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 sequences. However, nobody has succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles).

There are two reasons for the difficulty. One reason is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be considered is very large. The other reason for the difficulty is that there exist huge number of local minima in the energy function, and conventional simulation techniques 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 difficulty (or reviews, see References 1 and 2).

The goal of the present project is to further develop and test the effectiveness of generalize-ensemble algorithms in the protein folding problem and to succeed eventually in the prediction of tertiary structures of proteins from the first principles. We have been developing new generalited-ensemble algorithms. We found that the replica-exchange method and its extension are particularly promising.

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Development and Applications of Basic Theories for Chemical Reaction Dynamics and Their Control

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Reaction dynamics studies have now been extended to electronically nonadiabatic reactions. It is desirable to formulate accurate semiclassical theories by incorporating the Zhu-Nakamura theory of nonadiabatic transition due to potential curve crossing. Such theories should be able to deal with large reaction systems of chemical interest. In order to develop such theories, we have to investigate their validity first by applying to small systems which can be treated quantum mechanically accurately. As a such prototypical system, we have chosen the DH_2^+ reaction system in which two potential energy surfaces are involved. The quantum mechanical accurate numerical studies have been almost finished. As for the semiclassical treatment, we have first implemented the trajectory surface hopping method with use of the Zhu-Nakamura theory. The preliminary results are very promising, since the Zhu-Nakamura theory can deal with classically forbidden transitions properly. We further plan to incorporate the Zhu-Nakamura theory fully with all phases taken into account into semiclassical propagation methods.

In attempt to formulate hopefully a sort of unified theory of nonadiabatic transition which can cover both crossing and non-crossing cases, we have been working on exponential potential models. We have formulated a general framework for the case that the diabatic potentials and coupling are given by the same exponential function.

Control of molecular processes by manipulating time-dependent external fields would be one of the most important subjects in the coming new century. Using the intriguing phenomenon of complete reflection and our new idea of periodical sweeping of an external field to control nonadiabatic transitions, we have been working on controlling molecular processes such as photodissociation by lasers. The idea of periodic sweeping can also be applied to NMR such as cross polarization and may develop a methodology more effective than the conventional one.

The Energy Landscape for Solvent Dynamics in Electron Transfer Reactions: A Minimalist Model

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We employ the minimalist models for the solvent, *i.e.*, simpler models that include includes the basic features of a rough-energy landscape: multidimensional degrees of freedom, with each solvent molecule being treated independently; a disordered energy landscape with multiple minima; and a polarizable medium around a charged cavity.

Above the thermodynamic glass transition, it recovers the continuum dielectric limit, where the Marcus theory can be applied. At low temperatures, a polarization-dependent glassy phase appears and a slow non-self-averaging dynamics plays a role. Further investigation is made to address the validity of a collective reaction coordinate representation. Its connection to the study of energy landscapes opens a new theoretical framework to study the questions above.

Constructing Molecular Theory of Chemical Processes in Solution

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Our current research interests and activities are concentrated upon four important chemical processes in 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, D. molecular theory of electrode-solution interface. The RISM theory, an integral equation theory of molecular liquids, is our main machinery to attack the problems, which is coupled with other theoretical methodologies including the ab initio molecular oribital method, moelcular simulations, the generalized Langevin equation, and the density functional theory (DFT). Problems on which we have been wroking along the four lines are as follows:

1. Solvent effect on keto-enol tautomers of acetyl-acetone in aqueous solution.
2. Diels-Alder reactions in ambient and supercritical water.
3. Excited state dynamics of a molecule in polar solvent.
4. Solvent effect on NMR chemical shift in polar and non-polar solvents.
5. Partial molar volume of biomolecules in aqueous solution.
6. Salt effect on stability of a dipeptide in water.
7. Stability and folding of peptide and protein in aqueous solution.
8. Solvation dynamics and thermodynamics of ions.
9. Non-equlibrium free energy surface related to electron transfer reactions.
10. Dynamical coupling between intra- and inter molecular motions in liquids.
11. Description of collective excitation in liquds by interaction site model.
12. Time correlation function described by the interaction-site model of molecular liquids.
13. Dynamics of an ion in water.
14. Microscopic characterization of metal-liquid interface.
15. Path integral theory of a hydrated electron.

Imaging of Chemical Dynamics

SUZUKI, Toshinori; KOHGUCHI, Hiroshi; KATAYANAGI, Hideki

Femtosecond time-resolved photoelectron imaging method has been developed, for the first time. The scattering distributions of photoelectrons in [1+1’] REMPI of NO and [1+2’] REMPI of Pyrazine have been observed. Ultrafast decay of optically-prepared S_1 character and corresponding build-up of triplet character were visualized. Rotational coherence effect has been clearly observed in photoelectron intensity and angular distribution. Crossed beam ion imaging method has been applied to inelastic scattering of NO with Ar at the collision energy of 63 meV, and the differential cross sections were compared with scattering calculations by Millard Alexander using the newest *ab initio* surface.

Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

KOSUGI, Nobuhiro; HATSUI, Takaki

This project is being carried out in collaboration with UVSOR and Photon Factory (KEK-PF). We are interested in ionic fragmentations and electron emissions via inner-shell excitation of molecules and in their polarization dependence. In high-resolution C1s photoabsorption spectra of acetylene, C_2H_2, we have found that the lowest σ_u* state is embedded in the 3sσ_g Rydberg state and is dissociative through interaction with the lowest π* state with bent geometry due to the Renner-Teller effect, that the 3pσ_u and 3pπ_u Rydberg states are clearly resolved and show different vibrational structures, and that the C1s σ_g and σ_u ionization channels show different ionization thresholds, to which the Rydberg series are converging. We will extend our experimental and theoretical approaches to several open-shell and unstable molecules.

