SPECIAL RESEARCH PROJECTS

IMS has special research projects supported by national funds. Three projects in progress are:
(1) Development of microscopic environments with functionality and quantum steering for reactions(1995-)
(2) Study of molecular solid toward molecular electronics(1995-)
(3) Material control in multi-reaction centers(1993-1997)

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.

(1) Development of Microscopic Environments with Functionality and Quantum Steering for Reactions

Structures, Reactions and Spectroscopies of Molecules and Clusters

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Ab initio molecular orbital methods were applied to various chemical and physical problems. The density functional theory were also used in some of the studies. Most of works were carried out under close collaboration with several experimental groups. In addition, new theoretical techniques in molecular electronic calculations were developed. The followings are the titles of the topics we have worked in the last year.

A. Development of New Theoretical and Numerical Techniques in the Study of Molecular Structures
B. Water Clusters and Their Complexes with Atomic Ions
C. Structures and Vibrational Frequencies of Infinite Polymer Chains
D. Structures and Reactions of Atomic and Molecular Clusters
E. Accurate Studies of Excited States of Small Molecules
F. Application of ab initio Molecular Orbital Methods to Experimentally Relevant Systems

Folding Simulations of Protein Molecules by Generalized-Ensemble Algorithms

Yuko OKAMOTO, Ayori MITSUTAKE *(Grad. Univ. Adv. Stud.)* **and Hiroshi OHTSUKA** *(Grad. Univ. Adv. Stud.)*

Proteins are the most complicated molecules that exist in nature. Since protein structures are closely related to their biological functions, the prediction of their three-dimensional stuructures from the first principles (by minimizing their energy functions) is not only very challenging but also very important a problem in theoretical molecular science. To be more specific, it is widely believed that three-dimensional structure of proteins is determined by their amino-acidsequences. However, nobody has succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles.) There are two reasons for the difficulty. One reason is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be considered is very large.

The other reason for the difficulty is that there exist huge number of local minima in the energy function, and conventional simulation techniques necessarily get trapped in one of the local minima without ever finding the energy global minimum. Generalized-ensemble algorithms are new simulation algorithms that can alleviate this difficulty.

We proposed to apply one of such methods, multicanonical algorithm, to the protein folding problem.[1)] We have also developed a new generalized-ensemble algorithm that is effective for protein folding problem.[2)] The goal of the present project is to further test the effectiveness of generalized-ensemble algorithms in the protein folding problem and to succeed eventually in the prediction of tertiary structures of proteins from the first principles.

References

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Quantum Mechanical and Semiclassical Studies of Chemical Dynamics

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Quantum reaction dynamics of heavy-light-heavy systems, i.e. hydrogen atom transfer reactions between heavy atoms, have been clarified not only numerically but also mechanistically. The numerical calculations can now be carried out efficiently with use of the hyperspherical elliptic coordinates. The reaction mechanisms have been clarified by introducing the concepts of vibrationally adiabatic potential ridge lines and vibrationally nonadiabatic transitions at avoided

crossings among adiabatic potential curves. Rather small number of state-to-state reactions dictated by avoided crossings provide dominant contributions to the overall reactions. The calculations and analyses have been applied to $O(^3P)$ + HCl, an example of thermo-neutral HLH reactions, Cl + HCl, an example of symmetric HLH reactions and Cl + HBr, an example of exo- (or eudo-) thermic HLH reactions.

Studies of semiclassical theory of nonadiabatic transitions have been extended into various dimensions. First of all, the adiabatic phase integral in the two-state Landau-Zener type curve crossing has been further improved, and now our complete solutions of the Landau-Zener-Stueckelberg type curve crossing problems can cover virtually the whole range of diabatic coupling strength. In attempt to formulate a unified theory of nonadibatic transition, we are working on the exponential potential model. We have successfully derived a new semiclassical formula more general than that of Nikitin.

Another important development is a proposal of new way of controlling molecular nonadiabatic processes by a time-dependent external field. The basic idea is to control nonadiabatic transitions at avoided curve crossings by periodically sweeping the external field. Our theory of nonadiabatic transition enables us to formulate the problem analytically to find control parameters. In the case of laser field as an external field, we can use both frequency and intensity as control parameters, and utilize not only Landau-Zener-Stueckelberg type curve crossings but also Rosen-Zener-Demkov type non-crossing transitions, depending on the system we treat. As a demonstration, we have employed a ring puckering isomerization of tri-methyleneamine.

Quantum Fokker-Planck Equation Approach to Electron Transfer Problem in Two-Dimensional Displaced Potential Surfaces

Yoshitaka TANIMURA, Minhaeng CHO *(IMS and Korea Univ.)* **and Yutaka MARUYAMA** *(Grad. Univ. Adv. Stud.)*

The quantum Fokker-Planck equation is applied to study a multi-state system with two-dimensional harmonic potentials. A rigorous procedure for calculating the dynamics of nonadiabatic transitions in condensed phases and their monitoring by femtosecond pump-probe spectroscopy is developed using this equation. Model calculations for a harmonic system with various nonadiabatic coupling strengths and damping rates are presented. Nuclear wavepackets in phase space related to electronic coherence are shown to provide an insight into the mechanism of nonadiabatic transitions.

Constructing Molecular Theory of Chemical Processes in Solution

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Our current research interests and activities are concentrated upon four important chemical processes in solutions, in each of which solvent plays essential role.

A. the electronic structure of a molecule in solution,
B. solvation thermodynamics of protein and related biomolecules,
C. characterization of spatial and temporal density fluctuation in molecular liquids,
D. solid-liquid interface.

The RISM theory, an integral equation theory of molecular liquids, is our main machinery of attacking the problem, which is combined with other theoretical methodologies including the ab initio electronic structure theory, molecular simulations, and theories of non-equilibrium statistical mechanics. Problems on which we have been working along the four lines are as follows:

1. Dependence of autoionization of water or pKw in wide range of temperature and pressure including the super-critical condition.
2. Self-consistent determination of the electronic structure and liquid state properties of water.
3. Solvatochlomism of a triiodide ion in solutions.
4. Solvent effect on keto-enol tuatomerization.
5. Type II S_N2 reactions (Menshutkin reaction).
6. Salt effect on solubility of nonpolar solute in aqueous solution.
7. Solvation dynamics and thermodynamics of ions.
8. Stability of peptide and protein conformations in aqueous solution.
9. Non-equilibrium free energy surface related to electron transfer reaction.
10. Dynamical coupling between intra- and inter-molecular motions in liquids.
11. Description of collective excitations in liquids by interaction-site model.
12. Ion mobility in polar liquids.
13. Microscopic characterization of metal-liquid interface.
14. Electron transfer reactions at metal-liquid interface.

High-Resolution Terahertz Spectroscopy by a Compact Radiation Source Based on Photomixing with Diode Lasers in a Photo-conductive Antenna

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[*J. Mol. Spectrosc.* **187**, 97 (1998)]

Spectroscopy in the submillimeter-wave to far infrared region has been less exploited when compared with that in other regions, because high spectral purity and tunable radiation sources have not been available. In the former Annual Review[1)] we reported a development of a frequency-tunable far-infrared sideband

spectrometer suitable for the study of transient molecules. The performence of our spectrometer was exemplified by a study on the transient free radical NH_2.[2)]

We have investigated another possibility of high-resolution and high-sensitivity far infrared spectroscopy using a newly developed continuous-wave terahertz radiation source. The radiation source is a photomixing system with diode lasers in a low-temperature-grown GaAs photoconductive antenna (Figure 1) and has been developed originally at the Communication Research Laboratory.[3)] The source offers output power of several tens of nanowatts at the frequencies up to 2 THz with its long term frequency stability being anout 5 MHz. The pure rotational spectra of CH_3CN and isotopomers of CO (Figure 2) were measured with this source, and 1% absorption was clearly detected with a simple amplitude modulation technique. This indicates that the present system has a potential capability for high-resolution and high-sensitivity molecular spectroscopy.

References

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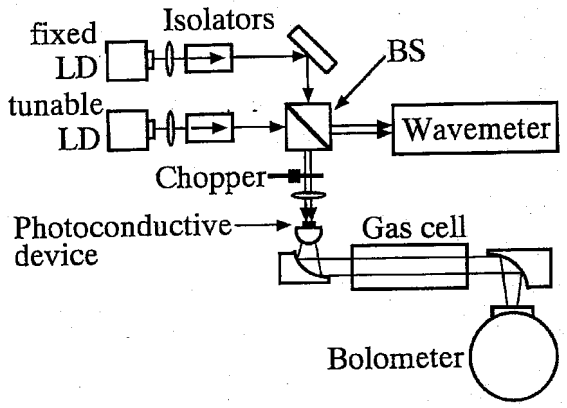

Figure 1. Schematic diagram of the photomixer spectrometer.

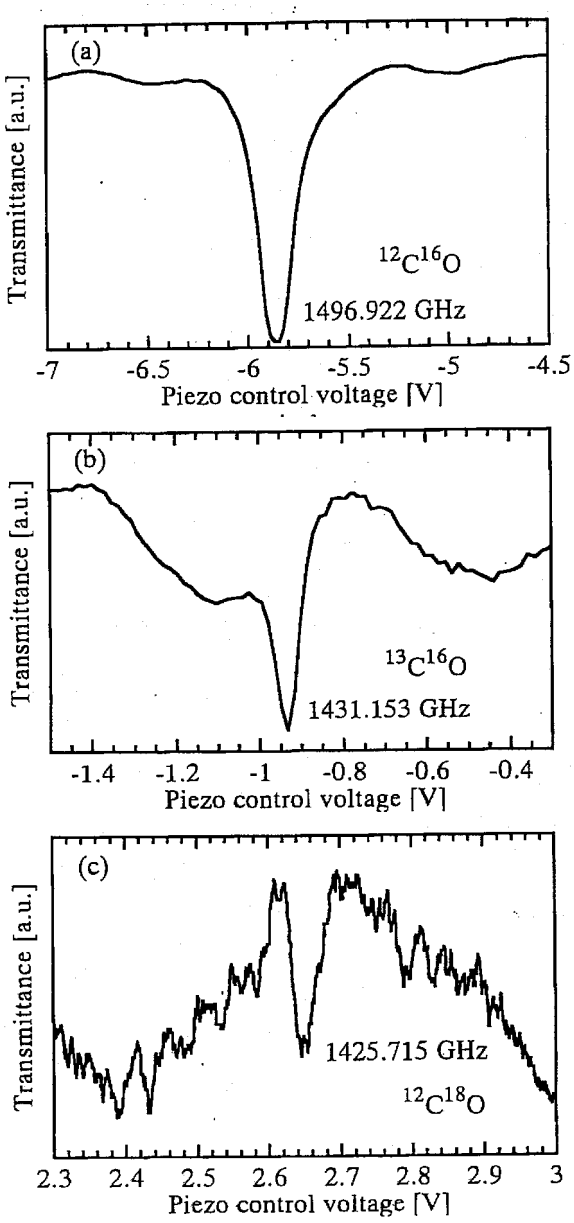

Figure 2. Pure rotational spectra of carbon monoxide and its isotopomers with natural abundance.

