SPECIAL RESEARCH PROJECTS

IMS has special research projects supported by national funds. Three projects in progress are:
(a) Chemical Reaction Dynamics
(b) Molecular Photophysics and Science
(c) Novel Material Science

These three projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

(a) Chemical Reaction Dynamics

Folding Mechanism of Protein Molecules Studied by Generalized-Ensemble Algorithms

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Proteins are the most complicated molecules that exist in nature. Since protein structures are closely related to their biological functions, the understanding of their folding mechanism from the first principles is not only very challenging but also very important 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-acid sequence information. However, nobody has completely succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles.)

There are two elements for the difficulty. One element is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be considered is very large. The other element for the difficulty is that there exist huge number of local minima in the energy function, and simulations by conventional techniques will necessarily get trapped in one of the local minima without ever finding the energy global minimum. Generalized-ensemble algorithms are new simulation algorithms that can alleviate this second difficulty (for reviews, see Refs.1-3). We have been developing new generalited-ensemble algorithms. We found that the replica-exchange method and its extension are particularly promising.3)

The goal of the present project is to further develop and test the effectiveness of generalize-ensemble algorithms in the protein folding problem and to succeed eventuallyin the prediction of tertiary structures of proteins from the first principles.

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Development and Applications of Basic Theories of Nonadiabatic Transitions, Chemical Reactions, and Their Control

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Based on the Zhu-Nakamura theory1) of non-adiabatic transition due to potential curve crossing, we are developing new semiclassical methods to effectively deal with electronically nonadiabatic chemical reactions. First, we incorporate our Zhu-Nakamura theory into the trajectory surface hopping (TSH) method. Taking the DH_2^+ system as a typical example of seam crossing, we have tested the idea in comparison with the old version of TSH based on the Landau-Zener formula and the exact quantum calculations. Not only the collinear but also 3D reaction systems are studied, and the Zhu-Nakamura theory was found to improve the method significantly. This is very encouraging, since this tells us that we can apply this new method to large reaction systems. We are planning to apply this method to conical crossing case also, which is an application of the nonadiabatic tunneling case of Zhu-Nakamura theory. We further plan to develop semiclassical methods with use of Zhu-Nakamura theory even with all the phase effects included.

In order to develop the above mentioned general methods, we have to further work out to formulate basic theories of nonadiabatic transitions applicable to other cases such as Renner-Teller type transition.

Another important project we are working on is the laser control of molecular processes. Here again, the various types of nonadiabatic transitions play essential roles, since in the so called dressed state picture we can create potential curve crossing by shining molecules by laser and further more we can control nonadiabatic transitions at the newly created avoided crossings by manipulating lasers. We have proposed the following two new ideas for that;1,2) (1) usage of the complete reflection phenomenon, and (2) control by a train of linearly chirped pulses. The first idea is based on the intriguing phenomenon occurring in the nonadiabatic tunneling type transition and can be realized by using a stationary laser field. The second is to use the interference phenomenon in nonadiabatic transitions induced by periodical chirping of laser frequencies. Since the basic analytical theories are available, we can design necessary conditions analytically. The idea can be applied to dynamic processes in an external field other than laser, namely to NMR and ESR problems.

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Proton Tunneling in a Dissipative Environment: Raman Response and ReactionRate

TANIMURA, Yoshitaka

A double well potential system coupled to a colored Brownian oscillators bath is considered to study tunneling dynamics in a dissipative environment. The quantum Fokker-Planck equation for a colored noise bath in a low temperature is reduced in a multi-dimensional hierarchy form. A chemical reaction rate and Raman response spectrum are calculated for various coupling strength and temperature. Compared with the classical results, which are obtained by solving classical Fokker-Planck equation, we investigate the effects of tunneling processes on the reaction rate and spectrum. In the quantal case, the low frequency peak is observed in the Raman spectrum, which is due to the level splitting of vibrational levels induced by tunneling.

Constructing Molecular Theory of Chemical Process in Solution

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Our current research interests and activities are concentrated upon three important chemical processes in solution, in each of which solvent plays essential role: (A) the electronic structure of a molecule in solution, (B) solvation thermodynamics of protein and related molecules, (C) characterization of spatial and temporal density fluctuation in molecular liquids, and (D) molecular theory of electrode-solution interface.

The RISM theory, an integral equation theory of molecular liquids, is our main machinery to attack the problem, which is coupled with other theoretical methodologies including the ab initio molecular orbital method, molecular simulations, and the generalized Langevin equation. Problems on which we have been working along the four lines are as follows:

1. Solvent effect on nuclear magnetic shielding of a molecule in solution.
2. Partial molar volume of biomolecules and their stability upon pressure.
3. Stability of peptide and protein conformations in aqueous solution.
4. Solvation dynamics and thermodynamics of ions and molecules.
5. Non-equilibrium free energy surface related to electron transfer reactions
6. Dynamical coupling between intra- and inter molecular motions in liquids.
7. Description of collective excitation in liquids by interaction site model.
8. Path integral theory of a hydrated electron.
9. Developing DFT theories of molecular liquids.
10. Gas-liquid phase transition.
11. Theory of liquids confined in porous media.
12. Structure of alcohol-water mixture.

Imaging of Chemical Dynamics

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We have constructed a crossed molecular beam apparatus and continued improving its performance over the past 6 years by introducing various new techniques of molecular beams and ion imaging. Its high performance has been proven by observing rotationally inelastic scattering of NO molecule with Ar, where state-resolved differential cross sections were observed, for the first time, for both fine-structure conserving and changing collisions. Based on this success, we set the next target of research at the O(^{1}D) reactions with hydrides, since it is important in the stratosphere. In the year of 2001, some modifications were made on the apparatus to increase the signal level. One is a new light path of 157 nm light for photolysis of molecular oxygen: a new configuration allows a straight through propagation of F2 laser light in the source chamber for which higher flux of 157 nm light. This required reconstruction of a bulkhead and readjustment of a skimmer and a pulsed valve. Another is introduction of pulsed valves that generate much shorter pulses of molecular beams than before. With the courtesy of Professor Uzi Even, we introduced solenoid valves that allow the pulse duration of only 50 microsecond or less. Such a short pulse duration reduces scattering of an molecular beam by a skimmer that would otherwise significantly reduce the flux of high intensity beam. In addition, an oil diffusion pump (2000 L/s) in the O(^{1}D) beam chamber was replaced with a hybrid turbo molecular pump (1600 L/s) to suppress the contamination of a focusing lens for 157 nm light by back streaming of pump oils. The backup pump was also changed from a rotary pump to an oil-free scroll pump. All of these improved the performance of our crossed beam machine, and we are currently working on reactive scattering experiments on O(^{1}D) + H_2 as a test case.

Stereodynamics and Active Control of Chemical Reactions by Using Electrostatic Hexapole State-Selector and Polarized Laser Excitation

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Since mutual orientation between colliding reactants plays a key role in chemical reaction, so-called “steric effect” becomes important for understanding stereodynamics of elementary reactions in the gas phase, and to control them actively. Although orientation dependences of “*atom (spherical)-molecule (vector)*” reactions have been studied, the steric effect of “*molecule (vector)-molecule (vector)*” reaction has not been studied so far using oriented molecules. Typical examples of the “*molecule-molecule*” reaction are the OH + NO radical reaction and the $(Si)_n$ + OH cluster reaction, which our special research project challenges. Our experimental strategy is to select molecular orientation by use of hexapole state-selector and/or linearly polarized laser. Thus, we have built a new crossed-beam apparatus with a 1-m long hexapole electric field and we have installed a new set of tunable YAG-dye laser system. There are three on-going objectives of our special project as presented in the following.

1) We investigate the photodissociation of the DCl dimer, which is preferentially size-selected by the hexapole electric field. We succeeded in detecting [ClDCl] transient species through the hydrogen elimination from $(DCl)_2$ by a Doppler-selected TOF technique. The structure of the observed TOF spectrum represents a vibrational state distribution of [Cl–D···Cl], reflecting strong perturbation from the adjacent Cl atom in [ClDCl].
2) We are investigating the reaction of oriented-OH with aligned-NO. The OH radicals are produced by a dc-discharge of H_2O seeded in Ar. We then state-select their orientation by the hexapole. NO is aligned by the linearly polarized UV laser. The hydrogen atom in the $OH + NO \rightarrow NO_2 + H$ reaction and NH product in the $OH + NO \rightarrow NH + O_2$ reaction are detected by REMPI and LIF, respectively. Orientation dependence of the branching ratio of the two reaction channels should provide an insight into details of stereodynamics.
3) We investigate the cluster reaction of OH with Si_n. Metal cluster source using laser vaporization is newly constructed. We temporarily obtain the result that Si monomer and dimer concentrations in the cluster beam can be control by changing the timing of the vaporization laser. Experiment is now being carried out to clarify steric effects on reactivity in van der Waals interaction within the cluster.

Monte Carlo Simulation of Chemical Gel

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Gel is an important material used in engineering and medicine. We studied the structure of chemical gel using Monte Carlo simulation with modeled radical reactions. Simulation is performed using beads-spring model in three-dimensional continuous space. For the criterion of gel, we apply the concept of percolation to our clusters; we calculate the maximum size in all directions for each cluster, and sum up the number of percolated direction for all percolated clusters in a system. We call this the number of percolation. We obtained structure information of system from plotting the average number of percolation. We can determine whether the system has percolated clusters, and also whether the polymer network has inhomogeneous structure.