Time-Resolved Spectroscopic Study of Photochemical Dynamics in Condensed Phase

TAHARA, Tahei; TAKEUCHI, Satoshi; FUJINO, Tatsuya; ARZHANTSEV, Sergei; MIZUNO, Misao; FUJIYOSHI, Satoru

Time-resolved spectroscopy is one of the most powerful tools for the studies of chemical reactions. It enables us to directly observe the temporal changes occurring in the course of chemical reactions. Recent progress of time-resolved spectroscopy relies on the drastic advance of the laser technology, and we are now able to examine ultrafast dynamics of the primary chemical processes with pico/femtosecond time-resolution. The aims of this project are (1) development of new technique and method in time-resolved spectroscopy, and (2) application of pico/femtosecond spectroscopy to the study of dynamics of molecules in condensed phase. Our research activities of this year can be summarized as follows, in the order of time-resolution of the experiments. First, we constructed experimental setups utilizing 'extremely-short' optical pulses (Δt ~ ten – a few tens of femtoseconds) and carried out time-resolved measurements to observe vibrational coherence (wavepacket motion) of the molecules in the excited state and the ground state. Especially, the vibrational coherence in the S_1 state of *trans*-stilbene is examined and discussed in detail. Secondly, with use of time-resolved fluorescence spectroscopy having a few hundreds femtoseconds time-resolution, we studied excited-state proton transfer of anthraquinone derivatives, isomerization of azobenzene, and relaxation process of the S_2 state of zinc(II) prophyrins. Thirdly, we applied picosecond time-resolved Raman spectroscopy to the study of photochemical dynamics of several fundamental aromatic molecules including p-nitroaniline. In addition, we examine the excitation profile of resonance hyper-Raman scattering of *all*-trans retinal by using picosecond amplified laser pulses. Finally, we started construction of a new apparatus for femtosecond infrared spectroscopy.

Production of Optical Knife—Site-Specific Fragmentation Following Core-Level Photoexcitation

NAGAOKA, Shin-ichi

Monochromatized synchrotron radiation can excite core electrons of an atom in a specific chemical environment selectively, discriminating the core electrons from those of like atoms having different chemical environments. This site-specific excitation often results in site-specific fragmentation, which is of importance in understanding localization phenomena in chemical reactions and which is potentially useful for synthesizing materials through selective bond breaking. Synchrotron radiation can indeed play the part of an optical knife for molecules. When bond dissociation around an atomic site is required in the synthesis, one can use the optical knife that has the photon energy corresponding to the specific excitation of that site. These site-specific phenomena have been of considerable interest to many researchers. To elucidate the site-specific fragmentation, we have used photoemission spectroscopy, the energy-selected-photoemission photoion coincidence method, and *ab initio* molecular-orbital calculations, and have studied site-specific phenomena in the C:1s and Si:2p photoexcitation of organic and organosilicon molecules condensed on a Si surface and in the vapor phase [$X_3Si-(CH_2)_nSi(CH_3)_3$ (X = F or Cl, n = 0–3), *trans*-$F_3SiCH=CHSi(CH_3)_3$, $F_3SiC\equiv CSi(CH_3)_3$, CF_3CH_3, $CF_3CH(OH)CH_3$ and $CF_3CD(OH)CH_3$]. An electron-ion coincidence spectrometer for vapor-phase site-specific-dynamics study is also being built now. The equipment consists of an electron gun, a cylindrical mirror analyzer (CMA) and a reflectron-type time-of-flight ion mass analyzer.

Theoretical Study on the Unimolecular Reaction Dynamics of Acetyl Radical $CH_3CO \rightarrow CH_3 + CO$

ITO, Masakatsu; NANBU, Shinkoh; AOYAGI, Mutsumi

We investigate the dissociation dynamics of acetyl radical with the classical trajectory method using the electronic model hamiltonian based on our ab initio calculations. At each time step in our classical trajectory calculations, the electronic hamiltonian is diagonalized to obtain the instantaneous adiabatic states and then the Hellmann-Feynmann forces are evaluated to drive the nuclear coordinates. Our hamitonian is based on the valence bond (VB) description of the electronic wavefunctions. Since acetyl radical and its dissociative products have different bonding characters, the wavefunctions along the dissociation process are approximately expanded by two correponding VB bases states. We found that the energy of the CCO bending excitation does not efficiently transfer into the dissociation coordinate (C–C) over the time period of 30 ps. It is suggested that this slow transfer or redistribution of internal energy could be one of the important sources for the discrepancy between the RRKM rate constants and the experimental results.

(b) Molecular Photophysics and Science

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

MORITA, Norio; MORIWAKI, Yoshiki; KUMAKURA, Mitsutaka

In studies on “laser cooling and trapping of metastable helium atoms,” the design and construction of a new laser cooling and trapping apparatus are now in progress. With this new apparatus we can expect to confine a much larger number of metastable He atoms at much lower temperature. On the other hand, in “laser spectroscopic studies of atoms and ions in liquid helium,” we have successfully measured some excitation and emission spectra of Yb^+ ions in liquid helium, and have well understood their spectral properties through our theoretical analyses (see II-B-1). Moreover, motivated by one of the results of this experiment, we have also measured fine structure changing cross sections of Ca^+ and Sr^+ ions in collisions with He atoms (see II-B-2).

Structures of Reaction Intermediates of Bovine Cytochrome c Oxidase Probed by Time-Resolved Vibrational Spectroscopy

KITAGAWA, Teizo

Structures of reaction intermediates of bovine cytochrome c oxidase (CcO) in its reactions of the fully reduced form with O_2 and the fully oxidized form with H_2O_2 were investigated with time-resolved resonance Raman (RR) and infrared spectroscopy. Six oxygen-associated RR bands were observed for the reaction of CcO with O_2. The isotope shifts for an asymmetrically labeled dioxygen, $^{16}O^{18}O$, have established that the primary intermediate of heme a_3 is an end-on type O_2 adduct, and the subsequent intermediate (P) has an oxoiron heme with Fe=O stretch ($\nu_{Fe=O}$) at 804/764 cm^{-1} for $^{16}O_2/^{18}O_2$ derivatives, although so far a peroxy structure has been postulated for it. The P intermediate is converted to the F intermediate having $\nu_{Fe=O}$ at 785/751 cm^{-1} and then to the ferric hydroxy species with $\nu_{Fe–OH}$ at 450/425 cm^{-1} (443/417 cm^{-1} in D_2O). The conversion rate from P to F intermediates is significantly slower in D_2O than in H_2O. The P intermediate was also generated by incubation of fully oxidized CcO with CO and O_2 but the F was not. The reaction of oxidized CcO with H_2O_2 yielded the same oxygen isotope-sensitive bands as those of P and F, indicating the identity of intermediates. Infrared spectra revealed the occurrence of deprotonation of one carboxylic acid side chain and protonation of the other upon deligation of a ligand from heme a_3. The protonation was not seen with a mixed valence enzyme. UVRR spectrum excited at 244 nm indicated deprotonation of Tyr244 at weakly alkaline pH and gave a prominent band assignable to the linoleoyl-type cis C=C stretch of phospholipids which must be tightly bound to purified CcO. The intensity titration with phosphatidylcholines indicated that twenty-one fatty acids chains are attached to one CcO molecule.