(1) Studies on Laser Cooling and Trapping of Neutral Atoms
(2) Laser Spectroscopic Studies of Atoms and Ions in Liquid Helium

Norio MORITA, Yoshiki MORIWAKI and Mitsutaka KUMAKURA

For studies on laser cooling and trapping of neutral atoms, we have continued the work on a magneto-optical trap of helium atoms. Especially, cold collision processes in the laser trap have been studied, and Penning ionization rate coefficients for both $^3He^*$-$^3He^*$ and $^4He^*$-$^4He^*$ cold collisions in the trap have been obtained. In addition, a remarkable isotopic difference in the Penning ionization rate coefficients obtained has successfully been explained through our theoretical calculation (see II-C-1). On the other hand, in laser spectroscopic studies of atoms and ions in liquid

helium, we have observed laser-induced spectra of Yb^+ ions in liquid helium (see II-D-1). In addition, we have also observed laser-induced spectra of neutral Yb atoms in liquid helium (see II-D-2). Furthermore, spectral properties of Mg atoms observed in our previous experiment have successfully been explained through our theoretical calculation based on a possible model of the Mg-He_{10} exciplex formation (see II-D-3).

Structure and Function of Transmembrane Electron Transfer System in Neuroendocrine Secretory Vesicles

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In neuroendocrine secretory vesicles, intravesicular ascorbate (AsA^-) functions as the electron donor for copper-containing monooxygenases. Upon these monooxygenase reactions, monodehydroascorbate (MDA) radical is produced by oxidation of AsA^-. The MDA radical is reduced back to AsA^- by membrane-spanning cytochrome b_{561} and subsequently the oxidized cytochrome b_{561} is reduced by cytosolic AsA^-. We found previously that purified cytochrome b_{561} contains two hemes B per molecule, each exhibiting an independent EPR signal in oxidized state.[1] The reaction of MDA radical with purified cytochrome b_{561} was investigated by the technique of pulse radiolysis.[2] Radiolytically generated MDA radical oxidized rapidly reduced cytochrome b_{561} to yield the oxidized form. Subsequently, the oxidized form was re-reduced by AsA^- in the medium. At excess MDA radical, only half of the heme was oxidized, indicating that only one of the two heme centers can react with MDA radical. We found that incubation of oxidized cytochrome b_{561} with diethylpyrocarbonate (DEP) caused a modification of only one histidyl imidazole group to form an N-carbethoxyhistidyl derivative. Radiolytically generated MDA radical was oxidized rapidly by the reduced form of DEP-modified cytochrome b_{561} with a similar second-order rate constant to that of the untreated sample. However, subsequent re-reduction of the oxidized heme with AsA^- was severely inhibited, indicating that one essential histidine residue close to the heme *b* center for the electron acceptance from AsA^- was selectively modified. These results suggest that the two heme *b* centers have distinct roles for the electron donation to MDA radical and the electron acceptance from AsA^-, respectively.[2]

References

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Time-Resolved Resonance Raman Study on Mechanism of Oxygen Reduction by Cytochrome *c* Oxidase

Teizo KITAGAWA

Reaction intermediates in the enzymatic reduction of O_2 by bovine cytochrome *c* oxidase (CcO) were investigated with time-resolved resonance Raman spectroscopy. Six oxygen-associated vibrations were identified in the $O_2 \rightarrow H_2O$ process. The isotopic shift of the Fe-O_2 stretching frequency for an asymmetrically labeled dioxygen, $^{16}O^{18}O$, has established that the primary intermediate of cytochrome a_3 is an end-on type O_2 adduct of Fe_{a_3} with the Fe-O-O angle of ~120°. The subsequent intermediates appearing around 0.1-3 ms following the start of the reaction yielded Raman bands at 804/764, 785/751, and 356/342 cm^{-1} for $^{18}O_2/^{16}O_2$ derivatives, respectively, in H_2O at pH 7.4. While these frequencies were the same between the H_2O and D_2O solutions, the final intermediate appearing around 3 ms gave the Raman bands at 450/425 cm^{-1} in H_2O and 443/417 cm^{-1} in D_2O. The last bands are reasonably assigned to the Fe_{a_3}-OH(D) stretching mode. The extended measurements at lower temperatures and longer delay times have demonstrated that the 804/764 cm^{-1} pair appears prior to the 785/751 cm^{-1} pair and that the conversion from the former to the latter species is significantly delayed in D_2O than in H_2O, suggesting that this step of electron transfer is tightly coupled with proton pumping. The experiments using $^{16}O^{18}O$ have established that all the 804/764, 785/751, and 356/342 cm^{-1} bands arise from the Fe=O heme, but definitely not from the Fe_{a_3}-O-O-Cu_B the presence of which has been long postulated. The same three sets of oxygen-isotope sensitive bands have also been observed for the reaction intermediates of oxidized CcO with H_2O_2, indicating the identity of intermediates.

Laser Raman Beat Detection of Magnetic Resonance

Tatsuhisa KATO and Michio MATSUSHITA

Laser Raman beat detection is a coherent optical-RF double resonance technique where the optical and RF field induce coherence within a three level system and a resultant Raman beat signal is detected using heterodyne detection. This technique can be applied to the study of electron paramagnetic resonance and nuclear magnetic resonance not only in the ground state of a molecule but also in the electronic excited state.

There are some causes to hide the Raman beat signal, that is, the inhomogeneity of the circumstance of the molecule, the fluctuation of the applied field, and the interference by the crystal phonon. It is the key to success in the Raman beat detection to eliminate these cause of the incoherence. Then it is needed to prepare the sophisticated single crystal sample, the highly stabilized magnetic field, and a cryostat of liquid helium. It has been completed to set up the apparatus, and the Raman beat detection was applied to the study on the quadrupole transitions of ^{139}La nuclei around Pr^{3+} doped in LaF_3, as reported in Section II-I-1, and on the delocalized excitation in molecular crystals of 1,4-dibromonaphthalene, in Section II-I-2.

Studies of Laser-Induced Photochemistry on Solid Surfaces, Thin Films, and Clusters

Yoshiyasu MATSUMOTO, Kazuya WATANABE,

Kazuo WATANABE, Michiharu OHTA *(Grad. Univ. Adv. Stud.)***, Ikuo KINOSHITA** *(Yokohama City Univ.)* **and Toshihisa ANAZAWA**

Light sources such as lasers and synchrotron radiation can be useful for the various processes in the fabrication of microelectronics, including etching, chemical vapor deposition, atomic layer epitaxy. On the other hand, it has also been well recognized that there is an important class of catalytic reactions with the aid of photon irradiation. Although those applications of light are practically useful and important, fundamental understanding of these processes is still lacking. Therefore, this project is mainly aimed for investigating how the interaction of light and adsorbates and /or substrates promotes chemical reactions from the fundamental point of view.

We have continuously performed the studies on surface photochemistry particularly of rare gas atoms adsorbed on semiconductor surfaces and methane on Pd clusters deposited thin Al_2O_3 films on a NiAl(110) substrate in this year. A UHV apparatus used is equipped with a retractable LEED/Auger electron spectrometer, a differentially pumped quadrupole mass spectrometer, an X-ray source, a photoelectron analyzer, an ion gun, a high precision sample manipulator, a closed cycle He refrigerator, and a gas doser. The main chamber was evacuated to a base pressure of 1×10^{-10} Torr by cascaded turbo-molecular pumps. With this apparatus, we can perform not only conventional analytical measurements in surface science including LEED, AES, temperature-programmed desorption, XPS, and work function measurements, but also measurements providing information on nuclei dynamics including angular-resolved time-of-flight spectroscopy of neutral species desorbed from the surface with sub-monolayer coverage.

In additon, we have developed an apparatus for multiphoton photoelectron spectroscopy that enables us to obtain electronically excited states of surface states of clean surfaces and those of adsorbates. The information of energetic positions and widths of the excited states is vital to understanding of excitation mechanisms in surface photochemistry. The apparatus is composed of light sources and a magnetically shielded UHV chamber. We have used two kinds of light sources: a tunable dye laser pumped by a Nd:YAG laser at a repetition rate of 10 Hz and a mode-locked Ti:Sapphire-seeded regenerative amplifier system (Spectra Physics, Spittfire) at a repetition rate of 1 and 50 kHz. We have also designed a VUV generation apparatus for 2-color pump-and-probe measurements.

Hydrogen Bond Network Fragmentation and Its Detection by Low Frequency Raman Spectroscopy

Nobuyuki NISHI, Takakazu NAKABAYASHI and Yoshiya INOKUCHI

Hydrogen bonding can generate two-dimensional or three-dimensional networks of molecules. Water and acetic acid are well known to form three- and two-dimensional networks, respectively. The COOH group takes quite important roles in biologically active systems. Glutamic acid, for example, is contained abundantly as a signal transfer material in neuron networks of our brains. We know so little about the role of the carboxyl group particularly in aqueous environment, where the anti-form isomer of acetic acid is nearly as stable as the syn-form ($\Delta E_{calc.}$ =1.7 kcal/mol by Sato & Hirata). Even the cluster structure in liquid acetic acid that is frequently cited in many textbooks is found to be inappropriate for explaining the low frequency Raman spectrum. The spectral change following the gradual crystal melting of acetic acid demonstrated the dramatic growth of the Rayleigh wing intensities in the region lower than 50 cm^{-1}. *Ab initio* calculation (at the HF6-31G(d,p) level) of acetic acid clusters with the same hydrogen bonding network structure as that of the crystal showed that the out-of-plane motions of the end molecules of the fragment clusters contribute to the very low frequency wing intensities of the Raman spectra. This scattering itself originates from the fluctuation lengths of the liquid and highly related to the average sizes of the fragment clusters. In order to obtain more detailed information, we are now going to construct a new hole burning laser system by combining a femtosecond high power (1-10 mJ) excitation source with a pico-second medium power high resolution hole-maker laser system. The former laser enables us to excite non-bonded acetic acid electronically and the wavelengths of the latter laser extend to longer than 10 μm. Time-resolved resonance Raman spectroscopy and transient absorption spectroscopy in a very wide region of 900-50,000 cm^{-1} will be challenged for the study of dynamics and structures of the hydrogen bonding networks.

Higher Vibrational States of Molecules and Clusters as Studied by Nonresonant Ionization Detected IR Spectroscopy

Masaaki FUJII

This special research project, started in April 1997 is planning to study spectroscopy and dynamics of molecules and clusters in higher vibrational state by the nonresonant ionization detected IR spectroscopy. The nonresonant ionization detected IR spectroscopy (shortly NID-IR) is a newly developed IR-UV double resonance spectroscopy which detects IR absorption by the selective ionization of a vibrationally excited molecule. Briefly, a jet-cooled molecule is excited to a vibrational level in the ground state by the IR laser. The vibrationally excited molecule is selectively ionized by the nonresonant two-photon process due to the UV laser. The simplest way of the selective ionization can be achieved by fixing the frequency of the UV laser to energy slightly less than a half of the ionization potential. Under this frequency condition, only the vibrationally excited molecule can be ionized by the two-photon process due to the UV laser. Therefore, the ion current is detected only when the IR laser is resonant to the vibrational level. This spectroscopy has an advantage in the sensitivity because of the weak background signal and the ionization

detection.

The experimental setup for the measurement of the nonresonant ionization detected IR spectroscopy is the same as that described in Annual Review 1997 and in the previous publications (*Chem. Phys. Lett.* **252**, 287 (1996), *Chem. Phys. Lett.* **283**, 243 (1998)), except for a near IR light source. An idler light of an OPO laser pumped by the third harmonics of YAG laser has been introduced to cover the region from 1.8 mm to visible. This light source has an advantage to cover wide energy region without replacing any optics and any crystals. In addition, its laser power is 10 times stronger than the previous light source due to the differential mixing. These advantage reduces experimental difficulty to measure the overtone transition.