The distributions of degree of polymerization for clusters obtained in this simulation show qualitatively good agreement with the experimental results. Linkers are classified to two types according to the roles in networks, and their ratios are discussed. The normal and weighted ratios of gel are defined using percolation theory. These ratios are compared with the changes in distribution.

Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

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This project is being carried out at the Beamline 4B of the UVSOR facility and at the Beamline I-511 of the MAX-II facility in collaboration with the Uppsala University. We are investigating linear polarization dependence of inner-shell resonant excitations for simple molecules. We are also investigating resonantly-emitted photoelectron and photon (fluorescence) spectroscopies for the same systems by tuning the photon energy to inner-shell resonances. In the UVSOR facility we are using crystal monochromators, which restrict the photon energy to the range higher than the Cu and Ni 2p edge (> 800 eV). Recently, we have decided to move our experimental apparatus to the BL 4B, which is a new beamline covering the lower photon energy (< 800 eV). In these studies theoretical investigation is essential and some theoretical approaches are also under development.

Time-Resolved Spectroscopic Study of Photochemical Dynamics in Condensed Phase

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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. Thanks to drastic advance of the laser technology, we are now able to study ultrafast dynamics of the primary chemical processes with pico/femtosecond time-resolution. The aims of this project are (1) development of new techniques and methods in time-resolved spectroscopy, and (2) application of pico/femtosecond spectroscopy to the study of the dynamics of the condensed-phase molecules. Our research activities of this year are summarized as follows, in the order of time-resolution of the experiments. First, by utilizing ‘extremely-short’ optical pulses (Δt ~ ten–a few tens of femtoseconds), we carried out time-resolved measurements to observe vibrational coherence (wavepacket motion) in the excited-state molecules. We observed the wavepacket motion of a photodissociating excited-state molecule in pump-probe measurements, and measured impulsive stimulated Raman scattering of an excited-state polyatomic molecule for the first time. Secondly, with use of time-resolved fluorescence and absorption spectroscopy having a few hundreds femtoseconds time-resolution, we studied excited-state proton transfer of hydroxy anthraquinone derivatives, isomerization of trans-azobenzene, and photodissociation of diphenylcyclopropenone. Thirdly, we applied picosecond time-resolved Raman spectroscopy to the study of solvated electrons and found a novel resonance Raman effect of the solvating molecules. We also demonstrated high potential of the up-conversion technique for temporal fluorescence rejection in Raman spectroscopy.

Theoretical Study of Vibrational States for AlNC/AlCN

MINAMINO, Satoshi; NANBU, Shinkoh; AOYAGI, Mutsumi

The character of the low-lying electronic states of AlNC strongly depends on the bond distance of Al-NC, because the covalent states are lying closely to the ionic states. Especially, due to the electronic ground state having the ionic character, the bending vibrational motion has a quite strong anharmonicity, and the motion is characterized as a large amplitude motion (LAM). Therefore, in general, the observed spectrum has the complicated vibronic structures and it is difficult to understand the molecular conformation having the LAM. In this study, we determined the global potential energy surfaces of the electronic ground state for the isomerization of AlNC/AlCN, and we elucidated the vibrational structures of the complicated vibronic states by solving the exact Schrödinger equation for the nuclear motion. Calculated results are in good agreement with the dispersed fluorescence spectra observed by Fukushima.

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Ultrafast Protein Dynamics Probed by Time-Resolved Resonance Raman Spectroscopy

KITAGAWA, Teizo

Ultrafast protein dynamics were examined with myoglobin (Mb) using picosecond time-resolved resonance Raman spectroscopy with a stress on structural and vibrational energy relaxation. Studies on the structural relaxation of Mb following CO photolysis revealed that the structural change of heme itself (core expansion), caused by CO photodissociation, is completed within the instrumental response time of the time-resolved resonance Raman apparatus used (~2 ps). In contrast, changes in the intensity and frequency of the iron–histidine (Fe–His) stretching mode upon dissociation of the trans ligand were found to occur in the picosecond regime. The Fe–His stretching band is absent for the CO-bound form, and its appearance upon photodissociation was not instantaneous, in contrast with that observed in the vibrational modes of heme, suggesting appreciable time evolution of the Fe displacement from the heme plane. The intensity reflected the out-of-plane displacement of iron, and 80% of the movement occurred in 2 ps but the remaining 20% occurred in 40 ps. The band position of the Fe–His stretching mode changed with a time constant of about 100 ps, indicating that tertiary structural changes of the protein occurred in a 100-ps range. This rate was dependent on viscosity of solvent ($k = \eta^{-0.3}$), indicating that the small change at the Fe–His bond is communicated to the protein surface through a conformation change, and conversely the change of Fe–His bond is controlled by the surface of the protein. Temporal changes of the aniti-Stokes Raman intensity of the ν_4 and ν_7 bands demonstrated immediate generation of vibrationally excited heme upon the photodissociation and successive decay of excited populations, whose time constants were 1.1 ± 0.6 and 1.9 ± 0.6 ps, respectively. This technique has been applied to identify an axial residue of a sensor protein, CooA, for which geminate recombination of photodissociated CO is very fast (τ = 70 ps) and therefore the Fe–His (His77) stretching Raman band could be detected only transiently with this technique.

(b) Molecular Photophysics and Science

Development of a Near-Field Ultrafast Spectroscopy System

IMURA, Kohei; OKAMOTO, Hiromi

We are constructing an apparatus for space- and time-resolved spectroscopic measurements, by combining near field optical microscopy and ultrafast time-resolved technique. With this apparatus, we aim at nanometer spatial resolution and femtosecond temporal resolution at the same time. Various photophysical phenomena probed under such extremely high space and time resolution can be of considerable significance not only in physics and chemistry but also in biology, and thus will open a new research activity. We plan to make use of this experimental methodology to investigate basic problems on chemical processes of mesoscopic structures. This technique also has a potential to shed a new light on nano-scale material science.

Experimental arrangement is schematically depicted in Figure 1. A spatial resolution of better than 100 nm is achieved by a nanometer-sized aperture of an optical fiber tip (SNOM tip). In so-called ‘illumination and collection’ mode, a sample is excited by the near-field radiation on the fiber tip introduced through the optical fiber, and emitted light is collected through the same fiber tip. The collected emission is dispersed in a monochromator and detected by a CCD detector. Ultrafast measurements are possible by a pump-probe optical correlation method with 100 fs pulses from a mode-locked Ti:sapphire laser.

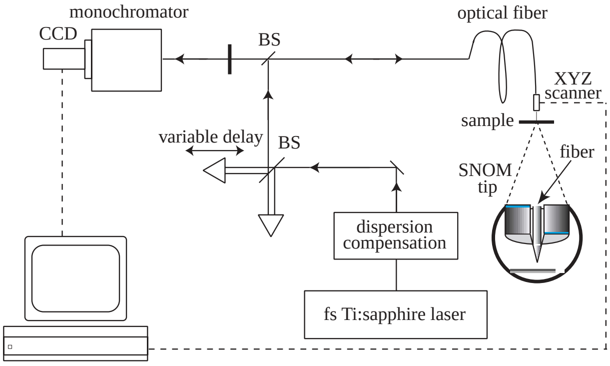

Figure 1. Schematic view of the experimental setup.

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

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In studies on “laser cooling and trapping of metastable helium atoms,” we have been constructing a new laser trapping apparatus for realizing the Bose-Einstein condensation of metastable He atoms. We have also been making additional LNA ($La_{1-x}Nd_xMgAl_{11}O_{19}$) lasers necessary for the new apparatus. On the other hand, in “laser spectroscopic studies of atoms and ions in liquid helium,” we have experimentally observed some interesting differences between spectra of Ca atoms in liquid ^4He and ^3He, and the cause of these differences has successfully been clarified through our theoretical calculation (see II-C-1). In addition, motivated by experimental results so far obtained in this project, we have also measured fine structure changing cross sections of Ba^+ ions in collisions with He atoms (see II-D-1) and of Ca^+, Sr^+ and Ba^+ ions in collisions with H_2 and D_2 molecules (see II-D-2).

Structure, Relaxation and Control of Reactive Cluster Studied by Two-Color Laser Spectroscopy

FUJII, Masaaki

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

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

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

Similarly, the IR spectrum of the ionic cluster can be measured by the depletion spectroscopy (mass-selected ion dip spectroscopy; see Figure 3). The ionic cluster can be prepared by the multiphoton ionization via S_1, and the ion current due to the cation cluster of the specific size can be measured through a mass-filter. When the ionic cluster is vibrationally excited by the IR laser, the cluster is dissociated by the vibrational predissociation. Therefore, the IR transition can be measured by the decrease of the parent cluster. The same spectrum can be obtained by monitoring the enhancement of fragments (mass-selected multiphoton dissociation spectroscopy). In addition to these "dip" spectroscopies, the PFI-ZEKE photoelectron spectroscopy[2] and the nonresonant ionization detected IR spectroscopy[3] are also important method to obtain the spectral information in the cation and the overtone states. Based on these spectroscopic techniques, we have measured the IR spectra of solvated clusters,[4] such as phenol/ammonia,[5] naphthol/alcohol,[6] carbazole/water[7] and 7-azaindole dimmers,[8] and have discussed the relation between the structure and intracluster reactions.

