defining the effective coupling for the relaxation.

VII-A-3 Vibrational Relaxation Time of CN⁻ Ion in Water Studied by Mixed Quantum-Classical Molecular Dynamics: Comparison with Fermi's Golden Rule and Influence Functional Theory

SATO, Masahiro; OKAZAKI, Susumu

[Mol. Sim. in press]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was compared with those based upon Fermi's golden rule with classical interaction and influence functional theory with classical bath. They are in good agreement with each other. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation.

VII-B Molecular Dynamics Study of Classical Complex Systems

VII-B-1 Molecular Dynamics Studies of Self-Organization of Amphiphilic Molecules in the Aqueous Solution

YOSHII, Noriyuki; IWAHASHI, Kensuke;

YAMADA, Atsushi; OKAZAKI, Susumu

Self-organization of amphiphilic molecules in water such as micelles and lipid bilayers is investigated. Potential of mean force between amphiphilic molecules is a target of this investigation. In order to accomplish this, general purpose program for large-scale molecular dynamics calculation has been coded in a suitable way for very highly parallel computing and grid computing. The program can be used to execute a calculation for the system of a million of atoms with arbitrary molecular configurations. Preliminary calculations have been done for many-body effect on the potential of mean force among small hydrophobic solutes.

VII-C Development of Simulation Algorithms for Quantum Many-Body Systems

VII-C-1 On the Solvation Structure of a Rare-Gas Solute in Superfluid Helium-4

MIURA, Shinichi

[J. Mol. Liq. in press]

Path integral hybrid Monte Carlo calculations have been performed for a system consisting of a single neon atom in the superfluid helium. An expression of the local superfluid density around the solute atom is introduced to analyze the microscopic density fluctuation around the solute in detail. We show that the superfluid component in the sovaltion shell dramatically increases with lowering temperature, although the radial number density profile itself is almost independent of temperature. We also compare the local superfluid density calculated by our expression with that by another commonly used one. Although both local superfluid densities show similar trend as a function of the radial distance from the solute atom, quantitative differences are found; the superfluid component is underestimated by the commonly used one. This is due to the fact that the commonly used definition of the local superfluid density does not give the bulk superfluid density by integrating it over whole space. New expression introduced in the present study is free from such a deficiency.

VII-D Theory of Sum Frequency Generation Spectroscopy

Sum Frequency Generation (SFG) spectroscopy in combination of infrared and visible lights has a wide range of applications to study interfacial structure, including ambient and buried surfaces not accessible by most other techniques. In contrast to the recent experimental progress, however, theoretical study of SFG is still in a relatively primitive stage. We recently proposed two theories which allow us to calculate SFG spectra via ab initio molecular orbital theory and molecular dynamics simulation, and applied them to the experimental SFG spectrum of water surface with considerable success. This project aims at extending this theory in two ways: (1) development of fundamental SFG theory toward quantitative interpretation of the experiments, and (2) application to other interfacial structures of interest using large-scale computation.

VII-D-1 Toward Computation of Bulk Quadrupolar Signals in Vibrational Sum Frequency Generation Spectroscopy

MORITA, Akihiro

[Chem. Phys. Lett. 398, 361–366 (2004)]

Although SFG is regarded as a surface-sensitive

spectroscopy, bulk contribution *via* quadrupole and other higher-order terms should not be negligible. Relative importance of surface and bulk signals has been a long standing issue, although quantitative discussion is rather scarce. This study provides theoretical expressions of the bulk signals, which are extension of our previous SFG theories and are readily implemented in molecular dynamics calculations.

VII-E Theory of Mass Transfer Kinetics at Liquid-Vapor Interfaces

Mass transfer kinetics at liquid-vapor interface is of fundamental importance in heterogeneous atmospheric chemistry, as it governs rates of heterogeneous reactions and nucleation. Observed uptake kinetics, however, is quite difficult to interpret in molecular level, since it is related to many kinetic factors including gas diffusion, liquid solubility and diffusion, interfacial mass accommodation, *etc.* We have demonstrated with the help of molecular dynamics and computational fluid dynamics calculations that those elemental kinetic resistances can be accurately decoupled in actual experimental conditions.

VII-E-1 Revised Kinetics in the Droplet Train Apparatus Due to a Wall Loss

HANSON, David R.¹; SUGIYAMA, Masakazu²; MORITA, Akihiro (¹NCAR; ²Univ. Tokyo)

[J. Phys. Chem. A 108, 3739–3744 (2004)]

Heterogeneous uptake experiments become further complicated when a wall loss effect is involved in addition to the interfacial mass transfer. In most experimental analyses of the droplet train flow reactor, the wall loss rate is simply subtracted as a constant background, assuming that it is independent from the uptake rate constant into droplets. However, we showed that this usual assumption is flawed because of radial concentration gradient in the flow tube. Accurate treatment of the wall loss effect is demonstrated using computational fluid dynamics calculations.

VII-E-2 Uptake of the HO₂ Radical by Water: Molecular Dynamics Calculations and Their Implications to Atmospheric Modeling

MORITA, Akihiro; KANAYA, Yugo¹; FRANCISCO, Joseph S.² (¹JAMSTEC; ²Purdue Univ.)

[J. Geophys. Res. 109, D09201, 10.1029/2003JD004240 (2004)]

 HO_2 plays many critical roles in radical-chain oxidation reactions in the troposphere. Although a substantial sink of HO_2 has been suggested to be the uptake into aerosols, its efficiency is largely uncertain. Therefore, we performed molecular dynamics calculations of HO_2 uptake into water surface, and found that the mass accommodation coefficient of HO_2 is close to unity. Implications of this result in the troposphere are examined by photochemical box model calculations for typical two cases of tropospheric boundary layers; remote marine air and polluted urban air. It is shown that HO_2 concentration is particularly sensitive to the heterogeneous uptake in the urban case.

VII-E-3 Mass Accommodation Coefficient of Water: Molecular Dynamics Simulation and Revised Analysis of Droplet Train/Flow Reactor Experiment

MORITA, Akihiro; SUGIYAMA, Masakazu¹; KAMEDA, Hirofumi¹; KODA, Seiichiro²; HANSON, David R.³ (¹Univ. Tokyo; ²Sophia Univ.; ³NCAR)

[J. Phys. Chem. B 108, 9111–9120 (2004)]

Mass accommodation coefficient of water α has been studied for a century, in relation to the cloud formation kinetics and many other implications. Most recent experiment using droplet train flow reactor reported $\alpha = 0.23$ at room temperature, which appears inconsistent to molecular dynamics value, $\alpha \sim 1$. This study resolved this discrepancy by reanalyzing the gas diffusion and flow conditions in the experimental reactor. Accurate calculations of the gaseous diffusion resistance yielded a value of α close to unity, which is fully consistent to the molecular dynamics and some other experiments.

VII-F Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States

VII-F-1 Millimeter-Wave Spectroscopy of the Internal-Rotation Band of the X-HCN Complex (X = He, Ne, and Ar) and the Intermolecular Potential Energy Surface

HARADA, Kensuke¹; TANAKA, Keiichi¹; TANAKA, Takehiko¹; NANBU, Shinkoh (¹Kyusyu Univ.)

Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the internal-rotation band of the X-HCN (X = He, Ne, and Ar) in the frequency region of 95-125 GHz. The observed transition frequencies were analyzed including their hyperfine splitting to yield an intermolecular potential energy surface, as improved from the one given by a coupled-cluster single double (triple) ab initio calculation. Regarding the He complex, the surface has a global minimum in the linear configuration (He···H–C–N) with a well depth of 30.2 cm^{-1} , and the saddle point located in the anti-linear configuration (H-C-N···He) is higher by 8.174 cm⁻¹ in energy than the global minimum. The distance $R_{\rm m}$ between the He atom and the center of mass of HCN along the minimum energy path shows a strong angular dependence; $R_{\rm m} = 4.169$ Å and 4.040 Å in the linear and antilinear forms, respectively, while it is 3.528 Å in a Tshaped configuration. The energy level diagram is consistent with the millimeter-wave observation. And now, we are trying to measure the stretching motion located just below the dissociation limits.

VII-F-2 Ab Initio Study of the Complexation Behavior of *p*-Tert-Butylcalix[5]arene Derivative toward Alkyl Ammonium Cations

CHOE, Jong-In¹; LEE, Sang Hyun¹; OH, Dong-Suk; CHANG, Suk-Kyu¹; NANBU, Shinkoh (¹Chung-Ang Univ.)

[Bull. Korean. Chem. Soc. 25, 190–194 (2004)]

The structures and complexation energies of penta-O-tert-butyl ester of p-tert-butylcalix[5]arene toward a series of alkyl ammonium guests have been optimized by ab initio HF/6-31G method. The calculated complexation efficiencies of the ester for alkyl ammonium guests have been found to be similar to the values of previously reported debutylated-calix[5]arene. Calculation results show that both of the calyx[5]aryl alkyl ammonium guests. The structural characteristics of the calculated complexes are discussed as a function of the nature of the alkyl substituents of the ammonium guests.

VII-F-3 Theoretical Transition Probabilities for the $\tilde{A}^2 A_1 - \tilde{X}^2 B_1$ System of H₂O⁺ and D₂O⁺ and Related Franck-Condon Factors Based on Global Potential Energy Surfaces

TOKUE, Ikuo¹; YAMASAKI, Katsuyoshi¹; NANBU, Shinkoh

(¹Niigata Univ.)

In order to elucidate the ionization dynamics, in particular the vibrational distribution, of $H_2O^+(\tilde{A})$ produced by the photoionization and the Penning ionization of H₂O and D₂O with He* $(2^{3}S)$ atoms, the Franck-Condon factors (FCFs) were presented for the H₂O(\tilde{X}) \rightarrow H₂O⁺(X,A) ionization and the transition probabilities were presented for the $H_2O^+(A-X)$ system. The FCFs were obtained by quantum vibrational calculations using the three-dimensional potential energy surfaces (PESs) of H₂O(\tilde{X}^1A_1) and H₂O⁺(\tilde{X}^2B_1 , \tilde{A}^2A_1 , \tilde{B}^2B_2) electronic states. The global PESs were determined by the multireference configuration interaction calculations with the Davidson correction and the interpolant moving least squares method combined with the Shepard interpolation. The obtained FCFs exhibit that the $H_2O^+(X)$ state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of $H_2O(\tilde{X})$, while the bending mode (v_2) is strongly enhanced for the $H_2O^+(\tilde{A})$ state; the maximums in the population of H_2O^+ and D_2O^+ are around $v_2 = 11-12$ and 15-17, respectively. These results are consistent with the distributions observed by photoelectron spectroscopy. Transition probabilities for the A-X system of H₂O⁺ and D_2O^+ show that the bending progressions consist of the great part of the A-X emission and that combination bands from the $(1, v_2) = 4-8, 0$ state are next important.

VII-F-4 Analysis of the Ultraviolet Absorption Cross Sections of Six Isotopically Substituted Nitrous Oxide Specie Using 3D Wavepacket Propagation

NANBU, Shinkoh; JOHNSON, Matthew S.¹ (¹Univ. Copenhagen)

[J. Phys. Chem. A 108, 8905–8913 (2004)]

The ultraviolet absorption cross sections of six isotopically substituted nitrous oxide species (14N14N16O, ¹⁴N¹⁴N¹⁷O, ¹⁴N¹⁴N¹⁸O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, and $^{15}N^{15}N^{16}O$) were computed using the wavepacket propagation technique to explore the influence of excited state dynamics, transition dipole surface and initial vibrational state. Three-dimensional potential energy surfaces for the electronic states of N₂O related to the experimentally observed photoabsorption between 170 and 220 nm were calculated using the ab initio molecular orbital (MO) configuration interaction (CI) method. The transition dipole moment surfaces between these states were also calculated. Numerous wave packet simulations were carried out and used to calculate the temperature-dependent photodissociation cross sections of the six isotopically substituted species. The photolytic isotopic fractionation constants determined using the calculated cross sections are in good

agreement with recent experiments. The results show that in addition to the effect of the changed shape of the ground state vibrational wavefunction with isotopic substitution, photodissociation dynamics play a central role in determining isotopic fractionation constants.

VII-F-5 Coarse-Grained Picture for Controlling **Quantum Chaos**

TAKAMI, Toshiya; FUJISAKI, Hiroshi¹; MIYADERA, Takayuki²

(¹Boston Univ.; ²Tokyo Univ. Sci.)

[Adv. Chem. Phys. in press]

We propose a coarse-grained picture to analyze control problems for quantum chaos systems. Using optimal control theory, we first show that almost perfect control is achieved for random matrix systems and a quantum kicked rotor. Second, under the assumption that the controlled dynamics is well described by a Rabi-type oscillaion between unperturbed states, we derive an analytic expression for the optimal field. Finally we numerically confirm that the analytic field can steer an initial state to a target state in random matrix systems.

VII-F-6 Coarse-Grained Picture for Controlling **Complex Quantum Systems**

TAKAMI, Toshiya; FUJISAKI, Hiroshi¹ (¹Boston Univ.)

[J. Phys. Soc. Jpn. 73, 3215-3216 (2004)]

We propose a coarse-grained picture to control complex quantum dynamics, *i.e.*, multi-level-multi-level transition with a random interaction. Introducing a Rabilike-oscillating state between two time-dependent states, we derive an analytic optimal field as a solution to optimal control theory. For random matrix systems, we numerically confirm that the analytic optimal field actually steers an initial state to a target state, which both contain many eigenstates.

RESEARCH ACTIVITIES VIII Coordination Chemistry Laboratories

Prof. Kazushi Mashima (Osaka Univ.) and Assoc. Prof. Masato Kurihara (Yamagata Univ.) took the position of Laboratory of Complex Catalyst from April 2004. Prof. Masahito Yamashita (Tokyo Metropolitan Univ.) and Prof. Naoto Chatani (Osaka Univ.) finished their term as Adjunct Prof. of Complex Catalyst in March 2004. Their effort during their term is gratefully appreciated. Prof. Hiroyuki Matsusaka (Osaka Prefecture Univ.) and Prof. Keiji Ueno (Gunma Univ.) continue the position of the Laboratory of Coordination Bond.

VIII-A Nano-Sciences of Advanced Metal Complexes

Recently, nano-sciences or nano-technologies have been attracting much attention because they show very interesting physical properties based on the non-linearity and quantum effect. There are two methods to obtain the nano-size materials, that is, "top-down" and "bottom-up" methods. The top-down method such as laser abrasion has a limitation to make particles with the sizes less than 100 nm. On the other hand, the bottom-up method is promising to control the nano-size since the chemical reactions are available. However, the researches based on the bottom-up methods are rare and such methods have not been accomplished so far. Then, I would like to focus on the bottom-up methods. As for the bottom-up methods, there are three types of the target materials such as inorganic compounds, organic compounds, and metal complexes. The inorganic compounds easily take three-dimensional bulk structures. The organic compounds easily take 0- and 1-dimesional bulk materials. Therefore, neither inorganic nor organic compounds are suitable for the nano-sciences. On the other hand, the metal complexes easily take nano-size clusters where they are surrounded with the organic ligands. Therefore, the nano-sciences of the advanced metal complexes are most promising. As for the non-linearity, we focus on the gigantic third-order optical non-linearity. As for the quantum effect, we focus on the single-molecule magnets, nano-wire molecule-magnets, and nano-network molecule-magnets.

VIII-A-1 A Three-Dimensional Ferrimagnet Composed of Mixed-Valence Mn₄ Clusters Linked by an {Mn[N(CN)₂]₆}^{4–} Unit

MIYASAKA, Hitoshi¹; NAKATA, Kazuya¹; SUGIURA, Ken-ichi¹; YAMASHITA, Masahiro²; CLÉRAC, Rodolphe³

(¹Tokyo Metropolitan Univ.; ²IMS and Tokyo Metropolitan Univ.; ³Cent. Recherche Paul Pascal)

[Angew. Chem., Int. Ed. 43, 707-711 (2004)]

A ferrimagnet with a 3D molecular network has been synthesized and characterized. This compound is composed of units of mixed-valence Mn_4 clusters, a unit that is well known for its single-molecule magnet properties, and Mn^{II} paramagnetic units. Both building blocks are linked by dicyanamide bridging ligand to form a covalent-bonded three-dimensional network. The compound becomes a ferrimagnet at 4.1 K that exhibits a spin-flip phenomenon under the influence of a magnetic field.

VIII-A-2 A Dimeric Manganese(III) Tertadentate Schiff Base Complex as a Single-Molecule Magnet

MIYASAKA, Hitoshi¹; CLÉRAC, Rodolphe²; WERNSDORFER, Wolfgang³; LECREN, Lollita²; BONHOMME, Claire²; SUGIURA, Ken-ichi¹; YAMASHITA, Masahiro⁴

(¹Tokyo Metropolitan Univ.; ²Cent. Recherche Paul Pascal; ³Laboratoire Louis Néel; ⁴IMS and Tokyo Metropolitan Univ.)

[Angew. Chem., Int. Ed. 43, 2801–2805 (2004)]

The complex $[Mn_2(saltmen)_2(ReO_4)_2]$ (saltmen^{2–} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)) is a simple out-of-plane dimmer of Mn^{III} ions that unambiguously exhibits single-molecule magnetic behavior. To date, this compound is the smallest magnetic unit which has been reported to behave as a magnet at the molecular level and to show quantum tunneling.

VIII-A-3 Tuning the Electronic Structure from Charge-Transfer Insulator to Mott-Hubbard and Peierls Insulators in One-Dimensional Halogen-Bridged Mixed-Metal Compounds

MATSUZAKI, Hiroyuki¹; IWANO, Kaoru²; AIZAWA, Takumi¹; ONO, Madoka¹; KISHIDA, Hideo¹; YAMASHITA, Masahiro³; OKAMOTO, Hiroshi¹

(¹Univ. Tokyo; ²KEK; ³IMS and Tokyo Metropolitan Univ.)

[Phys. Rev. B 70, 035204 (6 pages) (2004)]

The electronic structures of one-dimensional (1D) halogen-bridged mixed-metal compounds, $[Ni_{1-x}Pd_x (chxn)_2X]X_2$ (chxn = cychlohexanediamine; X = Cl, Br; 0 < x < 1), are investigated through optical and magnetic measurements. The results reveal that the system changes from charge-transfer (CT) insulator to Mott-

Hubbard (MH) insulator at around $x \sim 0.3$, and from MH insulator to Peierls insulator at $x \sim 0.9$ with increasing *x*. From the analysis of optical conductivity spectra using the 1D two-band extended Peierls-Hubbard model, electronic parameters such as Coulomb repulsion energy, *pd* hybridization, CT energy, and electronlattice interaction are determined.

VIII-A-4 A Square Cyclic Porphyrin Dodecamer: Synthesis and Single-Molecule Characterization

KATO, Aiko¹; SUGIURA, Ken-ichi¹; MIYASAKA, Hitoshi¹; TANAKA, Hiroyuki²; KAWAI, Tomoji²; SUGIMOTO, Manabu³; YAMASHITA, Masahiro⁴ (¹Tokyo Metropolitan Univ.; ²Osaka Univ.; ³Kumamoto Univ.; ⁴IMS and Tokyo Metropolitan Univ.)

[Chem. Lett. 33, 578-579 (2004)]

We prepared a square cyclic porphyrin dodecamer via the tetramerization of a trimer shaped like a right angle. The molecule was visualized by scanning tunneling microscopy to be square.

VIII-A-5 Visualization of Local Valence Structure in Quasi-One-Dimensional Halogen-Bridged Complexes [Ni_{1-x}Pd_x(chxn)₂Br]Br₂ by STM

TAKAISHI, Shinya¹; MIYASAKA, Hitoshi¹; SUGIURA, Ken-ichi¹; YAMASHITA, Masahiro²; MATSUZAKI, Hiroyuki³; KISHIDA, Hideo³; OKAMOTO, Hiroshi³; TANAKA, Hisaaki⁴; MARUMOTO, Kazuhiro⁴; ITO, Hiroshi⁴; KURODA, Shin-ichi⁴; TAKAMI, Tomohide⁵ (¹Tokyo Metropolitan Univ.; ²IMS and Tokyo Metropolitan Univ.; ³Univ. Tokyo; ⁴Nagoya Univ.; ⁵Visionarts Res. Inc.)

[Angew. Chem., Int. Ed. 43, 3171-3175 (2004)]

we have visualized the Mott-Hubbard and CDW states in quasi-1D halogen-bridged Ni and Pd complexes, respectively. In addition, we succeeded in visualizing the propagation of CDW coherence and the spin soliton in real space in the mixed-metal complexes $[Ni_{1-x}Pd_x(chxn)_2Br]Br_2$ for the first time.

VIII-A-6 A Dinuclear Ruthenium(II) Chelating Amido Complex: Synthesis, Characterization, and Coupling Reaction with Carbon Monoxide

TAKEMOTO, Shin¹; OSHIO, Shinya¹; KOBAYASHI, Tomoharu¹; MATSUZAKA, Hiroyuki²; HOSHI, Masatsugu³; OKIMURA, Hironobu³; YAMASHITA, Masayo³; MIYASAKA, Hitoshi³; ISHII, Tomohiko³; YAMASHITA, Masahiro⁴

(¹Osaka Prefecture Univ.; ²IMS and Osaka Prefecture Univ.; ³Tokyo Metropolitan Univ.; ⁴IMS and Tokyo Metropolitan Univ.)

[Organometallics 23, 3587–3589 (2004)]

[CpRuCl]₄ (Cp = η^5 -C₅Me₅) reacts with 2 equiv of dilithium 2,3-naphthalenediamide to afford the dinuclear bridging amido complex [(CpRu)₂{ μ_2 -(NH)₂-C₁₀H₆}] (**1b**) in moderate yield. Treatment of **1b** with CO (1 atm) resulted in the incorporation of three molecules of CO into the diruthenium core to give the carbamoyl amido bis(carbonyl) complex [CpRu(μ_2 -CO)-{ μ_2 -2,3-(CONH)(NH)C₁₀H₆}RuCp(CO)].

VIII-B Early Transition Metal Chemistry Directed to Olefin Polymerization

Recent development of well-defined single site transition metal catalysts enables us to precisely control not only catalytic activity for α -olefin polymerization but also microstructure of polymers. The nitrogen-based polydentate ligands such as phenoxyimine, 2,6-bis(*N*-aryliminomethyl)pyridine, and α -diimine derivatives, which serve the polymerization catalysts as supporting ligands, have attracted particular interest in terms of their advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features on the ligand. Despite these merits, the catalysts supported by these ligands have been found to be occasionally deactivated by the alkylation of the C=N bond of the ligand. The alkylation of the C=N moiety of the nitrogen-based ligand was thus anticipated to have a capability to make a cationic alkyl species more stable and, in particular case, enhance its catalytic activity compared to the corresponding catalyst bearing the unalkylated ligand. In this contribution, we have investigated such the alkylation of the ligand related to the polymerization activity and mechanism.

VIII-B-1 Intramolecular Benzylation of an Imino Group of Tridentate 2,5-Bis(*N*-aryliminomethyl)pyrrolyl Ligands Bound to Zircnoium and Hafnium Gives Amido-Pyrrolyl Complexes That Catalyze Ethylene Polymerization

TSURUGI, Hayato¹; YAMAGATA, Tsuneaki¹; MASHIMA, Kazushi² (¹Osaka Univ.; ²IMS and Osaka Univ.)

[Organometallics 23, 2797–2805 (2004)]

We already reported that an intramolecular benzylation of the imino moiety of bidentate iminopyrrolyl ligands afforded an amido-pyrrolyl complexes 1 and they exhibited better catalytic activity for ethylene polymerization compared to the corresponding bis-(iminopyrrolyl) dichloro complexes of zirconium. In this contribution, we prepared amido-pyrrolyl complexes of zirconium (3a-d) and hafnium (4a-f) by the reaction of tetrabenzyl-zirconium and -hafnium with 2,5-bis(*N*-aryliminomethyl)pyrrole ligands (2a-e), respectively. During the course of the reaction, one of two imino moieties of the ligand was selectively benzylated to give unique dianionic tridentate ligands, which stabilized dibenzyl complexes of zirconium and hafnium. The coordinative unsaturation around the metal center was compensated by not only the donation of the imino moiety but also the η^2 -coordination of one of the two benzyl ligands, as confirmed by spectral data together with X-ray analysis of 3b and 3c. The zirconium complexes **3b** and **3c** bearing bulky substituents at the nitrogen atoms of the ligand exhibited high catalytic activities (**3b**, 131 (kg-PE)(mol-cat)⁻¹h⁻¹ at 60 °C; **3c**, 458 (kg-PE)(mol-cat)⁻¹h⁻¹ at 75 °C) upon combined with 1000 equiv. of MMAO. Lewis-base free cationic alkyl complexes **5b**, **5c**, **6b**, and **6c** were prepared by alkyl abstruction from the corresponding dibenzyl complexes of zirconium **3b**,**c** and hafnium **4b**,**c** and the resulting cationic complexes **5c** and **6c** were found to catalyze the ethylene polymerization without MMAO.



VIII-C Linear Metal Clusters: Bonding and Reactivity

Assembled metal complexes with highly controlling their nuclearity and dimensionality have extensively investigated and quasi-one-dimensional materials, especially transition-metal linear-chain complexes, have attracted particular interest in view of their novel electronic, magnetic, and optical properties. In this contribution, we prepared two linear chain compounds comprised of Mo–Mo multiple bond in their chain.

VIII-C-1 An Infinite Zigzag Chain of Alternating CI–Pd–Pd–CI and Mo–Mo Units

MASHIMA, Kazushi¹; YI, JianJun²; MIYABAYASHI, Takayuki²; OHASHI, Masato²; YAMAGATA, Tsuneaki² (¹IMS and Osaka Univ.; ²Osaka Univ.)

[Inorg. Chem. 43, 6596–6599 (2004)]

Treatment of $Pd_2Cl_2(CNC_6H_3Me_2-2,6)_4$ (1) and $Mo_2(O_2CCF_3)_4$ (2) in dichloromethane afforded an infinite zigzag chain { $[Pd_2Cl_2(CNC_6H_3Me_2-2,6)_4][Mo_2(O_2CCF_3)_4]_n$ (3), where two metal-metal bonded dinuclear Pd-Pd and Mo-Mo units were bridged by chloro atoms (equation 1). The Mo-Mo distance (2.1312(3) Å) of 3 is significantly elongated compared to that of 2 (2.090(4)) Å) and lies in the range of that of the quadruple Mo-Mo bonded complexes (Figure 1). Such the elongation might be attributed to the axial donation of the chloro atoms of the Pd-Pd unit to the Mo-Mo moiety.





Figure 1. The structure of the infinite zigzag chain of **3**. Mo: yellow; Pd: green; Cl: orange; F: purple; O: red; N: blue; C: gray.

VIII-C-2 Unique Oxidative Metal–Metal Bond Formation of Linearly Aligned Tetranuclear Rh–Mo–Mo–Rh Clusters

MASHIMA, Kazushi¹; RÜFFER, Tobias²; OHASHI, Masato²; SHIMA, Asuka²; MIZUMOTO, Hitoshi²; KANEDA, Yutaka² (¹IMS and Osaka Univ.; ²Osaka Univ.)

[J. Am. Chem. Soc. 126, 12244–12245 (2004)]

The construction of one-dimensional, covalently bonded metal strings has attracted much interest in view of fundamental bonding nature as well as promising applications as extensive electronic and optoelectronic materials. Two major synthetic approaches to these compounds have been conducted by (a) using polydentate ligands such as oligo- α -pyridylamido ligands or by (b) partial oxidation of d⁸ square-planar complexes to form metal-metal bonds (e.g. platinum blue). Our effort has been focused on aligning transition metals by using a tridentate ligand 6-diphenylphosphino-2pyridonate (pyphos), in which three different elements, P, N, and O, were linearly laid out by the rigid pyridone framework and could act as coordination sites for arrangement of more than two kinds of transition metals in linear manner. And we have demonstrated linear hetelometallic clusters containing both group VI and group X metals by use of the quadruply-bounded dimolybdenum(II) complex, $Mo_2(pyphos)_4$ (1) as a core part of metal strings such as $Mo_2Pd_2Cl_2(pyphos)_4(2)$.

As the next stage of our continuous study, we confronted the synthesis of a new series of heterometallic tetranuclear clusters containing group IX metals with appropriate geometries of square planar as well as octahedral to be supported by the two PPh₂ groups. Herein we report the synthesis of linearly aligned tetranuclear complexes bearing the Rh–Mo–Mo–Rh array (equaition 2) and their unique oxidative reaction (equation 3). We found that rhodium metals at both axial positions of the Mo_2 in 4 electronically communicated through the Mo_2 core and, as a result, oxidative reaction Rh(I)/Rh(II) induced the formation of metal-metal bonds.



VIII-D Development of New Transformations Based on a Chelation-Assistance

We have developed a series of catalytic reactions, which involve the facile cleavage of unreactive bonds, such as C–H, C–C, C–F, and C–O bonds by taking advantage of the coordination of the directing group on the transition metals. Heteroatoms, such as carbonyl oxygen or sp^2 nitrogen, function as the directing group, and the coordination of the directing group to transition metals is a key step in those catalytic reactions. Various combination of directing group and catalysts would be expected to be available.

VIII-D-1 Ruthenium-Catalyzed C-H/CO/Olefin Coupling Reaction of *N*-Arylpyrazoles. Extraordinary Reactivity of *N*-Arylpyrazoles toward Carbonylation at C–H Bonds

ASAUMI, Taku²; CHATANI, Naoto¹; MATSUO, Takuya²; KAKIUCHI, Fumitoshi²; MURAI, Shinji² (¹IMS and Osaka Univ.; ²Osaka Univ.)

[J. Org. Chem. 68, 7538–7540 (2003)]

The reaction of 1-arylpyrazoles with CO and ethylene in the presence of $Ru_3(CO)_{12}$ resulted in regioselective carbonylation at the ortho C–H bonds. While it is found that the pyrazole ring also functions as the directing group for C–H bond cleavage, the efficiency of the reaction depends on position of the pyrazole ring.

VIII-D-2 A Chelation- Assisted Hydroesterification of Alkenes Catalyzed by Rhodium Complex

YOKOTA, Kazuhiko²; TATAMIDANI, Hiroto²; KAKIUCHI, Fumitoshi²; CHATANI, Naoto¹ (¹IMS and Osaka Univ.; ²Osaka Univ.)

[Org. Lett. 5, 4329–4331 (2003)]

The hydroesterification of alkenes with 2-pyridylmethanol catalyzed by $Rh_4(CO)_{12}$ is described. The reaction is accelerated by the presence of a pyridine ring in the alcohol. The reaction is applicable to various alkenes, both terminal and internal alkenes.

VIII-D-3 Ruthenium- and Rhodium-Catalyzed Direct Carbonylation of the *Ortho* C–H Bonds in the Benzene Ring of *N*-Arylpyrazoles

ASAUMI, Taku²; MATSUO, Takuya²; FUKUYAMA, Takahide²; IE, Yutaka²; KAKIUCHI, Fumitoshi²; CHATANI, Naoto¹ (¹IMS and Osaka Univ.; ²Osaka Univ.)

[J. Org. Chem. 69, 4433-4440 (2004)]

The direct carbonylation of C–H bonds in the benzene ring of *N*-phenylpyrazoles *via* catalysis by ruthenium or rhodium complexes is described. The reaction of *N*-phenylpyrazoles with carbon monoxide and ethylene in the presence of $Ru_3(CO)_{12}$ or $Rh_4(CO)_{12}$ resulted in the siteselective carbonylation of the *ortho* C–H bonds in the benzene ring to give the corresponding ethyl ketones. A variety of functional groups on the benzene ring can be tolerated. *N*-Phenylpyrazoles have higher reactivities than would be expected, based on the pK_a values of the conjugate acid of pyrazole. The choice of solvent for this reaction is significant, and *N*, *N*-dimethylacetamide (DMA) gives the best result.

VIII-D-4 Catalytic Cross-Coupling Reaction of Esters with Organoboron Compounds and Decarbonylative Reduction of Esters with HCOONH₄: A New Route to Acyl Transition Metal Complexes through the Cleavage of Acyl-Oxygen Bonds in Esters

TATAMIDANI, Hiroto²; YOKOTA, Kazuhiko²; KAKIUCHI, Fumitoshi²; CHATANI, Naoto¹ (¹IMS and Osaka Univ.; ²Osaka Univ.)

[J. Org. Chem. 69, 5615–5621 (2004)]

The Ru₃(CO)₁₂-catalyed cross-coupling reaction of esters with organoboron compounds leading to ketones is described. A wide variety of functional groups can be tolerated under the reaction conditions. Aromatic boronates function as a coupling partner to give aryl ketones. Acyl-alkyl coupling to dialkyl ketones is also achieved by the use of 9-alkyl-9-BBN in place of boronates. The Ru₃(CO)₁₂-catalyzed decarbonylative reduction of esters with ammonium formate (HCOONH₄) leading to hydrocarbons is also described. No expected aldehydes are produced, and controlled experiments indicate that aldehydes are not intermediate for the transformation. A hydrosilane can also be used as a reducing reagent in place of HCOONH₄. A wide variety of functional groups are compatible for both reactions. The key step for both catalytic reactions is the directing grouppromoted cleavage of an acyl carbon-oxygen bond in esters, leading to the generation of acyl transition metal alkoxo complexes.

VIII-E Development of Metal-Conjugated Multi-Electron Redox Systems in Metal-Dixolene Complexes

Dioxolenes act as a versatile electron-acceptor or -donor through the reversible two-electron redox reactions among the three oxidation states of catechol (Cat), semiquinone (SQ), and quinine (Q). The dioxolene ligands offer a wide range of the metal complexes with a unique metal-conjugated intramolecular electron transfer, which is a fascinating nature to design electrocatalysts and electronic molecular devices. The ruthenium-terpyridine-dioxolene complexes exhibit the reversible two-electron redox behavior and each oxidation state has been recognized as a resonance hybrid on account of the accessible redox potentials between the metal center and the dioxolene ligand. Ferrocene-attached dixolenes through π -conjugation provide a three-electron redox system, in which a new redox state of the ferrocenyl moiety is combined with the general two-electron redox reaction of the dioxolene moiety. The new oxidation state would be noninnocent, because the redox potentials of both moieties are close. Here we report the syntheses of a new ferrocene-attached dixolene ligand and its ruthenium-terpyridine complex, and the metalconjugated three reversible redox behavior.

VIII-E-1 Syntheses of Ferrocenylcatechol and Its Ruthenium-Terpyridine Complex and the Metal-Conjugated Redox Behavior

KURIHARA, Masato¹; OHIZUMI, Tomohiro²; SAKAMOTO, Masatomi²; WADA, Tohru; TANAKA, Koji

(¹IMS and Yamagata Univ.; ²Yamagata Univ.)

A ferrocene-attached dixolene, 4-ferrocenycatechol (Fc-CatH₂), and its ruthenium-acetato-terpyridine complex, [Ru^{II}(OAc)(SQ-Fc)(ph-terpy)] (1), were synthesized (Figure 1), where ph-terpy and SQ-Fc are 4'phenyl-2,2':6',2"-terpyridine and 4-ferrocenyl-1,2benzosemiquinone, respectively. The cyclic voltammogram of 1 shows three reversible redox waves at $E_{1/2}$ = -0.95, -0.15, and 0.40 V vs. Ag/Ag⁺, and the three redox couples correspond to $(1^{-}/1)$, $(1/1^{+})$, and $(1^{+}/1^{2+})$, respectively, based on the rest potential (-0.22 V) of 1. The UV-Vis-NIR absorption spectra of 1^- , 1, 1^+ , and 1^{2+} were investigated by controlled potential electrolyses at -1.30, -0.33, 0, and 0.50 V, respectively. The specific absorption of 1 in near-IR region was derived from superposition of two bands at 862 and 1015 nm. The higher energy band is similar to that of [Ru^{II}(OAc)] (SQ)(terpy)] (2) (SQ = 1,2-benzosemiquinone and terpy = 2,2':6',2''-terpyridine) at 878 nm, which is assigned to a metal-to-ligand charge transfer (MLCT) band (Ru(II) to SQ). This fact suggests that 1 has a similar structure, [Ru^{II}(OAc)(SQ-Fc)(ph-terpy)], to 2. The additional near-IR band is ascribable to another MLCT band (Fe(II) of the ferrocenyl group to SQ). In the absorption spectrum of 1^+ , an intense band at 674 nm appeared and the maximal wavelength is shifted to a lower energy region than that of the MLCT band (Ru(III) to SQ) in $[Ru^{III}(OAc)(SQ)(terpy)]^+$ (2⁺) at 556 nm. On the other hand, the absorption maximum at 1280 nm of a MLCT band in 1^+ is also shifted to a lower energy region compared with that (Fe(II) to SQ) of 1. The significant lower energy shift of the MLCT bands is understandable by consideration of the metal-conjugated resonance between Ru(III)-SQ-Fc \rightleftharpoons Ru(II)-Q-Fc \rightleftharpoons Ru(II)-SQ- Fc^+ (Q = 1,2-benzoquinone and $Fc^+ = Fe(III)$ form). The contribution of Ru(II)-SQ-Fc⁺ and Ru(II)-Q-Fc structures in 1^+ is responsible for the lower energy shift of the former and the latter MLCT bands, respectively.



Figure 1. The structure of 1.

VIII-F Reduction of CO₂ and Oxidation of Organic Molecules Aiming at Energy Conversion between Chemical Energy and Electricity

Electro- and photochemical reduction of CO₂ affording methanol has become crucial issue in line with the progress of fuel energy cells using methanol. Carbon dioxide easily forms η^{1-} and $\eta^{2-}CO_{2}$ adducts by the reaction with coordinatively unsaturated low-valent metal complexes. Metal complexes with $\eta^{1-}CO_{2}$ in protic media are smoothly converted to the corresponding metal-CO ones, which undergo reductive cleavages of the M–CO bonds by accumulation of electrons at the metal centers under electrolysis conditions. A number of metal complexes have proven to catalyze reduction of CO₂ to CO, but the process prevents the CO ligand from hydrogenation leading to methanol formation. To achieve electrochemical reduction of the carbonyl ligand derived from CO₂, we are designing new types of metal complexes that can provide electrons to carbonyl carbon through redox active ligands without increasing electron densities in the metal centers.

Metal complexes that have an ability to oxidize organic molecules at potentials more negative than the reduction potential of dioxygen enable the direct conversion from chemical energy of organic molecules to electricity. Metal-oxo complexes are possible candidates for the smooth oxidation of organic molecules, since metal-oxo species are believed to work as active centers in various metal enzymes, which oxidize various biological substrates under very mild conditions. Mechanistic understandings of the reactivity of metal-oxo species are limited because of the difficulty of selective formation of reactive M–O frameworks in artificial systems. On the other hand, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the corresponding Ru-OH₂ ones, and have proven to work as oxidants of organic molecules. We have succeeded smooth and reversible conversion between aqua and oxo ligands on Ru-dioxolene frameworks without using any oxidants by taking advantage of dioxolene as a redox active ligand. Along this line, we have been preparing a variety of metal-aqua complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal-oxo forms.

VIII-F-1 Regulation of Electron Donating Ability to Metal Center: Isolation and Characterization of Ruthenium Carbonyl Complexes with N,Nand/or N,O-Donor Polypyridyl Ligands

OOYAMA, Dai¹; KOBAYSHI, Takanori; SHIREN, Kazushi; TANAKA, Koji (¹Yamagata Univ.)

[J. Organomet. Chem. 665, 107–113 (2003)]

Polypyridyl ruthenium(II) dicarbonyl complexes with an N,O- and/or N,N-donor ligand, [Ru(pic)(CO)₂ Cl₂]⁻ (1), [Ru(bpy)(pic)(CO)₂]⁺ (2), [Ru(pic)₂(CO)₂] (3), and [Ru(bpy)₂(CO)₂]²⁺ (4) (pic = 2-pyridylcarboxylato, bpy = 2,2'-bipyridine) were prepared for comparison of the electron donor ability of these ligands to the ruthenium center. Salts of complexes 1 and 2 were characterized by x-ray crystallography. A carbonyl group of [Ru(L1)(L2)(CO)₂]^{*n*+} (L1, L2 = bpy, pic) successively reacted with one and two equiv of OH⁻ to form [Ru(L1)(L2)(CO)(C(O)OH)]^{(*n*-1)+} and [Ru(L1) (L2)(CO)(CO₂)]^{(*n*-2)+} (eq 1).

$$[\operatorname{Ru}(L1)(L2)(\operatorname{CO})_2]^{n+} \underbrace{\operatorname{OH}}_{H^+} [\operatorname{Ru}(L1)(L2)(\operatorname{CO})(\operatorname{CO})\operatorname{OH})]^{(n-1)+} \\ \underbrace{\operatorname{OH}}_{H^+} [\operatorname{Ru}(L1)(L2)(\operatorname{CO})(\operatorname{CO}_2)]^{(n-2)+} (1)$$

These three complexes exist as equilibrium mixtures in aqueous solutions and the equilibrium constants were determined potentiometrically. Electrochemical reduction of 2 in CO₂-saturated CH₃CN-H₂O at -1.5 V selectively produced CO.

VIII-F-2 Mono-Dithiolene Molybdenum(IV) Complexes of *cis*-1,2-Dicyano-1,2-Ethylene-Dithiolate (mnt^{2–}): New Models for Molybdenum Enzymes

SUGIMOTO, Hideki; SHIREN, Kazushi; TSUKUBE, Hiroshi; TANAKA, Koji

[Eur. J. Inor. Chem. 14, 2633–2638 (2003)]

New mono-dithiolene Mo(IV) complexes of cis-1,2dicyano-1,2-ethylenedithiolato [(mnt)²⁻] were synthesized as models for Mo enzymes, with 4,4'-di-tertbutyl-2,2'-bipyridine (Bu₂bpy) and, N,N'-tetraethylethylenediamine (Et₄en) as ancillary ligands, and characterized by IR, UV/visible, elemental anal., ESI-mass and electrochemical techniques. The temperature dependent ¹H NMR spectra, recorded in CD₃CN solution, indicated that [MoO(mnt)(Bu₂bpy)] (1) has a rigid structure but [MoO(mnt)(Et₄en)] (2) showed dynamic conformational inversion processes involving the chelating ethylenediamine unit. The complexes exhibited different reactivity toward O₂: 1 gave a single oxobridged dimolybdenum dimer complex [Mo₂O₃(mnt)₂ $(Bu_2bpy)_2$ (3), while 2 did not react with O_2 and kept its mononuclear structure. Both complexes have almost the same redox potential for Mo^{IV/V}, and so the steric bulkiness and conformational dynamics probably cause this marked contrast. The obtained dimolybdenum complex 3 was also structurally characterized and studied, and is a new dimolybdenum complex with one dithiolene per Mo. The crystal structure of the starting complex MoO₂Cl₂(Bu₂bpy) (4) is also reported.

VIII-F-3 Characterization of a Stable Ruthenium Complex with an Oxyl Radical

KOBAYASHI, Katsuaki; OHTSU, Hideki¹; WADA, Tohru; KATO, Tatsuhisa; TANAKA, Koji (¹CREST/JST)

[J. Am. Chem. Soc. 125, 6729-39 (2003)]

The ruthenium oxyl radical complex, [Ru^{II}(trpy) $(Bu_2SQ)O^{\bullet-}]$ (trpy = 2,2':6',2"-terpyridine, $Bu_2SQ =$ 3,5-di-tert-butyl-1,2-benzosemiquinone) was prepared for the first time by the double deprotonation of the aqua ligand of [Ru^{III}(trpy)(Bu₂SQ)(OH₂)](ClO₄)₂. [Ru^{III} (trpy)(Bu₂SQ)(OH₂)](ClO₄)₂ is reversibly converted to [Ru^{III}(trpy)(Bu₂SQ)(OH⁻)]⁺ upon dissociation of the aqua proton (p K_a 5.5). Deprotonation of the hydroxo proton gave rise to intramolecular electron transfer from the resultant O²⁻ to Ru-dioxolene. The resultant [Ru^{II} (trpy)(Bu₂SQ)O^{•-}] showed antiferromagnetic behavior with a Ru^{II}-semiquinone moiety and oxyl radical, the latter of which was characterized by a spin trapping technique. The most characteristic structural feature of $[Ru^{II}(trpy)(Bu_2SQ)O^{\bullet-}]$ is a long Ru–O bond length (2.042(6) Å) as the first terminal metal–O bond with a single bond length. To elucidate the substituent effect of a quinone ligand, [Ru^{III}(trpy)(4ClSQ)(OH₂)](ClO₄)₂ (4ClSQ = 4-chloro-1, 2-benzosemiquinone) was prepared and we compared the deprotonation behavior of the aqua ligand with that of [Ru^{III}(trpy)(Bu₂SQ) (OH₂)](ClO₄)₂. Deprotonation of the aqua ligand of [Ru^{III}(trpy)(4ClSQ)(OH₂)](ClO₄)₂ induced intramolecular electron transfer from OH⁻ to the [Ru^{III}(4ClSQ)] moiety affording [Ru^{II}(trpy)(4ClSQ)(OH•)]⁺, which then probably changed to [Ru^{II}(trpy)(4ClSQ)O^{•-}]. The antiferromagnetic interactions (J values) between Ru^{II}semiquinone and the oxyl radical for [Ru^{II}(trpy) $(Bu_2SQ)O^{\bullet-}]$ and for $[Ru^{II}(trpy)(4ClSQ)O^{\bullet-}]$ were 2J = -0.67 cm^{-1} and -1.97 cm^{-1} , respectively.

VIII-F-4 Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand

KOIZUMI, Take-aki; TOMON, Takashi; TANAKA, Koji

[Bull. Chem. Soc. Jpn. 76, 1969–1975 (2003)]

The Ru complexes bearing 1,8-naphthyridine (napy) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. The reaction of [RuCl₂(napy- k^2N ,N')(DMSO)₂] with **2** equiv of AgPF₆ and subsequent addition of LH and CO gave [RuL (napy- k^2N ,N')(CO)](PF₆)_n (**6a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, n = 2; **6b**: L = 2,6-di(2-pyridyl) phenyl, n = 1) *via* [RuL(napy- k^2N ,N')(DMSO)](PF₆)_n (**5a**: L = N-methyl-3,5-di(2-pyridyl)-4-pyridyl, n = 2; **5b**: L = 2,6-di(2-pyridyl)phenyl, n = 1). The crystal structures of **5a** and **6a** show distorted octahedral coordination with the tridentate (N,C,N)-ligand as merfashion, two nitrogens of bidentate napy and the S of DMSO (**5a**) or the C of the CO ligand (**6a**). Detailed expts. for irradn. and variable-temperature ¹H NMR

studies reveal a fluxional process of the chelated napy ligand in solutions.



VIII-F-5 Selective Formation of Inter- and Intramolecular A-D-A π - π Stacking: Solid-State Structures of Bis(pyridiniopropyl)benzenes

KOIZUMI, Take-aki; TSUTSUI, Kanako; TANAKA, Koji

[Eur. J. Org. Chem. 23, 4528-4532 (2003)]

The synthesis and mol. structures of bis(pyridiniopropyl)benzene derivatives $[p-(4-RC_5H_4N^+CH_2CH_2CH_2C_6H_4](X^-)_2 [R = H, X = I (I); R = CMe_3, X = Br (II)] have been investigated. I adopts a linear structure$ in the solid state and the crystal packing geometry canbe defined as isolated triplets formed by the phenylenering of one mol. and two pyridinium rings of two neighboring molecules. In contrast, II has an S-shapedarrangement, and an intramolecular acceptor-donoracceptor triplet is formed among the central phenylenering and two terminal pyridinium rings in the same mol.Such a distinct difference in the crystal structures of Iand II can be ascribed to the substituent on the pyridinium unit. The steric repulsion of the bulky*tert*-Bu group $hinders internal. A-D-A <math>\pi$ - π stacking.

VIII-F-6 Equilibrium of Low- and High-Spin States of Ni(II) Complexes Controlled by the Donor Ability of the Bidentate Ligands

OHTSU, Hideki¹; TANAKA, Koji (¹*IMS, CREST/JST*)

[Inorg. Chem. 43, 3024–30 (2004)]

Low-spin nickel(II) complexes containing bidentate ligands with modulated nitrogen donor ability, $Py(Bz)_2$ or MePy(Bz)₂ ($Py(Bz)_2 = N,N$ -bis(benzyl)-N-[(2pyridyl)methyl]amine, MePy(Bz)₂ = N,N-bis(benzyl)-N-[(6-methyl-2-pyridyl)methyl]amine), and a β -diketonate derivative, tBuacacH (tBuacacH = 2,2,6,6-tetramethyl-3,5-heptanedione), represented as [Ni(Py(Bz)_2) (tBuacac)](PF₆) (1) and [Ni(MePy(Bz)_2)(tBuacac)](PF₆) (2) have been synthesized. In addition, the corresponding high-spin nickel(II) complexes having a nitrate ion, [Ni(Py(Bz)_2)(tBuacac)(NO₃)] (3) and [Ni(MePy(Bz)_2) (tBuacac)(NO₃)] (4), have also been synthesized for comparison. Complexes 1 and 2 have tetracoordinate low-spin square-planar structures, whereas the coordination environment of the nickel ion in 4 is a hexacoordinate high-spin octahedral geometry. The absorption spectra of low-spin complexes 1 and 2 in a noncoordinating solvent, dichloromethane (CH₂Cl₂), display the characteristic absorption bands at 500 and 540 nm, respectively. On the other hand, the spectra of a CH₂Cl₂ solution of high-spin complexes 3 and 4 exhibit the absorption bands centered at 610 and 620 nm, respectively. The absorption spectra of 1 and 2 in N,N-dimethylformamide (DMF), being a coordinating solvent, are quite different from those in CH₂Cl₂, which are nearly the same as those of 3 and 4 in CH₂Cl₂. This result indicates that the structures of 1 and 2 are converted from a low-spin square-planar to a high-spin octahedral configuration by the coordination of two DMF molecules to the nickel ion. Moreover, complex 1 shows thermochromic behavior resulting from the equilibrium between low-spin square-planar and highspin octahedral structures in acetone, while complex 2 exists only as a high-spin octahedral configuration in acetone at any temperature.

Such drastic differences in the binding constants and thermochromic properties can be ascribed to the enhancement of the acidity of the nickel ion of 2 by the steric effect of the *o*-methyl group in the MePy(Bz)₂ ligand in 2, which weakens the Ni-N(pyridine) bond length compared with that of the nonsubstituted $Py(Bz)_2$ ligand in 1.



VIII-F-7 Acid-Base Equilibria of Various Oxidation States of Aqua-Ruthenium Complexes with 1,10-Phenanthroline-5,6-Dione in Aqueous Media

FUJIHARA, Tetsuaki; WADA, Tohru; TANAKA, Koji

[Dalton Trans. 645–52 (2004)]

Syntheses and pH dependent electrochemical properties of aqua-ruthenium(II) complexes, [Ru(trpy)(PDA-N,N')(OH₂)](ClO₄)₂ ([1](ClO₄)₂) and [Ru(trpy)(PD-N,N')(OH₂)](ClO₄)₂ ([**2**](ClO₄)₂) (trpy = 2,2':6',2"terpyridine, PDA = 6-acetonyl-6-hydroxy-1,10- phenanthroline-5-one, PD = 1,10-phenanthroline-5,6-dione) are presented. Treatment of $[Ru(trpy)(PD-N,N')C1](PF_6)$ with AgClO₄ in a mixed solvent of acetone and H₂O selectively produced the acetonyl-PD complex [1] $(ClO_4)_2$, and the similar treatment in a mixed solvent of 2-methoxyethanol and H_2O gave the PD complex [2] $(ClO_4)_2$. The molecular structures of both complexes were determined by X-ray structural analysis. The proton dissociation constants of various oxidations state of $[1]^{2+}$ and $[2]^{2+}$ were evaluated by simulation of $E_{1/2}$ values of those redox potentials depending on pH. The simulation revealed that the acetonyl-PD complex $[1]^{2+}$ underwent successive Ru(II)/Ru(III) and Ru(III)/Ru(IV)

redox couples though the two redox reactions were not separated in the cyclic voltammograms. The redox behavior of $[2]^{2+}$ in H₂O is reasonably explained by not only the similar successive metal-centered redox reactions but also simultaneous two-electron quinone/ catechol redox couple of the PD ligand including the contribution of hydration on a carbonyl carbon.

VIII-F-8 Syntheses and Electrochemical Properties of Ruthenium(II) Complexes with 4,4'-Bipyrimidine and 4,4'-Bipyrimidinium Ligands

FUJIHARA, Tetsuaki¹; WADA, Tohru; TANAKA, Koji

(¹IMS, CREST/JST)

[Inorg. Chim. Acta 357, 1205–1212 (2004)]

The syntheses and electrochem. properties of novel ruthenium(II) polypyridyl complexes with 4,4'bipyrimidine, [Ru(trpy)(bpm)Cl](X) ([1](X; X = PF₆⁻, BF₄⁻)) and with a quaternized 4,4'-bipyrimidinium ligand, [Ru(trpy)(Me₂bpm)Cl](BF₄)₃ ([2](BF₄)₃, trpy = 2,2':6',2"-terpyridine, bpm = 4,4'-bipyrimidine, Me₂ bpm = 1,1'-dimethyl-4,4'-bipyrimidinium) are presented. The bpm complex [1]⁺ was prepared by the reaction of Ru(trpy)Cl₃ with 4,4'-bipyrimidine in EtOH/H₂O. The structural characterization of [1]⁺ revealed that the bpm ligand coordinated to the ruthenium atom in a bidentate fashion. Diquaternization of the noncoordinating nitrogen atoms on bpm of [1]⁺ by Me₃OBF₄ in CH₃ CN gave [2](BF₄)₃. The electrochemical and spectroelectrochemical properties of the complexes are described.

VIII-F-9 Strong Interaction between Carbonyl and Dioxolene Ligands Caused by Charge Distribution of Ruthenium-Dioxolene Frameworks of Mono- and Dicarbonylruthenium Complexes

WADA, Tohru; FUJIHARA, Tetsuaki¹; TOMORI, Mizuno²; OOYAMA, Dai²; TANAKA, Koji (¹IMS, CREST/JST; ²Fukushima Univ.)

[Bull. Chem. Soc. Jpn. 77, 741-749 (2004)]

Monocarbonylruthenium complexes with a semiquinone ligand, $[Ru(CO)(sq)(L)]^{n+}$ (sq = 3,5-di-tertbutyl-1,2-benzosemiquinone, n = 1 or 0, L = 2,2':6',2''terpyridine ([**1**]⁺), 2,6-bis(*N*,*N*-dimethylaminomethyl) pyridine ($[2]^+$), 2,6-di-2'-pyridylphenyl ($[3]^0$), or 2-(2,2'-bipyridin-6-yl)phenolato ([4]⁰)), and dicarbonylruthenium complexes with two semiquinone ligands, $[Ru(CO)_2(sq)_2]$ ([5]⁰) and $[Ru(CO)_2(phsq)_2]$ (phsq = 9,10-phenanthrasemiquinone, $[6]^{0}$, were synthesized and the structures of $[1]^+$ and [6] were determined by xray crystal anal. Monocarbonyl Ru(II)-dioxolene complexes displayed the ligand localized catecholato/ semiguinone and semiguinone/quinone redox couples, and two sets of those redox couples were obsd. in the dicarbonyl Ru(II)-bis(dioxolene) complexes. Spectroelectrochemical study revealed that the Ru(II)-catecholato and Ru(II)-semiquinone complexes were stable in

solutions, while the Ru(II)-quinone complexes underwent fragmentation in solutions. One-electron reduction of the monocarbonyl Ru(II)-semiquinone complexes caused a red shift of the v(CO) bands at 41–56 cm⁻¹, which was substantially larger than those of carbonyl Ru(II)-polypyridyl complexes. Two v(CO) bands of dicarbonyl Ru(II)-bis(semiquinone) complexes also shifted to lower wavelength at 53–99 cm⁻¹ upon two electron reduction of the complexes. The unusually large red shift of v(CO) bands upon redn. of carbonyl Ru(II)-dioxolene complexes compared with those of Ru(II)-polypyridyl complex is ascribed to a strong electronic interaction between carbonyl and dioxolene ligands.

VIII-F-10 Synthesis and Crystal Structures of Mono- and Dinuclear Silver(I) Complexes Bearing 1,8-Naphthyridine Ligand

KOIZUMI, Take-aki; TANAKA, Koji

[Inorg. Chim. Acta 357, 3666–3672 (2004)]

Mononuclear and dinuclear silver(I) complexes bearing 1,8-naphthyridine (napy) were prepd. The crystal structures of $[Ag(napy-\kappa N)_2](PF_6)$ (1) and $[Ag_2(\mu-napy)_2](PF_6)_2 \cdot 3CH_3CN (2 \cdot 3CH_3CN)$ were determined by X-ray diffraction studies. In complex 1, intermol. π - π interaction of napy ligands between neighboring molecules forms left-handed hexagonal columns in the solid state. On the other hand, two napy ligands bridging two Ag ions in the dinuclear complex 2 shape a face-to-face π - π stacking with those of the neighboring molecule to form the dimeric unit. Besides, two of four napy ligands, which are located in a diagonal position in the dimeric unit, build intermolecular back-to-back π - π stackings with those of the adjacent dimeric unit, and a ladder-like stairway structure is generated in the solid state. Irrespective of such characteristic structures of 1 and 2 in the solid state, both complexes show very rapid dynamic behavior in solutions. No conversion between 1 and 2 took place even in the presence of excess amts. of Ag⁺ or napy in solutions.