Laser Raman Beat Detection of Magnetic Resonance

KATO, Tatsuhisa; MATSUSHITA, Michio

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

There are some causes to hide the Raman beat signal, that is, the inhomogeneity of the circumstance of the molecule, the fluctuation of the applied field, and the interference by the crystal phonon. It is the key to success in the Raman beat detection to eliminate these cause of the incoherence. Then it is needed to prepare the sophisticated single crystal sample, the highly stabilized magnetic field, and a cryostat of liquid helium. It has been completed to set up the apparatus, and the Raman beat detection was applied to the study on the delocalized excitation in molecular crystals of 1,4-dibromonaphthalene. The result was published in *Phys. Rev. Lett.* **83(10)**, 2018 (1999).

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 multiphoton ionization signal via S_1 is monitored. When the IR laser is resonant to a vibrational level of the cluster, the ion signal decreases much because of loss of the population in the vibrational ground state. Thus, the IR absorption spectrum of the cluster can be measured by this depletion spectroscopy. The same spectrum can be obtained when the fluorescence intensity from S_1 is monitored instead of the ion current.

The IR spectrum in the excited state S_1 can also be measured by the depletion spectroscopy, when the UV laser is introduced before the IR laser 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.

Here, we have obtained an example of the spectroscopy of the reactive cluster phenol/ammonia system.[4)] Recently, it has been pointed that the hydrogen transfer from phenol to ammonia occurs in the photoexcited phenol/ammonia cluster in addition to proton transfer. The application of the IR dip spectroscopy clearly proofs that the hydrogen transfer occurs in the photoexcited phenol $(NH_3)_{3,4}$ clusters. Figure 4 shows the transition scheme of the IR dip spectroscopy, which was employed in this work. The pump UV laser (ν_1) was tuned to the S_1–S_0 transition of $PhOH–(NH_3)_n$ ($n = 3, 4$). After a long delay time (180 ns), the IR laser (ν_{IR}) was irradiated and scanned in the energy region from 2700 cm^{-1} to 3700 cm^{-1}. Then, just after ν_{IR}, the ionization laser (ν_2) was irradiated. If ν_{IR} is resonant to a certain vibrational transition, the cluster is dissociated through the vibrational predissociation process, thus, the ion signal $(NH_3)_nH^+$ due to ν_2 decreases. Therefore, the vibrational transition of the reaction product which gives $(NH_3)_nH^+$ can be observed as a dip of the ion signal.

Figure 5a shows an IR dip spectrum which was obtained by fixing ν_1 to 35498 cm^{-1}, which corresponds to a lower vibronic band in the S_1 state of $PhOH–(NH_3)_3$. This frequency was chosen according to the work by Pino *et al.*[4)] The spectrum was measured by monitoring $(NH_3)_3H^+$. To measure the vibrational transition of the reaction product via S_1, ν_{IR} was introduced at the delay time of 180 ns from ν_1 (see Figure 4). The spectrum drawn by the solid curve was measured at a moderate intensity of ν_{IR} (0.2 mJ), while that shown by the dotted curve was obtained by using an intense ν_{IR} (0.4 mJ). As can be seen in the figure, two bands with comparable intensities were observed at 3180 and 3250 cm^{-1}, and a broad band was also found in the region of 2700~3100 cm^{-1}. In the energy region higher than 3300 cm^{-1}, we could not observe any bands, even when intense ν_{IR} was used.

In order to confirm that the IR dip spectrum shows the vibrational structure of the reaction product via S_1, we also observed the IR dip spectrum of $PhOH–(NH_3)_3$ in the ground state S_0. Figure 5b shows the IR dip spectrum of $PhOH–(NH_3)_3$ in S_0, which was obtained by introducing ν_{IR} earlier than ν_1 and ν_2. As can be seen in the figure, sharp bands at around 3400 cm^{-1}, and a broad band at ~3200 cm^{-1} can be observed on the very broad background signal. This spectral feature is very close to the IR dip spectrum of the 2-naphthol–$(NH_3)_3$ cluster in S_0.[5)] From an analogy of 2-naphthol–$(NH_3)_3$, we tentatively assigned the sharp bands at ~3400 cm^{-1}, the broad bands at ~3200 cm^{-1} and the broad background to ν_3 in NH_3, ν_1 in NH_3 and ν_{OH} in phenol, respectively. Though the vibrational assignment has not yet been confirmed, it is clear that the IR dip spectrum drastically changes before (Figure 5b) and after (Figure 5a) the electronic excitation to S_1 by the UV laser ν_1. It is concluded that the IR dip spectrum with a long delay (Figure 5a) shows the IR transitions of the reaction product. The possible reaction products from $PhOH–(NH_3)_3$ in S_1 are $PhOH(T_1)–(NH_3)_3$, $PhO^-(T_1)–(NH_3)_3H^+$ or $(NH_3)_3H$. The vibrational spectrum of $PhOH(T_1)–(NH_3)_3$ is thought to maintain some similarity to that of the cluster in S_0. It is thus natural to exclude the possibility of $PhOH(T_1)–(NH_3)_3$, because of the drastic change of the vibrational structure in comparison to the IR dip spectrum of the cluster in S_0 (Figure 5b). If the ion pair $PhO^-(T_1)–(NH_3)_3H^+$ is formed, the vibrational spectrum is expected to be similar to that of $NH_4^+(NH_3)_2$. The IR dip spectrum of $NH_4^+(NH_3)_2$ has been reported by Y. T. Lee's group.[6)] According to their assignments, the $NH_4^+(NH_3)_2$ cluster shows the NH stretch vibration of the NH_3 moiety at 3413.7 cm^{-1}, and the NH stretch vibration of NH_4^+ at 3395.4 cm^{-1}. In the IR dip spectrum of the reaction product, no bands are observed in the region higher than 3300 cm^{-1}. Such a large difference does not support the generation of the ion pair. Therefore, we concluded that the neutral radical $NH_4(NH_3)_2$ is formed via $PhOH–(NH_3)_3$ in S_1. This supports the hydrogen transfer of photo-excited $PhOH-(NH_3)_3$, as proposed by Pino *et al.*[4)]

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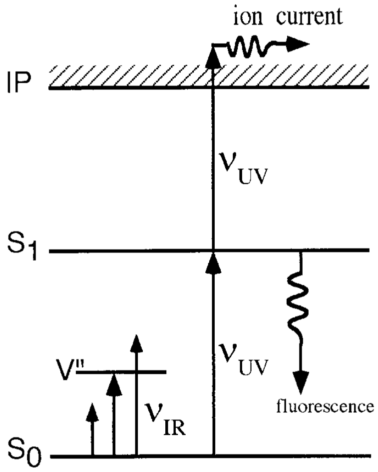

Figure 1. Principle of the IR Dip Spectroscopy. The IR transition in the ground state cluster can be measured.

