SPECIAL RESEARCH PROJECTS

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

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

(a) Chemical Reaction Dynamics

Folding Mechanism of Protein Molecules Studied by Generalized-Ensemble Algorithms

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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. To be more specific, it is widely believed that three-dimensional structures of proteins are determined by their amino-acid sequence information. However, nobody has completely succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles).

There are two elements for the difficulty. One element is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be taken into account is very large. The other element for the difficulty is that there exist a huge number of local minima in the energy function, and simulations by conventional techniques will necessarily get trapped in one of the local minima without ever finding the energy global minimum. 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 combination of multicanonical algorithm and replica-exchange method is particularly promising.2),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 eventually in the prediction of tertiary structures of proteins from the first principles.

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Theoretical Studies of Chemical Dynamics

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Various chemical quantum dynamics have been studied analytically as well as numerically. Quantum dynamics calculations have been carried out for the reactions in the $O(^1D)HCl$ system which is a prototypical electronically nonadiabatic triatomic reaction system.1)–3) Three potential energy surfaces are involved and reaction mechanisms on each surface are clarified. Effects of nonadiabatic transitions are planned to be further analyzed. In order to attack large chemical and biological nonadiabatic systems two types of semiclassical methodologies are developed with the Zhu-Nakamura theory of nonadiabatic transition4) incorporated into the formalisms. These are the TSH (trajectory surface hopping) and the semiclassical Herman-Kluk type of frozen Gaussian propagation method.

New powerful theories have been developed for treating two kinds of multi-dimensional tunneling effects. One is the energy splitting in a symmetric double well potential5),6) and the other is the decay of metastable state through tunneling.7) The first one was applied to nine atomic malonaldehyde molecule with use of the high level of ab initio quantum chemical calculations and an excellent agreement with experiment was obtained.8) A novel method to defect caustics along classical trajectory has also been successfully formulated. These theories can be incorporated into the TSH and the semiclassical prepagation method to take into account the tunneling effects.

Finally, new ideas of laser control of molecular processes have been devised. It was demonstrated that the photodissociation branching ratio of HI molecule can be controlled with use of the complete reflection phenomenon.9) Another idea is to use a sequence of chirped pulses to control nonadiabatic transitions among dressed states. This can be used to achieve selective and complete excitation of a particular state.10)

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Two-Dimensional Raman and Infrared Vibrational Spectroscopy for a Harmonic Oscillator System Nonlinearly Coupled with a Colored Noise Bath

KATO, Tsuyoshi; TANIMURA, Yoshitaka

Multi-dimensional vibrational response functions of a harmonic oscillator are reconsidered by assuming nonlinear system-bath couplings. In addition to a standard linear-linear(LL) system-bath interaction, we consider a square-linear(SL) interaction. The LL interaction causes the vibrational energy relaxation, while the SL interaction mainly responsible for the vibrational phase relaxation. The dynamics of the relevant system are investigated by the numerical integration of the Gaussian-Markovian Fokker-Planck equation under the condition of strong couplings with a colored noise bath, where the conventional perturbative approach cannot be applied. The response functions for the fifth-order nonresonant Raman and the third-order infrared (or equivalently the second-order infrared and the seventh-order non-resonant Raman) spectra are calculated under the various combinations of the LL and the SL coupling strengths. Calculated two-dimensional response functions demonstrate that those spectroscopic technique are very sensitive to the mechanism of the system-bath couplings and the correlation time of the bath fluctuation. We discuss the primary optical transition pathways involved to elucidate the corresponding spectroscopic features and to relate them to the microscopic sources of the vibrational nonlinearity which is induced by the system-bath interactions. Optical pathways for the fifth-order Raman spectroscopies from an "anisotropic" medium were newly found in this study, which were not predicted by the weak system-bath coupling theory or the standard Brownian harmonic oscillator model.

Experimental Exploration of Chemical Change at the Most Detailed Level

SUZUKI, Toshinori; KOHGUCHI, Hiroshi; KATAYANAGI, Hideki

Molecular reaction dynamics was explored at the level of state-to-state differential cross sections for photoionization, photodissociation, and molecular collisions using electron and ion imaging techniques. We introduced photoion imaging polarization analysis into the study of photodissociation dynamics and established theoretical frame work to analyze electron orbital alignment. Molecular scattering was investigated by using crossed beam ion imaging that provided the most accurate and detailed experimental results on open-shell collision dynamics. Femtosecond time-resolved photoelectron imaging was developed as a novel experimental means to visualize time-evolving molecular electronic state and electron configuration.

Computational Study of Quantum Dynamics of a Solute in Solution

OKAZAKI, Susumu; MIURA, Shinichi; IWAHASHI, Kensuke; TANAKA, Junji; MIKAMI, Taiji; SATO, Masahiro

Molecular mechanism of vibrational energy relaxation of a solute molecule in solution has been analyzed based upon path integral influence functional theory. Then, solvent normal modes were transformed to each molecular motion in order to examine the couplings in terms of solvent molecules. Coupling which has large contribution to relaxation could be attributed to a particular water molecule. Mixed quantum-classical molecular dynamics method has also been applied to the analysis of dynamic aspects of the coupling Component which is resonant with the solute wave function was extracted from the solute-solvent interaction <0|V|1>. In a short time-scale, *i.e.* sub ps, it shows almost random behavior. However, in longer time-scale, ~ps, it clearly shows relaxation.

Simulation method for quantum liquids has been investigated, too. A new hybrid Monte Carlo method has been developed to simulate liquid helium in superfluid state.

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 changes and vibrational energy relaxation of heme. 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 ($\tau = 70$ 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 Dynamic Spectroscopy Apparatus Having Nanometer Spatial Resolution

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

Recent technological progress in scanning near-field optical microscope (SNOM) has made it possible to perform optical measurements with very high spatial resolution beyond the diffraction limit. We have constructed apparatus for space- and time-resolved spectroscopic measurements, by combining SNOM and ultrafast time-resolved technique. With the apparatus, we have achieved ~ 100 nm spatial and ~ 100 fs 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 make use of this experimental methodology to investigate basic problems on chemical processes of mesoscopic systems. This technique also has a potential to shed a new light on nanoscale material science. Right now we have performed measurements to understand basic local optical properties of porphyrin aggregates and metal nanoparticles. The details of the apparatus and experimental results are reported in II-A.