The nonresonant ionization detected IR spectroscopy has been applied to jet-cooled phenol and various deuterated phenols. Vibrational transitions of jet-cooled phenol have been detected by nonresonant two-photon ionization due to UV laser from 3400 cm^{-1} to 14000 cm^{-1}. The UV frequency dependence of IR-UV double resonance signals is used for discussion on the mechanism of ionization. The spectrum shows a well-resolved structure due to the first to the fourth quantum of OH stretching vibrations, CH overtones and various combination vibrations. The vibrational frequency, anharmonisity and the dissociation energy of the OH stretching mode has been measured. The bandwidth of the OH overtone is found to decrease with increase in the vibrational quantum number. On the other hand, phenol-OD shows the opposite change that the band width increase in going to the higher overtone. Its mechanism has been discussed from the deuterated effect.

Laser Investigation of Elementary Reactions in the Gas Phase

Toshinori SUZUKI, Hiroshi KOHGUCHI, Hideki KATAYANAGI, Yuxiang MO and Li WANG

Detailed knowledge of elementary reactions in the gas phase is indispensable to understand combustion, plasma, and atmospheric chemistry. Knowledge on reaction dynamics is also important in seeking the possibility to steer the reactions by state-selective excitation. Scattering experiment is the most powerful means to study microscopic interaction potential. Since typical chemical reaction is low-energy event (< 10 eV), internal excitations of atoms and molecules cannot be neglected in the dynamics, so that the internal degrees of freedom of particles must be resolved in scattering experiment. Such requirement in chemical dynamics experiment can only be fulfilled by the use of laser spectroscopic means that provide ultimate state resolution. We have constructed a new crossed molecular beam machine equipped with the ion imaging apparatus to measure state-resolved differential cross sections for inelastic and reactive scattering.

Theoretical Study on the Electronic Structures of Atoms, Molecules, and Clusters

Eisaku MIYOSHI, Tapas Kumar GHOSH and Tomonari SUMI *(Kyushu Univ.)*

Using *ab initio* molecular orbital theory we have applied the model potential method to investigate the electronic structures of atoms, molecules, and clusters. In particular, our research interests are concentrated upon the electronic structures of complexes with coordinate bond between metals, which was recently found in experiments and is interesting because of its potential of application to new materials.

In addition, the electronic structures of weakly bound molecules such as van der Waals molecules were investigated by using sophisticated methods for electron correlation. The methods contain the model potential method, localized natural orbital technique, and multi-reference coupled pair approximation. It has been shown that such methods are necessary to compute accurate potential energy surfaces of weakly bound molecules.

Using potential energy surfaces obtained by *ab initio* molecular orbital calculations, molecular dynamics calculations were also performed to investigate physical and chemical properties of liquid mercury and other systems.

Preparation of Pt-Pd Bimetallic Clusters by Solvent Extraction

Tatsuya TSUKUDA *(Univ. Tokyo)***, Naoya KIMURA** *(Univ. Tokyo)* **and Takashi NAGATA**

[*European J . Phys.* submitted]

In view of the fundamental and technological importance of the noble-metal nanoparticles, several methods have been proposed recently for the chemical preparation of colloidal metal dispersions with a narrow particle-size distribution. In the present study, we have exploited two-phase system involving ligand exchange reactions of polymer-protected metal clusters for the preparation of thiol-stabilized Pt-Pd bimetallic clusters: Pt-Pd clusters protected by poly(*N*-vinyl-2-pyrrolidone) (PVP) in an aqueous solution[1)] are feasibly extracted via ligand-exchange reactions into toluene containing dodecanethiol (DT). The extraction efficiency, the size and shape distributions of the particles extracted into the organic phase were investigated as a function of DT concentration by the combination of UV-vis absorption spectroscopy and transmission electron microscopy (TEM). These measurements have revealed that the DT-stabilized clusters coalesce into different sizes and shapes, depending on the DT concentration in the organic phase (Figure 1). This indicates that the bimetallic clusters undergo reconstruction during the extraction, which opens up a new possibility for the size and shape control of metal clusters by ligand exchange reactions.

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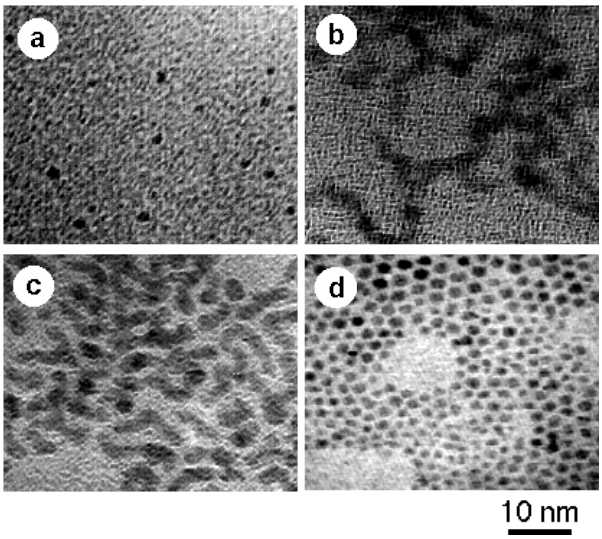

Figure 1. TEM images of Pt-Pd bimetallic clusters. (a) PVP-protected clusters dispersed sparsely in an aqueous solution (starting materials), (b) clusters arranged in a large network, which are obtained as floccules at low DT concentrations, (c) DT-stabilized clusters with worm-like shapes extracted at medium DT concentrations, and (d) DT-stabilized clusters extracted at high DT concentrations, which are nearly monodispersed and self-assembled.

Development of Pulsed-Jet Millimeter-Wave Spectrometer for the Detection of the Novel Unstable Species and the van der Waals Mode Transitions of Molecular Clusters

Kensuke HARADA, Asao MIZOGUCHI and Stéphane BAILLEUX and Keiichi TANAKA *(IMS and Kyushu Univ.)*

Molecular clusters have extremely low-frequency vibrations, so called van der Waals Vibrations, which sometimes falls in the submillimeter wave region below 30 cm^{-1}. For the detection of van der Waals vibrations of molecular clusters, we have developed pulsed-jet millimeter-wave spectrometer.[1)]

In the present work, we have newly revised our spectrometer. The main points of revisions are as follows.

1. Frequency region of the millimeter wave light source have been extended up to 330 GHz by using Gunn oscillator and frequency multipliers. The frequency region from 400 GHz to 800 GHz will be covered by a backward wave oscillator.
2. Accuracy and convenience of the measurement were revised by using cm wave synthesizer and a new frequency phase lock system.
3. The jet cell was evacuated by 600 m^3/hr roots pump which is sufficient for pulsed jet experiment even in the multi-nozzle configuration. The 10 inch diffusion pump will be attached in the experiment which need quite low rotational temperature.
4. Multi light pass experiment up to 4 light pass is possible using corner reflector and grid polarizer.

We have observed the van der Waals bending vibration of the Ar-DCN in the frequency region 180-300 GHz. The weak spectra near the band origins of the $\sum_1$-$\sum_0$ and $\prod_1$-$\prod_0$ subbands of the j = 1-0 van der Waals bending band have been observed and assigned. In the experiment, we found that the sample gas mixed with Ne buffer gas gives more efficient production of the cluster and narrower line width than that mixed with Ar buffer gas.

Reference

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Experimental Study of Ion-Induced Nucleation

Kenkichi NAGATO

Ultrafine particle formation by ion-induced nucleation has recently gained attention both in atmospheric science and in material processing. However, experimental results of ion-induced nucleation to date show significant deviations from theoretical predictions. One of the reasons is that nucleation theories have not taken account of chemical nature of ions. In order to improve theories, experimental investigations about the influence of ion species on the nucleation process are necessary. For this purpose, we have developed a high-resolution ion mobility/mass spectrometer which is capable of simultaneous measurements of mobility and mass spectra of cluster ions generated by ion-molecule reactions under atmospheric pressure. We will investigate clustering reactions of ions as an early stage of ion nucleation using this spectrometer. In particular, reactions of positive ions will be studied in detail because positive ions are known to grow to very large size under usual environmental and industrial conditions. Experiments will be extended to the study on the nucleation by ion-ion recombination.

Time-Resolved Spectroscopic Studies on Chemical Reactions using Ultrafast Laser and Synchrotron Radiation

Tahei TAHARA, Satoshi TAKEUCHI, Atsuhiko SHIMOJIMA, Nilmoni SARKAR and Misa KAYAMA

Time-resolved spectroscopy is one of the most powerful tools for the studies of chemical reactions. It enables us to directly observe the temporal changes occurring in the course of chemical reactions. Recent progress of time-resolved spectroscopy relies on the drastic advance of the laser technology, and we are now able to examine the dynamics of the primary processes of chemical reactions with pico/femtosecond time-resolution. Time-resolved spectroscopy based on ultrafast lasers is, and will continue, playing a crucial role in physicochemical studies on chemical reactions. Synchrotron radiation, on the other hand, has unique potentiality to be alternative light source in time-resolved spectroscopy. The potential of synchrotron radiation in time-resolved spectroscopy lies on the fact that it affords picosecond pulses in a very wide energy range from X-ray to far-infrared. Thus, synchrotron radiation may open up new possibility of time-resolved

spectroscopy in the energy region which is not accessible with the existing lasers. The aims of this project are (1) the development of new time-resolved spectroscopic methods and (2) their application to the studies on chemical reactions, taking advantage of these two light sources which are complementary to each other. We already constructed four experimental setups so far; a femtosecond time-resolved fluorescence up-conversion spectrometer, a femtosecond optical heterodyne detected impulsive stimulated Raman scattering (OHD-ISRS) spectrometer, a femtosecond UV-VIS-NIR transient absorption spectrometer and a picosecond time-resolved spontaneous Raman spectrometer. In this year, while continuing research about fundamental chemical reactions such as proton transfer and photoisomerization with use of these setups, we have also constructed a setup for generating femtosecond mid-infrared pulses down to 10 μm. In addition, in order to examine potentiality of synchrotron radiation for time-resolved measurements, we made attempts to measure time-resolved far-infrared spectra of several solid samples by using a setup at beamline BL6B in our synchrotron radiation facility (UVSOR).

Development of Scanning Tunneling Microscopy System for the Study of the Synchrotron-Radiation Stimulated Desorption of SiO_2 Films on Si(111) Surface

Takayuki MIYAMAE, Hironaga UCHIDA *(Toyohashi Univ. Tech.)*, **Tokukazu YAGI** *(Toyohashi Univ. Tech.)*, **Shinya HIRANO, Ian H. MUNRO** *(UMIST and IMS)* **and Tsuneo URISU**

A scanning tunneling microscopy (STM) system for the study of synchrotron radiation (SR) stimulated or excited reactions was constructed at the beamline 4B of UVSOR faculty. The design of our STM system is schematically shown in Figure 1. The STM (Rasterscope-3000 of DME Co.) is located in the left-hand side of the main chamber. A back-view LEED, oxygen and atomic hydrogen doser, and a heating device are located on the right-hand side of the chamber. The pumping of the system is carried out by 400 l/s ion pump, 400 l/s titanium sublimation pump, and a non-evaporable getter pump (SAES GETTERS Co., Ltd.) for the main chamber and a turbomolecular pump for the sample preparation chamber which is stopped during the STM experiments. The entire UHV chamber is mounted on a high-performance air-suspended vibration isolation table (resonance frequencies of 1.3 Hz for the horizontal direction and 1.6 Hz for the vertical direction, manufactured by Kurashiki Kako Co.). The vibration noise level and the acoustic noise level of the location where the STM system is placed currently is very high; approximately 12 gal in the x-y direction and 20 gal in the z direction, two or three orders of magnitude noisier than those under the normal environments. The STM chamber was covered by the sound proof mat because of the elimination of the acoustic noise during the STM measurements. Now the mechanisms for SR stimulated desorption from SiO_2 thin films on Si(111) surface have been investigated using the STM. The Si(111)-7×7 surface was clearly observed after two hours SR irradiationat a surface temperature of 700 °C. Analysis of the evolution in the STM topograph suggests that the desorption mechanism may be completely different between thermal and SR stimulated desorption of SiO_2 film.