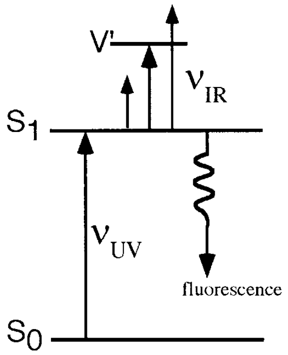

Figure 2. Principle of the UV-IR Fluorescence Dip Spectroscopy. The IR transition of the cluster in the S1 state can be obtained.

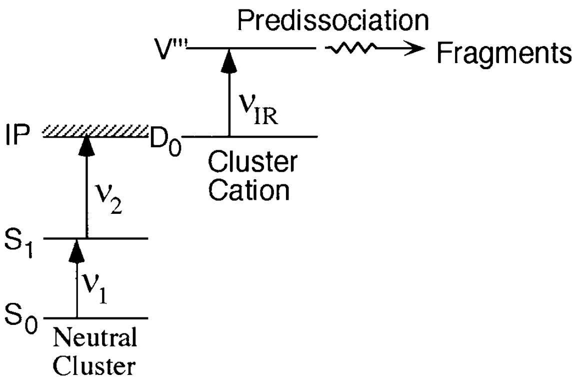

Figure 3. Principle of the mass-selected IR Ion Dip Spectroscopy. The IR transition of the cluster cation can be measured by the depletion of the parent cluster cation. The same spectrum can be measure by monitoring the enhancement of the fragments produced by the IR predissociation.

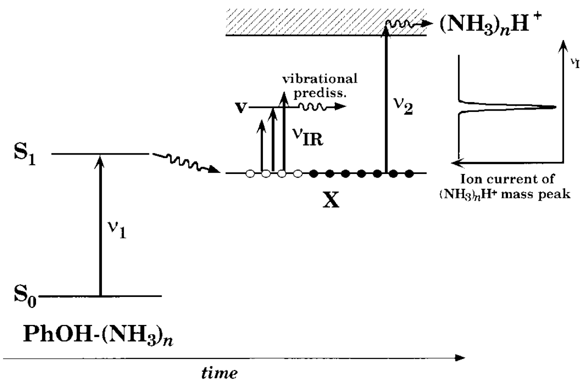

Figure 4. Schematic diagram showing the principle of IR dip spectroscopy which was employed in this work.

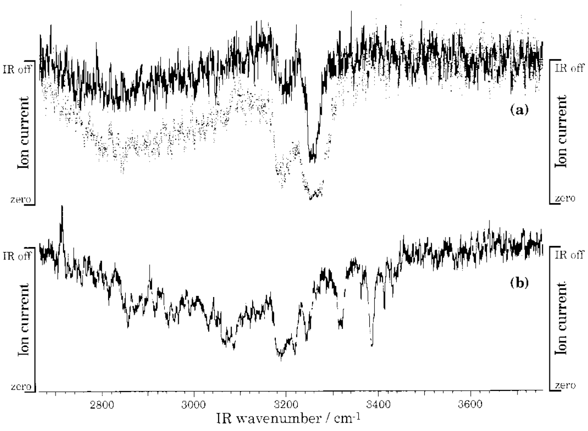

Figure 5. (a) IR dip spectrum of the reaction product which was observed by fixing ν_1 to the lower vibronic band in the S_1 state of PhOH–$(NH_3)_3$ (35498 cm^{-1}) and monitoring $(NH_3)_3H^+$. The third harmonics of the YAG laser was used as the ionization laser ν_2. The IR laser ν_{IR} was irradiated after 180 ns from the excitation to S_1 due to ν_1. The solid curves and the dotted curves show the spectra obtained by adjusting the laser power of ν_{IR} to 0.2 mJ and 0.4 mJ, respectively. (b) IR dip spectrum of PhOH–$(NH_3)_3$ in S_0. The IR laser ν_{IR} was irradiated before 20 ns from the excitation to S_1 due to ν_1.

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

MITSUKE, Koichiro; MIZUTANI, Masakazu; IWASAKI, Kota

Synchrotron radiation-laser combination techniques developed at UVSOR in Okazaki were employed for probing ionic and neutral photofragments produced in the vacuum ultraviolet. First, N_2^+ ($X\ ^2\Sigma_g^+$, $v_X = 0$ and 1) fragments resulting from direct ionization or autoionization of N_2 or N_2O were detected by laser induced fluorescence (LIF) excitation spectroscopy in the wavelength region of the $B\ ^2\Sigma_u^+ \leftarrow X\ ^2\Sigma_g^+$ transition. The partitioning of the excess energy impulsively released in dissociation was found to mainly determine the rotational distribution of N_2^+ from N_2O. Second, CN neutral fragments were dissociated from CH_3CN by excitation with synchrotron radiation of 15–20 eV. They were probed by LIF excitation spectroscopy utilizing the transition of $B\ ^2\Sigma^+\ v_B = 0 \leftarrow$

$X\ ^2\Sigma^+\ v_X = 0$. Either the dissociative ionization leading to CN + CH_3^+ or predissociation of superexcited states into CN + CH_3* may give rise to the CN fragments. We constructed a novel optics containing spheroidal and spherical mirrors and an optical fiber in order to improve the collection efficiency of the fluorescence. Third, the combination technique was incorporated into an apparatus for two-dimensional photoelectron spectroscopy to investigate photoionization dynamics of polarized atoms. Aligned Ar atoms formed by excitation with synchrotron radiation were ionized by irradiation of laser and the photoelectron angular distribution was measured with respect to the laser polarization. Derivation was made on the expressions which correlate asymmetry coefficients for the angular distribution with theoretical dynamic parameters including transition dipole matrix elements. The observed anisotropic angular distributions were reasonably explained, assuming that the matrix elements and phase shift differences are essentially independent of the total angular momentum quantum number of the final state and that the spin-orbit interaction in the continuous spectrum is small.