Studies on Laser Cooling and Trapping of Metastable Helium Atoms and Laser Spectroscopic Studies of Atoms and Ions in Liquid Helium

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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 helium atoms. Especially, we have developed a new metastable atomic beam source cooled by liquid helium, which can provide a metastable helium beam with a very small initial velocity. With this metastable source, it is greatly expected that the number of trapped atoms will dramatically be increased, and that Bose-Einstein condensation will more easily be realized (see II-B-1). On the other hand, in “laser spectroscopic studies of atoms and ions in liquid helium,” for both ^{4}He and ^{3}He we have extensively investigated the helium pressure dependence of inner shell transition spectra of Eu atoms over a very wide pressure range including the solidification region. We have found that some interesting differences in spectral behaviors between ^{4}He and ^{3}He in both liquid and solid states (see II-C-1). In addition, from the pressure dependence of the sideband profile of the spectra, we have found a proof for the inference that an unknown structure of the phonon sideband seen in our previous experiments for liquid ^{4}He is due to the roton spectrum (see II-C-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 photoexcitation, and consequently spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopy to the reactive clusters to reveal detailed mechanism of intracluster reaction. The originally developed spectroscopies, such as nonresonant ionization detected IR spectroscopy, UV-IR-UV ion dip spectroscopy, and the picosecond time-resolved IR dip spectroscopy, are described in the Research Activities of this group. By using these method, we have measured the IR spectra of solvated clusters, such as phenol/ammonia, naphthol/water and alcohol, carbazole/water and 7-azaindole dimers, and have discussed the relation between the structure and intracluster reactions. We also investigated the vibrational dynamics of those clusters in S_0 by picosecond time-resolved nonresonant ionization detected IR (NID-IR) spectroscopy and picosecond time-resolved transient fluorescence detected IR (TFD-IR) spectroscopy.

Dynamics of Superexcited States of Molecules and Fullerenes Studied by Electron, Fluorescence, and Laser Spectroscopy

MITSUKE, Koichiro

One of our main interests is to elucidate the spectroscopy and dynamics of superexcited states of molecules and fullerenes. Though these states often play crucial role in photoexcitation and bimolecular reactions in the VUV and soft X-ray regions, the knowledge of their characteristics is very limited. Owing to autoionization in a very short period and strong perturbation from neighboring neutral states, superexcited states experience various decay pathways such as neutral dissociation, internal conversion, and intramolecular vibrational redistribution. We have employed three experimental methods which serve as a means of providing insights into such processes: Photoelectron spectroscopy, dispersed fluorescence spectroscopy, and SR-laser pump-probe spectroscopy. Taking maximum advantage of the tunability of synchrotron radiation, we have obtained hundreds of spectra at different primary photon energies. Assembling and comparing these one-dimensional spectra enable us to uncover novel decay pathways. For example, superexcited states are often subject to neutral dissociation into electronically excited fragments. These fragments release their internal energy by emitting fluorescence. Dispersed fluorescence spectroscopy is helpful for us in assigning the dissociation products and determining their vibrational distribution. However, this is not sufficient. If we wish to decide on which precursor state gives rise to the fragments, we should carry on excitation spectroscopy for the particular emission band with changing the primary photon energy. Namely, the fluorescence intensity should be measured as a function of two variables, the initial synchrotron radiation photon energy and final fluorescence wavelength. Two-dimensional plots thus obtained allow us to investigate involved dissociation mechanism of a superexcited state, to evaluate the magnitudes of the electronic coupling with other neutral or ionic states, and to achieve description on the potential energy surface of the relevant dissociative state.

Theoretical Study on Photochromic Molecules and Electrochromic Amorphous

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Methylviologen dication is easily reduced to a monocation radical, and turned to be blue, forming a charge-transfer (CT) complex with a donor molecule. It is reported that photo-induced reduction and charge transfer complexes of this molecule in clathrates. We study this reduction and CT using quantum chemical calculations. The energy changes with the torsion angle of the two cations and the spectral change, solvent effect and the charge transfer between the dication and other guest molecules in the clathrates are investigated. The optimized geometry of the monocation radical was found to be planar while that of the dication is twisted, which is consistent with recent calculations for related compounds. The color change upon the photoreduction and CT was reproduced by the calculation. The solvent effect of acetonitrile was small for photoreduction but significant for the CT complex.

It is known that WO_3 films show color change when the charge was injected and remarkable change of its IR spectrum. With increasing of injected protons, the intensity of peak of ν(W–OH) increased and its position shifted hugely from 3200 to 2400 cm^{-1}. We calculated various bond-patterns of OH vibrations. Then OH vibrations accompanied with hydrogen bonds are plausible for observed OH peaks. On the other hand, with increasing of injected protons the intensity of peak of ν(W=O) bond also increased, but its position shifted a little. It is considered that parts of W–O–W–O–W bonds were broken by injected protons and then W=O bonds were brought about. It is suggested that the color change is associated with radical formation.

Decay and Dissociation Dynamics of Core Excited Molecules

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The dynamics of molecular inner-shell photoexcitation, photoionization, and subsequent decay processes is much more complex, in comparison to outer-shell photoionization which is still largely within the scope of the single electron picture. For instance, the excitation and ionization of valence electrons accompanies the inner-shell photoionization, which manifest themselves as shake-up and shake-off satellite structures in the corresponding photoelectron spectrum. The multi-electron processes due to the electron correlation are known to happen not only in the primary inner-shell hole creation processes, but also in their relaxation processes. It is advantageous to use various experimental techniques together with a high performance monochromator in the soft x-ray region, in order to investigate the related phenomena from different points of view. The high performance of the Varied-Line-Spacing Plane Grating Monochromator (VLS-PGM) at BL4B of the UVSOR facility provides us opportunities for performing various spectroscopic studies on molecular core-levels with high-resolution.