VIII-G Silanechalcogenolato Complexes

The development of synthetic routes to mixed-metal chalcogenido clusters is a critical prerequisite for study of these important materials. It is well known that $(Me_3Si)_2E$ (E = S, Se, Te) is a good chalcogen transfer reagent, which can replace a halide, alkoxide, acetate, and oxide with a chalcogen ligand by taking advantage of formation of Si–Cl and Si–O bonds. Therefore the corresponding M–ESiMe₃ species hold great promise for synthetic precursors of chalcogenido clusters. One of the important advantages of using this system is the possibility of controlling cluster-forming reactions by the choice of steric and electronic properties of the substituents on silicon. This approach has been widely used in organic syntheses, where silyl groups have proven to be useful as protecting agents of functional groups under various conditions. However, because of the high lability of Si–E bond, there is a strong tendency to restrict the use of silanechalcogenolato complexes. In this project, we have studied chemistry of silanechalcogenolato complexes, aiming at developing the rational synthesis of chalcogenido clusters.

VIII-G-1 Synthesis and Structural Characterization of Silanethiolato Complexes Having *tert*-Butyldimethylsilyl and Trimethylsilyl Groups

KOMURO, Takashi¹; MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki; TATSUMI, Kazuyuki¹ (¹Nagoya Univ.)

[Dalton Trans. 1618–1625 (2004)]

Treatment of cyclotrisilathiane (Me₂SiS)₃ with 3 equiv of RLi (R = Me, Bu^t) in hexane-Et₂O afforded the lithium silanethiolates LiSSiMe₂R, and the tmeda adduct [(tmeda)LiSSiMe₂Bu^t]₂ 1 (tmeda = N, N, N', N'tetramethylethylenediamine) was isolated in the case of $R = Bu^t$. Reaction of Fe(CH₃CN)₂(CF₃SO₃)₂, CoCl₂, and $[Cu(CH_3CN)_4](PF_6)$ with 1 gave rise to the silanethiolato complexes $M(SSiMe_2Bu^t)_2(tmeda)$ (M = Fe 2, Co 3), and $[Cu(SSiMe_2Bu^t)]_4$ 4, respectively. Complexes $(C_5H_5)_2Ti(SSiMe_2R)_2$ (R = Me 5, Bu^t 6) and $Ni(SSiMe_2R)_2(dppe)$ [R = Me 7, Bu^t 8; dppe = 1,2bis(diphenylphosphino)ethane] were prepared from treatments of $(C_5H_5)_2TiCl_2$ and $NiCl_2(dppe)$ with the corresponding lithium silanethiolates. Complex 7 readily reacted with (C₅H₅)TiCl₃ to produce the Ti-Ni heterobimetallic compound $(C_5H_5)TiCl(\mu-S)_2Ni(dppe)$ 9, in which silicon–sulfur bond cleavage took place.



Reagents and conditions: i) $Fe(CH_3CN)_2(CF_3SO_3)_2$, CH_3CN , rt; ii) $CoCl_2$, THF, rt; iii) $[Cu(CH_3CN)_4](PF_6)$, CH_3CN , 0 [°]C; iv) $(C_3H_3)_2TiCl_2$, Er_2O -toluene or THF, 0 [°]C or rt; v) $NiCl_2(dppe)$, Er_2O -THF or THF, 0 [°]C; vi) $(C_3H_3)TiCl_3$, toluene, rt.

VIII-H Coordination Chemistry of Sterically Hindered Ligands and Multidentate Ligands, and Activation of Small Molecules

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxide, thiolate, and amidinate. In addition, we set out to study metal complexes with sterically hindered arylthiolate ligands. Our recent efforts have been directed toward activation of small molecules.

VIII-H-1 Aryl-Oxygen Bond Cleavage by a Trihydride-Bridging Ditantalum Complex

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

[J. Am. Chem. Soc. 125, 14254–14255 (2003)]

Treatment of $[Ta(^{I}Bu-L)_2]_2$ with LiBHEt₃ gave $[Ta(^{I}Bu-L)]_2(H)_3Li(thf)_2$ (1). Complex 1 is a Ta(V) dimer, in which two metal center are bridged by three hydride ligands. The formation of 1 is believed to proceed *via* a Ta(III)–Ta(III) intermediate which undergoes intramolecular addition of a methylene CH bond of the

ligand. Complex 1 is thermally unstable and gradually undergoes rearrangement. The first step is likely the migration of one hydride to the methine carbon of the *bit-*^{*i*}Bu-L ligand to form a dihydirde Ta(IV)-Ta(IV)intermediate. Subsequent C–O scission occurs across the metal–metal bond, in which two electrons stored in metal–metal bonding is used to yield an oxo-dihydirde dimer 2. The final formation of 3 requires the migration of two hydrides to a methine and an aryl carbon, respectively. The overall transformation implies an internal redox process and dose not require electrons to be added to or removed from 1.



VIII-H-2 Triple Hydrogen Bridged Dititanium(III) and Dizirconium(IV) Aryloxide Complexes

MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki

[Organometallics 22, 5379–5381 (2003)]

The first example of triple hydrogen bridged dititanium(III) system, $[Li_3(thf)_3][Ti('Bu-L)]_2(\mu-H)_3$ (2) supported by the tridentate aryloxide ligand was synthesized by the reaction of $[Ti('Bu-L)Cl]_2$ (1) with LiBHEt₃ $[H_3('Bu-L) = 2,6$ -bis(4,6-methyl-*tert*-butylsalicyl)-4-*tert*-butylphenol]. On the other hand, the analogous reaction of Zr('Bu-L)Cl(thf)_2 (3) yielded the triple hydrogen bridged dizirconium(IV), $[Li_2Cl(thf)_4]$ $[Zr('Bu-L)]_2(\mu-H)_3$ (4). Structures of 2 and 4 were determined by X-ray crystallography. The titanium dimer adopts a face-sharing bioctahedral geometry with a very short Ti–Ti distance (2.621(1) Å). The diamagnetic nature and the dynamic behavior of 2 in solution were revealed by NMR studies.



VIII-H-3 Formation of an Iron(II) Carbene Thiolato Complex *via* Insertion of Carbon Monoxide into Si–C Bond

YUKI, Masahiro; MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki

[Angew. Chem., Int. Ed. 43, 1404–1407 (2004)]

The reaction of Fe(CF₃SO₃)₂(CH₃CN)₂ with Li₃ $[^{TMS}S_3Si]$ (H₃ $[^{TMS}S_3Si]$ = tris(3-trimethylsiyl-2mercaptophenyl)methylsilane) followed by addition of PPh4Br afforded (PPh₄)[Fe(^{TMS}S₃Si)(thf)] (1). Complex **1** reacted with CO to produce $(PPh_4)[Fe(^{TMS}S_3Si)]$ $(CO)_3$ (2). The carbonyl compound 2 is thermally unstable in solution. Stirring the solution of 2 at room temperature resulted in formation of the carbenethiolato complex 3, in which the insertion of CO into Si-C bond took place. A kinetic study of this reaction showed that this was first order in 2 with the appreciable positive entropy of activation. The crystal structures of 1 and 3 were determined by the X-ray analysis. The most remarkable feature in **3** is that the crystal structure exhibits substantial bonding interaction between the carbene carbon and the thiolato sulfur.


VIII-I Preparation and Properties of the Homo- and Heterometallic Clusters

This project focuses on the development of a systematic synthetic route to a series of the homo- and heterometallic clusters as templates or catalysts for new types of activation and transformation of organic, inorganic, and organometallic molecules at the well-defined multimetallic reaction sites. Especially, preparation and reactivity of dinuclear Ru(II) complexes having the bridging amido ligands has been extensively studied.

VIII-I-1 Reactivity of Amido Ligands on a Dinuclear Ru(II) Center: Formation of Imido **Complexes and C-N Coupling Reaction with** Alkyne

TAKEMOTO, Shin¹; KOBAYASHI, Tomoharu¹; MATSUZAKA, Hiroyuki²

(¹Osaka Prefecture Univ.; ²IMS and Osaka Prefecture Univ.)

[J. Am. Chem. Soc. 126, 10802–10803 (2004)]

Reactions of the dimeric Ru(II) anilido complex $[Cp*Ru(\mu_2-NHPh)]_2$ (1; $Cp* = \eta^5-C_5Me_5$) with CO, tbutyl isocyanide, a sulfur ylide Ph₂S=CH₂, and diphenylacetylene proceeded with an unexpected disproportionation of the u₂-anilido ligands to form free aniline and a series of new imidodiruthenium complexes **3–5** (Scheme 1). In the case of diphenylacetylene, the imido fragment underwent subsequent coupling reaction with the alkyne to produce an iminoalkenyl complex 6.



Existence of a Ru-Ru multiple bond is suggested by

electron counting and the short Ru-Ru distance that is close to those of some other compounds with Ru=Ru double bonds (2.417-2.629 Å). Orbital analysis of a DFT-B3PW91 optimized model compound [(CpRu)₂ $(\mu_2$ -CO) $(\mu_2$ -NH)] (3') has provided inshights into the Ru–Ru bond in 3. Although the first six of HOMOs of 3' are predominantly metal-based orbitals and constitute a formally nonbonded $\sigma^2 \sigma^{*2} \delta^4 \delta^{*4}$ configuration, the multiple bond order between the Ru atoms can be rationalized by back-donation from the filled Ru–Ru σ^* orbital into a π^* orbital of the CO ligand, and by donation from the imido and CO ligands into empty Ru-Ru π -bonding orbitals.

VIII-I-2 A Dinuclear Ru(II) Chelateing Amido Complex: Synthesis, Characterization, and **Coupling Reaction with Carbon Monoxide**

TAKEMOTO, Shin¹; OSHIO, Shinya¹; KOBAYASHI, Tomoharu¹; MATSUZAKA, Hiroyuki²; HOSHI, Masatsugu³; YAMASHITA, Masayo³; MIYASAKA, Hitoshi³; ISHII, Tomohiko³; YAMASHITA, Masahiro³

(¹Osaka Prefecture Univ.; ²IMS and Osaka Prefecture Univ.; ³Tokyo Metropolitan Univ.)

[Organometallics 23, 3587–3589 (2004)]

Results are summarized in Scheme 1. [Cp*RuCl]₄ $(Cp^* = \eta^5 - C_5 Me_5)$ reacts with 2 equiv of dilithium 2,3naphthalenediamide to afford a dinuclear bridging amido complex 7b in moderate yield. Treatment of 7b with CO (1 atm) resulted in the incorporation of three molecules of CO into the diruthenium core to give a carbamoyl amido bis(carbonyl) complex 8. Similar treatment of 7b with *tert*-butyl isocyanide resulted in the quantitative formation of a bis(isocyanide) complex 10, in which the two amido nitrogen atoms also occupy the terminal and bridging coordination sites.



Schime 1.

VIII-J Synthesis of Transition Metal Complexes Containing a Novel Metal-Silicon and Metal-Gallium Bonding

Synthesis of transition metal complexes with unprecedented bonds between a metal and a heavy main group element is one of current topics on inorganic chemistry. In this project, we have investigated the synthesis, structure, and reactivities of metal complexes containing metal-silicon and metal-gallium unsaturated bonding. We also investigated germylene-bridged diiron complexes having a triplet ground state.

VIII-J-1 Synthesis, Structure, and Reactivity of Cationic Base-Stabilized Gallyleneiron Complexes

UENO, Keiji¹; WATANABE, Takahito²; OGINO, Hiroshi³

(¹IMS and Gunma Univ.; ²Tohoku Univ.; ³Univ. Air)

[Appl. Organomet. Chem. 17, 403–408 (2003)]

Addition of 2,2'-bipyridine (bpy) to an acetonitrile solution of dichlorogallyliron complex FpGaCl₂ (1: Fp = $(\eta - C_5 H_5)Fe(CO)_2$) afforded almost quantitatively a salt consisting of a cationic base-stabilized gallylene complex $[FpGaCl \cdot bpy]^+$ ($[3a]^+$) and an anionic complex $[FpGaCl_3]^-$ ([4]⁻). Reaction of $Fp'GaCl_2$ (Fp' = Fp (1), Fp^* (2); $Fp^* = (\eta - C_5 Me_5)Fe(CO)_2$) with NaBPh₄ in the presence of a bidentate donor (Do2) gave [Fp'GaCl-Do₂]BPh₄ where Do₂ was bpy or 1,10-phenanthroline (phen). These cationic complexes may be useful precursors for the synthesis of gallyleneiron complexes with various substituents on the gallium atom. Indeed, reaction of $[Fp*GaCl phen]BPh_4$ ([**5b**]BPh_4) with NaS^PTol or Me₃SiS^PTol afforded the gallyleneiron complex $[Fp*GaS^{P}Tol \cdot phen]BPh_4$ ([6]BPh_4), the first example of a gallium-transition metal complex having a thiolate group on the gallium atom. The molecular structures of [5b]BPh₄ and [6]BPh₄ were determined by single crystal X-ray diffraction.



VIII-J-2 Synthesis and Structure of the First Dinuclear Complex Bridged by a Substituent-Free Gallium Atom

UENO, Keiji¹; WATANABE, Takahito²; TOBITA, Hiromi²; OGINO, Hiroshi³

(¹IMS and Gunma Univ.; ²Tohoku Univ.; ³Univ. Air)

[Organometallics 22, 4375–4377 (2003)]

The first dinuclear complex bridged by a substituentfree gallium atom, $Cp*Fe(dppe)(\mu-Ga)Fe(CO)_4$ (1, Cp*= η -C₅Me₅, dppe = Ph₂PCH₂CH₂PPh₂), was synthesized by the reaction of Cp*Fe(dppe)GaCl₂ with K₂[Fe (CO)₄]. Crystal structure analysis of complex 1 revealed that the geometry around the gallium atom is essentially linear and the Fe–Ga bonds are significantly shorter than that of usual single bonds. These structural features indicate that the Fe–Ga bonds bear significantly unsaturated character.



VIII-J-3 Direct Evidence for Extremely Facile 1,2- and 1,3-Group-Migrations on an FeSi₂ System

TOBITA, Hiromi¹; MATSUDA, Akihisa¹; HASHIMOTO, Hisako¹; UENO, Keiji²; OGINO, Hiroshi³

(¹Tohoku Univ.; ²IMS and Gunma Univ.; ³Univ. Air)

[Angew. Chem., Int. Ed. 43, 221-224 (2004)]

Photolysis of [Cp'Fe(CO)₂Me] (1a: Cp' = η^5 -C₅Me₅ (Cp*); 1b: Cp' = η^5 -C₅H₅ (Cp)) in the presence of HSi Me₂SiMes₂Me (2; Mes = mesityl (2,4,6-trimethylphenyl)) produced the first donor-free silyl(silylene)iron complexes [Cp'Fe(CO)(=SiMes₂)SiMe₃] (3a: Cp' = Cp*, 60%; 3b: Cp' = Cp, 38% yield, calculated by NMR spectroscopy). Complex 3a was isolated as orange crystals in 40% yield, whereas isolation of 3b was unsuccessful. When 3a was heated to 80 °C for 6 h in the presence of 'BuNC, a disilanyl complex [Cp*Fe (CO)(CN'Bu)SiMesMeSiMesMe₂] (4) was isolated as a main product in 25% yield. These results provide the most straightforward evidence for extremely facile 1,2and 1,3-group migrations of the substituents between two silicon atoms in silyl(silylene) complex systems.



VIII-J-4 Synthesis and Characterization of Triplet Germylene-Bridged Diiron Complexes and Singlet Stannylene-Bridged Diiron Complexes

MOHAMED, Bahaa. A. S.¹; KIKUCHI, Mami¹; HASHIMOTO, Hisako¹; UENO, Keiji²; TOBITA, Hiromi¹; OGINO, Hiroshi³

(¹Tohoku Univ.; ²IMS and Gunma Univ.; ³Univ. Air)

[Chem. Lett. 33, 112-113 (2004)]

Photoreaction of CpFe(CO)₂Me with sterically congested R₂GeH₂ [R = 2,4,6-C₆H₂^{*i*}Pr₃ (Tip), 2,4,6-C₆H₂Me₃ (Mes)] afforded paramagnetic germylenebridged diiron complexes having a triplet ground state, Cp₂Fe₂(μ -CO)₂(μ -GeR₂) (**3a**, R = Tip; **3b**, R = Mes), while the analogous reaction with R₂SnH₂ afforded diamagnetic complexes Cp₂Fe₂(CO)₂(μ -CO)(μ -SnR₂) (*trans*-**5a**, R = Tip; *trans*-**5b**, R = Mes). The structure of **3a** was determined by X-ray crystallography.





trans-5: R = Tip, Mes

RESEARCH ACTIVITIES IX Laser Research Center for Molecular Science

IX-A Developments and Researches of New Laser Materials

Although development of lasers is remarkable, there are no lasers which lase in ultraviolet and far infrared regions. However, it is expected that these kinds of lasers break out a great revolution in not only the molecular science but also in the industrial world.

In this project we research characters of new materials for ultraviolet and far infrared lasers, and develop new lasers by using these laser materials.

IX-A-1 Terahertz Radiation Mechanism from Femtosecond-Laser-Irradiated InAs (100) Surface

TAKAHASHI, Hiroshi¹; QUEMA, Alex; GOTO, Masahiro; ONO, Shingo; SARUKURA, Nobuhiko (¹GUAS)

[Jpn. J. Appl. Phys. 42, L1259 (2003)]

Terahertz (THz) radiation mechanism from femtosecond-laser-irradiated InAs surface is investigated by measuring the excitation-fluence dependence of THzradiation power. It is found that the THz-radiation is mainly generated by the surge-current, which originates from the different diffusion velocities between photoexcited electrons and holes. Furthermore, it is also found that the excitation fluence dependence of THzradiation is categorized into two regions depending on the excitation fluence. At low excitation fluence, a quadratic-dependent enhancement of the THz-radiation power is observed with increasing excitation fluence. In contrast, at high excitation fluence, the enhancement factor is gradually reduced, and the radiation power becomes proportional to a logarithm function of the excitation fluence. These results are explained by considering the photo-Dember field as the THz-radiation source.

IX-A-2 Broadband Terahertz Radiation Emitter Using Femtosecond-Laser-Irradiated *n*-Type InAs under Magnetic Field

TAKAHASHI, Hiroshi¹; HASSELBECK, Michael²; QUEMA, Alex; GOTO, Masahiro; ONO, Shingo; SARUKURA, Nobuhiko (¹GUAS; ²Univ. New Mexico)

[Jpn. J. Appl. Phys. 43, L221 (2004)]

We present the generation of broadband terahertz (THz) radiation using *n*-type InAs irradiated by ultrafast laser pulses. It is found that the high-frequency component of the THz-radiation spectrum originates from the hybrid modes of the plasmons and the longitudinal optical (LO) phonons, whose peak frequency shifts toward higher frequency with increasing doping density. For *n*-type InAs with a doping density of 3.1×10^{17} cm⁻³, the high-frequency components of THz-radiation

spectrum are observed at around 5.5 and 9 THz. Furthermore, the enhancement of THz-radiation power from these hybrid modes is achieved by applying an external magnetic field.

IX-A-3 Teflon Photonic Crystal Fiber as Terahertz Waveguide

GOTO, Masahiro; QUEMA, Alex; TAKAHASHI, Hiroshi; ONO, Shingo; SARUKURA, Nobuhiko

[Jpn. J. Appl. Phys. 43, L317 (2004)]

We demonstrate the construction of reasonably long and non-polarization changing photonic fiber waveguide using Teflon which is a readily available and highly flexible material. Due to its relatively low loss coefficient, the possibility of preparing longer photonic fiber waveguide, which has the potential of guiding intense THz radiation, can be easily attained.

IX-A-4 Growth and Charge Transfer Luminescence of Yb³⁺-Doped YAIO₃ Single Crystals

SHIM, Jan Bo¹; YOSHIKAWA, Akira¹; FUKUDA, Tsuguo¹; PEJCHAL, J.²; NIKL, M.²; SARUKURA, Nobuhiko; YOON, D. H.³

(¹Tohoku Univ.; ²Inst. Phys. ASCR; ³Sungkyunkwan Univ.)

[J. Appl. Phys. 95, 3063 (2004)]

Yb³⁺-doped YAlO₃ single crystals have been grown by the Czochralski method with a radio-frequency heating system. Starting melt compositions of $Y_{1-x}Yb_x$ AlO₃ were varied with x = 0.02, 0.1, 0.2, 0.3, and 0.45. The best Yb³⁺-doped YAlO₃ single crystals were obtained for a growth rate of 1.0 mm/h. The grown crystals were transparent and almost colorless. To investigate the homogeneity, the effective segregation coefficient of the Yb ion was estimated. The absorption, photoluminescence, and luminescence decay kinetics of Yb³⁺-doped YAlO₃ were investigated for the temperature range 4-300 K. Very fast charge transfer luminescence of Yb³⁺ from the near ultraviolet to visible spectral range and the high density of the Yb-rich YAlO₃ makes this material a promising candidate for fast scintillators.

IX-A-5 Terahertz Radiation from InAs with Various Surface Orientations under Magnetic Field Irradiated with Femtosecond Optical Pulses at Different Wavelengths

TAKAHASHI, Hiroshi¹; SAKAI, Masahiro; QUEMA, Alex; ONO, Shingo; SARUKURA, Nobuhiko; NISHIJIMA, Gen²; WATANABE, Kazuo²

(¹GUAS; ²Tohoku Univ.)

[J. Appl. Phys. 95, 4545 (2004)]

We present the magnetic-field dependence of terahertz (THz)-radiation power from femtosecondlaser-irradiated InAs with various surface orientations. Under 800 nm optical excitation, the magnetic field that provides the maximum THz-radiation power is found to be affected by the surface orientation, and InAs(111) exhibits it at lower magnetic fields than that of the other surfaces. In contrast, under 1560 nm excitation, the dependence on the surface orientation almost disappeared, and saturation is observed at a much smaller magnetic field than that in the 800 nm excitation case. Additionally, from the results of magnetic-field dependence up to 14 T, the shift of the peak in the THzradiation spectrum toward lower frequency is confirmed, depending on the magnetic field applied, which is possibly induced by the emergence of a magnetoplasma effect.

IX-A-6 Optical, Infrared and EPR Spectroscopy of CaF₂:Ce³⁺ Crystals Co-Doped with Li⁺ or Na⁺

YAMAGA, Mitsuo¹; YABASHI, Satoshi¹; MASUI, Yuki¹; TAKAHASHI, Hiroshi; SAKAI, Masahiro; SARUKURA, Nobuhiko; WELLS, J. -P. R.²; JONES, G. D.³

(¹Gifu Univ.; ²Univ. Sheffield; ³Univ. Canterbary)

[J. Lumin. 108, 307 (2004)]

Interconfigurational 4f \Leftrightarrow 5d VUV absorption and luminescence, intra-4f¹ IR absorption and X-band EPR measurements have been carried out on CaF₂:Ce³⁺ crystals co-doped with Na⁺ and Li⁺ ions. For both Li⁺ and Na⁺ co-doping, cubic, new tetragonal and rhombicsymmetry centres are observed. Cubic centres, which are readily observable by their infrared transitions, could not be identified and remain elusive in the EPR spectra.

IX-A-7 Effect of Ultrafast Optical Pulses with Different Pulse Duration on the Terahertz Radiation Spectrum of *n*-Type InAs

TAKAHASHI, Hiroshi¹; HASSELBECK, Michael²; QUEMA, Alex; GOTO, Masahiro; ONO, Shingo; SARUKURA, Nobuhiko (¹GUAS; ²Univ. New Mexico)

[Jpn. J. Appl. Phys. 43, L746 (2004)]

Terahertz (THz) radiation from n-type InAs irradi-

ated by ultrafast laser pulses is investigated under the existence of the magnetic field. It is found that the highfrequency component of the THz-radiation spectrum originates from the hybrid modes of the plasmons and the longitudinal optical (LO) phonons, and its intensity can be drastically enhanced by using the laser pulses with duration shorter than the oscillation period of the hybrid modes. Additionally, it is also found that the ratio of THz-radiation power from these two modes can be controlled by adjusting the pulse duration and the magnetic field strength.

IX-A-8 Physical Origin of Magnetically Induced Periodic Structure Observed in Terahertz Radiation Spectrum Emitted from InAs

TAKAHASHI, Hiroshi¹; QUEMA, Alex; GOTO, Masahiro; ONO, Shingo; SARUKURA, Nobuhiko; NISHIJIMA, Gen²; WATANABE, Kazuo² (¹GUAS; ²Tohoku Univ.)

[Jpn. J. Appl. Phys. 43, L1017 (2004)]

Terahertz (THz) radiation from femtosecond-laserirradiated InAs(100) surface is investigated. It is found that THz-radiation spectrum exhibits two inter-related phenomena in a strong magnetic field under the Voigt configuration. The peak shift of THz-radiation spectrum toward lower frequency is observed with increasing magnetic field. Additionally, THz-radiation spectrum is found to posses a periodic structure owing to the interference of THz-radiation pulses from the front and back surfaces of the InAs substrate. The physical origin of the latter phenomenon is discussed by considering the magneto-plasma effect, which affects both real and imaginary parts of refractive index for THz-radiation propagating in a direction perpendicular to the magnetic field.

IX-A-9 Design Proposal of Light Emitting Diode in Vacuum Ultraviolet Based on Perovskite-Like Fluoride Crystals

OUENZERFI, El Riadh¹; ONO, Shingo; QUEMA, Alex; GOTO, Masahiro; SARUKURA, Nobuhiko; NISHIMATSU, Takeshi¹; TERAKUBO, Noriaki¹; MIZUSEKI, Hiroshi¹; KAWAZOE, Yoshiyuki¹; YOSHIKAWA, Akira¹; FUKUDA, Tsuguo¹ (¹Tohoku Univ.)

[Jpn. J. Appl. Phys. 43, L1140 (2004)]

The variation of band gap energy, band structure and lattice constant of mixed LiBaF₃, LiCaF₃ and LiSrF₃ perovskites is studied. The band structure and transition type of these fluorides is predicted by *ab initio* band calculation based on the local density approximation. The design principle of vacuum ultraviolet light emitting diode is proposed. The lattice-matched double-hetero structure of different perovskite-like fluorides is found to be sufficiently feasible to fabricate with direct-band-gap compounds LiBa_xCa_ySr_(1-x-y)F₃ on LiSrF₃.

IX-B Development and Research of Advanced Tunable Solid State Lasers

Diode-pumped solid-state lasers can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Additionally, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. These kinds of advanced tunable solid-state light sources, so to speak "Chroma Chip Lasers," will assist the research of molecular science.

In this projects we are developing Chroma Chip Lasers based on diode-pumped-microchip-solid-sate lasers and advanced nonlinear frequency conversion technique.

IX-B-1 Saturation Factors of Pump Absorption in Solid-State Lasers

SATO, Yoichi; TAIRA, Takunori

[IEEE J. Quantum Electron. 40, 270–280 (2004)]

The precise formulation of the absorption coefficient is investigated, where the saturation factors of absorption for solid-state lasers are defined as depending on the pumping scheme. We also investigated theoretical and experimental evaluations of the pump saturation effect in Nd:YVO4 as an example, and proved the accuracy of this model describing the saturation effect (Figure 1), and the clipping of this effect by laser oscillation (Figure 2). This paper points out the following: even in the case of 1 µm oscillation in neodymium lasers, the selection of pump wavelength results in not only the different absorption cross sections, but also the different characteristics in the saturation of the pump absorption. This influence is especially important in the laser media with a large cross section, such as Nd: YVO₄. For example, in the direct pumping into the emitting levels ${}^{4}F_{3/2}$, the electrons in the laser upper level also connect to the stimulated emission to the ground state, which should not be observed in the conventional pumping into ${}^{4}F_{5/2}$ because of little distribution of the electrons in the ${}^{4}F_{5/2}$.



Figure 1. Absorption coefficient of 1 at.% Nd:YVO₄ in π -polarization as a function of pumping intensity.



Figure 2. Absorption coefficient of 1 at.% Nd:YVO₄ in π -polarization under lasing condition.

IX-B-2 Spectroscopic Properties and Laser Operation of Nd: Y_3 ScAl₄O₁₂ Polycrystalline Gain Media, Solid-Solution of Nd: Y_3 Al₅O₁₂ and Nd: Y_3 Sc₂Al₃O₁₂ Ceramics

SATO, Yoichi; SAIKAWA, Jiro; SHOJI, Ichiro; TAIRA, Takunori; IKESUE, Akio

[J. Ceram. Soc. Jpn. 112, S313–S316 (2004)]

Transparent Nd³⁺-doped Y₃ScAl₄O₁₂ (Nd:Y₃Sc Al₄O₁₂) ceramics with up to 5.0-at.% Nd³⁺-concentration (C_{Nd}) were fabricated by a solid-state reaction method using commercial 4N powders. Spectroscopic properties of this media, such as absorption and emission spectra, the fluorescence lifetime, and the influence of increasing $C_{\rm Nd}$ on these characteristics are discussed. It is shown that high absorption efficiency of the pump radiation that is necessary for efficient operation of a Nd:Y₃ScAl₄O₁₂ microchip laser can be obtained by increasing $C_{\rm Nd}$. One-micron laser operation with 113-mW output power (7.7% optical-to-optical overall efficiency) and 9.6% slope efficiency was demonstrated from a 1.0-mm thick, 5.0-at.% Nd:Y₃Sc Al₄O₁₂ uncoated sample under 808-nm pumping by a Ti:Sapphire laser (Figure 1). Further works are directed toward optimization of the fabricating process in order to reduce the optical losses that are found to increase with increasing $C_{\rm Nd}$.



Figure 1. Output power versus pump power for the Nd: Y_3Sc Al₄O₁₂ ceramics with 1.0 and 5.0-at.% Nd under 808-nm Ti:Sapphire pumping.

IX-B-3 High Energy Optical Parametric Oscillation Using 3-mm-Thick Periodically Poled MgO:LiNbO₃

ISHIZUKI, Hideki; SHOJI, Ichiro; TAIRA, Takunori

[Conf. Lasers Electro-Optics CTuA3 (2004)]

We presented high energy optical parametric oscillation (OPO) using 3-mm-thcik periodically poled MgO:LN (PPMgLN) device. Multipulses of ~10 kV were applied to the crystal at elevated temperature of ~100 °C to fabricate the PPMgLN device.

For OPO experiments, a Q-switched Nd:YAG laser (Spectra-Physics, LAB-170-30) was used as a pump source. The repetition rate was 30 Hz with the pulse width of 15 ns. The cavity length of single resonant OPO was fixed to 35 mm. The 1/e²-diameter of pump beam was set to 2.2 mm. Figure 1 shows the dependence of OPO output energy on input pump energy. The pump threshold was ~3 mJ, and the slope efficiency was 51% for total output (signal of 1.82 µm, idler of 2.56 µm) and 28% for the signal wave only. The maximum total output energy of 22 mJ at the pump energy of 46 mJ was obtained without photorefractive damages. This is the highest energy obtained from QPM-OPO operation using a PPMgLN device even at room temperature. The large-aperture PPMgLN devices would enable us to realize high-energy wavelength conversion, short pulse amplification, and pulse compression.



Figure 1. OPO output energy *vs.* input pump energy. Pump pulse width : 15 ns, Pump rep. rate : 30 Hz, Pump $1/e^2$ -diameter : 2.2 mm.

IX-B-4 Basic Enhancement of the Overall Optical Efficiency of Intracavity Frequency-Doubling Devices for the One-Micron Continuous-Wave Nd:Y₃Al₅O₁₂ Laser Emission

LUPEI, Voicu¹; PAVEL, Nicolaie²; TAIRA, Takunori (¹IAP-NILPRP, Romania; ²IMS and IAP-NILPRP, Romania)

[Appl. Phys. Lett. 83, 3653 (2003)]

Frequency-doubling of the efficient one-micron ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2} \text{ Nd}^{3+}$ lasers is currently the most used method to obtain light into the green region. If the intracavity frequency-doubling method is considered, the laser active material and a nonlinear crystal designed for phase matching conditions are placed in a laser resonator that confines the beam at the fundamental frequency ω inside the resonator, passes it through the doubling crystal and out-couples the frequency-doubled 2ω beam. The second-harmonic (SH) power $P_{2\omega}$ is determined by the intracavity emission intensity of the active material $I_{\omega \text{ int}}$ and by the characteristics of the doubling crystal

$$P_{2\omega} \sim I_{\omega, \text{int}}^{2} \cdot d_{eff}^{2} \ell^{2} / (n_{1}^{2} n_{2})$$
(1)

where d_{eff} is the effective nonlinear coefficient along the phase matching direction, l is the length of the nonlinear crystal and n_1 and n_2 are the refractive indices at the fundamental and SH wavelengths, respectively. The overall optical-to-optical efficiency of such a laser, i.e. the output power $P_{2\omega}$ obtained for a given pump power $P^{(j)}$, where j = i denotes the pump power incident on the laser material and j = ab denotes the absorbed power, can be optimized acting on these factors. In this work we discuss the possibility of basic enhancement of the overall optical-to-optical efficiency of intracavity frequency-doubling devices for the one-micron continuous-wave Nd lasers by direct pumping into the emitting level and by using concentrated laser materials.

The continuous wave (CW) Nd lasers are usually pumped using the strong absorption Nd^{3+} lines to energy levels placed above the emitting level ${}^{4}F_{3/2}$ and the absorbed excitation relaxes to the emitting level through electron-phonon interactions. Thus, the upper quantum defect between the pump level and the emitting level reduces the performances of the laser emission and contributes to the generation of heat. The upper quantum defect can be eliminated by pumping directly into the emitting level ${}^{4}F_{3/2}$: this modality of pumping was suggested in the first work on semiconductor diode excitation of Nd³⁺ emission¹⁾ and it was used in the first diode laser pumped Nd:YAG both in transverse and end-pumped configurations.^{2),3)} However, owing to the weak absorption into the level ${}^{4}F_{3/2}$ of Nd³⁺ in YAG, this was soon replaced by diode laser pumping at 808 nm into the strongly absorbing level ⁴F_{5/2}. The direct pumping of CW Nd lasers into the emitting level was reconsidered recently for Nd: YAG crystals and ceramics^{4),5)} as well as for other laser materials, such as Nd:YVO44),6) or Nd:GdCa4O $(BO_3)_3.7)$

A problem of concern in using the direct pumping into the emitting level is the low absorption η_a in some of the important laser materials, including Nd:YAG, for concentrations C_{Nd} around 1-at.% Nd that are traditionally used for construction of lasers. This could be overcome by using more concentrated materials. By estimating the quantum efficiency η_{qe} using the energy transfer data at low inversion, specific to the CW Nd: YAG lasers, it was shown that the product $\eta_a \eta_{qe}$ increases with $C_{\rm Nd}$ up to a critical value then decreases again.⁵⁾ The range of CNd for which this product is larger than for 1-at.% Nd could be quite wide: up to 8.0at.% for Nd:YAG and up to 3.0-at.% for Nd:YVO₄. Thus, working at the upper $C_{\rm Nd}$ limit would benefit both from a low threshold and from increased slope efficiency.

According to Eq. (1), the enhancement of the laser emission parameters at the frequency ω by direct pumping will be accentuated in the frequency-doubling device, resulting in a lower threshold for the SH emission and in a stronger dependence on the absorbed pump power. These concepts are investigated in this work by using 1.0-at.% and 2.4-at.% Nd:YAG crystals.

The frequency doubling is investigated with a Vtype folded laser resonator (Figure 1). The 3-mm long Nd:YAG crystals were coated as anti-reflection for 1064 nm and high transmission for 808 and 885 nm. A Ti:Sapphire laser whose radiation was focused into the crystals in a spot of 50-µm diameter was used for pumping. The M1 to M2 resonator arm is 70-mm long and contains also a Brewster glass plate (BP) to polarize the beam. The length of the M2 to M3 frequencydoubling arm was 55 mm and houses a 10-mm long LBO nonlinear crystal designed for type I critical phase matching condition ($\theta = 90^\circ$, $\phi = 11.4^\circ$) at 25 °C.

The 532-nm output power for the 1.0-at.% Nd:YAG crystal is shown in Figure 2. The threshold of green radiation is greatly reduced at 885 compared to 808-nm pumping (26 and respectively 50 mW), while the dependence on the absorbed power is enhanced. Moreover, the emission under 808-nm pumping shows signs of saturation induced by thermal effects in Nd:YAG for green emission larger than ~14 mW. The 532-nm emission under 885-nm pumping does not show such behavior even at the 20 mW obtained for the available absorbed power. As indicated by Figure 3a, the use of a more concentrated (2.4-at.% Nd) active crystal improves the 885-nm pump absorption efficiency, but increases the emission threshold in absorbed power, without changing the slope efficiency. However, the SH power obtained with this sample for a given incident power is larger (Figure 3b). Further improvement could be obtained with a longer active laser crystal and/or a higher C_{Nd} .

In conclusion this work demonstrates the advantages of using direct pumping into the emitting level and of more concentrated laser materials in intracavity frequency-doubling devices based on the 1064-nm CW laser emission of Nd:YAG. The improvement of emission parameters is accompanied by a drastically reduction of generation of heat that could enable scaling to higher emission powers. This approach could be particularly important for laser materials with higher absorption cross-section for the direct pumping.

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Figure 1. Schematic of the V-type resonator used in intracavity frequency-doubling experiments.



Figure 2. Green power *vs.* absorbed power for the 1.0-at.% Nd:YAG crystal under 808 and 885-nm pumping.



Figure 3. Green power for the 1.0 and 2.4-at.% Nd:YAG crystals under 885-nm pumping function of (a) absorbed, and (b) input power.

IX-B-5 High-Power Blue Generation from a Periodically Poled MgO:LiNbO₃ Ridge-Type Waveguide by Frequency Doubling of a Diode End-Pumped Nd:Y₃Al₅O₁₂ Laser

IWAI, Makato¹; YOSHINO, Takeshi¹; YAMAGUCHI, Shoichiro¹; IMAEDA, Minoru¹; PAVEL, Nicolaie²; SHOJI, Ichiro; TAIRA, Takunori

(¹NGK, Nagoya; ²IMS and IAP-NILPRP, Romania)

[Appl. Phys. Lett. 83, 3659 (2003)]

Continuous-wave (CW) blue laser radiation is of interest for various applications, such us display technologies, obtaining of high-density optical disk systems, high-resolution printing, or biological application. In order to obtain the blue light at 473 nm the secondharmonic generation (SHG) of the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition at 946 nm of Nd³⁺:Y₃Al₅O₁₂ (Nd:YAG) can be used. An attractive method to realize a compact bluelight source is SHG by quasi-phase matching (QPM) interaction: LiNbO₃ (LN), LiTaO₃ and KTiOPO₄ are in present widely known and used for fabricating of QPM devices. CW blue light at 473 nm of 81 mW was generated for a fundamental power of 1.13 W in a 15-mmlong periodically poled (PP) LiNbO₃ that operated at an elevated temperature of 140 °C.1) When using a PP KTiOPO₄ pumped at room temperature by a 946-nm Nd:YAG laser maximum blue power of 76 mW was obtained for 2.27 W of fundamental power.²⁾

Due to its high conversion efficiency, a waveguidetype QPM SHG device is a very promising solution for a compact blue-light source. The key points for obtaining efficient and high-power SHG waveguide devices include strong confinement of the fundamental light into the waveguide, good overlap of fundamental and second-harmonic modes, prevention of nonlinear properties degradation, maintaining of a high optical-damage resistance, particularly in the shorter wavelength region. MgO:LiNbO₃ (MgO:LN) was demonstrated to be a good nonlinear material for blue generation: compared with non-doped LN, it presents higher resistance to photorefractive damage, decreased coercive field and a large nonlinear coefficient $d_{33} \sim 25 ~(\pm 2.5) \text{ pm/V}.^{3),4)}$ CW blue power of 17.3 mW at 426 nm was demonstrated from a AlGaAs laser diode with 55-mW output power by using a MgO:LN proton-exchanged waveguide.⁵⁾ However, these waveguides has some limitations, such as mode field mismatching caused by dispersion and refractive index profiles, a trade-off between index change and nonlinearity⁶⁾ that degrades to about 90% of the original d_{33} value even after annealing.

In order to overcome these problems a fabrication process for realizing high efficiency and high power SHG waveguide devices by bonding and ultra-precision machining techniques was introduced by our group: thus, a ridge-type waveguide QPM-SHG MgO:LN device that preserves the original performances of the nonlinear crystal can be obtained. This research reports on our efforts toward scaling blue light obtained by frequency-doubling from a PP MgO:LN ridge-type waveguide using a diode end-pumped Nd:YAG laser operating at 946 nm as a fundamental source.

Based on the relation between the wavelength tuning of SHG and the periodicity of domain-inverted regions, a ridge-type MgO:LN waveguide of 4.6 µm periodicity was fabricated by ultra-precision machining to generate blue light at 473 nm. Figure 1 shows the procedure of fabrication. First, the periodically domain-inverted regions were formed on a MgO:LN substrate (3°-off Xcut) by the 2D high-voltage application technique (Figure 1a). Then a resin adhesive was used to glue the obtained comb-electrode-formed surface to a LN substrate (Figure 1b). In the next step (Figure 1c) the MgO: LN substrate was thinned by flat-grinding and surface finishing: thus, a 4 µm-thick planar waveguide was realized. In the final step (Figure 1d), the ridge-shaped structure was processed by machining to form a ridgetype waveguide.

A sketch of the experimental set-up is presented in Figure 2. The fundamental 946-nm radiation for frequency doubling was provided by a home-made Nd:YAG laser. For an absorbed pump power at 809 nm of 4.2 W the polarized output was 1.1 W in a Gaussian distribution ($\hat{M}^2 = 1.05$); the slope efficiency was 38%. Three periodically poled MgO:LN ridge-type waveguides, each of 1.4 mm-width, were prepared. First one has 8.5-mm length and both the input and output surfaces were cut at an angle $\alpha = 10^{\circ}$ and AR coated at 946 nm by SiO₂ monolayer. The second one of 6-mm length has the input and output surfaces cut at $\alpha = 10^{\circ}$, while the third one has 12-mm length and only the input surface cut at $\alpha = 6^{\circ}$; these two samples have no coating at 946 nm. No coating was provided at 473 nm for all the waveguides. The MgO:LN ridge-type waveguide was placed on an aluminum plate whose temperature was controlled within 0.1 °C accuracy.

The 473-nm power as a function of the 946-nm power coupled into the waveguide is presented in Figure 3. The maximum blue power of 189 mW was obtained for the 8.5-mm-long MgO:LN waveguide with a conversion efficiency of 49%. If the Fresnel loss on the waveguide output surface is considered, the maximum internal blue-light power is 222 mW, corresponding to a conversion efficiency of 58%. As the fundamental power before the waveguide was 670 mW the overall conversion efficiency is 28%; improving the 946 nm radiation coupling efficiency into the waveguide could increase the device overall efficiency. The maximum blue power for the 6-mm-long MgO:LN waveguide was 155 mW with 42% conversion efficiency (182-mW blue

internal power with 49% conversion efficiency), while 147 mW with a conversion efficiency of 48% (173-mW blue internal power with 56% conversion efficiency) were obtained for the 12-mm-long MgO:LN waveguide. The highest conversion efficiency of 63% (internal conversion efficiency of 74%) was obtained for a blue power of 99 mW from the longest waveguide used in experiments. During an hour measurement, the peak-topeak fluctuations for the 946-nm maximum power were $\pm 1.3\%$, while the blue power fluctuations were $\pm 4.0\%$. The phase matching temperature was 36.3 °C and the measured acceptance bandwidth ΔT was 2.3 °C, in very good agreement with the predicted theoretical value of 2.35 °C.

In conclusion, CW blue-light generation from a periodically poled MgO:LiNbO₃ waveguide by frequency-doubling of a diode end-pumped Nd:YAG laser operating at 946 nm is reported. The maximum output power at 473 nm was 189 mW with 49% conversion efficiency (222 mW internal power with 58% conversion efficiency), indicating the potential for high-power SHG of the ridge-type waveguide fabricated by ultraprecision machining.

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Figure 1. Fabrication steps of a periodically poled MgO:LN ridge-type waveguide by ultra-precision machining: (a) obtaining of the domain-inverted regions, (b) adhesion with a LN substrate, (c) flat grinding and polishing, and (d) ultra-precision grinding.



Figure 2. Schematic diagram of the experimental set-up. P: polarizer; L1: focusing lens; L2: collimating lens; F: 946-nm cut filter.



Figure 3. Output power at 473 nm versus the 946-nm power coupled into the waveguide. The inset shows a typical blue light far-field distribution.

IX-B-6 High-Power Continuous Wave Green Generation by Single-Pass Frequency Doubling of a Nd:GdVO₄ Laser in a Periodically Poled MgO:LiNbO₃ Operating at Room Temperature

MIZUUCHI, Kiminori¹; MORIKAWA, Akihiro; SUGITA, Tomoya¹; YAMAMOTO, Kazuhisa¹; PAVEL, Nicolaie²; SHOJI, Ichiro; TAIRA, Takunori

(¹Matsushita Co., Ltd., Osaka; ²IMS and IAP-NILPRP, Romania)

[Jpn. J. Appl. Phys. 42, L1296 (2003)]

Due to its high effective nonlinear coefficient and the possibility of obtaining non-critical phase matching in single-pass continuous wave (CW) pumping scheme, the periodically poled LiNbO₃ (PPLN) crystal continues to attract a great interest as a QPM device for generation in blue, green, or violet ranges. Employing a 50-mmlong first-order PPLN sample, CW powers of 2.7-W green¹⁾ and 60-mW blue²⁾ were demonstrated, respectively. It is known, however, that PPLN has significant problems for visible light radiation, such as greeninduced infrared absorption and optical damage. Although phase matching at high temperature close of 200 °C was used,²⁾ power instabilities and thermal lens effects could not be completely suppressed. Thus, to date, room temperature CW operation close or in excess of 1 W level was not obtained from a single-pass pumped PPLN crystal.

In order to overcome these problems, it was recently proposed³⁾ to utilize periodically poled MgO:LiNbO₃

(PPMgLN). Due to its larger nonlinear susceptibilities, higher resistance against photorefractive damage and shorter wavelength transparency compared with PPLN, PPMgLN is a very attractive material for generation of visible light through SHG by QPM process. Moreover, because of its low coercive field,⁴⁾ it was demonstrated that PPMgLN could be fairly easily fabricated by means of electric field poling. Recently, a novel high-voltage multi-pulse poling technique that suppress the penetration of poled region and produces uniform PPMgLN with domain period (Λ) as short as 1.4 µm was developed by our group.⁵⁾ This letter reports CW SHG at room temperature in a first-order PPMgLN with $\Lambda = 6.95$ mm that was fabricated by this technique.

In order to improve the domain pattern quality for short periodic structure a special attention was paid to understand the domain formation processes in a z-cut MgLN crystal. A large resistance reduction was found in a 0.5-mm-thick z-cut MgLN during a conventional electric-field-poling process. Large leakage current was observed in the electric circuit after poling process, which was explained by the resistance reduction in the poled region from 6×10^{11} to $7 \times 10^5 \Omega$ mm. This large resistance reduction may cause irregular side growth and non-uniformity of polarization inversion that, in turn, interrupts the fabrication of short-periodic structures. Such local penetrations under the electrode may shorten the surface and bottom electrodes and cause large leakage current between electrodes, which degrade uniformity of electric field. Then, in order to realize uniform PPMgLN structure over large areas, local penetration of polarization-inverted regions must be suppressed: a thick crystal and the multi-pulse application method⁶⁾ are used to overcome this last problem. The penetration of polarization inversion to the bottom of the crystal could be suppressed by employing thick samples. Shortening the growth time by using short width pulse would control the forward growth, while multiple pulses should supply enough charge for realizing a relatively deep polarizationinverted structure. Figure 1 shows the cross-sectional of the PPMgLN with $\Lambda = 6.95$ mm for various depths: the structure presents 50% duty cycle from the +Z surface to a depth of $\sim 300 \ \mu m$ and uniform periodicity was maintained from the surface to ~800-µm depth.

The 1063-nm radiation for frequency doubling was provided by a home-made diode end-pumped Nd: GdVO₄ laser that delivers CW 6.8 W output power (M^2 factor of 1.16) for an 808-nm pump power measured at the fiber end of 15.1 W; the slope efficiency was 57%. The output beam depolarization ratio was 1.2% and the power fluctuation during few hours of operation was ±1.1%. For SHG experiments a 10-mm length PPMgLN was used: the PPMgLN end-faces were optically polished and anti-reflection (AR) coated by SiO₂ monolayer for the 1063-nm fundamental wavelength; no coating was provided at 531 nm. The PPMgLN was placed on an aluminum plate whose temperature was controlled within 0.1 °C accuracy with a thermoelectric cooler. The 1063-nm radiation was focused into PPMgLN to a spot size of 17-µm radius.

Figure 2 shows the 531-nm green power after PPMgLN versus the 1063-nm fundamental power measured after the focusing lens. The maximum green

power of 0.89 W was obtained for an infrared incident power of 6.23 W, resulting a conversion efficiency of 14.3%. If the Fresnel loss (determined as ~14%) on the output surface is considered the maximum internal green-light power results as 1.03 W, corresponding to a conversion efficiency of 16.5%. The effective nonlinear coefficient was determined as 14 pm/V and the normalized conversion efficiency including the Fresnel loss by reflection was 2.7%/W. Figure 2 shows by continuous line the theoretical modeling using a quadratic relation with this value: a good agreement with the experimental results is observed. The phase matching temperature was 29.5 °C, stable within ± 0.3 °C on the entire pumping range.

In conclusion, irregular side growth of polarization inversion was suppressed in a 2-mm thick PPMgLN by using a multi-pulse application poling method. Uniform periodicity and 50% duty cycle with a 6.95- μ m domain period was fabricated on 10-mm length of interaction. This structure was used to obtain perfect first-order QPM in the bulk PPMgLN at 1063 nm wavelength: CW 531-nm green light of 0.89 W with 14.2% power conversion efficiency was obtained (internal power of 1.03 W and 16.5% conversion efficiency) in a singlepass pumping with a Nd:GdVO₄ laser.

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Figure 1. Cross-sectional view (Y face) of first-order PPMgLN with $\Lambda = 6.95 \,\mu\text{m}$: (a) general view, (b) near the surface, (c) at the depth of 300 μm , and (d) at 1-mm depth.



Figure 2. CW 531-nm output power (\Box - measured and \blacksquare - corrected with Fresnel losses) and phase matching temperature (\bigcirc) *vs.* the 1063-nm incident power.

IX-B-7 Continuous-Wave High-Power Nd:YAG-KNbO₃ Laser at 473 nm

PAVEL, Nicolaie¹; SHOJI, Ichiro; TAIRA, Takunori

(¹IMS and IAP-NILPRP, Romania)

[Opt. Laser Tech. 36, 581 (2004)]

During the past few years much work has been done in order to obtain an efficient and simple solid-state blue laser source, this device being of interest for applications such as display technologies, production of high-density optical disk systems, high-resolution printing, or medical diagnostics. Although the blue semiconductor diode laser is expected to reach the power level necessary for these applications, the frequency-doubling of the 946-nm ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition in Nd:YAG is a practical and the most used way that leads to blue radiation at 473 nm. Various resonator configurations and nonlinear crystals could be used for frequency-doubling of a Nd:YAG laser operating at 946 nm. The first continuous-wave (CW) diode-pumped Nd:YAG laser that delivered 42-mW at 946 nm was reported by Risk and Lendth,¹⁾ whereas an attempt of intracavity frequency-doubling by a LiIO₃ nonlinear crystal yielded 100 µW of blue light. Dixon et al. developed the first 946-nm Nd:YAG laser intracavity frequency-doubled by a KNbO3 crystal:²⁾ 5-mW power at 473 nm with 2% optical-to-optical conversion efficiency with respect to the pump power, $\eta_0^{(i)}$, was obtained. A compact source of CW single-frequency radiation at 473 nm with 500 mW output power was developed, employing a diode-pumped miniature Nd: YAG ring laser as a pump source and an external semimonolithic cavity with KNbO₃ crystal.³⁾ The best result to date at 473 nm is an output power of 2.8 W with $\eta_0^{(i)}$ = 13.3%: the experimental set-up was a three-arms resonator and BiB₃O₆ nonlinear crystal operating at room temperature was employed for frequencydoubling.4)

Some disadvantages of $KNbO_3$ are a small temperature and spectral acceptance bandwidths, photorefractivity effect, and that its domain structure is easily disturbed. However, because of its high value of the nonlinear coefficient and due to its ability to be birefringently phase-matched for second harmonic generation of the 946-nm wavelength this crystal was our choice. This paper reports on our work toward scaling blue light obtained by intracavity frequency-doubling of a diode end-pumped 946-nm Nd:YAG laser, using a KNbO₃ nonlinear crystal.

A 1.0-at.% Nd:YAG crystal (3-mm thickness) whose surfaces were anti-reflection (AR) coated at the pumping wavelength of 809 nm and also at 946 and 1064 nm was used in experiments. To achieve efficient heat removal the Nd:YAG crystal was placed in a copper mount whose temperature was kept at 12 °C, and an indium foil was used to improve the thermal contact between the Nd:YAG and the copper heat sink. A 400um diameter, 0.22-NA fiber-coupled diode (HLU32 F400, LIMO Co., Germany) was used for CW pumping; the fiber was imaged into the Nd:YAG crystal in a 300µm diameter spot. Two KNbO₃ crystals (Mitsui Chemicals Inc., Japan) of 1.0 and 2.0-mm thickness were cut for type I, critical-phase-matching condition (θ = 90°, ϕ = 59.2°) and placed in a copper holder whose temperature was controlled with 0.1 °C accuracy; the operation temperature was 29.2 °C. Both sides of each KNbO₃ were polished to parallel flat surfaces and AR coated at 473 and 946 nm.

The emission of a plane-concave resonator of 70mm length that contains the Nd:YAG crystal, the polarizing glass plate and the KNbO₃ crystal was first investigated. The output mirror has 100-mm radius and it was coated as high-reflection at 946 nm and hightransmission at 473 nm. The maximum power at 473nm for the 1.0-mm thick KNbO₃ crystal was 68 mW for an absorbed pump power of 3.1 W, as shown in Figure 1. The conversion of the available IR power was 10.5%. With the 2.0-mm thick KNbO₃ crystal the maximum blue power was 159 mW for an absorbed pump power of 3.3 W: thus $\eta_0^{(i)}$ was 2.7%, while the conversion of the IR power was determined as 21.4%. For these points of operation the transverse mode distribution was Gaussian ($M^2 < 1.05$), but a saturation of the blue power and decrease of the beam quality were obtained as the pump power was further increased.

In order to increase the blue power a V-type resonator, as shown in Figure 2, was designed. The distances M1 to M2 and M2 to M3 were 70 and 55 mm, respectively; the KNbO₃ nonlinear crystal was placed very close of mirror M3. Figure 3 shows the blue power versus the absorbed pump power. For the 1.0-mm thick KNbO₃ crystal a maximum blue power of 318 mW was obtained for an absorbed pump power of 3.8 W; the conversion efficiency of the IR power was 34.2%. An output power of 418 mW at 473 nm was recorded for the 2.0-mm thick KNbO₃ crystal with $\eta_0^{(i)} = 6.7\%$; the conversion of the available IR power was 50%. The 473-nm output beam was linearly polarized (> $1:10^3$) and orthogonal to the 946-nm radiation. Monitoring the maximum blue output power with a powermeter resulted in $\pm 2\%$ power fluctuations during few hours of operation. The stability on millisecond time scale was investigated with a fast photodiode: it shows no fluctuations, indicating no blue problem. No damage of the KNbO₃ crystals was observed during the experiments.

For modeling of blue power, the beam distribution inside the resonator was considered independent of the active medium refractive power induced by optical pumping, with the laser operating far of the threshold.^{5),6)} Experimentally we have determined the pump coupling coefficient $K_c = 0.032 \text{ W}^{-1}$ and the loss L as ~1.5% and ~2.0% for the resonators with the 1.0 and 2.0-mm thick KNbO₃, respectively. The beam radius in the Nd:YAG and in KNbO3 were considered independent of the absorbed power, namely 140 and 100 µm, respectively. Figure 3 also shows by continuous lines the modeling of the blue power using this model, where $d_{\text{eff}} = 13 \text{ pm/V}$ was the parameter used for fitting. The agreement between the experimental data and modeling is satisfactory, if one considers that the model assumes that the resonator parameters are optimized for each pump power, which is not the experimental case.

