JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institution, IMS undertakes joint studies programs for which funds are available to cover research expenses as well as travel and living expenses of individuals. The proposals from domestic scientists are reviewed and controlled by an inter-university committee. The programs are carried out under one of five categories:

(1) Joint Studies on Special Projects (a special project of significant relevance to the advancement of molecular science can be carried out by a team of several groups of scientists).
(2) Research Symposia (a symposium on timely topics organized by collaboration between outside and IMS scientists).
(3) Cooperative Research (a research program carried out by outside scientists with collaboration from an IMS scientist).
(4) Use of Facility (a research program carried out by outside scientists at the research facilities of IMS except the UVSOR facility).
(5) Joint Studies Programs Using beam lines at the UVSOR Facility.
A. Special Projects, B. Cooperative Research Projects, C. Invited Research Projects,
D. Use-of-UVSOR Projects.

In the fiscal year 1997, the numbers of joint studies programs accepted for categories (1) - (4) were 3, 8, 117 and 238, respectively, and those accepted for subcategories (5)A - (5)D were 3, 23, 1 and 153, respectively.

(1) Special Projects

A. Advanced Research of Carbon Clusters

Contributors: **Yusei MARUYAMA** *(Housei Univ.)*, **Kyuya YAKUSHI, Tadaoki MITANI** *(JAIST)*, **Yoshihiro IWASA** *(JAIST)*, **Yoji ACHIBA** *(Tokyo Metropolitan Univ.)*, **Tatsuhisa KATO, Hisanori SHINOHARA** *(Nagoya Univ.)*, **Hiroyoshi SUEMATSU** *(Univ. Tokyo)*, **Seiichi MIYAJIMA, Susumu SAITO** *(TIT)* **and Yahachi SAITO** *(Mie Univ.)*

The aim of this research has been to search for new families of fullerene materials and to obtain a comprehensive understanding of various unique features of fullerene materials. The reseach was carried out in a wide range covering physical chemistry of fullerene synthesis, solid state properties of fullerenes, and structural and electronic properties of carbon nanotubes. 1997 was the last year of this project. To summarize the accomplishemnt of the project and to stimulate our future collaborations, we have held a workshop on 20 and 21 December, 1997.

A-1 Formation of Thin Single-Wall Carbon Nanotubes by Laser Vaporization of Rh/Pd-Graphite Composite Rod

Single-wall carbon nanotubes (SWNTs) were synthesized in high yield by laser vaporization of Rh/Pd-graphite composite rod at 1200°C. Lattice constants of the bundle were estimated from transmission-electron-microscope images and were found to be distributed between 1.0 and 1.5 nm. Nine Raman peaks originating from the breathing modes were observed at 204, 215, 229, 247, 262, 272, 287, 303 and 328 cm^{-1}. These frequencies and lattice constants sharply indicate the presence of the SWNTs indexed from (5,5) to (8,8) which are thinner than the SWNTs obtained using Ni/Co catalyst. There are 40 independent chiral indexes between (5,5) and (8,8), and which lead to 40 different frequencies of the breathing modes. This result suggests the presence of a selection rule in the SWNT growth processes. A large softening of graphite sheet mode due to the curvature was also observed.

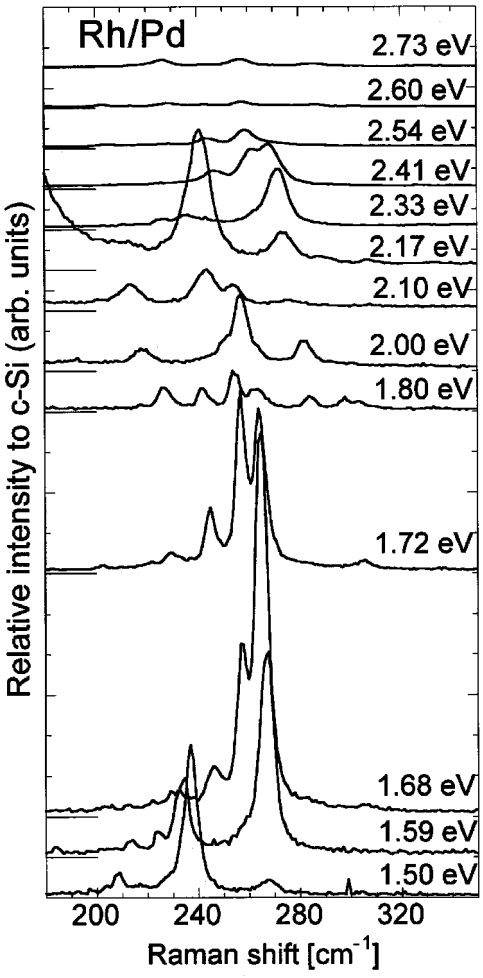

Figure 1. Low frequency Raman spectra of SWNTs using Rh/Pd with 13 different excitations, photon energies of which

are displayed in the figure. Intensities are normalized by that of crystalline silicon.

A-2 Size Dependent Optical Absorption of Single-Wall Carbon Nanotubes

Several kinds of single-wall carbon nanotubes (SWNTs) with different diameter distributions have been successfully synthesized in high yield by laser vaporization and electric arc methods using NiY, NiCo, Ni and RhPd catalysts. Diameter distributions were confirmed by transmission electron microscope observation and breathing mode frequencies in Raman spectra. Diameters of SWNTs synthesized using NiY catalyst are from 1.24 to 1.58 nm while those using RhPd are from 0.68 to 1.00 nm. Optical absorption spectra of these samples have been measured and three large absorption structures due to the optical transitions between spike like density of states in SWNTs were clearly seen in an infrared region. For example, SWNTs using NiY have absorption peaks at 0.68, 1.2 and 1.7 eV. Tight-binding zone-folding calculations indicate that the lowest two absorption peaks are due to semiconducting phases and the third one is due to metallic phases. These peaks shifted to higher photon energy side with decreasing diameters of SWNTs. For example, SWNTs using RhPd have absorption peaks at 1.1, 1.6 and 2.4 eV. These values are also explainable within a zone-folding scheme. Further, resonant Raman spectra with various laser wavelengths corresponding to the absorption by metallic phases were measured and could be assigned as a few metallic SWNTs. These results are consistent with previous works such as scanning tunneling spectroscopy by Dekker et al.