From 2001, we have been developing the new time-resolved IR spectroscopy for the reactive clusters. The pico-second time-resolved vibrational spectroscopy is one of the ideal way to reveal the reaction mechanism directly. Here, we will demonstrate its usefulness by applying the hydrogen transfer reaction in photoexcited PhOH–$(NH_3)_n$ cluster.[9] Figure 4 shows the principle of the picosecond time-resolved UV-IR-UV ion dip spectroscopy. The reactive cluster (PhOH–$(NH_3)_n$ in present case) is excited to S_1 by a picosecond UV laser ν_{UV} and the photochemical reaction (hydrogen transfer) is triggered. The final reaction product, *i.e.* $(NH_3)_{n-1}$-NH_4, is ionized by a nanosecond UV laser ν_{ION} which is irradiated after 100 ns from ν_{UV} and the population of the reaction product is monitored as a mass peak of $(NH_3)_{n-1}NH_4^+$. A picosecond tunable IR laser ν_{IR} is irradiated after t ps from ν_{UV} and is scanned over vibrational region. If ν_{IR} is resonant to vibrational levels of the transient species, the population of the final reaction product decreases due to the vibrational predissociation of the transient species. Therefore, the vibrational transitions of the transient species at t ps can be observed as decrease of ion current of $(NH_3)_{n-1}$-NH_4^+.

Figure 5 shows a diagram of the experimental apparatus rebuilt in the Laser Research Center of the Institute for Molecular Science. The femtosecond mode lock Ti:sapphire laser was regeneratively amplified at 10 Hz and was stretched to 3 ps (TSA 10/GCR-130: Spectra Physics). The typical power of the regeneratively amplified picosecond pulse was 5.6 mJ at 800 nm. Twenty percent of this pulse was frequency-doubled and was used to pump an optical parametric generator (OPG; TOPAS-400: Light Conversion). The signal light of this OPG was frequency-doubled and was used as the excitation laser ν_{UV}. Second OPG (TOPAS-800: Light Conversion) was pumped by 40% of the fundamental pulse. The frequency-doubled idler light of the second OPG and the remainder fundamental pulse were differentially mixed in a KTA crystal and were converted to the 3 µm IR laser ν_{IR}. The power of ν_{IR} was < 100 mJ. The pulse width of ν_{UV} and ν_{IR} was 3~4 ps. Third harmonic of nanosecond Nd^{3+}:YAG laser (INDI-40: Spectra Physics) was employed as the ionization laser ν_{ION}. Two YAG lasers (INDI-40 and GCR-130 which pumps the regenerative amplifier) were synchronized electrically within 1 ns-accuracy. Two UV lasers ν_{UV} and ν_{ION} were combined coaxially by a beam combiner and focused by a 250 mm focal lens. The IR pulse ν_{IR} was introduced into a vacuum chamber from the opposite side of the two UV lasers and was focused by a CaF_2 250 mm focal lens. The configuration that ν_{UV} and ν_{IR} are counter-propagated is convenient for the optical alignment, but this configuration lowers the time resolution than the pulse duration. The effective time resolution was ~20 ps.

The phenol vapor at room temperature was seeded in NH_3/Ne (0.5%) premix gas (2 atm) and the mixture was expanded into a vacuum chamber (typically 1×10^{-5} Torr) through a pulse valve (General Valve Series 9). The nozzle diameter was 400 mm. The laser beams were focused at 15 mm below the nozzle. The produced cations were pushed into a detector chamber by a repeller at an appropriate voltage (typically 15 $V \cdot cm^{-1}$), and were detected by a channel multiplier (Murata Ceratron) through a quadrupole mass filter (EXTREL). All laser systems were operated at 10 Hz, however, ν_{IR} was irradiated at 5 Hz through a chopper. Thus we could obtain a $\nu_{UV} + \nu_{IR} + \nu_{ION}$ signal and a $\nu_{UV} + \nu_{ION}$ signal alternatively. These two signals were separately integrated and stored in a digital boxcar system (4420/4422: EG&G PARC) after amplification by a pre-amplifier (5113: EG&G) . The integrated signal was recorded by a personal computer as a function of the IR laser frequency. The fluctuation of the condition of the pulse valve was suppressed by calculating the ratio between the two signals.

Time resolved UV-IR-UV ion dip spectra of phenol–$(NH_3)_3$ are shown in Figure 6. The numbers in the left hand sides of each spectrum indicate the delay time from ν_{UV} to ν_{IR}. Here the spectrum at –20 ns corresponds to the IR spectrum of PhOH–$(NH_3)_3$ in S_0, in which the sharp bands around 3400 cm^{-1}, the broad bands at ~3200 cm^{-1} and the very broad background are assigned to the degenerated antisymmetric stretch vibration ν_3 in NH_3, the totally symmetric stretch vibration ν_1 in NH_3 and the OH stretch vibration ν_{OH} in phenol, respectively.[5] The spectrum at +180 ns shows the vibrational transitions of the final reaction product via S_1, *i.e.* $(NH_3)_2NH_4$, and 1) two intense bands at 3180 cm^{-1} and 3250 cm^{-1} and 2) a broad band at 2700~3100 cm^{-1} which have been assigned to vibrational transitions concerned with NH_4.[5]

Let us discuss the time-resolved IR spectra from 0 to 100 ps, in which the excited state hydrogen transfer dynamics would be shown. One can see that the vibrational bands rise with increasing delay time. The spectral feature at +100 ps is already similar to that of the final reaction product (+180 ns). This time scale is consistent with that expected from previous studies.[5] Here, the intense band at 3250 cm^{-1} rises slower than the band at 3180 cm^{-1}. The relative intensities of the two bands become comparable at 40 ps, thereafter, the higher band at 3250 cm^{-1} clearly grows further. Thus, the rising time constant of the band at 3250 cm^{-1} is apparently different from that of the 3180 cm^{-1}-band. This remarkable difference between the two intense bands suggests that each vibrational transition is derived from different species. The existence of two transient species are naturally interpreted by considering the isomers of $(NH_3)_2NH_4$; the most stable $NH_3–NH_4–NH_3$ and the meta-stable $NH_4–NH_3–NH_3$. The co-existence of isomers is strongly supported by ab initio calculations.

In summary, it is demonstrated that the picosecond UV-IR-UV ion dip spectroscopy is a powerful tool to explore the dynamics of the intracluster reaction. We have successfully measured the picosecond time resolved IR spectra of the transient species for the ESHT of PhOH–$(NH_3)_3$ for the first time.

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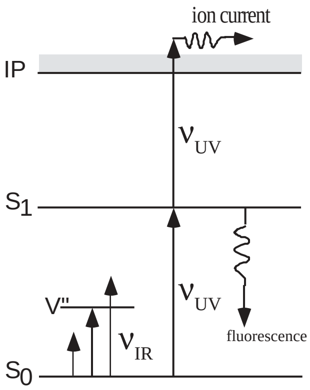

Figure 1. Principle of the IR Dip Spectroscopy. The IR transition in the ground state cluster can be measured.

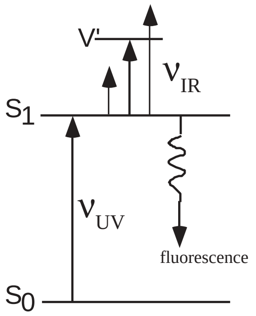

Figure 2. Principle of the UV-IR Fluorescence Dip Spectroscopy. The IR transition of the cluster in the S1 state can be obtained.

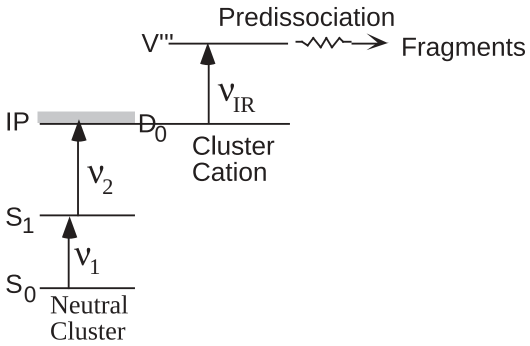

Figure 3. Principle of the mass-selected IR Ion Dip Spectroscopy. The IR transition of the cluster cation can be measured by the depletion of the parent cluster cation. The same spectrum can be measure by monitoring the enhancement of the fragments produced by the IR predissociation.

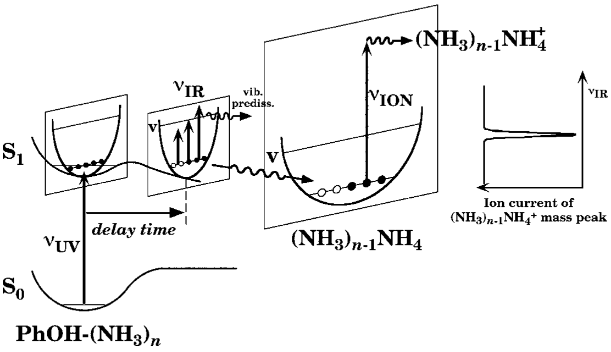

Figure 4. Principle of picosecond time-roselved UV-IR-UV ion dip spectroscopy. Potential curves of S_0 and S_1 are schematically drawn along O-H stretch coordinate. Potential curves in different sections on the S_1 O–H stretch coordinate are drawn along arbitrary N–H stretch coordinates.

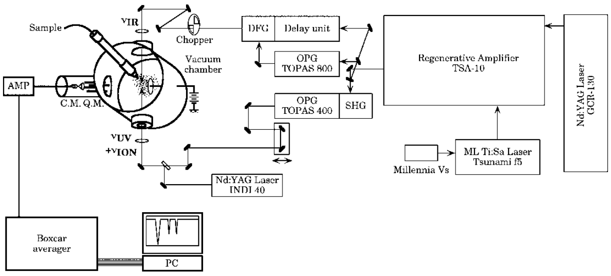

Figure 5. Schematic diagram of the experimental apparatus.