In conclusion, a continuous-wave diode-pumped Nd: YAG laser that operates on the 946-nm ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition and that is intracavity frequency-doubled to 473 nm using KNbO₃ nonlinear crystal is described. The blue maximum power was 418 mW, with 50% conversion of the available IR power, and the optical-tooptical conversion efficiency with respect to the pump power was 6.7%. To the best authors knowledge these are the highest results to date for a diode pumped Nd:YAG rod laser frequency-doubled by a KNbO₃ nonlinear crystal.

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Figure 1. Blue output power *vs.* the absorbed pump power for the linear resonator.



Figure 2. V-type resonator of the diode-pumped 946-nm Nd:YAG laser intracavity frequency-doubled by KNbO₃ crystal; BP: glass plate placed at the Brewster angle.



Figure 3. Blue output power *vs.* the absorbed pump power for the V-type resonator: signs for experiments and theory by the continuous lines.

IX-B-8 Room-Temperature, Continuous-Wave 1-W Green Power by Single-Pass Frequency Doubling in a Bulk Periodically Poled MgO:LiNbO₃ Crystal

PAVEL, Nicolaie¹; SHOJI, Ichiro; TAIRA, Takunori; MIZUUCHI, Kiminori²; MORIKAWA, Akihiro; SUGITA, Tomoya²; YAMAMOTO, Kazuhisa²

(¹IMS and IAP-NILPRP, Romania; ²Matsushita Co., Ltd., Osaka)

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Due to its significant advantages of phase-matching an arbitrary wavelength and of accessing high nonlinear coefficient by using an appropriate period of polarization inversion, the second-harmonic generation (SHG) by quasi-phase-matching (QPM) interaction is an attractive method to obtain a compact and high power laser emitting into visible or ultraviolet spectral regions. Because of its simplicity, the single-pass SHG scheme is a solution to obtain continuous wave (CW) operation in blue, green, or ultraviolet ranges. This scheme requires a high nonlinear coefficient and long interaction length with noncritical phase matching: these conditions are well fulfilled by the periodically poled LiNbO₃ (PPLN) crystal. It is known, however, that PPLN has significant problems for visible light radiation, such as green- or blue-induced infrared absorption and optical damage. Although phase matching at high temperature of 200 °C¹⁾ or 140 °C²⁾ was used, power instabilities and thermal lens effects could not be completely suppressed.

To overcome these problems, the use of periodically poled MgO:LiNbO₃ (PPMgLN) was proposed:³⁾ this crystal presents larger nonlinear susceptibilities, higher resistance against photorefractive damage and shorter wavelength transparency compared with PPLN. CW blue power of 17.3 mW at 426 nm was demonstrated from a PPMgLN waveguide that was single-pass pumped by a AlGaAs diode laser.⁴⁾ A novel highvoltage multi-pulse poling technique that suppress the penetration of poled region and produces uniform PPMgLN with domain period (Λ) as short as 1.4 μ m was developed by our group: ultraviolet light at 341.5 nm with a normalized conversion efficiency of 5.4%/W was thus demonstrated.⁵⁾ In this letter we report highpower CW frequency-doubling at room temperature in a first-order PPMgLN of $\Lambda = 6.95$ -µm fabricated by this technique and that was single-pass pumped with a Nd: GdVO₄ laser operating at one micron wavelength.

The experimental set-up is shown schematically in Figure 1. Taking into account the high thermal conductivity of Nd:GdVO₄ and the fact that the output beam is polarized, a diode-end pumped Nd:GdVO₄ laser (Z-type resonator) was build as a pump source: the laser delivers 6.8 W with 45% optical-to-optical efficiency, in a beam with M² factor of 1.15; the slope efficiency was 57%. The output beam depolarization ratio was 1.2% and the power fluctuation during few hours of operation was $\pm 1.1\%$. The laser spectrum, which was investigated by a spectrum analyzer (Q8384 Advantest Co., Japan) with 0.01-nm resolution, was centered at 1062.9 nm and presented four peaks separated by 0.08 nm, each peak with FWHM of ~0.01 nm; the spectrum width was ~0.24 nm.

The fabrication process of PPMgLN with $\Lambda = 6.95$ µm and long interaction length was as follows: To obtain a uniform PPMgLN structure over large areas, local penetration of polarization-inverted regions was suppressed by using a thick crystal and the multi-pulse application method.⁶⁾ A Z-cut 5-mol% MgO doped LN crystals of 2-mm thickness were used. First, a 100-nm thick Ta film was sputtered on the +Z and -Z faces of the crystals. Next, the patterned electrodes were covered with a 200-nm thick sputtered SiO₂ film. The applied voltage and pulse width were 10 kV and 1 ms, respectively. During the poling process, to lower the coercive field, the samples were heated at ~ 140 °C. After poling the substrate was etched in a 1:2 HNO₃+HF solution at 60 °C for several minutes to reveal the polarizationinverted region on both surfaces of the crystal. The cross sections were examined by cutting samples along Y-faces, polishing and etching. It was found that the structure has 50% duty cycle from the +Z surface to a depth of ~300 µm and uniform periodicity was maintained from the surface to ~800-µm depth; however, the polarization-inverted regions were not realized near the -Z face.

For SHG experiments PPMgLN crystals of 10- and 25-mm length were cut from the poled samples and the end-faces were optically polished and antireflection (AR) coated by SiO₂ monolayer for the 1063-nm wavelength; the SiO₂ coating has no AR effect at 531 nm. The PPMgLN were placed on an aluminum plate whose temperature was controlled within 0.1 °C accuracy using a thermoelectric cooler. A dichroic mirror M,

coated as high-reflectivity for 1063 nm and as high-transmission for 531 nm, was used to reflect the fundamental radiation left after PPMgLN.

A maximum CW green power of 0.89 W was measured for the 10-mm-long PPMgLN for an incident infrared power of 6.23 W. If the Fresnel loss (~14%) on the output surface of PPMgLN is considered the maximum internal green-light power results as 1.03 W, corresponding to a conversion efficiency of 16.5%. Figure 2a shows the internal green power and conversion efficiency versus the 1063-nm input power in PPMgLN. The effective nonlinear coefficient was determined as 14 pm/V; thus, the normalized conversion efficiency including the Fresnel loss by reflection was 3.0%/W. For the 25-mm long PPMgLN crystal a maximum green power of 1.18 W was measured. When the Fresnel loss is considered (Figure 2b) the internal power and conversion efficiency were 1.38 W and 19.6%, respectively, while the normalized conversion efficiency was ~3.3%/W; the continuous line of Figure 2b shows the expected results with this value.

The phase matching temperature was 29.5 °C, stable within ± 0.3 °C on the entire pumping range. The experimental data for the acceptance bandwidth ΔT was 3.9 °C, while the theoretical value obtained by taking into account the Sellmeier equations for LN crystal⁷) resulted as 3.4 °C; good agreement could be observed. During few hours of operation output power instabilities or variations of the green beam pattern that could be caused by thermal lens effects or optical damage of PPMgLN were not observed. Then, the strong resistance against photorefractive damage of MgO:LiNbO₃ enables achieving this green power level and highly efficient SHG efficiency in a CW single-pass pumping scheme.

In conclusion, CW power of 1.18 W at 531 nm with 16.8% power conversion efficiency was obtained from a 25-mm-long uncoated bulk PPMgLN in a single-pass frequency doubling scheme using a Nd:GdVO4 laser as pumping source; the PPMgLN internal power of and conversion efficiency were 1.38 W and 19.6%, respectively. To the authors best knowledge this is the highest power ever reported by quasi-phase matching at room temperature. The present result supports the prospect of obtaining compact and high power visible source based on bulk periodically poled MgO:LiNbO₃.

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Figure 1. The experimental set-up used for SHG generation. L: focusing lens, TEC: thermoelectric cooler, M1, M2, M3, M: mirrors.



Figure 2. Internal cw 531-nm output power and internal conversion efficiency versus the 1063-nm incident power for a) 10-mm and b) 25-mm long PPMgLN. Continuous lines shows the modeling with a quadratic dependence.

Research Center for Molecular-Scale Nanoscience

IX-C Nano-science and Nano-Technology toward Molecular Scale Electronics

Studies on electric properties of organic and in-organic nano structures are challenging field in material science. Those of aggregates, crystals, or polymers which are made from a large number of molecules or atoms have been already established. In contrast, electronics of nano scale materials which are constructed from small number or single molecules are the forefront of science and technology, and have been revealed gradually to show their diverse phenomena such as quantum conductance, the Kondo effect, the Coulomb blockade, and resonance tunneling. In order to promote this field further, we are studying preparation or fabrication of new organic and in-organic nano materials, and developing new methods to measure their physical properties.

IX-C-1 Bridging Nano-Gap Electrodes by *In Situ* Electropolymerization of a Bis-Terthiophenylphenanthroline Ruthenium Complex

ARAKI, Koiti^{1,3}; ENDO, Hiroaki^{1,2}; MASUDA, Gou²; OGAWA, Takuji¹ (¹IMS, JST; ³Ehime Univ.; ³Univ. São Paulo)

[Chem. Eur. J. 10, 3331–3340 (2004)]

A novel 3,8-bis-terthiophenyl-(1,10-phenanthroline) coordinated to [Ru(bpy)₂] was synthesized and characterized by electrochemical and spectroscopic techniques, and shown to be a suitable starting material for the electrodeposition of functionalized molecular wires in between nano-gap electrodes, generating stable molecular nano-devices. Temperature dependent nonlinear *I-V* curves were obtained in the 80 to 300 K range. The material can be deposited on ITO also, forming compact electrochromic films at surface concentrations lower than about 1×10^{-8} mol·cm², but a more loosely bond fibrous form is preferentially deposited at higher surface concentrations.



Scheme 1.



Scheme 2.

IX-C-2 Multi Curve Fitting Analysis of Temperature Dependent *I-V* Curves of Poly-Hexathiophenephenanthroline Bridged Nano-Gap Electrodes

ARAKI, Koiti^{1,3}; ENDO, Hiroaki^{1,2}; TANAKA, Hirofumi¹; OGAWA, Takuji¹ (¹IMS, JST; ²Ehime Univ.; ³Univ. São Paulo)

[Jpn. J. Appl. Phys. 43, L634–L636 (2004)]

Stable junctions were obtained by preparing polyhexathienylphenanthroline coordinated wires to $[Ru(bpy)_2]$ complexes directly in the Au electrode nanogaps by electropolymerization. Reproducible non-linear and strongly temperature dependent curves, similar to that found for π -conjugated dithiols and diisocyanides self-assembled inside nano-holes, were obtained rather than a tunneling behavior commonly found in alkane-thiol self-assembled monolayers. This is the first time that such a consistent series of data are collected for a polymer and interpreted based on a multi curve fitting method using a linear combination of tunneling, Frankel-Pool and hopping mechanism, suggesting that various independent conduction pathways may be present.



Figure 1.

IX-C-3 Position-Selected Molecular Ruler

TANAKA, Hirofumi; ANDERSON, Mary E.¹; HORN, Mark W.¹; WEISS, Paul S.¹ (¹Pennsylvania State Univ.)

[Jpn. J. Appl. Phys. 43, L950–L953 (2004)]

The molecular ruler method allows the precise control of the gap between a parent gold structure and a deposited daughter structure using a conveniently grown self-assembled molecular multilayer as a lithographic mask. However, we cannot choose a position where the gap should be placed, since the ruler attaches to all exposed gold surfaces. In this work, a convenient method of selecting the position of nano-gaps by further patterning the molecular multilayer using low-energy electron beam irradiation and piranha etchant is described.

The development of a convenient technique to fabricate precise nanostructures in large quantity is required for many types of application, such as electric devices, micromachines and biological equipment, since the "top-down" approach like electron lithography will reach its physical limit soon. Accordingly, it is urgently required to develop "bottom-up" techniques such as molecular self-assembly in order to achieve this goal.

Recently, many researchers have tried to create nano-gaps between electrodes to measure the electronic property of a single molecule or several molecules. For example, shadow evaporation, the break junction method and e-beam lithography have been investigated for this purpose. One of the most convenient approaches coupling the top-down and bottom-up approaches was developed as the molecular ruler method. This is based on the use of compact self-assembled molecular multilayers grown on a parent gold structure as a convenient photoresist. Gap width is precisely controlled by the length of the molecular ruler and the number of monolayers deposited on the top of parent structures, for example, prepared by conventional lithography techniques. One of the advantages of this method is that both sides of the gap are vertically parallel and the desired gap sides can be formed precisely. Another advantage is the position of the gap can be controlled. Multilayers are grown by the successive sequential deposition of monolayers of α, ω -mercaptoalkanoic acid (HS(CH₂)_xCOOH) and Cu²⁺ ions, until desired thickness is achieved.



Figure 1.



Figure 2.

IX-C-4 Advances in Nanolithography Using Molecular Rulers

ANDERSON, Mary E.¹; TAN, L. P.¹; TANAKA, Hirofumi²; MIHOK, M.¹; LEE, H.¹; HORN, Mark W.¹; WEISS, Paul S.¹

(¹Pennsylvania State Univ.; ²IMS and Pennsylvania State Univ.)

[J. Vac. Sci. Technol. B 21, 3116–3119 (2003)]

The combination of conventional lithographic techniques with chemical self-assembly allows for the creation of nanostructures whose spacing and edge resolution reach nanometer-scale precision. The controlled placement and thickness of self-assembled multilayers composed of alternating layers of $\alpha, \overline{\omega}$ -mercaptoalkanoic acids and coordinated metal ions form precise molecular ruler resists that enable the production of tailored and lithographically defined metal patterns. Initial structures created by conventional techniques are referred to as parents and subsequent structures generated by the molecular ruler process are identified as daughters. We report the further creation of subsequent generation structures ~granddaughters! that have sub-100 nm dimensions. The granddaughter structures are created by forming molecular rulers on parent and daughter structures, and can be isolated by removing sacrificial parent and/or daughter structures. This process has also been utilized in combination with parent structures created by the process of nanosphere lithography to produce arrays of metal features with 10 nm spacings. Since our original report, we have improved the throughput and reproducibility of the molecular ruler process by automating its iterative nature and by utilizing appropriate chemical lift-off solutions.

IX-C-5 Reactive Ligand-Protected Nano-Particles

ARAKI, Koiti^{1,3}; MIZUGUCHI, Eisuke^{1,2}; TANAKA, Hirofumi¹; OGAWA, Takuji¹ (¹IMS, JST; ²Ehime Univ.; ³Univ. São Paulo)

Gold nano-particles exhibit interesting bonding and electronic properties and have been proposed for many applications such as in photoelectrochemical devices, drug delivery systems and sensors. Such applications exploit the molecule-like electronic properties and the particle like behavior of such materials, behaving as highly dispersed solids possessing an exceedingly high functionalizable surface area. In fact, a very significant number of atoms constituting small nano-particles are in the surface and can bond species containing coordinating groups such as thiols, disulphides, phosphines, ammines, etc. This means that almost any molecular species can be anchored in the surface imparting their physico-chemical properties to them or leading to the appearance of new properties. On the other hand electronic properties such as light absorption, excited state and electron-transfer characteristics can be controlled by changing the size and the nature of the surface anchored species.

As pointed out above, the preparation of nanoparticles with narrow size distribution is a very important issue and some methods have being developed. For example, Brust et al developed a general method for the preparation of thiol-protected gold-nanoparticles with a narrow size distribution, based on the reduction of $AuCl_4^-$ in toluene with an aqueous NaBH₄ solution. The toluene solution also contains protecting species such as *n*-dodecanethiol, essential for the stabilization of the metal clusters, and tetraoctylammonium bromide (phase transfer agent). Teranishi *et al.* have shown that *n*dodecanethiol protected Au-nanoparticles with very narrow size distribution can be obtained by controlled thermal treatment of previously prepared solid samples.

Another main issue for the widespread use of goldnanoparticles is the sluggishness of the functionalization reactions, which in the case of *n*-dodecanethiol protected material generally can take more than a couple of days. To overcome such drawback more weakly binding protecting groups such as triphenylphosphine, amines and terc-dodecanethiol have being proposed. However, in the first case only very small ($\sim 1-2$ nm diameter) nanoparticles can be obtained and the reactivity are not so much higher in any case. For this reason, even very unstable gold-nanoparticle solutions, obtained in the absence of coordinating organic protecting groups, have been employed. This starting material is quite unstable and should be used soon after its preparation, making almost impossible its proper characterization before use. This is a main issue since can compromise their applications. We disclosed a method for the preparation of highly reactive ligand-protected nanoparticles.

IX-D Development of Organic Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on π -conjugated oligomers have been extensively studied as molecular thin-film devices. Organic semiconductors with low injection barriers and high mobilities are required for highly efficient OLEDs and OFETs. Radical cations or anions of an organic semiconductor have to be generated easily at the interface with an electrode (or a dielectric), and holes or electrons must move fast in the semiconducting layer. Compared with organic *p*-type semiconductors, organic *n*-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated oligomers are efficient electron-transport materials for OLEDs.

IX-D-1 Organic Thin-Film Transistors Based on Anthracene Oligomers

INOUE, Youji¹; TOKITO, Shizuo¹; ITO, Kaname; SUZUKI, Toshiyasu (¹NHK Sci. Tech. Res. Labs.)

[J. Appl. Phys. 95, 5795–5799 (2004)]

OFETs with an active layer based on the organic semiconducting anthracene oligomers, 2,2'-bianthracene (2A), 2,6-trianthracene (3A), and their dihexyl derivatives (DH-2A and DH-3A), were fabricated. It was found that thin films of anthracene oligomers deposited by thermal evaporation had lamellar structures with a high degree of molecular ordering. Consequently, the OFETs based on anthracene oligomers showed high field-effect mobilities. The mobility of the OFETs was increased by the oligomerization and the substitution of alkyl groups. DH-2A on a SiO₂/Si substrate showed the highest mobility of 0.13 cm²/V s. It was also found that the electrical characteristics of the OFETs were improved by using a Ta₂O₅ gate insulator.

IX-D-2 Perfluoropentacene: High-Performance *p*-*n* Junctions and Complementary Circuits with Pentacene

SAKAMOTO, Youichi; SUZUKI, Toshiyasu; KOBAYASHI, Masafumi¹; GAO, Yuan¹; FUKAI, Yasushi¹; INOUE, Youji²; SATO, Fumio²; TOKITO, Shizuo²

(¹Kanto Denka Kogyo; ²NHK Sci. Tech. Res. Labs.)

[J. Am. Chem. Soc. 126, 8138-8140 (2004)]

We report the synthesis and characterization of perfluoropentacene as an *n*-type semiconductor for OFETs. Perfluoropentacene is a planar and crystalline material that adopts a herringbone structure as observed for pentacene. OFETs with perfluoropentacene were constructed using top-contact geometry, and the electron mobility of 0.11 cm²/V s was observed. Bipolar OFETs with perfluoropentacene and pentacene function at both negative and positive gate voltages. The improved *p*-*n* junctions are probably because of the similar d-spacings of both acenes. Complementary inverter circuits were fabricated, and the transfer characteristics exhibit a sharp inversion of the output signal with a high voltage gain.





Figure 1. Structures of pentacene and perfluoropentacene.



Figure 2. Drain current (I_D) versus drain voltage (V_D) characteristics as a function of gate voltage (V_G) for a perfluoropentacene OFET.

IX-E Field-Effect Transistors with Organic Semiconductors

Considerable attention has recently focused on organic field-effect transistors (OFET) because of their potential use in low-cost flexible electronic devices. We have studied output characteristics of OFET devices based on newly synthesized organic compounds.

IX-E-1 Field-Effect Transistors Based on Dicyanopyrazinoquinoxaline Derivatives

NISHIDA, Jun-ichi¹; NARASO¹; MURAI, Shiro¹; FUJIWARA, Eiichi; TADA, Hirokazu; TOMURA, Masaaki; YAMASHITA, Yoshiro¹ (¹Tokyo Inst. Tech.)

[Org. Lett. 6, 2007–2010 (2004)]

Dicyanopyrazinoquinoxaline derivatives (Figure 1) have been prepared and characterized by using singlecrystal X-ray structure analysis and redox potential measurements. They have strong electron-accepting properties due to the pyrazinopyrazine skeletons as well as the cyano groups. Substituents can be easily introduced at the benzene ring and control the HOMO-LUMO energy gap and the molecular packing. Figure 2 shows output characteristics of a bottom-contact OFET based on compound 1a. It was found that the compound **1a** exhibited *n*-type semiconducting behavior with carrier mobility of 3.6×10^{-6} cm²/Vs. The compounds examined operated as N-type OFETs. The mobility and on/off ratio of the devices are summarized in Table 1.



Figure 1. Molecular structures of dicyanopyrazinoquinoxaline derivatives.



Figure 2. Output characteristics of the OFET based on compound **1a**. Gate voltages were varied from 0 to 100 V with an increment of 10 V.

Table 1. Field-effect mobilities and on/off current ratios ofFETs based on dicyanopyrazinoquinoxaline derivatives.

a 10. 100	padatature (maNV-s).	الم البيار	
34	1.6×10^{-6}	102	
Tb-	1.0×10^{-6}	18	
de .	2.1 × 10 ⁻⁷	107	
34	$8.5 = 101^{-9}$	184	
3.e	$Z.Z = 10^{-6}$	1.07	
11	5.5 × 10 ⁻²	102	
2			

IX-E-2 Low-Voltage Organic Field-Effect Transistors Based on Ta₂O₅ as Gate Insulator Material

SAKAI, Heisuke¹; FURUKAWA, Yukio¹; FUJIWARA, Eiichi; TADA, Hirokazu (¹Waseda Univ.)

[Chem. Lett. in press]

A thin film of Ta₂O₅ was prepared by sputtering on heavily-doped silicon substrates and used as a gate insulator of field-effect transistors. Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and pentacene were used as active semiconductors. Interdigital Au electrodes, which consisted of 25 pairs with 25 µm in spacing, 4 mm in width, and 50 nm in thickness, were prepared on the organic layer and used as the source and drain electrodes. Clear saturation in drain currents was observed at low drive voltage of about -3 V as shown in Figure 1. MEH-PPV and pentacence exhibited *p*-type semiconducting behaviors with mobilities of 4.6×10^{-4} cm²/V s and 0.8 cm²/V s, respectively.



Figure 1. Output characteristics of an FET based on MEH-PPV with a Ta_2O_5 gate insulator.

IX-E-3 Visible Light Emission from Polymer-Based Field-Effect Transistors

SAKANOUE, Tomo¹; FUJIWARA, Eiichi; YAMADA, Ryo; TADA, Hirokazu (¹GUAS) [Appl. Phys. Lett. 84, 3037-3039 (2004)]

Field-effect transistors (FETs) based on poly [2methoxy, 5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene] (MEH-PPV) were prepared with bottom-contact type interdigital electrodes of Cr/Au and Al/Au on the SiO₂/ Si substrates. MEH-PPV exhibited a *p*-type semiconducting behavior and orange light emission was observed when the devices were operated in vacuum. It was found that the luminescence efficiency of the FETs with Al/Au electrodes was higher than that of Cr/Au electrodes, as shown in Figure 1. The simultaneous injection of holes and electrons into MEH-PPV occurred efficiently with the application of Al/Au heteroelectrodes.



Figure 1. Luminescence intensity detected with a Si photodiode as a function of the gate voltage (a) and the drain current (b). The drain voltage was set at -150 V.

IX-F Molecular Assemblies on Silicon Surfaces *via* Silicon–Carbon Covalent Bonds

Preparation of molecular assemblies on inorganic semiconductors such as silicon and germanium has received a growing interest because of their potential application to stable regist for nano-patterning. We have prepared organic monolayers on silicon by wet process and studied film structures with IR and AFM.

IX-F-1 Temperature Dependence of the Structure of Alkyl Monolayers on Si(111) Surface *via* Si–C Bond by ATR-FT-IR Spectroscopy

YAMADA, Ryo; ARA, Masato¹; TADA, Hirokazu (¹GUAS)

[Chem. Lett. 33, 492–493 (2004)]

The temperature dependence of C–H stretching modes of alkyl monolayer formed on Si(111) surface was investigated by an attenuated total reflection Fourier transform infrared spectroscopy from room temperature up to 540 K. Continuous disordering of the monolayer was indicated from the gradual peak shifts toward higher frequency in C–H stretch modes upon heating. The irreversible conformational disorder was introduced in the monolayer above 440 K.

IX-F-2 Non-Contact Atomic Force Microscopy Using Silicon Cantilevers Covered with Organic Monolayers *via* Silicon–Carbon Covalent Bonds

ARA, Masato¹; SASAHARA, Akira²; OHNISHI, Hiroshi²; TADA, Hirokazu (¹GUAS; ²KAST) [Nanotechnology 15, S65–S68 (2004)]

Silicon cantilevers covered with dodecyl monolayers anchored *via* silicon–carbon covalent bonds were prepared by a wet process and used for non-contact atomic force microscopy (NC-AFM) of TiO₂(110) $-(1\times1)$ surfaces. Figure 1 shows an AFM image of the surface taken with the dodecyl-coated cantilevers. Clear images of atomic rows on atomically flat terraces were observed when the substrate was biased around 2.0 V with respect to the cantilevers. The bias voltage required to give clear images for alkyl-coated cantilevers was higher than that for uncoated ones. Since the cantilevers are thermally and chemically stable, they are applicable to various force microscopy to distinguish chemical species on surfaces.



Figure 1. NC-AFM image of the TiO₂ surface (10 nm \times 10 nm). The frequency shift and sample bias voltage were set at -186 Hz and 2 V, respectively.

IX-G Low Temperature Scanning Tunneling Microscopy and Spectroscopy of Organic Molecules on Metal Surfaces

The electronic structure of molecules adsorbed by metal surfaces is of growing interest in the field not only of surface science but also of molecular-scale electronic devices. Scanning tunneling microscopy and spectroscopy are powerful tool to investigate molecular arrangements and electronic structure with atomic resolution. We have prepared epitaxial films of phathalocyanine molecules on clean metal surfaces and studies there structures by scanning tunneling microscopy and spectroscopy at low temperature.

IX-G-1 Low Temperature Scanning Tunneling Microscopy of Phthalocyanine Multilayers on Au(111) Surfaces

TAKADA, Masaki¹; TADA, Hirokazu (¹GUAS)

[Chem. Phys. Lett. 392, 265–269 (2004)]

We have studied epitaxial trilayer films of cobaltphthalocyanine (CoPc) on Au(111)-22× $\sqrt{3}$ surfaces using a scanning tunneling microscope at 78 K. Figure 1 shows an STM image of a CoPc monoleyer on the Au(111) surface. Molecules in each layer were found to form square lattices and stacked along the [110] axis of the Au(111) surface. While CoPc molecules in the first layer were observed at bias voltages of -2.5 to +2.5 V, there were certain ranges of bias voltage in which molecules in the upper layers were invisible. The electronic structures of molecules in upper layers are more localized than those of the first layer, which is affected by the substrate surface.



Figure 1. STM image of CoPc molecules on the Au(111) surface (14.6 nm \times 14.6 nm).

IX-H Development of New Transport Mechanism Based on Wetting Gradients

Construction and control of wetting gradients on surfaces are of growing interest since the spatiotemporal control of wetting leads to non-mechanical pumping systems in micro-fluidic devices. The imbalance of surface tensions is known to play an important role in the movement of droplets on surfaces. We have succeeded in the reversible control of the direction, magnitude and position of the wetting gradient by in-plane regulation of the electrochemical potential of the thin-film substrate covered with a redox-active self-assembled monolayer. A small droplet of organic liquid was shown to move under the cyclic shift of wetting gradient in aqueous solutions.

IX-H-1 Electrochemically Generated Wetting Gradient and Its Application for the Transport of Droplets

YAMADA, Ryo; TADA, Hirokazu

The in-plane voltage (V_{bias}) was applied to the gold thin film substrate covered with 11-Ferrocenyl-1undecanethiol (FcC11SH) in addition to the conventional potentiostatic regulation of the potential of the substrate with respect to the reference electrode (RE) (Figure 1a). The current flowing through the substrate causes a continuous potential drop in it. The surface covered with FcC11SH monolayer is known to be hydrophobic and hydrophilic when Fc is reduced and oxidized, respectively. When the potential in the substrate crosses the oxidation potential of the FcC11 HS monolayer, a gradient in the extent of oxidation of the ferrocene, and thus, the wetting across the surface is generated (Figure 1b). The generation and regulation of wetting gradient by this method was confirmed by observing the shape of three droplets of nitrobenzene aligned in the biased direction. The one (Figure 2a; left was more negative) and two (Figure 2b) of the droplets got wet as the V_{bias} was increased. Since the electrochemical reaction of ferrocene is reversible, the observed wetting transition was reversible. Position of the wetting gradient can be moved by E_{offset} and direction and magnitude of it are controlled by V_{bias} in Figure 1a. The spatiotemporal control of the wetting gradient enabled us to manipulate a droplet on a substrate. Figure 3 shows the droplet moved in inchworm-like manner. Initially, the wetting gradient was positioned in the left of the picture and the left side of the substrate was wetting in Figure 3a. As wetting region reached the droplet, droplet spread into left, i.e., wetting area as

shown in Figure 3b. When the position of the wetting gradient was reversed, the droplet shrunk from the right side in Figure 3c. As a result, a net transport of the droplet took place.



Figure 1. (a) Schematic drawing of the experimental configuration. (b) Potential profile and wetting distribution on the substrate under the biased condition.



Figure 2. The formation of the wetting gradient by V_{bias} . V_{bias} was -0.6 V(a) and -0.7 V (b). E_{offset} was -300 mV vs. AuO_x .



Figure 3. Inchworm motion of the droplet in the solution. See text for details. $E_{\text{offset}} = (a) -300 \text{ mV}$, (b) -340 mV and (c) -300 mV.

IX-I Development of Precisely-Defined Macromolecules and Their Organization on Substrate Surfaces for Planar Molecular-Scale Electronics Circuits

The concept of molecular-scale electronics is now realized for individual components such as wire, diode, switch, and memory cell, but the fabrication of complete molecular-scale circuits remains challenging because of the difficulty of connecting molecular modules to one another. Molecular monolithic technology, which integrates the wiring, transistors and the required passive elements on a single macromolecule, has been proposed as a promising solution to this problem. In this project we have been trying to establish both the architecture of this novel class of macromolecules and the protocols for their purposive organization on metal/semiconductor substrate surfaces.

IX-I-1 Partially Insulated Molecular Wire as Components for Planar Molecule-Metal Junctions

TANAKA, Shoji

We have developed a series of "partially-insulated" multi-nanometer oligothiophenes to investigate systematically the nature of planar molecule-metal junctions as shown in Figure 1. Charge transport at planar junctions will be controlled by the degree of face-to-face interactions between π -system of conjugated molecules and electrode substrate. Therefore, to define exactly the areas of interactions, we have designed these molecules; the main chain consists of bare π -system as "charge-transfer interface" and insulated π -system possessing electron-donating amino groups as "positive charge-retention sites." Here we describe the electrochemical characterization of these molecules.

Figure 2 shows the cyclic voltammograms of the partially insulated oligothiophenes and the related molecules. In general multi-scan voltammogram of long oligothiophenes (> α -**6T**) is well known to be ill defined as shown in the voltammogram of oligomer 1. The complicated electrochemical behavior can be attributed to severe interchain interactions among the charged long oligomers that induce molecular aggregation and deposition on the electrode. During these processes, charges on an oligomer are dispersed and lost. In contrast, partially insulated oligothiophenes 3,4,6 as well as the fully insulated one 2 afforded reversible steady-state voltammograms. These findings suggest that only a one third coverage of the main chain of the α -9T-18T is enough to reduce the interchain interactions between the charged species and prevent the aggregation. In the case of oligomer 5, slight voltammogram deformation, a symptom of aggregation, was observed. This indicates that the steric hindrance of the alkyl substituents on the interchain interactions is minor but not negligible.

Figure 3 shows the differential pulse voltammograms of partially insulated oligothiophenes 2-4. Judging from the potential difference between the first and second peak, the magnitude of on-site Coulomb repulsion in these oligomers was found to decrease in this order: 4 > 2 > 3. This result may be explained based on the spatial arrangement of the insulated mantle. This component has electron-donating amino groups and tends to attract positive charges. Therefore, separate arrangement of them in the main chain is expected to isolate positive charges from each other resulting in reduction of on-site Coulomb repulsions as illustrated in Figure 3.



Flat nano-gap electrodes buried within insulating substrates

Figure 1. Molecular structure of partially insulated oligothiophenes.



Figure 2. Cyclic voltammograms of oligothiophenes.



Figure 3. Differential pulse voltammograms of oligothiophenes.

IX-J Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π -conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies. In this project new electron acceptors, donors, and donor-acceptor compounds based on heterocycles such as 1,2,5-thiadiazole and 1,3-dithiole were synthesized and their properties including those of the charge-transfer complexes or ion-radical salts were investigated. Unique crystal structures were constructed by using weak intermolecular interactions such as hydrogen bonding or heteroatom contacts.

IX-J-1 Preparation, Structures and Properties of Novel 1,3-Dithiol-2-Ylidene Derivatives Containing Bis(ethynylpyridine) Units

KUMAGAI, Tsutomu¹; TOMURA, Masaaki; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro² (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[Tetrahedron Lett. 44, 6845-6848 (2003)]

1,3-Dithiol-2-ylidene derivatives containing bis (ethynylpyridine) units were synthesized using a Pdcatalyzed reaction of the corresponding dibromide. X-Ray crystal analysis revealed unique crystal structures depending on the aromatic groups. The absorption spectra and redox properties indicated intramolecular charge-transfer interactions between the 1,3-dithiole unit and the pyridyl parts.



2-dipyridyl, 3-dipyridyl, 4-dipyridyl

IX-J-2 (1,3-Dithiol-2-ylidene)propanedinitrile

TOMURA, Masaaki; YAMASHITA, Yoshiro¹ (¹IMS and Tokyo Inst. Tech.)

[Acta Crystallogr., Sect. E 59, 01941–01943 (2003)]

In the crystal structure of the title compound, C₆H₂

 N_2S_2 , there is a tape structure, as a result of C-H···N hydrogen bonds is found. The molecules stack along the [120] direction in a head-to-tail fashion.



Figure 1. Packing diagram of the title compound viewed along the *c* axis. Dashed lines show the intermolecular $S \cdots N$ and $C-H \cdots N$ contacts.

IX-J-3 Crystal Structure of 4,7-Dibromo-2,1,3-Benzothiadiazole, $C_6H_2Br_2N_2S$

TOMURA, Masaaki; YAMASHITA, Yoshiro¹

(¹IMS and Tokyo Inst. Tech.)

[Z. Kristallogr. NCS 218, 555–556 (2003)]

The title compound crystallizes in a centrosymmetric $P2_1/c$ space group with two crystallographically independent molecules in the asymmetric unit. The considerable shortenings of the C1–C6, C4–C5, C7–C12 and C10–C11 bonds are observed. Such double bond fixation suggests the quinonoid character of the 2,1,3-benzothiadiazole ring. Short S…N and Br…Br intermolecular heteroatom contacts are found in the crystal. The S…N [3.226(4) and 3.238(4) Å] and the Br…Br [3.542(1) and 3.662(1) Å] distances are 3.4–3.7% and 1.0–4.3% shorter than the sum of the corresponding van der Waals radii, respectively.



Figure 1. Packing diagram of the title compound viewed along the *b* axis. Dashed lines show the short intermolecular $S \cdots N$ and $Br \cdots Br$ contacts.

IX-J-4 4,5-Diiodo[1,2,5]thiadiazolotetrathiafulvalene

TOMURA, Masaaki; YAMASHITA, Yoshiro¹

(¹IMS and Tokyo Inst. Tech.)

[Acta Crystallogr., Sect. E 60, 063-065 (2004)]

In the crystal structure of the title compound, 5-(4,5diiodo-1,3-dithiol-2-ylidene)-1,3-diaza-2,4,6-trithiapentalene, $C_6I_2N_2S_5$, a large number of short intermolecular heteroatom contacts, such as S…N, S…S, S…I, N…I, and I…I, are observed. The molecules, which are planar within 0.051 Å, stack along the *b* axis in a head-to-head fashion.



Figure 1. Packing diagram of the title compound viewed along the *b* axis. Dashed lines indicate the short intermolecular $S \cdots N$, $S \cdots I$ and $I \cdots I$ contacts.

IX-J-5 Synthesis and Characterization of Novel Dipyridylbenzothiadiazole and Bisbenzothiadiazole Derivatives

AKHTARUZZAMAN, Md.¹; TOMURA, Masaaki; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro² (¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[J. Org. Chem. 69, 2953–2958 (2004)]

Novel dipyridyl compounds containing a mono- and bisbenzothiadiazole unit were synthesized using the Stille coupling reaction. Their pyridinium salts, viologen analogues, were also prepared by the N-alkylation. The X-ray crystallographic analysis of the compounds containing a benzothiadiazole ring revealed nonplanar molecular structures and unique crystal structures depending on the nitrogen positions. The dipyridyl compounds are efficient fluorophores with high electron affinity. The derivative afforded complexes with chloranilic acid and cyanuric acid composed of hydrogen bonding networks. The methyl viologen analogues showed two-stage one-electron reduction waves.



2,2'-dipyridyl, 3,3'-dipyridyl, 4,4'-dipyridyl

IX-K Aquacatalysis

Catalytic organic transformations under mild, safe, and green conditions are important goals in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including π -allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. Rhodium-catalyzed hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids were also found to proceed smoothly in water. Here we wish to report recent progress in this subject.

IX-K-1 Catalytic Oxidation of Alcohols in Water under Atmospheric Oxygen by Use of an Amphiphilic Resin-Dispersion of Nano-Palladium Catalyst

UOZUMI, Yasuhiro; NAKAO, Ryu

[Angew. Chem., Int. Ed. 42, 194–197 (2003); Angew. Chem. 115, 204–207 (2003)]

An amphiphilic polystyrene-poly(ethylene glycol) resin-dispersion of palladium nanoparticles was designed and prepared with a view toward use for catalysis in water. The catalytic aerobic oxidation of various alcohols forming aldehydes, ketones, and carboxylic acids was achieved in water under atmospheric pressure conditions by use of the PS-PEG supported nano-palladium catalyst.



IX-K-2 PS-PEG Resin-Supported Palladium-MOP Complexes. Application in Asymmetric π -Allylic Reduction

UOZUMI, Yasuhiro; HOCKE, Heiko

Homochiral palladium complexes of polymeric 2'-, 6-, and 6'-anchored 2-diphenylphosphino-1,1'binaphthyl (MOP) ligands were prepared on polystyrene-poly(ethylene glycol) (PS-PEG) resin. The PS-PEG resin-supported palladium-MOP complexes exhibited high catalytic activity, stereoselectivity (up to 80% ee), and recyclability (6 times) in the asymmetric allylic reduction of 1-vinyl-1,2,3,4-tetrahydronaphth-1yl benzoate to give 1-vinyl-1,2,3,4-tetrahydronaphthalene.



IX-L Development of New Nanomaterials as Components in Advanced Molecular Systems

Nanometer-sized materials exhibit unique electronic behavior. In the quest of advanced redox catalysis, we are currently interested in combining nanometer-sized materials into molecular redox systems. As a basic architecture, a new type of dendrimers were synthesized and their dynamic behavior was examined.

IX-L-1 Synthesis and Properties of New, Spatially Relaxed Dendrons Containing Internal Carboxyl Groups

KIKUZAWA, Yoshihiro; NAGATA, Toshi

[Bull. Chem. Soc. Jpn. 75, 993–1000 (2004)]

We synthesized a series of new dendrons with up to fourteen internal carboxyl groups. These dendrons are made from a branching unit and a spacer unit with a carboxyl group. The growth reactions (formation of the benzylic ether bonds) completed within a few hours, which suggests the high reactivity at the "focal" point of the dendritic framework. The final deprotection of the internal ester groups also proceeded smoothly. These high reactivities were attributed to the presence of the spacer units, which caused spatially relaxed conformations of these molecules. The carboxylate salt form of the dendron produced both normal and reverse micelles in a THF/water mixed solvent according to the fraction.



Figure 1. The chemical structure of the dendron (generation 3).



Figure 2. Ball-and-stick representations of the dendron, (a) before the molecular dynamics (MD) run, (b) after 100-ps MD without solvent, (c) after 100-ps MD with explicit solvent (CHCl₃).

IX-M Designing Artificial Photosynthesis at Molecular Dimensions

Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

IX-M-1 Synthesis of Dendrimer-Linked Porphyrins Bearing Multiple Quinone Moieties at Internal Positions

KIKUZAWA, Yoshihiro; ITO, Hajime; HINO, Takami; NAGATA, Toshi

By use of dendrons described above, we synthesized dendrimer-linked porphyrins bearing up to fourteen quinone moieties at internal positions of the dendrimer. The CV (cyclic voltammetry) and DPV (differential pulse voltammetry) measurements revealed that all the quinone moieties were simultaneously reduced at -1.18 V. The steady-state fluorescence spectra showed reduced emissions (10–15%), which recovered by chemical reduction of quinones by sodium dithionite.

The quinones in these compounds were quantitatively converted to hydroquinone disilyl ethers by irradiation of these compounds in the presence of PhSSiMe₃. This suggests that even the quinones at the third-generation positions may accept electrons from the photoexcited porphyrin.



Figure 1. The structure of the quinone-dendrimer-linked porphyrins.



Figure 2. The CV and DPV voltammograms of the quinonedendrimer-linked porphyrin zinc complex.

IX-N Photochemistry on Well-Defined Surfaces

Upon the irradiation of light in the wavelength range from visible to ultraviolet, a number of adsorbed molecules on metal surfaces reveal variety of photochemical processes, including photo-stimulated desorption, rearrangement of adsorbed states, photodissociation, and photo-initiated reactions with coadsorbates. A central and fundamental question in the surface photochemistry is to clarify how adsorbate-substrate systems are excited by photon irradiation. In addition, since photo-initiated reactions can be induced without any thermal activation of reactants, they may provide good opportunities for studying a new class of surface reactions that may not be induced thermally. We have studied photochemistry of various adsorption systems on well-defined metal and semiconductor surfaces mainly by temperature-programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), x-ray photoelectron spectroscopy (XPS), work function measurements, near edge x-ray absorption fine structure (NEXAFS) and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation. In this year, the photochemistry of alkane on Pt(111) and Cu(111) surfaces was studied mainly by TPD, XPS, and IRAS.

IX-O Ultrafast Dynamics at Well-Defined Surfaces

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We demonstrate the real-time observations of surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces.

IX-O-1 Direct Time-Domain Observation of Ultrafast Dephasing in Adsorbate-Substrate Vibration under the Influence of a Hot Electron Bath: Cs Adatoms on Pt(111)

WATANABE, Kazuya¹; TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu (¹GUAS)

[Phys. Rev. Lett. 92, 57401 (4 pages) (2004)]

Femtosecond time-resolved second harmonic generation has been used to observe vibrational wavepacket dynamics at a Cs-covered Pt(111)surface. The creation and dephasing of vibrational coherence are monitored *via* the intensity modulations in the second harmonic of probe pulses as a function of pump-probe delay. The TRSHG trace obtained from the clean surface shows an instantaneous sharp rise right after the excitation. This is followed by a fast decaying component (t < 1 ps) and a slowly decaying one persistent to the longest delay (t = 6 ps) of the measurements. When the surface is covered with Cs, SH signals are enhanced by about 70 times and strongly modulated waveforms are superimposed on the TRSHG traces. The oscillatory signals are found in TRSHG signals upon the excitations at 580 and 800 nm, which are the manifestation of nuclear wavepacket dynamics on the surface. The Cscoverage dependence studied in detail indicates that the wavepacket dynamics of Cs-Pt stretching modes and Pt surface phonon modes are responsible for the TRSHG signals. The cos-like initial phase of the oscillatory signals and the coverage dependence of the initial amplitude suggest that the vibrational coherence is associated with the resonant excitation between Csderived states in the quantum well of the Cs overlayer. The rate of Cs-Pt vibrational dephasing increases with the surface temperature. This behavior cannot be accounted for by the increasing contribution from hot bands of low frequency modes. Instead, pure dephasing caused by anharmonic coupling between Cs-Pt stretching and parallel modes in the Cs overlayer is likely the dominant mechanism for the vibrational dephasing.

IX-P Multiphoton Photoelectron Spectroscopy of Electronic States of Nano-Structured Materials on Surfaces

Electronic structure and excited state dynamics of nano-structured materials on surfaces are very important for

exploring their properties, thermal reactivity and nonthermal processes including photochemistry and photo-induced charge transfer. For this purpose, we performed multiphoton photoelectron spectroscopy with the fs time resolution. In this year we applied this method to thin films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA).

IX-P-1 Ultrafast Excited State Dynamics in 3,4,9,10-Perylene Tetracarboxylic Dianhydride (PTCDA) Thin Films

INO, Daisuke¹; WATANABE, Kazuya¹; TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu (¹GUAS)

[Chem. Phys. Lett. 383, 261-265 (2003)]

Ultrafast decay dynamics of the excited state in the

thin films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) have been directly observed by using fs time-resolved two-photon photoelectron spectroscopy. The lifetimes were measured up to the excess energy of 2 eV above the S_1 state. The highly excited state presumably S_2 decays with $\tau = 70$ fs and S_1 with $\tau = 360$ ± 12 fs. The lifetime in the S_1 manifold decreases with increase of excess energy, which manifests itself in a time-dependent energy shift of the photoelectron peak originated from the S_1 state.

IX-Q Chemistry of One-Dimensional Nano-Surface Compounds Studied by Scanning Tunneling Microscopy

The fluctuating configurations of low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, one-dimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics, *i.e.*, one chain does not make a crystal. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured compounds.

IX-Q-1 Dynamic Formation of Reaction Sites at Nano-Structured One-Dimensional Surface Compounds

MATSUMOTO, Yoshiyasu; NAKAGOE, Osamu¹; WATANABE, Kazuya¹; TAKAGI, Noriaki¹ (¹GUAS)

[Proc. SPIE 5223, 232-240 (2003)]

It is well known that the adsorption of O on Ag(110) results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms.

AgO chains arrange periodically to form $(n \times 1)$ $(n = 2 \sim 7)$ depending on the fractional O coverage due to repulsive inter-chain interactions. Scanning tunneling microscopy is utilized to investigate the structural changes of AgO chains on clean and carbidic-carbon

containing Ag(110) surfaces under UV photoirradiation and CO exposure. Although AgO chains are arranged with the (2×1) structure on both of the surfaces, AgO chains are bundled to make the (2×1) bands on the Ccontaining surface, whereas they make much larger domains on the entire surface of clean Ag(110). The photo-induced elimination of O in AgO chains occurs only on the C-containing surface. Kinetics of oxygen elimination by CO exposure are very different between the two surfaces. Oxygen coverage decreases steadily on the C-containing surface with CO exposure, whereas the reaction is accelerated in the lower O coverage range where AgO chains with $(n \times 1)$ $(n \ge 4)$ configurations show significant structural fluctuation. Comparison between the two surfaces and simulations based on the Ising model indicate that the acceleration of the reaction originates from the dynamical formation of active O adatoms by fluctuation of AgO chains.

IX-R Adsorbate Structure and Surface Chemistry on Well-Defined Surfaces

Surface reactions have been playing an important role in production of many useful compounds and also fabrication of electronic devices. In particular, investigations on the structures of adsorbates and their reactivity are the first step for understanding more complicated catalytic reactions. We investigate surface reactions and kinetics

by means of various techniques including temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), work function measurements, Auger electron spectroscopy (AES), infrared reflection absorption spectroscopy (IRAS) and scanning tunneling microscopy (STM).

IX-R-1 Reactivity of Molecular Oxygen: Conversion of Methanol to Formate at Low Temperatures on Pt(111)

SAWADA, Takeshi¹; LIU, Zhengxin²; TAKAGI, Noriaki¹; WATANABE, Kazuya¹; MATSUMOTO, Yoshiyasu

(¹GUAS; ²System Engineers' Co.)

[Chem. Phys. Lett. 392, 334–339 (2004)]

The oxidation of methanol by molecular oxygen on a Pt(111) surface has been investigated by infrared reflection absorption spectroscopy and X-ray photoelectron spectroscopy. Formate is produced when the surface coadsorbed with molecular oxygen and methanol is annealed to 70 K; the temperature is far much lower than the dissociation temperature of molecular oxygen on a clean Pt(111) surface. The attractive interaction between the coadsorbates is postulated to lower a dissociation barrier of molecular oxygen. When a methanol-precovered Pt(111) surface is exposed to O₂, the sticking probability of O₂ decreases with increase of surface temperature and the major product of methanol oxidation is changed from formate to CO.

IX-S Structures, Stabilities and Physicochemical Properties of Organometallic Hybrid Clusters

Recently, metal clusters have gained much attention because they exhibit novel physicochemical properties that are beyond the prediction made by a dimensional scaling of those of the corresponding bulk. In this regard, metal clusters protected by thiolates or stabilized by polymers are promising candidates for elementary units of nano-scale devices. Our interests are focused on the following issues on the organometallic hybrid clusters: (1) a large-scale preparation of the subnanometer-sized clusters, (2) development of size–selection method, (3) determination of chemical compositions of size-selected clusters (*i.e.* the numbers of metal atoms and organic molecules), and (4) elucidation of effect of the core size, core shape, and interaction with organic molecules on stabilities, electronic structures, and chemical properties.

IX-S-1 Magic-Numbered Au_n Clusters Protected by Glutathione Monolayers (n = 18, 21, 25, 28, 32, 39): Isolation and Spectroscopic Characterization

NEGISHI, Yuichi; TAKASUGI, Yoshimitsu¹; SATO, Seiichi¹; YAO, Hiroshi¹; KIMURA, Keisaku¹; TSUKUDA, Tatsuya (¹Univ. Hyogo)

[J. Am. Chem. Soc. 126, 6518-6519 (2004)]

Small gold clusters (< 1 nm) protected by glutathione (GSH) monolayer were fractionated into six components by polyacrylamide gel electrophoresis (PAGE) and their chemical compositions were investigated by electrospray ionization (ESI) mass spectroscopy. The results demonstrate isolation of a series of magic-numbered gold clusters, Au₁₈(SG)₁₁, Au₂₁ $(SG)_{12}$, $Au_{25\pm 1}(SG)_{14\pm 1}$, $Au_{28}(SG)_{16}$, $Au_{32}(SG)_{18}$, and Au₃₉(SG)₂₃. Their optical absorption spectra are highly structured with clear absorption onsets, which shift toward higher energies with reduction of the core size. These molecular-like gold clusters exhibit visible photoluminescence. The results reported herein provide helpful guidelines or starting points for further experimental and theoretical studies on structures, stabilities and optical properties of small gold MPCs.

IX-S-2 Effect of Thiolate Ligation on Stabilization and Electronic Structures of Subnanometer-Sized Gold Clusters

NEGISHI, Yuichi; NOBUSADA, Katsuyuki; TAKASUGI, Yoshimitsu¹; SATO, Seiichi¹; YAO, Hiroshi¹; KIMURA, Keisaku¹; TSUKUDA, Tatsuya (¹Univ. Hyogo)

Small gold clusters protected by *N*-(2-mercaptopropionyl)glycine (MPG) and mercaptosuccinic acid (MSA) were prepared and isolated into several components by high-resolution PAGE. Mass analysis shows that the core sizes of the monolayer-protected gold clusters (gold MPCs) preferentially formed are dependent on the thiolate structures. This finding suggests the completion of the protecting shell plays an important role in stabilizing the gold MPCs with specific core sizes. In other words, it may be possible to prepare gold MPCs with any desired core size by proper design of the thiolate structures. Remarkable effect of thiolate ligation on the optical properties offers a new strategy toward fine-tuning of the fundamental properties of the MPCs through the degree of thiolate ligation as well as core size.

IX-S-3 Construction of Apparatus for Photodissociation and Surface-Induced Dissociation Studies of MPCs

NEGISHI, Yuichi; TSUKUDA, Tatsuya

Photo-dissociation and surface-induced dissociation of MPCs provide direct information on their thermodynamic stabilities. Such information also helps in the understanding of the origin of the preferential formation of certain-sized MPCs. Thus, we have improved our ESI-TOF mass spectrometer by introducing two components: a quadrupole ion trap and a reflectron coupled with an in-line MCP detector with a center hole. The continuous beam of the MPC ions formed in the ESI source is guided to the quadrupole ion trap. The ions accumulated in the trap are extracted into a primary TOF mass spectrometer typically operated at 10 Hz. The mass-selected cluster ions are irradiated by a pulsed laser or allowed to collide with the solid surface mounted at the end of the reflectron. The fragment ions generated are detected by a secondary TOF mass spectrometer.

IX-S-4 Construction of Low-Temperature Optical Spectroscopy System

NEGISHI, Yuichi; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya

We have demonstrated that subnanometer-sized gold clusters exhibit clear structures in their optical spectra even at room temperature. In order to minimize the influence from vibration excitation of internal modes and/or isomers (if present), the measurement at low temperature is required. The system under construction is composed of a sample holder supported on a cold head (~22 K), a vacuum chamber, and a turbo-molecular pump. The system can be coupled to a spectrophotometer (HITACHI, U-2010) or a spectrofluorometer (JASCO, FP-6600) to obtain optical data of the neat film of the clusters.

IX-S-5 Heat Induced Long-Range Ordering of Small Gold Nanoparticles with Tunable Interparticle Spacings

KANEHARA, Masayuki¹; KODZUKA, Etsushi¹; NEGISHI, Yuichi; TSUKUDA, Tatsuya; TERANISHI, Toshiharu¹ (¹Univ. Tsukuba)

The monodisperse Au nanoparticles smaller than 2 nm were prepared by the reduction of HAuCl₄·4H₂O in DMF/H₂O in the presence of a series of ligands, 2,6bis(1'-(*n*-thioalkyl)benzimidazol-2-yl)pyridine (TC_nBIP, n = 8, 10, 12), and formed hexagonal close packed (*hcp*) two-dimensional (2D) superlattices with tunable interparticle spacings from 1.9 to 2.5 nm by the ligand length. Then we present the new methodology to fabricate the long range ordered 2D superlattices of 1.5nm Au nanoparticles at the air-water interface, which includes a heat-induced rearrangement of *hcp* domains into long range ordered *hcp* superlattices stabilized by interligand π - π interaction. The large-scale *hcp* 2D superlattices of 1.5-nm Au nanoparticles were obtained, and advantageously transferable onto any substrate.

IX-S-6 Colloidal Gold Nanoparticles as Catalyst for Carbon–Carbon Bond Formation: Application to Aerobic Homocoupling of Phenylboronic Acid in Water

TSUNOYAMA, Hironori; SAKURAI, Hidehiro; ICHIKUNI, Nobuyuki¹; NEGISHI, Yuichi; TSUKUDA, Tatsuya (¹Chiba Univ.)

[Langmuir 20, 11293–11296 (2004)]

Gold nanoparticles ($\phi < 2$ nm) stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP NPs) were prepared by reduction of AuCl₄⁻ with NaBH₄ in the presence of PVP and characterized via array of methods including optical absorption spectroscopy, TEM, XRD, XANES, EXAFS, and XPS. It is found for the first time that the Au:PVP NPs act as catalyst toward homocoupling reactions of phenylboronic acid in water under aerobic conditions. Suppression of the biphenyl formation under anaerobic condition indicates that molecular oxygen dissolved in water is intimately involved in the coupling reactions. Effect of the particle size and the PVP coordination upon the catalytic activity is discussed.



Figure 1. (a) TEM image, (b) optical absorption spectrum, (c) XRD profile, (d) Au L_3 -edge XANES, (e) FT-EXAFS, (f) XPS of Au:PVP(K-30).

 Table 1. Homocoupling Reactions of Phenylboronic Acid in

 Water Catalyzed by Au:PVP NPs^a.

	- #0Hg #0Hg	0	\bigcirc	Ģ	нон
entry	catalyst	yield $(\%)^b$		$)^{b}$	$d (nm)^d$
		1 ^c	2	3	
1 2 2	Au:PVP(K-15) Au:PVP(K-30)	16 3	62 72	22 23 25	3.1±0.7 2.9±0.4
5 4 ^e 5 6	Au:PVP(K-90) Au:PVP(K-30) recovered from $#2^{f}$	26 43	64 trace 61 49	trace 13 8	- 3.4±0.5 3.4±0.6

^aThe reactions were carried out at room temperature under air for 24 h. ^bEstimated from NMR analysis. ^cDetected as anhydride. ^dParticle diameter after the reaction determined by TEM measurement. ^eThe reaction was carried out under nitrogen. ^fThe Au:PVP NPs were collected by centrifugal ultrafiltration by a filter with10 kDa cutoff.