Electronic Structure and Optical Properties of III-V Nitrides

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The soft X-ray absorption (SXA) around nitrogen *K*-edge (N-*K*) have been measured to investigate the electronic structure of the wurtzite III-V nitrides, especially the structure of the unoccupied states. The N-*K* absorption spectra of III-V nitrides near the N *K*-edge in principle represent the partial density of the final states with *p* symmetry according to the selection rule. Since the core levels are strictly localized in space, the N-*K* absorption spectrum gives us the site-specific information. The N-*K* absorption spectrum also gives us the information about the final states symmetry p_{xy} and p_z, because the incidence soft X-ray light is linearly polarized. Under this project, the first results of N-*K* SXA spectra of wurtzite $Al_{1-x}In_xN$ (x = 0, 0.53, 0.78, 1) have been measured. The results of x = 0.53 and 0.78 reflect on their unstable crystallinity. The SXA spectra show the structure-less features and the incidence angle dependence of the SXA spectra is also unclear compared with that of wurtzite $Al_{1-x}Ga_xN$ and $In_{1-x}Ga_x$-N. However, the successional change of the spectral shape as the function of x can be seen.

Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; GEJO, Tatsuo

Recently the influence of nuclear motion within the core-hole lifetime to the dissociation dynamics becomes an extraordinarily intriguing subject in the research field of molecular core-level spectroscopy. The dynamics of molecular inner-shell excitation and relaxation processes is complex even for simple molecules, and thus it is advantageous to use various experimental techniques together with high performance monochromators in the soft x-ray region. At the UVSOR, there is only one monochromator available for high-resolution spectroscopy in the photon energy region of interest (100–550 eV), where the core edges of chemically important elements lie. In 1999 design study for a new monochromator at BL4B was started in order to improve the situation. A Varied-line-spacing Plane Grating Monochromator (VPGM) has been chosen for this work. Thanks to the availability for high quality gratings and simple scanning mechanism, VPGM seems to be one of the most promising monochromators to realizing high resolution in the soft x-ray range.

All the optical elements needed for the present (four mirrors and one grating) have been successfully fabricated. The vacuum chambers for the mirrors and grating and other beamline components were also manufactured in good condition and conveyed to the experimental hall of the UVSOR. It is expected that the first light through the new monochromator will be available in near future and the performance tests for it to be terminated in 2000.

(c) Novel Material Science

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

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([1]GUAS)

Electron correlations in low-dimensional molecular materials are essential for the understanding of novel electronic phases and their dynamical properties. i) In quasi-one-dimensional organic conductors $(TMTCF)_2X$, various changes in electronic properties can be interpreted from the viewpoint of dimensional crossovers. For weak interchain hopping, one-particle motion is effectively confined into the chains by electron correlation. The three-dimensionally ordered, antiferromagnetic phase is achieved from a charge-localized phase. For weak dimerization, electron correlation is so weak that three-dimensionality is first achieved in one-particle motion to produce a Fermi liquid, and then the nesting of the Fermi surface induces the magnetically ordered phase. Even in the latter case, the optical conductivity spectra with different polarization vectors and excitation energies show that quantum-mechanical motion of electrons is confined into the chains as the energy scale increases. Local excitation spectra for infinitely long, one-dimensional systems are studied by the thermodynamic density-matrix renormalization-group method. ii) In one-dimensional halogen-bridged binuclear metal complexes, M_2L_4X, competition between electron-lattice and electron-electron interactions brings about variety of charge and lattice ordering phases. The stability of each electronic phase is studied from the strong-coupling limit. The dependence of the electronic phase on the ligand, the halogen ion and the counter ion is qualitatively understood in a model with strong on-site repulsion and electron-lattice couplings. However, a long-range part of the electron-electron interaction is needed to reproduce the optical conductivity by the exact-diagonalization method. iii) The charge-ordering and magnetic-coupling patterns of two-dimensional organic conductors θ-$(BEDT\text{-}TTF)_2X$ are understood on the basis of the anisotropy in Coulomb repulsion strengths and transfer integrals. Some of the optical properties may indicate importance of electron-phonon interaction as well, so that both static and dynamical properties are consistently studied with unconstrained Hartree-Fock and random-phase approximations.

Size-Controlled Synthesis of Colloidal Metal Clusters

NEGISHI, Yuichi; TSUKUDA, Tatsuya

Colloidal metal clusters have gained much attention because of their noble catalystic reactivities. Because the reactivity of the cluster depends on their size and shape, the synthesis of clusters while controlling these parameters is critical especially from the viewpoint of applications. Most of the preparative methods reported so far involve the reduction of the relevant metal ions in the presence of a ligand reagent, which stabilizes the resultant clusters and prevents further coalescence. Under these conditions, the cluster size and shape can be controlled by adjusting the relative concentration of the ligands over the metal ions. We have been exploiting a method to prepare the clusters having a well-defined size and shape by taking advantage of hollow structures of various host molecules. The transmission electron microscopy observations have revealed that the Pd clusters stabilized by cyclodextrins have diameters in the range of 2–5 nm. The experimental conditions will be further optimized so as to narrow the width of the cluster size distributions with a help of mass spectrometry.

Spectroscopic and Physico-Chemical Studies of Organic Conductors

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

The reflectivity of an organic conductor provides us with a wealth of information on the electronic structure. For instance, the anisotropy of a band structure, band width, effect of electron-electron correlation, and electron-molecular vibration (*e-mv*) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. Raman spectroscopy is a complementary method to reflection spectroscopy for investigating molecular vibrations (local phonons). For the past year, we have obtained the following results. (1) The reflectivity of $(EO\text{-}TTP)_2AsF_6$ can be almost perfectly fitted down to 600 cm^{-1} by Drude model. The complete fitting by Drude model is rather exceptional for organic metals. From the analysis of the reflectivity, we determined the temperature dependence of the intra-chain and inter-chain transfer integrals. (2) The reflectivity of $(BEDT\text{-}ATD)_2X$(solvent) ($X = PF_6, AsF_6, BF_4$; solvent = THF, DHF, DO) shows a remarkable deviation from Drude model. This strongly correlated system shows a Peierls-Hubbard type of $4k_F$ phase transition. The fluctuation of the lattice distortion is observed above the phase transition temperature. (3) We investigated the C=C stretching modes in the Raman and infrared spectra of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$. We found a large factor group splitting, which was attributed to the inter-dimer interaction inside the conducting layer.

Recently, a charge-ordered ground state has been found in several organic conductors. We are investigating the charge ordering (CO) or charge disproportionation phenomena in organic conductors using the technique of vibrational spectroscopy. We have obtained the following results. (1) The C=C stretching modes of θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$ show noticeable variations in the Raman spectrum below the phase transition temperature. The low-temperature vibrational spectrum was successfully explained in terms of the charge ordering. (2) The interpretation was confirmed by investigating the isotopic compound, in which the two carbon atoms at the central C=C bond of BEDT-TTF was replaced by ^{13}C. (3) In θ-(BDT-TTP)$_2$-Cu(NCS)$_2$, we found a second-order phase transition at 250 K, which was proved to be accompanied by a charge disproportionation by the use of Raman spectrum. (4) We found a magnetic phase transition at 5 K in θ-(BDT-TTP)$_2$Cu(NCS)$_2$. The ground state is a non-magnetic state.