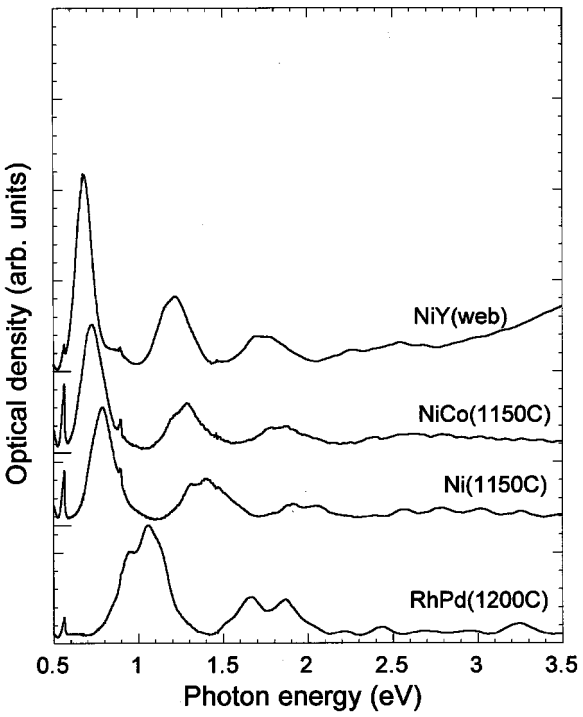

Figure 1. Optical absorption spectra of four kinds of SWNTs with different diameter distributions. Background absorption due to the π plasmon was subtracted. Electric arc method was used for NiY catalyst case and all the other samples were synthesized by laser ablation method. Peaks at 0.55 and 0.9 eV are absorption by the quartz substrate.

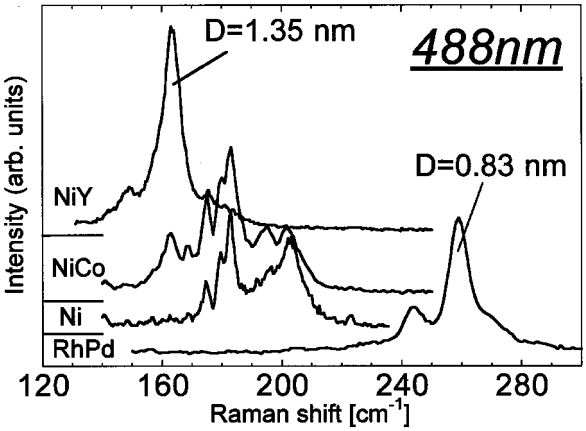

Figure 2. Low frequency Raman spectra of the SWNTs. Breathing mode frequencies provide a rough estimation of the diameter distribution.

A-3 Characterization by STM and Electrical Conductivity of Single-Walled Carbon Nanotubes

Single-walled carbon nanotubes (SWCNT) prepared by a DC-Arc-Discharge and purified by a hydrothermal treatment followedby several steps of procedures including heating, burning, extracting and acid-washing are investigated by a conventional STM technique morphologically and spectroscopically. The electical resistivities of compacted pellets (mats) of SWCNT are measured as a function of temperature in the range from the room-temperature to 1.5K. The behaviors seems to be essentially originated in the metallic nature ofindivisual SWCNT.

A-4 Magnetism and Electrical Conductivity of Vapour-Phase Grown Crystals of TDAE-C_{60}

The ferro-or antiferro-magnetic behaviors of TDAE-C_{60} crystals at low temperatures have recently been studied in rather elaborated way by Blinc et al. In the present work we have grown first TDAE-C_{60} crystals in the vapour-phase with subliming C_{60} and evaporating TDAE separately. Obtained crystals have clear indication of ferromagnetic behavior below 16K and antiferromagnetic transition at around 50K in the measurements by an SQUID magnetometer. ESR signal also shows the strong ferromagnetic component, but it shows no indication for the antiferromagnetic trnsition. The resistivity is 15,000 Ohm-cm at room temperature and it is almost temperature independent down to 80K.

A-5 Transport Properties of Carbon Nanotubes

Magnetoconductance oscillates periodically as a function of a magnetic flux passing through the circular cross section of the tube below about 30 K. It is understood as an appearance of the Aharonov-Bohm effect which have not yet been observed experimentally. Because the result shows that the electron interference effect along the circumference becomes effective only at low temperature, it is suggested that

carbon nanotubes in this system show the graphite-like feature at high temperature and that the nature of the tubular-figure and of the honeycomb-network appears only at low temperature.

A-6 Structural and Physical Properties of Metallofullerenes

We have succeeded to synthesize single crystals of solvent-free La@C82 for the first time in metallofullerenes. We have investigated the low temperature x-ray diffraction measurement. We revealed that the crystal undergoes a structural phase transition from face-centered-cubic lattice to simple-cubic lattice at about 120 K with decreasing temperature. Our present structural analysis supports that this transition is due to an order-disorder phase transition with respect to the arrangement of the molecular electric dipoles.

A-7 Structural and physical properties of Ammoniated Fulleride Compound

X-ray diffraction measurement of $(NH_3)K_3C_{60}$ have revealed a structural phase transition at Ts = 150 K, which is attributed to the order-disorder transition of the K-NH_3 pair at the octahedral site of the C_{60} lattice. The low-temperature phase has a face-centered-orthorhombic structure derived by doubling the unit vectors of the high-temperature phase along three axes. The superlattice intensity increases continuously below Ts, which means that the transition is second order. At 100K < T < Ts, a negative thermal expansion is observed along the a- and b-axes. This is closely related to the contraction of K-N interatomic distance. We now focus on the relation between the superconductivity and the local symmetry.

A-8 High Yield Selective Synthesis of C_{60} Dimers

Polymeric fullerenes have attracted considerable interest because of their variety in structure and properties. Both neutral and doped polymers have been synthesized by various techniques. While doped polymers are found to be formed spontaneously by slow cooling to room temperature, polymerization in the neutral state requires activation of C_{60} in terms of light-irradiation or application of external pressure at high temperature. An advantage of high pressure synthesis is that by tuning the temperature and pressure, one can selectively synthesize one- and two-dimensional polymers in a bulk amount by tuning the temperature and pressure.

To control the dimensionality and the degree of polymerization, we found a novel method of squeezing the crystals of a molecular compound of C_{60} and ET, where ET denotes bis(ethylenedithio)tetrathiafulvalene. Squeezing $(ET)_2C_{60}$ at 5 GPa and 200 °C followed by removing unreacted ET molecules produces C_{60} dimers, with an yield of about 80%.

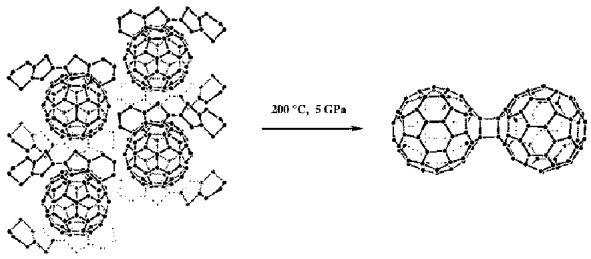

Figure 1. Squeezing organic crystal $(ET)_2C_{60}$ yields a C60 dimer.