IX-S-7 Fabrication of Model Catalytic System by Use of Monolayer-Protected Metal Clusters as Precursor

TSUNOYAMA, Hironori; NEGISHI, Yuichi; TSUKUDA, Tatsuya

Metal clusters supported on a surface have been regarded as an ideal model for the study of heterogeneous catalysts.¹⁾ In these studies, metal clusters with a given size were softly deposited on the surface, and the catalytic activity was investigated as a function of the cluster size. However, following difficulties are encountered in this approach: (1) the clusters tend to aggregate at high coverage, (2) the structures of the clusters deposited on a surface may not be uniform because of isomers present in the beam or surfaceinduced structural rearrangement. In order to circumvent these difficulties, we have been developing a new scheme to fabricate an ordered array of size-selected metal clusters. An ordered array of size-selected MPCs is transferred to a solid substrate by using a Langmuir-Brodgett technique. As an initial step, we prepared the monolayer of alkanethiolate-protected gold clusters on a carbon-coated copper grid. In the monolayer obtained, the gold MPCs are arranged regularly with interparticle distance determined by the thickness of the thiolate monolayer.²⁾ The substrate is subsequently transferred into a UHV chamber which accommodates a magnetron-type plasma source. The organic layer of the MPCs is etched by exposure of the oxygen and/or hydrogen plasma. The structures of the resulting clusters are characterized by XPS and AFM. The activity of the model catalysts thus prepared is investigated in situ by means of thermal desorption spectroscopy.

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IX-T Fundamental Study on Electrostatic Manipulation of Biomolecules and Its Application to Gene Analysis

Since conventional DNA sequencing method can determine up to 1000 base pairs at one time, longer DNA must be cut into small fragments. However, order information among these fragments is inevitably lost resulting in tremendous post sequencing process to do a puzzle. To cope with the problem, we have studied DNA sequencing method based on one-by-one DNA handling. The method includes (1) electrostatic manipulation of genomic DNA, (2) fixation in a stretched from, (3) cut from the terminus, (4) recovery and amplification of the fragments.

IX-T-1 On-Demand Mixing Droplet Spotter for Preparing Picoliter Droplets on Surfaces

YOGI, Osamu¹; KAWAKAMI, Tomonori¹; MIZUNO, Akira

(¹Hamamatsu Photonics K. K.)

[Anal. Chem. 76, 2991–2996 (2004)]

An on-demand mixing droplet spotter for generating and mixing picoliter droplet has been developed for ultrasmall reaction vessels. The droplets were generated by appling a ~500 V, ~2 ms pulsed voltage to the tips of capillary tubes (o.d. ~20 μ m; i.d. ~12 μ m) filled with solution. The mixing process was achieved using electrostatic force. The initial droplet was formed by applying the pulsed voltage between one capillary and the substrate, and the second jet of the other solution was generated from the other capillary and collided with the initial droplet automatically because the electric field lines concentrated on the initial droplet. Using this mixing process, a microarray having a concentration gradient was obtained by spotting ~6 pL droplets on a surface with a density of one spot per 75 × 75 μ m².

IX-T-2 Ice-Water Interface Migration by Temperature Controlling for Stretching of DNA Molecules

KOMATSU, Jun¹; NAKANO, Michihiko¹; KURITA, Hirofumi¹; TAKASHIMA, Kazunori¹; KATSURA, Shinji¹; MIZUNO, Akira²

(¹Toyohashi Univ. Tech.; ²IMS and Toyohashi Univ. Tech.)

[J. Biomol. Struct. Dyn. accepted]

This report shows a new DNA stretching method using migration of an ice-water interface. DNA molecules were stretched accompanying the migration of the solid-liquid interface and immobilized in frozen area. This simple method needs no chemical modification to keep DNA in the stretched form. For full stretching of DNA molecules, one terminus of the DNA molecules were anchored on silanized substrate. The anchored DNA molecules were stretched by freezing the DNA solution. The stretched DNA molecules were observed after sublimation of the frozen solution keeping its stretched form on silanized surface which had no attractive interaction with DNA molecules except for the SH-modified terminus in solution. An infrared (IR) laser beam was introduced to a frozen DNA solution through an objective lens for local area melting of the solution. Scanning of the laser irradiation caused stretching and enclosing of DNA molecules in the frozen area followed by migration of the solid-liquid interface.

IX-T-3 Activation of Restriction Enzyme by Electrochemically Released Magnesium Ion

KATSURA, Shinji¹; HARADA, Noriaki¹; MAEDA, Yukihiro¹; KOMATSU, Jun¹; MATSUURA, Shunichi¹; TAKASHIMA, Kazunori¹; MIZUNO, Akira² (¹Toyohashi Univ. Tech.; ²IMS and Toyohashi Univ. Tech.)

[J. Biosci. Bioeng. accepted]

Observation and cutting of DNA molecules at intended positions permit several new experimental methods that are completely different from conventional molecular biology methods; therefore several cutting methods have been proposed and studied. In this paper, a new cutting method for a DNA molecule by localizing the activity of a restriction enzyme is presented. Since most restriction enzymes require magnesium ions for their activation, local restriction enzyme activity can be controlled by the local concentration of magnesium ions. Applying a dc voltage to a needle electrode of metallic magnesium made it possible to control the local magnesium ion concentration at the tip of the needle. The restriction enzyme was activated only when magnesium ions were electrochemically supplied.

IX-U Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Electron Impact at Large Momentum Transfer

Binary (e,2e) or electron momentum spectroscopy (EMS) is a high-energy electron-impact ionization experiment in which kinematics of all the electrons are fully determined by coincident detection of the two outgoing electrons. The method enables us to look at individual molecular orbitals in momentum space, based on the so-called electron Compton scattering. However, EMS has long been plagued by the fact that the present experiments measure averages over all orientations of gaseous targets. The spherical averaging results in enormous loss of versatile information on electronic structure, in particular that on anisotropy of the target wavefunction. Consequently, one must be content to use EMS only as a stringent test for the target wavefunction model employed. Under these historical circumstances, we have successfully developed an electron-electron-fragment ion triple coincidence apparatus that makes it possible to carry out molecular frame EMS experiments for the first time, opening up the possibilities for detailed studies of bound electronic wavefunctions of molecules.

IX-U-1 (e,2e) Ionization-Excitation of H₂

TAKAHASHI, Masahiko¹; KHAJURIA, Yugal; UDAGAWA, Yasuo²

(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[Phys. Rev. A 68, 042710 (7 pages) (2003)]

Binary (e,2e) measurements are reported for simultaneous ionization-excitation processes of H₂. The experiments were performed at impact energies of 1200, 1600 and 2000 eV using an energy- and momentumdispersive spectrometer. Momentum profiles for transitions to the $2s\sigma_g$ and $2p\sigma_u$ excited final ion states are presented as normalized intensities relative to the cross section of the primary ionization to the $1s\sigma_g$ ground ion state. The results are compared with theoretical calculations of Lermer et al. [Phys. Rev. A 56, 1393 (1997)] using the first-order plane-wave impulse approximation. Certain features of the discrepancies between experiment and theory can be explained by incorporating contributions from the second-order twostep mechanisms into the (e,2e) cross sections. Furthermore, the present results suggest that $2s\sigma_g$ and $2p\sigma_u$ cross sections approach their high-energy limits in different ways.

IX-U-2 Electron Momentum Spectroscopy of $N_2 O$

KHAJURIA, Yugal; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²

(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[J. Electron Spectrosc. Relat. Phenom. 133, 113–121 (2003)]

An electron momentum spectroscopy study of the outer valence orbitals of N_2O is reported. The experiments were performed at impact energies of 1000, 1200, 1600 and 1800 eV by using a recently developed multichannel (e,2e) spectrometer. The experimental momentum profiles are compared with each other to examine their impact energy dependence. The results are used for comparisons with Hartree-Fock (HF) and density func-

tional theory (DFT) calculations using various basis sets. The DFT and HF calculations with large basis sets are in good agreement with the measured electron momentum profiles, with the exception of that of the 6σ orbital for which the HF method underestimates the cross sections in the low momentum region.

IX-U-3 Triple Differential Cross-Section of Ne(2s²) in Coplanar to Perpendicular Plane Geometry

CHEN, Li Q.¹; KAHJRIA, Yugal; CHEN, Xian J.¹; XU, Ka Z.¹ (¹USTC)

[Eur. Phys. J. D 26, 141–146 (2003)]

The distorted wave Born approximation (DWBA) with spin average static exchange potential has been used to calculate the triple differential cross sections (TDCSs) for Ne(2s²) ionization by electron impact in the coplanar to perpendicular plane geometry at 110.5 eV incident energy. The present theoretical results at gun angles $\Psi = 0^{\circ}$ (coplanar symmetric geometry) and $\Psi = 90^{\circ}$ (perpendicular plane geometry) are in satisfactory agreement with the available experimental data. A deep interference minimum appears in the TDCS in the coplanar symmetric geometry and a strong peak at a scattering angle $\xi = 90^{\circ}$ caused by the single collision mechanism has been observed in the perpendicular plane geometry. The TDCSs at the gun angles $\Psi = 30^{\circ}$, and $\Psi = 60^{\circ}$ are predicted.

IX-U-4 A High Sensitivity Electron Momentum Spectrometer with Two-Dimensional Detectors and Electron Momentum Distributions of Several Simple Molecules

TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo² (¹*IMS and Tohoku Univ.;* ²*Tohoku Univ.*)

[J. Electron Spectrosc. Relat. Phenom. **137-40**, 387–391 (2004)]

Electron momentum spectroscopy (EMS) makes it

possible to examine orbital patterns of individual molecular orbitals in momentum space. A new spectrometer for electron-electron coincidence experiments for EMS has been developed to obtain orbital patterns quantitatively. Using a spherical analyzer and positionsensitive two-dimensional detectors combined with fast electronics, simultaneous measurements of energy and angular correlations between the two outgoing electrons can be made. This spectrometer features high sensitivity and an ease of changing impact energies. Details of the apparatus are described and impact energy dependence of electron momentum distributions of the HOMO of H_2 and biacetyl are compared.

IX-U-5 Practical Means for the Study of Electron Correlation in Atoms

VAN BOEYEN, Roger W.¹; WATANABE, Noboru²; DOERING, John P.¹; MOORE, John H.³; COPLAN, Michael A.³

(¹Johns Hopkins Univ.; ²IMS and Tohoku Univ.; ³Univ. Maryland)

[Phys. Rev. Lett. 92, 223202 (4 pages) (2004)]

Electron correlation is basic to the understanding of a diverse range of physical and chemical phenomena, yet, there have been no direct measurements of the correlated motion of electrons. Measurement of the correlated momenta of atomic electrons is possible via electron-impact double ionization provided that the ionizing collisions are both impulsive and binary, and the three-body scattering mechanism is known. The results reported here satisfy these conditions, and a practical means for the study of atomic electron correlation through measurement of two-electron momentum densities is presented.

IX-U-6 Development and Use of a Multichannel (e,2e) Spectrometer for Electron Momentum Densities of Molecules

TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo² (¹*IMS and Tohoku Univ.; ²Tohoku Univ.)*

[J. Phys. Chem. Solids 65, 2055–2059 (2004)]

We have developed an (e,2e) spectrometer with the introduction of modern multiparameter techniques. In particular, the high sensitivity achieved by simultaneous detection in energy and momentum is remarkable, opening up the possibilities of more precise and more advanced studies on the electronic structure of atoms and molecules. To illustrate some of the features, an overview of our recent results is presented. Highlights are applications to collision dynamics of H_2 and development of a method for a complete three-dimensional mapping of electron momentum densities in gaseous molecules. Both of these studies are based on the high sensitivity of the spectrometer.

IX-U-7 Electron Momentum Spectroscopy of Valence Satellites of Neon

WATANABE, Noboru¹; KHAJURIA, Yugal; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo² (¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[J. Electron Spectrosc. Relat. Phenom. in press]

Electron momentum spectroscopy (EMS) study of the neon valence satellites is reported. The experiments were performed at impact energies of 1250, 1450 and 1670 eV using a multichannel spectrometer that features high sensitivity. Binding energy spectra up to 100 eV and momentum profiles for the $2p^{-1}$ and $2s^{-1}$ primary transitions as well as the satellites are presented. The results are used to examine impact energy dependence of the relative intensities and shapes of the satellite momentum profiles. The results are also used to determine symmetries and spectroscopic factors of the satellites, and are compared with the previous experiments by EMS and photoelectron spectroscopy and sophisticated theoretical calculations. The present study has largely resolved controversies in the previous studies.

IX-U-8 Observation of Molecular Frame (e,2e) Cross Section Using an Electron-Electron-Fragment Ion Triple Coincidence Apparatus

TAKAHASHI, Masahiko¹; WATANABE, Noboru¹; KHAJURIA, Yugal; NAKAYAMA, Kazuya²; UDAGAWA, Yasuo²; ELAND, John H. D.³ (¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³IMS and Oxford Univ.)

[J. Electron Spectrosc. Relat. Phenom. 141, 83–93 (2004)]

An apparatus for electron-electron-fragment ion triple coincidence experiments has been developed to examine binary (e,2e) scattering reaction in the molecular frame. In the axial recoil limit of fragmentation of the residual ion, measurements of vector correlations among the three charged particles are equivalent to (e,2e) experiments with fixed-in-space molecules. Details and performance of the apparatus are reported, together with preliminary result of collision dynamics study on ionization-excitation processes of fixed-inspace H₂ molecules. We believe that this is the first observation of molecular frame (e,2e) cross sections.

IX-U-9 (e,3e) Collisions on Mg in the Impulsive Regime Studied by Second Born Approximation

WATANABE, Noboru¹; COOPER, John W.²; VAN BOEYEN, Roger W.³; DOERING, John P.³; MOORE, John H.²; COPLAN, Michael A.² (¹IMS and Tohoku Univ.; ²Univ. Maryland; ³Johns Hopkins Univ.)

[J. Phys. B: At., Mol. Opt. Phys. submitted]

Five-fold differential cross sections for electronimpact double ionization of the 3s electrons of magnesium have been calculated in the second Born approximation in the impulsive regime. Comparing these results with calculations carried out in the first Born approximation demonstrates the dominant contribution of the second Born term. The second Born calculation shows that contribution of the two-step 2 (TS2) process becomes large under the condition where sequential binary collisions on the Bethe ridge can occur. The effect of electron correlation in the initial target state is also examined by using a configuration interaction wavefunction.

IX-U-10 Molecular Frame (e,2e) Cross Sections Observed for Ionization-Excitation Processes of H₂

TAKAHASHI, Masahiko¹; WATANABE, Noboru¹; KHAJURIA, Yugal; UDAGAWA, Yasuo²; ELAND, John H. D.³

(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³IMS and Oxford Univ.)

[Phys. Rev. Lett. submitted]

We report on first kinematically complete experiment of (e,2e) scattering by molecules using the electron-electron-fragment ion triple coincidence technique. Vector correlations among the two outgoing electrons and the fragment ion have been measured for ionizationexcitation processes of H₂. The results are used to obtain (e,2e) cross section in the molecular frame and to observe the collision stereodynamics, the phenomenon that has never been explored so far.

IX-U-11 Double Ionization of He by (e,3-1e) at Large Momentum Transfer

KHAJURIA, Yugal; WATANABE, Noboru¹; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²; POPOV, Yuri V.³; KOZAKOV, Konstantin A.³; VINITSKY, Pavel S.³; CHULUUNBAATAR, Ochbadrakh⁴

(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³Moscow State Univ.; ⁴JINR)

[Phys. Rev. A to be submitted]

The present (e,3-1e) experiment aims at investigating double ionization at large momentum transfer that would provide direct information on electron correlation in the target initial state. The (e,3-1e) method involves coincident detection of the two fast outgoing electrons while keeping the slow outgoing electron undetected. It has been found from comparison between experiment and theory that (e,3-1e) momentum profile is very sensitive to the target electron correlation, as expected. In fact, the experimental profile shape is reproduced well by first Born calculations using highly correlated wavefunctions. However, there is noticeable intensity difference between experiment and theory. The calculation underestimates the experimental cross sections significantly by a few times of magnitude, suggesting need of incorporating higher Born terms and/or more accurate description of correlated electron pair in helium.

IX-U-12 (e,2e) Study on Distorted Wave Effects in the Xe 4d⁻¹ Ionization Process

KHAJURIA, Yugal; WATANABE, Noboru¹; YOSHINO, Tae²; SAKAI, Yasuhiro²; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo³ (¹IMS and Tohoku Univ.; ²Toho Univ.; ³Tohoku Univ.)

[J. Phys. B: At., Mol. Opt. Phys. to be submitted]

Momentum profiles for the Xe $4d^{-1}$ ionization process have been studied by means of binary (e,2e) at various impact energies. The results are found to exhibit considerable intensity near the momentum origin that the plane-wave impulse approximation (PWIA) theory can not predict. The discrepancy from PWIA is substantially reduced by distorted-wave theory. Furthermore, momentum profiles for the core $4d_{3/2}$ and $4d_{5/2}$ orbitals of Xe are compared with associated theoretical momentum profiles generated using Dirac-Fock wavefunctions to investigate relativistic effects in the ionization process.

IX-U-13 The Impact Energy Dependence of Momentum Profile of Acetone and Comparison with Theory at Its High-Energy Limit

CHO, Tegyon¹; KHAJURIA, Yugal; WATANABE, Noboru²; TAKAHASHI, Masahiko²; UDAGAWA, Yasuo¹

(¹Tohoku Univ.; ²IMS and Tohoku Univ.)

[J. Phys. B: At., Mol. Opt. Phys. to be submitted]

We report an electron momentum spectroscopy study of the outermost orbital of acetone. The experiments were performed at impact energies of 800, 1200, 1600 and 2000 eV by using a recently developed multichannel (e,2e) spectrometer. The results at 2000 eV are compared with plane-wave impulse approximation calculations using Hartree-Fock (HF) and density functional theory (DFT). While the DFT calculations reproduce the observations better than HF, noticeable discrepancy between experiment and theory still remains.

IX-V Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Photon Impact

The group takes another, photon-impact, approach to issues of electronic structure and collision dynamics, since photon-impact and electron-impact or photoelectric effects and Compton scattering are complementary to each other.

IX-V-1 N 1s Photoionization Cross Sections of the NO Molecules in the Shape Resonance Region

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2}; TAKAHASHI, Masahiko³; YAGISHITA, Akira^{1,2} (¹Univ. Tokyo; ²KEK-PF; ³IMS and Tohoku Univ.)

[J. Phys. B: At., Mol. Opt. Phys. 36, 4617–4629 (2003)]

The N 1s partial photoionization cross sections of NO leading for the ${}^{3}\Pi$ and ${}^{1}\Pi$ ionic states have been measured in the shape resonance region for the first time. The twin local maxima in the cross sections have been tentatively assigned, based on the simple models for the photoabsorption intensities and for the branching ratio of the ${}^{3}\Pi$ and ${}^{1}\Pi$ ionic states from the σ^{*} shape resonance state.

IX-V-2 Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹; FURUYA, Shuusaku³; SOEJIMA, Kouich³; TAKAHASHI, Masahiko⁴; YAGISHITA, Akira^{1,2}; SEMENOV, Sergei K.⁵; CHEREPKOV, Nikolai A.⁵ (¹Univ. Tokyo; ²KEK-PF; ³Niigata Univ.; ⁴IMS and Tohoku Univ.; ⁵State Univ. Aerospace Instrum.)

[Phys. Rev. Lett. 91, 163001 (4pages) (2003)]

Angular distributions of C1s photoelectrons from fixed-in-space CO molecules have been measured with vibrational resolution. A strong dependence of the angular distributions on the vibrational states of the residual molecular ion has been found for the first time in the region of the shape resonance. Calculations in the relaxed core Hartree-Fock approximation have reproduced the angular distributions fairly well in the general shapes of the angular distributions due to the correct description of nuclear motion as an average of the internuclear-distance-dependent dipole amplitudes.

IX-V-3 Photoelectron-Photoion-Photoion Coincidence in Ar Dimers

FANIS, Albert De^{1,2}; OURA, Masaki³; SAITO, Norio⁴; MACHIDA, Masatake^{3,5}; NAGOSHI, Mitsuru⁵; KNAPP, Alexandra⁶; NICKLES, Jurgen⁶; CZASCH, Achim⁶; DÖRNER, Reinhard⁶; TAMENORI, Yusuke¹; CHIBA, Hisashi⁷; TAKAHASHI, Masahiko⁷; ELAND, John H. D.⁸;

UEDA, Kiyoshi²

(¹JASRI; ²Tohoku Univ.; ³RIKEN; ⁴Natl. Metrology Inst.; ⁵Himeji Inst. Tech.; ⁶Univ. Frankfurt; ⁷IMS and Tohoku Univ.; ⁸Oxford Univ.)

[J. Phys. B: At., Mol. Opt. Phys. 37, L1-L8 (2004)]

Photoelectron-photoion-photoion coincidence momentum imaging was applied to study 2p photoemission from Ar dimmers. We present measurements of the kinetic energy released in fragmentation of Ar_2^{++} , angular distributions of energetic fragments, angular distributions of photoelectrons in the laboratory frame and in the molecular frame. The mean kinetic energy of fragment Ar⁺ ions, 2.2 eV, is larger than the value estimated from the Coulomb explosion model with the equilibrium Ar-Ar distance. No significant differences between the photoelectron angular distributions of monomers and dimmers can be found in the laboratory frame. The photoelectron angular distributions of dimmers in the molecular frame show a minimum for electron emission along the dimmer axis at low energies (1.2 and 3.4 eV) and become isotropic at higher kinetic energies.

IX-V-4 Multiplet-Specific N 1s Photoelectron Angular Distributions from the Fixed-in-Space NO Molecules

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2}; TAKAHASHI, Masahiko³; YAGISHITA, Akira^{1,2}; LIN, Ping⁴; LUCCHESE, Robert R.⁴ (¹Univ. Tokyo; ²KEK-PF; ³IMS and Tohoku Univ.; ⁴Texas A&M Univ.)

[J. Phys. B: At., Mol. Opt. Phys. 37, L49–L55 (2004)]

Angular distributions of multiplet-specific N 1*s* photoelectrons from the fixed-in-space NO molecules have been measured for the first time. The dynamics of the σ^* shape resonance appeared in the channel leading to the ${}^{3}\Pi$ and ${}^{1}\Pi$ ionic states has been made clear from the analyses of the angular distributions. Multiplet-specific multichannel calculations have reproduced the observed angular distributions fairy well.

IX-V-5 Angular Distributions of Vibrationally Resolved C 1s Photoelectrons from Fixed-in-Space CO Molecules: Vibrational Effect in the Shape-Resonant C 1s Photoionization of CO

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹; FURUYA, Shuusaku³; SOEJIMA, Kouich³; TAKAHASHI, Masahiko⁴; YAGISHITA, Akira^{1,2}; **SEMENOV, Sergei K.⁵; CHEREPKOV, Nikolai A.⁵** (¹Tokyo Univ.; ²KEK-PF; ³Niigata Univ.; ⁴IMS and Tohoku Univ.; ⁵State Univ. Aerospace Instrum.)

[J. Electron Spectrosc. Relat. Phenom. **137-40**, 243–248 (2004)]

We have measured molecular-frame photoelectron angular distributions (MF-PAD) for the vibrationally resolved C1s photoelectron from CO molecule in the σ shape resonance region. The MF-PAD's for the $v_f = 0$, 1, and 2 levels in the C1s $\rightarrow \epsilon \ell \sigma$ channel are apparently different each other at each incident photon energy. These MF-PAD's agree with the present theoretical results from the averaging the nuclear distance dependent dipole matrix elements with the relaxed core Hartree-Fock calculations. The present results show that the internuclear distance dependences of the phase and of the magnitude of the dipole matrix element play a crucial role in the C1s photoionization of CO.

IX-V-6 Coulomb Hole in N₂, CO and O₂ Deduced from X-Ray Scattering Cross Sections

WATANABE, Noboru¹; KAMATA, Yohei²; YAMAUCHI, Kota²; UDAGAWA, Yasuo²; MÜLLER, Thomas³

(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³Res. Cent. Jülich)

[Mol. Phys. 102, 649-657 (2004)]

Accurate total (elastic + inelastic) x-ray scattering cross sections $\sigma_{ee}(q)$ of N₂, CO and O₂ were measured by the use of the energy dispersive method up to a momentum transfer of q = 12 a.u. The radial electron pair distribution function $P(r_{12})$ was extracted from the cross sections. The Coulomb hole, defined as the difference between the exact $P(r_{12})$ and the corresponding function evaluated at Hartree-Fock limit, has been derived from experimental data for the first time. Comparison of multi reference configuration interaction (MRCI) and averaged quadratic coupled cluster (MR-AQCC) calculations indicate substantial shortcomings of MRCI due to the lack of size extensivity. The overall agreement with experiment is good but some differences between the theoretical and experimental results remain.

IX-V-7 Absolute Surface Coverage Measurement Using a Vibrational Overtone

PIPINO, Andrew C. R.¹; HOEFNAGELS, Johan P. M.²; WATANABE, Noboru³

(¹Natl. Inst. Standards Tech.; ²Eindhoven Univ. Tech.; ³IMS and Tohoku Univ.)

[J. Chem. Phys. 120, 2879–2888 (2004)]

Determination of absolute surface coverage with sub-monolayer sensitivity is demonstrated using evanescent-wave cavity ring-down spectroscopy (EW-CRDS) and conventional CRDS by employing conservation of the absolute integrated absorption intensity between gas and adsorbed phases. The first C-H stretching overtones of trichloroethylene (TCE), cis-dichloroethylene, and trans-dichloroethylene are probed using the idler of a seeded optical parametric amplifier having a 0.075 cm⁻¹ line width. Polarized absolute adsorbate spectra are obtained by EW-CRDS using a fused-silica monolithic folded resonator having a finesse of 28500 at 6050 cm⁻¹, while absolute absorption cross sections for the gas-phase species are determined by conventional CRDS. A measure of the average transition moment orientation on the surface, which is utilized for the coverage determination, is derived from the polarization anisotropy of the surface spectra. Coverage measurement by EW-CRDS is compared to a mass-spectrometer-based surface-uptake technique, which we also employ for coverage measurements of TCE on thermally grown SiO₂ surfaces. To assess the potential for environmental sensing, we also compare EW-CRDS to optical waveguide techniques developed previously for TCE detection.

IX-V-8 Direct Observation of a Symmetry Lowering in Core-Electron Ionization for Highly Symmetric Molecules

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2}; GOLOVIN, Alexander V.²; TAKAHASHI, Masahiko³; TERAMOTO, Takahiro¹; WATANABE, Noboru³; YAGISHITA, Akira^{1,2} (¹Tokyo Univ.; ²KEK-PF; ³IMS and Tohoku Univ.)

(*Nature* to be submitted)

The Jahn-Teller theorem governs stable structures of crystalline solids and molecules with an element of symmetry. This is because electro-vibrational (vibronic) coupling splits degenerate adiabatic-states by lowering the symmetry. The symmetry lowering occurs quite often in the ionization of a core electron of equivalent constituent-atoms for highly symmetric molecules since the core-hole states of those molecules are generally quasi-degenerate and therefore couple over non-totally symmetric vibrational modes. Such couplings, referred as quasi-Jahn-Teller couplings, have been clearly investigated for the most basic example of CO₂; the relation between the symmetry lowering and core-hole localization has been proved. The symmetry lowering which removes the equivalence of two oxygen atoms causes a fundamental quantum mechanical question; is it possible to decide whether the core hole is localized on the right oxygen atom or on the left? Here we report the direct observation of the symmetry lowering of the CO₂ induced by O1s photoionization.

IX-W Study of Electronic Structure of Organic Thin Film and Organic/Inorganic Interface

Organic semiconductors have gained increasing interest because of their highly potential uses in various molecular devices. To clarify the electronic processes at the organic/inorganic interface, various characterization techniques such as high-resolution ultraviolet photoemission spectroscopy (UPS) and near-edge x-ray absorption fine structure (NEXAFS) have been performed for organic thin film systems, because the origin of the energy position and the bandwidth of UPS spectra are keys to understand the interface properties such as the energy level alignment at the interface, intermolecular or molecule-substrate interactions, and carrier transport process. Energy, vibronic coupling and lifetime of a hole created in the highest occupied molecular orbital (HOMO) state in the organic thin film play a crucial role in the hole transport through the film and the electron injection from an electrode to the ionized molecule. The HOMO band in UPS spectra in principle involves such information about the hole, and thus offers a variety of key information that is necessary to unravel fundamental mechanism in carrier transport properties in organic devices.

IX-W-1 Impact of an Interface Dipole Layer on Molecular Level Alignment at an Organic-Conductor Interface Studied by UPS

KERA, Satoshi; YABUUCHI, Yousuke¹; YAMANE, Hiroyuki¹; SETOYAMA, Hiroyuki¹; OKUDAIRA, K. Koji¹; KAHN, Antoine²; UENO, Nobuo¹ (¹Chiba Univ.; ²Princeton Univ.)

[Phys. Rev. B 70, 085304 (6 pages) (2004)]

The effect of an interface dipole layer on the energy level alignment at organic-conductor interfaces is studied on a copper phthalocyanine (CuPc) monolayer/ electric dipole layer/graphite system via ultraviolet photoemission spectroscopy (UPS) and metastable atom electron spectroscopy (MAES). An oriented monolayer of the OTi-phthalocyanine molecule (OTiPc), which has an electric dipole moment, is grown on graphite to yield a well-defined dipole layer with the vacuum side negatively charged. The CuPc monolayer is sequentially deposited on the dipole layer kept at 123 K. This weakly interacting system made of a very thin organic layer on top of a very thin dipole layer is in thermodynamic equilibrium. The UPS data from the system grown with and without the interface dipole layer show that the binding energy of the highest occupied state of the CuPc monolayer decreases when the dipole layer is inserted. The binding energy shift is in excellent agreement with the increase in vacuum level energy of the graphite substrate upon deposition of the dipole layer. The results show that the Fermi level of the CuPc shifts toward the valence states when the interface dipole layer is inserted.

IX-W-2 HOMO-Band Fine Structure of OTi- and Pb-Phthalocyanine Ultrathin Films: Effects of the Electric Dipole Layer

YAMANE, Hiroyuki¹; HONDA, Hiroyuki¹; FUKAGAWA, Hirohiko¹; OHYAMA, Mitsuharu¹; HINUMA, Yoyo¹; KERA, Satoshi; OKUDAIRA, K. Koji¹; UENO, Nobuo¹ (¹Chiba Univ.)

[J. Electron Spectrosc. 137-140, 223–227 (2004)]

Ultraviolet photoelectron spectra were measured for titanyl- and lead-phthalocyanine ultrathin films prepared on graphite in order to study effects of the electric dipole layer on the organic energy levels. Each of these molecules has an electric dipole perpendicular to the molecular plane, and hence a well-defined electric dipole layer could be intentionally prepared by using oriented monolayer of these molecules. For as-grown films the observed highest occupied molecular orbital (HOMO) band consists of many peaks that could be assigned to different molecular orientations/aggregations. For well-oriented monolayer films obtained by annealing the as-grown films, we observed a very sharp HOMO band with two satellites for both molecules as for copper phthalocyanine. Difference of binding energy of HOMO bands between the oriented monolayer and the doublelayer in which molecular dipoles are cancelled was found to agree with the vacuum level shift for both molecules, leading to important conclusions that (1) the molecular energy level with respect to the substrate Fermi level is changed when the molecule is in the dipole-layer and (2) the binding-energy shift corresponds with the vacuum level shift.

IX-W-3 Photoelectron Fine Structures of Uppermost Valence Band for Well-Characterized CIAI-Phthalocyanine Ultrathin Film: UPS and MAES Study

KERA, Satoshi; YAMANE, Hiroyuki¹; HONDA, Hiroyuki¹; FUKAGAWA, Hirohiko¹; OKUDAIRA, K. Koji¹; UENO, Nobuo¹ (¹Chiba Univ.)

[Surf. Sci. 566-568, 571-578 (2004)]

Metastable atom electron spectroscopy was used to characterize monolayer formation of chloroaluminum phthalocyanine (ClAlPc) prepared on graphite. For asgrown film, molecules form island structure of staggered doublelayers on the substrate. By annealing the film, molecules diffuse to form a uniform monolayer where all the molecules are oriented flat with Cl atom directed to the vacuum. After the confirmation of the oriented monolayer formation, high-resolution ultraviolet photoelectron spectra were measured to study effects of the molecular orientation on the energy levels. ClAlPc has an electric dipole perpendicular to the molecular plane, hence a well-defined electric dipole layer could be intentionally prepared by using the oriented monolayer. Difference of binding energies of HOMO bands between the oriented monolayer and the doublelayer was found to agree with the vacuum level shift, leading to a conclusion that the molecular energy level with respect to the substrate Fermi level is changed when the molecule is in the dipole-layer field.

IX-W-4 Study of Excited States of Fluorinated Copper Phthalocyanine by Inner Shell Excitation

OKUDAIRA, K. Koji¹; SETOYAMA, Hiroyuki¹; YAGI, Hideki¹; MASE, Kazuhiko²; KERA, Satoshi; KAHN, Antoine³; UENO, Nobuo¹

(¹Chiba Univ.; ²AIST; ³Princeton Univ.)

[J. Electron Spectrosc. 137-140, 137-140 (2004)]

Near edge X-ray absorption fine structure (NEXA FS) spectra of hexadecafluoro copper phthalocyanine (FCuPc) films (thickness of 50 Å) on MoS₂ substrates were observed near the carbon (C) and fluorine (F) Kedges. From the analysis of the dependence of C and F K-edge NEXAFS spectra on the photon incidence angle (α) , the average molecular tilt angle was determined to be 30°. The lowest and second lowest peaks in the F Kedge NEXAFS were assigned to the transition to σ^* . In the ion time-of-flight mass spectra of FCuPc excited by photons near the F K-edge, F⁺, CF⁺, and CF₃⁺ ions were mainly observed. These results indicate that C-C bonds as well as C-F bonds are broken by the photon irradiation. From the analysis of the partial ion yield spectra of F⁺ and CF⁺ near the F K-edge, the lowest and second lowest peaks in the F K-edge NEXAFS spectra could be assigned to transitions to $\sigma(C-F)^*$ and $\sigma(C-C)^*$, respectively.

IX-W-5 Simulation Study of Angle-Resolved Photoemission Spectra and Intramolecular Energy-Band Dispersion of a PTFE Oligomer Film

YOSHIMURA, Daisuke¹; ISHII, Hisao²; OUCHI, Yukio³; MIYAMAE, Takayuki⁴; HASEGAWA, Shinji⁵; OKUDAIRA, K. Koji⁶; UENO, Nobuo⁶; SEKI, Kazuhiko³

(¹IMS and Nagoya Univ.; ²Tohoku Univ.; ³Nagoya Univ.; ⁴AIST; ⁵Fuji Xerox; ⁶Chiba Univ.)

[J. Chem. Phys. 120, 10753-10762 (2004)]

Theoretical simulations of the angle-resolved ultraviolet photoemission spectra for the oligomer of poly (tetrafluoroethylene) ((CF₂)_n; PTFE) was performed using the independent-atomic-center (IAC) approximation combined with *ab initio* molecular orbital (MO) calculations. Previously observed normal-emission spectra for the end-on oriented sample (with long-chain axis being perpendicular to the surface) showed the incident photon-energy (hv) dependence due to the intramolecular energy-band dispersion along the onedimensional chain,¹⁾ and the present simulations successfully reproduced this hv-dependence of the observed spectra. We employed the experimentally observed helical structure for PTFE oligomers for the simulations. We also calculated the density of states (DOS) for the planar zigzag structure, and examined the changes in the electronic structure due to the difference in the molecular structure by comparing the DOS for the helical and planar zigzag structures. Only little change in the DOS was found between these structures, showing little change of the electronic structure between these conformations. We also evaluated the innerpotential V_0 , which is the parameter defining the energy origin of the free-electron-like final state, and checked the validity of the value of -10 eV estimated in our previous study using the experimentally observed hvdependence of the peak intensity.¹⁾ The estimation of V_0 was performed by pursuing the best agreement between the energy-band dispersion (E = E(k)) relation along the chain direction obtained from the simulated spectra and the experimentally deduced one. An excellent agreement in the topmost band was achieved when the assumed inner potential V_0 was set about zero. This value of V_0 is much different from the value of $V_0 = -10$ eV in the previous study, suggesting the invalidity of the previous assumption at the estimation of V_0 from the peak intensity variation with hv. Using the presently obtained V_0 , we could derive more reliable E = E(k)dispersion relation from the observed ARUPS spectra. The comparison of this newly derived relation gave good agreement with theoretically calculated E = E(k)relations, in contrast to the poor agreement for the previous results with $V_0 = -10$ eV.

Reference

 T. Miyamae, S. Hasegawa, D. Yoshimura, H. Ishii, N. Ueno and K. Seki, *J. Chem. Phys.* **112**, 3333–3338 (2000).

IX-X Effects of High Magnetic Field on Chemical and Physical Processes

We have studied the effects of high magnetic field on chemical reaction and physical processes of diamagnetic and paramagnetic materials to unravel the mechanisms of the interaction of matter and magnetic field and to develop unique methods controlling chemical and physical processes and improving chemical and physical properties of functional materials. Currently we are using a vertical superconducting magnet which can generate high magnetic fields (15 T, 1500 T²/m) in a 40 ϕ bore tube. Last year, we have succeeded, for the first time, to induce 3-dimensional morphological chirality in zinc silicate membrane tube using a high magnetic field. This year, from *in situ* observation, we have verified the mechanism. The Lorentz force on ions induces remarkable convection of a solution in silicate garden reaction. Some other interesting effects of magnetic fields were also studied.

IX-X-1 3-Dimensional Morphological Chirality Induction in Silicate Garden Reaction Using a Magnetic Field

DUAN, Wenyong¹; UECHI, Ichiro¹; KITAMURA, Shu²; FUJIWARA, Yoshihisa²; TANIMOTO, Yoshifumi¹

(¹IMS and Hiroshima Univ.; ²Hiroshima Univ.)

We have reported that three-dimensional morphological chirality can be induced in silicate membrane tubes formed from the reaction of sodium silicate aqueous solution and zinc sulfate crystals by using vertical magnetic fields (5–15 T).¹⁾ In magnetic fields right-handed helical tubes grow along the inner surface of the vessel wall, whereas left-handed tubes grow along the outer surface of the glass rod placed in the vessel. In order to examine whether this new effect is generally observed in silicate garden reaction, we have studied many silicate garden reactions using different metal salt crystals. Morphological chirality is induced in membrane tubes prepared from magnesium chloride, copper sulfate, manganese sulfate, and iron sulfate crystals, indicating that this effect is common in silicate garden reaction. Paramagnetism of metal ion such as copper ion is unimportant for chirality induction, indicating that magnetic force cannot induce morphological chirality. Furthermore, in magnetic fields membrane tubes grown apart from the vessel wall are twisted to the opposite direction to those grown along the inner surface of the wall, as shown in Figure 1.

In order to verify the mechanism, *in situ* observation of the reaction using magnesium salt crystals was carried out in a bore tube of a magnet. At zero field, no convection of sodium silicate aqueous solution was observed regardless of magnesium chloride crystals. In the presence of 15 T vigorous convection was observed only when the crystals were added to the solution. It was shown that helical tubes near the vessel wall grow along the convection, whereas tubes apart the wall are twisted by the convection. It is now verified that Lorentz force on ions blowing out from the membrane tubes induces remarkable convection of the bulk solution.

Reference

1)I. Uechi, A. Katsuki, L. Dunin-Barkovskiy and Y. Tanimoto, J. Phys. Chem. B 108, 2527–2530 (2004).



Figure 1. Photos of zinc silicate membrane tubes grown apart from a vessel wall at zero field (left) and 12 T (right). (Magnification; 175)

IX-X-2 *In Situ* Observation of the Effects of a High Magnetic Field on the Growth of Silver Dendrites

KATSUKI, Akio¹; TANIMOTO, Yoshifumi (¹Shinshu Univ.)

We have showed 3-dimensional morphology and chemical yields of silver dendrites generated by the liquid/solid redox reaction between silver ion and copper metal were remarkably affected by vertical high magnetic fields.¹⁾ In order to clarify the mechanisms, we have undertaken in situ observation of the silver dendrite formation reaction in 2-dimensional system. A thin plate of zinc metal (0.1 mm \times 20 mm \times 5 mm) was sandwiched with two plastic plates (2 mm \times 20 mm \times 55 mm), and silver nitrate aqueous solution was added to the space between two plates. At zero field, dendrites on the upper side of the metal plate grew steadily and no convection of the solution was observed. At 15 T, the top of dendrites underwent precession with bottom fixed. This unique phenomenon indicates that the solution near the dendrites undergoes convection due to the Lorentz force on the flow of ions. Because of concentration gradient of silver ions near the reactive zone of dendrites, silver ions move to dendrite surface and Lorentz force affects the flow of silver ions, leading to the convection of the solution near dendrites. Since dendrites are composed of many small crystals, they are not rigid but flexible. Circular convection of the solution near the dendrites induces precession of the flexible dendrites. This means that Lorentz force is very important for the reaction where concentration gradient of ions is induced during the reaction.

Reference

1) A. Katsuki, I. Uechi and Y. Tanimoto, *Bull. Chem. Soc. Jpn.* **77**, 275–279 (2004).

IX-X-3 Formation of Protein Crystals (Orthorhombic Lysozyme) in a Pseudo-Microgravity Environment Obtained by a Superconducting Magnet

YIN, D. C.¹; WAKAYAMA, N. I.²; HARATA, K.³; FUJIWARA, Masao; KIYOSHI, T.²; WADA, H.²; HUANG, W. D.⁴; TANIMOTO, Yoshifumi (¹NIMS and Northwestern Polytechnical Univ., China; ²NIMS; ³AIST; ⁴Northwestern Polytechnical Univ., China)

[J. Cryst. Growth 270, 184–191 (2004)]

As one of the best candidates for simulating the microgravity conditions in space, low gravity environments provided by applying an upward magnetic force has been considered to grow protein crystals. Since 2002, the stable and long-time durable microgravity generated by a superconducting magnet has been available for protein crystal growth. In this paper, for the first time, we grew protein crystals (orthorhombic lysozyme crystals) at pseudo- microgravity. The present study showed that pseudo-microgravity improves the crystal quality effectively and reproducibly. The application of strong magnetic field also improves the crystal quality. Further verification of the combined effects of microgravity and magnetic field itself may lead to a more general means to grow high quality protein crystals.

IX-X-4 Magnetic Field Effects upon Macroscopic Plastic Deformation of Diamagnetic Single Crystals Containing Paramagnetic Impurity

DUNIN-BARKOVSKIY, L. R.; MORGUNOV, R. B.¹; TANIMOTO, Yoshifumi (¹IMS and ISSIP, Chernogolovka)

It is known that macroscopic magnetoplastic effects in inorganic crystals containing paramagnetic impurity are mainly caused by spin-dependent solid reactions in the system of crystal structure defects. In spite of wide interest to the topic, there is so long a lack of understanding of the mechanisms of such effects. In this work we studied magnetic field effects on plastic deformation of NaCl:Eu single crystals. The crystals were annealed at 770 K and quenched to room temperature. Then they were deformed at room temperature in the absence and presence of a magnetic field (15 T). The field affects the shape of stress-strain diagram, in particular decreases the yield stress by approximately 100%, as shown in Figure 1. Besides, partial or complete suppression of the drop deformation (i.e., Portevin-Le Chaterlier effect), caused by dynamic interaction between movable dislocations and atoms of dissolved impurity, was observed for the first time.



Figure 1. Magnetic field effects on stress-strain diagram of NaCl:Eu single crystal.

IX-X-5 Effect of Horizontal High Magnetic Field on the Movement of *E. coli*

TANIMOTO, Yoshifumi¹; OGAWA, Seiji²; FUJITANI, Kiyomi²; FUJIWARA, Yoshihisa²; IZUMI, Shunsuke²; HIRATA, Toshifumi² (¹IMS and Hiroshima Univ.; ²Hiroshima Univ.)

[Environ. Sci. in press]

Effects of a high magnetic field gradient (8 T, *ca*. 400 T²/m, horizontal) on the behavior of *E. coli* were examined. An *E. coli* suspended solution was injected in one end of a glass tube (5 mm $\phi \times 150$ mm) filled with viscous medium containing sodium nitrate. They move along the tube axis because of chemotaxis to nitrate ion. The speeds for movement from a high (8 T) to a low field (1.5 T) and for the opposite movement are 1.35 and 0.49 cm/h, respectively; it is 0.65 cm/h at a zero field. It is found that the magnetic force hastens the downfield movement of *diamagnetic E. coli* and impedes the upfield movement.

IX-Y Theoretical and Computational Study on Gas Phase Reactions

- 1. Quantum chemical calculations are used to produce potential energy surface (PES) to do reaction dynamics simulations. We develop the methodology to generate PES efficiently and automatically using quantum chemical calculation results. The method does not need any derivative information in quantum chemical calculations.
- 2. We search a reasonable pathway to form H_2 and the other interstellar molecules *via* PAH related catalysts.
- 3. We also calculate (electronic) CD spectra to determine the absolute configuration of several chiral molecules in collaboration with experimentalists.

IX-Y-1 Aromatic Character of Annelated Dimethyldihydropyrenes

AIHARA, Jun-ichi¹; ISHIDA, Toshimasa

(¹Shizuoka Univ.)

[J. Phys. Org. Chem. 17, 393–398(2004)]

Aromaticity is one of the fascinating concepts in modern organic chemistry. It has been defined in structural, magnetic and energetic terms. Historically, many chemists have discussed aromaticity most conveniently in terms of ¹H chemical shifts. Mitchell and coworkers noted that ¹H chemical shifts of the internal methyl groups in dimethyldihydropyrene (DDP) and its annelated derivatives serve to assess the relative local aromaticities of the DDP nuclei. They recently estimated the order of aromaticity for DDP nuclei in annelated derivatives using nucleus-independent chemical shifts (NICS). We found that two graphtheoretically defined energetic quantities, percentage topological resonance energy (% TRE) and bond resonance energy (BRE), can be used to predict readily the relative aromaticities of these hydrocarbons and their DDP nuclei, respectively. Since these quantities are not dependent on the areas of individual rings, they are better suited for estimating the degree of aromaticity.

IX-Y-2 Possible Molecular Hydrogen Formation Mediated by the Inner and Outer Carbon Atoms of Typical PAH Cations

HIRAMA, Mutsumi¹; ISHIDA, Toshimasa; AIHARA, Jun-ichi¹ (¹Shizuoka Univ.)

[Chem. Phys. 305, 307–316 (2004)]

We have been exploring the possibility of H_2 formation mediated by the radical cations of gaseous polycyclic aromatic hydrocarbons (PAHs). In this study, we estimated the catalytic ability of the inner carbon atoms of some typical PAH cations at the B3LYP/6-31G** level of theory and compared it with that of the outer carbon atoms. We presumed as before that H_2 is formed by way of two elementary reactions, the addition of an H atom to a PAH cation and the H abstraction from the resulting arenium ion by another H atom to yield H_2 . We found that both reactions proceed without any activation energy. It follows that almost all carbon atoms of a PAH cation give sites for molecular hydrogen formation. Since there are large compact PAHs abundantly in space, the H_2 formation at the inner carbon atoms of such PAH cations can never be overlooked. Even if inner carbon atoms might be less reactive than peripheral ones, there are many inner carbon atoms in large compact PAH cations.

IX-Y-3 One-Pot Synthesis of Helical Aromatics: Stereoselectivity, Stability against Racemization, and Assignment of Absolute Configuration Assisted by Experimental and Theoretical Circular Dichroism

WATANABE, Masashi¹; SUZUKI, Hiroshi¹; TANAKA, Yasutaka; ISHIDA, Toshimasa; OSHIKAWA, Tatsuo²; TORII, Akiyoshi³ (¹Shizuoka Univ.; ²Numazu College Tech.; ³Saga Univ.)

[J. Org. Chem. in press]

Helical aromatics (1) were synthesized via one step in good quantity by solvent-free condensation of N,N'*p*-phenylenediamine (2) and various carboxylic acids in the presence of Lewis acid. Microwave irradiation greatly facilitated the condensation reaction to furnish 1 with a 100% diastereo- and a 50% enantioselectivity, when a chiral carboxylic acid was utilized. **1f**, derived from 2-methylglutaric acid, was quite stable, no racemization taking place even at 200 °C. The assignment of the absolute configurations to the helical aromatics has been attempted by CD exciton chirality method and comparison of experimental and theoretical CD spectra calculated by time-dependent density functional theory.

IX-Y-4 A Local Interpolation Scheme Using No Derivatives in Potential Sampling: Application to OH + H₂ System

ISHIDA, Toshimasa; SCHATZ, George C.¹ (¹Northwestern Univ.)

[in preparation]

We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and the modified Shepard interpolation proposed by Collins are employed to describe potential energy surfaces. This IMLS/Shepard scheme is applicable to do potential interpolation with quantum chemical results for which analytical derivatives are not available. We applied the scheme to a four atomic system $OH + H_2 \rightarrow H_2O + H$ reaction. As for the former system, we compared the results with those based on the modified Shepard interpolation using second order Taylor expansions. An analytical surface is used to define the potential function so that errors in the interpolation function may accurately be determined. We found that the energy and gradient errors in the present scheme is comparable to those in the modified Shepard scheme. Note that the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does. The accuracy in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

IX-Y-5 Possible Interstellar Molecule Formations Mediated by Naphthalene Cation

HIRAMA, Mutsumi¹; ISHIDA, Toshimasa; AIHARA, Jun-ichi¹ (¹Shizuoka Univ.)

[in preparation]

We have studied the possibilities of interstellar molecule formation mediated by the radical cations in the gas phase. In this letter, we explored the catalytic role of a typical PAH cation, a naphthalene cation, at the both B3LYP/6-31G** and MP2/6-31G** levels of theory. We presumed that interstellar molecule is formed by way of two elementary reactions: the addition of an H atom to a PAH cation and the H abstraction from the resulting arenium ion by one interstellar molecular species to form another interstellar molecular species. It was found that the first reactions proceed with no activation energies. Refinement of the activation energies with both spin-projected and unrestricted MP2 procedures confirmed no or very small activation energies for the second reactions.

We employ the simplest PAH, a naphthalene, as molecular catalyst and consider that the naphthalenium ion is one of the key intermediates not only in the formation of molecular hydrogen but also in the formation of interstellar molecular species. We studied some formations of their species, i.e., HCCH, CH₄, HCN, HNC, H₂O, NH₃, NH₂, CH₃, and CH₂. All of these species and these precursors have observed in space.

IX-Y-6 Molecular Rattles Using Excited States and Non-Adiabatic Transition

ISHIDA, Toshimasa; NANBU, Shinkoh; NAKAMURA, Hiroki

[in preparation]

Non-adiabatic phenomena play crucial roles in the molecular science, in particular, in the molecular material field. Nakamura and Nanbu proposed the idea for the molecular switching with aggressive use of the phenomena although the virtual system composed of an ideal one-dimensional finite periodic potential system was used. The key-phenomena in the idea are the complete reflection and complete transmission. Once we find the appropriate condition for those phenomena in the corresponding system, the molecular motion can be completely controlled without any exception.

We newly propose the application of our idea to the transmission of hydrogen atom through cyclic molecule. This may be regarded as a model of encapsulation by carbon nanotubes.

We explored lots of systems with theoretical calculations, and finally it is found that several model systems seem to be suitable. Two of them are (1) cyclopentadienyl radical (C_5H_5) + H reaction model and (2) C_9H_9 + alkaline atom system.

In these systems, we found complete transmission and reflection, which is based on two non-adiabatic transition of non-adiabatic tunneling type. We will discuss possible application to real systems.

IX-Y-7 Quantum Chemical Study of H₂ Formation Reaction via the Benzene Cation Catalyst

HIRAMA, Mutsumi¹; AIHARA, Jun-ichi¹; ISHIDA, Toshimasa

(¹Shizuoka Univ.)

[in preparation]

We have been exploring a possibility that polycyclic aromatic hydrocarbon (PAH) cations may catalyze the H₂ formation because PAHs are ubiquitous in interstellar space and are probably partly ionized by stellar UV radiation. Benzene is not a PAH, but is an aromatic hydrocarbon, so that it is expected to give similar energy profile to PAHs. Thus, we undertake to use benzene cations to investigate the effect of more sophisticated method for electron correlation on the energy profile of the H₂ formation reaction.

 $\begin{array}{c} C_6H_6^+ + H \xrightarrow{\rightarrow} C_6H_7^+ \\ C_6H_7^+ + H \xrightarrow{\rightarrow} C_6H_6^+ + H_2 \end{array}$

We employed coupled cluster singles and doubles (CCSD) and its modification with the third order perturbation energy (CCSD(T)) as well as QCISD(T) at the MP2-optimized geometries to make comparison of the results with the B3LYP and MP2 ones to estimate higher correlation effects. In addition, use of both the B3LYP and MP2 results proposed by Turecek was valuated. CCSD, CCSD(T), and QCISD(T) calculations gave us activation energies between B3LYP and MP2 values. From these results, hybrid use of B3LYP and MP2 would be justified to estimate activation energies for larger PAH cation catalyst systems.

IX-Z Macromolecular Self-Assembly Opens the Way for Development of Novel Materials That Have Characteristics of Cellular Systems

Methods to integrate functional molecules into well-defined nano structures is a key for fabrication of future materials. Nano-integrated circuits may be afforded by elaborate arrangements of various molecular- and nano-devices. Self-assembly is a strong tool for integration of molecules into various nano structures. Self-assembly, however, tends to give polymorphism and structural defects in the assembled structures. Furthermore, functions of elaborate molecular systems should be sensitive to small structural damages and heat dissipation. For development of the future materials, thus, one should employ a self-assembly process that selectively affords a single, well-defined supramolecular structure to suppress polymorphism. It is also necessary that the formed device is repairable to be robust to damages and defects. We examine such a design strategy that has not yet been examined to date (Figure 1; see also Special Research Project (c)).

Figure 1. A concept of the nano-device that functions on-demand. The device does not function until ondemand self-assembly of nano functional blocks, and can easily be decomposed into the reusable components on demand.

IX-Z-1 Fabrication of Nano-Devices on the Principle of Cellular Supramolecular System

OBA, Toru; HANASAKI, Mitsuru¹; SATO, Michihiro¹; MINABE, Masahiro¹ (¹Utsunomiya Univ.)

> [Photosynthesis: Fundamental Aspects to Global Perspectives in press]

Development of molecular devices has attracted much attention in the field of electronics and photoelectronics. For global, sustainable development, molecular devices and nano-devices should be reusable, repairable, and bio-degradable, which has not been considered to date. We thus aimed at development of an artificial photosynthetic device as a prototype of the flexible (supra)molecular system that functioned on demand (Figure 1). We employed naturally occurring nano-tube, 'microtubule' (MT), to integrate functional molecules into a nano ordered structure. We prepared tubulins (Tubs), component proteins of MT, conjugated with a fluorophore for light-harvesting and with a photosensitizer-labeled hemoprotein for charge separation, respectively, and mixed them simply. Each time these functional blocks self-assembled to form MTs in the assembly/disassembly cycle, solar energy absorbed by the antenna fluorophore migrated to the sensitizer, leading to charge separation between the sensitizer and the heme. The nano-device can easily be decomposed into the components on demand, and the components can readily reassemble on demand to recover the function again.





nano-molecules (loss of function) nano-device (gain of function)

IX-Z-2 Synthesis and Properties of Novel Cationic Chlorophyll Derivatives

OBA, Toru; TAKATOYA, Haruki¹; TOBITA, Hiromi¹; UGAJIN, Aya¹; OGURA, Koji¹; MINABE, Masahiro¹

(¹Utsunomiya Univ.)

[Photosynthesis: Fundamental Aspects to Global Perspectives in press]

Not only metal nano particles but also biomolecules such as DNA, phospholipids, proteins and their supramolecules have been studied for development of molecular devices. It is of much interest to conjugate chlorophylls (Chls), quite abundant photofunctional molecules in nature, with these biomolecules in water for fabrication of novel photofunctional materials such as artificial photosynthetic devices. Chl derivatives that carry cationic charges may be advantageous for interaction with anionic surfaces of the biomolecules and their supramolecules. The conjugation is, however, quite difficult, because, in general, Chls are insoluble in water, resulting in facile formation of higher aggregates. We prepared Chl derivatives that had cationic polymer moiety. Condensation of cationic polymer improved water-solubility, lowered the aggregation number, and enabled conjugation with proteins. The cationic, watersoluble Chl derivative is thus a useful tool for various investigations and applications.

IX-Z-3 Physicochemical Studies on the Molecular Mechanism of Photosynthesis

OBA, Toru; TAMIAKI, Hitoshi¹

(¹*Ritsumeikan Univ.*)

[Photosynthesis: Fundamental Aspects to Global Perspectives in press]

Since chlorophylls (Chls) and bacteriochlorophylls (BChls) are highly asymmetric molecules, an external ligand can coordinate to the central Mg atom of (B)Chls from either of the two sides of the chlorin macrocycle. We found that the 'back' side (Figure 1) is favored for the ligand coordination, by survey of the highly resolved crystal structures of photosynthetic proteins and by theoretical calculations of model molecules. We have recently found that the 'back' type complex is also the major isomer in two newly resolved photosynthetic proteins. In light-harvesting complex II, 6 of 8 Chl a and 4 of 6 Chl b are the 'back'-type complexes, respectively. Among 28 ligand-identified Chls in the photosystem 2 core complex, 22 are the 'back' stereoisomers. Further calculations on the virtual chlorin molecules revealed the origin of the energy gap between the 'back' and the 'face' stereoisomers. We also discuss yet undetermined nomenclatures for the macrocycle faces of (B)Chls.