A high luminosity double toroidal analyzer (DTA) equipped with a two-dimensional detector enables the simultaneous measurement of the angular distribution and kinetic energy of electrons/ions. In the first performance test of DTA at BL4B, the LMM Auger spectra of Ar atoms have been observed at last. However, considerable a considerable amount of noise after the accidental discharge of the microchannel plates were experienced, which may lead to inhomogeneous and unexpected geometrical patterns on the images around the symmetry axis of DTA. In order to obtain threshold electron spectra including the symmetry information on the excited states, symmetry-resolved threshold electron spectra, which are based on the combination between a threshold electron spectroscopy and an angle-resolved photoion spectroscopy, have been measured on BL27SU at the SPring-8 after the careful tuning of the apparatus on BL4B and BL7B. The results obtained so far are not yet close to satisfaction, and further improvement of our experimental setup is obviously necessary for achieving a much higher counting rate for the coincidence signals.

A new project towards the practical usability of the free electron laser (FEL) developed at UVSOR has been continued since 2000. Two-photon double-resonant excitation spectrum of the autoionization Xe* $5p^54f$ resonance via the Xe* $5p^55d$ intermediate state has been successfully derived in 2001. Recently we have performed pressure-dependent measurements concerning the same system. The results gained, strongly suggest the formation of Xe dimmers in the intermediate states prepared by the initial pump processes.

(c) Novel Materials Science

Parallel Algorithm of Semi-In-Core Calculations of Large Molecular Systems

ISHIMURA, Kazuya; NAGASE, Shigeru

In material science, it is currently of great interest to perform reliable and high-speed calculations for large molecular systems using ab initio molecular orbital or density functional methods. An important bottleneck for high-speed calculations is time-consuming two-electron integrals. By using effectively many distributed memories available for large PC clusters and parallelization algorithm, we have developed a semi-in-core method to calculate two-electron integrals, which is essential for the high-speed ab intio and density functional calculations of large molecular systems. The method is implemented in the representative quantum chemistry program packages such as GAMESS.

Statistical Mechanics of Interfacial Fluids

HIRATA, Fumio; KOVALENKO, Andriy F.; YAMAZAKI, Takeshi; TANIMURA, Ayumi; OMELYAN, Ihor

Microscopic structure of fluid interfaces has been drawing a lot of attention due to recent development in the experimental techniques devised particularly to probe the interface. However, there are many open questions remained unanswered. For example, how wide is the interfacial region, how does it depend on the chemical species consisting the solution? Is the interface more or less homogeneous in terms of density or concentration of the two fluids, or is it spatially inhomogeneous? If it is inhomogeneous, what is the spatial extent of the inhomogeneity?

Answering those questions is the most difficult and challenging tasks for theoretical physics and chemistry, and not much progress has been made in the past, especially from a molecular view point. The difficulty arises from the fact that the interface makes the density of fluid non-uniform, which violates the standard requirement for the liquid state theory, or the uniformity of the system. The requirement can be removed by applying a density functional theory for a non-uniform fluids.

In the present project, we develop the theory of non-uniform fluids, which employs a density functional theory of fluids developed by Lovett, Mou, Buff, and Wertheim (LMBW). The basic idea of the theory is to solve the problem in two stages. The first stage is to obtain the one-particle density along the direction normal to the fluid interface, which is a functional of a pair correlation function of the fluids. The second stage is to obtain the pair correlation function in the fluid, which, in tern, is a functional of the one-particle density. Therefore, the two equations which relate the one-particle density and the pair correlation function should be solved iteratively.

We have applied the theory to two problems concerning interfacial fluids, which are essentially the same in terms of the theoretical view point: a Lennard-Jones fluid at vapor-liquid interface, and molecular fluids at liquid-liquid interface.

The density profile at the vapor-liquid interface is shown in Figure 1. The density profile indicates that the width of the interfacial region is about 1 nano-meter for the system in concern. The pair correlation functions (PCF) in planes parallel to the interface are shown in Figure 2. The thin solid line, thick solid line and dashed line depict, respectively, the PCF in the plane at $z = -10\sigma$(vapor), $z = +10\sigma$(liquid), and $z = 0$(interface), where z denotes the distance from the interface, and σ is the Lennard-Jone diameter of a molecule. The behavior of PCFs at $z = -10\sigma$ at $z = +10\sigma$ are typical to those in bulk gas and liquids, respectively, while the PCF at $z = 0$ has an unusually long lasting tail. The long range behavior in PCF is a characteristic of the "critical point" of fluids, which is a manifestation of the density fluctuation in pheno-menological scale.

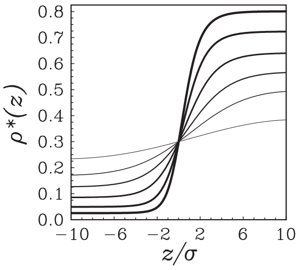

Figure 1.

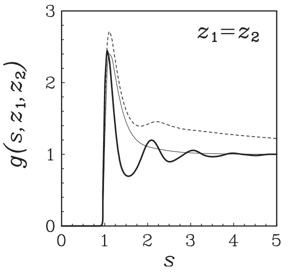

Figure 2.

Theory for Equilibrium and Non-Equilibrium Properties of Low-Dimensional Molecular Materials with Strong Correlation

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In low-dimensional molecular materials, the effects of different interactions appear not only in their ground states or in their equilibrium phases but also in the non-equilibrium time-evolution of their inhomogeneous domains. i) In the mixed-stack organic charge-transfer complex, TTF-CA, neutral-ionic and dimerization-induced ferroelectric phase transitions are observed. At ambient pressure, they occur simultaneously and discontinuously. Under high pressure, these transitions take place at different temperatures, that is, its phase diagram contains a paraelectric ionic phase in addition to the ferroelectric ionic and neutral phases. To treat both the ionicity (*i.e.*, degree of charge transfer from the donor to acceptor molecules) and the dimerization, which causes a finite polarization, we employ a classical spin-1 model called Blume-Emery-Griffiths model. To reproduce the observed solid-liquid-gas phase diagram, we show the inter-stack electrostriction effect is necessary. This complex shows ionic-to-neutral and neutral-to-ionic transitions after sufficiently strong photoirradiation. We have solved the time-dependent Schrödinger equation for an extended Peierls-Hubbard model under an oscillating electric field during the photoirradiation. In the ionic-to-neutral transition, there is threshold photo-absorption intensity above which the ionicity globally changes. In the neutral-to-ionic transition, however, the degree of charge transfer is proportional to the number of absorbed photons, although it is still a highly nonlinear function of the amplitude and duration time of the oscillating electric field. ii) Among halogen-bridged binuclear metal complexes, the iodine-bridged binuclear platinum complexes with ligand pop show a discontinuous transition from the charge-polarization to charge-density-wave phases upon increasing pressure. A photo-induced transition is observed in the hysteresis loop, but only from the metastable charge-density-wave to stable charge-polarization phases. The threshold photo-absorption intensity is explained by drawing the diabatic potentials of the two phases in a Peierls-Hubbard model. The one-way transition is shown to be due to very different inter-unit charge-transfer processes for the two transitions. iii) Among organometal spin-crossover complexes, some show two-step transitions from a high-temperature high-spin phase to a mid-temperature mixed-spin phase to a low-temperature low-spin phase due to a short-range interaction favoring high-spin-low-spin neighbors. We study a two-sublattice Ising-like model accompanied with intra-dimer "antiferromagnetic" coupling and inter-dimer "ferromagnetic" coupling. Monte Carlo simulations show complex behavior under continuous photoexcitation, *i.e*., threshold behavior, phase separation, and step-like evolution of the high-spin fraction.