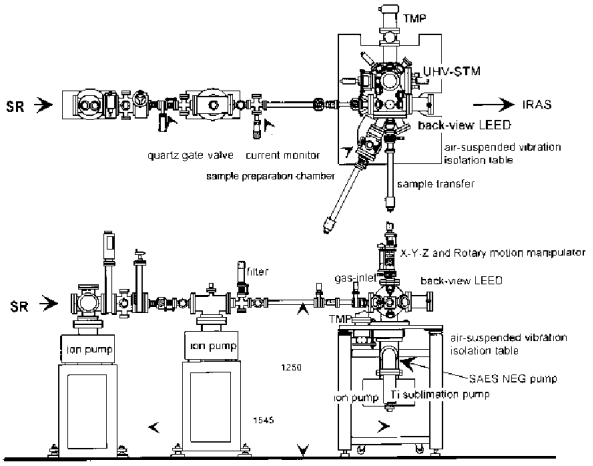


Figure 1. Schematic of the STM system to study the SR-stimulated reaction on the BL4B beamline of UVSOR facility.

Pump-Probe Spectroscopy of Atoms and Molecules with a Combination of Synchrotron Radiation and a Mode-Locked or Pulsed Laser

Koichiro MITSUKE, Masakazu MIZUTANI, Hiromichi NIIKURA *(Grad. Univ. Adv. Stud.)* **and Kota IWASAKI**

There is a growing interest in combining synchrotron radiation with the laser, since high-resolution or ultra-fast lasers are expected to open a new field for studies on dynamical behaviors of excited states in the VUV or soft X-ray region. Nevertheless, only a few attempts have been made at pump-probe experiments of atoms and molecules using the combination technique. Our group have developed the following three systems at cooperative and in-house beamlines in UVSOR. (1) An ultraviolet mode-locked Ti:sapphire laser synchronizing precisely with the undulator radiation from the UVSOR storage ring in a multibunch operation mode. With this system two marked results have been obtained: (a) two-photon ionization of helium atoms studied as the prototype of the time-resolved experiment, and (b) fluorescence excitation spectroscopy of $N_2^+(X^2\sum_g^+)$ ions produced by synchrotron radiation photoionization of N_2 or N_2O. (2) A pulsed dye laser pumped by an excimer laser. The second harmonic of the dye laser is tunable in the range of 265-280 nm with a pulse energy of ca. 2 mJ $pulse^{-1}$ at a repetition rate of 10 - 100 Hz. By employing resonance enhanced multiphoton ionization (REMPI) spectroscopy we can observe neutral species produced by neutral photofragmentation, via superexcited states, induced by synchrotron radiation excitation of OCS. (3) A high-power pulsed Nd:YAG laser incorporated in the experimental station of two-dimensional photoelectron spectroscopy. We perform photoelectron spectroscopy of polarized atoms using linearly-

polarized laser light, aiming at a complete quantum-mechanical photoionization experiment. Initial excitation with a linearly polarized synchrotron radiation permits ensemble of atoms to be aligned along the electric vector of the light. From an angular distribution of photoelectrons from polarized atoms, we are able to gain insight into the magnitude and phase shift difference of dipole transition moments of each final channel which is allowed by selection rules.

Vibrational Spectroscopy on Cryogenic Surfaces using Synchrotron Radiation

Makoto SAKURAI and Masuaki MATSUMOTO

Vibrational Spectroscopy makes it possible to analyze dynamical aspects of molecules adsorbed on surfaces. Molecular layers on cryogenic surfaces show specific structures which depend on the interaction between molecules and substrate, and the vibrational spectra reveal the details of the interaction. Infrared reflection absorption spectroscopy (IRAS) and high-resolution electron energy loss spectroscopy (HREELS) are useful tools for vibrational spectroscopy on surfaces, and they have complemental characteristics, that is, IRAS is superior in resolution and stability whereas HREELS has higher sensitivity. Utilization of IRAS with HREELS in an identical vacuum system brings advantageous apparatus for researches of dynamical aspects of adsorbed molecules.

Under this project, we develop an apparatus for vibrational spectroscopy of molecules on cryogenic surfaces. The apparatus comprises both measurement systems (IRAS and HREELS), a cryogenic sample holder and tools for preparation and characterization of surface cleanliness. The IRAS system has optical system for inlet and outlet of synchrotron radiation in far-infrared (FIR) and infrared (IR) regions, since synchrotron radiation is brighter light source than conventional ones in this regions taking into account that the light source necessary for IRAS should have low emittance.

Formation of Ordered Array of Quantum Dots Using Synchrotron Radiation-Stimulated Etching and Selective Growth

Youichi NONOGAKI, Tsuneo URISU and Yoshikazu TAKEDA *(Nagoya Univ.)*

Semiconductor structures with reduced dimensionality are subject of significant interest in modern solid state physics and device application. Recently the formation of quantum-sized InAs and InGaAs dots self-organized on GaAs surfaces using molecular beam epitaxy (MBE) was demonstrated. We have been studying formation of InAs dots on InP substrate by novel droplet heteroepitaxy, because the quantum dots can emit light at technologically important wavelength of 1.5 μm. Although emission from the single dot has very sharp line, the total emission from the sample has a broad full width at half maximum of about 100-150 meV, probably due to fluctuation in dot size. Suppression of the fluctuation is necessary to fabricate the new optical devices which have higher performance than quantum laser diodes.

We suggested a new method to form ordered array of the quantum dots, which includes synchrotron radiation (SR) -excited etching process and selective growth technique. The SR excited etching process has a potential to fabricate nano-meter scale holes with vertical side wall. Furthermore, damage induced by the etching will be much lower than conventional reactive ion etching, because SR-excited etching involves no sputter process.

SR-stimulated etching of SiO_2 on Si substrate were investigated by exposing to SR irradiation in SF_6 ambient. Figure 1 shows etched depth as a function of SF_6 pressure, keeping the irradiation dose constant of 10,000 mA·min. The etching rate increases in the region of 10^{-3}-10^{-2} Torr and saturates at around 10^{-1} Torr. It indicates that rate limiting processes are different between low and high SF_6 pressure regions. In the low SF_6 pressure region, mass-transport process of SF_6 would limit the rate, on the other hand, photon flux in the high SF_6 pressure region. The irradiation-dose dependence of the etched depth was shown in Figure 2. The depth increases with the irradiation dose linearly, which shows high controllability of SR-stimulated etching.

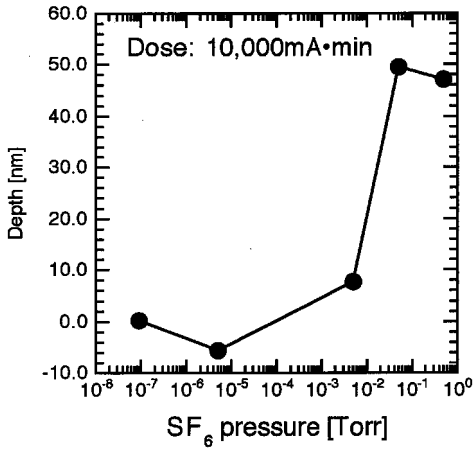


Figure 1. SF_6 pressure dependence of etched depth for SiO_2 on Si substrate.

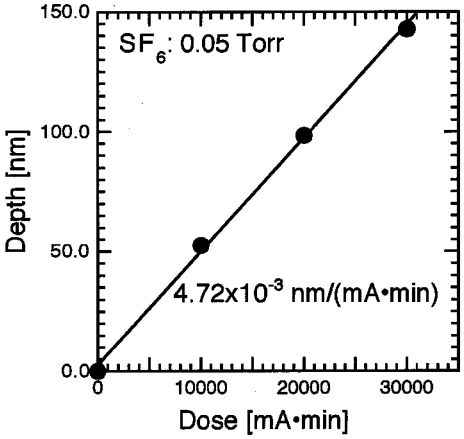


Figure 2. SR irradiation dose dependence of etched depth for SiO_2 on Si substrate.

Similarity Transformed Preconditioners for Green Function Evaluation in Cumulative Reaction Probability Calculations

Masakatsu ITO, Shinkoh NANBU, Mutsumi AOYAGI and Albert F. WAGNER *(Argonne Nat. Lab.)*

The micro-canonical rate constant of interest for unimolecular reaction is given in terms of the cumulative reaction probability $N(E)$, $k(E) = N(E)/\{h \rho_r(E)\}$, where $\rho_r(E)$ is the density of reactant states per unit energy. The calculation of $N(E)$ is based on a discrete variable representation(DVR) of Hamiltonian and the use of absorbing boundary conditions (ABC). Recently Seidemann, Manthe and Miller showed that $N(E)$ was given as the eigenvalue sum of the probability operator $P(E)$. $P(E)$ is expressed in terms of the ABC Green function $G^{(\varepsilon)}(E)$,

$$P(E) = 4\, \varepsilon_r^{1/2}\, G^{(\varepsilon)}(E) \varepsilon_p\, G^{(\varepsilon)}(E) \varepsilon_r^{1/2}.$$

The use of ABC provides the well-behaved representation of the Green function without having to include information regarding the asymptotic region. Since it is difficult to reproduce a global structures of the potential energy surface for a many-atom molecule with an analytic function, this feature is efficient for realistic applications.

We employ iterative methods for diagonalizing $P(E)$ and for evaluating $G^{(\varepsilon)}(E)$. Since the ill-conditioned linear problem of this kind cannot be solved with ordinary iterations, we proposed Kyrlov subspace methods with numerical preconditioning in order to reach a convergence. The resulting iterative expansion with the preconditioner corresponds to the distorted-wave Born expansion of the Green's function.

$$G = G_0 + G_0 \Delta G_0 G_0 + G_0 \Delta G_0 \Delta G_0 + \cdots$$

The acceleration with the preconditioning is most effective when the preconditioner is closest to the Green's function. We found that the banded matrix extracted from $E\text{-}H\text{-}i\varepsilon$ effectively accelerate the convergence, and GMRES and Davidson method can get a convergence even when the bandwidth is only 3 % of the matrix size. The LU decomposition of this banded preconditioner, however, needs extremely large amount of memory when the molecule has many degrees of freedom. We overcome this difficulty by employing the similarity transformed preconditioner.

$$M = U \,\text{Band}\, (U^{+}\, (E\text{-}H\text{-}i\varepsilon)\, U)\, U^{+},$$

where U is prepared for block-diagonalizing the Hamiltonian to reduce the memory requirement. We showed that this kind of preconditioner is as effective as the 'fat' preconditioner.