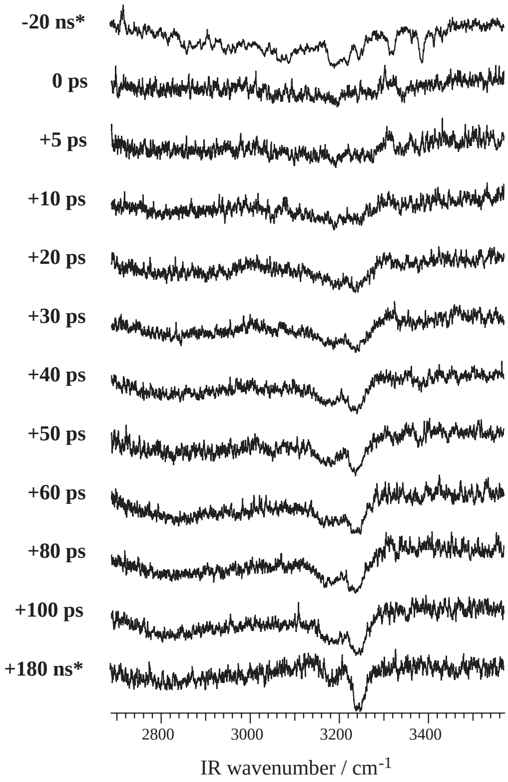

Figure 6. Picosecond time-resolved UV-IR-UV ion dip spectra of the transient species from the electronically excited PhOH–$(NH_3)_3$ which was observed by fixing ν_{UV} to the low vibronic band in the S_1 state of PhOH–$(NH_3)_3$ (281.49 nm) and monitoring $(NH_3)_2NH_4^+$ due to ν_{ION} (355 nm). Times indicated at the left side of each spectrum mean the delay times between ν_{UV} and ν_{IR}. The spectra whose delay times are –20 ns and +180 ns (indicated by *) are obtained by nanosecond laser system, which have been reported in the previous paper.[5)]

SR-Pump and Laser-Probe Experiments for the Photofragmentation Dynamics of Molecules

MITSUKE, Koichiro

Synchrotron radiation-laser combination techniques developed at UVSOR in Okazaki were employed for probing ionic and neutral photofragments produced in the vacuum ultraviolet. First, CN neutral fragments were dissociated from CH_3CN by excitation with synchrotron radiation in the photon energy E_{SR} range of 13.6 to 18.6 eV [*J. Electron Spectrosc. Relat. Phenom.* **119**, 155 (2001)]. Observed CN radicals were in the vibronically ground state. The laser induced fluorescence (LIF) signal was measured as a function of E_{SR} with the laser wavelength fixed at the CN ($B\ ^2\Sigma^+$, $v_B = 0 \leftarrow X\ ^2\Sigma^+$, $v_X = 0$) transition. The laser and monitored wavelengths were chosen at 388 and 420.8 nm, respectively. We constructed a novel optics containing spheroidal and spherical mirrors and an optical fiber in order to improve the collection efficiency of the fluorescence. The onset of 15.4 eV of the fluorescence signal indicates that the detected CN ($X\ ^2\Sigma^+$) radicals result from dissociative ionization of CH_3CN

$$CH_3CN^+ \rightarrow CN\ (X\ ^2\Sigma^+) + CH_3^+\ (X\ ^1A_1'). \qquad (1)$$

The partial cross section for the formation of CN ($X\ ^2\Sigma^+$) is estimated to be 0.1–0.5 Mb and is in a reasonable agreement with that for the CH_3^+ formation previously reported.

Second, N_2^+ ($X\ ^2\Sigma_g^+$, v_X = 0 and 1) ions resulting from direct ionization or autoionization of N_2 were detected by the LIF excitation spectroscopy using the $B\ ^2\Sigma_u^+ \leftarrow X\ ^2\Sigma_g^+$ transition. The LIF signal counts were measured in the E_{SR} range of 15.6 to 16.6 eV where numerous Rydberg states converging to N_2^+ ($A\ ^2\Pi_u$) exist. The fluorescence yield curves for the v_X = 0 and 1 vibrational levels were comparable with the relative partial photoionization cross sections for the respective levels. Several Rydberg states are found to exhibit stronger peak intensities in the v_X = 1 curve, suggesting enhancement in the branching ratio of the v_X = 1 level. We performed Franck-Condon calculations to evaluate the relative partial cross sections by using an approximate expression:

$$\sigma(v_X) \propto n^{*-3} \left|\langle v_g | v_R \rangle\right|^2 \left|\langle v_R | v_X \rangle\right|^2 \Big/ \sum_{v'_X} \left|\langle v_R | v'_X \rangle\right|^2 \qquad (2)$$

Here, we assumed that the neutral ground state N_2 ($X\ ^1\Sigma_g^+$, $v_g = 0$) is primarily photoexcited to the Rydberg state having a vibrational level v_R and an effective principal quantum number n^* and subsequently autoionized into N_2^+ ($X\ ^2\Sigma_g^+$, v_X).

Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; GEJO, Tatsuo

The new grazing incidence monochromator (Varied-line-spacing Plane Grating Monochromator; VLS-PGM) on BL4B at UVSOR has been successfully installed by the end of December 2000. The first photons through this monochromator were observed on the 16th of January in 2001, and from that day on, the performance tests for the monochromator have been initiated. As a consequence, it turned out that the maximum resolving power achieved, is more than 3000 at the entire photon energy region of interest, and the throughput photon flux measured by a calibrated silicon photodiode ranges from 10^8 to 10^9 photons/sec/100mA when the resolving power in the regular spectral region is set to be more than 3000. The performance of the present VLS-PGM is high enough to perform various spectroscopic investigations on molecular core-levels with high-resolution. The dynamics of molecular inner-shell excitation and relaxation processes is complex even for simple molecules, and thus advantageous to use various experimental techniques together with such a high performance monochromator in the soft x-ray region.

Two types of electron-ion coincidence experiments are in planning and the construction of the related spectrometers has been started; a high luminosity double toroidal analyzer (DTA) and a threshold electron analyzer. DTA equipped with a two-dimensional detector makes it possible to measure the angular distribution and kinetic energy of electrons/ions simultaneously. The combination of the present DTA with a time-of-flight mass spectrometer can be a powerful tool to study the state-to-state photodissociation dynamics following the molecular core-level excitation and ionization. Threshold electron spectroscopy has proved to be very powerful in the investigation of electron correlation phenomena not only in atoms but also in molecules. In the angle-resolved photoion spectroscopy applied to the inner-shell excitations of linear molecules, the parallel and perpendicular transitions are distinguishable. Thus, it is expected that the combination between a threshold electron spectrometer and an angle-resolved photoion spectrometer can provide a rare opportunity to obtain threshold electron spectra including the symmetry information on the excited states, which can be called as symmetry-resolved threshold electron spectra. We are hoping that the basic tunings of the apparatuses will be finished before the end of November 2001.

A new project towards utilizing the free electron laser (FEL) developed at UVSOR has been initiated in 2000. Two-photon double-resonant excitation of the autoionization Xe* $5p^5 4f$ resonance via the Xe* $5p^5 5d$ intermediate state has been chosen to demonstrate the practical usability of FEL, since the resulting spectrum has already been measured at LURE in France using the combination of a conventional mode-locked laser and synchrotron radiation (SR). Finally, the similar spectrum has been successfully derived. It is found that the spectrum obtained is characterized by a typical asymmetric Fano-type line profile. We are now planning on performing further detailed investigations on atomic photoionization processes utilizing the combination between FEL and SR.

(c) Novel Material Science

Theory for Electronic Properties of Molecular Conductors and Insulators: Dimensional Crossovers Induced by Correlation

YONEMITSU, Kenji; KISHINE, Jun-ichiro; MORI, Michiyasu[1]; KUWABARA, Makoto[2]; MIYASHITA, Naoyuki[3]
([1]Tohok Univ.; [2]Kobe Univ.; [3]GUAS)

In low-dimensional molecular materials, electron correlations are essential for the understanding of novel electronic phases. i) Variation of physical properties in quasi-one-dimensional organic conductors, $(\mathrm{TMTTF})_2X$ and $(\mathrm{TMTSF})_2X$, under physical or chemical pressure can be viewed as a dimensional crossover. With increasing inter-molecular overlaps between the neighboring chains and/or reducing electron correlation, the electronic dimensionality in the normal phase above the phase transition temperatures continuously changes from one to three. The optical conductivity spectra are also known to show a similar crossover with lowering energy scale. Anisotropic excitation spectra are studied by using the finite-temperature DMRG technique for a spinless-fermion model on a two-leg ladder. *Intra*-chain electron correlation is found to sensitively affect the *inter*-chain excitation spectrum, while the *inter*-chain inter-molecular overlap to sensitively affect the *intra*-chain spectrum. These results are opposite to the intuition, but nicely explained by the collective motion and/or confinement of fermions in the chains. ii) Quasi-one-dimensional π-d hybrid electron systems, $(\mathrm{DCNQI})_2M$, are known to show a metal-insulator transition originating from the collaboration of the Peierls and Mott mechanisms. Strong commensurability effects on the insulator phase with lattice modulation of period three are studied by using the exact diagonalization and DMRG techniques. With strong electron correlation among the d electrons, self-consistent lattice modulation strongly block the charge transfer between the π and d orbitals in order to keep the commensurability condition even the π-d level difference is widely varied. A transition to the incommensurate phase requires a large deviation of the π-d level difference from the optimal case. iii) Among quasi-two-dimensional organic conductors, the θ-phase compounds are known to show metal-insulator transitions accompanied with charge ordering. Although long-range Coulomb repulsion is believed to be essential to the paramagnetic charge-ordered phase, the optical conductivity spectra do not show an excitonic band expected from our random-phase-approximation calculations. Then additional interaction terms might be important for the charge-ordering transitions. In fact, $(\mathrm{BEDT\text{-}TTF})_2\mathrm{RbZn(SCN)}_4$ shows a discontinuous transition accompanied with lattice modulation at a rather high temperature. The transition temperatures are lower when lattice modulation does not take place in similar compounds. Exact diagonalization calculations and the second-order perturbation theory from the strong-coupling limit show indeed that weak electron-lattice coupling enhances the effect of long-range Coulomb repulsion on the charge order coexisting with paramagnetism.