Figure 1. Molecular structure of the 'back' type chlorophyll *a*-imidazole complex.

Equipment Development Center

IX-AA Development of New Instrument

The technical staff of the Equipment Development Center is partly engaged in planning, researching, designing and constructing high technology experimental instruments in collaboration with the scientific staff. And these experimental instruments are incorporated with new manufacturing technology and new mechanical idea.

IX-AA-1 Development of a High-Precision Slit for Soft-X-Ray Emission Studies

MATSUSHITA, Koji¹; YOSHIDA, Hisashi; SUZUI, Mitsukazu; HORIGOME, Toshio; HATSUI, Takaki; KOSUGI, Nobuhiro

(¹IMS and Nagoya Univ.)

An exit-slit system for the soft x-ray emission end station of the BL3U beamline has been developed. The slit comprises a set of two high-precision blades manufactured by using Electrolytic in-process dressing (ELID) grinding in collaboration with Nagoya University. The slit opening is adjustable from 5 to 100 micron by moving one of the blades in the direction perpendicular to the edge of the blades. The blade is connected to a piezo actuator *via* a solid metal flexure with a magnification of approximately 10. The blade (and the slit opening) is feedback controlled by a position stabilization system equipped with a capacitance-based sensor, which monitors the slit opening. The whole system has been constructed and is now under fine adjustment of the feedback control.

The slit system will be installed in August 2004, and be used in combination with the novel soft-x-ray emission spectrometer constructed by the department of vacuum UV photoscience.

IX-AA-2 Design and Fabrication of Undulator Beamline for STM Observations of Synchrotron Radiation Stimulated Reactions

MATSUSHITA, Koji¹; SUZUI, Mitsukazu; NONOGAKI, Youichi; URISU, Tsuneo (¹IMS and Nagoya Univ.)

The undulator beamline of BL7U at UVSOR was designed and fabricated for Chemical Dynamics Division in Department of Vacuum UV Photoscience. In the BL7U, the undulator radiation were focused by two Pt-coated cylindrical mirrors on the sample surface in the STM chamber set at end station of this beamline. The first mirror was located at 5100 mm downstream from the middle of the undulator. This mirror can move linearly by ± 15 mm to adjust optical path. The second mirror was located at 2000 mm downstream from the first mirror. This mirror can move linearly by ± 15 mm to adjust optical path. The second mirror was located at 2000 mm downstream from the first mirror. This mirror can move linearly by ± 15 mm to the surface normal direction and rotates around both two axes of the vertical and horizontal directions by $\pm 2^{\circ}$, to adjust the spot position on the sample surface.

The ideal design of the two rotating axes is that they are just on the mirror plane for easy beam positioning. However, horizontal rotating axis should be located far from mirror surface by the size of rotating mechanism, because rotating mechanism interfere the optical path. By using elastic hinges that have smaller size than ball bearings, we realized the small gap of \sim 4 mm between the mirror surface and the rotating axis in this system.

The beam positioning system and other beamline components have been constructed at UVSOR BL7U and used for synchrotron irradiation study.

UVSOR Facility

IX-BB Development of the UVSOR Light Source

IX-BB-1 Successful Commissioning of UVSOR-II

KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; HAYASHI, Kenji; HORI, Yo-ichiro¹; HONDA, Toru¹; HAGA, Kai-ichi¹; TAKASHIMA, Yoshifumi²; KOSEKI, Tadashi³; KODA, Shigeru⁴; KITAMURA, Hideo⁵; HARA, Toru⁵; TANAKA, Takashi⁵

(¹KEK-PF; ²Nagoya Univ.; ³RIKEN; ⁴Kyushuu Sync. L. R. C.; ⁵RIKEN/SPring-8)

In 2003, UVSOR was successfully converted to a high brilliance synchrotron light source, UVSOR-II, which has eight straight sections and small emittance of 27 nm-rad. All the reconstruction works were completed within three months, from April to June 2003. The commissioning and the machine tuning were completed until the end of August. User experiments were started in September. The filling beam current is 350 mA. The light source is operated for 12 hours a day with an injection interval of 6 hours. Although a small beam emittance of 27 nm-rad was achieved in the machine studies, the light source is currently operated for users with a moderately small emittance of 60 nm-rad, which gives a longer beam lifetime. The low emittance operation for users will be started after the reinforcement of the RF accelerating system, which is planned in spring, 2005.

IX-BB-2 Commissioning of In-Vacuum Undulator for BL3U

MOCHIHASHI, Akira; KATOH, Masahiro; HOSAKA, Masahito; YAMAZAKI, Jun-ichiro; HAYASHI, Kenji; HORI, Yo-ichiro¹; HONDA, Toru¹; HAGA, Kai-ichi¹; TAKASHIMA, Yoshifumi²; KOSEKI, Tadashi³; KITAMURA,

Hideo⁴; HARA, Toru⁴; TANAKA, Takashi⁴

(¹KEK-PF; ²Nagoya Univ.; ³RIKEN; ⁴RIKEN/SPring-8)

During the construction of UVSOR-II, an in-vacuum undulator was installed, whose period length was 38 mm and the number of the periods was 50. This undulator provides high brilliance soft X-rays to the newly constructed beam-line, BL3U. In the machine studies, it was confirmed that the storage ring could be operated with the small pole gap of 15 mm without reducing the beam lifetime. No beam instabilities, such as the resistive wall instability, were observed. The newly developed control system can correct the electron orbit shift due to the pole gap changes with a precision better than 10 microns. The users can change the pole gap and the photon energy at their experimental station anytime.

IX-BB-3 UVSOR Free Electron Laser

HOSAKA, Masahito; KATOH, Masahiro; MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; HAYASHI, Kenji; TAKASHIMA, Yoshifumi¹; HAMA, Hiroyuki²

(¹Nagoya Univ.; ²Tohoku Univ.)

The upgrade of UVSOR increased the brightness of the electron beam. The improved quality of the beam is of great advantage to the storage ring FEL. We expect increase of the FEL gain by about one order with the present FEL system. In December, 2003, we have succeeded in oscillating the FEL for the first time after the upgrade. We confirmed the increase of the FEL gain. To improve the performance of the FEL further and deliver shorter wavelength laser to user, we are designing a new FEL system, which includes a new invacuum optical klystron type undulator optimized to lasing in the deep UV and VUV region.

IX-CC Researches by the Use of UVSOR

IX-CC-1 Autoionization Selectivity of Ne⁺ Rydberg States Converging to Ne²⁺(¹S^e)

HIKOSAKA, Yasumasa; AOTO, Tomohiro¹; SHIGEMASA, Eiji; ITO, Kenji¹ (¹KEK)

[J. Phys. B 37, 2823 (2004)]

Indirect double photoionization processes of Ne have been studied in the photon energy range from 65.5 to 68.3 eV by using a threshold-photoelectron-photoelectron coincidence method, where intermediatelyformed Ne⁺ states have been defined by the detection of threshold photoelectrons and fast electrons from their autoionizing decay have been analyzed in coincidence. The present investigation revealed that each Ne⁺ Rydberg series converging to Ne²⁺(¹S^e) shows notable selectivity in the autoionizing decay to the final Ne²⁺ states.

IX-CC-2 Dissociative Double Photoionisation of CO below the CO⁺⁺ Threshold

HIKOSAKA, Yasumasa; ELAND, John¹ (¹*Phys. Theor. Chem. Laboratory*)

[Chem. Phys. 299, 147 (2004)]

Dissociative double photoionisation of CO below the adiabatic double ionisation threshold has been studied by the time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) and the velocity imaging photoionisation coincidence (VIPCO) methods. By combining the results from the two methods which give complementary information, the double photoionisation process is identified to $CO + hv \rightarrow CO^{+*} + e^{-} \rightarrow$ $C^{+}(^{2}P) + [O^{+}(^{2}D/^{2}P)]nl + e^{-} \rightarrow C^{+}(^{2}P) + O^{+}(^{4}S) + 2e^{-}.$ The high energy resolution of the TOF-PEPECO spectrometer enables us to resolve individual fragment $[O^{+}(^{2}D/^{2}P)]nl$ states and also intermediate CO^{+*} states. The angular correlations between electrons and ions, deduced from the VIPCO data, imply that the nuclear dissociation is faster or at least comparable in the time scale with molecular rotation, and that the second electron emission occurs after the C⁺ and O^{*} atoms are far apart. A possible generic identification of the intermediate states is suggested.

IX-CC-3 Sub-Natural Linewidth Auger Electron Spectroscopy of the 2s Hole Decay in H₂S

HIKOSAKA, Yasumasa; LABLANQUIE, Pascal¹; PENENT, Francis²; LAMBOURNE, Joe²; HALL, Richard²; AOTO, tomohiro^{3,4}; ITO, kenji³ (¹Univ. Paris Sud; ²Univ. Pierre Marie Curie; ³Univ. Tsukuba; ⁴KEK)

[J. Electron Spectrosc. Relat. Phenom. 137, 287 (2004)]

Threshold photoelectron-Auger electron coincidence spectroscopy has been applied to the sulphur 2s region of H₂S, where the Auger electron spectrum is measured in coincidence with threshold electrons. Formation of H₂S⁺⁺[(S2p)⁻¹(V)⁻¹] states *via* the $L_1L_{2,3}V$ Coster-Kronig transitions is observed above the S 2s photoionization threshold. Even below threshold, formation of these H₂S⁺⁺ states is seen and is due to direct double ionization. A sub-natural linewidth regime is achieved with this coincidence method and three structures resulting from overlaps of the H₂S⁺⁺ [(S2p)⁻¹(V)⁻¹] states appear in the spectra. The three structures probably correspond to H₂S⁺⁺ states with the 2b₁, 5a₁ and 2b₂ holes.

IX-CC-4 Formation of Fluorescent and Metastable Fragments by Photoexcitation of Some Diatomic Molecules in the Vacuum Ultraviolet Region

HIKOSAKA, Yasumasa; LABLANQUIE, Pascal¹; AHMAD, Muthanna²; PENENT, Francis²; ELAND, John³; HALL, Richard²

(¹Univ. Paris Sud; ²Univ. Pierre Marie Curie; ³Phys. Theor. Chem. Laboratory)

[J. Phys. B 37, 283 (2004)]

The formation of fluorescent and metastable fragments from four diatomic molecules, *i.e.* O_2 , N_2 , NO and CO, has been investigated in the vacuum ultra-

violet region. The neutral particles are detected by using a microchannel plate stack, where retarding electric potentials prevent charged particles from reaching the detector. Every diatomic molecule investigated here shows formation of fluorescent and metastable fragments in particular photon energy regions. Three Rydberg states of O₂ converging to $O_2^+(a^4\Pi_u)$ undergo both neutral dissociation processes forming fluorescent $[O^+(^4S)]_{3s} {}^3S_1$ and metastable $[O^+(^4S)]_{3s} {}^5S_2$, the yield curve for each fragment is determined. Direct and cascade formation of the fluorescent $[N^+(^{3}P)]3s$ ⁴P fragment from N₂ are separated, and it is found that the dissociation of the 4so Rydberg state converging to $N_2^+(C^2\Sigma_u^+)$ preferably produces $[N^+(^3P)]_{3p}$ fragments, but not or weakly the $[N^+(^{3}P)]3s$ ⁴P fragment. High-*n* Rydberg states converging to NO+($c^{3}\Pi$) and CO⁺($D^{2}\Pi$) undergo neutral dissociation described by the core ion model, resulting in large peaks for neutral particle formation.

IX-CC-5 New Molecular Inner-Shell Spectroscopy for Probing Multiple Excitations

SHIGEMASA, Eiji; NAKAMURA, Eiken; GEJO, Tatsuo¹

(¹Himeji Inst. Tech.)

[AIP Conf. Proc. 705, 1118 (2004)]

A new experimental setup for probing multi-electron processes in molecular inner-shell ionization regions has been developed at the UVSOR facility, IMS. A zerokinetic-energy electron (ZEKE) analyzer is composed of a lens system on the basis of the penetrating field technique and an electrostatic analyzer. Two identical ion detectors with regarding grids are utilized for detecting the fragment-ions emitted at 0 and 90 degrees relative to the electric vector of the light, which correspond to the symmetry-resolved photoabsorption spectra. The symmetry-resolved ZEKE spectra have been measured by scanning the photon energy with monitoring the intensity of the coincidence signals between the ZEKE electrons and fragment-ions. The results obtained using the new setup are reported.

IX-CC-6 Optical Conductivity of a Non-Fermi-Liquid Material YbRh₂Si₂

KIMURA, Shin-ichi; NISHI, Tatsuhiko¹; SICHELSHMIDT, Joerg²; VOEVODIN, Vladimir²; FESTEL, Jung²; GEIBEL, Charls²; STEGLICH, Frank²

(¹GUAS; ²Max-Planck-Inst. Chem. Phys. Stoffe, Germany)

[J. Magn. Magn. Mater. 272-276, 36–37 (2004)]

The temperature-dependent electronic structure of a pronounced non-Fermi-liquid material YbRh₂Si₂ has been investigated by the optical conductivity measurement in the photon energy range of 10 meV–30 eV at several temperatures of 2.7–300 K: The optical conductivity spectrum as well as the electronic structure changes at two temperatures of 80 and 20 K: At 80 K;

the heavy quasiparticles develop and at 20 K; the non-Fermi liquid behavior appears in the optical conductivity spectra.

IX-CC-7 New Infrared and Terahertz Beamline **BL6B at UVSOR**

KIMURA, Shin-ichi; NAKAMURA, Eiken; YAMAZAKI, Jun-ichiro; KATOH, Masahiro; NISHI, Tatsuhiko¹; OKAMURA, Hidekazu²; MATSUNAMI, Masaharu²; CHEN, Lin²; NANBA, Takao²

(¹GUAS; ²Kobe Univ.)

[AIP Conf. Proc. 705, 416–419 (2004)]

We have designed a new infrared beam line BL6B at UVSOR for infrared and terahertz spectroscopies including microspectroscopy with high brilliance and high flux. The beam line will be replaced in the spring of 2004 from the infrared beam line, BL6A1, at UVSOR. The beam line has a large acceptance angle of $215(H) \times 80(V) \text{ mrad}^2$ and a so-called "magic mirror" is adopted to get the perfect focusing of the bending magnet radiation. The optics and expected performance (focus size, photon flux and brilliance) are reported.

IX-CC-8 Change of Electronic Structure Induced by Magnetic Transitions in CeBi

KIMURA, Shin-ichi; OKUNO, Mitsuru¹; KITAZAWA, Hideaki²; ISHIYAMA, Fumihiko³; SAKAI, Osamu⁴

(¹Kobe Univ.; ²Natl. Inst. Mater. Sci.; ³NTT; ⁴Tokyo Metropolitan Univ.)

[J. Phys. Soc. Jpn. 73, 2041–2044 (2004)]

The temperature dependence of the electronic structure of CeBi arising from two types of antiferromagnetic transitions based on optical conductivity was observed. The optical conductivity spectrum continuously and discontinuously changes at 25 and 11 K, respectively. Between these temperatures, two peaks in the spectrum rapidly shift to the opposite energy sides as the temperature changes. Through a comparison with the band calculation as well as with the theoretical optical conductivity spectrum, this peak shift was explained by the energy shift of the Bi 6p band due to the mixing effect between the Ce 4f Γ_8 and Bi 6p states. The singlelayer antiferromagnetic transition from the paramagnetic state was concluded to be of the second order. The marked changes in the optical conductivity spectrum at 11 K, however, indicated the change in the electronic structure was due to a first-order-like magnetic transition from a single-layer to a double-layer antiferromagnetic phase.

IX-CC-9 Para- to Antiferro-Magnetic Phase Transition of CeSb Studied by Ultrahigh-**Resolution Angle-Resolved Photoemission** Spectroscopy

ITO, Takahiro; KIMURA, Shin-ichi; KITAZAWA,

Hideaki¹

(¹Natl. Inst. Mater. Sci.)

Temperature-dependent angle-resolved photoemission spectroscopy has been performed on CeSb to study the origin of its complicated magnetic phase transition. In the paramagnetic phase $(T \ge 30 \text{ K})$, we have found that the electronic structure near the Fermi level ($E_{\rm F}$) consists of the hole-like Sb 5p band at the Γ point and the electron-like Ce 5d bands at the X point. With decreasing temperature across Néel temperature $(T_{\rm N} = 10 \text{ K})$, both the energy shift and the energy splitting of the bands appear along the ΓX highsymmetry line. While the energy shift of the bands is consistent with the pf mixing model, the energy splitting has not been expected in the model so far. On the other hand, by comparing with the recent calculation based on the pf+dp mixing model, we found a qualitative agreement between the experiment and the calculation. This result suggests the importance of the dp mixing effect to interpret the mechanism of the magnetic phase transition of CeSb.

IX-CC-10 Optical Study on *c*-*f* Hybridization States in Mixed-Valent Yb Compounds: Metallic YbAl₃ vs Semiconducting YbB₁₂

OKAMURA, Hidekazu¹; MICHIZAWA, Takahiro¹; MATSUNAMI, Masaharu¹; NANBA, Takao¹; KIMURA, Shin-ichi; EBIHARA, Takao²; IGA, Fumitoshi³; TAKABATAKE, Toshiro³

(¹Kobe Univ.; ²Shizuoka Univ.; ³Hiroshima Univ.)

[J. Magn. Magn. Mater. 272-276, e51-e52 (2004)]

We have measured the optical conductivity spectra of YbB₁₂ and YbAl₃; which are typical mixed-valent Yb compounds. The measured optical conductivity spectra in the mid-infrared region are quite similar for the two compounds, with a pronounced peak centered near 0.2 eV: This result demonstrates that the Kondo semiconductor YbB₁₂ and the highly metallic YbAl₃ share very similar electronic structures near the Fermi level, in spite of their very different transport properties at low temperatures. This observation is discussed in terms of c-f hybridization states in these compounds.

IX-CC-11 The Origin of the Phase Separation in Partially Deuterated κ-(ET)₂Cu[N(CN)₂]Br Studied by Infrared Magneto-Optical Imaging Spectroscopy

NISHI, Tatsuhiko¹; KIMURA, Shin-ichi; TAKAHASHI, Toshiharu²; ITO, Takahiro; IM, Hojun; KWON, Yong-seung; MIYAGAWA, Kazuya³; TANIGUCHI, Hiromi⁴; KAWAMOTO, Atsushi⁵; KANODA, Kazushi³

(¹GUAS; ²Kyoto Univ.; ³Univ. Tokyo; ⁴Saitama Univ.; ⁵Hokkaido Univ.)

The direct observation of the phase separation between the metallic and insulating states of 75%deuterated κ -(ET)₂Cu[N(CN)₂]Br (d33) using infrared magneto-optical imaging spectroscopy is reported, as well as the associated temperature, cooling rate, and magnetic field dependencies of the separation. The distribution of the center of spectral weight ($\langle \omega \rangle$) of d33 did not change under any of the conditions in which data were taken and was wider than that of the non-deuterated material. This result indicates that the inhomogenity of the sample itself is important as part of the origin of the metal - insulator phase separation.

IX-CC-12 Auger Electron Spectroscopy in Coincidence with Photoelectrons

ITO, Kenji; HIKOSAKA, Yasumasa; SHIGEMASA, Eiji

We have developed Auger-photoelectron coincidence spectroscopy, which involves measuring Auger electrons in coincidence with corresponding photoelectrons, to elucidate the decay dynamics of the innershell hole states followed by the production of doubly charged atomic and molecular ions. Two analyzers for the Auger electrons and photoelectrons have been installed in a vacuum chamber, and we have successfully obtained the first coincidence spectrum for OCS at BL4B in spring 2004. In our experiment, we measure threshold photoelectrons as photoelectrons to attain high detection efficiency. Tuning photon energy at the S 2s ionization threshold, the Auger electron spectra are recorded in coincidence with the threshold photoelectrons. We have observed the Auger lines associated with the formation of OCS⁺⁺[(S 2p)⁻¹(V)⁻¹] states via the $L_1L_{2,3}V$ Coster-Kronig transitions, which are rather faster than usual Auger decay processes such as the LVV transitions. The corresponding Auger spectra measured in the ordinary way show broad structures due to the lifetime effect of the 2s hole states, however, at least five peaks can be observed in the coincidence spectra where the experimental resolution is restricted only by the instrumental resolution.

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RESEARCH ACTIVITIES X Okazaki Institute for Integrative Bioscience

X-A Single-Molecule Physiology

A single molecule of protein (or RNA) enzyme acts as a machine which carries out a unique function in cellular activities. To elucidate the mechanisms of various molecular machines, we need to observe closely the behavior of individual molecules, because these machines, unlike man-made machines, operate stochastically and thus cannot be synchronized with each other. By attaching a tag that is huge compared to the size of a molecular machine, or a small tag such as a single fluorophore, we have been able to image the individual behaviors in real time under an optical microscope. Stepping rotation of the central subunit in a single molecule of F_1 -ATPase has been videotaped, and now we can discuss its detailed mechanism. RNA polymerase has been shown to be a helical motor that rotates DNA during transcription. Myosin V and VI are also helical motors that move as a left- or right-handed spiral on the right-handed actin helix. Single-molecule physiology is an emerging field of science in which one closely watches individual, 'live' protein/RNA machines at work and examines their responses to external perturbations such as pulling and twisting. I personally believe that molecular machines operate by changing their conformations. Thus, detection of the conformational changes during function is our prime goal. Complementary use of huge and small tags is our major strategy towards this end.

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X-A-1 Catalysis and Rotation of F₁ Motor: Cleavage of ATP at the Catalytic Site Occurs in 1 ms before 40° Substep Rotation

SHIMABUKURO, Katsuya¹; YASUDA, Ryohei²; MUNEYUKI, Eiro¹; HARA, Kiyotaka Y.³; KINOSITA, Kazuhiko, Jr.; YOSHIDA, Masasuke^{1,3} (¹Tokyo Inst. Tech; ²Cold Spring Harbor Laboratory; ³ERATO)

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F₁, a water-soluble portion of F₀ F₁-ATP synthase, is an ATP hydrolysis-driven rotary motor. The central ysubunit rotates in the $\alpha_3\beta_3$ cylinder by repeating the following four stages of rotation: ATP-binding dwell, rapid 80° substep rotation, interim dwell, and rapid 40° substep rotation. At least two 1-ms catalytic events occur in the interim dwell, but it is still unclear which steps in the ATPase cycle, except for ATP binding, correspond to these events. To discover which steps, we analyzed rotations of F_1 subcomplex ($\alpha_3\beta_3\gamma$) from thermophilic Bacillus PS3 under conditions where cleavage of ATP at the catalytic site is decelerated: hydrolysis of ATP by the catalytic-site mutant F₁ and hydrolysis of a slowly hydrolyzable substrate ATPγS (adenosine 5'-[γ -thio]triphosphate) by wild-type F₁. In both cases, interim dwells were extended as expected from bulk phase kinetics, confirming that cleavage of ATP takes place during the interim dwell. Furthermore, the results of ATP γ S hydrolysis by the mutant F₁ ensure that cleavage of ATP most likely corresponds to one of the two 1-ms events and not some other faster undetected event. Thus, cleavage of ATP on F1 occurs in 1 ms during the interim dwell, and we call this interim dwell catalytic dwell.

X-A-2 Mechanically Driven ATP Synthesis by F₁-ATPase

ITOH, Hiroyasu^{1,2}; TAKAHASHI, Akira¹; ADACHI, Kengo; NOJI, Hiroyuki³; YASUDA, Ryohei⁴; YOSHIDA, Masasuke⁵; KINOSITA, Kazuhiko, Jr.

(¹Hamamatsu Photonics; ²CREST; ³Univ. Tokyo; ⁴Cold Spring Harbor Laboratory; ⁵ERATO)

[Nature 427, 465-468 (2004)]

ATP, the main biological energy currency, is synthesized from ADP and inorganic phosphate by ATP synthase in an energy-requiring reaction. The F₁ portion of ATP synthase, also known as F1-ATPase, functions as a rotary molecular motor: *in vitro* its y-subunit rotates against the surrounding $\alpha_3\beta_3$ subunits, hydrolysing ATP in three separate catalytic sites on the β -subunits. It is widely believed that reverse rotation of the y-subunit, driven by proton flow through the associated F_0 portion of ATP synthase, leads to ATP synthesis in biological systems. Here we present direct evidence for the chemical synthesis of ATP driven by mechanical energy. We attached a magnetic bead to the γ-subunit of isolated F1 on a glass surface, and rotated the bead using electrical magnets. Rotation in the appropriate direction resulted in the appearance of ATP in the medium as detected by the luciferase-luciferin reaction. This shows that a vectorial force (torque) working at one particular point on a protein machine can influence a chemical reaction occurring in physically remote catalytic sites, driving the reaction far from equilibrium.

X-A-3 Chemomechanical Coupling in F₁-ATPase Revealed by Simultaneous Observation of Nucleotide Kinetics and Rotation

NISHIZAKA, Takayuki^{1,2,6}; OIWA, Kazuhiro¹; NOJI, Hiroyuki³; KIMURA, Shigeki¹; MUNEYUKI, Eiro⁴; YOSHIDA, Masasuke^{4,5}; KINOSITA, Kazuhiko, Jr. (¹Kansai Adv. Res. Cent.; ²PRESTO; ³Univ. Tokyo; ⁴Tokyo Inst. Tech; ⁵ERATO; ⁶Gakushuin Univ.)

[Nat. Struct. Mol. Biol. 11, 142-148 (2004)]

F₁-ATPase is a rotary molecular motor in which unidirectional rotation of the central γ subunit is powered by ATP hydrolysis in three catalytic sites arranged 120° apart around γ . To study how hydrolysis reactions produce mechanical rotation, we observed rotation under an optical microscope to see which of the three sites bound and released a fluorescent ATP analog. Assuming that the analog mimics authentic ATP, the following scheme emerges: (i) in the ATP-waiting state, one site, dictated by the orientation of γ , is empty, whereas the other two bind a nucleotide; (ii) ATP binding to the empty site drives an $\sim 80^{\circ}$ rotation of γ ; (iii) this triggers a reaction(s), hydrolysis and/or phosphate release, but not ADP release in the site that bound ATP one step earlier; (iv) completion of this reaction induces further $\sim 40^{\circ}$ rotation.

X-A-4 Unconstrained Steps of Myosin VI Appear Longest among Known Molecular Motors

ALI, Md. Yusuf¹; HOMMA, Kazuaki²; IWANE, Atsuko H.³; ADACHI, Kengo; ITOH, Hiroyasu^{4,5}; KINOSITA, Kazuhiko, Jr.; YANAGIDA, Toshio³; IKEBE, Mitsuo²

(¹Shahjalal Univ., Bangladesh; ²Univ. Massachusetts Medical School, USA; ³Osaka Univ.; ⁴Hamamatsu Photonics; ⁵CREST)

[Biophys. J. 86, 3804–3810 (2004)]

Myosin VI is a two-headed molecular motor that moves along an actin filament in the direction opposite to most other myosins. Previously, a single myosin VI molecule has been shown to proceed with steps that are large compared to its neck size: either it walks by somehow extending its neck or one head slides along actin for a long distance before the other head lands. To inquire into these and other possible mechanism of motility, we suspended an actin filament between two plastic beads, and let a single myosin VI molecule carrying a bead duplex move along the actin. This configuration, unlike previous studies, allows unconstrained rotation of myosin VI around the right-handed double helix of actin. Myosin VI moved almost straight or as a right-handed spiral with a pitch of several micrometers, indicating that the molecule walks with strides slightly longer than the actin helical repeat of 36 nm. The large steps without much rotation suggest kinesin-type walking with extended and flexible necks, but how to move forward with flexible necks, even under a backward load, is not clear. As an answer, we propose that a conformational change in the lifted head would facilitate landing on a forward, rather than backward, site. This mechanism may underlie stepping of all two-headed molecular motors including kinesin and myosin V.

X-B Bioinorganic Chemistry of Heme-Based Sensor Proteins

Studies of heme-containing gas sensor proteins have revealed a novel function for heme, which acts as an active site for sensing the corresponding gas molecule of a physiological effector. Heme-based O_2 , NO, and CO sensor proteins have now been found in which these gas molecules act as a signaling factor that regulates the functional activity of the sensor proteins. Our research interest focuses on the elucidation of structure-function relationships of CO sensor protein (CooA) and O_2 sensor protein (HemAT).

X-B-1 Activation Mechanisms of Transcriptinal Regulator CooA Revealed by Small-Angle X-Ray Scattering

AKIYAMA, Shuji¹; FUJISAWA, Tetsuro¹; ISHIMORI, Koichiro²; MORISHIMA, Isao²; AONO, Shigetoshi

(¹RIKEN Harima Inst./SPring 8; ²Kyoto Univ.)

[J. Mol. Biol. 341, 651–668 (2004)]

CooA, a heme-containing transcriptional activator, binds CO to the heme moiety and then undergoes a structural change that promotes the specific binding to the target DNA. To elucidate the activation mechanism coupled to CO binding, we investigated the CO-dependent structural transition of CooA with small-angle X-ray scattering (SAXS). In the absence of CO, the radius of gyration R_g and the second virial coefficient (A₂) were $25.3(\pm 0.5)$ Å and $-0.39(\pm 0.25) \times 10^{-4}$ ml mol g⁻², respectively. CO binding caused a slight increase in R_g (by 0.5 Å) and a marked decrease in A_2 (by 5.09 × 10⁻⁴ ml mol g^{-2}). The observed decrease in A_2 points to higher attractive interactions between CO-bound CooA molecules in solution compared with CO-free CooA. Although the minor alternation of R_g rules out changes in the overall structure, the marked change in the surface properties points to a CO-induced conformational transition. The experimental $R_{\rm g}$ and SAXS curves of the two states did not agree with the crystal structure of CO-free CooA. We thus simulated the solution structures of CooA based on the experimental data using rigid-body refinements as well as low-resolution model reconstructions. Both results demonstrate that the hinge region connecting the N-terminal heme domain and Cterminal DNA-binding domain is kinked in CO-free CooA, so that the two domains are positioned close to each other. The CO-dependent structural change observed by SAXS corresponds to a slight swing of the DNA-binding domains away from the heme domains coupled with their rotation by about 8 degrees around the axis of 2-fold symmetry.

X-B-2 Structure and Function of the CO-Sensor Protein CooA

AONO, Shigetoshi; YOSHIOKA, Shiro; INAGAKI, Sayaka

CooA is a heme-containing and CO-sensing transcriptional activator whose activity is regulated by CO, which is the first example of a transcriptional regulator containing a heme as a prosthetic group and of a heme protein in which CO plays a physiological role. A protoheme acts as a CO sensor in CooA. Mutagenesis and spectroscopic studies on CooA from R. rubrum (Rr-CooA) have revealed that the heme in Rr-CooA shows several unique features as described in the following: (1) The exchange of the axial ligand of the heme takes place during the change in the oxidation state of the heme iron. Cys⁷⁵, one of the axial ligands of the ferric heme, is replaced by His⁷⁷ when the heme in CooA is reduced, and vice versa. (2) Hysteresis is observed in electrochemical redox titration, i.e., the observed reduction and oxidation midpoint potentials are -320 mV and -260 mV, respectively. (3) Although the ferrous heme is 6-coordinate with two endogenous axial ligands, CO reacts with the ferrous heme to form the CO-bound heme under physiological conditions. Only CO-bound Rr-CooA is active as the transcriptional activator.

A CooA homologue from a thermophilic CO oxidizing bacterium, *C. hydrogenoformans*, (Ch-CooA) has also been studies. Ch-CooA shows different properties from Rr-CooA for the coordination structure and redox properties. Some information of what is essential for CooA function have been elucidated by comparing the properties between Ch-CooA and Rr-CooA.

X-B-3 Structure and Function of the Oxygen Sensing Signal Transducer Protein HemAT from *Bacillus subtilis*

AONO, Shigetoshi; YOSHIOKA, Shiro; KOBAYASHI, Katsuaki; YOSHIMURA, Hideaki

HemAT-Bs is a heme-containing signal transducer protein responsible for aerotaxis of *Bacillus subtilis*, where the heme acts as an oxygen sensor. We have characterized the recombinant HemAT-Bs to elucidate the mechanisms of oxygen-sensing and signal transduction by HemAT-Bs. HemAT-Bs shows similar uv/vis spectra to those of myoglobin (Mb). Site-directed mutagenesis reveals that His123 is the proximal ligand of the heme in HemAT-Bs.

Oxygen binding and dissociation rate constants are determined to be $k_{on} = 32 \ \mu M^{-1} \ s^{-1}$ and $k_{off} = 23 \ s^{-1}$, respectively, revealing that HemAT-Bs has a moderate oxygen affinity similar to that of sperm whale Mb. The rate constant for autoxidation at 37 °C is 0.06 h⁻¹, which is also close to that of Mb. Although the electronic absorption spectra of HemAT-Bs are similar to those of Mb, HemAT-Bs shows some unique characteristics in its resonance Raman spectra. Oxygen-bound HemAT-Bs gives the v(Fe–O₂) band at a noticeably low frequency (560 cm⁻¹), which suggests a unique hydrogen bonding between a distal amino acid residue and the proximal atom of the bound oxygen molecule. Deoxy HemAT-Bs gives the v(Fe–His) band at a higher frequency (225 cm⁻¹) than those of ordinary His-coordinated deoxy heme proteins.

HemAT-Bs consists of two domains, a N-terminal sensor domain and a C-terminal signaling domain. We have also prepared a truncated mutant consisting of the only N-terminal sensor domain. The heme environmental structure is perturbed by truncating the C-terminal domain. The resonance Raman spectroscopy reveals that a hydrogen bonding pattern toward the heme-bound oxygen is different from each other between wild-type and sensor domain mutant. The rate constant for autoxidation is 0.6 h⁻¹ for the sensor domain mutant. The oxygen binding kinetics are also changed for the sensor domain mutant to be $k_{on} = 69 \ \mu M^{-1} \ s^{-1}$ and $k_{off} = 1.2 \ s^{-1}$, indicating the binding affinity of oxygen increases in this mutant compared with wild-type HemAT-Bs.

X-C Electronic Structure and Reactivity of Active Sites of Metalloproteins

Metalloproteins are a class of biologically important macromolecules that have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloproteins have been thought to depend on the ligands from amino acid, coordination structures, and protein structures in immediate vicinity of metal ions. In this project, we are studying the relationship between the structures of the metal active sites and functions of metalloproteins.

X-C-1 A Salen Iron Complex as a Model for Non-Heme Iron Enzymes; Electronic Structure and Reactivity of the Two-Electron-Oxidized State

KURAHASHI, Takuya; KOBAYASHI, Yoshio¹; FUJII, Hiroshi (¹RIKEN)

High-valent iron-oxo species are proposed to be the key reactive intermediate in oxidation reactions catalyzed by both heme and non-heme iron enzymes. Although oxo-iron (IV) porphyrin π -cation radical and related model species have been extensively investigated in the field of heme chemistry, non-heme counterparts are not well understood. We employ the salen ligand as a non-heme iron model complex, and attempt to isolate a transient oxidizing intermediate. Herein, we describe spectroscopic properties of oxidizing intermediates and discuss the structure-reactivity relationship. We synthesize the salen iron complex 1 having bulky mesityl substituents to avoid an undesirable dimmerization. A low-temperature electrochemical oxidation generates one and two-electron oxidized forms of the complex 1. Spectroscopic investigation by use of UV-Vis, CV, EPR, Mössbauer, and ESI mass spectroscopy indicates that the phenoxy radical iron complex is formed. The reactivity of the oxidized intermediate is also investigated. In contrast, the salen manganese complex 2 exhibits different spectroscopic behavior. In this study, the electronic structure of the oxidized intermediate from 2 is also discussed.



1 M = Fe; 2 M = Mn

Figure 1. Structure of Sterically Hindered Salen Complexes prepared in this study.

X-C-2 A Superoxo-Ferrous State in a Reduced Oxy-Ferrous Hemoprotein and Model Compounds

DAVYDOV, Roman¹; SATTERLEE, James²; FUJII, Hiroshi; SAUER-MASARWA, Alexandra³; BUSCH, Daryle H.³; HOFFMAN, Brian M.¹

(¹Northwestern Univ.; ²Washington State Univ.; ³Univ. Kansas)

[J. Am. Chem. Soc. 125, 16340–16346 (2003)]

Cryoreduction of the $[FeO_2]^6$ (n = 6 is the number of electrons in 3d orbitals on Fe and π^* orbitals on O₂) dioxygen-bound ferroheme through (irradiation at 77 K generates an $[FeO_2]^7$ reduced oxy-heme. Numerous investigations have examined $[FeO_2]^7$ centers that have been characterized as peroxo-ferric centers, denoted $[FeO_2]^{7}_{per}$, in which a ferriheme binds a dianionic peroxo-ligand. The generation of such an intermediate can be understood heuristically if the $[FeO_2]^6$ parent is viewed as a superoxo-ferric center and the injected electron localizes on the O-O moiety. We here report EPR/ENDOR experiments which show quite different properties for the [FeO₂]⁷ centers produced by cryoreduction of monomeric oxy-hemoglobin (oxy-GMH3) from Glycera dibranchiata, which is unlike mammalian globins in having a leucine in place of the distal histidine, and of frozen aprotic solutions of oxy-ferrous octaethyl porphyrin and of the oxy-ferrous complex of the heme model, cyclidene. These $[FeO_2]^7$ centers are characterized as superoxo-ferrous centers, ($[FeO_2]^7_{sup}$), with nearly unit spin density localized on a superoxo moiety which is end-on coordinated to a low-spin ferrous ion. This assignment is based on their g tensors and ¹⁷O hyperfine couplings, which are characteristic of the superoxide ion coordinated to a diamagnetic metal ion, and on the absence of detectable endor signals either from the in-plane ¹⁴N ligands or from an exchangeable H-bond proton. Such a center would arise if the electron that adds to the [FeO₂]⁶ superoxo-ferric parent localizes on the Fe ion, to make a superoxo-ferrous moiety. Upon annealing to T > 150 K the $[FeO_2]^7_{sup}$ species recruit a proton and converts to peroxo/hydroperoxo-ferric ([FeO₂H]⁷) intermediates. These experiments suggest that the primary reduction product is $[FeO_2]^{7}_{sup}$, and that the internal redox transition to $[FeO_2]^7_{per}/[FeO_2H]^7$ states is driven at least in part by Hbonding/proton donation by the environment.

X-C-3 Synthesis and Characterization of Copper(I)-Nitrite Complexes as a Model for a Reaction Intermediate of Copper Nitrite Reductase

KUJIME, Masato; FUJII, Hiroshi

Cu-containing nitrite reductase (NiR) contains a pair of Cu, a type1 Cu ion and a type2 Cu ion, which catalyze the reduction of NO₂⁻ to NO. In the catalytic reduction, type 2 Cu site receives one electron from type 1 Cu site, and reduce Cu-bound NO₂⁻ ion to NO with addition of two protons. In this study, we synthesized Cu(I)-nitrite complexes with various tridentate ligands, TACN^{iPr}Cu(NO₂) (1), TIC^{iPr}Cu(NO₂) (2), TPM^{iPr}Cu (NO₂) (3), and TPM^{Me}Cu(NO₂) (4), as a model for a reaction intermediate of NiR. Reaction of $1 \sim 3$ with acetic acid or trifuluoroacetic acid afforded Cu(II) species, which characterized by UV-Vis and ESR. NO gas generated in the reaction was trapped with Fe(II)octaethylporphyrinate and detected as a NO-Heme complex by ESR. In addition, two equivalent of proton was required for quantitative generation of NO. Therefore, the complexes $1 \sim 3$ produce NO upon addition of two protons and one-electron to the Cu-bound NO₂⁻, similar to native NiR. The rate of NO evolution was accelerated by the use of trifuluoroacetic acid instead of acetic acid, suggesting that the rate-determining step is the protonation of Cu-bound NO_2^{-} .



Figure 1. X-ray Crystal Structure of Copper(I)-Nitrite Complex.

X-D Molecular Mechanism of Heme Degradation and Oxygen Activation by Heme Oxygenase

Heme oxygenase (HO), an amphipathic microsomal protein, catalyzes the regiospecific oxidative degradation of iron protoporphyrinIX (heme) to biliverdinIXa, carbon monoxide, and iron in the presence of NADPH-cytochrome P-450 reductase, which functions as an electron donor. Heme oxygenase reaction is the biosynthesis processes of bile pigments and CO, which is a possible physiological messenger. Recent development in the bacterial expression of a soluble form of heme oxygenase has made it possible to prepare in the large quantities for structural studies. In this project, we are studying the molecular mechanism of heme degradation and the oxygen activation by heme oxygenase using various spectroscopic methods.

X-D-1 Kinetic Isotope Effects on the Rate-Limiting Step of Heme Oxygenase Catalysis Indicate Concerted Proton Transfer/Heme Hydroxylation

DAVYDOV, Roman¹; MATSUI, Toshitaka²; FUJII, Hiroshi; IKEDA-SAITO, Masao²; HOFFMAN, Brian M.¹

(¹Northwestern Univ; ²Tohoku Univ.)

[J. Am. Chem. Soc. 125, 16208–16209 (2003)]

Heme oxygenase (HO) catalyzes the O_2 and NADPH/cytochrome P450 reductase-dependent conversion of heme to biliverdin, free iron ion, and CO through a process in which the heme participates as both dioxygen-activating prosthetic group and substrate. We earlier confirmed that the first step of HO catalysis is a monooxygenation in which the addition of one electron and two protons to the HO oxy-ferroheme produces ferric-meso-hydroxyheme (**h**). Cryoreduction/EPR and ENDOR measurements further showed that hydroperoxo-ferri-HO converts directly to **h** in a single kinetic step without formation of a Compound I. We here report details of that rate-limiting step. One-electron 77 K cryoreduction of human oxy-HO and annealing at 200 K generates a structurally relaxed hydroperoxo-ferri-HO species, denoted R. We here report the cryoreduction/ annealing experiments that directly measure solvent and secondary kinetic isotope effects (KIEs) of the ratelimiting $\mathbf{R} \rightarrow \mathbf{h}$ conversion, using enzyme prepared with meso-deuterated heme and in H₂O/D₂O buffers to measure the solvent KIE (solv-KIE), and the secondary KIE (sec-KIE) associated with the conversion. This approach is unique in that KIEs measured by monitoring the rate-limiting step are not susceptible to masking by KIEs of other processes, and these results represent the first direct measurement of the KIEs of product formation by a kinetically competent reaction intermediate in any dioxygen-activating heme enzyme. The observation of both solv-KIE(298) = 1.8 and sec-KIE(298) = 0.8 (inverse) indicates that the rate-limiting step for formation of h by HO is a concerted process: proton transfer to the hydroperoxo-ferri-heme through the distal-pocket H-bond network, likely from a carboxyl group acting as a general acid catalyst, occurring in synchrony with bond formation between the terminal hydroperoxo-oxygen atom and the α -meso carbon to form a tetrahedral hydroxylated-heme intermediate. Subsequent rearrangement and loss of H₂O then generates h.



Figure 1. Mechanism of a proton transfer.

X-D-2 Essential Amino Acid Residues Controlling the Unique Regioselectivity of Heme Oxygenase in *Pseudomonas aeruginosa*

FUJII, Hiroshi; ZHANG, Xuhong¹; YOSHIDA, Tadashi¹

[J. Am. Chem. Soc. 126, 4466–4467 (2004)]

Heme oxygenase (HO), an amphipathic microsomal protein, catalyzes the oxygen-dependent degradation of heme (iron-protoporphyrinIX) to -biliverdin, CO, and free iron ion. Interestingly, all of HO regiospecifically oxidize the α -meso position of the heme to formbiliverdin isomer while nonenzymatic heme degradation forms all four possible α -, β -, γ -, δ -biliverdin isomers at nearly identical yield. Recently, an interesting example has been found in HO (PigA) of the Gram-negative bacterium Pseudomonas aeruginosa, which does not produce α -biliverdin at all, but forms the mixture of β and δ -biliverdins at a ratio of 3:7. While studying the mechanism of the unique regioselectivty of PigA, we found essential amino acid residues, Lys34, Lys132, and Phe189, controlling the unique regioselectivity of PigA. In this communication, we show that Lys34 and Lys132 are essential amino acid residues to hold the rotated heme in the active site of PigA via hydrogen-bonding interaction with the heme propionate and that Phe189 controls the product ratio of β - and δ -biliverdins via steric interaction with heme substituents. These interactions place the β - or δ -meso position of the heme at the oxidation site of PigA, leading to the unique regioselectivity.



Figure 1. Active Site Structure of PigA-HO proposed in this study.

X-E Biomolecular Science

Elucidation of a structure-function relationship of metalloproteins and structural chemistry of amyloid are current subjects of this group. The primary technique used for the first project is the stationary and time-resolved resonance Raman spectroscopy excited by visible and UV lasers. Various model compounds of active site of enzymes are also examine with the same technique. IR-microscope dichroism analysis and AFM are the main techniques for the second project. The practical themes that we want to explore for the first project are (1) mechanism of oxygen activation by enzymes, (2) mechanism of active proton translocation and its coupling with electron transfer, (3) structural mechanism of signal sensing and transduction by heme-based sensor proteins, (4) higher order protein structures and their dynamics, and (5) reactions of biological NO. In category (1), we have examined a variety of terminal oxidases, cytochrome P450s, and peroxidases, and also treated their reaction intermediates by using the mixed flow transient Raman apparatus and the Raman/absorption simultaneous measurement device. For (2) the third-generation UV resonance Raman (UVRR) spectrometer was constructed and we are going to apply it to a giant protein like cytochrome c oxidase with $M_r = 210,000$. Recently, we succeeded in pursuing protein folding of apomyoglobin by combining UV time-resolved Raman and rapid mixing device. We also determined the carboxylic side chains of bovine cytochrome oxidase which undergo protonation/deprotonation changes and hydrogen-bonding status changes in response with electron transfers between metal centers or ligand dissociation from heme a_3 . Currently, we focus our attention on detecting tyrosine radical for the P intermediate of terminal oxidases. In (3) we are interested in a mechanism of ligand recognition specific to CO, NO or O_2 and a communication pathway of the ligand binding information to the functional part of the protein. Several gas sensor heme proteins were extensively treated in this year. For (4) we developed a novel technique for UV resonance Raman measuremnts based on the combination of the first/second order dispersions of gratings and applied it successfully to 235-nm excited RR spectra of several proteins including mutant hemoglobins and myoglobins. Nowadays we can carry out time-resolved UVRR experiments with nanosecond resolution to discuss protein dynamics. With the system, we have succeeded in isolating the spectrum of tyrosinate in ferric Hb M Iwate, which was protonated in the ferrous state, and the deprotonated state of Tyr244 of bovine cytochrome c oxidase. The study is extended to a model of Tyr244, an imidazole-bound para-cresol coordinated to a metal ion, was synthesized and its UV resonance Raman was investigated. For (5) we purified soluble guanylate cyclase from bovine lung and observed its RR spectra in the presece of allosteric effectors. To further investigate it, we are developing an expression system of this protein. For the amyloid study, we examined FTIR spectra of β_2 -microglobulin and its #11-21, K3, and K3-K7 peptides which form a core part of amyloid fibril.

X-E-1 Construction of a Square-Planar Hydroperoxo-Copper(II) Complex Inducing a Higher Catalytic Reactivity

FUJII, Tatsuya¹; NAITO, Asako¹; YAMAGUCHI, Syuhei¹; WADA, Akira¹; FUNAHASHI, Yasuhiro¹; JITSUKAWA, Koichiro¹; NAGATOMO, Shigenori; KITAGAWA, Teizo; MASUDA, Hideki¹ (¹Nagoya Inst. Tech.)

[Chem. Commun. 2700-2701 (2003)]

A novel hydroperoxo-copper(II) complex with a square-planar geometry has been prepared, which has exhibited a higher selectivity and catalytic reactivity for dimethyl sulfide, in contrast to that with a trigonal-bipyramidal one.

X-E-2 Copper Hydroperoxo Species Activated by Hydrogen-Bonding Interaction with Its Distal Oxygen

YAMAGUCHI, Syuhei¹; NAGATOMO, Shigenori; KITAGAWA, Teizo; FUNAHASHI, Yasuhiro¹; OZAWA, Tomohiro¹; JITSUKAWA, Koichiro¹; MASUDA, Hideki¹ (¹Nagoya Inst. Tech.)

[Inorg. Chem. 42, 6968-6970 (2003)]

A novel copper(II)-OOH complex with functional ligand that can form a hydrogen bond with the distal oxygen of hydroperoxide has been designed and prepared as a structural/functional model of dopaminehydroxylases, whose spectroscopic characterization and decomposition rates have indicated that the hydroperoxide is activated through the hydrogen-bonding interaction with the distal oxygen.

X-E-3 Thermal Stability and Absorption Spectroscopic Behavior of (μ-Peroxo)dicopper Complexes Regulated with Intramolecular Hydrogen Bonding Interactions

YAMAGUCHI, Syuhei¹; WADA, Akira¹; FUNAHASHI, Yasuhiro¹; NAGATOMO, Shigenori; KITAGAWA, Teizo; JITSUKAWA, Koichiro¹; MASUDA, Hideki¹ (¹Nagoya Inst. Tech.)

[Eur. J. Inorg. Chem. 2003, 4378–4386 (2003)]

In order to clarify the effect of hydrogen bonding on the stabilities of (μ -peroxo)dicopper complexes with a *trans*-1,2-peroxo form, novel copper complexes with intramolecular hydrogen bonding interaction sites have been synthesized, and their spectroscopic properties and thermal stabilities studied. The selected tripodal tetradentate ligands were tris(2-pyridylmethyl)amine (TPA) derivatives bearing pivalamido and amino groups at the 6-position of the pyridine ring in TPA, {[6-(pivalamido) pyrid-2-yl]methyl}bis(pyrid-2-ylmethyl)amine (MPPA) and [(6-aminopyrid-2-yl)methyl]bis(pyrid-2-ylmethyl) amine (MAPA). The single-crystal X-ray structure of a monomeric Cu^{II} complex with N₃⁻ namely [Cu(mppa) N₃]ClO₄ (1a), revealed an interligand hydrogen bonding interaction between the substituent NH group of MPPA and the azide nitrogen atom in the axial position. The Cu^I complexes of MPPA and MAPA were immediately oxygenated with dioxygen in acetone solution at -78 °C to give the µ-peroxo dinuclear copper(II) complexes $[{Cu(mppa)}_{2}(O_{2})]^{2+}$ (1b) and $[{Cu(mapa)}_{2}(O_{2})]^{2+}$ (2b). These complexes exhibited two kinds of characteristic absorption bands ($\pi^*_{\sigma} \rightarrow d_{\sigma}, \pi^*_{v} \rightarrow d_{\sigma}$) originating from the ligand-metal charge transfer (LMCT) of O_2^{2-1} to Cu. Affected by the hydrogen bonding interaction, the π^*_d CT band shifted significantly to a higher energy region and the $\pi^*_v \rightarrow d_\sigma$ CT absorbance decreased due to stabilization of the π^* orbital and restriction of the Cu–O bond rotation. The thermal stabilities of the (µperoxo)dicopper(II) complexes were estimated from their decomposition rates which decreased in the order, **2b** $[{Cu(tpa)}_2(O_2)]^{2+}$ (**3b**) > **1b** >> $[{Cu(6-metpa)}_2(O_2)]^{2+}$ (**4b**) $\{6-MeTPA = [(6-methylpyrid-2-yl)methyl]$ bis(pyrid-2-ylmethyl)amine}. The above findings indicate that the interligand hydrogen bonding interaction, although overcome to some extent by the adverse effect of the steric bulk of the NH group, is inclined to stabilize (µ-peroxo)dicopper(II) complexes.

X-E-4 CO Binding Study of Mouse Heme-Regulated eIF-2 α Kinase: Kinetics and Resonance Raman Spectra

IGARASHI, Jotaro¹; SATO, Akira²; KITAGAWA, Teizo; SAGAMI, Ikuko³; SHIMIZU, Toru¹ (¹Tohoku Univ.; ²GUAS; ³Tohoku Univ. and Kyoto Prefectural Univ.)

[Biochim. Biophys. Acta 1650, 99-104 (2003)]

Heme-regulated eukaryotic initiation factor (eIF)-2a kinase (HRI) regulates the synthesis of globin chains in reticulocytes with heme availability. In the present study, CO binding kinetics to the 6-coordinated Fe(II) heme of the amino-terminal domain of mouse HRI and resonance Raman spectra of the Fe(II)-CO complex are examined to probe the character of the heme environment. The CO association rate constant, k_{on} , and CO dissociation rate constant, k_{off} , were 0.0029 μ M⁻¹s⁻¹ and $0.003\ s^{-1},$ respectively. These values are very slow compared with those of mouse neuroglobin and sperm whale myoglobin, while the koff value of HRI was close to those of the 6-coordinated hemoglobins from Chlamydomonas and barley (0.0022 and 0.0011 s⁻¹). The dissociation rate constant of an endogenous ligand, which occurs prior to CO association, was 18.3 s^{-1} , which was lower than those (197 and 47 s^{-1}) of the same 6-coordinate hemoglobins. Resonance Raman spectra suggest that the Fe-C-O adopts an almost linear and upright structure and that the bound CO interacts only weakly with nearby amino acid residues.

X-E-5 Resonance Raman Study on Synergistic Activation of Soluble Guanylate Cyclase by Imidazole, YC-1 and GTP

PAL, Biswajit; LI, Zhengqiang¹; OHTA, Takehiro; TAKENAKA, Shigeo²; TSUYAMA, Shingo²; KITAGAWA, Teizo

(¹IMS and Jilin Univ.; ²Osaka Prefecture Univ.)

[J. Inorg. Biochem. 98, 824-832 (2004)]

Soluble guanylate cyclase (sGC), a physiological nitric oxide (NO) receptor, is a heme-containing protein and catalyzes the conversion of GTP to cyclic GMP. We found that 200 mM imidazole moderately activated sGC in the coexistence with 3-(5'-hydroxymethyl-2'-furyl)-1-benzylindazole (YC-1), although imidazole or YC-1 alone had little effect for activation. GTP facilitated this process. Resonance Raman spectra of imidazole complex of native sGC and CO-bound sGC (CO-sGC) have demonstrated that a simple heme adduct with imidazole at the sixth coordination position is not present for both sGC and CO-sGC below 200 mM of the imidazole concentration and that the Fe-CO stretching band (v_{Fe-CO}) appears at 492 cm⁻¹ in the presence of imidazole compared with 473 cm⁻¹ in its absence. Both frequencies fall on the line of His-coordinated heme proteins in the v_{Fe-CO} vs v_{C-O} plot. However, it is stressed that the CO-heme of sGC becomes photo-inert in the presence of imidazole, suggesting the formation of five-coordinate CO-heme or of six-coordinate heme with a very weak trans ligand. These observations suggest that imidazole alters not only the polarity of heme pocket but also the coordination structure at the fifth coordination side presumably by perturbing the heme-protein interactions at propionic side chains. Despite the fact that the isolated sGC stays in the reduced state and is not oxidized by O₂, sGC under the high concentration of imidazole (1.2 M) yielded v_4 at 1373 cm⁻¹ even after its removal by gel-filtration, but addition of dithionite gave the strong v_4 band at 1360 cm⁻¹. This indicated that imidazole caused autoxidation of sGC.

X-E-6 Heme Structures of Five Variants of Hemoglobin *M* Probed by Resonance Raman Spectroscopy

JIN, Yayoi¹; NAGAI, Masako¹; NAGAI, Yukifumi¹; NAGATOMO, Shigenori; KITAGAWA, Teizo (¹Kanazawa Univ.)