Developments of Advanced Lasers for Chemical Reaction Controls

Shin-ichiro SATO

The chemical reaction controls with laser lights are undoubtedly one of the most important subjects of chemistry. The coherence of laser lights has not been considered seriously in the old fashion of the laser controls. Recent theoretical studies have shown that the optimized laser coherence may be important for the more sophisticated controls of chemical reactions. We are planning to develop an arbitrary photo-waveform shaper of ultra-short laser pulses. The pulse shaping is based on the spatial masking of spectral components of an ultra short laser pulse: The spectral components of the incident pulse are spatially dispersed with a grating, modulated with a spatial mask on the Fourier plane and recombined with an another grating. Roughly speaking, an output of pulse sequence will be generated with a time separation of t, if an incident pulse is modulated with a period of $\omega = 1/t$. The choice of mask material is a key point in relation to the location of mask in the whole laser system, since the fairly high peak energy of laser pulse is necessary to promote chemical reactions via highly excited vibrational states.

Developments and Researches of New Laser Materials

Nobuhiko SARUKURA, Hideyuki OHTAKE, Zhenlin LIU, Shinji IZUMIDA and Shingo ONO

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

Takunori TAIRA and Jiro SAIKAWA

The use of diode lasers to pump solid-state lasers leads to favorable performance characteristics. Diode-pumped solid-state lasers are compact, long-lived, and efficient sources of coherent radiation. They can provide excellent spatial mode quality and narrow linewidths. Because of the improved beam quality of diode-pumped solid-state lasers, nonlinear frequency conversion can readily be applied. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Recently attention has been directed the trivalent ytterbium ion doped YAG. The advantages of Yb:YAG lasers for a high power, high stability and wide tunability laser operation are well recognized due to its a smaller quantum defect, a longer upper state life time and a wider gain width.

In other hand, quasi phase matching (QPM) is new technique to birefringent phase matching for compensating phase velocity dispersion in frequency conversion applications. Inasmuch as the pool of mature nonlinear optical materials is limited and the development cycle for new materials is long and costly,

QPM is a useful method for extending the range of available nonlinear optical materials. The ability to pattern QPM structure allows the nonlinear material to be engineered for the desired interaction.

In this projects we research and develop new Diode-Pumped-Solid-Sate lasers and new frequency conversion devices. Especially, we will focus on the combination of Yb-doped lasers and QPM devices. These kind advanced tunable solid-state light sources will assist the research of molecular science.

UHV Tribometer

Tatsuharu TORII, Takuhiko KONDOH, Shuji ASAKA and Michio WATANABE

A surface treatment which is excellent in anti-galling is important for actuators with sliding surfaces to operate smoothly in ultra-high-vacuum (UHV). Last year we produced a UHV tribometer to evaluate existing surface treatments and to develop new and better surface treatments. We have newly improved the device to achieve the following points:

(1) Vacuum of tribometry atmosphere up to 6.3×10^{-11} Torr,
(2) Rotational speed of sample up to 1700 r.p.m., and
(3) Automatic stopping of friction test when coefficient of friction reaches a certain point.

The improved tribometer (Figure 1) enabled us to evaluate several kinds of existing surface treatments.

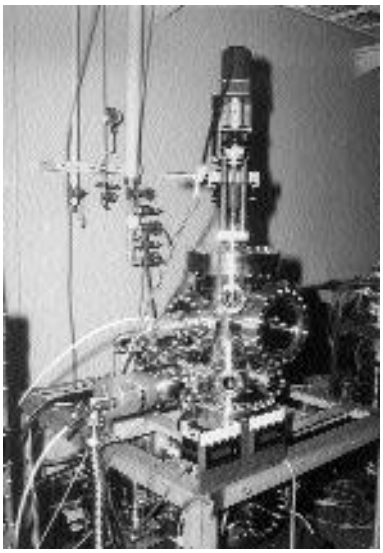


Figure 1. Outer view of the UHV tribometer.

Investigation of Electronic Structures of Solid/Surface by Using Synchrotron Radiation

Masao KAMADA and Shin-ichiro TANAKA

Insulator surface is one of the interesting targets for scientific reseaches, but usual surface techniques such as UPS, Auger, and LEED are not avilable because of the charging of samples. Therefore we have grown thin insulator films on semiconductor surfaces and investigated their electronic structures, using photo-electron and optical spectroscopy with synchrotron radiation from the UVSOR storage ring. For examples, the valence band structures of BaF_2, CsCl, PbF_2, and $PbCl_2$, which are interesting materials for optical properties, have been observed.

We have been investigating the photon-stimulated desorption (PSD) in recent years, since PSD is interesting and promising field from a point of view from the application to micro-fabrication and the basic surface science. The photoelectron and ion coincidence technique and the laser-induced fluorescence method are powerful to understand the PSD dynamics on semiconductor (H_2O/Si) and insulator (KCl) surfaces.

It is important subject to develop new experimental systems and methods with synchrotron radiation for scientific researches. In recent years, we have constructed new beamline consisted of the helical undulator, high-resolution monochromator, and spin-resolved photoelectron spectrometer. High-resolution photoelectron spectrometer was also installed in 1997. The combinational use of synchrotron radiation and short-pulse laser is also promising for solid/surface studies. In recent years, we have developed this method to two-photon excitation spectroscopy for optical and photoelectron studies (See UVSOR ACTIVITY REPORT 1998).

Non-Linear Phenomena and Related Beam Physics in Storage Ring Free Electron Lasers

Hiroyuki HAMA, Masahito HOSAKA and Hitoshi TANAKA *(SPring-8)*

Simulation study for longitudinal phase space of the electron bunch including effects of potential-well distortion and FEL interaction has been performed for both positive and negative momentum compaction factors on a storage ring. Trend of the bunch lengthening is well interpreted by the wake field due to inductive impedance. Above the upper bound of the Haissinski equation for the negative momentum compaction operation, the simulation shows the bunch is lengthened by increasing the energy spread, which is in good agreement with the experimental data. Even the energy spread is enhanced at the negative momentum compaction, the FEL oscillation is possible and there particularly seems an advantage for the Q-switched macropulse because the electron population is centered in the bunch.

Studies of Solids and Surfaces by Photoelectron Spectroscopy

Toyohiko KINOSHITA, Yuichi HARUYAMA and Krishna Gopal NATH

We are studying the electronic structures of solids, solid surfaces, interfaces and adsorbates by using photoelectron spectroscopy, especially with synchrotron radiation from the UVSOR storage ring. Since 1995, we have constructed the new equipment for photoelectron spectro-microscopy measurements. In 1997, a sample preparation chamber which is equipped with a LEED optics, evaporation guns, a quartz thickness monitor and

so on has been connected with the photoelectron spectro-microscopy system (see, the annual review 1997, p. 224). The apparatus has been connected to the 2 beamlines (BL5B and BL7A). The use of the new sample preparation chamber enables us to perform the photoelectron spectro-microscopy studies for many kinds of samples. By using this apparatus, several photoemission studies for small samples, magnetic materials and thin films are now in progress. We have also studied the resonant photoemission spectra of heavy rare earth compounds around the excitation threshold of 4*d*-4*f* and 3*d*-4*f* resonant regions at BL2B1 and BL1A. The details of these photoemission studies are appeared in this issue (Research activities at ultraviolet synchrotron orbital radiation facility; UVSOR).

Further, in order to perform photoelectron spectro-microscopy measurements as a function of temperature, a He cryostat and a laser annealing system have been constructed. The latter can also be used for the heating source for sample cleaning, especially, of small samples and small area of surfaces.

(2) Study of Molecular Solid toward Molecular Electronics

Theory of Electronic Phases in Molecular Conductors and Insulators: Electron Correlations and Dimensional Crossovers

Kenji YONEMITSU, Jun-ichiro KISHINE, Takuhiro OGAWA, Michiyasu MORI, Makoto KUWABARA, Masao OGATA *(Univ. Tokyo and IMS)***, Xin SUN** *(Fudan Univ. and IMS)* **and Yutaka IMAMURA** *(Grad. Univ. Adv. Stud.)*

Competitions among different transport and magnetic properties and their origins in one-, quasi-one, and two-dimensional, correlated electron systems have been theoretically studied with various techniques; (i) a path integral formulation of the adiabatic approximation, combined with many-body tight-binding, instanton, constrained lattice dynamics, and many-body exact diagonalization techniques for Berry phases and pairing symmetry in the high-T_c copper oxides; (ii) a two-loop renormalization-group approach (a) to superconductivity and dimensional crossovers in the doped ladder system, $Sr_{14-x}Ca_xCu_{24}O_{41}$, (b) to antiferromagnetism and dimensional crossovers in the quasi-one-dimensional organic conductors, $(TMTCF)_2X$, and (c) to pseudogap and suppression of the quasiparticle weight in the high-T_c copper oxide, $Bi_2Sr_2CaCu_2O_8$; (iii) the density-matrix renormalization-group method for long-range interaction, exchange coupling, and metal-insulator transition in the one-dimensional π-d electron system, $CoPc(AsF_6)_{0.5}$; (iv) the Hartree-Fock approximation and the strong-coupling expansion in the second order for possibility of different magnetic orders in the 1D-2D hybrid, metal-assembled complex, $Me_4Z[Pd(dmit)_2]_2$; (v) the Hartree-Fock approximation for mysterious coexistence of the spin density wave and the $2k_F$ charge density wave in the quasi-one-dimensional organic conductor, $(TMTSF)_2PF_6$; (vi) the adiabatic approximation and molecular dynamics studies for possibility of negative polarizability in conducting polymers; and (vii) the ab initio molecular orbital theory and the full configuration interaction method for antiferromagnetic correlation and $4k_F$ charge ordering in the quasi-one-dimensional, quarter-filled band system, $(DCNQI)_2M$ (M = Li, Ag).

π-d Interaction in Molecular Metals

Kyuya YAKUSHI, Yukako YONEHARA, Iakov L. KOGAN and Mkhital SIMONYAN

We have undertaken a systematic study on the solid molecular systems in which transition metals are embedded in a π-conjugated system from the viewpoint of the future design of the superconducting material. The highly conductive phthalocyanine salts such as $CoPc(AsF_6)_{0.5}$ and $NiPc(AsF_6)_{0.5}$ are the prototype of the one-dimensional conductors in which the d- and π-orbitals form a double-chain and two-band system.

Subsequently to the high-pressure experiment, we performed the reflectivity measurement in 600-30000 cm^{-1} range and Raman scattering spectra of the mixed crystals $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$. Although the data collection is still in progress, the reflectivity of $CoPc(AsF_6)_{0.5}$ and Raman spectra of the mixed crystals suggest the band formation of the $3d_{z^2}$-orbital and the charge-transfer interaction between $Ni3d_{z^2}$ and $Co3d_{z^2}$. (See IV-A-1)

Instead of high pressure, we made an attempt to shift the Fermi energy of the wide π-band by using electrochemical method. An electrode was built embedding solid phthalocyanine into poly-bisphenol-A-carbonate. PF_6^- ions were doped into and dedoped from the solid phthalocyanine in the polycarbonate controlling the electrochemical potential. This doping and dedoping was characterized by X-ray diffraction, ESR, optical absorption spectrum, electrical resistance and thermoelectric power. It was found, however, that the band filling control by this method is difficult in $PtPc(PF_6)_x$ system due to the formation of the domians of two phases. (see IV-A-2)

Search for Negative-*U* Materials in Molecular Solid

Kyuya YAKUSHI, Mikio URUICHI, Jianyong OUYANG, Yoshiro YAMASHITA, Chikako NAKANO, Makoto INOKUCHI and Mkhital SIMONYAN

The negative-U material comprises the molecule which has a negative on-site Coulomb energy or, in other words, an attractive force between two electrons within the molecule. We are looking for such compounds from the two directions: (1) a strong electron-molecular vibration coupling and (2) a strong nearest neighbor Coulomb repulsion. (1) A strong electron-molecular vibration interaction may overcome the repulsive force within the molecule and stabilize a on-site bipolaron state. The similar state has been found

in the insulating compound, Cs_2SbCl_6, superconducting compound, $BaPb_{1-x}Bi_xO_3$, and conducting polymer, polypyrrole, but never been in a organic charge-transfer compound. (2) The molecular distance between the neighboring molecules is about 3.4 Å, whereas recently synthesized long conjugated molecule has more than 15 Å. If we use the long conjugated molecule which is stacked in an eclipsed overlapping mode, the on-site Coulomb repulsion energy happens to be smaller than the nearest neighbor Coulomb repulsion occasionally.