Pulsed Methods of Electron Spin Resonance Spectyroscopy

KATO, Tatsuhisa; FURUKAWA, Ko

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of ESR spectroscopy enables us to investigate the transient phenomena in detail. The pulsed ESR spectroscopy gives us the prototyped demonstration of the time-dependent spectroscopy. Some time-dependent measurements were experimentally performed and compared with the theoretical model calculation. The advanced ESR method was applied to the study on the high spin state of $\mathrm{Gd@C_{82}}$ described in section II-H-1, of an inclusion complex of a cyclic dimmer of metalloporphyrin with $\mathrm{La@C_{82}}$ in section II-H-2, and of dications of aromatic amines in section II-I-2, and to the study on the reaction mechanism in the heterogeneous system on CaO surface in section II-I-1.

Synthesis of Palladium Clusters Stabilized by Molecular Capsules and their Catalytic Properties

SAKURAI, Hidehiro[1]; HIRAO, Toshikazu[1]; NEGISHI, Yuichi; TSUKUDA, Tatsuya
([1]Osaka Univ.)

Recently, colloidal dispersions of transition metal clusters with nanometer scale have gained much attention as a new class of catalysts. They show superior catalytic properties for some organic reactions compared with the monometallic complexes due to their unique electronic and geometric structures. The important task for understanding their size–specific properties and wide range of applications is to exploit a preparative method of the clusters having a well-defined size and morphology. We have addressed these issues by utilizing various host molecules, such as cyclodextrines (CD) and calixarene compounds, as stabilizing reagents of the metal clusters. Chemical reduction of palladium ions in the presence of these molecular capsules results in the formation of stable colloidal solutions as shown in Figure 1. The size distributions of the Pd clusters fall in the range of 2–6 nm in all the cases. By considering the fact that these clusters are too large to be accommodated into an internal cavity of a single molecule, a number of molecules are involved in the stabilization of a single cluster. Namely, the Pd cluster is encapsulated as a guest into the hydrophobic space made by several CDs or calixarenes.

Their catalytic activities toward Suzuki-Miyaura coupling reactions are also studied, motivated by the fact that palladium (0) complexes, such as $\mathrm{Pd(PPh_3)_4}$, act as good catalysts for the cross-coupling reactions between organic halides and organometallic compounds. We found the Pd clusters promotes the coupling reactions of *m*-iodophenol and phenylboronic acid at room temperature leading to the formation of hydroxybiphenyls with excellent yields. Studies concerning the detailed mechanisms of the reactions are now underway.

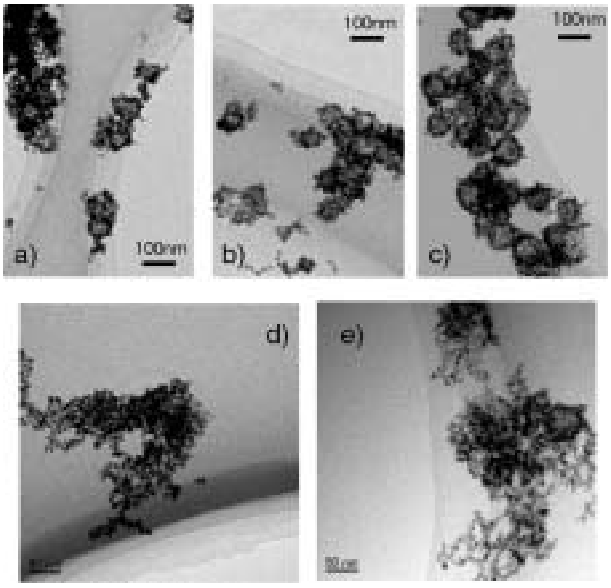

Figure 1. TEM images of Pd clusters stabilized by a) α–CD, b) β–CD, c) γ–CD, d) calix [6] arene *p*–sulfonic acid, and e) calix [8] arene *p*–sulfonic acid.

Spectroscopic and Physico-Chemical Studies of Organic Conductors

YAKUSHI, Kyuya; YAMAMOTO, Kaoru; URUICHI, Mikio; NAKANO, Chikako; DING, Yuqin; DROZDOVA, Olga; MAKSIMUK, Mikhail; SIMONYAN, Mkhitar

Photo-excitation spectrum within visible and infrared region contains much information on the local and extended electronic structure in the organic charge transfer (CT) salts. Our main research implements are the microscopic reflection and Raman spectroscopies, which enable us to perform polarized measurements on small single crystals of CT salts. Among the various information that can be extracted from these spectroscopies, we have particular interest on the molecular vibrations and possible collective excitations to investigate charge localization and superconducting phenomena.

Vibrational signals in the spectra allow us to investigate the local charge density on each molecule through the frequency shift and spectral selection rule. Based on the properties, we are now investigating the charge ordering (CO) or charge disproportionation phenomena in one-dimensional systems, $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Ag}$ and $(\mathrm{EDO\text{-}TTF})_2\mathrm{PF}_6$, and two-dimensional systems, $\theta\text{-}(\mathrm{BEDT\text{-}TTF})_2\mathrm{RbZn(SCN)}_4$, $\theta\text{-}(\mathrm{BDT\text{-}TTP})_2\mathrm{Cu(NCS)}_2$, and $(\mathrm{BEDT\text{-}TTF})_2\mathrm{CuBr}_4$ via the two spectroscopies.

On the other hand, electric transport properties are governed by the band structure and collective low-energy excitations. Particularly, it is widely recognized that the latter one is essential to be studied to understand characteristic phenomena realized in highly correlated systems. These excitations appear in the far-infrared spectrum of which observation requires exceptionally large single crystals, and thus the infrared study has remained an uncultivated field in the CT salt research. We are trying to observe good quality far-infrared spectra of organic superconductor $\kappa\text{-}(\mathrm{ET\text{-}d_8})_2\mathrm{Cu(CN)[N(CN)_2]}$. We have revealed so far that almost no Drude peak can be found in the optical conductivity down to far-infrared region and most of the spectral weight is contained in the broad mid-infrared peak in spite of the tight-binding band calculation predicting the presence of free electron excitations.

We have studied the electronic structures of certain phthalocyanine metal complexes, in which unpaired d-electrons localizing on phthalocyanine molecules coexist in the itinerant conjugated π-electron system. Such a d-π double band structure is a reminiscent of the f-electron system, in which a narrow f-band coexists with a wide s-band and they are hybridized near the Fermi level. To make sure the presence of d-π interaction, we prepared mixed crystal of NiPc and CoPc, and then investigated the ESR, magnetic susceptibility, reflectance and Raman spectra.

Broad-Line Solid State NMR Investigation of Electronic States in Molecular-Based Conductors

NAKAMURA, Toshikazu; FUJIYAMA, Shigeki

Broad-line solid state NMR is a powerful method that gives us crucial information about the fundamental electronic properties and about the detailed electronic structures of molecular based compounds. Investigation of such electronic phases in molecular based conductors is important to understand the unsolved fundamental problems in the field of solid state physics. The aim of this project is to clarify the electronic states (charges and spins) of molecular based compounds by microscopic point of view.

Quasi-one-dimensional organic conductors, $(\mathrm{TMTTF})_2X$, have been extensively studied so far because of their various ground states such as spin-Peierls, AF, IC-SDW and superconductivity. The temperature dependences of resistivity of TMTTF salts have broad minima around 100 K. The insulating states at low temperatures have been believed as Mott-Hubbard insulators since strong dimerization of the donor molecules might reduce the system half-filled. However a recent report of ac-conductivity suggesting strong ferroelectric response for TMTTF series provokes a new question about validity of the simple Mott-Hubbard ground state. To investigate the low temperature electronic phases, we synthesized $^{13}\mathrm{C}$ substituted TMTTF molecules; the two central carbon sites, of which hyperfine coupling constants are much larger than those of hydrogen sites, have been labeled with $^{13}\mathrm{C}$. We investigated the charge configurations and spin dynamics in the low temperature phases of $(\mathrm{TMTTF})_2X$.

The following topics are also now going on.

[1] Magnetic investigation of itinerant and local hybrid

spins system, (CHTM-TTP)$_2$TCNQ

[2] Low temperature Electronic Phases in (EDT-TTF)$_2$-*X*.

[3] Magnetic properties of organic spin-ladder systems, (BDTFP)$_2X$

[4] Magnetic structures of the antiferromagnetic states in Pd(dmit)$_2$ families

In this project, we are preparing a new NMR system to study more detailed electronic structure from microscopic points of view. We also try to carry out experiments with new devices under unconventional circumstance.