A-9 Superconducting and Normal State Properties of Nonavalent Fullerides

Cointercalation of fullerenes with alkali metals and alkaline earth metals provides new opportunities to control the band-filling of fullerides. $A_3Ba_3C_{60}$ (A = K, Rb, and Cs) forms an isostructural series of compounds with a body-centered-cubic structure and tunable lattice parameter, while the nominal molecular valence as C_{60}^{9-}. In sharp contrast with the trivalent face-centered-cubic A_3C_{60}-type superconductors, the density of states at the Fermi energy and Tc decreases with increasing lattice parameter. Analysis by a phonon-mediated pairing model gives relevant parameters which considerably differ from those proposed for the A_3C_{60} superconductors.

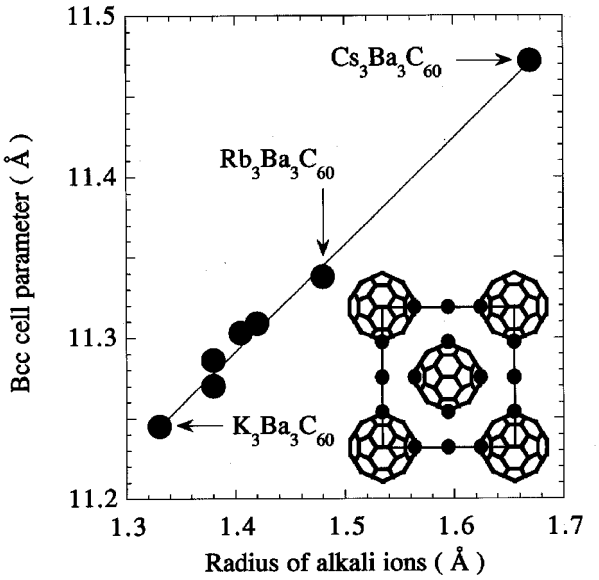

Figure 1. Bcc cell parameter against the ionic radius of alkali metals. The solid line is a guide to the eye. The inset shows a schematic (100) view of the bcc lattice.

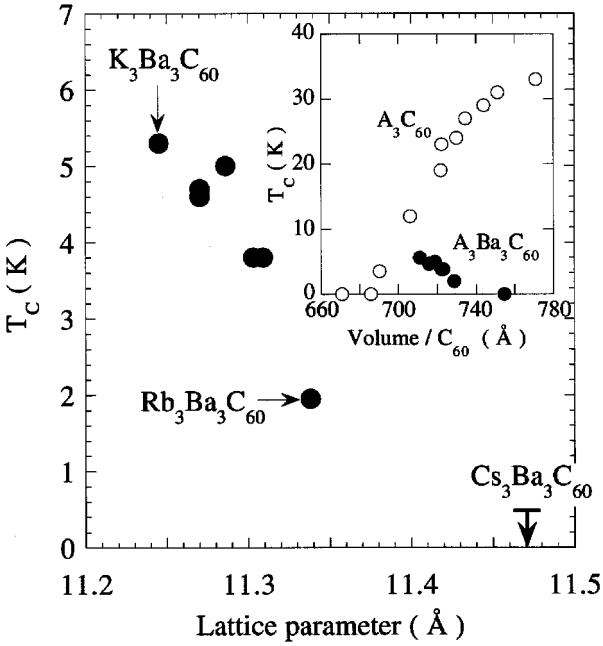

Figure 2. Relation between Tc and the cell parameter for $A_3Ba_3C_{60}$ compounds. The inset shows a direct comparison of Tc-V/C_{60} correlation in A_3C_{60} and $A_3Ba_3C_{60}$.

B. Dioxygen Activation with Chemical Models of Metalloenzymes

Contributors: **Yoshinori NARUTA** *(Kyushu Univ.)*, **Yoshito WATANABE, Fumito TANI** *(Kyushu Univ.)*, **Nobufumi NAKAMURA** *(Kyushu Univ.)*, **Kanako ICHIHARA** *(Kyushu Univ.)* **and Takao SASAKI** *(Kyushu Univ.)*

The aim of this research project is the molecular-level understanding of the reaction mechanism of metalloenzymes participating the molecular conversion of oxygen, i. e., cytochrome P-450, cytochrome c oxidase, oxygen-evolving complex in plant PSII, and sMMO by use of artificial chemical models and the development of new oxidation systems with these catalysts.

B-1 Modeling of Cytochrome P-450 Active Center with New Chiral Porphyrins bearing a Thiolate Axial Ligand

Cytochrome P-450 has an array of polar peptide residues around its O_2-binding/activation site. These groups are assumed to play a key role in proton relay and the acceleration of O-O bond cleavage. As a model compound, we prepared an Fe complex of 'twin-coronet' porphyrin (**TC**) which has hydroxyl groups at the proximal position of the Fe ion inside one cavity and a thiolate ligand in other cavity. Its EPR signal at the oxidized form appeared at $g \approx 2$ which is characteristic of RS^- bound low spin Fe^{III}. The ferric form exhibit higher stability under aerobic conditions at ambient temperature than the relating model compounds ever reported. The reduced form exhibited reversible O_2 binding and the resultant oxy form was assigned by various spectroscopic methods. This is the first example what a heme model bearing a thiolate axial ligand indicated its reversible O_2 binding. The high stability of this complex allows us its high utility as a P-450 model compound.

B-2 New Modeling System of CuB-heme a_3 Site in Cytochrome c Oxidase

Cytochrome c oxidase (CcO) is a member of the super family of terminal oxidases which reduce dioxygen to water with concomitant translocation of proton through a membrane. Though the detailed oxygen reduction mechanism has not well revealed, it is believed that $Fe^{IV}(=O)$ or $Fe^{IV}(=O)P^{+\cdot}$ is involved in the catalytic cycle. As a model of the oxygen metabolic center (heme a_3-CuB site) in CcO, tris(pyridylmethyl)-amino group (TPA)-linked porphyrin derivatives were prepared. In dry CH_3CN, the reduced form Fe^{II}-Cu^I gave the corresponding O_2 complex at ambient temperature. As the result of its structural assignment by resonance Raman, UV-vis, ESI-MS, and EPR spectroscopies. μ-1,2-peroxo bond is present in the oxy form. This is the first example what the structure of the oxy form in CcO model complex was undoubtedly assigned. We also proposed this structures as a 'resting state' model of CcO before the report regarding the enzyme resting-state strucute by X ray. The finding and assignment of the peroxo form allow us the proposal of the new O_2 activation intermediate involving the Cu ion, whose role in the catalytic reaction has been ignored so far. The kinetics and thermodynamic properties of the O_2-complex formation and the decomposition of the peroxy form has also been studied.