In some charge-transfer salts of phthalocyanine, localized unpaired d-electrons coexist with itinerant π-electrons. We are investigating these π-d electron systems from the viewpoint that it is analogous to an f-electron system, in which a narrow f-band coexists with a wide s-band. We have obtained the following results. (1) The magnitude of the π-d exchange interaction was determined from the analysis of the temperature dependence of the *g* value and linewidth of the ESR signal in the dilute alloy system $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$. The estimated Kondo temperature was 10^{-5} K. (2) We measured the pressure dependence of the resistivity of $CoPc(AsF_6)_{0.5}$ down to 50 K. In contrast to NiPc-$(AsF_6)_{0.5}$, the temperature of the resistivity minimum decreases down to 100 K at 0.9 GPa. (3) We found an antiferromagnetic (AF) phase transition at 12 K in newly prepared π-d system, (DMTSA)FeCl$_4$. The heat capacity experiment suggested that the magnetic moment of Fe^{2+} (S = 5/2) took in part in the AF state and the AF interaction has a low-dimensional character.

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

NAKAMURA, Toshikazu; TSUKADA, Hiroshi

Competition of the electronic phases in molecular based conductors has attracted much attention. The aims of this project are to clarify these electronic phases stabilized at low temperatures and to explore novel electronic phases in molecular-based conductors by microscopic investigation. It is worth noting that spin-Peierls (spin-singlet), commensurate spin density wave (C-SDW), incommensurate spin density wave (IC-SDW), and superconducting phases can be realized by applying appropriate pressures even in the same system. Investigation of such electronic phases in molecular based conductors is important to understand the unsolved fundamental problems in the field of solid state physics.

Broad-line solid state NMR is a powerful measurement to clarify the fundamental electronic properties. In this project, we are preparing the second 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.

The following topics are in progress.

[1] Successive SDW transition in (EDT-TTF)$_2$AuBr$_2$.
[2] Magnetic properties of organic spin-ladder systems, (BDTFP)$_2$X.
[3] NMR and ESR investigation of organic conductors based on TTP derivatives.
[4] Magnetic structures of the antiferromagnetic states in Pd(dmit)$_2$ families.
[5] Competition between local and itinerant electrons in charge-transfer salts: (CPDT-STF)-TCNQ.

Development of New Organic Conductors and Their Physical Properties

KOBAYASHI, Hayao; FUJIWARA, Hideki; FUJIWARA, Emiko; ADACHI, Takafumi; NARYMBETOV, Bakhyt Zh.; TANAKA, Hisashi; TAMURA, Itaru; KOBAYASHI, Akiko[1]
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In order to contribute for further development of solid state physics and chemistry of molecular materials, we have tried to develop new types of molecular conductors and to improve the conventional methods of X-ray structure analysis and resistivity measurements at high pressure. The main results obtained in the last one year are as follows: (1) we have recently found the first single-component molecular metal. Since the discoveries of the semiconducting properties of phtalocyanines and aromatic hydrocarbones around 1950, many chemists have dreamed to develop metallic crystal composed of simgle molecules. Our fingings will open a way to develop molecular metals or even superconductors soluble in organic solvents. (2) Following after the first discovery of antiferromagnetic organic superconductor κ-BETS$_2$FeBr$_4$, the second antiferromagnetic organic superconductor κ-BETS$_2$-FeCl$_4$ was discovered. Neel temperature (T_N = 0.45 K) and the superconducting transition temperature (T_c = 0.1 K) are much lower than those of κ-BETS$_2$FeBr$_4$ (T_N = 2.4 K, T_c = 1.1 K). In these systems, the π-d interaction between π conduction electrons in BETS layers and magnetic d electrons in the anion sites is considered to be mediated by halogen atoms of FeX_4^- anions. The microscopic mechanism of magnetic interaction between Fe^{3+} ions below T_c will be of special interest because π conduction electrons are in the superconducting state. (3) We have succeeded to obtain the accurate resistivity data of organic single crystal up to 15 GPa by adopting diamond-anvile four-probe technique. In the course of these studies, we have examined the possiblity of the superconducting transition of (TMTTF)$_2$PF$_6$, the sulfur-analog of the first organic superconductor (TMTSF)$_2$PF$_6$ and found the superconducting transition above 52 kbar. Bechgaars salt with PF$_6$ anion is the first “TM system” whose superconductivity was found in both Se- ans S-analogs. (4) The development of “pure organic magnetic conductor” based on stable organic radicals is one of the next important targets of the chemists in the fields of molecular conductors and molecular magnets. We are now trying to prepare candidate molecules suitable to construct such systems.

Constraction of a Catalase Active Site by Site Directed Mutagenesis of Myoglobin

HARA, Isao; MATSUI, Toshitaka; OZAKI, Shin-ichi; WATANABE, Yoshihito

A double mutant protein of myoglobin (Mb) that exhibits altered axial ligation has been prepared by site-directed mutagenesis. The original axial ligand residue, histidine 93(F8), was replaced with glycine, and also histidine 64(E7) was replaced with tyrosine as an axial ligand, resulting in H64Y/H93G Mb. Tyrosine coordination to the ferric heme iron is verified by optical absorption, EPR and resonance Raman spectroscopy. The optical absorption spectrum of a ferric form of H64Y/H93G Mb is characteristic of high spin heme and similar to those observed in bovine liver catalase and natural occurring mutants of hemoglobin having a tyrosinate ligand. In contrast, wild-type and H64Y/H93G Mb exhibit almost the same spectra in ferrous and carbon monoxy forms, suggesting coordination of a histidine residue, possibly histidine 97(FG3), in the reduced forms of the mutant. The tyrosinate ligation in the ferric H64Y/H93G Mb is confirmed by the observation of $\nu_{\text{Fe-O}}$ band at 597 cm^{-1} in a resonance Raman spectrum. Although EPR spectrum of ferric H64Y/H93G Mb consists of at least two sets of rhombic high spin signals, the major component is similar to bovine liver catalase in the *g*-values. These results indicate successful conversion of Mb into a catalase-like protein in terms of coordination structure and electronic properties of the heme iron.