Development of New Organic Conductors and Their Physical Properties

KOBAYASHI, Hayao; FUJIWARA, Hideki; FUJIWARA, Emiko; TANAKA, Hisashi; TAMURA, Itaru; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

With the aim of development of solid state physics and chemistry of molecular materials, we have tried to develop new types of molecular metals and superconductors and to improve the methods of X-ray structure analysis at high pressure. The main results obtained in the last year are as follows. (1) development of single-component molecular metal: Although a vast number of molecular metals have been developed, the mechanism of carrier generation in the organic metals ever developed is rather simple. That is, every system utilizes the charge transfer phenomena between the molecules forming conduction band and other chemical species to generate the carriers. We have recently reported the first single-component molecular metal. As one of the next targets, we are going to start to examine the possibility of the development of ferromagnetic molecular metal composed of single-component molecules (2) discovery of field-induced superconducting state: In contrast to the isomorphous system without magnetic moments λ-(BETS)$_2$GaCl$_4$, λ-(BETS)$_2$FeCl$_4$ undergoes a unique π-d coupled antiferromagnetic insulating transition around 8 K, which was suppressed by applying magnetic field higher than 11 T. Firthermore, we have recently found field-induced superconductivity at $17\text{ T} < H < 41$. In addition, we have also found that the superconductivity of the first antiferromagnetic organic superconductor κ-(BETS)$_2$-FeBr$_4$ to be a “bi-functional molecular system” whose superconducting state can be switched on or switched off by controlling the magnetic state of anions. (3) high-pressure single crystal X-ray structure analysis on organic metal: We have recently made the accurate X-ray crystal structure analysis on α-ET$_2$I$_3$ by using diamond anvile high-pressure cell up to 2 GPa. There seems no special difficulty to elevate the applied pressure (up to 10 GPa).

Preparation and Characterization of Highly Ordered Molecular Films on Silicon Bound Through Si–C Covalent Bond

ARA, Masato[1]; GRAAF, Harald; TADA, Hirokazu
([1]GUAS)

Self-assembled monolayers (SAMs), have received considerable attention because of their potential applications to molecular scale electronic devices. Covalently bond alkane SAMs formed by reaction between alkene and hydrogen terminated silicon are of increasing interest as nano-interface for molecular electronics devices fabricated on silicon microstructures. We have studied (a) growth manner and electronic structure of Si-C junction using scanning probe microscope such as STM (scanning tunneling microscope), AFM (atomic force microscope) and KFM (Kelvin force microscope), (b) surface morphology of SAMs formed by the reaction between 1-dodecene, octadecene and methyl 10-undecenoate prepared on hydrogen terminated silicon (111) surfaces, and (c) degradation process of alkane monolayer film due to the a positive bias voltage at the substrate.

As a consequence, we have achieved atomically flat terraces on both p and n type Si(111) surfaces by means of chemical etching technique. The atomically flat surface was confirmed to be maintained after the growth of SAMs, indicating that the molecules formed highly oriented films. Detail investigation on the electronic structure at the interface using KFM and ultraviolet photoelectron spectroscopy is under progress. In addition, we succeeded in a preparation of a lithographically patterned alkane monolayer on silicon surface (Figure) by controlling the degradation of the film via the bias voltage applied on the AFM tip. The patterned area is available for different kinds of advanced techniques: 1) covering the oxide with other self-assembled monolayer by trichloro- or trimethoxy siliyl compounds; 2) removing of the silicon oxide by NH$_4$F-solution and using the established hydrogen terminated silicon for light or heat induced reaction with other alkenes or using the electrical conductive for metal plating; 3) etching of ditches by NH$_4$F/H$_2$O$_2$ solution and fill this ditches with metal by plating.

Design and Synthesis of Organic Ferrimagnets

HOSOKOSHI, Yuko; KATOH, Keiichi; INOUE, Katsuya

Molecule-based magnets have attracted current interests. After the discovery of an organic ferromagnet in 1991, construction of an organic ferrimagnet is one of today’s challenging targets in material science. Alternant alignment of two kinds of spins with different spin-multiplicities yields spontaneous magnetizations. Ferrimagnetism is an effective strategy to give spontaneous magnetizations to molecular materials. The use of antiferromagnetic exchange couplings, is advantageous to obtaining magnet with higher T_C. We can control the antiferromagnetic interactions easier than ferromagnetic ones. Although a number of ferrimagnets are realized in inorganic-organic hybrid systems, a genuine organic ferrimagnet has not yet been realized. All the reported ferrimagnets include at least two magnetic components: bimetallic compounds or metal complexes with organic radicals. In order to achieve this challenging subject of an organic ferrimagnet from a different viewpoint, we propose a single-component strategy: utilizing a triradical including an *S*

= 1 and an S = 1/2 units within a molecule and connecting the S = 1 and S = 1/2 units by intra- and intermolecular antiferromagnetic interactions. We have succeeded in synthesizing the first example of a genuine organic ferrimagnetic material having well-defined chemical and crystal structure. This material undergoes the 3D phase transition at 0.28 K. The advantage of utilizing organic molecules is demonstrated aiming to a single component ferrimagnet. (see V-D).

Formation of Nano-Reaction Field and Integration of Bio-Functional Materials on Si

URISU, Tsuneo

Integration of biofunctional materials such as lipids and proteins are expected to find important applications in biosensors, developments of new medicines, and diagnosis of intractable diseases etc. Up to now, almost of all these kinds of works have been made on the surfaces of gold. In the present work, we are considering to integrate bio-functional materials on Si surfaces, for which various structures, even nano-structures can be made easily by using conventional semiconductor processes and good matching with high density electric circuits is expected. We are going to make highly controlled nanostructures on Si surfaces by using synchrotron radiation etching, and after that, by area selective deposition of several kinds of alkyl monolayers on the surface, functionalized surfaces such as hydrophobic, hydrophilic and amphiphilic surfaces are made. By these area selectively functionalized surfaces, we expect that biofunctional materials such as lipids and membrane proteins are arranged with position and orientation controlled. In this year, we have attained the construction of the synchrotron radiation beam line for the etching experiments, clean rooms for the preparation of biomaterials, and draft for the self assembled monolayer depositions on Si. We have succeeded the good quality of self assembled alkyl monolayers on Si and SiO_2.

Development of New Materials Based on Fullerene and Carbon Nanotube in Nanometer Scale

KUBOZONO, Yoshihiro; TAKABAYASHI, Yasuhiro; FUJIKI, Satoshi; KANBARA, Takayoshi

New materials based on fullerenes and carbon nanotubes with novel physical properties are studied in various scale from bulk to nanometer size. In 2000, the superconducting transition temperature, T_c, of 52 K was reported in a field effect transistor (FET) with C_{60} crystals. The T_c was the highest among fullerene superconductors. Very recently, the T_c increases to 117 K in FET with C_{60}-tribromomethane crystals. The T_c is comparable to that of copper oxide-based ceramics. This clearly shows a possibility for C_{60}-based superconducting device which can be used in high-speed computing and medical imaging. Fullerene and fullerene based materials showed various novel physical properties in bulk solid. Through 1990s, solid state chemistry and physics contributed to the development of fullerene-based new materials in solid state. The appearance of C_{60}-based FET superconductor opened a way to develop new materials by combination of chemistry, physics and electronics. In the FET, the atomic level control of interface is very important to bring out its functionality. In the present project, we propose a development of new materials in various scale from bulk to nanometer size. Now, we prepare FET with C_{60} thin films which should have higher potential in application than crystal-based FET. Further, the superconductors with higher T_c are searched in FET with C_{60} encapsulating atoms (M@C_{60}) and carbon nanotube encapsulating fullerenes (peapod). Further, the studies on heterojunction diodes with metallofullerenes and peapod are now in progress. These studies are linked to development of device in nanometer scale. The STM/STS and AFM dual probe methods will be applied to study atomic level structures and interface structures in the devices.

Asymmetric Transition Metal Catalysis in Aqueous Media

UOZUMI, Yasuhiro; SHIBATOMI, Kazutaka; HOCKE, Heiko; YASOSHIMA, Kayo; NAKAO, Ryu; TANAKA, Hirotaka; NAKAZONO, Maki; YAMANOI, Yoshinori

Catalytic asymmetric reactions have attracted significant interest for their synthetic utility. One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the novel and basic chiral units. Homochiral organic molecules bearing hetero atoms (*e.g.* nitrogen, phosphorus, *etc.*) occupy a prominent position in organic chemistry as both useful synthetic reagents and molecules of biological interest. In this specail project, highly functionalized optically active pyrrolo[1,2-*c*]-imidazolone framework was identified as a novel basic chiral unit through a diversity-based approach.

A parallel library of optically active bicyclic tertiary amines bearing N-chiral bridgehead nitrogen atoms was readily prepared by condensation of primary amines, cyclic amino acids, and aldehydes. The enantio-controlling ability of each of the library members was examined for the asymmetric alkylation of benzaldehyde with diethylzinc, and (3*R*,6*R*,7a*S*)-(2,3-diphenyl-6-hydroxy)hexahydro-1*H*-pyrrolo[1,2-*c*]-imidazol-1-one, which contains β-amino alcohol unit, showed high enantioselectivity. Enantioselective desymmetrization of meso compounds is a powerful synthetic means of preparing enantiomerically enriched products where plural stereogenic carbon centers are generated in one step. Enantioselective ring opening of meso cyclic anhydrides is one of the cases. Asymmetric methanolysis of meso cyclic carboxylic anhydrides including hexahydrophthalic anhydride proceeded in toluene in the presence of (6*R*,7a*S*)-(2-aryl-6-hydroxy)-hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one to give the corresponding desymmetrized mono ester acids (*e.g.* (1*S*,2*R*)-2-(methoxycarbonyl)cyclohexane-1-carboxylic acid) with enantiomeric excesses of up to 89%.