B-3 Formation and Characterization of Convergent High-Valent Mn Oxo Porphyrins as a Model Complex of Oxygen-Evolution in PSII

Manganese porphyrin dimers having appropriate Mn-Mn separation showed catalytic activity toward O_2 evolution by water oxidation under anodic oxidation. In order to determine the active intermediate and the reaction mechanism of this reaction, oxidation of the dimanganese complex with peroxy acid has been carried out. Detailed analysis of the course of the oxidation revealed the stepwise formation of $Mn^V(=O)$ intermediate through the corresponding Mn^{III} perbenzoate complex, then intramolecular electron transfer between Mn^V to Mn^{IV} to result in the formation of the $Mn^{IV}{}_2$. In this way, we succeeded the formation of $Mn^{IV}(OH)_2$ dimer and its assignment by spectroscopic methods, which is considered to be the S_3 stae of OEC.

B-4 Preparation of Diiron Complexes with a Polyazamacrocyclic Ligand

In soluble methane oxygenase (sMMO) and some copper enzymes, dinuclear iron (or copper) core is assigned to be its active site. sMMO catalytically oxidizes saturated hydrocarbons including methane to the corresponding alcohols. In many enzyme models so far reported, the preferential ligand oxidation over a

substrate is one of the most serious problem in their dioxygen activation chemistry. In order to prevent the undesired ligand oxidation, we designed polyazamacrocycles as ligands, which can keep the ligand methylene group away from the active metal site and can fix the two metal ions with keeping the suitable separation between them as well. By treatment of the ligand with suitable iron salt, we can obtained the diiron complex in a good yield. Its separation and purification has also been established.

C. Multi-Functional Molecular Solids with π-d Electronic Structures

Contributors: **Hayao KOBAYASHI, Susumu KITAGAWA** *(Tokyo Metropolitan Univ.)***, Masahiro YATASHITA** *(Nagoya Univ.)***, Norimichi KOJIMA** *(Univ. Tokyo)***, Toshiaki ENOKI** *(Tokyo Inst. Tech.)* **and Hiroshi KITAGAWA** *(JAIST)*

Recently the electric, magnetic and optical properties of molecular crystals have attracted an increasing interest from the viewpoint of the development of new functional molecular solids. The aim of this research project is the development of multi-functional molecular solids, especially the magnetic molecular metals. In spite of many recent efforts, there seems to be no good example of organic conductor showing the important role of the interaction between π conduction electrons and localized magnetic moments of anions incorporated in the crystal. Here we present an example of our recent studies on the π-d conducting systems.

C-1 Organic Metals and Superconductors incorporating Magnetic Anions

Since the first discovery of semiconducting nature of crystals of phtalocyanine and the condensed aromatic hydrocarbons about a half of a century ago, a great progress has been achieved in the field of molecular conducting systems. Contrary to the old idea that the molecular crystals are poor conductors, a large number of organic superconductors have been developed recently and the organic superconductors are no more rare materials. In order to cultivate new field in the organic conductors, we have tried to obtain the electrically and magnetically active molecular systems by incorporating magnetic ions and found a new series of organic metals and superconductors, λ-$BETS_2Fe_xGa_{1-x}Br_yCl_{4-y}$ where π-d interaction between conduction electrons of BETS layers and 3d localized magnetic moments of tetrahalide anions play a crucial role. With varying the mixing ratio of metal atoms (Fe, Ga) and/or halogen atoms (Br, Cl), we could control finely the electric and magnetic properties of the system. Recently we have discovered the unprecedented super-conductor-to-insulator transition of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ and proposed a characteristic π-d coupled antiferromagnetic spin structure in λ-$BETS_2FeCl_4$. Figure 1 shows the unique susceptibility behavior of λ-$BETS_2FeCl_4$ around the metal-insulator transition temperature (TMI), which suggests the development of π-d coupled antiferromagnetic spin structure below TMI. In addition, we have found that λ-$BETS_2FeCl_4$ becomes the first antiferromagnetic organic metal at high pressure. Although the details of the newly found various novel physical properties of λ-$BETS_2Fe_xGa_{1-x}Br_yCl_{4-y}$ remains to be clarified, it may be said that λ-$BETS_2Fe_xGa_{1-x}Br_yCl_{4-y}$ has opened a new stage of the organic conducting systems.

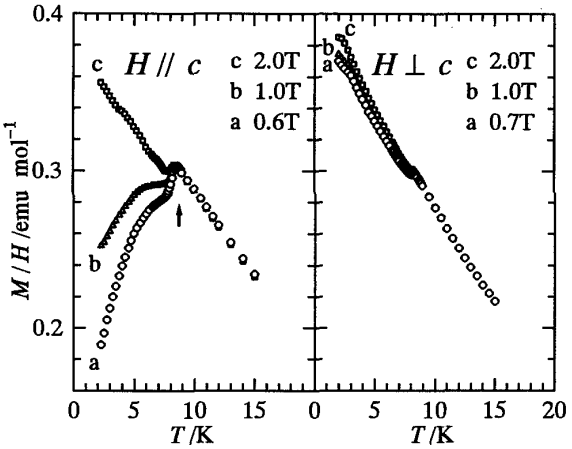

Figure 1. Magnetic susceptibility of λ-$BETS_2FeCl_4$.

D. Molecular Theory of Chemical Reactions in Solution

Contributors: **Fumio HIRATA, Masahiro KINOSHITA** *(Kyoto Univ.)***, Hirofumi SATO, Song-Ho CHONG** *(Kyoto Univ.)***, Tateki ISHIDA** *(Kyoto Univ.)* **and Katsura NISHIYAMA** *(Osaka Univ.)*

There are two aspects in chemical reactions: the reactivity or chemical equilibrium and the reaction dynamics. The reactivity of molecules is a synonym of the free energy difference between reactant and product. Two important factors determining the reactivity in solution are the changes in the electronic structure and the solvation free energy. Those quantities can be evaluated by the coupled quantum and the extended RISM equations, or RISM-SCF theory.

The exploration of the reaction dynamics is much more demanding. The reaction dynamics in solutions has two elements to be considered. One of those is the determination of reaction paths, the other the time evolution along the reaction path. The reaction path can be determined most naively by calculating the free energy map of reacting species. The RISM-SCF procedure can be employed for such calculations. If the rate-determining step of the reaction is an equilibrium between the reactant and the transition state, the reaction rate can be determined from the free energy difference of the two states based on the transition state theory. On the other hand, for such a reaction in which dynamics of solvent reorganization determines the reaction rate, the time evolution along the reaction path may be described by a coupled RISM and the genralized Langevin equation (GLE) with the same spirit as the Kramers theory: the time evolution along a reaction path can be viewed as a stochastic barrier crossing driven by thermal fluctuations and damped by friction. Our treatment features microscopic treatment of solvent structure in the level of the density pair

correlation functions, which distinguishes from the ealier attempts using phenomenological solvent models.