To look for such molecules, multi-step-oxidation properties of electron donors are one of the key parameters. Generally, the difference (ΔE) between the first and second oxidation potentials is thought to be a measure of the on-site Coulomb energy in the organic conductor. Subsequently to the study of the charge-transfer salts of BDNT, we conducted the spectroscopic study of the charge-transfer salts of BEDT-ATD which has very small ΔE (90 mV). The compounds were found to be narrow-band metal with quasi-one-dimensional nature. The shape of the conduction electron absorption suggests the strong electron correlation and strong electron-molecular-vibration coupling. Howevrer, we still do not have evidence for the negative-*U* state. (IV-B-6)

Nearest neighbor Coulomb repulsion is largest in the molecular conductor having half-filled band. Generally such a system becomes a Mott insulator. However, DMTSA-BF_4 shows a metallic behavior above 100 K. Through the polarized reflection spectroscopy, this compound is characterized as the Peierls system with a metallic property. In this compound, the effective on-site Coulomb energy U-V is still positive but overcomed by the large transfer integral t = 0.30 eV, which makes this compound metallic. We found a strong fluctucation effect accompaying the Peierls transition in DMTSA-BF_4 (See IV-B-1).

We examined the electronic structure of new organic metals based on a long conjugated molecule BDT-TTP, $(BDT\text{-}TTP)_2X$ (X=SbF_6, AsF_6, ClO_4). These compounds were found to be two-dimensional metals with large anisotropy. The correlation effect and the electron-molecular-vibration coupling are small in this β-type arrangemnt.

The negative-*U* state is a dynamic state of the charge disproportionation: the paired charge is moving coherently. Contrary to this state, some charge-transfer salts in a mixed valent state show a static charge disproportionation state. The Raman spectroscopy is a efficeint method to detect this kind of charge distribution. We examined $(BEDT\text{-}ATD)_2PF_6(THF)$ (See IV-B-5), $(Et_4N)(DMe\text{-}TCNQ)_2$ (See IV-B-6), and α'-$(BEDT\text{-}TTF)_2IBr_2$ (See I-B-7).

Exploring Novel Electronic Phases in Molecular-Based Conductors

Toshikazu NAKAMURA and Yasuhiro NAKAZAWA

The aims of this project are to explore novel electronic phases and new functional materials after investigating the electronic state of molecular-based conductors from a microscopic point of view. Molecular-based conductors are very advantageous because of several features as follows: (1) low-dimensional and simple Fermi surfaces, (2) clean system, (3) various ground states, and (4) molecular internal-freedom. We will perform the investigation with the following procedure: firstly we will understand the fundamental electronic properties by static magnetic susceptibility, EPR and transport measurements. Secondly we study the detailed electronic structure and mechanism of the phase transition by means of (a) EPR g-tensor analyses, (b) EPR relaxation time measurement, and (c) NMR measurements for selectively isotope substituted samples. We also try to carry out experiments with new devices under unconventional circumstance.

In the next several years, we will plan to study on these topics.

[1] investigation of the charge distribution in uniform stacked systems
[2] competition between local and itinerant electrons in charge-transfer salts
[3] understanding of the electronic structure of conducting metal complex from a microscopic point of view

This program has just been opened, and preparations for measurements is now in progress.

Development of New Organic Metals and Superconductors

Hayao KOBAYASHI, Hideki FUJIWARA, Akane SATO, Emiko ARAI, Takafumi ADACHI, Hisashi TANAKA *(Univ. Tokyo)* **and Akiko KOBAYASHI** *(Univ. Tokyo)*

We have recently studied the following three subjects: (1) novel electric and magnetic properties of a series of λ-type BETS conductors incorporating magnetic ions, $\lambda\text{-}BETS_2Fe_xGa_{1-x}Br_yCL_{4-y}$ (2) development of a new organic donor containing an organic radical part (3) and solid state properties of organic systems at high pressure. Main results achieved in the last year are as follows.

(1a) We have studied the unprecedented superconductor-to-insulator transition found in $\lambda\text{-}BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.5$) at ambient pressure. An evidence of the bulk nature of this transition was obtained from the ac susceptibility. The insulating ground state takes an antiferromagnetic spin structure. The superconductor-to-insulator transition was also discovered in $\lambda\text{-}BETS_2Fe_xGa_{1-x}BrCl_3$ ($x \approx 0.5$) at high pressure. Furthermore, a superconductor-to-metal transition was disclosed in $\lambda\text{-}BETS_2Fe_xGa_{1-x}BrCl_3$ ($x \approx$ 0.1-0.2). The role of the magnetic moments of Fe^{3+} is essential. It might be said that a completely new class of organic superconductor appears after two decades of the first discovery of organic superconductor.

(1b) The development of ferromagnetic or antiferromagnetic organic metals is one of the largest current topics in the field of the molecular conducting systems. We have examined the high-pressure susceptibility of $\lambda\text{-}BETS_2FeCl_4$ under the collaboration with Dr. Hosokoshi of this institute and found the

evidence that the antiferromagnetic ordering of Fe^{3+} spins coexists with π metal electrons above 2 kbar. Thus, λ-$BETS_2FeCl_4$ becomes the first antiferromagnetic organic metal.

(1c) Although λ-$BETS_2FeCl_4$ does not show the superconducting transition, we have found the superconductivity in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.9$) at high pressure. Similar to the representative organic superconductors such as Bechgaard salts and κ-type BEDT-TTF superconductors, this system has an antiferromagnetic insulating state neighboring on the superconducting state. In these representative organic superconductors, the spin excitation is expected to be related to the superconducting mechanism. However, it is quite doubtful that the existence of antiferromagnetic phase is favorable for the superconductivity of λ-$BETS_2FeCl_4$.

(2) With the aim of the development of pure organic magnetic metals, we have prepared a new organic donor with neutral radical part, TEMPOET. ESR spectra showed three absorption lines characteristic of TEMPO radical and almost quantitative spin concentration. The CV examination indicated the possibility of the formation of the conducting cation radical salts.

(3) In order to examine the transport properties around the pressure region of 50 kbar, we have recently tried to perform the four-probe resistivity measurements of $TMTTF_2PF_6$, which has a spin-Peiels ground state at ambient pressure. In order to confirm the superconductivity of this salt, the resistivity measurements up to 45 kbar and down to 0.5 K seems to be required. We have recently observed the stabilization of the metallic state down to 2 K at 46 kbar.

NMR Studies of Liquid Crystals

Osamu OISHI, Daisuke KUWAHARA, Hiroki FUJIMORI *(Nihon Univ.)*, **Jean-Pierre BAYLE** *(Univ. Paris XI)*, **Toshihito NAKAI** *(Univ. Tsukuba)* **and Seiichi MIYAJIMA**

Extensive high resolution NMR studies were conducted to investigate the microscopic mechanism of dynamics and orderings of liquid crystals. (1) Pulsed field gradient spin echo (PGSE) NMR study revealed an inversion of self-diffusion anisotropy in smectic A liquid crystal. (2) Complete assignment of ^{13}C NMR lines was accomplished for an antiferroelectric liquid crystal MHPOBC, and the orientational order parameter was analyzed on the basis of a number of intramolecular rotation models. (3) Transient coherent effect in the cross-polarization dynamics was applied to the analysis of intramolecular motion in MHPOBC. (4) Transient ^{13}C-^{1}H nuclear Overhauser effect was found significant in liquid crystal, and the time-evolution of the magnetization was reproduced quatitatively by a coupled spin model. (5) ^{13}C NMR and neutron diffraction studies were conducted for a reentrant liquid crystal.

Construction and Characterization of Chiral Molecule-Based Magnets

Katsuya INOUE, Hitoshi KUMAGAI and Shinya HAYAMI

The design of molecular materials with interesting electrical and/or magnetic properties is one of the major challenges of science in the last few years. It's possible to modify the molecular structure in the molecule-based magnetic materials. Recently, we introduced a strategy of using π-conjugated polyaminoxyl radicals with high-spin ground states as bridging ligands for magnetic metal ions in order to assemble and align the electron spins on a macroscopic scale. The crystal structures of these complexes are known, and some cases, the magnetic structures are analyzed.

By the way, a new magneto-optical phenomena was expected in the transparent chiral magnets by theoretical considerations. In 1984 Barron and Vrbancich, they call "magneto-chiral dichroism" (MChD) for this phenomena. It's important to make the fully chiral molecule-based magnets, which expected to be strong MChD effect. There are still no examples of molecule-based chiral magnet. Novel properties are expected for such compounds.

When we use a chiral bisaminoxyl radical for the ligand, a chiral one-dimensional structure was expected. Brown crystals of $\{\mathbf{1}\cdot Mn(II)(hfac)_2\}_n$ were obtained by mixing the chiral triplet bisaminoxyl radical, 1,3-Bis(*N*-oxy-*tert*-butylamino)-5-{(*S*)-2'-methylbutyloxy}-*iso*-propylbenzene **1** and bis(hexafluoroacetylacetonato)-manganese(II) $\{Mn(II)\cdot(hfac)_2\}$ in diethyl ether/n-heptane. An X-ray crystal structure analysis revealed the formation of a DNA strand type (*R*)-helical one-dimensional polymeric structure. It not only contains a (*S*) chiral carbon center but also (*R*) *C2* chiral skeleton of the organic ligand. Each of the two aminoxyl radical centers which are mutually coupled ferromagnetically within the organic radical molecule is coupled antiferromagnetically to the d^5 manganese(II) ions. The temperature dependence of the magnetization revealed that the heterospin system behaves as a metamagnet below 5.4 K. This complex is first example of transparent and fully chiral molecular metamagnet. The observation of MChD effect of this complex is now underway.

Quantitative Analysis of Organic Thin Films Using Angle-Resolved UPS

Nobuo UENO, Shinji HASEGAWA, Yasushi AZUMA, Koji K. OKUDAIRA *(Chiba Univ.)*, **Yoshiya HARADA** *(Chiba Univ.)*, **Hisao ISHII** *(Nagoya Univ.)* **and Kazuhiko SEKI** *(Nagoya Univ.)*

Angle-resolved photoelectron spectroscopy (ARUPS) is a well-known technique to investigate the electronic structure of surfaces. One can in principle determine the orientation and electronic states of molecules adsorbed on crystal surfaces by the quantitative analysis of the photoelectron angular distribution. For thin films of functional organic molecules, which are promising candidates to realize new electronic devices, the determination of molecular orientation and the electronic structure in the ultrathin films is of fundamental importance, since the molecular orientation is different from that in a bulk crystal, and

thus new electronic states appear owing to the molecule /substrate, molecule/overlayer and molecule/molecule interactions which depend on the molecular orientation. Although ARUPS experiments have been widely performed on such thin films, the quantitative analysis of the ARUPS intensity and the determination of molecular orientation have little been realized due to the difficulty of quantitative analysis of the photoelectron angular distribution. We have recently succeeded to analyze the photoelectron angular distributions from thin films of large functional organic molecules.