On the other hand, catalytic organic transformations in water using recyclable immobilized catalysts is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including π-allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. A novel *P*,*N*-chelate chiral ligand, (3*R*,9a*S*)-(2-aryl-3-(2-diphenylphosphino)-phenyl)-tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one having pyrrolo[1,2-*c*]-imidazolone framework was designed, prepared, and immobilized on an amphiphilic polystyrene-poly-(ethylene glycol) graft copolymer (PS-PEG) resin. A palladium complex of the PS-PEG resin-supported *P*,*N*-ligand catalyzed the allylic substitution of both cyclic and acyclic allylic esters in water with high enantioselectivity. Reactions of cyclopentenyl, cyclohexenyl, and cycloheptenyl carbonates with dialkyl malonate gave the corresponding alkylated products with enantiomeric excess ranging from 89 to 98% ee. The PS-PEG supported Pd complex was readily recovered by simple filtration and reused without loss of catalytic activity or enantioselectivity.

Heterolytic Cleavage of C–H bond in Alkanes

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([1]Shizuoka Univ.; [2]IMS)

Alkanes were understood to be inert toward the heterolytic cleavege of their C–H bonds in a mild reaction condition. In particular the p*Ka* value for the methane C–H ($\equiv$C–H $\rightleftarrows$ H$^+$ + $\equiv$C$^-$) is about 49. When one of four protons was substituted with an electron withdrawing group such as nitro the p*Ka* potently decreases; *e.g.*, nitromethane has the p*Ka* value of 10.2 in water. If an aryl group was adopted as the substituent the decrease in the p*Ka* value was also observed. Thus, several aromatics undergo H-D exchange reaction of protons in a methyl side chain which is covalently bound to the aromatic ring. The mechanism of this type of reaction could also be considered as being initiated by nucleophilic attack of a base ion on a methyl hydrogen resulting in heterolytic cleavage of the C–H bond to afford a carbanion and a proton. Consequently, the presence of a strong base and/or vigorous conditions such as high temperature are inevitably required. Among aromatic nuclei, acridines and their derivatives are still attracting considerable attention because of the many functions which they possess, including biomimetic redox reactivities, chemiluminescence, and the interaction with DNA as an intercalator. In particular the 9 position, the pare position from acridine nitrogen, in acridinium exhibits strong electrophilicity and reacts with alcohols giving rise to 9-alkoxy-acridanes. 9-methyl substituted acridinium exhibited a slightly different reactivity with basic alcohol, affording the corresponding 9-alkoxyacridanes followed by an olefinic species, 9-methyleneacridane, through the 9-methyl proton abstraction by an alkoxide. Therefore, the 9 position in acridinium appears to have different electric and steric conditions as compared to the other positions, giving rise to expectations of more unique reactivity. We report on the unusual acidity of protons in methyl groups substituted onto acridinium skeleton at the 9 position. The p*Ka* of these methyl protons was estimated to be slightly higher than that of acetic acid at room temperature, showing that the methyl protons in the acridinium are functioning as an organic protic acid.

Reductive Activation of Carbon Monoxide derived from Carbon Dioxide and Oxidative Activation of Hydroxy- and Oxo-Groups Derived from Water

TANAKA, Koji: WADA, Tohru; MIZUKAWA, Tetsunori; KOBAYASHI, Katsuaki; TOMON, Takashi

An electrophilic attack of CO_2 to coordinatively unsaturated low valent metal complexes affords M-η^1-CO_2 complexes, which are easily converted to M-CO ones in both protic and aprotic media. Organic synthesis through M-CO complexes derived from CO_2 is highly desired from the viewpoint of utilization of CO_2 as C1 resources. A major problem of the reduction of CO_2 using homogeneous catalysis is reductive cleavages of M-CO bonds under reductive conditions because of accumulation of too much electrons in the central metals. Such unfavorable CO evolution in the reduction of CO_2 is expected to depress effectively by utilization of ligand localized redox reactions rather than metal centered one. A flexible ligand having an ability to change the bonding modes among monodentate, bidentate and bridging form to connect metals and carbonyl carbon of M-CO bonds would meet the requirements of smooth M-η^1-CO_2 formation and depression of reductive cleavage of M–CO bond under reductive conditions.

Neutralization energy generated by reactions between acids and bases is merely wasted as thermal energy into air. 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. $\Delta p = \Delta\psi - Z\Delta\mathrm{pH}$ ($Z = 2.303RT/F$). Proton gradient is equivalent to the neutralization energy because the neutralization reaction takes place upon removal of separating membrane. Thus, neutralization energy results from the formation of water. Biological system effectively creates and consumes neutralization energy in various reactions. Acids and bases, therefore, have potential energy sources, which are provided by chemical bondings (chemical energy). Along this line, we tried to convert the neutral energy to electronic energy by using ruthenium-aqua complexes.

Rational Synthesis of Metal-Chalcogenido Clusters

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Metal–chalcogenide clusters are of fundamental interest by virtue of their relevance to bioinoganic chemistry, catalysis, and materials science. One of challenging topics in this chemistry is to develop rational syntheses or stepwise syntheses of metal-chalcogen clusters, whereby small metal-chalcogen fragments assemble into desirable higher molecularity sulfur complexes. For this purpose, we find it attractive to utilize silanechalcogenolato complexes as precursors to metal-chalcogenolato clusters. The use of silanechalcogenolates has the two following advantages in exploring the synthetic method for clusters. First, silicon–chalcogen bond is labile and is readily cleaved in a mild condition. Secondly, the reactivity of silanethiolato ligands can be regulated by steric and electronic properties of substituents on silicon. However, the coordination chemistry of silicon-chalcogen ligands has yet to be explored. In this project, we have prepared silanecalcogenolate complexes of transition metals. Studies of reactions of silicone-chalcogen bonds coordinated at a metal center are now in progress.

Developments and Researches of New Laser Materials

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Although development of lasers is remarkable, there are no lasers which lase in ultraviolet and far infrared regions. However, it is expected that these kinds of lasers break out a great revolution in not only the molecular science but also in the industrial world.

In this project we research characters of new materials for ultraviolet and far infrared lasers, and develop new lasers by using these laser materials.

Development and Research of Advanced Tunable Solid State Lasers

TAIRA, Takunori; KURIMURA, Sunao; SHOJI, Ichiro; PAVEL, Nicolaie; SATO, Yoichi; SAIKAWA, Jiro

The use of diode lasers to pump solid-state lasers opens new horizon in laser science. Diode-pumped solid-state lasers are compact, reliable, and efficient sources of coherent radiation. They can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Recently attention has been directed to the trivalent 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 small quantum defect, long upper-state life time and wide gain width.

On the other hand, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. Inasmuch as the pool of mature nonlinear optical materials is limited and development of new materials takes time and cost, QPM is a useful method for extending the range of available nonlinear optical materials. The ability to pattern a QPM structure allows the nonlinear materials to be engineered for desired interactions, meaning molecular-science-specified lasers are obtainable through these artificial materials.

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 kinds of advanced tunable solid-state light sources which based on microchip lasers will be powerful tools in the research of molecular science.

Diode-pumped solid-state lasers can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Additionally, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. These kinds of advanced tunable solid-state light, so to speak “Chroma-Chip Lasers,” will assist the research of molecular science. In this projects we are developing Chroma Chip Lasers based on diode-pumped-microchip-solid-sate lasers and advanced nonlinear frequency conversion technique.

Generation of Reactive Species via Electron Transfer on Metal Complexes, as Basis of Chemical Energy Conversion Systems

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This project aims at developing redox catalysis reactions suitable for chemical energy conversion. Our current interest focuses on modeling photosynthesis, that is, driving endothermic chemical transformation by using light energy via photoinduced electron transfer. Progress has been made in the following topics during the last year:

A. Examination of various terdentate ligands as candidates for new electrocatalysis. 2,2’:6’,2”-Terpyridine (terpy) has been the ligand of choice for application of metal complexes on electrocatalysis. We found, however, that terpy tended to stabilize the complexes with first-row transition metals at their lower oxidation states (Fe(II), Mn(II), *etc.*), which prevented these complexes to serve as electrocatalysis at low overpotentials. We therefore examined other terdentate ligands that were to replace terpy. 2,2’:6’,2”-Terpyridine-1,1”-dioxide was a promising ligand which showed lower M(III)/M(II) potentials than the terpy analogs. Also being investigated are pyrrole-containing ligands, 2,6-bis(2-pyrrolyl)pyridine and 6-(2-pyrrolyl)-2,2’-bipyridine.
B. Multistep redox-active polymers were combined with photoactive pigment (porphyrin). This is another necessary step towards realizing photosynthesis in artificial molecular systems. Multiple electron transfers from the polymer to quinones were

successfully observed. Development of other types of redox pools using dendrimer-related substances are currently under way.