One of prerequisites of developping such a treatment is a theory to describe liquid dynamics in molecular level. In the past year, we have proposed a new theory based on the interaction site model, in which the liquid dynamics is decoupled into the collective modes of density fluctuation: the acoustic and optical modes corresponding, respectively, to translational and rotational motion of molecules.From the point of view, transport coefficients such as the friction can be realized as a response of the collective modes of solvent to the perturbation due to solute. It is the first step of developping a theory of reaction dynamics to describe the stochastic barrier crossing in terms of the collective fluctuatuions of solvent to reacting species along a reaction coordinate properly chosen.

References

1)S. Chong and F. Hirata, *Phys. Rev. E* **57**, 1691 (1998).
2)S. Chong and F. Hirata, *J. Chem. Phys.* **108**, 7339 (1998).

(2) Research Symposia

(from September '97 to August '98)

1. Strongly Correlated Electronic Phases and Dimensional Crossovers in Organic to Inorganic Materials
   (December 11th-13th, 1997)
   Chair: **Kenji YONEMITSU**

2. Development of Molecular Spinics
   (December 12th-13th, 1997)
   Chair: **Katsuya INOUE**

3. Structure and Function of the Complex Integrated Metal Centers in the Biological Systems and Novel Approaches
   (January 12th-14th, 1998)
   Chair: **Takeshi SAKURAI**

4. Recent Advances in Photophysics of Gaseous and Condensed Molecular Systems
   (February 12th, 1998)
   Chair: **Nobuyuki NISHI**

5. Recent Development of Molecular Solids with New Electronic Functions
   (March 5th-6th, 1998)
   Chair: **Hayao KOBAYASHI**

6. Symposium on Physical Chemistry for Young Researchers of Molecular Science
   (June 3rd, 1998)
   Chair: **Okitsugu KAJIMOTO** *(Kyoto Univ.)*

(3) Cooperative Research

This is one of the most important categories that IMS undertakes for conducting its own research of the common interest to both outside and IMS scientists by using the facilities at IMS. During the first half of the fiscal year of 1997 ending on September 30, 52 outside scientists joined Cooperative Research programs and during the second half, 65 outside scientists did. The names and affiliations of those collaborators are found in Research Activities.

(4) Use of Facility

The number of projects accepted for the Use-of-Facility Program of the Computer center during the fiscal year of 1997 amounted to 188 (719 users) and computer time spent for these projects is 60071 hours (converted to the HITAC M-680H time), and amounted to 70% of the total annual CPU time used. The numbers of projects accepted for the Use-of-Facility Program during the fiscal year of 1997 amounted to 11 for the Laser Research Center for Molecular Science and 39 for the Research Center for Molecular Materials.

(5) UVSOR

In the UVSOR Facility with the 750 MeV electron storage ring, there are twenty beam lines available for synchrotron radiation research (see "UVSOR ACTIVITY REPORT 1997"). The experimental facility of each beam line is described also in this report. Under the following programs, a number of synchrotron radiation studies have been carried out by many users outside and inside IMS: A. the UVSOR Special Projects, B. the UVSOR Cooperative Research Projects, C. the UVSOR Invited Research Projects, and D. the Use-of-UVSOR Projects.

A. UVSOR Special Projects

In the fiscal year of 1997, the following UVSOR special projects were carried out.

1. Title: Construction of multilayer monochromator system for photochemical reactions
   Beam Line: 4A
   Representative: **Tsuneo URISU**
2. Title: Upgrade of VUV beam line with installation of new monochromator
   Beam Line: 7B
   Representative: **Hideyuki NAKAGAWA** *(Fukui Univ.)*
3. Title: Improvement of the double crystal monochromator at BL7A
   Beam Line: 7A
   Representative: **Toyohiko KINOSHITA**

B. UVSOR Cooperative Research Projects

Under these joint studies programs, many synchrotron radiation experiments have been carried out with the beam lines of in-house staff in cooperation with scientists who were invited from other institutions. The total number of the projects in this category was 23 in the fiscal year of 1997.

C. UVSOR Invited Research Projects

Under these joint studies programs, several scientists were invited from other institutions of help for construction of new beam lines, improvement of the UVSOR storage ring and other cooperative works. The total number of the projects in this category was 1 in the fiscal year of 1997.

D. Use-of-UVSOR Projects

Eleven out of the total of twenty UVSOR beam lines are available for general users outside and inside IMS for their synchrotron radiation studies in the field of molecular science. The total number of the projects in this category was 153 in the fiscal year of 1997.

FOREIGN SCHOLARS

Visitors from abroad are always welcome at IMS and they have always played an important role in the research activities of the Institute. The foreign scientists who visited IMS during the past year (Aug. 1997 - Aug. 1998) are listed below.

*1 indicates attendance at an Okazaki Conference; *2 a MONBUSHO (the Ministry of Education, Science, Sports and Culture, Japan) or JSPS (the Japan Society for the Promotion of Science) Invited Fellow; *3 an IMS councillor; *4 an IMS visiting professor or associate professor from abroad (period of stay from 6 to 12 months); *5 a JSPS Post-Doctoral or Ronpaku Fellow; *6 an IMS visiting scientist and *7 a visitor to IMS.

Scientists who would like to visit IMS under programs *2 and *4 are invited to make contact with IMS staff in their relevant field.