UHV Systems for MOKE, MSHG, XMCD and XAFS Measurements

NAKAGAWA, Takeshi; YOKOYAMA, Toshihiko; MARUYAMA, Koichi; WATANABE, Hirokazu

The magneto-optical Kerr effect (MOKE) is usually the most suitable method to characterize magnetic properties of ultrathin films. In the case of in-plane magnetization, however, the rotation angle is sometimes too small to discuss detailed magnetic properties. The magnetic second-harmonic generation (MSHG) method is superior for such purposes. Since last year we have been constructing an ultrahigh vacuum (UHV) MOKE system containing an UHV electromagnet (max. 3000 G, static). The installation was completed and some experiments are being conducted. For MSHG, a Ti: sapphire laser (800 nm) and the detection system were installed in autumn 2003. Using the UHV MOKE-MSHG system, we will investigate magnetic properties of ultrathin metal films, nanowires and nanodots, especially control of magnetism using surface chemical techniques such as gas deposition.

The x-ray magnetic circular dichroism (XMCD) technique is also quite useful since it provides information on element-specific magnetization and on the orbital magnetic moment because of its importance for discussion on magnetic anisotropy. The up-grade project of UVSOR was almost completed and we have installed a new surface analysis chamber at Beamline 4B. In the UHV system, we can perform typical sample treatments for surface analysis (sputtering, annealing, cooling, evaporation of metals, gas adsorption, *etc.*) and verify the surface order and cleanliness of the single crystal substrate using LEED, RHEED (reflection high energy electron diffraction), and XAFS (x-ray absorption fine structure). In order to measure XMCD a similar UHV-compatible electromagnet is installed. The XMCD and XAFS spectra are recorded by the partial electron yield mode using a microchannel plate (for zero magnetic field) or by the total electron yield mode (drain current, for applied field). The installation was completed in autumn 2003.

Pulsed Methods of Electron Spin Resonance Spectroscopy

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 $Eu@C_{82}$ and $Eu@C_{74}$ described in section II-I-1, of water soluble C_{60} and metallofullerenes described in section II-I-3,of a discrete self-assembled metal array in artificial DNA described in section II-J-1, and of multi-cations of aromatic amines in section II-J-4. The spin state of anion species of $La_2@C_{80}$ was characterized by X-band and W-band ESR observation combined with the detailed simulation analysis as described in section II-I-2. Hyperfine Interactions in $La@C_{82}$ was studied by W-band ESR and ENDOR spectroscopy described in section II-I-5.

Charge Ordering in Organic Conductors

YAKUSHI, Kyuya; YAMAMOTO, Kaoru; URUICHI, Mikio; YAMAMOTO, Takashi; DROZDOVA, Olga; SUZUKI, Kenji

The charge ordering is originated from the localization of charges owing to the on-site and inter-site Coulomb interactions which are stronger than the energy gain by the delocalization charges. Since these competing energies are comparable with each other, many organic conductors are situated in the boundary between delocalized and localized states. Organic conductors exhibits various electronic states such as charge-density wave (CDW), spin-density wave (SCD), antiferromagnetic state (AF), spin-Peierls state (SP), and superconducting state (SC) *etc*. through the electron-phonon, Coulomb, and exchange interactions. Recently, the charge-ordered state (CO) participates in the ground state. The boundary with a superconducting state has been drawing attention, since theoretical studies suggest a charge-fluctuation-mediated superconducting mechanism. We are investigating the charge ordering (CO) in organic conductors using the technique of infrared and Raman spectroscopy, and obtained the following achievements. (1) Subsequently to the thorough study of θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$, we have investigated θ-type BEDT-TTF salts that has more narrow bandwidth than θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$ such as orthorhombic and monoclinic θ-$(BEDT\text{-}TTF)_2TlZn(SCN)_4$ and θ-$(BEDT\text{-}TTF)_2Cu_2(CN)[N(CN)_2]_2$. All of these compounds showed a metal-insulator phase transition accompanying charge order and structural change. We characterized the CO pattern of orthorhombic θ-$(BEDT\text{-}TTF)_2TlZn(SCN)_4$ and θ-$(BEDT\text{-}TTF)_2Cu_2(CN)[N(CN)_2]_2$ as a horizontal stripe and that of monoclinic θ-$(BEDT\text{-}TTF)_2TlZn(SCN)_4$ as a diagonal stripe. The latter compound is the first example for the diagonal stripe. (2) We found a precursory phenomenon of charge ordering above the CO transition temperature in the very narrow-bandwidth system, monoclinic θ-$(BEDT\text{-}TTF)_2TlZn(SCN)_4$ and θ-$(BEDT\text{-}TTF)_2Cu_2(CN)[N(CN)_2]_2$. (3) We found a similar precursory phenomenon at room temperature in the metallic phase of β”-(BEDT-TTF)(TCNQ). Very interestingly, this precursory phenomenon continuously disappeared at low temperature, where the resistivity continuously decreased from the room temperature. We consider that our spectroscopic experiment catches the dynamics of the charges in organic conductors. (4) We examined the β”-type BEDT-TTF salts such as β”-$(BEDT\text{-}TTF)_3(ReO_4)_2$ and β”-$(BEDT\text{-}TTF)_4M(CN)_4\text{-}H_2O$ (M = Ni, Pd, Pt), and found that the metal-insulator phase transitions of all these compounds were accompanied by charge ordering. It is known that the latter compounds shows superconductivity under high pressure. Therefore, we confirmed that the latter compounds are the candidate for the materials at the boundary between CO and SC. (5) We elucidated that the charges in the insulating phase of $(EDO\text{-}TTF)_2X$ (X = PF_6, AsF_6) were almost completely localized at the inner two molecules in a tetramer unit. This unique CO pattern with BOW (bond order wave) was verified in these compounds for the first time. (6) We have conducted a theoretical consideration of the frequency and intensity of the Raman-active and infrared-active vibronic band that are interacting with electronic excited state through the electron-molecular-vibration (*e-mv*) interaction. We provided a theoretical support that the charge disproportionation induces a strong Raman-active vibronic band and infrared-active overtone and combination tone, when the vibrational mode has a large *e-mv* coupling constant.