The goal of our project is to obtain quantitative information on the full geometrical structure of ultrathin films of functional organic molecules as well as the electronic structure typical of the thin films which consist of large organic molecules by the quantitative analysis of photoelectron angular distribution, and open a door to realize quantitative chemical analysis of organic ultrathin films using ARUPS with synchrotron radiation.

In order to perform the project, a new ARUPS spectrometer, which enable us to measure accurate photoelectron angular distributions from functional organic thin films, were constructed at the BL8B2 of the UVSOR facility. The spectrometer consists of a 75 mm hemispherical sector analyzer with two-axes rotations, electrostatic lens of various operation offering various angles of acceptance, multi-channel detection system and a μ-metal UHV chamber. The spectrometer station is shown in Figure 1.

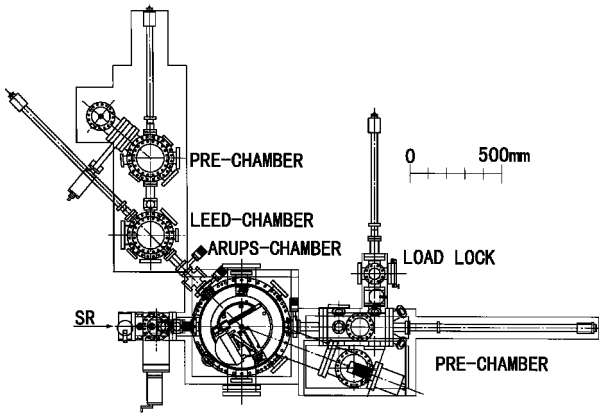


Figure 1. A drowing of the new ARUPS apparatus for organic thin films at the BL8B2.

New Advanced Organic Materials Based on Novel Heterocyclic Compounds

Yoshiro YAMASHITA, Shoji TANAKA and Masaaki TOMURA

We have succeeded in preparing new electron donors with extended π-conjugation. For example, novel viologen derivatives containing 1,2,5-thiadiazole units were prepared by reductive coupling of pyridinium compounds. They are stronger electron donors than TTF and afforded PF_6 and AsF_6 salts of the cation radical. X-ray analyses revealed that a tape-like network of the donor molecules is formed by short S···N contacts. TTF vinylogues bearing various substituents at the vinyl positions have been prepared using an oxidative dimerization reaction of 1,4-dithiafulvenes with an aminium salt. The derivatives with *o*-substituted phenyl groups show stepwise reversible oxidation potentials, suggesting that the cation radicals are thermodynamically stable where the aryl part is twisted and the TTF vinylogue skeleton is planar. Some compounds afforded cation radical salts upon electrochemical oxidation. X-ray analysis revealed the planar structure of the TTF vinylogue part and an interesting two-dimensional columnar structure. We have also prepared novel π-extended TCNQ analogues containing sulfur atoms. Thus, thiophene-TCNQ and bithiophene-TCNQ derivatives containing fused pyrazine rings have been prepared using the reaction of TCNEO. X-ray analyses revealed the interesting crystal structures where intermolecular networks are formed by short S···N contacts. Furthermore, we have synthesized a promising building block for molecular-scale electronic wires; *N*-silyl protected tetraaminoquaterthiophene. This molecule has a rigid and coplanar main chain surrounded by the electrically-inert alkyl substituents. Details of these works are described in VIII-E section.

Design and Synthesis of New Tellurium-Containing Donors

Hayao KOBAYASHI, Toshiyasu SUZUKI, Hideki FUJIWARA, Takafumi ADACHI, Akane SATO and Emiko ARAI

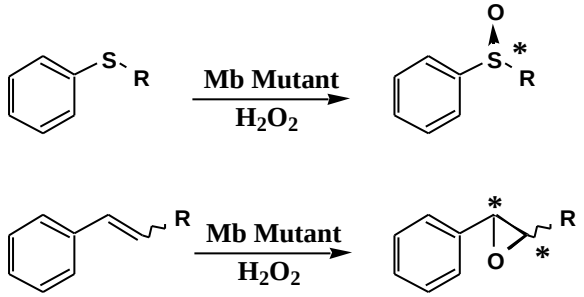
In the field of molecular conductors, systems based on tellurium-containing donor molecules have not received as much attention as systems based on sulfur- or selenium-containing donors. By incorporating heavy chalcogen atoms such as tellurium into donor molecules, a new metallic system with a wider bandwidth and a higher dimensionality is expected to appear. We have designed dimeric donor molecules containing two HM-TTeF moiety and been trying to synthesize them. After obtaining these molecules, we are planning to study their crystal structures and physical properties of both neutral and oxidized states.

(3) Material Control in Multi-Reaction Centers

Asymmetric Oxidation Catalyzed by Myoglobin Mutants

Shin-ichi OZAKI, Hui-Jun YANG, Toshitaka MATSUI, Yoshio GOTO and Yoshihito WATANABE

The sperm whale myoglobin active site mutants (L29H/H64L and F43H/H64L Mb) have been shown to catalyze the asymmetric oxidation of sulfides and olefins. Thioanisole, ethyl phenyl sulfide, and *cis*-β-methylstyrene are oxidized by L29H/H64L Mb with more than 95 % enantiomeric excess (% ee). On the other hand, the F43H/H64L mutant transforms *trans*-β-methylstyrene into *trans*-epoxide with 96 % ee. The dominant sulfoxide product in the incubation of alkyl phenyl thioethers is the *R* isomer; however, the mutants afford dominantly the *S* isomer of aromatic bicyclic sulfoxides. The results help us rationalize the difference in the preferred stereochemistry of the Mb mutants-catalyzed reactions. Furthermore, the Mb mutants exhibit the improvement of the oxidation rate up to 300-fold with respect to wild type, and the Phe-43 → His and His-64 → Leu double mutation endow with the ability to perform the hydroxylation reaction, which is not normally catalyzed by wild type Mb.



Two Dimensional Coordination Chemistry at the Interface towards Molecular Protonic Devices

Masa-aki HAGA, Hideaki MONJUSHIRO, Yasushi KAWATA, Md. Delower HOSSAIN and Kezhi WANG

The control of molecular architecture at the surface is one of the important and attractive area in the supramolecular chemistry. In order to control the molecular arrays or layers in two dimensions, the incorporation with coordination bond has advantage compared to the other molecular interactions such as hydrogen bonding and electrostatic interaction from the viewpoint of strength of interaction and molecular geometry around metal ion. However, the incorporation with coordination bond at the interface has not extensively studied so far. Research efforts in our group are aimed at building up the molecular assembly on solid surface towards molecular protonic devices. We have developed the chemical principle underlying the proton-induced switching in 2-(2-pyridyl)benzimidazole Ru complexes. In order to achieve the proton-induced switching systems, the interlocking between the potential change by protonation/deprotonation and the pKa change by Ru(II) to Ru(III) oxidation is responsible. The judicious molecular design of the Ru complexes containing benzimidazole ligands allows us to synthesize the novel supramolecular metal complexes with bistable property not only in solution but also at the surface. We examined two methodologies; one is the self-assembled monolayer (SAM) method on gold, and the other is Langmuir-Blodgett (LB) techniques. New bridging, anchoring, or amphiphilic ligands based on tridentate 2,6-bis(benzimidazol-2-yl)pyridine-($bbimpH_2$) were synthesized and used as a molecular module. (1) SAM of Ru complexes on Au surfaces. The oxidative peak potential of the Ru complex modified on Au is linearly dependent on the solution pH, which strongly indicates the proton-coupled electron transfer reactions on the SAM. Proton release by oxidation of the Ru complex on the SAM was detected by a pH fluorescent probe. (2) LB films of amphiphilic Ru complexes. A π-A isotherm of [Ru-(L18)($bbimpH_2$)]$^{2+}$ complex (C18 = 2,6-bis(N-octadecyl-benzimidazolyl)-pyridine) shows a strong dependence on the subphase pH. The monolayer was transferred onto a hydrophilic glass plate as a LB Y-type films.

Peroxide Adduct of Hydroxo(oxo)iron Clusters as a Cause of Neurodegenerative Diseases

Yuzo NISHIDA

Increased brain iron concentration have been described in several neurodegenerative diseases, most notably in those diseases characterized by nigral degeneration, such as Parkinson's disease (PD) and Alzheimer's disease (AD). The cause of nigral cell death in these disorders is unknown, but considerable experimental evidence supports the hypothesis that the celluar degeneration results from the oxidative stress. At present, it is generally accepted that the oxidative stress is essentially associated with toxic process involving highly reactive oxygen species such as hydroxyl radical. We examined the so-called "general" method to detect the hydroxyl radical, and found that the detection of hydroxyl radical by the use of ESR spin-trapping agents such as DMPO is not adequate, and the results obtained by this technique are all doubtful.

We have recently observed that some binuclear iron(III) or iron clusters containing hydroxo or oxo-bridge exhibit high activity for a) hydroxylation of and oxidative degradation of nucleosides, b) DNA cleavage, c) protein degradation, and d)lipid peroxidation, in the presence of hydrogen peroxide, and pointed out that the peroxide adduct of iron clusters in the serum should be a main cause of neurodegenerative diseases in brain, and the investigation on this problem is now in progress.

Assembled Metal Centers in Enzymes

Takeshi SAKURAI, Hidemi NAGAO, Nobuhiko SAKURAI, Hong-wei HUANG, Isao HARA, Hideyuki KUMITA and Hiroki MATSUMOTO

Metal centers as the active site in metalloproteins and metalloenzymes do not exist as isolated centers but as functionally related centers or as metal clusters to exert integrated functions such as electron-transfer, activation of small molecules like dioxygen, NOx, SOx, etc. Laccase, ascorbate oxidase, ceruloplasmin, and bilirubin oxidase, which belong to a super family of multicopper oxidase are such the enzymes. The active site of these enzymes is composed of the three types of coppers, the type 1 Cu (blue Cu) the type 2 Cu (non-blue Cu), and a pair of the type 3 Cu's (EPR non-detectable Cu at the resting state). The latter two types of copper form the unique trinucelar site, at which electrons transferred from the type 1 Cu site by the intramolecular long range process are pooled and a dioxygen is reduced to two water molecules. Such the four-electron reduction of dioxygen is performed only by multicopper oxidases and the Cu-Fe center in terminal oxidases in the respiration process. Our goal of the study is to reveal the unique steric structure and magnetic property of the Cu trinuclear center and the four-electron reduction of dioxygen by using absorption, CD, MCD, EPR, SQUID, electrochemistry, stopped flow etc. Another target of our study is NO reductase from denitrifying bacteria. Although special attention has been paid for NO for these years, many studies have been focused on to forming and detecting this inorganic hormone. We have establish the purification method of this membrane protein and started the biophysical characterization of it. NO reductase is apparently a complex of *b* type and *c* type cytochromes. The aim is not only to reveal the structure of each active site but also to reveal the integrated function of them. Since NO reductase is apparently the ancestor enzyme of heme-Cu terminal oxidases, the architecture of the enzyme, the arrangement of the metal centers and their roles in comparison with those of Heme-Cu terminal oxidases are interested. Transfers of protons to be reacted are also studied in connection with proton transfers to be pumped and to be reacted in terminal oxidases.