Prof. L. G. Marzilli*2*5	Emory Univ.	(U.S.A.)	-Aug. '97
Dr. P. A. Marzilli*6	Emory Univ.	(U.S.A.)	-Aug. '97
Prof. M. Cho*2	Korean Univ.	(Korea)	-Aug. '97
Dr. Janvan Elp*7	Inst. of Phys. and Astronomy Univ. of Aarhus	(Denmark)	Aug. '97
Dr. Roman Tatchyn*7	SSRL, SLAC	(U.S.A.)	Aug. '97
Dr. G. N. Kulipanov*7	Synchrotron Radiation Laboratory	(Russia)	Aug. '97
Dr. M-E. Couprie*7	Univ. de Paris Sud.	(France)	Aug. '97
Prof. Volker Saile*7	CAMD,Luisiana Univ.	(U.S.A.)	Aug. '97
Dr. C. G. Khanmalek*7	Luisiana State Univ.	(U.S.A.)	Aug. '97
Prof. Jik Chin*6	McGill Univ.	(Canada)	Aug. '97
Prof. A. Rosen*7	Chalmers Univ. of Tech.	(Sweden)	Aug. '97
Prof. I. H. Munro*7	Univ. of Manchester Inst. of Sci. and Tech.	(U.K.)	Aug. '97
Prof. E. Morikawa*7	CAMD, Louisiana State Univ.	(U.S.A.)	Aug. '97
Prof. V. Zaile*7	CAMD, Louisiana State Univ.	(U.S.A.)	Aug. '97
Prof. R. V. Nandedkar*7	Centre for Advanced Tech.	(India)	Aug. '97
Prof. Y. Ufuktepe*6	Cukurova Univ.	(Turkey)	Aug.-Sep. '97
Prof. J. N. Onuchic*2	Univ. of California	(U.S.A.)	Aug.-Nov. '97
Mr. P. Severino*6		(Italy)	-Sep. '97
Dr. S. C. Jeoung*6	Korea Res. Inst. of Standards and Sci.	(Korea)	-Sep. '97
Prof. A. P. Hitchcock*6	McMaster Univ.	(Canada)	Sep. '97
Prof. D. N. Hendrickson*7	UC, San Diego	(U.S.A.)	Sep. '97
Dr. M. W. George*7	Dept. of Chemistry, Univ. of Nottingham	(U.K.)	Sep. '97
Dr. M. Marsi*7	Trieste, Elettra	(Italy)	Sep. '97
Dr. M. Neeb*7	Julich Research Center	(Germany)	Sep. '97
Prof. H. Ågren*7	Linköping Univ.	(Sweden)	Sep. '97
Prof. R. B. Lyubovskii*7	Inst. of Chemical Physics in Chernogolovka	(Russia)	Sep. '97
Dr. A. Chasse*7	Martin-Luther-Universitat Halle-Wittenberg	(Germany)	Sep. '97
Prof. Leo Meerts*7	Univ. of Nijmegen	(Holland)	Sep.-Oct. '97
Dr. G. Milinikov*6	Inst. of Structural Macrokinetics Russian Acad. of Sci.	(Russia)	Sep.-Nov. '97
Prof. O. Vasyutinskii*2	Russian Academy of Science	(Russia)	-Oct. '97
Prof. B. J. Robert*2	Wuppertal Univ.	(Germany)	Oct. '97
Prof. J. Havacek*2	Charles Univ.	(Czech)	Oct. '97
Dr. S. Hayward*7	Bioson Research Inst. Groninger	(U.K.)	Oct. '97
Prof. S. Berry*7	Univ. of Chicago	(U.S.A.)	Oct. '97
Dr. Li Yumin*6		(China)	Oct.-Dec. '97
Dr. Andriy Kovalenko*4	Inst. for Condensed Math. Phys. Ukrainan Acad.	(Ukraina)	Oct. '97-Jul. '98
Prof. Jiri Horacek*7	Charles Univ.	(Czech)	Oct. '97
Prof. I. H. Munro*2	Univ. of Manchester Inst. of Sci. and Tech.	(U.K.)	Oct. '97-Aug, '98
Dr. M. P. Roach*5	Univ. of South Carolina	(Canada)	Nov. '97-
Dr. Chin-Kun Hu*6	Inst. of Phys. Academia Sinsia	(Taiwan)	Nov. '97
Prof. A. A. Pavlychev*6*7	St. Petersburg Univ.	(Russia)	Nov. '97
Mr. H. P. N. J. Gunasekara*7	Ceylon Inst. of Sci. and Indnstrial Research	(Srilanka)	Nov.-Dec. '97
Dr. T. Steffen*7	Univ. Groningen	(Holland)	Nov'97-Jan. '98
Dr. Haiyang Li*6	Dalian Institute of Physics	(China)	-Nov. '97
Prof. A. S. Markosyan*5	Moscow State Univ.	(Russia)	-Dec. '98
Dr. J. Hrusak*2	Acad. of Sci. of the Czech Republic	(Czech)	Dec. '97
Dr. J. S. Villarrubia*7	National Inst. of Standard and Tech.	(U.S.A.)	Dec. '97
Prof. M. J. Wojcik*4	Jagiellonian Univ. , Faculty of Chem.	(Poland)	Dec. '97-
Dr. K. Mohanalingham*6	Waseda Univ.	(Japan)	-Jan. '98
Prof. N. G. Hwang*7	Dankook Univ.	(Korea)	Jan. '98
Dr. Vladmir Chern*6	Rochester Univ.	(U.S.A.)	Jan. '98
Prof. Minhaeng Cho*2	Korea Univ.	(Korea)	Jan.-Feb. '98