Broad-Line Solid State NMR Investigation of Molecular-Based Conductors

NAKAMURA, Toshikazu; FUJIYAMA, Shigeki

Magnetic resonance measurements may be mature techniques as devices of the so-called chemical analyses. However, from the viewpoint of the solid state material science, magnetic resonance measurement is challenging area still in under the special condition such cases as the extreme low temperature, strong magnetic field, high pressure, electric field ,optical response and so on. Moreover they are advantageous for studying the fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Soft materials such as molecule based conductors show huge response to environments from the outside. In fact, competition of the electronic phases in molecular based conductors has attracted much attention. Magnetic resonance measurements under the special condition are absolutely necessary to search of the materials with new functions.

The development of the understanding of the electronic phases of molecular based conductors enables us systematic investigations of low-dimensional highly correlated electrons systems. For example, $(TMTTF)_2X$, have been extensively studied so far because of their various ground states such as spin-Peierls, AF, IC-SDW and superconductivity. However the origin of the para-magnetic insulating states is an open question. Recent progress of the investigation shows possibility of charge ordering and/or charge disproportionation states also in this family. We performed ^{13}C NMR measurements to investigate the charge configurations and spin dynamics in the low temperature phases of $(TMTTF)_2X$ in which the two central carbon sites were labeled with ^{13}C.

In this project, we are constructing our third NMR system. We also try to carry out experiments with new devices under unconventional circumstance.

The following projects are also now going on.

[1] Charge Configurations and Spin Dynamics of $(TMTTF)_2X$
[2] ^{13}C NMR study of two-component spins system, (BEDT-TTF)-TCNQ
[3] Charge and spin dynamics in organic conductors
[4] Low temperature electronic phases in $(EDT\text{-}TTF)_2X$

Development of New Molecular Conductors

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Since the discovery of the first organic superconductors more than two decades ago, extremely large number of the organic conductors including many superconductors have been developed based on the π donor molecules with TTF (tetrathiafulvalene) skeletons and inorganic anions. Though the development of new organic superconductors is still promoted very actively especially in Japan, traditional Bechgaard-type organic superconductors, D_2X (D = TTF-like π donor, X =

inorganic anion) seem to become rather trivial. The development of the completely new types of molecular systems with novel electronic functions will be highly desired for further progress. We have continued to try to develop new functional molecular systems. The main results are as follows. (1) Recently a considerable attention has been attracted to the unconventional conducting molecular systems such as single-component molecular conductor, nano-wires, molecular wire junctions and even DNA. Though the intriguing reports on these new types of molecular systems are rapidly increasing in number, there seem to be many systems where the origins of the charge carriers and/or transport mechanisms still remain unclear. We have observed the de Haas van Alphen oscillation in the recently discovered first single-component molecular metal, Ni(tmdt)$_2$ by using piezoresistive cantilever technique, which revealed unambiguously the presence of the single-component neutral molecular crystal with three-dimensional Fermi surfaces. The angle dependence of the oscillation frequencies agrees well to the band structure calculated by local density approximation (LDA) and *ab initio* plane-wave norm-conserved pseudo potential method. We have also observed the extremely low energy electronic excitations in the single-component molecular conductors. To our best knowledge, the absorption maxima observed around 2200 cm^{-1} in Ni(tmdt)$_2$ and Ni(dmdt)$_2$ are the smallest absorption energy ever reported for single-component molecular systems. The general feature of the *ir* electronic spectra of Ni(tmdt)$_2$ and analogous systems, especially the blue shift of the electronic absorption spectra in the semiconducting systems was well explained by the calculated joint density of states. (2) We have developed single-component molecular metal, Au(tmdt)$_2$ which has the crystal structure isostructural to Ni(tmdt)$_2$. The ESR and SQUID measurements revealed that Au(tmdt)$_2$ undergoes a magnetic transition around 100 K without loss of its high conductivity, indicating the possibility of the future development of molecular metals with magnetic order around room temperature. We have also prepared new types of magnetic organic conductors based on the p donor molecules with stable organic radical parts. In the system with magnetic anions such as FeCl$_4^-$, the first example of organic π conductors with two kinds of spin systems could be obtained. (3) We have tried to develop new *bi*-functional molecular systems by using the microporous frame works constructed of magnetic transition metal atoms and organic ligands and suitable guest molecules. Several ferrimagnetic porous molecular materials have been prepared.

Deposition of Phospholipid Layers on SiO$_2$ Surface Modified by Alkyl-SAM Islands

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Nano-bioelectronics is one of the most attractive and desirable fields in these days. The surface modification with self-assembled monolayers (SAMs), on semiconductor or insulting materials such as Si and SiO$_2$ is one of the key-techniques. It plays an important role for anchoring and/or immobilization of supported membranes and many kinds of biofunctional materials. In this study, we will report about dipalmitoyl phosphatidylcholine (DPPC) monolayers and bilayers on the SiO$_2$ surface modified with SAM islands of octadecyltrichlorosilane (OTS) by means of atomic force microscopy (AFM).