[Biochemistry 43, 8517-8527 (2004)]

The α -abnormal Hb Ms show physiological properties different from the β -abnormal Hb Ms, that is, extremely low oxygen affinity of the normal subunit and extraordinary resistance to both enzymatic and chemical reduction of the abnormal met-subunit. To get insight into the contribution of heme structures to these differences among Hb Ms, we examined the 406.7-nm excited resonance Raman (RR) spectra of five Hb Ms in the frequency region from 1700 to 200 cm⁻¹. In the highfrequency region, profound differences between met- α and met- β abnormal subunits were observed for the inplane skeletal modes (the $v_{C=C}$, v_{37} , v_2 , v_{11} and v_{38} bands), probably reflecting different distortions of heme structure caused by the out-of-plane displacement of the heme iron due to tyrosine coordination. Below 900 cm⁻¹, Hb M Iwate [α (F8)]His \rightarrow Tyr], exhibited a distinct spectral pattern for the v_{15} , γ_{11} , $\delta(C_bC_aC_b)_{2,4}$ and $\delta(C_bC_cC_d)_{6,7}$ compared to that of Hb M Boston [$\alpha(E7)$] His \rightarrow Tyr], although both heme irons are coordinated by Tyr. The β -abnormal Hb Ms, namely, Hb M Hyde Park [β (F8)]His \rightarrow Tyr], Hb M Saskatoon [β (E7)]His \rightarrow Tyr], and Hb M Milwaukee [β (E11)]Val \rightarrow Glu], displayed RR band patterns similar to that of metHb A, but with some minor individual differences. The RR bands characteristic of the met-subunits of Hb Ms totally disappeared by chemical reduction and the ferrous heme of abnormal subunits was no more bonded with Tyr or Glu. They were bonded to the distal (E7) or proximal (F8) His, and this was confirmed by the presence of the $v_{\text{Fe-His}}$ mode at 215 cm⁻¹ in the 441.6nm excited RR spectra. A possible involvement of heme distortion in differences of reducibility of abnormal subunits and oxygen affinity of normal subunits is discussed.

X-E-7 Vibronic Coupling between Soret and Higher Energy Excited States in Iron(II) Porphyrins: Raman Excitation Profiles of A_{2g} Modes in the Soret Region

EGAWA, Tsuyoshi¹; SUZUKI, Noriyuki²; DOKOH, Takashi²; HIGUCHI, Tsunehiko²; SHIMADA, Hideo³; KITAGAWA, Teizo; ISHIMURA, Yuzuru³ (¹IMS and Keio Univ.; ²Univ. Tokyo; ³Keio Univ.)

[J. Phys. Chem. A 108, 568–577 (2004)]

Resonance Raman spectra were observed for heme proteins and iron(II) porphyrins including ferrous-CO and ferrous-isocyanide derivatives of cytochrome P450_{cam}, a synthetic iron(II) porphyrin complex having a thiolate axial ligand, ferrous-isocyanide derivative of myoglobin, and synthetic iron(II) porphyrin complexes having either an imidazole or a sulfide axial ligand. Among them, the former three were found to be a hyperporphyrin, giving red and blue Soret absorption bands, whereas others were normal porphyrins giving a single Soret band. When Raman scattering was excited within the Soret region, an anomalously polarized (ap) Raman line, which was assignable to the v_{19} mode belonging to the A_{2g} species, was observed at 1537-86 cm⁻¹ for all these compounds. Both the synthetic iron (II) porphyrins having the imidazole and sulfide ligands also showed another ap Raman line at 1230 cm⁻¹, which was assigned to v_{26} of A_{2g} symmetry. Raman excitation profiles of the v_{19} and v_{26} modes showed a maximum that was displaced from the 0-0 component of the Soret or red Soret band toward higher frequencies by the frequency of the corresponding mode, indicating the 0-1 component. Although Raman lines of these modes were also observed upon excitation at the 0-0 component, they were significantly more intense at the 0-1 component. These results, together with nonadiabatic theories about vibronic contribution to Raman intensity, indicated the presence of vibronic coupling between the Soret (or red Soret) excited state and some other electronic excited state(s) located in the blue of the Soret band. The present study hence demonstrates that lower occupied orbitals other than those described in the ordinary four-orbital model and its extended form, which is applicable to the hyperporphyrins, contribute to the Soret (or red Soret) excited states.

X-E-8 Dioxygen Reactivity of Copper(I) Complexes with Tetradentate Tripodal Ligands Having Apliphatic Nitrogen Donors: Synthesis, Structures, and Properties of Peroxo and Superoxo Complexes

KOMIYAMA, Kazuya¹; FURUTACHI, Hideki¹; NAGATOMO, Shigenori; HASHIMOTO, Akifumi¹; HAYASHI, Hideki¹; FUJINAMI, Shuhei¹; SUZUKI, Masatatsu¹; KITAGAWA, Teizo

(¹Kanazawa Univ.)

[Bull. Chem. Soc. Jpn. 77, 59-72 (2004)]

Oxygenation of copper(I) with tetradentate tripodal ligands (L) comprised of a tris(aminoethyl)amine (tren) skeleton having sterically bulky substituent(s) on the terminal nitrogens has been investigated, where L = tris(*N*-benzylaminoethyl)amine (L^{H,Bn}), tris(*N*-benzyl-*N*-methylaminoethyl)amine ($L^{Me,Bn}$), or tris(*N*,*N*dimethylaminoethyl)amine (L^{Me,Me}). All the copper(I) complexes reacted with dioxygen at low temperatures to produce superoxocopper(II) and/or trans-(µ-1,2peroxo)-dicopper(II) complexes depending on the steric bulkiness of the terminal nitrogens and the reaction conditions. The reaction of a copper(I) complex [Cu $(L^{H,Bn})]^+$ at -90 °C in acetone resulted in the formation of a superoxo complex $[Cu(L^{H,Bn})(O_2)]^+$ as a less stable species and a peroxo complex $[\{Cu(L^{H,Bn})\}_2(O_2)]^{2+}$ as a stable species. The structures of $[Cu(L^{H,Bn})]_2(O_2)]^{2+}$ as a $[{Cu(L^{H,Bn})}_2(O_2)](BPh_4)_2 \cdot 8(CH_3)_2CO \text{ were determined by X-ray crystallography. } [{Cu(L^{H,Bn})}_2(O_2)]^{2+}$ has a trans-(u-1,2-peroxo)-dicopper(II) core with a trigonal bipyramidal structure. The O-O bond distance is 1.450(5) Å with an intermetallic Cu-Cu separation of 4.476(2) Å. The resonance Raman spectrum of [{Cu $(L^{H,Bn})$ ₂(O₂)]²⁺ measured at -90 °C in acetone-d6 showed a broad v(O–O) band at 837–834 cm⁻¹ (788 cm^{-1} for an ¹⁸O labeled sample) and two v(Cu-O) bands at 556 and 539 cm⁻¹, suggesting the presence of two peroxo species in solution. $[Cu (L^{Me,Bn})]^+$ also produced both superoxo and *trans*-u-1,2-peroxo species, $[Cu(L^{Me,Bn})(O_2)]^+$ and $[\{Cu(L^{Me,Bn})\}_2(O_2)]^{2+}$. At a lower concentration of $[Cu (L^{Me,Bn})]^+$ (~0.24 mM) and higher dioxygen concentration ($P(O_2) = -1$ atm), the superoxo species is predominantly formed, whereas at a higher concentration of $[Cu(L^{Me,Bn})]^+$ (~1 mM) and lower dioxygen concentration ($P(O_2) = -0.02$ atm) the formation of the peroxo species is observed. The resonance Raman spectrum of $[Cu(L^{Me,Bn})(O_2)]^+$ (~1 mM) in acetone- d_6 at ~-95 °C exhibited a v(O-O) band at 1120 cm⁻¹ (1059 cm⁻¹ for an ¹⁸O labeled sample) and that of $[{Cu(L^{Me,Bn})}_2(O_2)]^{2+}$ (~3 mM) in acetone-*d*₆ at ~-90 °C showed two v(O–O) bands at 812 and 797 cm⁻¹ (767 and 753 cm⁻¹ for an ¹⁸O labeled sample), respectively. A similar observation was also made for $[{Cu (L^{Me,Me})}_2(O_2)]^{2+}$. Relationships between the energies of the LMCT and *d*–*d* transitions and those of the v(O–O) and v(Cu–O) stretching vibrations and the steric constraints in the Cu(II)–(O₂^{2–})–Cu(II) core are discussed.

X-E-9 Dinuclear Copper-Dioxygen Intermediates Supported by Polyamine Ligands

TERAMAE, Shinichi¹; OSAKO, Takao²; NAGATOMO, Shigenori; KITAGAWA, Teizo; **FUKUZUMI**, Shunichi¹; ITOH, Shinobu² (¹Osaka Univ.; ²Osaka City Univ.)

[J. Inorg. Biochem. 98, 746–757 (2004)]

Reactivity of the dicopper(I) and dicopper(II) complexes supported by novel polyamine ligands L1 (1,11-bis(6-methylpyridin-2-yl)-2,6,10-triaza-2,6,10tribenzylundecane) and L2 (5-benzyl-1,9-bis(6-methylpyridin-2-yl)-2,8-bis(6-methylpyridin-2-ylmethyl)-2,5,8-triazanonane) towards O_2 and H_2O_2 , respectively, has been investigated in order to shed light on the ligand effects on Cu₂/O₂ chemistry. The dicopper(I) complex of L1 (1a) readily reacted with O2 in a 2:1 ratio at a low temperature (-94 °C) in acetone to afford a mixture of $(\mu - \eta^2 : \eta^2 - \text{peroxo})$ dicopper(II) and bis $(\mu - \text{oxo})$ dicopper (III) complexes. The formation of these species has been confirmed by the electron spin resonance (ESR) silence of the solution as well as their characteristic absorption bands in the UV-visible region [max = 350]and 510 nm due to the peroxo complex and ~400 nm due to the $bis(\mu$ -oxo) complex] and the resonance Raman bands at 729 cm⁻¹ [$\Delta v({}^{16}O_2 - {}^{18}O_2) = 38 \text{ cm}^{-1}$] due to the peroxo complex and at 611 and 571 cm⁻¹ $[\Delta v({}^{16}O_2 - {}^{18}O_2) = 22 \text{ and } 7 \text{ cm}^{-1}, \text{ respectively}] \text{ due to}$ the bis(μ -oxo) complex. The peroxo and bis(μ -oxo) complexes were unstable even at the low temperature, leading to oxidative N-dealkylation at the ligand framework. The dicopper(I) complex of L2 (2a) also reacted with O_2 to give (μ -hydroxo)dicopper(II) complex $(2b^{OH})$ as the product. In this case, however, no active oxygen intermediate was detected even at the low temperature (-94 °C). With respect to the copper(II) complexes, treatment of the $(\mu$ -hydroxo)dicopper(II) complex of L1 $(1b^{OH})$ with an equimolar amount of H_2O_2 in acetone at -80 °C efficiently gave a (µ-1,1hydroperoxo)dicopper(II) complex, the formation of which has been supported by its ESR-silence as well as UV-vis (370 and 650 nm) and resonance Raman spectra $[881 \text{ cm}^{-1}; \Delta v({}^{16}\text{O}_2 - {}^{18}\text{O}_2) = 49 \text{ cm}^{-1}].$ The (µ-1,1hydroperoxo)dicopper(II) intermediate of L1 also decomposed slowly at the low temperature to give similar oxidative N-dealkylation products. Kinetic studies on the oxidative N-dealkylation reactions have been performed to provide insight into the reactivity of the active oxygen intermediates.

X-E-10 Structural Characterization of a Binuclear Center of a Cu-Containing NO Reductase Homologue from *Roseobacter denitrificans*: EPR and Resonance Raman Studies

MATSUDA, Yuji¹; UCHIDA, Takeshi; HORI, Hiroshi²; KITAGAWA, Teizo; ARATA, Hiroyuki¹ (¹Kyushu Univ.; ²Osaka Univ.)

[Biochim. Biophys. Acta 1656, 37-45 (2004)]

Aerobic phototrophic bacterium Roseobacter denitrificans has a nitric oxide reductase (NOR) homologue with cytochrome c oxidase (CcO) activity. It is composed of two subunits that are homologous with NorC and NorB, and contains heme c, heme b, and copper in a 1:2:1 stoichiometry. This enzyme has virtually no NOR activity. Electron paramagnetic resonance (EPR) spectra of the air-oxidized enzyme showed signals of two low-spin hemes at 15 K. The high-spin heme species having relatively low signal intensity indicated that major part of heme b_3 is EPR-silent due to an antiferromagnetic coupling to an adjacent Cu_B forming a Fe-Cu binuclear center. Resonance Raman (RR) spectrum of the oxidized enzyme suggested that heme b_3 is six-coordinate high-spin species and the other hemes are six-coordinate low-spin species. The RR spectrum of the reduced enzyme showed that all the ferrous hemes are six-coordinate low-spin species. v(Fe-CO) and v(C-O) stretching modes were observed at 523 and 1969 cm⁻¹, respectively, for CO-bound enzyme. In spite of the similarity to NOR in the primary structure, the frequency of v(Fe-CO) mode is close to those of aa_3 - and bo_3 -type oxidases rather than that of NOR.

X-E-11 Model Complexes of the Active Site of Galactose Oxidase. Effects of the Metal Ion Binding Sites

TAKI, Masayasu¹; HATTORI, Haruna¹; OSAKO, Takao¹; NAGATOMO, Shigenori; SHIRO, Motoo²; KITAGAWA, Teizo; ITOH, Shinobu¹ (¹Osaka City Univ.; ²Rigaku Agency)

[Inorg. Chim. Acta 357, 3369–3381 (2004)]

Model compounds of the active site of galactose oxidase have been developed by using new cofactor model ligands, L1H (2-methylthio-4-tert-butyl-6-[{bis(pyridin-2-ylmethyl)amino}methyl]phenol) and L2H (2-methylthio-4-tert-butyl-6-[{bis(6-methylpyridin-2-ylmethyl)amino methyl]phenol). Treatment of the ligands with copper(II) and zinc(II) perchlorate in the presence of triethylamine followed by anion exchange reaction with NaPF₆ or NaBPh₄ provided the corresponding copper(II) and zinc(II) complexes, the crystal structures of which have been determined by Xray crystallographic analysis. All the copper(II) and zinc(II) complexes have been isolated as a dimeric form in which the phenolate oxygen of each ligand acts as the bridging ligand to form a rhombic $Mv(OAr)_2$ core (M = Cu or Zn). The dimeric complexes can be converted into the corresponding monomer complexes by the treatment with exogenous ligand such as acetate ion. The redox potential and the spectroscopic features of the monomer complexes have also been examined. Furthermore, the copper(II)- and zinc(II)-complexes of the phenoxyl radical species of the ligands have been generated in

situ by the oxidation of the phenolate complexes with $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (CAN) in CH₃CN, and their spectroscopic features have been explored. The structures and physicochemical properties of the phenolate and phenoxyl radical complexes of **L1** and **L2** have been compared to those of the previously reported copper(II) and zinc(II) complexes of **L3** (2-methylthio-4-*tert*-butyl-6-[{bis(2-pyridin-2-ylethyl)amino}methyl]phenol) in order to get insights into the interaction between the metal ions and the organic cofactor moiety.

X-E-12 Refolding Processes of Cytochrome P450_{cam} from Ferric and Ferrous Acid Forms to the Native Conformation

EGAWA, Tsuyoshi¹; HISHIKI, Takako²; ICHIKAWA, Yusuke²; KANAMORI, Yasukazu²; SHIMADA, Hideo²; TAKAHASHI, Satoshi³; KITAGAWA, Teizo; ISHIMURA, Yuzuru² (¹IMS and Keio Univ.; ²Keio Univ.; ³IMS and Osaka Univ.)

[J. Biol. Chem. 279, 32008–32017 (2004)]

Changes in heme coordination state and protein conformation of cytochrome P450_{cam} (P450_{cam}), a btype heme protein, were investigated by employing pH jump experiments coupled with time-resolved optical absorption, fluorescence, circular dichroism, and resonance Raman techniques. We found a partially unfolded form (acid form) of ferric P450_{cam} at pH 2.5, in which a Cys-heme coordination bond in the native conformation was ruptured. When the pH was raised to pH 7.5, the acid form refolded to the native conformation through a distinctive intermediate. Formations of similar acid and intermediate forms were also observed for ferrous P450_{cam}. Both the ferric and ferrous forms of the intermediate were found to have an unidentified axial ligand of the heme at the 6th coordination sphere, which is vacant in the high spin ferric and ferrous forms at the native conformation. For the ferrous form, it was also indicated that the 5th axial ligand is different from the native cysteinate. The folding intermediates identified in this study demonstrate occurrences of non-native coordination state of heme during the refolding processes of the large *b*-type heme protein, being akin to the well known folding intermediates of cytochromes c, in which *c*-type heme is covalently attached to a smaller protein.

X-E-13 Simultaneous Resonance Raman Detection of the Heme a_3 -Fe-CO and Cu_B-CO Species in CO-Bound ba_3 -Cytochrome cOxidase from *Thermus thermophilus*

PINAKOULAKI, Eftychia¹; OHTA, Takehiro; SOULIMANE, Tewfik²; KITAGAWA, Teizo; VAROTSIS, Constantinos³

(¹Univ. Crete; ²Paul Scherrer Inst.; ³IMS and Univ. Crete)

[J. Biol. Chem. 279, 22791-22794 (2004)]

Understanding of the chemical nature of the dioxygen and nitric oxide moiety of ba_3 -cytochrome c

oxidase from Thermus thermophilus is crucial for elucidation of its physiological function. In the present work, direct resonance Raman (RR) observation of the Fe-C-O stretching and bending modes and the C-O stretching mode of the Cu_B-CO complex unambiguously establishes the vibrational characteristics of the heme-copper moiety in ba_3 -oxidase. We assigned the bands at 507 and 568 cm^{-1} to the Fe–CO stretching and Fe-C-O bending modes, respectively. The frequencies of these modes in conjunction with the C-O mode at 1973 cm⁻¹ showed, despite the extreme values of the Fe-CO and C-O stretching vibrations, the presence of the *a*-conformation in the catalytic center of the enzyme. These data, distinctly different from those observed for the caa3-oxidase, are discussed in terms of the proposed coupling of the a-and b-conformations that occur in the binuclear center of heme-copper oxidases with enzymatic activity. The Cu_B-CO complex was identified by its v(CO) at 2053 cm⁻¹ and was strongly enhanced with 413.1 nm excitation indicating the presence of a metal-to-ligand charge transfer transition state near 410 nm. These findings provide, for the first time, RR vibrational information on the EPR silent $Cu_B(I)$ that is located at the O₂ delivery channel and has been proposed to play a crucial role in both the catalytic and proton pumping mechanisms of heme-copper oxidases.

X-E-14 Detection of a Photostable Five-Coordinate Heme a_3 -Fe-CO Species and Functional Implications of His384/ α 10 in CO-Bound ba_3 -Cytochrome *c* Oxidase from *Thermus thermophilus*

OHTA, Takehiro; PINAKOULAKI, Eftychia¹; SOULIMANE, Tewfik²; KITAGAWA, Teizo; VAROTSIS, Constantinos¹

(¹Univ. Crete; ²Paul Scherrer Inst.; ³IMS and Univ. Crete)

[J. Phys. Chem. B 108, 5389-5491 (2004)]

Resonance Raman (RR) spectra are reported for the fully reduced carbon monoxy derivative of ba3-cytochrome c oxidase from Thermus thermophilus. The RR spectra show the formation of a photolabile six-coordinate heme-CO and a photostable five-coordinate heme Fe-CO species. The latter species is formed by the cleavage of the proximal heme Fe-His384 bond and is the first five-coordinate Fe-CO species detected in hemecopper oxidases. The frequency of the Fe-CO species observed at 526 cm⁻¹ correlates with either the C-O stretching modes observed at 1967 or 1982 cm⁻¹ and lie on the correlation line of v(Fe-CO) vs v(C-O)for all known five-coordinate heme Fe-CO complexes. The loss of intensity of the heme Fe-His384 mode observed at 193 cm⁻¹ in the photostationary CO-bound spectra is attributed to the loss of the non-hydrogen bonded heme Fe-His384…Gly359 conformer. Taken together, the data indicate that the environment of theruptured His384 that is a part of the Q-proton pathway and leads to the highly conserved among all hemecopper oxidases, H₂O pool, is disrupted upon CO binding to heme a_3 .

X-E-15 Heme Environment in Aldoxime Dehydratase Involved in Carbon–Nitrogen Triple Bond Synthesis

OINUMA, Ken-Ichi¹; OHTA, Takehiro; KONISHI, Kazunobu¹; HASHIMOTO, Yoshiteru¹; HIGASHIBATA, Hiroki¹; KITAGAWA, Teizo; KOBAYASHI, Michihiko¹ (¹Univ. Tsukuba)

[FEBS Lett. 568, 44-48 (2004)]

Resonance Raman spectra have been measured to characterize the heme environment in aldoxime dehydratase (OxdA), a novel hemoprotein, which catalyzes the dehydration of aldoxime into nitrile. The spectra showed that the ferric heme in the enzyme is six-coordinate low spin, whereas the ferrous heme is five-coordinate high spin. We assign a prominent vibration that occurs at 226 cm⁻¹ in the ferrous enzyme to the Fe-proximal histidine stretching vibration. In the CObound form of OxdA, the correlation between the Fe–CO stretching (512 cm⁻¹) and C–O stretching (1950 cm⁻¹) frequencies also supports our assignment of proximal histidine coordination.

X-E-16 Interactions of Soluble Guanylate Cyclase with Diatomics as Probed by Resonance Raman Spectroscopy

PAL, Biswajit; KITAGAWA, Teizo

[J. Inorg. Biochem. in press]

Soluble guanylate cyclase (sGC, EC 4.6.1.2) acts as a sensor for nitric oxide (NO), but is also activated by carbon monoxide in the presence of an allosteric modulator. Resonance Raman studies on the structurefunction relations of sGC are reviewed with a focus on the CO-adduct in the presence and absence of allosteric modulator, YC-1, and substrate analogues. It is demonstrated that the sGC isolated from bovine lung contains one species with a five coordinate (5c) ferrous high-spin (HS) heme with the Fe-His stretching mode at 204 cm⁻¹, but its CO adduct yields two species with different conformations about the heme pocket with the Fe–CO stretching (v_{Fe-CO}) mode at 473 and 489 cm⁻¹, both of which are His- and CO-coordinated 6c ferrous adducts. Addition of YC-1 to it changes their population and further addition of GTP yields one kind of 6c $(v_{Fe-CO} = 489 \text{ cm}^{-1})$ in addition to 5c CO-adduct $(v_{Fe-CO} = 521 \text{ cm}^{-1})$. Under this condition the enzymatic activity becomes nearly the same level as that of NO adduct. Addition of γ -S-GTP yields the same effect as GTP does but sGMP and GDP gives much less effects. Unexpectedly, ATP cancels the effects of GTP. The structural meaning of these spectroscopic observation is discussed in detail.

X-E-17 Resonance Raman Evidence for the Presence of Two Heme Pocket Conformations with Varied Activities in CO-Bound Bovine Soluble Guanylate Cyclase and Their Conversion LI, Zhengqiang¹; PAL, Biswajit; TAKENAKA, Shigeo²; TSUYAMA, Shingo²; KITAGAWA, Teizo (¹IMS and Jilin Univ.; ²Osaka Prefecture Univ.)

[*Biochemistry* in press]

It was noted previously that resonance Raman (RR) spectra of soluble guanylate cyclase (sGC) observed by five independent research groups were categorized into two types; sGC₁ and sGC₂ (Vogel, K. M., Hu, S. Z., Spiro, T. G., Dierks, E. A., Yu, A. E., and Burstyn, J. N., J. Biol. Inorg. Chem. 4, 804-813 (1999)). We demonstrate here that the RR spectra of sGC isolated from bovine lung contains only sGC₂ but both species for CO-bound form (CO-sGC). The relative population of the two forms was changed from the initial CO-sGC₂ form dominant with the Fe–CO (v_{Fe-CO}) and C–O stretching modes (v_{CO}) at 472 and 1990 cm⁻¹, respectively, to the CO-sGC1 form with ν_{Fe-CO} and ν_{CO} at 488 and 1973 cm⁻¹ by adding a zenobiotic, YC-1. Further addition of a substrate, GTP, completed the change. GDP and cGMP had much less effects but a substrate analogue, GTP-y-S was found to have the same effect as GTP. In contrast, ATP has the reverse effect, namely deleted the effect of YC-1 and GTP. In the coexistence of YC-1 and GTP, vinyl vibrations of heme are largely influenced and new CO-isotope sensitive bands were observed at 521, 488, 363, and 227 cm⁻¹. The 521 cm⁻¹ band was assigned to the five-coordinate (5c) species from the model compound studies using ferrous ironprotoporphyrin IX in CTAB micelles. Distinctively from the 472 cm^{-1} species, both the 488- cm^{-1} and 521cm⁻¹ species were apparently unphotodissociable when an ordinary Raman spinning cell was used, meaning rapid recombination of photodissociated CO. On the basis of these observations, binding of YC-1 to the heme pocket is proposed.

X-E-18 SOUL in Mouse Eyes Is a Novel Hexameric Heme-Binding Protein with Characteristic Optical Absorption, Resonance Raman Spectral and Heme Binding Properties

SATO, Emiko¹; SAGAMI, Ikuko²; UCHIDA, Takeshi; SATO, Akira³; KITAGAWA, Teizo; IGARASHI, Jotaro¹; OLSON, John S.⁴; SHIMIZU, Toru¹

(¹Tohoku Univ.; ²Tohoku Univ. and Kyoto Prefectural Univ.; ³GUAS; ⁴Rice Univ.)

[*Biochemistry* in press]

SOUL is specifically expressed in the retina and pineal gland, and displays more than 40% sequence homology with p22HBP, a heme protein ubiquitously expressed in numerous tissues. SOUL was purified as a dimer in the absence of heme from the *E. coli* expression system, but displayed a hexameric structure upon heme binding. Heme-bound SOUL displayed optical absorption and resonance Raman spectra typical of 6coordinate low-spin heme protein, with one heme per monomeric unit for both the Fe(III) and Fe(II) complexes. Spectral data additionally suggest that one of the axial ligands of the Fe(III) heme complex is His. Muta-

tion of His42 (the only His of SOUL) to Ala resulted in loss of heme binding, confirming that this residue is an axial ligand of SOUL. The K_d value of heme for SOUL was estimated as 4.8×10^{-9} M from the association and dissociation rate constants, suggesting high binding affinity. On the other hand, p22HBP was obtained as a monomer containing one heme per subunit, with a K_d value of 2.1×10^{-11} M. Spectra of heme-bound p22HBP were different from those of SOUL, but similar to those of heme-bound bovine serum albumin in which heme bound to a hydrophobic cavity with no specific axial ligand coordination. Therefore, the heme-binding properties and coordination structure of SOUL are distinct from those of p22HBP, despite high sequence homology. The physiological role of the new heme binding protein, SOUL, is further discussed in this report.

X-E-19 Quaternary Structures of Intermediately Ligated Human Hemoglobin A and Influences from Strong Allosteric Effectors; Resonance Raman Investigation

NAGATOMO, Shigenori; NAGAI, Masako¹; MIZUTANI, Yasuhisa²; YONETANI, Takashi³; KITAGAWA, Teizo

(¹Kanazawa Univ.; ²IMS and Kobe Univ.; ³Univ. Pennsylvania)

[Biophys. J. submitted]

The Fe-histidine stretching (v_{Fe-His}) frequency was determined for deoxy subunits of intermediately ligated human hemoglobin A in equilibrium and CO-photodissociated picosecond transient species in the presence and absence of strong allosteric effectors like inositol (hexakis)phosphate (IHP), bezafibrate (BZF) and 2,3bisphosphoglycerate (BPG). The v_{Fe-His} frequency of deoxyHb A was unaltered by the effectors. The T to R transition occurred around $m = 2 \sim 3$ in the absence of effectors but m > 3.5 in their presence, where m is the average number of ligands bound to Hb and was determined from the intensity of the v_4 band measured in the same experiment. The α_1 - β_2 subunit contacts revealed by UV resonance Raman spectra, which were distinctly different between the T and R states, remained unchanged by the effectors. This observation would solve the recent discrepancy that the strong effectors remove the cooperativity of oxygen binding in the low affinity limit whereas the ¹H NMR spectrum of fully ligated form exhibits the pattern of R state.

X-E-20 Oxygen Sensing Mechanism of HemAT from *Bacillus subtilis*: A Resonance Raman Spectroscopic Study

OHTA, Takehiro; YOSHIMURA, Hideaki; YOSHIOKA, Shiro; AONO, Shigetoshi; KITAGAWA, Teizo

[J. Am. Chem. Soc. submitted]

HemAT-*Bs* is a heme-based signal transducer protein responsible for aerotaxis of *Bacillus subtilis*, which detects oxygen and transmits the signal to regulatory proteins that control the direction of flagella rotation. CO and NO are also caught at the same position as O_2 but the signals would be differentiated. Binding of oxygen to the sensor domain of this protein is supposed to alter the protein conformation in the vicinity of heme, which is propagated to the signaling domain through the linker region in a way different from the other case in binding of other gases.

Specific sensing of O₂, CO, and NO might have been required for the aerophilic bacteria in the early times of the earth, when CO and NO were more abundant than O₂. In support of this idea our previous resonance Raman (RR) study of the oxygen bound form of HemAT-Bs has demonstrated that the Fe-O2 stretching (v_{Fe-O_2}) frequency (560 cm⁻¹) is noticeably lower than those of general oxygen bound hemoproteins, but similar to the frequencies observed for invertebrate, plant, and bacterial Hbs, suggesting that the bound oxygen is incorporated into a unique hydrogen bonding network in the distal environment. Here we present RR evidences for structural linkage between the distal heme pocket and the signaling domain by using the linker-lacking protein as well as the wild type and the Y70F and T95A mutants of full-length

X-E-21 The Interaction of Covalently Bound Heme with the Cytochrome *c* Maturation Protein CcmE

UCHIDA, Takeshi; STEVENS, Julie M.¹; DALTROP, Oliver¹; HARVAT, Edgar M.¹; HONG, Lin¹; FERGUSON, Stuart J.¹; KITAGAWA, Teizo (¹Univ. Oxford)

[J. Biol. Chem. submitted]

The heme chaperone CcmE is a novel protein that binds heme covalently via a histidine residue as part of its essential function in the process of cytochrome cbiogenesis in many bacteria as well as plant mitochondria. In the continued absence of a structure of the holoform of CcmE, identification of the heme ligands is an important step in understanding the molecular function of this protein and the role of covalent heme binding to CcmE during the maturation of *c*-type cytochromes. In this work we present spectroscopic data that provide insight into the ligation of the heme iron in the soluble domain of CcmE from E. coli. Resonance Raman spectra demonstrated that one of the heme axial ligands is a histidine residue and the other is likely to be Tyr134. In addition, the properties of the heme resonances of the holo-protein compared with those of a form of CcmE with non-covalently bound heme provide evidence for the modification of one of the heme vinyl side chains by the protein, most likely the 2-vinyl group.

X-E-22 Role of Tyr288 at the Dioxygen Reduction Site of Cytochrome *bo* Studied by Stable Isotope Labeling and Site-Directed Mutagesis

UCHIDA, Takeshi; MOGI, Tatsushi¹; NAKAMURA, Hiro²; KITAGAWA, Teizo (¹Univ. Tokyo, Tokyo Inst. Tech. and ERATO(JST); ²RIKEN Harima Inst. and Yokohama City Univ.)

[J. Biol. Chem. submitted]

To explore the role of a cross-link between sidechains of Tyr288 and His284 at the heme-copper binuclear center, we prepared cytochrome bo where D_4 -, 1-¹³C-, or 4-¹³C-Tyr has been biosynthetically incorporated. Unexpectedly, the D₄-Tyr-labeled enzyme showed the large decrease in the ubiquinol-1 oxidase and CO-binding activities. Optical absorption and resonance Raman spectra identified the defect in the distal side of the heme-copper binuclear center. In the CO-bound D₄-Tyr-labeled enzyme, a large fraction of the $v_{(Fe-C)}$ mode was shifted from the normal 520 cm⁻¹band to a broad band centered around 491 cm⁻¹, as found for the Y288F mutant. Our results suggest that the substitution of ring hydrogens of Tyr288 with deuteriums slows down the formation of the His-Tyr crosslink essential for the dioxygen reduction at the binuclear center.

X-E-23 Resonance Raman Characterization of the PAS-A Domain of the Nobel CO-Dependent Gene Regulatory Protein, NPAS2

UCHIDA, Takeshi; SATO, Emiko¹; SATO, Akira²; SAGAMI, Ikuko³; SHIMIZU, Toru¹; KITAGAWA, Teizo

(¹Tohoku Univ.; ²GUAS; ³Tohoku Univ. and Kyoto Prefectural Univ.)

[J. Biol. Chem. submitted]

Neuronal PAS domain protein 2, a newly discovered as a heme protein, is expressed in the mammalian forebrain and acts as a CO-dependent transcriptional activator. This protein consists of the N-terminal basic helix-loop-helix domain, and two heme-containing PAS domains (PAS-A and PAS-B). In this study we prepared the isolated PAS-A domain and its mutants, and measured resonance Raman spectra. The CO-bound form gave the ν_{Fe-CO} and ν_{C-O} bands at 497 and 1967 cm⁻¹, respectively, and the correlation plot between v_{Fe-CO} and v_{C-O} suggested that a neutral His is a trans ligand of CO. The ferric form is constituted of the dominant 6-coordinate low-spin species and minor 5and 6-coordinate high-spin species. When its Raman spectrum was excited at 363.8 nm, an intense band assignable to the Fe^{3+} -S stretching was observed at 332 cm⁻¹, whereas it disappeared in the C170A mutant, suggesting that Cys170 is an axial ligand in the ferric state. The spectrum of the wild-type ferrous PAS-A domain shows a mixture of 5-coordinate high-spin and 6-coordinate low-spin hemes. In the H119A and H171A mutants, the 5-coordinate species increased, while no change was observed for the C170A mutant, which suggest that His119 and His171, not Cys170, are the axial ligands in the ferrous heme, and ligand replacement from Cys to His takes place upon heme reduction. The marker band v_{11} of the reduced form, which is sensitive to the donor strength of the axial ligand, was shifted to a lower frequency than that of cytochrome c_3 , suggesting the coordination of a deprotonated histidine. Taken together, the present results support a mechanism that CO binding to heme causes conformation change in the His171-Cys170 moiety, which leads to physiological signaling.

X-F Molecular Mechanism of Photosensory Protein Function, Excitation Energy Transfer and Electron Transfer in Biological Systems

We are interested in photochemistry, photophysics, photoenergy conversion and photosignal transduction in living orgamisms. Above all, the primary interest in our laboratory is the molecular mechanism of photosensory proteins including rhodopsin and photoactive yellow protein. Using theoretical/computational techniques, we study what happens in these photosensory proteins after light illumination and how these proteins convert light energy into conformational changes.

Excitation energy transfer is a significant process in biophysics. The light-harvesting antenna system in photosynthetic purple bacteria collects and transfers photoenergy efficiently by its unique mechanism. We study this mechanism theoretically.

The electron transfer in biological systems is mostly long-range electron transfer that occurs by the electron tunneling through the protein media. Using theoretical/computational methods, we calculate the electron tunneling current in the protein matrix and analyze how intraprotein electron transfer occurs.

X-F-1 Torsion Potential Works in Rhodopsin

YAMADA, Atsushi¹; YAMATO, Takahisa²; KAKITANI, Toshiaki¹; YAMAMOTO, Shigeyoshi³ (¹Nagoya Univ.; ²IMS and Nagoya Univ.; ³Chukyo Univ.)

[Photochem. Photobiol. 79, 476–486 (2004)]

We investigate the role of protein environment of rhodopsin and the intramolecular interaction of the chromophore in the cis-trans photoisomerization of rhodopsin by means of a newly developed theoretical method. We theoretically produce modified rhodopsins in which a force field of arbitrarily chosen part of the chromophore or the binding pocket of rhodopsin is altered. We compare the equilibrium conformation of the chromophore and the energy stored in the chromophore of modified rhodopsins with those of native rhodopsins. This method is called site-specific force field switch (SFS). We show that this method is most successfully applied to the torsion potential of rhodopsin. Namely, by reducing the twisting force constant of the C11=C12 of 11-cis retinal chromophore of rhodopsin to zero, we found that the equilibrium value of the twisting angle of the C11=C12 bond is twisted in the negative direction down to about -80 degrees. The relaxation energy obtained by this change amounts to an order of 10 kcal/mol. In the case that the twisting force constant of the other double bond is reduced to zero, no such large twisting of the bond happens. From these results we conclude that a certain torsion potential is applied specifically to the C11=C12 bond of the chromophore in the ground state of rhodopsin. This torsion potential facilitates the bond-specific cis-trans photoisomerization of rhodopsin. This kind of the mechanism is consistent with our torsion model proposed by us more than a quarter of century ago. The origin of the torsion potential is analyzed in detail on the basis of the chromophore structure and protein conformation, by applying the SFS method extensively.

X-F-2 Role of Protein in the Primary Step of the Photoreaction of Yellow Protein

YAMADA, Atsushi¹; ISHIKURA, Takakazu¹; YAMATO, Takahisa²

(¹Nagoya Univ.; ²IMS and Nagoya Univ.)

[Proteins: Struct., Funct., Genet. 55, 1063–1069 (2004)]

We show the unexpectedly important role of the protein environment in the primary step of the photoreaction of the yellow protein after light illumination. The driving force of the *trans*-to-cis isomerization reaction was analyzed by a computational method. The force was separated into two different components: the term due to the protein-chromophore interaction and the intrinsic term of the chromophore itself. As a result, we found that the contribution from the interaction term was much greater than that coming from the intrinsic term. This accounts for the efficiency of the isomerization reaction in the protein environment in contrast to that in solution environments. We then analyzed the relaxation process of the chromophore on the excitedstate energy surface and compared the process in the protein environment and that in a vacuum. Based on this analysis, we found that the bond-selectivity of the isomerization reaction also comes from the interaction between the chromophore and the protein environment.

X-F-3 Direct Measure of Functional Importance Visualized Atom-by-Atom for Photoactive Yellow Protein: Application to Photoisomerization Reaction

YAMADA, Atsushi¹; ISHIKURA, Takakazu¹; YAMATO, Takahisa² (¹Nagoya Univ.; ²IMS and Nagoya Univ.)

[Proteins: Struct., Funct., Genet. 55, 1070–1077 (2004)]

Photoreceptor proteins serve as efficient nanomachines for the photoenergy conversion and the photosignal transduction of living organisms. For instance, the photoactive yellow protein derived from a halophilic bacterium has the *p*-coumaric acid chromophore, which undergoes an ultrafast photoisomerization reaction after light illumination. To understand the structure-function
relationship at the atomic level, we used a computational method to find *functionally important atoms* for the photoisomerization reaction of the photoactive yellow protein. In the present study, a "direct" measure of the functional significance was quantitatively evaluated for each atom by calculating the *partial atomic driving force* for the photoisomerization reaction. As a result, we revealed the reaction mechanism in which the specific role of each functionally important atom has been well characterized in a systematic manner. In addition, we observed that this mechanism is strongly conserved during the thermal fluctuation of the photoactive yellow protein.

RESEARCH FACILITIES

The Institute for Molecular Science includes five research facilities. This section describes their latest equipment and activities. For further information please refer to older IMS Annual Review issues (1978–2003).

Laser Research Center for Molecular Science

This center was established in 1997 by reorganization of a part of the Instrument Center. The new Center is composed of three research groups which are asked to develop new lasers suitable for pioneering researches in the new field of molecular science. The three groups are

- 1. Advanced Lasers for Chemical Reaction Studies,
- 2. Advanced Lasers for Synchrotron Radiation Applications,
- and
- 3. Advanced UV and IR Tunable Lasers.

The Laser Research Center is equipped with excimer lasers and solid-state light sources in various temporal and spectral regions, including femtosecond optical parametric oscillators (OPO). The synchronously pumped femtosecond (OPO) (OPAL; Spectra Physics) is tunable from 1.1 µm up to 1.6 µm.

The Laser Center also has general instruments and spectrophotometers. A fluorescence spectrophotometer (Fluorolog II; Spex) is composed of a xenon lamp house for excitation, double and single monochromators for spectroscopy, and changeable detectors (CCD and photomultiplier tube). Other instruments are UV-VIS and IR spectrophotometers, circular dichroism dispersion photometer, and general-purpose electronic instruments. Using these instruments, researchers can carry out various experiments not only in the ultrafast temporal region but also in the steady state regime.

Research Center for Molecular-scale Nanoscience

This center was established in April 2002 after reorganization including the Research Center for Molecular Materials, the Department of Electronic Structure and the Department of Molecular Assemblies. The Center is supposed to play a principal role to integrate the innovative progress that IMS has achieved in the fields of molecular science and material science. Its mission is to develop a new field of science systematizing new finding in physical and chemical properties of new molecular materials and nano structures, by elucidation and controling the structure and function of the materials at the atom/molecular level. In addition, the center promote colaboration with internal and external researchers by providing technical services of common research facilities which are indispensable for nano science research.

The center is comprised of four divisions: (A) Molecular-scale electronics, (B) Nanocatalysis, (C) Nano-scale photoscience, and (D) Advanced molecular science, where the last devision consists of visiting faculty members. The respective research activities of each divisions are reported in other sections in this Review. Technical staffs are also important members of the center, who manage the common equipments and facilities of the center, provide liquid nitrogen and helium, and take care of the elemental analyses.

Equipment Development Center

Design and fabrication of the instruments, and research and developments of the new instruments necessary for the molecular science research are the mission of this center, which consists of the mechanical, electronic and glass work sections.

Design and fabrication works of this fiscal year Head of microchip Yb:YAG laser Diebonding system Water manifold for LD Lens holder in diode-pump module Improvement of diebonding system for laser crystal Accurate diebonding system using SiC heater Laser cooling system Micro-laser and holder Double stage acceleration time-of-flight mass spectrometer Auger yield detection system Micro-manipulator Research and developments of the new instruments High-Precision slit Beam positioning system Activities are described in detail in the section "RESEARCH ACTIVITIES."

UVSOR Facility

The UVSOR accelerator complex consists of a 15 MeV injector linac, a 600 MeV booster synchrotron, and a 750 MeV storage ring. The magnet lattice of the storage ring is the so-called double-bend achromat. The double RF system is routinely operated for the user beam time, and the lifetime of the electron beam has been improved to about 6 hours at 200 mA. The storage ring is normally operated under multi-bunch mode with partial filling. The single bunch operation is also conducted about two weeks per year, which provides pulsed synchrotron radiation (SR) for time-resolved experiments. Initial beam currents stored under multi-bunch and single-bunch modes are 300 mA and 70 mA, respectively.

Eight bending magnets and three insertion devices are available for utilizing SR. The bending magnet with its radius of 2.2 m provides SR, whose critical energy is 425 eV. After completing the upgrade project, there are 16 beamlines operational at UVSOR, which can be classified into two categories. 8 of them are so-called "Open beamlines," which are open to scientists of universities and research institutes belonging to the government, public organizations, private enterprises and those of foreign countries. The rest of the 8 beamlines are so-called "In-house beamlines," which are dedicated to the use of the research groups within IMS. We have 1 soft X-rays (SX) station equipped with a double-crystal monochromator, 7 EUV and SX stations with a grazing incidence monochromator, 3 VUV stations with a normal incidence monochromator, 1 (far) infrared station equipped with FT interferometers, 1 station with a multi-layer monochromator, and 3 non-monochromatized stations for irradiation of white-light.

The replacement of the old planar undulator into an in-vacuum type one with 2-m long has been successfully accomplished in 2003. The length of the undulator period and the number of the periods are 38 mm and 50, respectively. This new undulator covers the spectral region from 50 to 120 eV with its first harmonic radiation. The carbon, nitrogen, and oxygen K-edge regions, which are main targets on the novel in-house beamline BL3U, can be covered with the use of the third and fifth harmonics. The helical undulator was installed in 1996, which can also be used as the helical optical klystron for free electron laser (FEL) experiments. The undulator supplies the perfect circular polarization in the photon energy range of 2–45 eV, and the elliptic polarization up to 200 eV.

Discussion with users, concerning the improvements and upgrades of the beamlines at UVSOR, has been continuously made as series of UVSOR workshops. Discussion for the rebuilt and rearrangement of several old beamlines has been initiated more recently, on the basis of the review and evaluation report on the present status of UVSOR in 2000. According to the decision through the discussion, the reconstruction of BL3U and BL6, and the introduction of high-resolution photoelectron spectrometer to BL5U have begun in 2002. The upgrade project of the storage ring, which is intended to realize much smaller emittance (27nm-rad) and create new straight sections, was funded in FY2002 and the construction of accelerator components, beamlines, and the spectrometer has begun in 2002. All the reconstruction work has been completed by the end of July in 2003, and then the commissioning of the upgraded UVSOR, UVSOR-II, has started. The operation of UVSOR-II for users has been started successfully from the first week of September 2003, and so far there has been no serious trouble on the machine operation of UVSOR-II.

All users are required to refer to the beam-line manuals and the UVSOR guidebook (latest revision in 1999), on the occasion of conducting the actual experimental procedures. Those wishing to use the open and in-house beamlines are recommended to contact with the stationmaster/supervisor and the representative, respectively. For updated information of UVSOR, http://www.uvsor.ims.ac.jp/.

Safety Office

The Safety Office was established in April 2004. The Office is supposed to play a principal role in the institute to secure the safety and health of the staffs by achieving a comfortable workplace environment, and improvement of the working conditions. In concrete terms, it carries out planning, work instructions, fact-findings, and other services for safety and health in the institute. The office is comprised of the following staffs: the director of the office, safety and health administrators, safety and health office personnel, operational chiefs, and other staff members appointed by the Director General.

Okazaki Research Faciities (related to IMS) Research Center for Computational Science

Research Center for Computational Science, Okazaki Research Facilities, National Institutes of Natural Sciences, provides up-to-date computational resources to academic researchers in molecular science and related fields. As of March 2004, this facility is used by 550 scientists in 133 project groups.

The computer systems, currently consisting of Fujitsu VPP5000, SGI 2800/Origin3800, NEC SX-7, NEC TX-7 and Hitachi SR8000, cover a wide range of computational requests in quantum chemistry, molecular simulation, chemical reaction dynamics and solid state physics. These systems are linked to international networks through Super Science Information Network (super SINET). Detailed information on the hardware and software of the Center is available on the web site (http://ccinfo.ims.ac.jp/).

The Center provides a number of program suites, including Gaussian 03, GAMESS, Molpro2002, Hondo2002, AMBER, etc, which are installed to the computer systems and kept updated for immediate use of the users. The Center also maintains and offers the Quantum Chemistry Literature Database (QCLDB, http://qcldb2.ims.ac.jp/),

which has been developed by the Quantum Chemistry Database Group in collaboration with staff members of the Center. The latest release, QCLDB Release 2004, contains 68,468 data of quantum chemical studies.

In addition to offering computer resources to a wide range of molecular scientists, another vital aspect of the Center is to perform leading computational researches with massive computations. Since 2003 the Center is participating in the National Research Grid Initiative (NAREGI) project, a five-year national project by National Institute of Informatics (NII) and IMS. This joint project aims at developing grid computing system (NII) and thereby realizing extremely large-scale computational studies in the frontier of nanoscience (IMS). For these purposes, two supercomputer systems, Hitachi SR11000 and HA8000, were introduced to the Center in 2004, with combined performance exceeding 10 TFlops. Further information on the NAREGI project and the computer systems at the Center is found on the web site (http://nanogrid.ims.ac.jp/nanogrid/).

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SPECIAL RESEARCH PROJECTS

IMS has special research projects supported by national funds. Three projects in progress are:

- (a) Chemical Reaction Dynamics
- (b) Molecular Photophysics and Science
- (c) Novel Materials Science

These three projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

(a) Chemical Reaction Dynamics

Folding Mechanism of Protein Molecules Studied by Generalized-Ensemble Algorithms

OKAMOTO, Yuko; OKUMURA, Hisashi; KAWASHIMA, Yukio; ONO, Yuriko; KOKUBO, Hironori; ITOH, Satoru¹ (¹GUAS)

Proteins are the most complicated molecules that exist in nature. Since protein structures are closely related to their biological functions, the understanding of their folding mechanism from the first principles is not only very challenging but also very important. To be more specific, it is widely believed that three-dimensional structures of proteins are determined by their amino-acid sequence information. However, nobody has completely succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles).

There are two elements for the difficulty. One element is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be taken into account is very large. The other element for the difficulty is that there exist a huge number of local minima in the energy function, and simulations by conventional techniques will necessarily get trapped in one of the local minima without ever finding the energy global minimum. Generalizedensemble algorithms are new simulation algorithms that can alleviate this second difficulty (for reviews, see Refs. 1–3). We have been developing new generalitedensemble algorithms. We found that the combination ofmulticanonical algorithm and replica-exchange method is particularly promising.

The goal of the present project is to further develop and test the effectiveness of generalize-ensemble algorithms in the protein folding problem and to succeed eventually in the prediction of tertiary structures of proteins from the first principles.

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Theoretical Studies of Chemical Dynamics

NAKAMURA, Hiroki; MIL'NIKOV, Gennady V.; KONDORSKIY, Alexey; ZHAO, Yi¹; ZOU, Shiyang; NANBU, Shinkoh; TAMURA, Hiroyuki; OLOYEDE, Ponmile²; ISHIDA, Toshimasa³ (¹IMS and Univ. Sci. Tech. China, China; ²GUAS; ³Shizuoka Univ.)

Various types of chemical dynamics have been studied analytically as well as numerically. In order to treat multi-dimensional non-adiabatic chemical dynamics by taking into account important quantum mechanical effects, we have developed a general TSH (trajectory surface hopping) method and a semiclassical frozen Gaussian wave packet propagation method by incorporating the Zhu-Nakamura theory.^{1),2),3)} Furthermore, new formulations have been made for direct evaluation of thermal rate constant of electronically nonadiabatic chemical reactions by incorporating the Zhu-Nakamura theory. In order to take into account the tunneling effects in the dynamics, we have developed a general method to find caustics along classical trajectories in multi-dimensional system.⁴⁾

Our theory of tunneling splitting⁵⁾ has been successfully appield to real polyatomic molecules such as malonaldehyde, vinyl radical, and formic acid dimer.⁶⁾ The calculated results are in very good agreement with experiment and have proved the power of our theory.

As is well known, nonadiabatic transitions play crucial roles in various types of molecular functions such as photochromism and encapsulation of atoms in nanotubes. We have studied the transformation between cyclohexadiene and hexatriene by a high level of quantum chemical calculations and found a conical intersection important for the transformation. As a model of encapsulation, we have investigated the system composed of $C_{20}H_{10}$ and H quantum chemically and dynamically. The nonadiabatic transition is found to play crucial role and it is possible to transmit H through the ring molecule $C_{15}H_{10}B_5$ with high efficiency.

Laser control of molecular processes is another important subject of our activities. A numerically efficient new semiclassical optimal control theory (OCT) has been successfully formulated and is expected to be applicable to multi-dimensional systems.⁷⁾ Electronic transition of wave packet is an important element of controlling chemical dynamics and is found to be controlled efficiently by using quadratically chirped pulses.⁸⁾ Combination of this idea with the semiclassical OTC would enable us to treat realistic multi-dimensional chemical dynamics.

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Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

KOSUGI, Nobuhiro; HATSUI, Takaki

This project is being carried out at the Beamlines 4B and 3U on the UVSOR-II ring. We have three subprojects: (A) spin-orbit, exchange, and molecular field splittings in S 2p and P 2p excited states, (B) molecules and radicals in condensed phase and in rare gas matrix, and (C) ionic fragmentations following the inner-shell resonance excitation. In (A), we have found some spinforbidden ionized and excited states in non-radiative (photoelectron emission) and radiative (photon emission) deexcitation spectra. In (B), we have discussed blueshift and redshift in inner-shell excitation energy by relating to exchange repulsion and polarization stabilization from surrounding molecules. In (C), we are concentrating on theoretical interpretation of our experimental data measured for recent several years.

Computational Study of Quantum Dynamics of a Solute in Solution

OKAZAKI, Susumu; MIURA, Shinichi; MIKAMI, Taiji; SATO, Masahiro

Dynamics of molecular vibration in solution has been investigated based upon two simulation methods. The first one is an application of path integral influence functional theory assuming harmonic oscillations bath. The second is mixed quantum-classical molecular dynamics calculation with mean field approximation for the force on the classical solvent molecules.

Based upon the first method, dynamics of coherence between vibrational states of a solute molecule in the solution has been analysed. The formalism of the present method was compared with that of the Redfield theory. The method was applied to the vibrational relaxation of CN^- ion in water. The calculated $Rep_{01}(t)$ showed an oscillatory behavior, whose amplitude was damped as a function of time. This is an annihilation of the coherence. Further, inhomogeneous environment for the system of interest clearly showed a dephasing when the function is averaged over a number of solute molecules.

Population decay mechanism in the fluid, *i.e.* collision or resonance, has also been analysed based upon mixed quantum-classical molecular dynamics calculation. It was clarified that it depends upon temperature, density, and transition frequency as well as the interaction, *i.e.* long-ranged coulombic one or short-ranged one of LJ type.

Chemical Reactions at Surfaces and Nano-Structured Materials Studied by Spatio-Temporally Resolved Spectroscopy

MATSUMOTO, Yoshiyasu; WATANABE, Kazuya; MATSUMOTO, Taketoshi

Chemical reactions on solid surfaces are typical heterogeneous reactions. Studies in the time domain such as kinetics are useful to understand reaction mechanisms, but these are not enough to have a full understanding of the reaction mechanisms because reactions depend on local environment of reactants. Therefore, it is necessary to perform studies both in the time and spatial domains. This project aims for developing spatio-temporally resolved methods to probe various processes at surfaces. In the time domain, we perform fs time-resolved nonlinear spectroscopy including multiphoton photoelectron spectroscopy (MPS), second harmonic generation (SHG), and sum frequency generation (SFG). MPS is very suitable to investigate the unoccupied states of adsorbates and how they decay. This method is applied to ultrafast electron transfer at surfaces and interfaces. SHG is used for monitoring the dephasing processes of vibrational motions at surfaces coherently prepared by impulsive resonance Raman excitation. This is a first step toward coherent control of surface processes. SFG provides time-resolved vibrational spectra of adsobates, which is useful to detect reaction intermediates. On the other hand, in the spatial domain we perform scanning tunneling microscopy (STM) in ultrahigh vacuum conditions. Observations of temporal progresses in STM images while surface reactions take place make it possible to confirm active sites of the reactions. Furthermore, a variable temperature STM allows us to monitor changes in surface geometry with the atomic resolution during surface reactions. This capability is extremely useful to monitor spatial propagation of surface reactions, in particular, autocatalytic reactions.

Fundamental Study on High Speed DNA Sequencing Method

MIZUNO, Akira; KATSURA, Shinji¹ (¹Toyohashi Univ. Tech.)

Fundamental study on high speed DNA sequencing method was carried out using field ion microscope (FIM), which has atomic-level resolution of the surface morphology. For the sample preparation of FIM obser-

vation, immobilization of DNA molecules on an electropolished Au wire serving as a high voltage electrode was studied. Optical microscopic observation of the fluorescently labeled DNA molecules showed that DNA molecules of which terminus was modified with -SH group were immobilized on the Au tip through specific reaction between Au and -SH groups. For the FIM observation, positive high voltage was applied to the Au tip on which DNA molecules were immobilized. As a result, FIM image was observed at lower applied voltage compared with the sample without DNA molecules. The difference in on-set voltage of the FIM images seems to be attributed to the difference in the surface morphology especially the difference in evenness; thin DNA molecules must have introduced atomically uneven surface to the Au tip.

Development of Molecular Frame (e,2e) Spectroscopy: Towards Complete Mapping of Molecular Orbitals

TAKAHASHI, Masahiko¹; WATANABE, Noboru¹; KHAJURIA, Yugal; UDAGAWA, Yasuo²; ELAND, John H. D.³; JAGUTZKI, Ottmar⁴

(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³IMS and Oxford Univ.; ⁴Univ. Frankfurt)

Through the last three decades of studies of binary (e,2e) spectroscopy or electron momentum spectroscopy (EMS), it has been demonstrated that the ionization reaction near the Bethe ridge is a sensitive probe for electronic structure and electron correlation. Under the high-energy Bethe ridge conditions, where the collision kinematics most nearly corresponds to collision of two free electrons with the residual ion acting as a spectator, EMS allows us to measure individual orbital momentum densities or to look at individual molecular orbitals in momentum space. In spite of the remarkable feature of the technique, however, EMS has not yet reached the stage of full use of its ability for intensive investigation on electronic structure of molecules. The reason for this may have been twofold; (1) a more complete knowledge of the binary (e,2e) reaction mechanism is an everincreasing necessity as sophistication of experiments increases, and (2) the present EMS experiments measure averages over all orientations of gaseous molecules, resulting in enormous loss of information on electronic structure, anisotropy of the target wavefunction in particular.

To resolve the historical issues, we have proposed a method for complete mapping of the electron momentum densities in the molecular frame.^{1),2)} In the axial recoil limit of fragmentation of the residual ion, measurements of vector correlations among the two outgoing electrons and the fragment ion are equivalent to (e,2e) experiments with fixed-in-space molecules, which should be designated as (e,2e+M) spectroscopy. Our apparatus has already been used to explore the phenomena of H₂ and O₂ for which detailed theoretical explanations are eagerly awaited. We believe that these are the first observation of molecular frame (e,2e) cross sections, which visualize collision stereodynamics.

However, there is ample room for improvements mainly in collection efficiency, which could be achieved by detection of the outgoing electrons in the momentum dispersive plane around full 2π azimuth and detection of the fragment ion over the full 4π solid angle. With these further technical developments the method would exploit a new area for studies on collision dynamics and electronic structure in the molecular frame.