Construction and Characterization of Chiral Molecule-Based Magnets in a Systematic Way

INOUE, Katsuya; KUMAGAI, Hitoshi; IMAI, Hiroyuki

The design of multi-functional molecular materials is one of the current interests. Especially the molecular magnetic materials with conducting and/or optical properties are one of the challenging target in the last few years. The synthesis and study of optical properties on molecular-based magnetic materials being transparent for light, are of great interest. Novel magneto-optical phenomena, MChD effect, have been theoretically predicted and observed in chiral paramagnetic materials in 1997. Although novel properties are expected for such compounds, few examples of chiral molecular-based magnetic materials are still known. To get more insight in their properties it is therefore important to construct such chiral molecule-based magnets in a systematic way. We designed and synthesized a chiral organic radical which was can be employed to construct chiral molecular-based magnets. We have introduced a strategy of using π-conjugated high-spin oligonitroxide radicals which can be used as bridging ligands for paramagnetic transition metal ions in order to assemble and align the electron spins on a macroscopic scale. By this strategy, we have made a chiral metamagnet with a T_N = 5.5 K and a ferrimagnet with a T_C = 4.5 K. (see V-E). The observation of MChD effect of this complex is now underway.

STM Study on Synchrotron-Radiation Stimulated SiO_2 Desorption on Si (111) Surface

NONOGAKI, Youichi; URISU, Tsuneo

We have been developing UHV-STM systems with special process chambers for synchrotron radiation (SR) irradiation. Using the UHV-STM systems, we have investigated SR-stimulated SiO_2 desorption on Si (111) surface which is one of most interesting topics not only for surface science but for nano-fabrication in the Si-based device engineering. We expect that SR-stimulated SiO_2 desorption become most significant etching techniques for the fine pattern fabrication on the Si surfaces. Since the SiO_2 desorption was induced by surface photochemical reaction without physical sputtering, the etching is expected to be very low damage and high precision processes.

It was found that an atomically flat surface was obtained after two hours SR irradiation even at a low temperature of ~700 °C. The surface has bilayer atomic steps and 7×7 reconstruction on the terrace. The bilayer steps tend to pass along crystallographic axis. This is in sharp contrast to Si surfaces after thermal desorption of SiO_2 at temperatures of 880 °C, where the steps are much more irregular. It indicates that the bilayer atomic steps reach thermodynamic equilibrium under synchrotron radiation at temperatures much lower than those necessaries for thermal desorption.

We conclude that SR-stimulated SiO_2 desorption occurs and shows different characteristics from thermal desorption. However, we still do not know the mechanisms how the SiO_2 desorb from the surface and how the steps rearrange. To consider these mechanisms, time dependence of STM images observed at the same area would be good help. Now, we plan to use Si wafer with marks for position detection, which is made by conventional lithography and wet chemical etching.

Design and Construction of UVSOR-BL4A2 Beam Line for Nano-Structure Processing

TAKEZOE, Noritaka; YANAGIDA, Hideaki[1]; KUROSAWA, Kou; NONOGAKI, Youichi; NODA, Hideyuki; MEKARU, Harutaka[2]; URISU, Tsuneo
([1]IMS and Univ. Miyazaki; [2]Himeji Inst. Tech.)

[7th International Conference on Synchrotron Radiation Instrumentation]

We have designed and constructed a new beam line BL4A2 at UVSOR mainly for nano-structure fabrication based on synchrotron radiation stimulated surface photochemical reactions. In order to obtain high-photon flux, we use white ray beam focused with only one mirror. The beam line is connected with ultra-high vacuum scanning tunneling microscope for in-situ atomic scale pbservations, low energy electron diffraction and Auger electron spectroscope for surface crystal structure characterization, and photo-stimulated surface reaction chamber. In order to monitor the optical properties with atomic scale, a near field optical microscope is planned to be installed.

Study on RF-Photocathode for Compact X-Ray Sources

TAKASHIMA, Yoshifumi; KOBAYAKAWA, Hisashi[1]; KIMURA, Kenichi[1]; SUGIYAMA, Harue[1];

FURUTA, Fumio[1]; NAKANISHI, Tsutomu[1]
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When a charged particle is passing through a object with a relativistic velocity, atoms in the object feel a pulse of electromagnetic field which causes electromagnetic radiations from the objects. Cherenkov radiation is one of this kind of radiation. If a object has a periodical structure, a coherent x-ray called "Parametric x-ray Radiation(PXR)"[1,2] is generated. PXR has good monochromaticity and is radiated in a conical direction away from a direction of incident charged particles. Thus PXR is a good candidate of a hard x-ray source. However, in spite of optimizing the thickness of the target radiator of crystal, the highest intensity of PXR achieved up to now is about 10^{-5} photons/e^- and is not enough to use in practical applications unless we use a very high current electron beam.

RF-photocathode would produce high peak current of electron beam so that it is useful as a electron source. Figure 1 shows a plan of our system. Now we are studying the photocathode made of cesium telluride and constructing the RF system.

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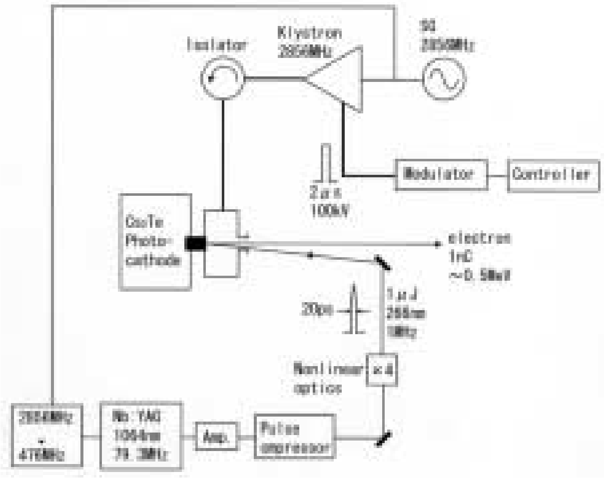

Figure 1. System of RF-gun.

Reductive Activation of Metal-Carbonyl Complexes Derived from Carbon Dioxide and Oxidative Activation of Metal-Hydroxy and -Oxo Complexes Derived from Water

TANAKA, Koji: WADA, Tohru: MIZUKAWA, Tetsunori; SHIREN, Kazushi; WADA, Hiroaki[1]; KOBAYASHI, Katsuaki; TOMON, Takashi
([1]RIKEN)

Some of metal-carbonyl complexes are obtained through metal-CO_2 adducts which are produced by an attack of CO_2 to the reduced form of those metal-complexes and subsequent oxide transfer from the CO_2 group to free CO_2. Accordingly, organic synthesis through M-CO_2 and M-CO complexes is highly desired in the view point of the development of a new C1 resources. A major problem of the reduction of CO_2 using homogeneous catalysis is reductive cleavages of M-CO bonds under reductive conditions. Accumulation of too much electrons in the central metals in the reduction of CO_2 can be avoided by using ligand localized redox reactions rather than metal centered ones. Ligands which can flexibly change the coordination modes among monodentate, bidentate and bridging form which connects 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.