Prof. V. Osherov[*1]	Rossian Acad. of Sci.	(Russia)	Jan.-Mar. '98
Dr. Wang Li[*6]	Dalian Inst. of Chem. Phys.	(China)	Feb. '98-
Prof. Ingolf Hertel[*7]	Max-Born Institute	(Germany)	Feb. '98
Dr. E. E. B. Campbell[*7]	Max-Born Institute	(Germany)	Feb. '98
Ms. Ja-Young Han[*7]	Korea Advanced Inst. of Sci. and Tech. (KAIST)	(Korea)	Feb. '98
Mr. H. S. Cho[*7]	Soul National Univ.	(Korea)	Feb. '98
Dr. Yong-Ki Kim[*7]	National Inst. of Standards and Tech.	(U.S.A.)	Feb. '98
Prof. Jiri Horacek[*2]	Charles Univ.	(Czech)	Feb.-Apr. '98
Dr. Mikhail Vener[*2]	Karpov Inst. of Physical Chemistry	(Russia)	Feb.-Apr. '98
Dr. Nakul C. Maiti[*5]	Tata Inst. for Fundamental Res.	(India)	Feb. '98-
Dr. M. Basharov[*6]	Inst. of Theol. and Exper. Biophy. Russian Acad. of Sci.	(Russia)	Mar. '98
Prof. D. P. Ballou[*6]	Univ. of Michigan	(U.S.A.)	Mar. '98
Dr. J. V. Yakhmi[*6]	High-Tc Research, Chemistry Division, Bhabha, Atomic Research Centre	(India)	Mar. '98
Dr. Miroslav Mensik[*7]	Acad. of Sci. of the Czech Republic	(Czech)	Mar. '98
Prof. John C. Light[*6]	The Univ. of Chicago	(U.S.A.)	Mar. '98
Prof. R. D. Levine[*3]	The Hebrew Univ. of Jerusalem	(Israel)	Mar. '98
Dr. F. Remacle[*7]	Univ. de Lieql	(Belgium)	Mar. '98
Dr. N. Kouchtsh[*7]	Inst. of Chemical Physics, Russian Acad. of Sci.	(Russia)	Mar. '98
Prof. C. C. Martens[*7]	Univ. of California	(U.S.A.)	Mar. '98
Prof. G. A. Voth[*7]	Univ. of Utah	(U.S.A.)	Mar. '98
Dr. Tsu-Fan Cheng[*7]	National. Tsing Hua Univ.	(Taiwan)	Mar. '98
Dr. C-Hsiung Chan[*7]	National. Tsing Hua Univ.	(Taiwan)	Mar. '98
Prof. T. N. Truong[*7]	Univ. of Utah	(U.S.A.)	Mar. '98
Dr. Robert Gareth[*7]	Cambridge Univ.	(U.K.)	Mar. '98
Dr. Albert Stolow[*7]	Steacie Inst. ,NRC	(Canada)	Mar. '98
Prof. Todd Martinez[*7]	Department of Chemistry, Univ. of Illinois	(U.S.A.)	Mar. '98
Prof. V. Aquilanti[*7]	Univ. of Perugia	(Italy)	Mar. '98
Prof. Michael Baer[*7]	Soreq Nuclear Research Center	(Israel)	Mar. '98
Prof. Michael Robb[*7]	King's College London	(U.K.)	Mar. '98
Prof. Mark S. Child[*7]	Physical and Theoretical Chemistry Laboratory	(U.K.)	Mar. '98
Prof. G. D. Billing[*7]	Univ. of Copenhagen	(Denmark)	Mar. '98
Prof. J-Kang Hwng[*7]	National. Tsing Hua Univ.	(Taiwan)	Mar. '98
Prof. Lee Yoon Sup[*7]	Korea Advanced Inst. of Sci. and Tech.	(Korea)	Mar. '98
Prof. Seokmin Shin[*7]	Seoul National Univ.	(Korea)	Mar. '98
Dr. Michael Ward[*7]	Univ. of Bristol	(U.K.)	Mar. '98
Prof. P. J. Knowles[*7]	Univ. of Birmingham	(U.K.)	Mar. '98
Dr. Ilya Rips[*7]	Weizmanr Inst. of Sci.	(U.S.A.)	Mar. '98
Prof. Casey Hynes[*7]	Centre Natl. Recherche Sci. (CNRS)	(France)	Mar. '98
Prof. A. Kahn[*7]	Prinston Univ.	(U.S.A.)	Mar. '98
Prof. H. Meyer[*6]	Univ. of Georgia	(U.S.A.)	Mar. '98
Prof. Richang Lu[*6]	Dalian Inst. of Chem. Phys.	(China)	Mar. '98
Prof. Hanna Reisler[*6]	Univ. of South California	(U.S.A.)	Mar. '98
Prof. K. M. Dethlefs[*7]	Univ. of York	(U.K.)	Mar. '98
Prof. M. Shapiro[*7]	Weizmann Inst. of Sci.	(Israel)	Mar. '98
Prof. A. N. Brito[*6]	Brazil Univ.	(Brazil)	Mar. '98
Prof. G. A. Blake[*7]	California Inst. of Tech.	(U.S.A.)	Mar. '98
Prof. S. Nespurek[*2]	Acad. of Sci. of the Czech Republic	(Czech)	Mar.-Apr. '98
Prof. B. Hamilton[*6]	Univ. of Manchester Inst. of Sci. and Tech.	(U.K.)	Mar.-Apr. '98
Prof. B. N. Viktorovich[*6]	Physical Faculty, Ural State Univ.	(Russia)	Mar.-May '98
Dr. S. Nilmoni[*5]	RIKEN	(Japan)	Mar.-Jun. '98
Dr. S. Mukhopadhyay[*5]	Ind. Assoc. for the Cultivation of Science	(India)	Mar. '98-
Dr. A. Fiedler[*5]		(Germany)	-Apr. '98
Prof. Xin Sun[*4]	Fudan Univ.	(China)	-Apr. '98
Prof. Mishra Manoj[*7]	Department of chemistry IIT Bombay	(India)	Apr. '98
Prof. C. Varotsis[*2]	Univ. of Crete	(Greece)	Apr.-Jul. '98
Prof. James M. Lisy[*2]	Univ. of Illionis	(U.S.A.)	Apr.-Aug. '98
Dr. B. Stephane[*5]	Universite des Sci. s & Technologiede Lille	(France)	Apr. '98-
Mr. A. Tiagilev[*7]	Russian Research Inst. "Kurchatov Inst. "	(Russia)	May. '98
Dr. M. Vadim[*7]	Russian Research Inst. "Kurchatov Inst. "	(Russia)	May. '98
Prof. V. Stankevitch[*6]	Russian Research Inst. "Kurchatov Inst. "	(Russia)	May. '98
Dr. Olga O. Drozdova [*7]	Russian Acad. of Sci.	(Russia)	May. '98
Mr. U. Prawatwong[*7]	Natl. Synchrotron Res. Center Suranaree Univ. of Techrology	(Thailand)	May. '98

Dr. P. Songsiriritthigul[*7]	Natl. Synchrotron Res. Center Suranaree Univ. of Techrology	(Thailand)	May. '98
Prof. Kimoon Kim[*7]	Pohang Univ. of Sci. and Tech.	(Korea)	May. '98
Prof. Sutclifle Brian[*7]	Univ. of York	(U.K.)	May. '98
Prof. Jean-Pierre Tuchagues[*7]	Univ. Panl Sabatier	(France)	Jun.-Jul. '98
Prof. K-Koo Baeck[*2]	Kang-Nung Univ.	(Korea)	Jun.-Aug '98
Prof. Seokmin Shin[*6]	Seoul National Univ.	(Korea)	Jun.-Aug '98
Prof. Y. Kim[*2]	Hankuk Univ. of Foreigh Studies	(Korea)	Jun. '98-
Dr. M. V. Simonyan[*4]	Inst. for Phys. Res. of Armenian National Acad. of Sci.	(Armenia)	Jun. '98-
Prof. Xian-He Bu[*2*6]	Nankai Univ.	(China)	Jun. '98-
Dr. Olga O. Drozdova[*7]	Russian Acad. of Sci.	(Russia)	Jul. '98
Prof. Gang Ho Lee[*7]	Kyungpook National Univ.	(Korea)	Jul. '98
Prof. Maochun Hong[*7]	Fujian Inst. of Res. on the structure of Matter	(China)	Jul. '98
Mr. Lee Martin[*2]	The Royal Institution of Great Britain	(U.K.)	Jul.-Aug. '98
Dr. Olga O. Drozdova[*7]	Russian Acad. of Sci.	(Russia)	Aug. '98
Prof. Takashi Yonetani[*4]	Univ. of Pennsylvania	(U.S.A.)	Aug. '98
Dr. Lars Pettersson[*4]	Stockholm Univ.	(Sweden)	Aug. '98-

AWARDS

Emeritus Professor Kimura's Scientific Achievements

Dr. Katsumi Kimura, a professor emeritus (professor: 1979-1992), was honored as the 1998 Purple Ribbon by the Government for his distinguished contributions to physical chemistry. The Purple Ribbon is given to distinguished people in science and art in Japan. His scientific achievements are summarized as following.