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Efficient Generation of Potential Energy Surfaces

ISHIDA, Toshimasa; SCHATZ, George C.¹ (¹Northwestern Univ.)

We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and the modified Shepard interpolation proposed by Collins are employed to describe potential energy surfaces. This IMLS/Shepard scheme is applicable to do potential interpolation with quantum chemical results for which analytical derivatives are not available. We applied the scheme to a four atomic system $OH + H_2 \rightarrow H_2O + H$ reaction and H_4 .

As for the former system, we compared the results with those based on the modified Shepard interpolation using second order Taylor expansions. An analytical surface is used to define the potential function so that errors in the interpolation function may accurately be determined. We found that the energy and gradient errors in the present scheme is comparable to those in the modified Shepard scheme. Note that the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does.

For H_4 system, in order to take advantage of the full symmetry of nuclear permutation of it, we generalized our code to handle the symmetry. This reduces the computational time as well as memory storage. In addition, we parallelized our code. We used an analytical surface by Boothroyd et al to test the IMLS/Shepard scheme. They employed a global function to fit their ab initio points with the error of several kcal/mol, but our scheme use all the points and there is no errors at least at the points.

The accuracy and convenience in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

(b) Molecular Photophysics and Science

Spatiotemporal Dynamics in Nanometric Molecular Assemblies by Near-Field Spectroscopy

OKAMOTO, Hiromi; IMURA, Kohei; NAGAHARA, Tetsuhiko; LIM, Jong Kuk

Recent technological progress in scanning near-field optical microscope (SNOM) has made it possible to perform optical measurements with very high spatial resolution beyond the diffraction limit. We have constructed apparatus for space- and time-resolved spectroscopic measurements, by combining SNOM and ultrafast time-resolved pump-probe technique. With the apparatus, we have achieved ~50 nm spatial and ~100 fs temporal resolution at the same time. Using continuum generation in a photonic crystal fiber, we have also succeeded in near-field pump-probe experiments in wide-range probe wavelength. Various photophysical phenomena probed under such extremely high space and time resolution can be of considerable significance not only in physics and chemistry but also in biology, and thus will open a new research activity. We make use of this experimental methodology to investigate basic problems on physical and chemical processes in nanometric systems. Right now we have performed measurements to understand basic local optical properties of porphyrin aggregates and metal nanoparticles. On porphyrin aggregates, we have obtained information on inhomogeneity of spectroscopic character and dynamic behavior. On metal nanoparticles, we have succeeded in direct imaging of resonant plasmon modes. The details of the apparatus and experimental results are reported in II-A.

Studies on Laser Cooling and Trapping of Metastable Helium Atoms and Laser Spectroscopic Studies of Atoms and Ions in Liquid Helium

MORITA, Norio; MORIWAKI, Yoshiki¹ (¹Toyama Univ.)

In "studies on laser cooling and trapping of metastable helium atoms," we have improved the vacuum system at the trapping section by introducing a nonevaporative getter pump in order to extend the lifetime of the trap. On the other hand, in "laser spectroscopic studies of atoms and ions in liquid helium," we have measured emission spectra of Mg atoms in cold helium gas in order to confirm the inference presented in our previous work, in which the formation of Mg(3s3p ¹P)He₁₀ exciplex in liquid helium is inferred. The spectrum obtained in the present experiment has shown good agreement with a theoretical spectrum calculated based on the model of the exciplex formation, and this result strongly supports the previous inference (see II-B-1). In addition, we have also measured emission spectra of Eu atoms in liquid and solid helium over a wide pressure range across the solidification pressure. As a result, we have found that the behavior of the spectral

intensity across the solidification pressure remarkably differs between ³He and ⁴He; while for ⁴He the intensity drastically increases above the solidification pressure, no significant change is seen for ³He across the solidification pressure. We have interpreted this difference as a manifestation of the difference between mobilities of Eu atoms in solid ³He and ⁴He, and have inferred that such a difference in mobility is caused by the difference in mass between the two helium species and also depends on whether the solid is a Bose condensate or not (see II-B-2).

Structure, Relaxation and Control of Reactive Cluster Studied by Two-Color Laser Spectroscopy

FUJII, Masaaki

A molecular cluster is a microscopic system of solution and/or crystal, and is thought to provide detailed information on relaxation and reaction dynamics in condensed phase. However the molecular clusters which have been studied are mainly static system which has no reaction pathway after photo-excitation, and consequently spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopy to the reactive clusters to reveal detailed mechanism of intracluster reaction. The originally developed spectroscopies, such as nonresonant ionization detected IR spectroscopy, UV-IR-UV ion dip spectroscopy, and the picosecond time-resolved IR dip spectroscopy, are described in the Research Activities of this group. By using these method, we have measured the IR spectra of solvated clusters, such as phenol/ammonia, naphthol/water and alcohol, carbazole/water and 7-azaindole dimers, and have discussed the relation between the structure and intracluster reactions. We also investigated the vibrational dynamics of those clusters in S_0 by picosecond time-resolved nonresonant ionization detected IR (NID-IR) spectroscopy and picosecond time-resolved transient fluorescence detected IR (TFD-IR) spectroscopy.

Development of Attosecond Coherent Control and Its Application

OHMORI, Kenji

Coherent control is based on manipulation of quantum phases of wave functions. It is a basic scheme of controlling a variety of quantum systems from simple atoms to nanostructures with possible applications to novel quantum technologies such as bond-selective chemistry and quantum computation. Coherent control is also expected to serve as an effective tool for the fundamental test of quantum theory. We have developed an "attosecond phase modulator (APM)," which we have applied to vibrational wave packets in molecules to realize an unprecedented high-precision quantum interferometry. In this research project, we utilize our present APM as a sensitive decoherence meter for the fundamental test of quantum theory. Also the APM will be developed to a more fexible quantum-phase modulator. And they will be applied to (1) fundamental test and control of decoherence, (2) high-precision reaction control, (3) control of highly-nonlinear processes in intense laser fields, and (4) molecule-based quantum information processing.

Probing Ultrafast Molecular Dynamics by Extremely Short Laser Pulses

TAKAHASHI, Eiji J.; HISHIKAWA, Akiyoshi

Highly excited molecules often undergo ultrafast nuclear dynamics with a time scale less than 100 fs as observed in intense laser fields (see VI-C). This special research project is aimed to trace in real time the evolution of such ultrafast nuclear motion by extremely short laser pulses with the duration less than 15 fs. For this purpose, a new Ti:Sapphire amplifier system has been introduced. The output from the Ti:Sapphire oscillator (800 nm, 20 fs, 600 mW) is amplified by a regenerative amplifier and a double path main amplifier. The typical output power is 2.5 W at the repetition frequency of 1 kHz. The pulse compression system of the amplifier output with the pulse duration of ~35 fs to deliver high power, sub-15fs laser pulses is under construction.

Dynamics of Superexcited States of Molecules and Fullerenes Studied by Electron, Fluorescence, and Laser Spectroscopy

MITSUKE, Koichiro; KOU, Junkei; MORI, Takanori

One of our main interests is to elucidate the spectroscopy and dynamics of superexcited states of fundamental molecules. Though these states often play crucial role in photoexcitation and bimolecular reactions in the VUV and soft X-ray regions, the knowledge of their characteristics is very limited. Autoionization usually takes place in a very short period, but strong interactions caused by neighboring neutral states often lead the superexcited states to various decay pathways such as neutral dissociation, internal conversion, and intramolecular vibrational redistribution. We have employed three experimental methods which serve as a means of providing insights into such processes: Photoelectron spectroscopy, dispersed fluorescence spectroscopy, and synchrotron radiation-laser pumpprobe spectroscopy. Taking maximum advantage of the tunability of synchrotron radiation, we have obtained hundreds of spectra at different primary photon energies. Assembling and comparing these one-dimensional spectra enable us to uncover novel decay pathways. For example, superexcited states are often subject to neutral dissociation into electronically excited fragments. These fragments release their internal energy by emitting fluorescence. Dispersed fluorescence spectroscopy is helpful for us in assigning the dissociation products and determining their vibrational distribution. However, this is not sufficient. If we wish to decide on which precursor state gives rise to the fragments, we should carry on excitation spectroscopy for the particular emission band with changing the primary photon energy. Namely, the fluorescence intensity should be measured as a function of two variables, the initial synchrotron radiation photon energy and final fluorescence wavelength. Two-dimensional plots thus obtained allow us to investigate involved dissociation mechanism of a superexcited state, to evaluate the magnitudes of the electronic coupling with other neutral or ionic states, and to achieve description on the potential energy surface of the relevant dissociative state.

Theoretical Development of Vibrational Sum Frequency Generation Spectroscopy

MORITA, Akihiro

The sum frequency generation (SFG) spectroscopy is a powerful technique for interface characterization, owing to a number of unique, useful features. It has a sufficient surface sensitivity in a molecular scale as a surface vibrational spectroscopy. It can be applied to surfaces in both vacuum and ambient conditions, and even to buried interfaces such as liquid-liquid or liquidsolid interfaces. By utilizing the time resolution of short-pulse lasers, this technique possesses high potential applicability to dynamics studies at interfaces.

Although SFG spectra involve rich structural information of interfaces in molecular level, their microscopic interpretation is often not straightforward to determine the interfacial structure. Theoretical calculations to help assign the experimental spectra are therefore greatly needed to fully exploit the potential of SFG spectroscopy. We proposed theories of SFG spectroscopy, ^{1),2),3)} which enable us to compute SFG spectra in non-empirical ways by molecular simulation.

The present project started this year after Dr. Morita moved to the IMS. This project develops our SFG theories toward general and practical use for experimental interpretation. We have two sub-projects in this category: (1) development of fundamental SFG theory toward quantitative interpretation of the experiments, and (2) application to other interfacial structures of interest using massive computation. This year we have developed a theory for bulk contribution to SFG spectra, which is readily implemented in molecular dynamics simulation. Numerical calculation of the bulk contribution is now in progress.

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Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; HIKOSAKA, Yasumasa

The dynamics of molecular inner-shell photoexcitation, photoionization, and subsequent decay processes is

much more complex, in comparison to outer-shell photoionization which is still largely within the scope of the single electron picture. For instance, the excitation and ionization of valence electrons accompanies the inner-shell photoionization, which manifest themselves as shake-up and shake-off satellite structures in the corresponding photoelectron spectrum. The multielectron processes due to the electron correlation are known to happen not only in the primary inner-shell hole creation processes, but also in their relaxation processes. It is advantageous to use various experimental techniques together with a high performance monochromator in the soft x-ray region, in order to investigate the related phenomena from different points of view. The high performance of the Varied-Line-Spacing Plane Grating Monochromator (VLS-PGM) at BL4B of the UVSOR facility provides us opportunities for performing various spectroscopic studies on molecular core-levels with high-resolution.

A "double toroidal" electron analyzer, which has been originally developed by a French group, has been constructed at UVSOR. The conical symmetry of the lens system limits the detection angle of electrons to 54.7° with respect to the cylindrical symmetry axis of the analyzer. The incident electrons are focused by the lens, and then dispersed in energy between the double toroidal deflectors, and reach a delay-line-type imaging detector mounted on the output plane. The imaging detection without any exit slit enables us to observe electrons within an energy range more than 10% of the pass energy. Recently the performance of the analyzer has been improved considerably after careful tuning, but an insulation failure on the detector has occurred and might be damaged beyond repair. The introduction of a new detector system will be seriously considered.

Vacuum ultraviolet (VUV) fluorescence may be a unique probe for identifying the multielectron processes, because it is expected that such processes may lead to highly-excited molecular ions, fragment ions, and neutral fragments produced after Auger decays. We have constructed a 0.3-m Seya-Namioka-type fluorescence spectrometer, for observing the VUV fluorescence following the molecular inner-shell excitation. The dispersed fluorescence is detected by a position sensitive detector composed of three microchannel plates and a resistive anode encoder, where the front microchannel plate is coated by CsI. The position sensitive detector installed enables us to observe the fluorescence spectrum with its spectral range about 300 Å simultaneously. Preliminary results for some simple molecules such as N2, O2, and N2O have been gained at BL4B.

Parallel to the developments of the apparatus mentioned above, several trial experimental setups have been made for observing minor products, such as highly excited neutral species and anions after the molecular inner-shell excitations and their performance tests have been conducted with success. However, due to the insufficient intensity of the monochromatized soft Xrays at BL4B, it is difficult to obtain the reliable data for the minor products including the VUV fluorescence. The utilization of the new undulator beamline BL3U is highly desired, in order to overcome such a situation.

(c) Novel Materials Science

Quantum Chemistry Calculations of Large Molecules

ISHIMURA, Kazuya; NAGASE, Shigeru

In order to make reliable quantum chemistry calculations possible for large molecular systems, we have developed a new program code that is suitable for the high-speed parallel treatments of two-electron integrals as well as the generation and diagonalization of Fock matrices, these being essential for molecular orbital and density functional theory calculations. By using this code, test calculations are performed using Pentinum 4 3.0GHz PC clusters, for example, for a taxol molecule $(C_{47}H_{51}NO_{14})$ without symmetry at the HF/6-31G level (a total of 660 contracted functions). The speedup ratios are 2.0, 4.2, 10.2, and 32.7 for 2, 4, 8, and 16 CPUs, respectively. As the number of CPUs increases, it is evident that the speedup is highly enhanced and a superlinear parallelization is achieved. To incorporate effects of electron correlation, we are now developing a program code of second-order Møller-Plesset perturbation (MP2) calculations that are applicable to non-covalent interactions playing an important role in host-guest chemistry, molecular recognition, and sele-assembly.

Statistical Mechanics of Interfacial Fluids: Electric Double-Layer in Carbon Nano-Pore and Super-Capacitor

HIRATA, Fumio; MIYATA, Tatsuhiko; TANIMURA, Ayumi; MARUYAMA, Yutaka; ISHIZUKA, Ryosuke¹; KOVALENKO, Andriy F.²; OMELYAN, Ihor³

(¹GUAS; ²NRCC; ³Inst. Cond. Matt. Phys.)

Materials with randomly distributed pores such as charcoal are attracting much attention as "new materials" for industrial applications. In fact, so called 'super capacitor' or 'electric-double-layer capacitor (ELC),' which consists of a porous carbon and an electrolyte solution, has been among latest targets of industrial research due to its high capability of storing charges; million to 10 million time greater than traditional capacitor using metal electrodes. Theoretical investigation of such materials, however, has been largely limited simply by the difficulty of describing or modeling randomly distributed pores, electrolyte solutions, and their interface.

Recently, we have devised a new theory for modeling the interface of solution and materials with randomly distributed pores based on the RISM theory and the replica method developed in the field of the spin glass: the liquid phase is described by the RISM theory and the disordered porous material is modeled by branched polymeric chains of nano-spheres, which are quenched into a matrix spatial configurations. The averaging of the free energy of solution over the matrix configurations is carried out by the replica trick.

Using the method, we could have successfully accounted the liquid-vapor phase transition of water and

methanol sorbed in nanoporous carbons. The theory is also successful to predict the large capacity exhibited by the electric-double-layer capacitor. A research is in progress to figure out possible factors which produce such high capability of storing charges: electrolyte concentrations, ionic species, shape of pores, and so on.

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Theory for Equilibrium and Non-Equilibrium Properties of Low-Dimensional Molecular Materials with Strong Correlation

YONEMITSU, Kenji; YAMASHITA, Yasufumi; OTSUKA, Yuichi; INOUE, Hitoshi; MAESHIMA, Nobuya

In low-dimensional molecular materials, effects of different interactions appear not only in their equilibrium phases but also in their non-equilibrium timeevolution. i) Mixed-stack organic charge-transfer complexes show neutral-ionic and dimerization-induced ferroelectric phase transitions. In the most famous TTF-CA complex, they occur simultaneously at ambient pressure but at different temperatures under high pressure. Thus we treat both the ionicity and the dimerization using the Blume-Emery-Griffiths model. Long-time evolution is studied by solving the master equation during and after photoirradiation of the complex. As a first step, we use the mean-field approximation that does not distinguish the intra- and inter-chain couplings. We find photoinduced breaking of the inversion symmetry and spontaneous ordering of electric polarizations leading to the ferroelectric ionic phase after the neutral phase is photoexcited and converted into the paraelectric ionic phase. This would explain the recent experimental findings with intra-molecular excitations. ii) Recent experimental data on photoinduced phase transitions of the materials with strong electron-lattice coupling show different degrees of coherence. In the TTF-CA complex also, the coherent oscillation of neutral-ionic domain walls is observed. In order to study the effect of coherence in the ionic-toneutral transition, we use the one-dimensional extended Peierls-Hubbard model with alternating potentials. A double pulse of oscillating electric field is introduced in the time-dependent Schrödinger equation. The two pulses constructively interfere with each other if the interval is a multiple of the period of the optical lattice vibration, while they destructively interfere if the interval is a half-odd integer times the period, in the

processes toward the neutral phase. The interference is strong especially when the pulse is strong and short because the coherence is also strong. Here we have observed the coherence in domino-like photoinduced phenomena for the first time, *i.e.*, in photoinduced phenomena which spontaneously proceed once triggered. iii) Some spin-crossover complexes show two-step transitions by changing temperature between high-spin and low-spin phases in equilibrium. In [Fe(2pic)3]Cl2·EtOH, high-spin-low-spin ordering is recently observed on the 50% plateau of high-spin fraction at intermediate temperatures. However, the time evolution of this material under continuous photoirradiation does not clearly show the high-spin-low-spin-ordered phase even transiently. We employ a two-sublattice classicalspin model, where an intra-dimer inter-sublattice antiferroic coupling prefers the intermediate phase while an inter-dimer intra-sublattice ferroic coupling the uniformly high-spin or low-spin phase. Although an inter-dimer inter-sublattice coupling plays the same role with the intra-dimer inter-sublattice coupling at the mean-field level, we find by Monte Carlo simulations that their effects are different especially when the material is under photoirradiation. This fact can explain why the high-spin-low-spin-ordered phase is hardly realized under photoirradiation.

UHV Systems for MOKE, MSHG, XMCD and STM Measurements

NAKAGAWA, Takeshi; YOKOYAMA, Toshihiko; WATANABE, Hirokazu; MARUYAMA, Koichi

The magneto-optical Kerr effect (MOKE) is usually the most suitable method to characterize magnetic properties of ultrathin films. We have constructed an ultrahigh vacuum (UHV) MOKE system equipped with an UHV-compatible electromagnet (max. 3000 G, static). While information from the MOKE is basically attributed to the whole films, information only on surfaces and interfaces can be given by the magnetic second harmonic generation (MSHG) technique. We have installed a Ti:sapphire laser (800 nm) and the detection system in the same chamber, and the preliminary MSHG data have been recorded.

The x-ray magnetic circular dichroism (XMCD) technique is also quite useful since it provides information on element-specific magnetization and on the orbital magnetic moment because of its importance for discussion on magnetic anisotropy. We have constructed another UHV chamber that is installed at Beamline 4B in UVSOR-II. In order to measure XMCD a similar UHV-compatible electromagnet is installed. X-ray absorption fine structure (XAFS) spectra of adsorbates are also obtainable in the same chamber for the determination of the surface structure.

In order to characterize surface structure, we are also now constructing a new surface analysis system based on UHV scanning tunneling microscopy (STM). The performance test was completed and we observed good STM images of graphite at ~10 K as well as at room temperature.

Some experimental results concerning MOKE and XMCD have already been obtained and are described in

the section of Research Activities. Using the MOKE, MSHG, XMCD and STM techniques, we will investigate surface magnetism that can be controlled by surface chemical adsorption and reactions.

Advanced Use of Electron Spin Resonance Spectyroscopy

KATO, Tatsuhisa; FURUKAWA, Ko

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of ESR spectroscopy enables us to investigate the transient phenomena in detail as well as the high spin state. The pulsed ESR spectroscopy gives us the prototyped demonstration of the time-dependent spectroscopy. Some time-dependent measurements were experimentally performed and compared with the theoretical model calculation. The combined use of the different frequency ESR spectrometers, i.e. X-band (9 GHz), Qband (35 GHz) and W-band (95 GHz) spectrometers, gave the detail information of the high spin state. The advanced ESR method was applied to the study on the high spin state of Ce@C₈₂ described in section II-G-1, of La@C₈₂ derivatives described in section II-G-2. And the high-field high-frequency ESR method was also applied to the biological system, the manganese cluster in oxygen evolving complex of photosystem II in the S₂-state, described in section II-H-1.

Charge Ordering in Organic Conductors

YAKUSHI, Kyuya; YAMAMOTO, Kaoru; URUICHI, Mikio; YAMAMOTO, Takashi; DROZDOVA, Olga; SUZUKI, Kenji

The charge ordering is originated from the localization of charges driven by the on-site and inter-site Coulomb interactions which are stronger than the energy gain by the delocalization charges. Since these competing energies are comparable with each other, many organic conductors are situated in the boundary between delocalized and localized states. Organic conductors exhibits various electronic ground states such as charge-density wave (CDW), spin-density wave (SCW), antiferromagnetic state (AF), spin-Peierls state (SP), and superconducting state (SC) etc. through the electron-phonon, Coulomb, and exchange interactions. Recently, the charge-ordered state (CO) participates in the ground state. The boundary with a superconducting state has been drawing attention, since theoretical studies suggest a charge-fluctuation-mediated superconducting mechanism. We are investigating the charge ordering (CO) in organic conductors using the technique of infrared and Raman spectroscopy, and obtained the following achievements. (1) We have investigated the infrared and Raman properties of all θ -type ET salts, θ - $(ET)_2Cu_2(CN)[N(CN)_2]_2, \theta_m-(ET)_2TlZn(SCN)_4, \theta_o (ET)_2TlZn(SCN)_4$, θ - $(ET)_2RbZn(SCN)_4$, θ - $(ET)_2CsZn$ (SCN)₄, and θ -(ET)₂I₃ in the sequence of the bandwidth. All of these compounds showed a metal-insulator transition except θ -(ET)₂I₃. The metal-insulator transitions are accompanied by charge order and structural change except for θ -(ET)₂CsZn(SCN)₄ We characterized the CO pattern of θ -(ET)₂RbZn(SCN)₄, θ_0 -(ET)₂ TlZn(SCN)₄, and θ -(ET)₂Cu₂(CN)[N(CN)₂]₂ as a horizontal stripe and that of θ_m -(ET)₂TlZn(SCN)₄ as a diagonal stripe. The Raman spectra of these θ -type ET compounds show a systematic change depending upon the bandwidth. (2) We found a precursory phenomenon of charge ordering above the CO transition temperature in the θ -type ET compounds which show the CO phase transition. The electronic state of this unusual hightemperature phase is not well understood. (3) We found a similar phenomenon at room temperature in the metallic phase of β "-(BEDT-TTF)(TCNQ) last year. To verify that this compound is located near the boundary between delocalized and localized states, we applied hydrostatic pressure to contract the crystal lattice. We found that the hydrostatic pressure worked in the same way as the temperature lowering. (4) We examined the β "-type ET salts, β "-(ET)₃X₂ (X = ReO₄, HSO₄, ClO₄), and found that the metal-insulator phase transitions of all these compounds were accompanied by charge ordering. The difference in the CO pattern between X = ReO_4 and $X = HSO_4$, ClO_4 was reasonably explained from the structural point of view. (5) We have conducted a theoretical consideration of the frequency and intensity of the Raman-active and infrared-active vibronic band that are interacting with electronic excited state through the electron-molecular-vibration (*e-mv*) interaction. We provided a theoretical support that the charge disproportionation induces a strong Ramanactive vibronic band and infrared-active overtone and combination tone, when the vibrational mode has a large *e-mv* coupling constant. This theoretical work succeeded to explain the dip structures in the electronic absorption band in the frequency range of 2000-3000 cm⁻¹, which have been universally observed in various organic charge-transfer compounds. Another important result of this theoretical work is that the Raman-active vibronic band is insensitive to the site charge when the EMV coupling constant is large, even if this mode is very sensitive to the molecular ionicity in the free molecule. (6) We have detected the charge disproportionation in (DI-DCNQI)₂Ag through the measurement of infrared-active b_{μ} molecular vibrations. Combining with the selection rule of the infrared- and Raman-active modes of a_g molecular vibration, we proposed the CO pattern as 0110 that is different from the 0101 pattern proposed based on NMR experiment.

Broad-Line Solid State NMR Investigation of Molecular-Based Conductors

NAKAMURA, Toshikazu; FUJIYAMA, Shigeki

Magnetic resonance measurements may be mature techniques as devices of the so-called chemical analyses. However, from the viewpoint of the solid state material science, magnetic resonance measurement is challenging area still in under the special condition such cases as the extreme low temperature, strong magnetic field, high pressure, electric field, optical response and so on. Moreover they are advantageous for studying the fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Soft materials such as molecule based conductors show huge response to environments from the outside. In fact, competition of the electronic phases in molecular based conductors has attracted much attention. Magnetic resonance measurements under the special condition are absolutely necessary to search of the materials with new functions.

TMTTF family salts are now attracted attention by the observation of the charge ordering (CO) phenomena. We investigated the ESR linewidth anisotropy at low temperatures for a series of $(TMTTF)_2X$, and proposed that the variation of ESR behaviors have their origins in the variation of the charge-ordering patterns at low temperatures, such as -O-O-o-o- and -O-o-O-oalong the stacking axes. In order to clarify the CO mechanisms of the TMTTF salts, we synthesized perdeuterio-TMTTF, TMTTF- d_{12} . It is well known that deuteration often gives a great influence on the electronic states of organic conductors as a chemical pressure. We found that the deuteration does not affect the anion ordering transition temperature. However, the CO transition temperatures show large increases with the deuteration. It is likely negative pressure effects with deuteration for TMTTF salts. To check the possibility of the anion effect through the hydrogen bonds between proton on donors and fluorine, we performed ¹⁹F and ¹³C NMR. According to the experimental results, we found that the CO phenomena are independent from the counter anion motion.

Multi-Frequency ESR Investigation for Molecular-Based Materials

FURUKAWA, Ko; HARA, Toshifumi; MAEDA, Keisuke; NAKAMURA, Toshikazu

In general, high frequency (high field) ESR measurements are advantageous because they are high sensitive and high resolution spectroscopy. So we can get ESR signals even for very tiny samples. Moreover, as for the solid compounds, *i.e.* conducting and/or magnetic materials, multi-frequency measurements give us information about frequency (magnetic field) dependent ESR parameters. For example, the frequency dependence of the *g*-values tells us the development of the short-range order for the paramagnetic states. In the magnetic long-range order phases, we can estimate the dispersion of their collective mode. From the frequency dependence of the linewidth, we can estimate the characteristic time of the spin diffusive motion, the development of the spin-spin correlation time for the paramagnetic phases. Such kind of information is very important to understand the electronic interaction in functional materials.

We performed the multi frequency, *i.e.* X-, Q-, and W-band ESR measurements for several molecular-based materials in order to clarify low-temperature electronic phase. The following projects are now going on.

- [1] Charge Configurations and Spin Dynamics of $(TMTTF)_2X$
- [2] ESR study on low-dimensional antiferromagnet α -(BEDT-TTF)₂PF₆ and ζ -(BEDT-TTF)₂PF₆ (THF)
- [3] Charge and spin dynamics in molecular based compounds.

Development of New Functional Molecular Systems

KOBAYASHI, Hayao; TAKAHASHI, Kazuyuki; CUI, HengBo; OKANO, Yoshinori; OTSUKA, Takeo; FUJIWARA, Emiko¹; KOBAYASHI, Akiko¹ (¹Univ. Tokyo)

Since the discovery of the first organic superconductors about a quarter century ago, extremely large progress has been made not only in the field of physics of organic conductors but also in the chemistry of molecular conductors. We have recently discovered antiferromagnetic organic superconductors, fieldinduced organic superconductors and single-component molecular metals. Though the development of Bechgaard-type organic conductors, D_2X (D = TTF-like π donor, X = inorganic anion) is still actively pursued especially in Japan, the renewal of the chemistry of conducting molecular materials seems to be highly desired. The main results of our group in the last year are as follows. (1) In the last two years we have tried to observe the de Haas van Alphen oscillation of the first single-component molecular metal Ni(tmdt)₂ by using piezoresistive cantilever technique. The angle dependence of the oscillation frequencies agrees well with the results of band structure calculations base on the local density approximation (LDA) and ab initio plane-wave norm-conserved pseudo potential method. Thus, the existence of the molecular crystal where the metal electrons are automatically produced by self-assembling the identical molecules was finally proved in the most rigorous sense. (2) We have developed various singlecomponent molecular conductors based on the transition metal complex molecules with extended-TTF ligands. The antiferromagnetic transition of Au(tmdt)₂ previously observed by ESR and SQUID measurement around 100 K was confirmed by NMR experiments ($T_{\rm N} \approx 85$ K), which revealed another magnetic transition at lower temperature. (3) We are continuing to try to prepare various magnetic organic conductors based on the π donor molecules with stable organic radical parts. (4) We are also going to try to develop new molecular systems with tailored dielectric properties by using the porous molecular systems based on transition metal complexes.

Lipid Membrane Formation by Vesicle Fusion on Silicon Dioxide Surfaces Modified with Alkyl Self-Assembled-Monolayer Islands

TERO, Ryugo; TAKIZAWA, Morio; LI, Yanjun; YAMAZAKI, Masakazu¹; URISU, Tsuneo (¹Shizuoka Univ.)

[Langmuir 20, 7526–7531 (2004)]

We have investigated the formation of the dipalmitoylphosphatidylcholine (DPPC) membrane by the vesicle fusion method on SiO₂ surfaces modified with self-assembled monolayer (SAM) islands of octadecyltrichlorosilane (OTS) with sizes comparable to those of the vesicles by means of atomic force microscopy. OTS-SAM islands with various size and coverage

can be constructed on the SiO₂ surfaces prepared by thermal oxidation followed by partial hydroxylation in a H_2O_2/H_2SO_4 solution (Figure 1. a, b). When vesicles are sufficiently smaller than the SiO₂ domains, DPPC bilayers and DPPC/OTS layers form on the SiO₂ and OTS domains, respectively (Figure 1. c). However, the adhesion of larger vesicles onto SiO₂ is prevented by the OTS islands, therefore only DPPC/OTS layers form without formation of DPPC bilayers on the SiO₂ domains (Figure 1. d). On surfaces with domains in tens to hundreds nanometer scale, the relative size between the hydrophilic domains and the vesicles becomes important factor in the membrane formation by the fusion of vesicles.



Figure 1. (a, b) AFM images of OTS-SAM islands on chemically oxidized SiO₂ surfaces with different treatment times in a H_2O_2/H_2SO_4 solution. Observed in air. (c, d) OTS/SiO₂ surfaces prepared the same as (b) were incubated in the suspensions of sonicated (c) and 200-nm-filtered (d)

Reduction of CO₂ and Oxidation of Organic Molecules Aiming at Energy Conversion between Chemical Energy and Electricity

vesicles. Observed in a buffer solution.

TANAKA, Koji

Electro- and photochemical reduction of CO_2 affording methanol has become crucial issue in line with the progress of fuel energy cells using methanol. Carbon dioxide easily forms η^{1-} and $\eta^{2-}CO_2$ adducts by the reaction with coordinatively unsaturated low-valent metal complexes. Metal complexes with $\eta^{1-}CO_2$ in protic media are smoothly converted to the corresponding metal–CO ones, which undergo reductive cleavages of the M–CO bonds by accumulation of electrons at the metal complexes have proven to catalyze reduction of CO_2 to CO, but the process prevents the CO ligand from hydrogenation leading to methanol formation. To achieve electrochemical reduction of the carbonyl ligand derived from CO₂, we are designing new types of metal complexes that can provide electrons to carbonyl carbon through redox active ligands without increasing electron densities in the metal centers.

Metal complexes that have an ability to oxidize organic molecules at potentials more negative than the reduction potential of dioxygen enable the direct conversion from chemical energy of organic molecules to electricity. Metal-oxo complexes are possible candidates for the smooth oxidation of organic molecules, since metal-oxo species are believed to work as active centers in various metal enzymes, which oxidize various biological substrates under very mild conditions. Mechanistic understandings of the reactivity of metaloxo species are limited because of the difficulty of selective formation of reactive M-O frameworks in artificial systems. On the other hand, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the corresponding Ru-OH2 ones, and have proven to work as oxidants of organic molecules. We have succeeded smooth and reversible conversion between aqua and oxo ligands on Ru-dioxolene frameworks without using any oxidants by taking advantage of dioxolene as a redox active ligand. Along this line, we have been preparing a variety of metal-aqua complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal-oxo forms.

Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

The chelate effect in coordination and organometallic chemistry has most pronounced kinetic and thermodynamic consequences. Complexes supported by multidentate ligands are known to have intriguing coordination and reactivity compared to metals supported by monodentate ligands, because the presence of the bridging units imposes a strong geometry constraint to the coordination groups. In this context, we have begun to study the coordination chemistry of multidentate ligands derived from aryloxides and arylthiolates. Our recent work concentrate on the synthesis, structural characterization, and reactivity of hydride Group 4 and 5 metal complexes supported by multidentate aryloxide (arylthiolate) ligands. According to preliminary results, the use of multidentate aryloxide(arylthiolate) ligands with constrained geometry has led to some highly unusual chemistry not seen in previously reported transition metal aryloxide(arylthiolate) complexes or in related metallocene hydrides. Further studies of these and hybrid ligand systems are in progress,

Developments and Researches of New Laser Materials

SARUKURA, Nobuhiko; ONO, Shingo; GOTO, Masahiro; QUEMA, Alex; MURAKAMI, Hidetoshi; DIWA, Girbert; KAMEI, Takayuki¹ (¹Tokyo Univ. Sci.)

Although development of lasers is remarkable, there are no lasers which lase in ultraviolet and far infrared

regions. However, it is expected that these kinds of lasers break out a great revolution in not only the molecular science but also in the industrial world.

In this project we research characters of new materials for ultraviolet and far infrared lasers, and develop new lasers by using these laser materials.

Development and Research of Advanced Tunable Solid State Lasers

TAIRA, Takunori; SHOJI, Ichiro; PAVEL, Nicolaie; TSUNEKANE, Masaki; DASCALU, Traian; ISHIZUKI, Hideki; SATO, Yoichi; SAIKAWA, Jiro

The use of diode lasers to pump solid-state lasers opens new horizon in laser science. Diode-pumped solid-state lasers are compact, reliable, and efficient sources of coherent radiation. They can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Recently attention has been directed to the trivalent neodymium and ytterbium ion doped materials. The advantages of Yb:YAG lasers for a high power, high stability and wide tunability laser operation are well recognized due to its small quantum defect, long upper-state life time and wide gain width. Recently developed transparent ceramic material enhances the flexibility of the solid-state laser, for example, the doping ions and host structures for the advanced laser systems.

On the other hand, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. Inasmuch as the pool of mature nonlinear optical materials is limited and development of new materials takes time and cost, QPM is a useful method for extending the range of available nonlinear optical materials. The ability to pattern a QPM structure allows the nonlinear materials to be engineered for desired interactions, meaning molecularscience-specified lasers are obtainable through these artificial materials.

In this projects we research and develop new diodepumped-solid-sate lasers and new frequency conversion devices. Especially, we will focus on the combination of microchip lasers and QPM devices. These kinds of advanced tunable solid-state light, so to speak "Chroma-Chip Lasers," will assist the research of molecular science.

Studies on Development of Molecules and the Device Fabrications for Molecular Scale Electronics

OGAWA, Takuji; TANAKA, Hirofumi

The aim of this special project is to study the electric and photonic properties of individual single molecules, and to establish the fundamental of molecular nanoscience. The project is composed of two parts; (1) design and synthesis of novel molecules which are important in molecular nano-science and (2) construction of a "molecular tester" which is comprised of double probe conductive AFM. The "molecular tester" is capable of measuring the electric properties of individual molecules by using two conductive cantilevers like proves of conventional electric testers. The machine can be extended to include SNOM-type cantilever as the third prove, which will be used to measure the photonic properties of the individual molecules. The essential parts of the machine will be furnished within the end of December 2004.

The following molecules or molecular composites have been designed and synthesized.

(a) Sub-micro meter long fully conjugated porphyrin wires, which were designed to work as the basic framework of more elaborated nano-scale molecular structures. Those molecules were designed to have high solubility toward ordinal organic solvents despite the high molecular weights, and can be deposited on a variety of substrate surfaces without making the agglomeration, thus the individual molecules were clearly observed by AFM.

(b) Supramolecular sub-micro meter long porphyrin wires were prepared by utilizing LB trough and detergent. These molecules were designed to have more rigid structure than those described above, which enables easier measurement of individual molecules by scanning probe techniques and/or nano-gap electrodes method.

(c) One dimensional aggregates of gold nano-particles were prepared by utilizing structures of porphyrin molecules.

These newly prepared molecular wires and one dimensional nano structures are now elucidated their electronic and photonic properties by SPM and/or nano-gap electrodes.

Synthesis of Iridium Complexes with Ethylphenylcarbazole Dendrons and Applications for Organic Light-Emitting Diodes

SHIRASAWA, Nobuhiko; SUZUKI, Toshiyasu

We have synthesized novel iridium complexes with ethylphenylcarbazole dendrons up to the second generation. These dendrimers are soluble in common organic solvents and form good amorphous films. Light-emitting diodes using these complexes as the emitting material show high external quantum efficiencies up to 8%.

Visible Light Emission from Polymer-Based Field-Effect Transistors

SAKANOUE, Tomo¹; FUJIWARA, Eiichi; YAMADA, Ryo; TADA, Hirokazu (¹GUAS)

[Appl. Phys. Lett. 84, 3037–3039 (2004)]

Field-effect transistors (FETs) based on poly [2methoxy, 5-(2'-ethyl-hexoxy)-1, 4-phenylenevinylene] (MEH-PPV) were prepared with bottom-contact type interdigital electrodes of Cr/Au and Al/Au on the SiO₂/Si substrates. MEH-PPV exhibited a p-type semiconducting behavior and orange light emission was observed when the devices were operated in vacuum. It was found that the luminescence efficiency of the FETs with Al/Au electrodes was higher than that of Cr/Au electrodes, as shown in Figure 1. The simultaneous injection of holes and electrons into MEH-PPV occurred efficiently with the application of Al/Au heteroelectrodes.



Figure 1. Luminescence intensity detected with a Si photodiode as a function of the gate voltage (a) and the drain current (b). The drain voltage was set at -150 V.

Development of Multi-Function Integrated Macromolecules Directed toward Molecular Scale Electronics

TANAKA, Shoji

In this project we have been trying to establish general architecture for "planar and multi-function integrated" π -conjugated macromolecules, which will be the key components for the fabrication of ultra-dense molecular-scale circuits. As the building blocks we have developed and characterized i) "insulated molecular modules," ii) "energy-gap tuning modules," iii) "molecule-anchor modules," and iv) "molecule-junction modules." Recent progress in fabricating technologies has enabled us to obtain "flat nano-gap electrodes buried within insulating substrates" optimized for planar molecular-metal junctions. Charge transport at planar junctions will be controlled by the degree of the "faceto-face interactions" between π -system of conjugated molecules and electrode substrate. Therefore, to define exactly the positions and areas of the interactions, we have designed "partially insulated" oligothiophenes consisting of non-insulated chain moiety as "chargetransfer interface" and insulated chain moiety as "charge-retention site." We have prepared a series of 3-6 nm long partially insulated oligothiophenes and investigated the redox features by electrochemical methods.

Asymmetric Transition Metal Catalysis

UOZUMI, Yasuhiro

Catalytic asymmetric reactions have attracted significant interest for their synthetic utility. One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the novel and basic chiral units. Homochiral organic molecules bearing hetero atoms (e.g. nitrogen, phosphorus, etc.) occupy a prominent position in organic chemistry as both useful synthetic reagents and molecules of biological interest. In this specail project, highly functionalized optically active pyrrolo[1,2-c] imidazolone framework was identified as a novel basic chiral unit through a diversity-based approach. A variety of new chiral ligands having a pyrrolo[1,2-c]imidazolone backbone were prepared by condensation of anilides of homochiral cyclic amino acids with 2-(diphenylphosphino)benzaldehyde. Of these ligands, (3R,9aS)-(3-(2-diphenylphosphino)phenyl-2-phenyl)tetrahydro-1Himidazo[1,5-a]indole-1-one was identified to be effective for various palladium-catalyzed asymmetric transformations. Thus, for example, catalytic asymmetric allylic amination of cycloalkenyl carbonates (methyl cyclohexen-2-yl carbonate, methyl cyclohepten-2-yl carbonate, methyl 5-methoxycarbonylcyclohexen-2-yl carbonate, methyl cyclohexenyl carbonate, t-butyl 5methoxycarbonyloxy-1,2,5,6-tetrahydropyridinedicarboxylate) with dibenzylamines ((C₆H₅CH₂)₂NH, (C₆H₅CH₂)(4-CH₃OC₆H₄CH₂)NH, (4-CH₃OC₆H₄CH₂)₂ NH) was achieved in water under heterogeneous conditions by use of a palladium complex of (3R,9aS)-3-[2-(diphenylphosphino)phenyl]-2-phenyltetrahydro-1H-imidazo[1,5-a]indole-1-one anchored on polystyrene-poly(ethylene glycol) copolymer resin to give the corresponding cycloalkenylamines with high enantiomeric selectivity (90-98% ee). Novel pincer palladium complexes having chiral hexahydro-1Hpyrrolo[1,2-c]imidazolone groups were also designed and prepared. Catalytic asymmetric Michael addition of isopropyl 2-cyanopropionate to ethyl vinyl ketone was catalyzed by the chiral pincer palladium complex to give isopropyl 2-cyano-2-methyl-5-oxoheptanoate with high enantioselectivity (up to 83% ee).

Construction of Advanced Redox Materials Based on Organic Molecules and Metal Complexes, as Basis of Chemical Energy Conversion Systems

NAGATA, Toshi; KIKUZAWA, Yoshihiro; NAGASAWA, Takayuki; HOSOKAWA, Youichi; MAKI, Suguru

The goal of this project is to develop advanced redox catalysis reactions suitable for chemical energy conversion. Our current interest focuses on modeling photosynthesis, that is, driving chemical transformation by using light energy *via* photoinduced electron transfer. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, transition metal complexes, and metal nanoparticles.

During the last year, we have made progresses on construction of unimolecular redox pools by use of our newly developed dendrimers. These dendrimers have "internal" carboxylate functionality that are readily accessible from exterior even after construction of the dendritic framework. We demonstrated introduction of up to fourteen ferrocenyl and quinone groups inside the dendrimer, and examined photochemistry of the porphyrin moiety attached at the core of the dendrimer.

Synthesis of Buckybowls and Heterobuckybowls

SAKURAI, Hidehiro; HIGASHIBAYASHI, Shuhei

Bowl-shaped π -conjugated compounds including partial structures of the fullerenes, which are called "buckybowls," are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowlto-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, heterobuckybowls, some of whose carbon atoms in the framework are substituted to the appropriate heteroatoms such as N, O, S, Se, Si, B *etc.*, have been expected to exhibit unique physical characters based on the heteroatom induced effects.

However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure. In addition, most of thus-reported procedures are performed under severe reaction conditions, limiting the sort of the introducible atoms/ functional groups. In the present project, we develop the rational route to the various kinds of buckybowls/ heterobuckybowls using the organic synthesis approach. Targets of this year are as follows:

A. Novel and versatile route to C_5 symmetric corannulene and its derivatives.

B. Synthesis of C_2 symmetric C_{60} and C_{70} fragments.

C. Synthesis of nitrogen-containing heterobuckybowls.

Toward Tailor-Made Synthesis of Monolayer-Protected Metal Clusters

NEGISHI, Yuichi; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya

Monolayer-protected clusters (MPCs) have been potential candidates for building blocks for novel nanostructured material. In order to fabricate tailor-made materials with the MPCs, it is important to understand how the basic properties evolve as functions of the core size and ligation numbers of thiolates. We have developed a large-scale synthesis of small gold clusters protected by carboxylated thiolates, high-resolution separation by polyacrylamide gel electrophoresis (PAGE), and compositional analysis by electrospray ionization (ESI) mass spectrometry. The most remarkable finding throughout these efforts is that the magic core sizes do not always take the same value but vary according to the structures of the thiolates. This result indicates that the core sizes of the gold MPCs are not determined solely by intrinsic stability of the gold cores themselves but also affected by thiolate ligation. The optical measurements of isolated clusters reveal that the

thiolate structure has nontrivial effect on the electronic structure of the MPCs, probably due to thiolate-induced core deformation. These finding offer helpful guidelines for further experimental and theoretical studies on structures, stabilities and optical properties of small gold MPCs and a strategy toward fine-tuning of the fundamental properties of the MPCs.

Effects of Vertical Magnetic Field in Material Science

DUAN, Wenyong; FUJIWARA, Masao; TANIMOTO, Yoshifumi

[Jpn. J. Appl. Phys. 43, 8213-8216 (2004)]

Magnetic control of chemical processes has been one of the most interesting and hot topics in material science. A vertical magnetic field can provide us a novel composite environment useful in material science where influence of gravity is negligibly small and various mechanisms of magnetic field effects are operative.

In order to examine the effects of high vertical magnetic fields on the reaction in liquid solution, we have carried out in situ observation of laser-induced convection of benzene solution of a photochromic compound, 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene (CMTE), in vertical high magnetic fields (up to 15 T and 1500 T^2/m). When a CMTE solution is irradiated by a 308-nm laser from the bottom of a vessel $(10 \text{ mm} \times 10 \text{ mm} \times 40 \text{ mm})$, CMTE undergoes photoisomerization reaction to its photo-isomer (PI) and the color of the solution changes from pale yellow to red. At zero field the PI solution formed on the bottom surface of the vessel removes at a 5 s delay after laser excitation and then moves upward. At $-1300 \text{ T}^2\text{m}^{-1}$ it removes at a 9 s delay and moves upwards, whereas at $+1000 \text{ T}^2\text{m}^{-1}$ it dose at a 3 s delay, moves upward and then finally moves downward.

The removal of the PI solution from the bottom surface will be explained by taking into account of the pressure in solution. The pressure difference of the bulk CMTE solution and the PI solution can be calculated by the following equation.

$$\Delta P = (\Delta \rho_{\text{solution}})gh + (\Delta \chi_{\text{benzene}})(1/\mu_0)hB\partial B/\partial z + (\chi_{\text{PI}} - \chi_{\text{CMTE}})c(1/\mu_0)hB\partial B/\partial z$$
(1)

The first term of the right-hand side of eq. 1 is the density change of the solution induced by photoirradiation, the second is the magnetic susceptibility change of benzene due to temperature change and the third is the magnetic susceptibility change of solute due to photo-isomerization. It is estimated that at $-1300 \text{ T}^2\text{m}^{-1} \Delta P$ is about one order of magnitude smaller than that at zero field, whereas at $+1000 \text{ T}^2\text{m}^{-1}$ it is about 1.7 times larger than that at zero field. This is why the departure time of the PI solution is different in three cases.

The downward movement of the PI solution at $+1000 \text{ T}^2/\text{m}$ is attributed to the smaller magnetic susceptibility of PI than that of CMTE.

In conclusion, vertical high magnetic fields are a useful tool to control convection in solution. The fact suggests that we can use high vertical magnetic fields to control chemical yield and morphology of functional materials formed in solution.

Development of Self-Healing Nano-Materials

OBA, Toru; HANASAKI, Mitsuru¹; FUJIWARA, Umihito¹; MINABE, Masahiro¹ (¹Utsunomiya Univ.)

[Photosynthesis: Fundamental Aspects to Global Perspectives in press]

For development of elaborate nano-devices, we utilized naturally occurring nano-tube, 'microtubule' (MT), formed by self-assembly of the component protein, tubulin (Tub), to integrate functional molecules into a nano ordered structure (Figure 1). Tub/MT system is not in a simple equilibrium, because the Tubassembly requires hydrolysis of GTP bound to each Tub. GTP hydrolysis in the MT lattice weakens proteinprotein interactions between Tubs, which facilitates release of Tubs from the end of the MT. Bulk, undamaged Tubs exchange their nucleotides, then reassemble again to form and elongate MTs. All Tubs in a MT lattice are, thus, exchanged constantly with free Tubs in this cycle regardless of whether their structures are damaged or undamaged. For this metabolism-like behavior, the functionalized MT can be regarded as a prototype of self-healing devices. Future works to refine the system by using Tub and/or other nano-particles would give unique supramolecular systems (see also IX-Z).



Figure 1. A concept of the on-demand nano-devices. The device possessing an ordered nano-structure is formed by self-assembly of nano building blocks conjugated with various functional molecules. The device functions only in the assembled form. The device can easily be decomposed into the component functional blocks on demand (loss of function), and the blocks can readily be reconstituted on demand (gain of function).

Observation of Coherent Synchrotron Radiation at UVSOR-II

KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; KIMURA, Shin-ichi; TAKAHASHI, Toshiharu¹; TAKASHIMA, Yoshifumi²

(¹Kyoto Univ.; ²Nagoya Univ.)

At a 750MeV electron storage ring, UVSOR-II,

possible coherent synchrotron radiation was observed in the wavelength region between 0.2 and 3.0 mm. Bursts of far infrared emission were detected when the ring was operated in single bunch mode and the beam current exceeded a certain threshold current, typically around 100 mA. Typical duration and interval of the bursts are about 200 µsec and 10–15 msec, respectively. Each burst contains many peaks and shows quasiperiodicity of about 30 µsec. The peak intensities of the bursts are 10000 times higher than that of normal synchrotron radiation in the same wavelength region. The threshold current depends on the operation condition of the storage ring, especially that of the RF system.

Optical and Photoelectrical Studies on Fermiology of Strongly Correlated Electron Systems

KIMURA, Shin-ichi; ITO, Takahiro; KWON, Yongseung; SAKURAI, Yoko; NISHI, Tatsuhiko; IM, Hojun

Strongly correlated electron systems attract much attention because of their various physical properties. To investigate the interaction between the carriers and the localized magnetic moments, we are investigating the electronic structure near the Fermi level (Fermiology) by infrared and photoemission spectroscopies using synchrotron radiation. In this year, we measured optical reflectivity spectra of rare-earth compounds CeNi_{1-x}Co_xGe₂ (x = 0, 0.3, 0.6 1), alkali-metal and alkali-earth skutterudites, AFe_4Sb_{12} (A = Na, K, Ca, Ba) and a clathrate, $Sr_6Ga_{16}Ge_{30}$, and the 4d-4f and 3d-4f resonant photoemission spectra of CeNi_{1-x}Co_xGe₂. Infrared spectroscopy under multi-extreme conditions of low-temperature, high-field and high-pressure has been also started in this year.

Regulation of Biological Function by the Heme-Based Gas-Molecule Sensor Proteins

YOSHIOKA, Shiro; KOBAYASHI, Katsuaki; INAGAKI, Sayaka; YOSHIMURA, Hideaki; AONO, Shigetoshi

A variety of gas molecules serve as substrates and/or reaction products in many enzymatic reactions including oxygen respiration, denitrification, nitrogen fixation and methanogenesis. Recently, a novel physiological function of gas molecules, that act as a signaling molecules, has been elucidated and studied extensively. So far, ethylene, O₂, NO, and CO are known to act as physiological effectors in the control of various biological functions. The corresponding receptor (sensor) proteins are required for these gas molecules to act in this way. A gas molecule that plays the role of the input signal is sensed by an active site of a sensor domain. An intramolecular signal transduction is induced following the detection of the gas molecule, which controls the functional activity in response to the input signal. Generally, a conformational change in the sensor protein facilitates this intramolecular signal transduction.

All of the gas sensor proteins so far reported have a metal-containing prosthetic group at the sensor active site. Specific interactions between protein and gas, for which the metal-containing prosthetic group is used, are required for the gas sensor protein to detect its physiological effector gas.

In this project, we elucidate the structure and function relationships of the heme-based CO and O_2 sensor proteins, CooA and HemAT-Bs, respectively, by molecular biological and spectroscopic techniques.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

FUJII, Hiroshi; KURAHASHI, Takuya; KUJIME, Masato

Metalloenzymes are a class of biologically important macromolecules that have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloenzymes have been thought to depend on the coordination structure of the active site in the protein matrices; the ligand donors, the geometry, and the coordination mode of reactant and substrate. Furthermore, it has been thought that protein structures in immediate vicinity of active metal ion are related to enzymatic function, regio-selectivity, and stereo-selectivity. In this project, we are studying the molecular mechanism of activation of molecular oxygen mediated by metalloenzymes.

(1) High-valent iron-oxo species are proposed to be the key reactive intermediate in oxidation reactions catalyzed by both heme and non-heme iron enzymes. We employ the salen ligand as a non-heme iron model complex, and attempt to isolate a transient oxidizing intermediate.

(2) Cu-containing nitrite reductase (NiR) contains a pair of Cu, a type1 Cu ion and a type2 Cu ion, which catalyze the reduction of NO_2^- to NO. In the catalytic reduction, the type 2 Cu site receives one electron from the type 1 Cu site and reduce Cu-bound NO_2^- ion to NO with addition of two protons. In this study, we synthesized Cu(I)-nitrite complexes with various tridentate ligands as a model for a reaction intermediate of NiR.

(3) Heme oxygenase (HO), an amphipathic microsomal protein, catalyzes the oxygen-dependent degradation of heme (iron-protoporphyrinIX) to α -biliverdin, CO, and free iron ion. Recently, an interesting example has been found in HO (PigA) of the Gram-negative bacterium Pseudomonas aeruginosa, which does not produce α biliverdin at all, but forms the mixture of β - and δ biliverdins at a ratio of 3:7. We show that Lys34 and Lys132 are essential amino acid residues to hold the rotated heme in the active site of PigA via hydrogenbonding interaction with the heme propionate and that Phe189 controls the product ratio of β - and δ -biliverdins via steric interaction with heme substituents. These interactions place the β - or δ -meso position of the heme at the oxidation site of PigA, leading to the unique regioselectivity.

Molecular Science of Proteins Based on Vibrational Spectroscopy

KITAGAWA, Teizo

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Proteins have a static structure as determined by xray crystallographic analysis, but its higher order structure, which is easily altered by small energy, is directly related with a function of the molecule. Vibrational spectroscopy can provide essential information on the higher order structure of proteins and its dynamics. It is the purpose of this study to apply resonance Raman and IR spectroscopy to observe vibrational spectra of proteins in aqueous solutions and to elucidate the structure-function relation in a level of molecular science.

In the visible resonance Raman spectroscopy, we intend to explore the relation between the structure of chromophore and its reactivity by observing time-resolved spectra. In the UV resonance Raman spectroscopy, we focus on the structure of aromatic side chains like Trp and Tyr as well as a polypeptide skeleton. The two techniques will be combined to elucidate the allosteric effects in gas-sensing heme proteins as well as in hemoglobin and myoglobin. The study will be extended to DNA-photolyse and ogygenase enzymes and their model compounds. We are going to develop IR microscopy to reveal structural chemistry involved in amyloid formation of β_2 -microglobulin. IR spectroscopy will also be used to reveal the coupling mechanism of proton and electron transfers by terminal oxidases.

OKAZAKI IMS CONFERENCE

Okazaki IMS Conference 2003

International Symposium on Functional Clusters and Cluster-Based Nano-Materials December 15–18, Main Conference Room of Okazaki Conference Center

Clusters with several to several hundred atoms or nano-particles with several thousand atoms exhibit various properties dependent on their size and has lately attracted considerable attention as functional materials in the next generation. With the 20 invited speakers from abroad, we discussed the following 6 subjects from the points of future development of this field.

1) thermodynamic properties of gas phase clusters, 2) geometrical and electronic structures of gas phase clusters, 3) reactivity of clusters,4) structure and reaction dynamics of molecular clusters, 5) supported clusters, 6) magnetic properties of clusters and single domain magnets, nano-particles, and nano-clusters.

Following to the welcome address by the director general, Prof. Koji Kaya, Prof. A. W. Castleman presented a plenary lecture titled "Cluster reactions and properties: Laying the foundation for cluster assembled materials." He introduced the ways of making metal alloys with carbon. Dr. B. Simard introduced the methods of dispersing iron oxide nanoparticles in a polymer film and gold-silver alloy formation in the liquid phase. Prof. H. Haberland reported the size effect of sodium clusters on the thermodynamic properties. They found that the some specific clusters show negative heat capacities. Prof. M.F. Jarrold presented the experiments and theoretical analyses on the structure and the binding energies of $Na^+(NaCl)_n$ (n = 20-40) clusters. Prof. Kaya introduced the research of his group in Keio University. Prof. K. Bowen reported the size dependence on the ionization potentials and magnetic dipole moments of nickel and aluminum clusters. A very interesting report on gold clusters was presented by Prof. L. -S. Wang who found aromatic properties in the gold clusters with planer wheel-type structures. Prof. R. Whetten from Georgia Institute of Technology reported electrode formation with C76 and capacitance properties of silver clusters with super-shell structures. Prof. Landman from the same university introduced the consideration on electric properties of several metallic and semiconductor clusters from the points of free energy and entropy. In addition to the 20 invited talks, 9 Japanese speakers also presented original works and young people displayed 52 poster presentations.