The SiO$_2$ layers were formed by thermal oxidation of cleaned Si wafers at 1000 degree C, followed by immersion into the H_2O_2/H_2SO_4 solution. It resulted in the flat and hydrophilic SiO$_2$ layer. OTS was deposited in water-saturated toluene at 22 degree C for 3–5 sec. Unilamellar vesicles of DPPC were prepared by extruding the DPPC suspension in buffer solution (150 mM NaCl, 1.0 mM CaCl$_2$, 10 mM HEPES/NaOH (ph 7.0)) through a 100 nm polycarbonate filter. The suspension was kept above 41 degree C during vesicle preparation. After the sample wafer was incubated in the vesicle suspension at 45 degree C for 2 h, the DPPC layer was deposited on the surface. AFM observations were performed under the buffer solution using an SPI3800 scanning probe microscopy system (Seiko Instruments Inc.) in contact mode.

Figure 1 shows AFM images of OTS-modified SiO$_2$/Si surfaces before and after deposition of DPPC. OTS islands with typical shapes and heights[1)] were successfully prepared as shown in Figure 1a. After the DPPC deposition, the height of OTS islands regions increased from 2.9 nm to 4.1 nm as shown in Figure 1b. It indicates the deposition of the DPPC membrane on OTS islands. The height increment of 1.2 nm corresponds to the half value of DPPC monolayer, therefore DPPC would be sparsely deposited on OTS islands. Whether DPPC was deposited on SiO$_2$ region or not was confirmed by scratching the surface with the AFM tip applying a strong force.[2)] In the case of as filtered vesicles (Figure 1b), no scratch trace was observed, indicating that depositions did not occur on the SiO$_2$ region. In the case of vesicles with the smaller size, which were obtained by the sonication of 100 nm-filtered vesicles, DPPC layers were formed on the SiO$_2$ region as well as on OTS islands. It will be due to the difference in adhesion and fusion processes between on OTS islands and on SiO$_2$ regions.

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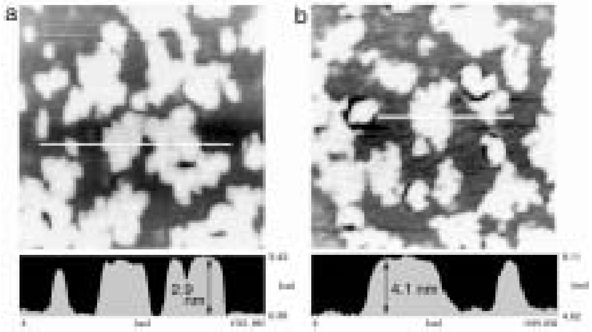

Figure 1. AFM images (2.0 × 2.0 nm^2) and line profiles of OTS/SiO_2 surfaces (a) before and (b) after deposition of DPPC vesicles. The images were successively obtained using the same tip.

Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aiming at Reversible Conversion between CO_2 and Organic Molecules

TANAKA, Koji

Multi-electron reduction of CO_2 aiming at smooth conversion to organics is highly desired in the viewpoints of not only the utilization of C1 resources but also the decrease of the concentration in the air. Carbon dioxide easily reacts with coordinatively unsaturated low-valent metal complexes to form η^1- or η^2-CO_2 adducts, the former of which are easily converted to metal-CO complexes in protic media. Accumulation of much electrons on metal centers usually accelerates not only reduction of CO_2 but also metal–CO bond cleavages. As a result, CO is the main product in photo- and electro-chemical reduction of CO_2 catalyzed by metal complexes. It is, therefore, highly desired to develop new methodologies that can supply electrons to the carbonyl ligand of metal-CO complexes derived from CO_2 without accumulation of electrons at the central metals. Along the line, we are designing new types of metal complexes that have an ability to provide electrons to carbonyl carbon through metallacycle rings involving the CO groups aiming at catalytic generation higher organic molecules by the electro- and photo-chemical reduction of CO_2.

Oxygenations and oxidations of organic molecules by high valent metal-oxo complexes are of current interest from the viewpoints of the enzymatic activities of P-450. Mechanistic understandings of the reactivity of metal-oxo species derived from O_2, however, have been limited because of the difficulty of selective cleavage of the O–O bond of M–O_2 frameworks in artificial systems. Alternatively, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the Ru–OH_2 frameworks, and some of Ru=O complexes have proven to work as oxidants of organic molecules. Introduction of quinone molecules, which are reduced to semiquinone and catecholate in a wide range of potentials, into M–OH_2 frameworks also induces sequential electron and proton loss of the Ru–OH_2 ones without addition of oxidizing agents. Such acid-base equilibria of the aqua ligands by taking advantages of smooth redox reactions of quinone ligands can be applied for energy conversion from pH gradients to electronic energy.

Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

The ability of RE^- (E = O, S) ligands to support and promote various important organic/inorganic reactions at metal centers has been known for many years. In this context, they complement the well-studied cyclopentadienyl-based systems, with the major difference being the greater reactivity of the former complexes due to their relatively higher unsaturation and lower coordination numbers for a $(RE)_nM$ fragment. However, ligand redistribution reaction is a common reaction pathway through which coordinatively unsaturated metal complexes decompose. These undesired ligand redistribution reactions are occasionally a severe obstacle to synthetic efforts. One of strategies for overcoming this problem is to use covalently linked ancillary ligands, thereby limiting ligand mobility and leaving little possibility to reorganize the molecule. This strategy has been a very useful concept in coordination chemistry and has allowed the isolation of transition metal complexes in unstable oxidation states or in unusual coordination geometries, and many with diverse highly-reactive functionalities. In this scenario, we prepared complexes of group 4, 5, and 6 transition metal complexes incorporating linear linked aryloxide trimers. Additionally we have designed and synthesized arylthiolate multidentate ligands new ancillary ligands. Studies the coordination chemistry of these complexes and their derivatives are 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

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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 microchip lasers and QPM devices. These kinds of advanced tunable solid-state light, so to speak “Chroma-Chip Lasers,” will assist the research of molecular science.

Synthesis of Perfluorinated Tetracene and Pentacene and Applications for Organic Field-Effect Transistors

SAKAMOTO, Youichi; SUZUKI, Toshiyasu

We have synthesized perfluorotetracene (**PF-TC**) and perfluoropentacene (**PF-PC**). These compounds are reddish orange and dark blue crystalline solids, respectively. **PF-TC** is slightly soluble in some organic solvents, but **PF-PC** is almost insoluble in common organic solvents. Their reduction potentials shifted positively by 500–600 mV relative to parent acenes, indicating that they should be good candidates for the *n*-type semiconductors of OFETs.