Synthesis and Electron-Transport Properties of Perfluorinated Oligonaphthalenes

SAKAMOTO, Youichi; KOMATSU, Shingo; SUZUKI, Toshiyasu

We have synthesized perfluoro-2,6-ternaphthalene (**PF-3N**) and -quaternaphthalene (**PF-4N**). These oligomers are colorless crystalline solids, which showed sharp melting endotherms at 263 and 371 °C, respectively. **PF-3N** is slightly soluble in some solvents, but **PF-4N** is insoluble in common organic solvents. The cyclic voltammogram of **PF-3N** in THF exhibited a reversible reduction at –1.88 V. OLEDs were fabricated using these oligomers as the electron-transport layer. The luminance-voltage curves of **PF-3N** and **-4N** are almost identical to that of Alq_3. The maximum luminance of **PF-4N** reached 15940 cd/m^2 at 12.6 V. The low electron mobility of Alq_3 could be responsible for the saturation of luminance and current density.

Slurry Mixer for Bonded Lubricating Films

WATANABE, Michio; YOSHIDA, Hisashi; KONDOH, Takuhiko; MIYASHITA, Harumi; TAKAMATU, Gunzo

This year we have newly built a Slurry Mixer for Bonded Lubricating Films (Figure 1) to product bonded lubricating films.

Now we are evaluating the performance both in antigalling and in coefficient of friction for some samples by Ball on Disk Tribometer.

Figure 1. Slurry Mixer for Bonded Lubricating Films.

Investigation of Dynamics on Photo-Excited Solids and Surfaces by Using the Combination of Synchrotron Radiation and Laser

KAMADA, Masao; TAKAHASHI, Kazutoshi

Dynamics on solids and surfaces, which are excited by photons, has attracted much interest from both of basic and application sides, since it may provide new scientific fields and photo-controllable devices. We have been investigating the photo-induced phase transition using photoelectron spectroscopy based on the combination of synchrotron radiation and laser. Core-level and valence-band photoelectron spectra of organo-metalic complex showed clearly the characteristics of the photo-induced phase transition.

We have been also investigating the photo-induced phenomena on semiconductor surfaces using the combination of synchrotron radiation and laser. Photo-induced core-level shifts observed on GaAs (100) can be interpreted in terms of surface photo-voltage effects. This work is now extended to the super-lattice systems and another semiconductors such as GaN. We have constructed the experimental system for investigating the time-response on the semiconductor surfaces using photoelectron spectroscopy.

The dynamics on the photo-excited semiconductors is also observed in the optical response. We have conducted the two-photon excitation experiments using synchrotron radiation and laser. Excited carriers changed the surface band structures, resulting in the reflectivity spectra. The experiments are in progress on GaAs and ZnSe.

Development of Combined-function Focusing Magnet

KATOH, Masahiro; HAYASHI, Kenji; HORI, Yoichiro[1]; HOSAKA, Masahito; KINOSHITA, Toshio; KODA, Shigeru; TAKASHIMA, Yoshifumi; YAMAZAKI, Jun-ichiro
([1]IMS and KEK-PF)

In the upgrade plan proposed for UVSOR, the original magnetic lattice will be modified to reduce the emittance and to increase the number of straight sections for insertion devices. We have completed the lattice design. We are designing and developing the lattice components, such as quadrupole/sextupole magnets and the vacuum chambers. Because of the space limitation, sextupoles will be integrated in quadrupoles. We have constructed a prototype of the combined-function magnets. Field measurements are in progress. It has been shown that the magnet is capable of producing required field strengths.

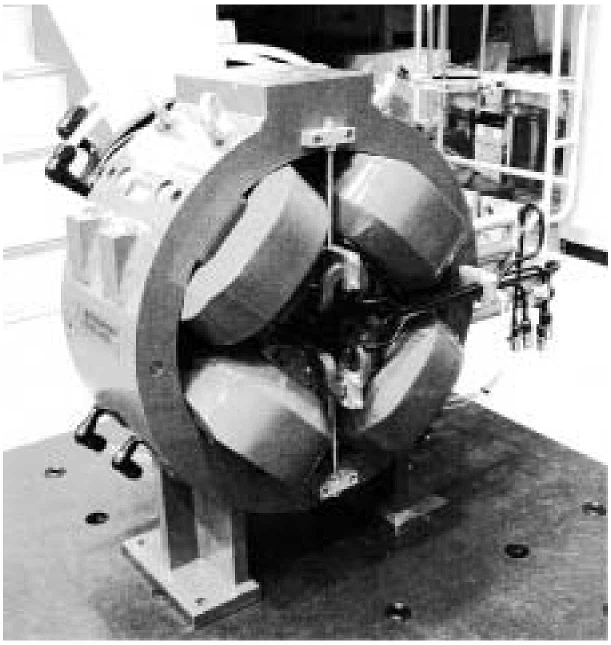

Figure 1. Prototype of the combined-function magnets.

Roles of Val-68 on the Oxidation Activity and Enantioselectivity by Sperm Whale Myoglobin

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([1]Tohoku Univ.; [2]Yamagata Univ.)

In the course of structural studies on H64D myoglobin (Mb) mutant, which is the first Mb mutant to afford compound I in its reaction with H_2O_2, we have solved the crystal structure of H64D/V68A Mb. The carboxylic acid in Asp-64 is found to interact with Arg-45 through a hydrogen bonding. According to the hydrogen bonding, a distal site immediate above the heme becomes vacant. In addition, the amino acid residue at the position of 68 appears to construct a big obstacle for incoming organic substrate such as sulfides and olefins. Thus, we have prepared H64D Mbs bearing a series of substituent for Val-68 whether or not the enzymatic activities could be regulated by the Va-l68 variants, so called H64D/V68X Mbs. A series of Mb mutants have been prepared by replacing Val-68 with Gly, Ala, Ser, Leu, Ile, and Phe in H64D Mb. All the mutant proteins, except for H64D/V68G Mb, are stable enough to be purified. The oxidation of thioanisole by compound I of H64D/V68X Mb (Mb-I) was directly monitored by stopped-flow spectrometer, and the sulfoxidation rate constants are found to increase in the order of Phe < Val < Leu < Ala < Ile. Unfortunately, H64D/V68S Mb-I is rapidly decay to Mb-II; therefore, the rate of Mb-I reduction with thioanisole was not determined accurately. The results suggest that the volume of hydrophobic residue at the 68 position influences the sulfoxidation activity. A similar trend is observed for the catalytic sulfoxidation of thioanisole by H64D/V68X Mbs with H_2O_2. The dominant product in the catalytic sulfoxidation is the (R)-isomer for the H64D/V68A and H64D/V68S mutants, with more than 84% enantiomeric excess (% ee). However, increasing the polarity of the distal pocket by substituting Ala-68 with Ser in H64D Mb decelerates the rate of sulfoxidation by 2-fold. On the other hand, the H64D/V68I mutant affords dominantly the (S)-enantiomer with the highest rate (*i.e.* 413 turnover/min). The substitution of Val-68 with Leu has little effect on enantioselectivity in the catalytic sulfoxidation but increases the reactivity with H_2O_2. Both the values of % ee and rate in the catalytic sulfoxidation decrease for H64D/V68F Mb in comparison with the values for H64D/V68A Mb, implying that a large benzyl side chain of phenylalanine at the 68 position inhibits the access of substrate to the heme pocket. In order to understand details of the transition state of the oxo-transfer step, we have examined enantioselective binding of (R)- and (S)-1-phenylethylamine to H64D/V68X Mb mutants, since the structure of 1-phenylethylamine–Mb adduct is expected to be very similar to the transition state of the thioanisole sulfoxidation (transition state analogue). Therefore, enantioselectivity sulfoxidation and enantioselective amine binding are compared. Finally, we have concluded that the enantioselectivity in the sulfoxidation is determining the step prior to the oxo-transfer step, possibly the substrate access step.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

FUJII, Hiroshi

Metalloenzymes are a class of biologically important macromolecules which have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloenzymes have been thought to depend on the coordination structure of the active site in the protein matrices; the ligand donors, the geometry, and the coordination mode of reactant and substrate. Furthermore, it has been thought that protein structures in immediate vicinity of active metal ion are related to enzymatic function, regio-selectivity, and stereo-selectivity. In this project, we are studying the molecular mechanism of activation of molecular oxygen mediated by metalloenzymes.

(1) To understand the structure-function relationship of 3,4-PCD, there have been attempted over several decades to prepare inorganic model complexes that mimic the ferric iron site of 3,4-PCD, however, no ferric iron complex with the same coordination structure that in the enzyme has been characterized definitively. We have succeeded in an attainment to the ferric iron active site of 3,4-PCD by using sterically hindered salen ligand. Characterization of the model complex revealed the roles of the iron bound water ligand in the enzyme on the unique trigonal bipyramidal structure and the catechol degradation reaction.

(2) Cytochrome c oxidase (CcO) is the terminal oxidase that reduces molecular oxygen to water, coupling with proton pumping across the mitochondrial inner membrane. To reveal the reaction mechanism of CcO, we have synthesized model complexes of the heme-a_3 site of cytochrome c oxidase. We have

succeeded in the preparation of a high valent oxo iron porphyrin complexes as models for the intermediates P and F, which are detected as reaction intermediates in the catalytic cycle of CcO, by the oxidation of the ferric model complexes with m-chloroperbenzoic acid or ozone.

(3) Heme oxygenase catalyzes the regiospecific oxidative degradation of iron protoporphyrin IX (heme) to biliverdin, CO and Fe, utilizing molecular oxygen and electrons donated from the NADPH-cytochrome P450 reductase. To investigate the functionality of highly conserved polar amino acids in the distal helix of HO-1, we have prepared alanine mutants: T135A, R136A, D140A, and S142A, and found drastic changes in the heme degradation reactions of D140A. All of the experimental data clearly indicated that the carboxylate at position 140 has essential role on the activation of iron bound dioxygen and hydroperoxide.