Many exciting reports presented in this conference made us confirm that the development of cluster science and technology will give us more opportunities of finding more interesting properties of new cluster systems and nano-particles of new composite atoms and molecules. On the last day we had fruitful discussion time in Gamagoori Prince Hotel and enjoyed the garden and the beach area. This meeting will be taken over in the two symposia of PacifiChem 2005, "Frontiers in Structural and Functional Studies of Atomic and Molecular Clusters, and Nano-particles," and "Advances in Cluster Sciences and Nanoparticles Technologies."

PROGRAM

December 15 (Monday)

- 8:50–9:00 **K. Kaya** (Director General, IMS) Opening Address
- 9:00–9:50 A. W. Castleman (Pennsylvania State University) Cluster reactions and properties: Laying the foundation for cluster assembled materials
- 9:50–10:35 **B. Simard** (National Research Council of Canada) Transition metal clusters in the gas phase and in solutions—Towards the fabrication of functional materials
- 10:50–11:35 **H. Haberland** (University of Freiburg) Experimental thermodynamics of small systems: Melting and boiling of clusters
- 11:35–12:20 M. F. Jarrold (Indiana University) Melting of clusters and nanocrystals 13:40–14:25 K. Kaya (IMS)
- Cluster science in Keio: Creation and development of cluster chemistry
- 14:25–15:10 **M. Kappes** (Universitat Karlsruhe) Physical and chemical properties of coinage metal clusters
- 15:10–15:55 **J. H. Parks** (Rowland Institute at Harvard) Electron diffraction of trapped metal clusters
- 16:15–17:00 **K. H. Bowen** (Johns Hopkins University) Photoelectron spectroscopy of cluster anions
- 17:00–17:45 **L.-S. Wang** (Washington State University) Planar clusters: from aromaticity to molecular wheels
- 17:45–18:05 **A. Nakajima** (Keio University) Photoelectron spectroscopy of binary cluster anions
- 18:05–18:25 A. Terasaki (Toyota Institute of Technology) Laser spectroscopy of free, trapped, and deposited cluster ions

December 16	(Tuesday)
9:00-9:45	T. Kondow (Toyota Institute of
	Technology)
	Size-dependent physical and chemical
	properties of metal clusters
9:45-10:30	P. Armentrout (University of Utah)
	Bond energies of molecular fragments to
	transition metal clusters
10:50-11:35	R. L. Whetten (Geogia Institute of
	Technology)
	Selected gold and metal-oxide clusters as
	model low-temperature oxidation
	catalysts
11:35–12:20	A. Rosen (Göteburg University)
	Molecular dynamics study of catalysed
	carbon nanotube growth within the vapor-
	liquid-solid model
13:30–14:15	J. M. Farra (University of Rochester)
	Size-dependent electron density
	redistribution in polar solvent-alkaline
	earth cluster ions
14:15–14:35	F. Misaizu (Tohoku University)
	Excited state charge-transfer process and
	dissociation dynamics of Mg+-methyl
14.05 14.55	halide complexes
14:35-14:55	K. Fuke (Kobe University)
	Electronic propeties of hypervalent
15.15 16.00	Clusters
15:15-16:00	S. K. Kim (Seoul National University)
	Conformation dependent structure and
16.00 16.20	aynamics of amino acid and its clusters
10:00-10:20	NI. FUJII (TOKYO INStitute of Technology)
	Picosecond time-resolved IR
	Pridge from eluster to solution
16.20 16.40	H Selving (Krushu University)
10:20-10:40	H. Sekiya (Kyushu University)
	dynamics in doutorated 7 againdala
	dimore studied by hele hyrning
	spectroscopy
	specification

16:40–17:00 **A. Fujii** (Tohoku University) Infrared spectroscopy of large sized water containing cluster cations: Development of the three-dimensional hydrogen bond network with the cluster size

17:00–19:00 Poster Session

December 17 (Wednesday)

9:00–9:45 U. Landman (Geogia Institute of Technology) Small is different: self-selection, assembly, and nonscalable evolution of nanoclusters

9:45–10:05 **J. Murakami** (National Institute of Advanced Industrial Science) Low-temperature activation and direct oxidation of dinitrogen on supported tungsten nanoclusters

10:25–11:10 **C. Brechignac** (CNRS) Nanosystems from cluster deposition: formation, stability and organization

- 11:10–11:55 **M. Broyer** (CNRS and Universite Lyon) Clusters on surfaces and embedded in matrix: organization, optical properties and dynamics
- 13:10–13:55 M. B. Knickelbein (Argonne National Laboratory) Toward molecular magnetic materials: Molecular beam characterization of magnetic clusters and complexes
 13:55–14:15 N. Nishi (IMS) Air-stable Fe nanoparticles and nanorods
- with graphitic carbon-skins
 14:15–14:35 T. Yamase (Tokyo Institute of Technology) Quantum tunneling of magnetization of VO²⁺-triangle-containing polyoxo-tungstates and self-assembly of polyoxo-molybdates and -tungstates to nano-ring superclusters
- 14:35–14:55 **K. Sumiyama** (Nagoya Institute of Technology) Composite state control of two different clusters *via* gas phase
- 15:15–16:00 **D. J. Schiffrin** (University of Liverpool) Functionalised nanoparticles and molecular linkers: optical and electrical properties
- 16:00–16:45 **J. Cheon** (Yonsei University) Novel anisotropic inorganic nanocrystals: diamonds, wires and stars
- 16:45–17:05 **T. Teranishi** (Advanced Institute of Science and Technology) Planar patterning of gold nanoparticles for nanoelectronic devices
- 17:05–17:25 **T. Tsukuda** (IMS) Photochemical and photophysical properties of subnanometer-sized gold clusters
- 17:25–17:35 N. Nishi Closing Address

JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institute, IMS undertakes joint studies programs for which funds are available to cover research expenses as well as travel and living expenses of individuals. The proposals from domestic scientists are reviewed and controlled by an inter-university committee.

- The programs are carried out under one of the following categories:
- (1) Joint Studies on Special Projects (a special project of significant relevance to the advancement of molecular science can be carried out by a team of several groups of scientists).
- (2) Research Symposia (a symposium on timely topics organized by collaboration between outside and IMS scientists).
- (3) Cooperative Research (a research program carried out by outside scientists with collaboration from an IMS scientist).
- (4) Use of Facility (a research program carried out by outside scientists at the research facilities of IMS except the UVSOR facility).
- (5) Invited Research Project
- (6) Joint Studies Programs using beam lines of UVSOR Facility.
- (7) Use of Facility Program of the Computer Center (research programs carried out by outside scientists at research facilities in Computer Center).

In 2003 Oct.–2004 Sep., the numbers of joint studies programs accepted for the categories (1)–(7) were 5, 8, 92, 57, 1, 131, and 121, respectively.

(1) Special Projects

A. Ultrafast Time-Resolved Study on Photochromic Reactions in the Isolated State and Condensed Phase

SEKIYA, Hiroshi¹; IRIE, Masahiro¹; OKABE, Chie; NAKABAYASHI, Takakazu²; INOKUCHI, Yoshiya³; NISHI, Nobuyuki

(¹Kyushu Univ.; ²Hokkaido Univ.; ³Univ. Tokyo)

In this joint project we investigated photochromic reactions of diarylethene derivatives and \hat{N} -salicylideneaniline (SA). The cyclization and cycloreversion reactions of diarylethene derivatives have been studied with picosecond time-resolved Stokes and anti-Stokes Raman spectroscopy. We obtained information on the vibrational relaxation and the energy partitioning in the cycloreversion process in 1,2-bis(3,4-dimethyl-5phenyl-2-thyenyl)perfluorocyclopentene. We also measured the fluorescence excitation and dispersed fluorescence spectra of the open-ring form of 1, 2-bis(3methyl-2-thienyl)perfluorocylclopentene and SA in a supersonic jet expansion. The spectra reveals that an ultrafast internal conversion (IC) occurs from the photoexcited ²A state to ¹A state that correlates to the ¹A state of the closed-ring form. The vibronic pattern in the fluorescence excitation spectrum of SA suggested that a very fast occurs from the photoexcited $S_1(\pi\pi^*)$ state of the enol form in addition to the excited-state doubleproton transfer. We have first to investigate the ultrafast excited-state dynamics in photochromic SA by femtosecond time-resolved REMPI spectroscopy. The excited-state dynamics of SA in both the enol and cisketo forms has been clarified. There is a close similarity in the dynamics of diarylethene derivatives and SA; The initially photoexcited state is located above an electronic-dipole forbidden state, and IC plays an important role in photochromic reaction.

A-1 Ultrafast Excited-State Dynamics in Photochromic *N*-Salicylideneaniline Studied by Femtosecond Time-Resolved REMPI Spectroscopy

Ultrafast processes in photoexcited N-salicylideneaniline (SA) have been investigated with femtosecond time-resolved resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The ion signals via the $S_1(n,\pi^*)$ state of the enol form as well as the protontransferred cis-keto form emerge within a few hundred femtoseconds after photo-excitation to the first $S_1(\pi,\pi^*)$ state of the enol form. This reveals that two ultrafast processes, excited-state intramolecular proton transfer (ESIPT) reaction and an internal conversion (IC) to the $S_1(n,\pi^*)$ state, occur on a time scale less than a few hundred femtoseconds from the $S_1(\pi,\pi^*)$ state of the enol form. The rise time of the transient corresponding to the production of the proton-transferred cis-keto form is within 750 fs when near the red-edge of the absorption is excited, indicating that the ESIPT reaction occurs within 750 fs. The decay time of the $S_1(\pi,\pi^*)$ state of the *cis*-keto form is 8.9 ps by exciting the enol form at 370 nm, but it dramatically decreases to be 1.5 ~ 1.6 ps for the excitation at 365 ~ 320 nm. The decrease in the decay time has been attributed to the opening of an efficient non-radiative channel; an IC from $S_1(\pi,\pi^*)$ to $S_1(n,\pi^*)$ of the *cis*-keto form promotes the production of the *trans*-keto form as the final photochromic products. The two IC processes provide opposite effect on the quantum yield of photochromic products: IC in the enol form may substantially reduce the quantum yield, but IC in the *cis*-keto form increases it. The time constants and reaction processes in SA obtained from present study are summarized in Figure 1.



Figure 1. Excited-state dynamics in SA obtained from femtosecond time-resolved study.

B. Structural Chemistry of High Oxidation State Intermediate of Terminal Oxidases

KITAGAWA, Teizo; OGURA, Takashi¹; ODA, Kenji²; TAKAHASHI, Toshinari²; YAMAGUCHI, Satoru¹; MIKAMI, Jun¹; KADOKAWA, Toshifumi¹; YOSHIKAWA, Shinya¹; MURAMOTO, Kazumasa¹; ITOH, Kyoko¹; SHIMADA, Hideo³; MUKAI, Masahiro⁴; SHIMOKATA, Kunitoshi⁴; KATAYAMA, Yukie⁴; TAKAHASHI, Satoshi⁵; AOYAMA, Hiroshi⁶; VAROTSIS, Constantinos⁷; KIM, Younkyoo⁸ (¹Himeji Inst. Tech.; ²Univ. Tokyo; ³Keio Univ.; ⁴JBIC; ⁵Osaka Univ.; ⁶RIKEN Harima Inst.; ⁷Univ. Crete; ⁸Hankuk Univ. Foreign Studies)

Ogura's group have moved to Himeji Inst. Tech. and Takahashi was promoted to Osaka University during this program. The purpose of this project is to characterize the P intermediate of cytochrome c oxidase. Ogura's group carried out time-resolved resonance Raman as well as time-resolved absorption spectroscopy. Yoshikawa analyzed x-ray crystallographic structure of this enzyme. Okuno of Grad. Univ. of Adv. Stud. and Kitagawa examined IR spectra of the protein moiety of this enzyme to elucidate the proton pumping mechanism. Kim produced the P intermediate by incubation of oxidized enzyme with CO and investigated UV resonance Raman spectra. Varotsis brought bacterial terminal oxidases with him from Crete Univ. to Okazaki and measured its resonance Raman spectra. Prof. Shimada prepared a chimeric enzyme which consists of a bacterial subuit I and mammalian subunits II-VII. Prof. Pawel Kozlowski of Lousvile Univ. also joined this collaborative research to perform DFT calculations on the P intermediate. The all members got together on January 8, 2004 to discuss the structure of P intermediate.

It was pointed out that although the P intermediate generated by incubation of oxidized enzyme with CO exhibits the absorption and resonance Raman spectra quite similar to those of the P intermediate generated during the reduction of O_2 by fully reduced enzyme, the two P intermediates are distinct from each other, because the former becomes ferric state without showing the F intermediate but the latter shows it. The presence of an extra oxidation equivalent of the P intermediate on a heme was suggested from the DFT calculations and its compatibility with resonance Raman spectra became a highlight of discussion.

C. Exchange and Spin-Orbit Interactions in Molecular Inner-Shell Excitation

KOSUGI, Nobuhiro; GEJO, Tatsuo¹; ISHIDA, Toshimasa²; HIYAMA, Miyabi; RÜHL, Eckart³; HATSUI, Takaki

(¹Univ. Hyogo; ²Shizuoka Univ.; ³IMS and Würzburg Univ.)

In the orbital interaction theory,¹⁾ the electron-hole interaction between occupied and unoccupied orbitals is related to short-range interaction, delocalization (DL) or charge transfer (CT), and long-range interaction, polarization (PL) or local excitation. On the other hand, the electron-electron interaction in two occupied orbitals is related to short-range exchange repulsion (EX) and long-range electrostatic interaction (ES). The spin-orbit (SO) interaction is inherently of atomic character. EX and SO interactions involving core electrons of the firstrow and second-row elements such as carbon 1s and sulfur 2p are relatively small in comparison with intravalence EX and deep-core SO, but have been recently essential to understand fine structures newly found in high-resolution and sophisticated measurements of inner-shell phenomena using third-generation synchrotron radiation (SR) facilities.

There are some types of EX. EX in closed-shell electrons results in an *exclusion* effect on the electrons in the interacting region. This is completely different from electrons sharing in the interacting region and forming covalent bonds. The interatomic core-core and core-valance EX interactions²⁾ are important in discussing core hole localization in the core ionization and resonant phenomena such as multi-atom resonant photoemission. The core excitation in the closed-shell system creates an open-shell valence and/or Rydberg electron. In this case, the intra-atomic core-valence and core-Rydberg EX result in large and small singlet-triplet (ST) exchange splittings, respectively, where the core electron is localized on an atom and the intra-atomic EX component is predominant. On the other hand, the Rydberg electron may have relatively large intermolecular EX interaction with surrounding molecules in cluster, liquid, solid, and adsorbate phases, because of its diffuse character. In the core excitation and ionization of the open-shell system, EX causes more complicated multiplet splittings (MS). The core-valence EX sometimes competes with the intra-valence EX in core excitations of open-shell molecules composed of firstrow elements.²⁻⁵⁾

The SO splitting on the core electron is directly observed in X-ray photoelectron spectroscopy. Even in 2p photoabsorption spectroscopy, the 2p SO splitting of third-row and heavier elements is large and is easily distinguishable. The singlet and triplet (ST) 2p excited states are strongly and indistinguishably mixed with each other through SO or jj coupling. However, in second-row elements such as phosphor and sulfur, 2p SO is not satisfactorily analyzed due to a small and comparable splitting to the intra-atomic core-valence EX splitting. SO is still a major factor in the core-toRydberg excited state with a small ST (EX) splitting, but is only one of some important factors in the core-tovalence excited state with a large ST (EX) splitting.⁶) Recent high-resolution photoelectron spectroscopy is possible to reveal another small splitting in the $2p_{3/2}$ manifold due to the molecular filed (MF) effect.⁷)

Now we have to consider SO, MF, and EX splittings in interpreting 2p excitation spectra of molecules involving second-row elements. Furthermore, de-excitation or resonant inner-shell spectroscopy may indicate additional features *via* triplet components in intermediate core-excited states; that is, triplet valence excitation in resonant inelastic X-ray scattering and quartet valence ionization in resonant photoelectron or Auger electron emission. In the present special project, we will discuss various types of EX and intermediate couplings between SO and EX to analyze experimental evidence in inner-shell spectra of some simple molecules.

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D. Integration of Bio-Molecular Recognition Reaction System on Solid Surfaces and the Structure Analysis

URISU, Tsuneo; TERO, Ryugo; NONOGAKI, Youichi; MORIGAKI, Kenichi¹; WATANABE, Hidekazu²; AOYAGI, Mutsumi²; HARADA, Kensuke²; TANAKA, Keiichi² (¹AIST; ²Kyushu Univ.)

Membrane protein biosensors and biochips are most important research targets in the post-genome. However, their developments are surprisingly delayed. One of the reason is due to the difficulty in integrating the membrane proteins on solid surfaces without loosing their physiological activities. They express their physiological activity only when they are reconstructed in the lipid bilayers under the water. In this research project, we are going to develop elementary technologies of constructing membrane protein/lipid bilayer systems on Si surfaces and conduct the analysis of their structures by AFM (Atomic force microscopy) and BML-IRRAS (Infrared reflection absorption spectroscopy using buried metal layer substrates).

D-1 Lipid Membrane Formation by Vesicle Fusion on Silicon Dioxide Surfaces Modified with Alkyl Self-Assembled-Monolayer Islands

We have investigated the formation of the dipalmitoylphosphatidylcholine (DPPC) membrane by the vesicle fusion method on SiO2 surfaces modified with self-assembled monolayer (SAM) islands of octadecyltrichlorosilane (OTS) with sizes comparable to those of the vesicles by means of atomic force microscopy. OTS-SAM islands with various size and coverage can be constructed on the SiO2 surfaces prepared by thermal oxidation followed by partial hydroxylation in a H₂O₂/ H₂SO₄ solution. When vesicles are sufficiently smaller than the SiO₂ domains, DPPC bilayers and DPPC/OTS layers form on the SiO₂ and OTS domains, respectively (Figure 1). However, the adhesion of larger vesicles onto SiO₂ is prevented by the OTS islands, therefore only DPPC/OTS layers form without formation of DPPC bilayers on the SiO₂ domains (Figure 1). On surfaces with domains in tens to hundreds nanometer scale, the relative size between the hydrophilic domains and the vesicles becomes important factor in the membrane formation by the fusion of vesicles.



Figure 1. AFM images $(5.0 \times 5.0 \ \mu\text{m}^2)$ of the OTS-modified SiO₂ surfaces ($\theta_{\text{OTS}} = 0.71$) obtained in the buffer solution (a) before and (b) after the deposition of 200-nm-filtered vesicles and (c) sonicated vesicles.

D-2 Characterization of Dipalmitoylphosphatidylcholine/Cholesterol Langmuir-Blodgett Monolayers Investigated by AFM and FT-IR

The addition effects of cholesterol on the dipalmitoylphosphatidylcholine (DPPC) Langmuir-Blodgett (LB) monolayer have been investigated by atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRRAS). The phase transformation from the pure DPPC to the DPPC/cholesterol phase proceeds through two stages: initial drastic changes in the surface morphology and the conformation of the DPPC acyl chains below 10% cholesterol, and the gradual homogenization of the morphology towards the liquid ordered phase up to 35% cholesterol (Figure 1). The IRRAS peak position indicates that the conformational disorder of the acyl chain becomes almost liquid level at the 10% cholesterol addition. In the homogeneous liquid-ordered phase at 35% cholesterol, the terminal methyl groups of the DPPC are aligned in good order as the solid-like gel phase, whereas the acyl chains have liquid level disordered conformation.



Figure 2. AFM images $(5 \times 5 \ \mu m^2)$ of DPPC/ cholesterol LB monolayers transferred onto the mica surface at the surface pressure of 10 mN m⁻¹. The concentrations of cholesterol are: a) 0% (pure DPPC), b) 10%, c) 20%, d) 30%, e) 35% and f) 100% (pure cholesterol) in the molar ratio. g) The profile of the line drawn in d). The scale of the inserts of c) and d) is $1.34 \times 1.34 \ \mu m^2$.

D-3 Theoretical Analysis of the Oxygen Insertion Process in the Oxidation Reactions of $H_2O + H/Si(100)$ and $2H + H_2O/Si(100)$; Calculation of an Ab Initio Molecular Orbital Method and an Analysis of the Tunneling Reaction

The reaction paths were analyzed, by an ab initio molecular orbital method, for the surface reaction systems, $2H + H_2O/Si(100)-(2\times1)$ and $H_2O + H/Si(100)-(2\times1)$, in which SiH₂ species with one or two oxygen atom-inserted back bonds have been observed as new stable reaction products. It was found that common metastable states exist in both systems, and the initial energy is sufficiently higher than all transition state energies in the former system, while in the latter system, the energy of the highest transition state is much higher than the initial energy, and thus a tunneling effect plays an important role (Figure 1, and 2).



Figure 1. Energy diagrams for the oxygen insertion reactions, $H_2O + H/Si(100)-(2\times1)$ and $2H + H_2O/Si(100)-(2\times1)$. The dissociation limit $H_2O + H/Si(100)-(2\times1)$ is set on the energy standard. The zero-point vibration energy correction is summed into the energies.



Figure 2. Fully optimized structures of the local minima and the transition states in the oxygen migration processes. Several bond lengths concerned with the migration reaction is expressed in Å.

D-4 Integration of Membrane Protein on Si and Application to the Biosensor

Membrane proteins such as receptors and ion channels play an important in the regulation of the physiological condition and the signal transduction in the central nervous system, and they are considered to be the important target of the medical development based on the genome information. Concerning the membrane proteins, however, not only the structure analysis but also the development of the analysis method of the protein molecular recognition reaction are significantly delayed. It is considered to be due to that usual protein chip technologies of immobilizing the protein on the solid surface can not be applied for the membrane protein which shows the physiological activity only when reconstructed in the lipid bilayers. The supported membrane, the lipid bilayer with reconstructed membrane protein system on the solid surface, are attracting a significant attention as a new analytical method for analyzing a membrane protein molecular recognition interaction. It also provides an interesting tool for the study of the cell membrane surface reaction. The supported membranes are classified to the beads type¹⁾ and the planer type.^{2),3)} Although the higher sensitivity is expected for the beads type, the planer type, however, has several advantages such as; (1) The precise structure control, which is important in the ion channel and the trans membrane receptor, can be made, and (2) Not only the membrane surface but also the inside information such as channel current can be obtained.

We are now developing the elementary process technologies necessary for the fabrication of the supported membrane structure shown in Figure 1. The important elementary processes are, (a) Surface structure control of the supporting substrate. Especially, it is pointed out that the decrease of the surface roughness is required.²⁾ (b) Surface chemical modifications necessary for immobilizing the lipid bilayer and or proteins on the surface, and for depressing the edge leak current. (c) Formation of the planer lipid bilayer and the reconstruction of membrane proteins. In this symposium, I am going to introduce the recent results about each elementary process developments.

(a) Surface structure control of the supporting substrate: We have almost succeeded in developing the super flat surface Si substrate with buried $AgCl/Ag/CoSi_2$ electrode, for which the interface potential between buffer solution/electrode and electrode/Si(100) can be controlled.

(b) Surface chemical modifications: We have succeeded in deposition and patterning of OTS (octadecyltrichlorosilane) self-assembled monolayers, which we are going to use for the depression of the edge leak current. The surface modification by –COOH group has been attained keeping the surface roughness less than 1 nm. This was used for immobilization of avidin molecules on the substrate surface. The immobilization was certified by molecular recognition AFM and the IR absorption spectroscopy by BML-IRRAS.

(c) The tethered single lipid bilayers of DPPC and DMPC using avidin immobilized on the surface have been successfully deposited. The structure was certified by under-water-AFM. Several membrane protein molecules were successfully reconstructed in these lipid bilayers and their single molecule images were obtained by the same AFM technique.

We are going to continue these effort to attain the measurement of the function of the supported membrane systems in the succeeding research.

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Figure 1. Supported membrane biosensor device.

E. Development and Application of Short Wave Length Free Electron Laser

KATOH, Masahiro; HOSAKA, Masato; MOCHIHASHI, Akira; TAKASHIMA, Yoshifumi¹; HAMA, Hiroyuki²; GEJO, Tatsuo³; NISHINO, Hideo⁴; HARA, Toru⁵; COUPRIE, Marie-Emmanuelle⁶; BIELAWSKI, Serge⁷ (¹Nagoya Univ.; ²Tohoku Univ., ³Hyogo Univ.; ⁴JST; ⁵RIKEN; ⁶LURE; ⁷Univ. Sci. Tech. Lille)

The free electron laser developed at UVSOR has some characteristics such as tunability in wave length, variability in polarization, high average power and natural synchronization with synchrotron light pulses. We achieved the average output power of 1.2 W in the visible region, which is the world highest record in storage ring free electron lasers. We have successfully carried out a two-photon double-resonant excitation on Xe atoms utilizing the SR pulses as a pump and the FEL pulses as a probe light.

As the next step, we are trying to realize a stable and high power oscillation in the UV region, hopefully shorter than 200 nm. The upgraded UVSOR, UVSOR-II, has a small beam emittance of 17 nm-rad in the FEL operating mode. This smaller emittance gives a larger FEL gain, especially in the shorter wave length. In December, 2003, we have succeeded in oscillating the FEL in visible wavelength region for the first time at UVSOR-II. We have confirmed the increase of the FEL gain. We are trying to oscillate the FEL at around 250 nm. The circular polarized FEL around 250 nm will be used for the experiment on absolute asymmetric photoreactions of amino acids.

(2) Research Symposia

(From 2003 Oct. to 2004 Sep.)

- Dynamics of Biomolecules in its Relation to Function and Structure (Dec. 22–24, 2003) Chair: KITAO, Akio
- Size Effect in Nano-Scale Reaction Field (Jan. 19–20, 2004) Chair: MAFUNE, Fumitaka
- Physical Chemistry of Molecular Functions—New Development in Theoretical/Computational Chemistry and Spectroscopy (July 21–23, 2004) Chair: ISHIDA, Toshimasa
- Advanced Molecular Science and Its Frontiers (May 21–22, 2004) Chair: SUZUKI, Toshinori
- Magnetic Structure and Magneto-Optical Effect of Chiral Molecule-Based Magnets (July 15–16, 2004) Chair: INOUE, Katsuya
- 6. Physical Chemistry Symposium for Young Researchers (June 2, 2004) Chair: NAKAJIMA, Atsushi
- Particle Correlations in Elementary Reactions Involving Atoms and Molecules (June 3–4, 2004) Chair: KOCHI, Noriyuki
- Conference on Molecular Electronics (April 8–10, 2004) Chair: MATSUMOTO, Takuya

(3) Cooperative Research

This is one of the most important categories that IMS undertakes for conducting its own research of the common interest to both outside and IMS scientists by using the facilities at IMS. In 2003 Oct.–2004 Mar., 117 outside scientists from 45 research groups joined the Cooperative Research programs, and 128 outside scientists from 47 research groups in 2004 Apr.–2004 Sep. The names and affiliations of those collaborations are found in the Research Activities sections in this Review.

(4) Use of Facility

The number of projects accepted for the Use of Facility in 2003 Oct.–2004 Mar. amounted 3, 23, and 0 for the Laser Research Center for Molecular Science (LRCMS), for the Research Center for Molecular-scale Nanoscience (RCMN) and for the Equipment Development Center (EDC), respectively. In 2004 Apr.–2004 Sep., the number of projects accepted amounted 1, 29, and 1 for LRCMS, for RCMN, and for EDC, respectively.

(5) Invited Research

Under this joint-study program, several scientists were invited from other institutions of help for construction and improvement of instruments in IMS. The total number of the projects in this category was 1.

(6) Use of UVSOR Projects

In the UVSOR Facility with the 750 MeV electron storage ring, there are sixteen beam lines available for synchrotron radiation research (see UVSOR ACTIVITY REPORT 2003). Under the Use of UVSOR Projects, many synchrotron radiation experiments have been carried out by outside scientists on eight beam lines in close cooperation with the UVSOR staff. The total number of the projects in this category was 131 (68 in 2003 Oct.–2004 Mar., and 63 in 2004 Apr.–2004 Sep.).

(7) Use of Facility Program of the Computer Center

Computer Center provides three types of research programs for outside scientists: (a) Use-of-Facility Program; (b) Cooperative Research Program; (c) Advanced Research Program. The numbers of projects accepted for each programs during the fiscal year of 2003 were (a) 111 with 525 users, (b) 8 with 13 users and (c) 2 with 4 users. Computer time distributed for these projects amounted to 65% of the total annual CPU time available.

FOREIGN SCHOLARS

Visitors from abroad are always welcome at IMS and they have always played an important role in the research activities of the Institute. The foreign scientists who visited IMS during the past year (September 2003-August 2004) are listed below.

The mark ^{*1} indicates attendance at an Okazaki IMS Conference; ^{*2} a MONKASHO (Ministry of Education, Culture, Sports, Science and Technoogy, Japan) or JSPS (Japan Society for the Promotion of Science) Invited Fellow; ^{*3} an IMS councillor; ^{*4} an IMS visiting professor or associate professor from abroad (period of stay from 6 to 12 months); ^{*5} a JSPS Post-Doctoral or Ronpaku Fellow; ^{*6} an IMS visiting scientist and ^{*7} a visitor to IMS. Scientists who would like to visit IMS under programs ^{*2} and ^{*4} are invited to make contact with IMS staff in

their relevant field.

Prof. Kovalenko Andriy ^{*6}	Natl. Inst. for Nanotechnology, Univ. of Alberta	(U.S.A.)	Sep. '03
Prof. Holovko Myroslav ^{*2}	Inst. for Condeused Matter Phys.	(Ukraine)	Sep.–Dec. '03
Dr. Da Silva Eirik Falck ^{*6}	Norwegian Univ. of Sci. and Tech.	(Norway)	Sep. '03–Mar. '04
Prof. H. Köhler Frank ^{*1}	Tech. Univ. München	(Germany)	Sep.'03
Dr. Dascalu Traian ^{*6}	Natl. Inst. for Lasers, Plasma and Rediation Phys.	(Rumania)	Oct. '03–Mar. '04
Dr. Carr G. Lawrence ^{*1}	Brookhaven Natl. Lab.	(U.S.A.)	Oct '03
Dr. Simonyan Mkhitar ^{*6}	Inst. for Phys. Res. Armenian Natl. Acad. of Sci.	(Armenia)	Oct. '03–Mar. '04
Dr. Ohrwall Gunnar ^{*1}	Uppsala Univ.	(Sweden)	Oct '03
Prof. Gel'mukhanov Faris ^{*1}	Royal Inst. of Tech.	(Sweden)	Oct '03
Dr. Toman Petr ^{*2}	Acad. of Sci. of the Czech Rep.	(Czech Republic)	OctNov. '03
Prof. Duan Wenyong ^{*6}	Nankai Univ. Tianjin	(China)	Nov. '03–Mar. '04
Prof. Ali Md. Yusuf ^{*6}	Shahjalal Univ. of Sci. and Tech.	(Bangladesh)	Oct. '03–Jan. '04
Dr. Zhao Yi ^{*2}	Univ.of Sci. and Tech. of China	(China)	Nov. '03–Nov. '05
Prof. Josef Stepanek ^{*6}	Inst. of Phys. Charles Univ.	(Czech Republic)	NovDec. '03
Dr. Jizba Petr ^{*1}	Univ. of Tsukuba, Inst. of Phys.	(Czech Republic)	Nov. '03
Prof. Constantinos Varotsis ^{*6}	Univ. of Crete	(Greece)	NovDec. '03
Prof. Ashot Markosyan ^{*6}	Lab. of Problems for Magnetism	(Russia)	Dec. '03–Mar. '04
Prof. Yoon Cheol min ^{*2}	Korea Univ.	(Korea)	Dec. '03–Feb. '04
Prof. Yi Jonghoon ^{*2}	Yongnm Univ.	(Korea)	Dec. '03–Jan. '04
Dr. Pavel Nicolaie ^{*1}	Inst. of Atomic Phys.	(Rumania)	JanFeb. '04
Prof. Kim Younkyoo ^{*2}	Hunkuk Univ. of Foreign Studies	(Korea)	Dec. '03–Feb. '04
Dr. Hammer Thomas ^{*1}	Siemens AG Corporate	(Germany)	Feb. '04
Prof. Castleman Albert Wlford Jr.*	¹ Pennsylvania State Univ.	(U.S.A.)	Dec. '03
Prof. Brover Michel ^{*1}	Univ. Lvon 1	(France)	Dec. '03
Prof. Simard Benoit ^{*1}	Natl. Res. Council of Canada	(Canada)	Dec. '03
Prof. Schiffrin David L ^{*1}	Univ. of Liverpool	(England)	Dec. '03
Prof Wang Lai-Sheng ^{*1}	Washington State Univ	(USA)	Dec. '03
Prof. Knickelbein Mark B. ^{*1}	Argonne Natl. Lab.	(U.S.A.)	Dec. '03
Prof. Rosen Arne E. ^{*1}	Gothenburg Univ.	(Sweden)	Dec. '03
Prof. Haberland Helmut ^{*1}	Univ. of Freiburg	(Germany)	Dec. '03
Prof Brechignac Catherine ^{*1}	Centre Natl de la Res Sci	(France)	Dec. '03
Prof Farrar James M ^{*1}	Univ of Rochester	(USA)	Dec. '03
Prof Whetten Robert L ^{*1}	Georgia Inst. of Tech	(U S A)	Dec. '03
Prof Jarrold Martin F ^{*1}	Indiana Univ	(USA)	Dec. '03
Prof Kappes Manfred ^{*1}	Univ Karlsruhe	(Germany)	Dec. '03
Prof Armentrout Peter B *1	Univ. of Itah	(USA)	Dec. '03
Prof Parks Ioel H ^{*1}	Rowland Inst. at Harverd	(USA)	Dec. '03
Prof Kim Seong Keun ^{*1}	Seoal Natl Univ	(Korea)	Dec. '03
Prof Landman Uzi ^{*1}	Georgia Inst. of Tech	(IISA)	Dec. '03
Prof Bowen Kit H Ir ^{*1}	Johns Honkins Univ	(USA)	Dec. '03
Prof Jinwoo Cheon ^{*1}	Vonsei Univ	(V.J.A.) (Korea)	Dec. 03
Prof Klaus Muller Dathlafs ^{*1}	Univ. of Vork	(Kolca) (England)	Dec. 05
Drof Arich Dan Naim ^{*6}	Univ. Of TOIK	(Lingianu)	Dec. 05 Eab. Mar '04
Prof. Mondon Dominique ^{*1}	Leuis Desteur Univ.	(Islael) (Eronoo)	Feb Mai. 04
Dr. Lablanguia Dagaal ^{*]}	LUDE	(France)	Feb. 04
Dr. Cuo Unigina ^{*6}	LUKE Heldreide Univ	(France)	reb. 04 Apr 204 Mar 205
Dr. Guo Haiqilig	HOKKAIGO UIIIV.	(Japan) (Commoniu)	Apr. 04–Mar. 05
Dr. Znang Fapel - Draf, Dracht Ealaget*?	Leioniz Inst. for Solid State and Mater. Res.	(Germany)	Apr. 04–Apr. 06
Prof Ion Shih Chana ^{*6}	w ucizourg Univ. Me Mester Univ	(Germany)	AprJul. 04
Prof. Change ing Ling	Tioniin Univ.	(Callada)	Dec. 03
Prof. Unang-jun Liu ~	Lianjin Univ.	(Cnina)	Dec. 05
Prof. Haymet Anthony	Csiro Marine Kes.	(Australia)	Jan. 04
Prof. Zhou Kuhong	Columbia Univ. Cent.	(U.S.A.)	Apr. '04

Prof. Chen Kuo-mei ^{*6}	Natl. Sun Yat-sen Univ.	(Taiwan)	Mar. '04
Prof. Lee Yuan-Pern ^{*6}	Natl. Tsing Nua Univ.	(Taiwan)	Mar. '04
Prof. Chang Bor-chen ^{*6}	Natl. Central Univ.	(Taiwan)	Mar. '04
Dr. Tzeng Wen-Bih ^{*6}	Inst. for Atomic and Molecular Sci. Acad. Sinica	(Taiwan)	Mar. '04
Dr. Lin Jim-Jr-Min ^{*6}	Inst. for Atomic and Molecular Sci. Acad. Sinica	(Taiwan)	Mar. '04
Dr. Lee Shih-Huang ^{*6}	Natl. Synchrotron Res.Cent.	(Taiwan)	Mar. '04
Prof Ioo Taiha ^{*6}	Pohang Univ of Sci and Tech	(Korea)	Mar '04
Prof Kim Dongho ^{*6}	Yonsei Univ	(Korea)	Mar '04
Prof. Lim Manho ^{*6}	Pusan Natl Univ	(Korea)	Mar '04
Drof Shin Sookmin ^{*6}	Socul Natl Univ.	(Korca)	Mar. 04
Draf Chai Jana Ha ^{*6}	Verse Univ.	(Korea)	Mar. 04
PIOL CHOI JOIIg-HO	Korea Univ.	(Korea)	Mar. 04
Dr. Lee Sang Won ^o	Korea Univ.	(Korea)	Mar. '04
Prof. Pulay Peter ¹²	Arkansas Univ.	(U.S.A.)	Jan.–May '04
Prof. Kozlowski Pawel ^{*2}	Univ. of Louisville	(U.S.A.)	Apr.–Aug. '04
Dr. Pavel Nicolaie	Natl. Inst. for Laser	(Rumania)	Apr. '04–Mar. '05
Dr. Redshaw Carl ^{*1}	Univ. of East Anglia	(England)	May '04–0 '0
Ms. Biswas Raka ^{*1}	Univ. of Kalyani	(India)	May '04
Ms. Chang I-Ya ^{*1}	Natl. Tsing Hua Univ.	(Taiwan)	May '04
Ms. Chang YeWon ^{*1}	Sungkyunkwan Univ.	(Korea)	May '04
Mr. Choi Hyeonho ^{*1}	Seoul Natl.Univ.	(Korea)	May '04
Mr. Kim Hyungiun ^{*1}	KAIST	(Korea)	May '04
Prof Lee Yoon S ^{*1}	KAIST	(Korea)	May '04
Prof Liang WanZhen ^{*1}	Univ of Sci and Tech of China	(China)	May '04
Prof L o Chi Eqi ^{*1}	Chinese Univ. of Hong Kong	(Unita) (Hong Kong)	$M_{\rm av}$ '04
M_r Lo Loo $Ping^{*1}$	Chinese Univ. of Hong Kong	(Holig Kolig)	May '04
Mr. LO LOC Fillg	Vegeteert Univ. of Holig Kolig	(Clilla) (Thailand)	Mary 04
Ms. Maitarad Phornphimon	Kasetsart Univ.	(Inaliand)	May 04
Dr. Nunrium Peerapol	Kasetsart Univ.	(Inailand)	May 04
Prof. Orbell John D. ⁴	Victoria Univ.	(Australia)	May '04
Ms. Poolmee Ptjaman ¹	Kasetsart Univ.	(Thailand)	May '04
Dr. Tonmunphean Somsak ^{*1}	Chulanlongkorn Univ.	(Thailand)	May '04
Prof. Wang Bo-Cheng ^{*1}	Tamkang Univ.	(Taiwan)	May '04
Dr. Wang Feng ^{*1}	Swinburne Univ. of Tech.	(Australia)	May '04
Ms. Wong C. Hoi-Shan ^{*1}	Hong Kong Polytechnic Univ.	(HongKong)	May '04
Dr. Yu Jen-Shinag K. ^{*1}	Natl. Chiao Tung Univ.	(Taiwan)	May '04
Dr. Rungrotmongkol Thanyada*	Kasetsart Univ.	(Thailand)	May '04
Dr. Treesuwan Witcha ^{*1}	Kasetsart Univ.	(Thailand)	May '04
Mr. Chanmongkolpanich Krit ^{*1}	Thammasat Univ.	(Thailand)	May '04
Ms. Cho Sung-sil ^{*1}	Sungkyunkwan Univ.	(Korea)	May '04
Dr. Hannonghua Supa ^{*1}	Kasetsart Univ	(Thailand)	May '04
Mr. Kim Changho ^{*1}	KAIST	(Korea)	May '04
Dr. Parasuk Waraporn ^{*1}	Kasatsart Univ	(Thailand)	May '04
Mr. Siyanrakasam Drasanna ^{*1}	School of Dhamaon dawn	(India)	May '04
Ma Vana Mar V ^{*1}	Chinese University of Henry Kenry	$(\Pi \Pi \Pi a)$	Mary 04
Ms. Yeung Man Yi $\frac{1}{2}$	Unitese Univ. of Hong Kong	(China)	May 04
Dr. Ghosh D. C.	Univ. of Kalyani	(India)	May 104
Dr. Radom Leo ¹	Univ. of Sydney	(Australia)	May '04
Dr. Baeck Kyoung K. ¹	Kangnung Natl. Univ.	(Korea)	May '04
Dr. Chandra Amalendu ¹	Indian Inst. of Tech.	(India)	May '04
Dr. Collins "Michael, A. ^{*1}	Australian Natl. Univ.	(Australia)	May '04
Dr. Coote Michelle C. ^{*1}	Australian Natl. Univ.	(Australia)	May '04
Dr. Das Bhanu Pratap ^{*1}	Indian Inst. of Astrophysics	(India)	May '04
Dr. Fang Wei-Hai ^{*1}	Beijing Normal Univ.	(China)	May '04
Prof. Gadre Shridhar ^{*1}	Univ. of Pune	(India)	May '04
Dr Javatilaka Dylan ^{*1}	Univ of Western Australia	(Australia)	May '04
Dr. Jiang Hua-Liang ^{*1}	Shanghai Inst. of Materia Medica	(China)	May '04
Dr. Lee Fok Kyun ^{*1}	KAIST	(Korea)	May '04
Dr. Lee Lok Kyun Dr. Lee Jin Vong *1	Chonnam Natl Univ	(Korea)	May $'04$
$Dr. Li Shuhuo^{*1}$	Nonjing Univ.	(Koica)	May '04
Dr. Li Shuhua ⁻	Dalias Lai	(China)	May 04
Dr. Liu wenjian $\frac{1}{2}$	reking Univ.	(China)	Iviay 04
Dr. Lin Znenyang		(Cnina)	Iviay 04
Dr. Lu Shih-l ⁻¹	Fooyin Univ.	(laiwan)	May 04
Dr. Ma Ida N. L. 1	Inst. of High Performance Computing	(Singapore)	May '04
Dr. Pal Sourav ^{*1}	Natl. Chem. Lab.	(India)	May '04
Dr. Parasuk Vudhichai ^{*1}	Univ. Chualongkorn	(Thailand)	May '04
Dr. Park Seung, C. ^{*1}	Sungkyunkwan Univ.	(Korea)	May '04

*1			
Prof. Pulay Peter ^{*1}	Univ. of Arkansas	(U.S.A.)	May '04
Dr. Schwerdtfeger P. ^{*1}	Univ. of Auckland	(New Zeland)	May '04
Dr. Shin Seokmin ^{*1}	Seoul Natl. Univ.	(Korea)	May '04
Prof. Wong Richard M. W. ^{*1}	Univ. of Singapore	(Singapore)	May '04
Dr. Yang Zhong-Zhi ^{*1}	Liaoning Normal Univ.	(China)	May '04
Dr. Yates Brian ^{*1}	Univ. of Tasmania	(Australia)	May '04
Dr. Yu Chin-hui ^{*1}	Natl. Tsing Hua Univ.	(Taiwan)	May '04
Prof. Jiang Yuansheng ^{*1}	Nanjing Univ.	(China)	May '04
Prof. Kim Kwang S. ^{*1}	Pohang Univ. of Sci. and Tech.	(Korea)	May '04
Prof. Mukherjee Debashis ^{*1}	Indian Association for the Cultivation of Sci.	(India)	May '04
Prof. Wu Yun-Dong ^{*1}	Hong Kong Univ. of Sci. and Tech.	(China)	May '04
Prof. Couprie Marie-Emmanuelle*	² Comissariat al' Energie Atomique	(France)	Jun.–Sep. '04
Prof. Cindy L Berrie ^{*1}	Univ. of Kansas	(U.S.A.)	May '04
Prof. Ward H Thompson ^{*1}	Univ. of Kansas	(U.S.A.)	May '04
Dr. Lei Sheng-Bin ^{*6}	Chinese Acad. of Sci.	(China)	May-Nov. '04
Prof. Boo Bong Hyun ^{*2}	Chungnam Natl. Univ.	(Korea)	Jul.–Aug. '04
Prof. Rubensson Jan-Erik ^{*1}	Uppsala Univ.	(Sweden)	JunJul. '04
Prof. Jing Lu ^{*6}	Peking Univ.	(China)	Jul '04
Dr. Huang Wei ^{*6}	Nanjing Univ.	(China)	Jul. '04–Jun. '06
Prof. Girard Bertrand ^{*6}	Univ. of Paul Sapatie	(France)	JulAug. '04
Prof. Levis Robert.J ^{*6}	Temple Univ.	(U.S.A.)	Jul.–Aug. '04
Mr. Guhr Markus ^{*6}	Freie Univ. Berlin	(Germany)	Aug. '04
Dr. Ottmar Jagutzki ^{*6}	Inst. für Kemphysik	(Germany)	Jun. '04
Mr. Markus Schoffler ^{*6}	Inst. für Kemphysik	(Germany)	Jun. '04
Prof. Bopp Philippe ^{*1}	Univ. of Bordeaux	(France)	Jun. '04
Prof. Wan Lijun ^{*2}	Chinese Acad. of Sci. Inst. of Chem.	(China)	JulOct. '04
Mr. Lim Jong Kuk ^{*6}	Seoul Natl. Univ.	(Korea)	AprOct. '04
Prof. Boulanger Benoit ^{*6}	Univ. Joseph Fourier	(France)	Jul '04
Dr. B ielawski Serge ^{*6}	Univ. des Ŝci. et Tech. de Lille	(France)	Aug. '04
Prof. Gu Yuzong ^{*2}	Henan Univ.	(China)	Jul. '04–Jul. '06
Dr. El-Mashtoly Samir ^{*6}	Ain Shams Univ.	(Eygpt)	JulSep. '04
Prof. Fejer Martin ^{*6}	Stanford Univ.	(U.S.A.)	Aug. '04
Prof. Laurell Fredrik ^{*6}	KTH Phys.	(Sweden)	Aug. '04
Prof. Kim Dongho ^{*6}	Yonsei Univ.	(Korea)	Aug. '04
Prof. Chong Song-Ho ^{*1}	Univ. Montpellier 2	(France)	Aug. '04
Dr. Riadh Sahnoun ^{*1}	Tohoku Univ.	(Japan)	Aug. '04
Prof. Milan Melnik ^{*1}	Slovak Tech.Univ.	(Slovakia)	Jun. '04
Dr. Zhang Dao ^{*6}	Nanjing Normal Univ.	(China)	Nov. '03-Nov. '04

264 FOREIGN SCHOLARS

AWARDS

Professor lijima's Scientific Achievements

Professor Sumio Iijima, a visiting professor of Department of Electronic Structures, has been selected as a Person of Cultural Merits in 2003 for his outstanding contribution to the discovery and elucidation of geometrical structures of carbon nanotubes by means of high-resolution electron microscpy. His scientific achievements not only have an enormous impact on the rapidly growing field of nanoscale material science but also open up a possibility toward application in various fields, such as fuel cells, catalysts, sensors, STM probes, and panel display.

Associate Professor Taira's Scientific Achievements

Associate professor Takunori Taira of Laser Research Center for Molecular Science received the Award of 2004 Commendation by the Minister of Education, Culture, Sports, Science and Technology (Persons of scientific and technological research merits) for his contribution to "Miniaturization and Improvement in Performance of Solid-State Lasers."

This award is given to the persons who made a great contribution in scientific technologies. Dr. Taira realized a microchip laser composed of a 500-µm Nd:YVO₄ crystal for the first time. He improved its output power and efficiency and succeeded also in realizing lasers made of Yb:YAG and Nd:YAG ceramics. These developments opened a new field of microchip lasers and variety of applications including experiments using a satellite in space.

Research Associate Fujiwara's Scientific Achievement

Research associate Dr. Hideki Fujiwara of Department of Molecular Assemblies (who moved to Osaka Prefecture Univesity on October, 2003) has received the 2004 Chemical Society of Japan Award for Young Chemists for his contribution to "Development of the first Antiferromagnetic Organic Superconductor." About a quarter century ago, the era of organic superconductors was opened by the discovery of the first organic superconductors, which stimulated greatly the chemists to search for new molecular superconductors. However, the overwhelming discovery of the cupper oxide superconductors around 1986–87 requested them to find a new way to develop new types of functional molecular conductors. Then, the research for developing magnetic organic conductors was started around 1992. Around 1999 Dr. Fujiwara and co-workers examined the electric and magnetic properties of organic metal, κ -(BETS)₂FeBr₄ at low temperature and found the antiferromagnetic transition at 2.5 K and the superconductor. The coexistence of three-dimensional magnetic order and superconductivity was definitely proved by the subsequent physical measurements by Dr. Fujiwara. The discovery of the antiferromagnetic organic superconductor is one of the recent prominent achievements in the field of molecular conductors.

Mr. Yamanaka's Technological Achievements

Mr. Takaya Yamanaka, the chief of the technical section of Laser Research Center for Molecular Science, received the Award of the Technological Development in Chemistry for 2003.

The Chemical Society of Japan awards every year a person who has contributed to the development or improvement of experimental techniques in chemistry or chemical engineering. Mr. Takaya Yamanaka is recognized for his contribution to "Advanced Instrumentation for Spectroscopic Measurements and the Development of Online Booking System of Equipments for the Use of Molecular Scientists." Mr. Yamanaka developed the following useful systems for the investigators in molecular science: (1) the computer-controlled apparatus for fluorescence-lifetime measurements with ns-time resolution by using fast transient memories, (2) the apparatus for time-resolved spectroscopic measurements for ultraviolet synchrotron orbital radiation facility, (3) the maintenance of ultrafast lasers and the development of acquisition systems in ultrafast time-resolved measurements, and (4) the online booking system of equipments for the use of molecular scientists. In particular, the apparatus for fluorescencelifetime measurements has provided molecular scientists in use since 1984. This is one of the most heavily used apparatus originally developed in IMS and applied to the studies including not only the spectroscopy of molecules in the gas phase, but also clusters and photo-catalysts.

Research Associate Miura's Scientific Achievement

Dr. Shinichi Miura received the Scientific Award of Molecular Simulation Society, Japan in 2004 for his contribution to "Computational Theory for Quantum Liquids." Dr. Shinichi Miura started his career in molecular simulation in Prof. Go's group at Kyoto University in collaboration with Prof. Hirata and obtained his Ph.D in 1995 from Kyoto University. After the stay at Prof. Klein's group at University of Pennsylvania, he moved to Tokyo Institute of Technology as a Joshu of Okazaki group, and is, now, working for Institute for Molecular Science.

He has been engaged in simulation study for quantum liquids for more than ten years. First, he studied proton transfer reaction between two formic acid molecules based upon ab initio path integral molecular dynamics calculation and clarified energy profile along the reaction coordinate. Second, he extended RISM integral equation theory to the quantum system and applied it to solutions of quantum solvent, that is alkali metal atom in liquid helium and rare gas molecule in it, and succeeded in analyzing the microscopic solvation structure of snowball and bubble models for these solutions, respectively. Third, he is challenging to include the exchange effect of particles in the calculation, that is, the simulation for Boson and Fermion. Along this way, he proposed one possible way to simulate quantum dynamics of Boson and Fermion based upon a pseudo-potential method. Further, he secceeded in simulating liquid helium in superfluid state using his new hybrid path integral Monte Carlo method, which has a suitable form to include a solute in the fluid. And, now, he is extending his calculation to open a new field of solution chemistry, that is, solvation of a solute in quantum solvent in the super fluid state.

Research Associate Dr. Imura's Scientific Achievement

Dr. Kohei Imura, Research Associate of Department of Molecular Structure, received the Young Scientist Award for the Presentation of an Excellent Paper in the Annual Meeting of The Japan Society of Applied Physics (2004 spring). His title of paper was "Observation of two-photon emission and dynamics of gold nanoparticles by near-field microscopy." He constructed an apparatus for near-field spectroscopy using a femtosecond Ti:sapphire laser as a light source, where the pulse duration at the near-field probe tip was < 100 fs. Using this apparatus, he succeeded in measuring two-photon induced emission from gold nanoparticles with a spatial resolution as high as ~50 nm, and in analyzing the origin of that as well. He also succeeded in direct imaging of spatial distribution of surface plasmon modes for nanorods. At the same time, he found by time-resolved measurements that the ultrafast relaxation process (especially the electron-phonon relaxation) is strongly dependent on position in single nanorods. These results are important for fundamental understanding and application of optical properties of metal nanoparticles, and those of plasmon resonances in nanometric systems.
LIST OF PUBLICATIONS

Department of Theoretical Studies

Y. MAEDA, G. M. A. RAHMAN, T. WAKAHARA, M. KAKO, M. OKAMURA, S. SATO, T. AKASAKA, K. KOBAYASHI and S. NAGASE, "Synthesis and Characterization of Tetrakis-Silylated C₆₀ Isomers," J. Org. Chem. 68, 6791-6794 (2003).

T. WAKAHARA, Y. MAEDA, M. KAKO, T. AKASAKA, K. KOBAYASHI and S. NAGASE, "Silylation of Fullerenes with Active Species in Photolysis of Polysilane," J. Organomet. Chem. 685, 177-188 (2003).

T. TAJIMA, K. HATANO, T. SASAKI, T. SASAMORI, N. TAKEDA, N. TOKITOH, N. TAKAGI and S. NAGASE, "Syntheses and Structures of Silicon Analogues of Cyclopropabenzenes," J. Organomet. Chem. 686, 118-126 (2003).

M. T. H. LIU, Y. -K. CHOE, M. KIMURA, K. KOBAYASHI, S. NAGASE, T. WAKAHARA, Y. NIINO, M. ISHITUKA and T. AKASAKA, "The Effect of Substituents on the Thermal Decomposition of Diazirines: Experimental and Computational Studies," J. Org. Chem. 68, 7471–7478 (2003).

J. LU, S. NAGASE, L. PENG and S. ZHANG, "Strongly Size-Dependent Electronic Properties in C₆₀-Encapsulated Zigzag Nanotubes and Lower Size Limit of Carbon Nanopeapods," Phys. Rev. B 68, 121402 (4 pages) (2003).

T. WAKAHARA, Y. MATSUNAGA, A. KATAYAMA, Y. MAEDA, M. KAKO, T. AKASAKA, M. OKAMURA, T. KATO, Y. -K. CHOE, K. KOBAYASHI, S. NAGASE, H. HUANG and M. ATA, "A Comparison of the Photochemical Reactivity between N@C₆₀ and C₆₀: Photolysis with Disilirane," Chem. Commun. 2940-2941 (2003).

Z. SLANINA, K. KOBAYASHI and S. NAGASE, "Temperature Development in a Set of C₆₀H₃₆ Isomers," Chem. Phys. Lett. 382, 211-215 (2003).

Z. CHEN, A. HIRSCH, S. NAGASE, W. THIEL and P. v. R. SCHLEYER, "Spherical Sila- and Germa-Homoaromaticity," J. Am. Chem. Soc. 125, 15507-15511 (2003).

B. CAO, T. WAKAHARA, Y. MAEDA, A. HAN, T. AKASAKA, T. KATO, K. KOBAYASHI and S. NAGASE, "Lanthanum Endohedral Metallofulleropyrrolidines: Synthesis, Isolation, and EPR Characterization," Chem. Eur. J. 10, 716-720 (2004).

Z. CHEN, S. NAGASE, A. HIRSCH, R. C. HADDON, W. THIEL and P. v. R. SCHLEYER, "Side-Wall Opening of Single-Walled Carbon Nanotubes (SWCNTs) by Chemical Modification: A Critical Theoretical Study," Angew. Chem., Int. Ed. 43, 1552-1554 (2004).

Z. SLANINA, K. KOBAYASHI and S. NAGASE, "Ca@C₈₂ Isomers: Computed Temperature Dependence of Relative Concentrations," J. Chem. Phys. 120, 3397-3400 (2004).

Z. SLANINA, K. ISHIMURA, K. KOBAYASHI and S. NAGASE, "C72 Isomers: The IPR-Satisfying Cage is Disfavored by Both Energy and Entropy," *Chem. Phys. Lett.* **384**, 114–118 (2004). **S. RE and S. NAGASE**, "How is the CH/π Interaction Important for Molecular Recognition?" *Chem. Commun.*

658-659 (2004).

S. IWAMATU, T. UOZAKI, K. KOBAYASHI, S. RE, S. NAGASE and S. MURATA, "A Bowel-Shaped Fullerene Encapsulates a Water into the Cage," J. Am. Chem. Soc. 126, 2668-2669 (2004).

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