1. Vacuum ultraviolet photoelectron spectroscopic studies of whole valence electron structure for various fundamental organic molecules.
2. The development and application of synchrotron radiation ionization spectroscopy for studying molecular clusters.
3. The development and application of laser multi-photon ionization photoelectron spectroscopy for studying excited-state molecules.
4. The development and application of zero-kinetic-energy photoelectron spectroscopy for cation vibrational spectroscopy of jet-cooled molecules and van der Waals complexes.

Associate Professor Suzuki's Scientific Achievements

Associate Professor Toshinori Suzuki of the Department of Electronic Structure received the Award of the Spectroscopical Society of Japan in 1998 for his contribution entitled "Studies on Chemical Reaction Dynamics by Photoion Imaging" published in Journal of the Spectroscopical Society of Japan.

The final state distribution of products and their dependence on the initial state of reactants are key to understanding the chemical reaction mechanism. The photoion imaging presented by Professor Suzuki enables us to measure the product distribution in space and energy with a single quantum state selectivity. Professor Suzuki has combined the photoion imaging with laser spectroscopy and has revealed the photodissociation mechanism of a small molecule, such as NO_2 and OCS with clear experimental evidence. His works summarized in the paper were thus evaluated as the creative contribution in spectroscopy and dynamics in the year.

Associate Professor Inoue's Scientific Achievements

Associate Professor Katsuya Inoue of Department of Applied Molecular Science received the Morino Science Award for Molecular Scientists in 1997 for his contribution to "The Design and Synthesis of Molecular-based Magnets by the Self-Assemblage of Nitroxide Radicals and Transition Metal Ions". His scientific achivements relevant to the award are summarized as follows.

1. Synthesis of high-spin polynitroxides.
2. Construction of molecular-based ferrimagnets by self-assemblage of transition metal ions with high-spin polynitroxide radicals.

Associate Professor Sarukura's Scientific Achievements

Associate professor Nobuhiko Sarukura of Laser Research Center for Molecular Science received the Researcher Paper Award (original) of the Laser Society of Japan in 1998 for their contributions on "Broad-Band, Low-Loss Mirror for Tunable Laser", together with Dr. N. Yamamura, Dr. R. Uchimura, Dr. M. Maeda, Dr. S. Kimura, and Dr. Izawa in Showa Optronics Corporation.

Their main scientific contribution is that they developed an extremely broad-band, super high reflection mirror. Typically, it is requested to change 4 sets of optics for obtaining full tuning of Ti:sapphire laser (670-1100 nm). This inconvenience was due to the restricted performance of a dielectric coated mirror. Owing to the sophisticated design of gradually varying thickness quarter wave dielectric coatings and improved electron-beam deposition technique, they have succeeded in fabricating broad-band, high reflection mirrors which meet the requirements for full tuning of a cw Ti:sapphire laser. Using these mirrors in a Ti:sapphire laser, they have demonstrated the tuning from 663 nm to 1095 nm. This technological breakthrough will make all tunable-laser systems including Ti:sapphire lasers and OPO's much more powerful and attractive.

Emeritus Professor Iwamura's Scientific Achievements

Emeritus Professor Hiizu Iwamura, currently Professor of National Institution for Academic Degrees, received the Fujiwara Science Award in 1998 for his contribution to "The Design and Synthesis of Molecular-based Magnetic Materials by the Assembly and Spin Ordering of Free Radicals". His scientific achivements relevant to the award are summarized as follows.

1. Synthesis of super-high-spin polycarbenes (up to $S = 9$).

2. Systematization of the molecular ferromagnetic couling units.
3. Synthesis of a number of stable triplet bis- and quartet trisaminoxyl radicals.
4. Construction of molecular-based ferro- and ferrimagnets (Tc in the range 3.4-46 K) by self-assemblage of magnetic metal ions with high-spin oligoaminoxyl radicals as ligands.
5. Approaches to photomagnetic ferri- and ferromagnetic materials.

It is to be noted that the original work was initiated in the early 80s at IMS when he was Director and Professor of Division of Applied Molecular Science.

Nagakura Award to Mr. Takeshi Tomita

This award was founded in 1995 on the basis of donation from Prof. Saburo Nagakura, the first president of the Graduate University for Advanced Studies, to encourage students to open a new field of science and/or to challenge some pioneering work and is yearly given to a few promising students of this university. T. Tomita is the first winner in this institute.

Mr. Tomita has graduated from the Engineering Department of Kyoto University, where he learned theoretical chemistry based on ab initio MO calculations (Prof. Hiroshi Nakatsuji's lab). Subsequently he studied solvent extraction under the under the supervision of Prof. Masakazu Matsui in Institute of Chemistry, Kyoto University. After two years of master course in analytical chemistry, he entered into the Graduate University for Advanced Studies, and started the investigation of structure-function relationship of hemeproteins in my laboratory.

Tomita has succeeded in isolating soluble guanylyl cyclase (sGC), which is a physiological receptor of NO in animal tissues and catalyzes the formation of cGMP from GTP. He used rat brain first but he could not observe even the strongest absorption band for the preparations obtained from 100 pieces of rats. Second he tried bovine lung. After long struggles including chemical modifications of column materials, he succeeded in obtaining 3 mg of sGC from 4 kg of bovine lung. Accordingly, he established the method of purification. He found that this protein has one heme per a molecule consisting of two subunits and is ADP-ribosylated in the presence of a toxin similar to general G proteins. The enzymatic activity of the ADP-ribosylated enzyme became higher ~ 10 fold but it was only the β subunit that underwent ADP-ribosylation. Upon binding of NO to sGC, the enzymatic activity was raised by 200 fold. Resonance Raman spectra of the NO-bound sGC indicated cleavage of the Fe-histidine bond which is stable before incorporation of NO. Furthermore, Tomita found that the NO stretching Raman band of the NO-bound sGC exhibits splitting as the proceed of the enzymatic reaction. He ascribed it to the binding of a product, cGMP, to the heme pocket, and inferred it a negative feedback regulation. To understand the meaning of splitting of the NO stretching band, he investigated resonance Raman spectra of the NO complex of myoglobin and its mutants at neutral and acidic pH. He observed a shift of NO stretching mode upon mutation of some residues and deduced the origin of the splitting in sGC from the studies of myoglobin.

He worked not only very hard but also challenged difficult problems with an indomitable will. He leanred something from failures. I want to bless him and wish his good luck as a research associate in Tohoku University.

Mr. Liu's Scientific Achievements

Mr. Zhenlin Liu, who is a graduate student studying in the Laser Research Center for Molecular Science, received the Excellent Presentation Award of the Laser Society of Japan in 1998 for his contributions on "All Solid State Tunable Ultraviolet Picosecond Ce:$LuLiF_4$ Laser".

This award is given to young scientists (under 35 years old) who made contributions to the development of laser science and gave excellent presentation at the Annual Meeting of the Laser Society of Japan.

LIST OF PUBLICATIONS

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