Friction Force Microscopy Using Silicon Cantilevers Covered with Organic Monolayers *via* Silicon-Carbon Covalent Bonds

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Cantilevers covered with hydrocarbon (CH) and fluorocarbon (CF) monolayers *via* Si–C covalent bonds were prepared and used for adhesion force measurements and friction force microscopy of the surface patterned also with CH and CF areas. The adhesion and friction forces on CF areas were larger than those on CH areas, especially using CF cantilevers. Large polarizabilities of CF molecules compared to CH molecules are found to enhance the contrast in adhesion and friction images. The cantilevers covered with organic monolayers via covalent bonds are useful for chemical force microscopy with contact and noncontact mode atomic force microscopy in various atmospheres since the interface between molecules and cantilevers is thermally and chemically stable.

Development of Multi-Function Integrated Macromolecules Directed toward Molecular Scale Electronics

TANAKA, Shoji

The emerging field of molecular-scale electronics is the new frontier of molecular science and technology. In recent years there have been demonstrations worldwide of molecular-scale diode, switches, transistors, logic circuits, and memory cells. However, the fabrication of ultra-dense molecular-scale circuits remains extremely challenging because of the difficulty in assembling a large number of molecular functional modules. As a promising solution to this problem, molecular monolithic technology based on “planar and multi-function integrated” π-conjugated macromolecules has become a subject of intensive research. In this project we have been trying to establish practical architecture for this novel class of tailor-made macromolecules. As the building blocks we have developed and characterized i) “insulated molecular modules,” ii) “energy-gap tuning modules,” iii) “molecule-anchor modules,” and iv) “molecule-junction modules” for constructing planar grid-type molecular frameworks. Furthermore we have composed various type of “processible” and “multifunctional” oligoheterocyles based on these modules, and characterized them on substrate surfaces using the high-resolution STM/STS.

Asymmetric Transition Metal Catalysis

UOZUMI, Yasuhiro

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

New chiral ligands having a pyrrolo[1,2-*c*] imidazolone backbone were prepared by condensation of anilides of homochiral cyclic amino acids with 2-(diphenylphosphino)benzaldehyde. Of these ligands, (3*R*,9a*S*)-(3-(2-diphenylphosphino)phenyl-2-phenyl)-tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one was found to be effective for palladium-catalyzed asymmetric allylic alkylation of cycloalkenyl carbonates with dimethyl malonate to give the corresponding dimethyl cycloalkenylmalonates with up to 89% *ee*.

Various homochiral binaphthyl derivatives having functional groups at the 6-position are important key intermediates for the immobilization of binaphthyl compounds on various solid-supports and have been prepared from commercially available 1,1'-bi-2-naphthol *via* controlled monopivalation of the 2-hydroxyl group and electrophilic aromatic substitution at the 6-position. (*S*)-2,2'-Bis-((*S*)-4-alkyloxazol-2-yl)-6-(2-methoxycarbonyl)ethyl-1,1'-binaphthyls (6-functionalized (*S*,*S*)-boxax)) were prepared and immobilized on various polymer supports including PS-PEG, PS, PEGA and MeO-PEG resin.

Construction of Advanced Redox Materials Based on Organic Molecules and Metal Complexes, as Basis of Chemical Energy Conversion Systems

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The goal of this project is to develop advanced redox catalysis reactions suitable for chemical energy conversion. Our current interest focuses on modeling photosynthesis, that is, driving endothermic chemical transformation by using light energy via photoinduced electron transfer. Progress has been made in the following topics during the last year:

A. Mechanistic details of light-driven oxidation of alcohols by a TEMPO/quinone/porphyrin system were investigated. The kinetic analyses were consistent with the intermediacy of the triplet radical pair of porphyrin and quinone, followed by one-electron oxidation of TEMPO by the porphyrin cation radical.

B. A new series of dendrimers were prepared. These dendrimers have “internal” carboxylate functionality that are readily accessible from exterior even after construction of the dendritic framework. We demonstrated introduction of up to fourteen ferrocenyl groups inside the dendrimer. These materials will serve as single-molecular models of biological redox pools.

C. New tripod molecules for stabilization of metal nanoparticles were developed. These molecules are designed so that a single molecule can enclose a single metal nanoparticle to give a “molecular” nanoparticle complex.

Fabrication of Model Catalytic Systems with the Use of Monolayer-Protected Metal Clusters as Starting Materials

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The size-dependent catalytic properties of metal clusters have been one of the most important subjects in nanoscience. In order to study the catalytic properties, it is necessary to be able to prepare samples of monodispersed clusters supported on well-characterized substrates. The most elegant method for the preparation of such model catalytic systems is based on the soft landing of the size-selected metal clusters onto the clean surface placed in the UHV condition. In this project, we aim to develop an alternative approach to this subject by using the monodispersed metal clusters prepared by chemical methods. The monolayer-protected metal clusters (MPCs) are chosen as the starting materials because of the following reasons: (1) they can be prepared in a large quantity as stable entities; (2) the core size can tuned through the synthetic conditions and further selected by chromatographic method; (3) they are self assembled into two dimentional crystal on a flat surface. One obvious difficulty in the fabrication of the catalytic system lies in the removal of the thiolate ligands from the cluster surfaces. To this end, we have constructed an apparatus which accommodates a plasma source, where the MPCs on a surface are exposed to the oxygen and/or hydrogen plasma. The etching processes of the organic layers of the MPCs will be monitored by XPS and AFM.

Local Distribution of Photoexcited States on a Semiconductor Surface as Observed by Scanning Tunneling Spectroscopy

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The photocatalytic processes occurring on a semiconductor catalyst surface may be divided into two parts: physical processes that are initiated by photoexcitation of titania electrons, and following chemical processes which are the so-called heterogeneous catalysis. The former physical processes are commonly described within the framework of band model which assumes infinite array of three-dimensional (3-D) unit cells that give rise to a periodic potential, with which the electronic band structure is defined. Thus upon UV light illumination electrons in the valence band of titania are excited to its conduction band, leaving holes in the valence band, and they migrate within each band following the energy gradient until they annihilate each other, trapped in some (defect) sites, or consumed by subsequent chemical processes. However, at the solid surfaces and in superfine particles which are the common forms of practical photocatalysts, this infinite array of unit cells in three dimensions no longer exist, and their electronic band structure are known to be quite different from that of bulk.