Novel Phosphorus Ligands for Supramolecular Catalyst System

Yasushi TSUJI

Phosphorus ligands are the most important to activate and regulate catalysis. Stereo- and regio-selectivities are successfully controlled by these ligands, and even some chiral phosphorus ligands are utilized in industrial productions. We are now trying to make some novel phosphorus ligand systems having host-guest ability. These phosphorus ligands will realize unique and highly selective supramolecular catalytic reactions.

Bio-Inspired Molecular Architecture

Mitsuhiko SHIONOYA, Kentaro TANAKA, Motoyuki TASAKA *(Grad. Univ. Adv. Stud.)***, Kazuki SHIGEMORI** *(Grad. Univ. Adv. Stud.)***, Akihiko HATANO** *(Grad. Univ. Adv. Stud.)***, Hiromasa MORISHITA** *(Grad. Univ. Adv. Stud.)***, Honghua CAO** *(Grad. Univ. Adv. Stud.)* **and Xian-He BU** *(Nankai Univ., China and IMS)*

Nature has produced a limited number of molecular modules such as nucleosides and nucleotides, amino acids, and lipids. However, the chemical diversity of these biomolecules and the different ways they can be polymerized or assembled into precisely-defined three-dimensional shapes provide a wide range of possible structures and functions. Furthermore, owing to advances in chemical synthesis and biotechnology we can combine or chemically modify these molecular building blocks, almost at will, to produce new functional molecules that have not yet been made in Nature. Based on these concepts, we have been working on the following research projects. Our research programs also consciously focus on structures and functions that have been unknown in living, biological systems.

(1) Artificial DNAs: metal alignment at the axis of ds-DNA with artificial chelate nucleobases.
(2) Cyclic metallopeptides: efficient cyclization of oligopeptides linked to functional metal complexes.
(3) Molecular recognition of DNA sequences by self-assembling metal complexes.
(4) A bottom-up approach to highly controlled hierarchical structures of metal complexes.

Stereochemistry of Six-Coordinated Octahedral Silicon(IV) Complexes Containing 2,2'-Bipyridine

Hong Ling LIU *(Okayama Univ.)***, Yasuharu OHMORI** *(Okayama Univ.)***, Masaaki KOJIMA** *(Okayama Univ.)* **and Yuzo YOSHIKAWA**

[*J. Coord. Chem.* **43**, 257 (1998)]

$[Si(bpy)_3]^{4+}$ (bpy=2,2'-bipyridine), synthesized from SiI_4 and 2,2'-bipyridine, was optically resolved by a chromatographic method using an SP-Sephadex C-25 column as an adsorbent and a 0.16 M aqueous solution of sodium (2*R*,3*R*)-(-)-O,O'-dibenzoyltartrate as an eluent. The optical isomers were characterized by measurement of their electronic absorption, circular dichroism, and ^{1}H NMR spectra. The chromatographic resolution of $[Si(bpy)_3]^{4+}$ was also attempted by the use of an aqueous solution of potassium [(2*R*,3*R*)-(+)-tartrato]antimonate(III), sodium (2*R*,3*R*)-(+)-bitartrate, and sodium (2*R*,3*R*)-(+)-tartrate as eluents. Force-field calculations were used to elucidate the chromatographic elution mechanism. $[Si(OH)_2(bpy)_2]I_2$ was also synthesized from SiI_4 and 2,2'-bipyridine. The optical resolution of this complex was achieved with sodium [(2*R*,3*R*)-(+)-tartrato]antimonate(III).

Activation of Carbon Dioxide Directed toward Carbon-Carbon Bond Formation and Energy Conversion from Proton Gradients to Electricity

Koji TANAKA, Kiyoshi TSUGE, Hideki SUGIMOTO, Tetsunori MIZUKAWA, Tohru WADA and Takashi TOMON

Direct electrochemical reduction of CO_2 is not thermodynamically favorable process because of the large negative redox potential of $E°(CO_2/CO_2^-)$ at -2.21 V (*vs.* SCE). A variety of metal complexes have been used as catalysts precursors for the reduction of CO_2, though the reduction products are usually limited to CO and/or HCOOH. We have found that depression of cleavage of metal-CO bonds derived from CO_2 under reductive conditions enables multi-electron reduction of CO_2 accompanied by carbon-carbon bond formation. Selective ketone formation is also achieved in the reduction of CO_2 catalyzed by metal complexes with chelating ligands which have the function of ring-opening and -closing in a catalytic cycle. Site opening and closing of the reaction centers greatly contributes to stabilization, inhibition of side reactions, and promotion of eliminating the products from the reaction site. An equilibrium of chelation and dechelation of ligands with a little configuration barrier greatly improves a catalytic activity of the reduction of CO_2.

ATP synthesis utilized proton gradient is the key reaction for maintenance of biological activity. The proton gradient (Δp) between inside and outside of a cell is depicted as the sum of electric activity ($\Delta\psi$) and chemical activity (ΔpH) components. $\Delta p = \Delta y - Z\Delta$pH ($Z = 2.303RT/F$) Artificial energy conversion from proton gradients to other energy forms except for thermal energy has not been established so far. Biological system creates various valuable energies from the proton gradients, that is the neutralization energy. Basically, neutralization energy is originated from the binding energy of acid and base, namely is one of the chemical energies, which are expected to be converted directly to valuable chemical, electric or mechanical energy in 100% efficiency in principal. Along this line, we tried to convert the neutral energy to electronic energy by using metal complexes. The purpose of the two projects is to create new electron sources which can be used in catalytic reduction of CO_2 directed toward carbon-carbon bond formation.

Self-Assembling Molecular Systems

Makoto FUJITA, Takahiro KUSUKAWA, Shuichi HIRAOKA *(CREST)***, Youichi SAKAMOTO, Nobuhiro TAKEDA** *(CREST)***, Masaki TAKAHASHI** *(JSPS)***, Shu-Yan YU** *(JSPS)***, Delower HOSSAIN** *(Mie Univ.)***, Fumiaki IBUKURO** *(Grad. Univ. Adv. Stud.)***, Masaru AOYAGI** *(Grad. Univ. Adv. Stud.)***, Hirokazu ITO** *(Grad. Univ. Adv. Stud.)***, Norifumi FUJITA** *(Grad. Univ. Adv. Stud.)* **and Kazuhiko UMEMOTO** *(Grad. Univ. Adv. Stud.)*

We have been studying the self-assembly of finite and infinite structures based on coordination chemistry, where metal-coordination induces the generation of defined structures. Our studies are focused on the self-assembly of finite structures such as macrocycles, catenanes (interlocked molecules), cages, tubes, and capsules, as well as infinite network structures. In the construction of the discrete structure, our strategy may be charcterized by the use of palladium's 90 degree coordination. Based on this concept, we have obtained the following results during 1998.

- Made-to-Order Assembling of [2]Catenanes from Palladium(II)-Linked Rectangular Molecular Boxes: eight building blocks - four metals and four ligands - are found to self-assemble into [2]catenanes consisting of two rectangular molecular boxes.
- Self-assembled Molecular Ladders: Coordination of a pyridine-based bridging ligand, 1,4-bis(4-pyridyl-methyl)benzene, with cadmium nitrate afforded an infinite ladder complex.
- Coordination Polymers Self-assembling from Cadmium(II) Ions and Flexible Pyridine-based Bridging Ligands: Coordination polymers are prepared by self-assembly from cadmium nitrate and flexible bridging ligands, Py-X-Py (Py = 4-pyridyl, X = CH_2, C(=CH_2), CH_2CH_2).
- Nanometer-sized Macrotricyclic Complexes Self-assembled from Ten Small Component Molecules: Self-assembly of nanoscale, highly positive charged macrotricycles with a general formula of $[M_6L_4]^{12+}$ (where M = (en)Pd(II), L = tripyridyl ligands) is achieved.
- Encapsulation of Large, Neutral Molecules in a Self-assembled Nanocage Incorporating Six Palladium(II) Ions: It is shown that self-assembled M_6L_4 type cage can hold as many as four adamantane molecules or *o*-carborane (8 Å in diameter) inside its nanosized cavity.
- A Thermally Switchable Molecular Lock. The Guest-Templated Synthesis of a Kinetically Stable Nano-Sized Cage: Stable nano-sized M_6L_4 type cage complex (M = Pt(II)) self-assembled upon heating and converted into an inert (stable) form by cooling.
- Spontaneous Assembling of Ten Small Components into a Three-dimensionally Interlocked Compound Consisting of the Same Two Cage Frameworks: Two cage complexes efficiently bind each other through giving rise to a ten-component self-assembly into a three-dimensionally interlocked molecule
- A Nonometer-sized Hexahedral Coordination Capsule Assembled from Eighteen Metal Ions and Six Triangular Organic Ligands: The transition metal-induced assembly of a stable, nano-meter sized coordination capsule are achieved from twenty-four small components; eighteen metals and six triangular organic ligands.
- "Ship-in-a-bottle" Formation of Stable Hydrophobic Dimers of cis-Azobenzene and -Stilbene Derivatives in a Self-assembled Coordination Nanocage: "C-shaped" molecules such as cis-azobenzene and -stilbene are enclathrated in the cavity of a nano-sized M_6L_4 type cage complex through "ship-in-a-bottle assembly" into a hydrophobically interacted dimer.

Molecular Mechanism of Heme Degradation and Oxygen Activation by Heme Oxygenase

Hiroshi FUJII, Tadashi YOSHIDA *(Yamagata Univ.)*

and Masao IKEDA-SAITO *(Case Western Reserve Univ.)*

Heme oxygenase (HO), an amphipathic microsomal proteins, catalyzes the regiospecific oxidative degradation of iron protoporphyrin IX (heme) to biliverdinIXα, 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 oxygen activation by heme oxygenase using various spectroscopic methods.

(1) We prepared oxy and deoxy forms of cobalt-porphyrin-HO complex as a model for those of heme-HO complex. The EPR measurements first demonstrated the formation of a hydrogen bond interaction between the bound dioxygen and the amino acid residue in the distal pocket of the enzyme.
(2) We have prepared the heme, α-hydroxyheme, and verdoheme complexes of heme oxygenase, and their reactions with oxygen and carbon monoxide have been studied. The heme complexes of heme oxygenase isoforms-1 and -2 have different from myoglobin in oxygen and carbon monoxide binding properties.
(3) To identify the axial heme ligand of HO-2, His-45 to Ala(ΔH45A) and His-152 to Ala(ΔH152A) mutants have been prepared using this expression system. We conclude that His-45, but not H152, in heme oxygenase isoform-s is the proximal ligand of the heme and is essential for the heme degradation aciticty of the enzyme.

Generation of Reactive Species on Multinuclear Metal Complexes as Molecular Components in Energy Conversion Systems

Toshi NAGATA and Katsuji AIKAWA

Multinuclear transition-metal complexes are expected to provide unique environment for chemical transformation through delocalization of electrons among the metal centers. This research project aims at activation of water and other small molecules on multinuclear metal complexes by means of electron and/or proton transfer. We also plan to combine the chemistry of multinuclear metal complexes and photosynthesis model compounds (such as porphyrins) so as to construct efficient light-energy conversion systems. Currently, we are working on developing organic ligands capable of assembling metal centers in suitable geometry, as well as adjusting the redox properties of metals.