Acids or bases generated in industrial process are just wasted after neutralization. Proton gradient (Δp) between inside and outside of a cell is represented as the sum of electric activity ($\Delta\Psi$) and chemical activity (ΔpH) components. $\Delta p = \Delta\Psi - Z\Delta pH$ ($Z = 2.303RT/F$) Proton gradient is equivalent to the neutralization energy because the neutralization reaction takes place to form water if the separating membrane is removed. 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 provided by chemical bondings (chemical energy). Along this line, we tried to convert the neutral energy to electronic energy by using ruthenium-aqua complexes.

Developments and Researches of New Laser Materials

SARUKURA, Nobuhiko; OHTAKE, Hideyuki; LIU, Zhenlin; KAWAHATA, Eiji; KOZEKI, Toshimasa; ONO, Shingo[1]
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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.

New Advanced Organic Materials Based on Novel Heterocyclic Compounds

YAMASHITA, Yoshiro; TANAKA, Shoji; TOMURA, Masaaki

We have succeeded in preparing new electron donors and acceptors with extended π-conjugation. For example, TTF vinylogues bearing various substituents at the vinyl positions have been prepared using an oxidative dimerization reaction of 1,4-dithiafulvenes. We have prepared derivatives bearing cyano or bromo substituents which can induce intermolecular interactions. Novel bis(1,3-dithiole) electron donors containing an azulene spacer unit were also synthesized.

They have small HOMO-LUMO gaps and show the longest absorption maxima at 733–762 nm. As electron acceptors, bithiazole analogues of tetracyanodiphenoquinodimethane (TCNDQ) were prepared using Pd-catalyzed coupling reaction of dicyanomethanide to the corresponding dibromide precursors. Heterocyclic TCNQ analogues containing thiophene and benzothiadiazole units were also prepared using the similar Pd-catalyzed reaction. They are polarized molecules and show strong absorptions at longer wavelengths than 500 nm. They gave charge transfer complexes with various electron donors. Decamethylferrocenium salts of anilate anions were obtained as single crystals. The unique crystal structures involving intermolecular interactions such as hydrogen bonding were revealed by X-ray analysis. A new type of hydrogen-bonding system has also been developed by using dipyridylacetylenes as proton acceptor and chloranilic acid as proton donor. The component molecules are combined via three-center hydrogen bonded interactions. Furthermore, we have prepared thiophene oligomers as promising molecular-scale electronic wire which have small energy gaps with a rigid and coplanar main chain. Details of these works are described in VIII-C section.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

FUJII, Hiroshi; FUNAHASHI, Yasuhiro; MIZUTANI, Mamoru; IKEUE, Takahisa

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) Resonance Raman(RR) spectra are reported for two models of the compound I intermediates of oxidative heme proteins; namely, the imidazole (Im) and 2-methyl-imidazole (2-MeIm) complexes of the ferryl π-cation radical derivative of iron-(5,10,15,20-tetramesitylporphyrin). While the observed shifts in the frequencies of the core modes are in agreement with those expected upon formation of the π-cation radical, the results suggest that the isolated effect of macrocycle oxidation on the Fe=O stretching frequency is rather small.
(2) To reveal the electronic states of these intermediates and to understand the reaction mechanism of cytochrome c oxidase, 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 complex as a model for the intermediate P by the oxidation of the ferric model complex with mCPBA 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. The regioselective oxidation of the α-meso position by HO is quite unique, in contrast to the non-enzymatic heme degradation. We have shown the first evidence of the formation of biliverdin isomers other than biliverdinIXα by HO mutants.

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

NAGATA, Toshi; ITO, Hajime; ITO, Kaname

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. Application of photoinduced electron transfer as a synthetic tool, where photoexcited organic molecules (like porphyrins) are considered from a synthetic point of view as short-lived reducing/oxidizing reagents. Two reaction systems, reductive silylation of quinones and diketones and oxidation of alcohols, have been discovered.
B. Development of binary ligands that allow control over the metal coordination environment. A new class of binary ligands, terpyridine-salicylaldehyde, were prepared and studies on the redox properties of the metal complexes are currently under way.

Design and Synthesis of New Tellurium-Containing Donors

KOBAYASHI, Hayao; SUZUKI, Toshiyasu; FUJIWARA, Hideki; OJIMA, Emiko

In the field of molecular conductors, systems based on tellurium-containing donor molecules have not received as much attention as systems based on sulfur- or selenium-containing donors. By incorporating heavy chalcogen atoms such as tellurium into donor molecules, a new metallic system with a wider bandwidth and a higher dimensionality is expected to appear. We have synthesized two TTeF derivatives of 1-Benzyl-2,5-dihydropyrrole and 1-Methyl-2,5-dihydropyrrole. The X-ray structure analyses showed that the intermolecular Te-Te distances are shorter than the sum of the van der Waals radii (3.95 and 3.96 Å, respectively).

Ball on Disk Tribometer

WATANABE, Michio; KONDOH, Takuhiko; MIYASHITA, Harumi

This year we have newly built a Ball on Disk Tribometer (Figure 1) to clear frictional phenomena of metals,ceramics,macromolecular materials and surface modificated materials.

Now we are evaluating the performance both in antigalling and in coefficient of friction regard to some samples.

Figure 1. Ball on Disk Tribometer.

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 excited by photons has attracted much interest from both of basic and application sides. We have been investigating the photo-induced phenomena 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. To understand the non-equilibrium dynamics of the negative-electron affinity on GaAs surfaces is an interesting subject and is useful for producing a practical spin-polarized electron emitter. We have investigated the time-response on the negative-electron affinity GaAs surfaces using photoelectron spectroscopy.

It is also important subject to investigate photo-induced phase transition using photoelectron spectroscopy based on the combination of synchrotron radiation and laser. Core-level and valence-band photoelectron spectra showed clearly the characteristics of the photo-induced phase.

We have been also investigating the two-photon excitation experiments using synchrotron radiation and laser in recent years, since simultaneous excitation with two photons (SR and laser) is interesting and promising field to understand the symmetry-forbidden states and excited-state dynamics. The experiments are in progress on BaF_2 and ZnSe.