This very surface is where the chemical part, namely heterogeneous catalysis, occurs. It is a highly local process: individual reactant molecules adsorb on a solid catalyst surface, react in one or more steps, and the product molecules leave the surface in the process called desorption. The adsorption and/or reaction sites in heterogeneous catalysis are often very specific, in terms of their atomic and/or electronic configuration: some reactant may need particular arrangements of atoms that is present on the catalyst surface, and others may need particular electronic states of the surface atoms to provide unique adsorption or reaction sites.

Despite these vastly different descriptions between the two processes occurring in heterogeneous photocatalysis, namely the physical process that is described by infinite 3-D or 2-D array of unit cells, and the chemical process that necessitates very local description of catalyst surface, no efforts to bridge this gap are known to the authors. The present work is the first of such attempts, and examines the local electronic characters of titania surface upon UV-light illumination by means of scanning tunneling microscopy (STM).

Photoexcited states on rutile $TiO_2(110)$ surface have been examined with ultrahigh vacuum scanning tunneling microscopy. Mesoscopic as well as atomic level excitation was observed. The observed excitation appeared to be associated with oxygen deficiency on the surface. The results were interpreted in terms of reported experimental as well as theoretical band structures.

Electronic Structures of Excited States for Organic Thin Films by Inner-Shell Excitation

OKUDAIRA, Koji K.

Organic devices such as organic light-emitting diodes (OLEDs) in general consist of *p*-type and *n*-type organic thin films. However, there are not so many *n*-type organic materials which are stable and show high electron mobilities. To develop highly efficient organic devices, it is important to clarify the characteristics of unoccupied states of electron-transport layer. As the inner shell electron is excited in the near-edge absorption fine structure (NEXAFS) spectroscopy, the character of unoccupied state can be easily studied. However, the assignment is not so easy due to the interaction between photogenerated holes and electrons. The analysis of photon energy ($h\nu$) dependence of photon-stimulated ion desorption (PSID) is expected to help the assignment of NEXAFS spectra, since the chemical bond scission by inner-shell excitation depends on the electronic configuration of the excited state.

We reported that partial ion yields (PIY) for poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) thin films show strong photon energy dependencies near fluorine(F) and carbon(C) *K*-edges. The excitation from fluorine 1*s* to σ(C–F)* is specially efficient for F^+ ion production for both PTFE and PVDF.

The PIY of perfluorinated oligo(*p*-phenylene) (PF-8P) which is an efficient *n*-type semiconductor with high electron mobilities were observed near F and C *K*-edges PIY spectra of PF-8P show clear hn dependence near F and C *K*-edges. Especially, near F *K*-edge, the PIY spectra of F^+ increase remarkably at $h\nu$ = 689.2 eV, which corresponds to the lowest peak in NEXAFS. From the comparison with the results of PIY of PTFE and PVDF, the lowest peak in the NEXAFS near F *K*-edge is assigned to the transition from F1*s* to σ(C–F)* not to π*. Furthermore, from the analysis of PIY spectra of PF-8P near carbon *K*-edge, the peak at $h\nu$ = 289.5 eV is ascribed to the transition from C1*s* to σ(C–F)*.

Preliminary Study on Photoemission Thickness Dependence of Cesium Telluride Irradiated by Polarized Photon

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Cesium telluride is a good candidate for a material to be used as a photocathode for RF-gun because of its high quantum efficiency and long life. The quantum efficiency of the photocathode measured with changing the thickness of the cesium telluride gives us important information about the effective thickness of the photocathode.

We measured the quantum efficiency of cesium telluride by using linear polarized photon. Figure 1 shows a sketch of our experimental set up. A Xe lamp was used as a light source. The light from the Xe lamp passed through a monochrometer and polarized light enter a vacuum chamber in which cesium telluride was evaporated on molybdenum block as a photocathode.

Figure 2 shows the thickness dependence of the quantum efficiency of the cesium telluride irradiated by the light of 250nm wavelength. Closed circles show the experimental data and solid line shows a function proportional to (1-R), where R is reflectivity of the incident light from the photocathode surface.

We assume that the quantum efficiency is proportional to (1-R) in order to estimate the most effective thickness of the photocathode of cesium telluride. The maximum quantum efficiency is given at 10 nm for 250nm light.

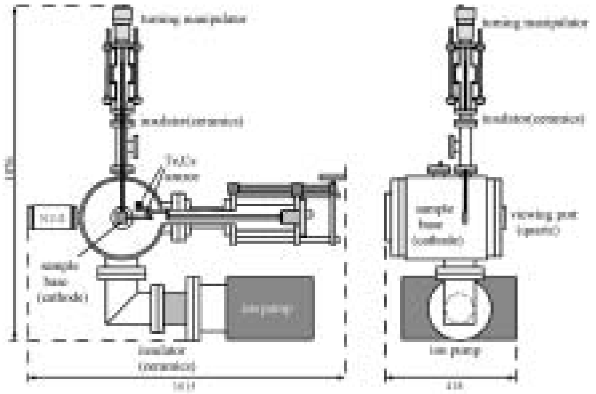

Figure 1. Sketch of experimental set up.

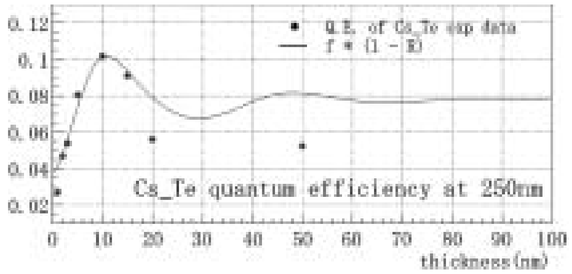

Figure 2. Quantum efficiency of cesium telluride with the thickness the cathode. The wavelength of the light is 250 nm. Closed circles show the quantum efficiency for the experimental data and solid line shows the calculation.

Development of New Materials Based on Fullerenes and Carbon Nanotubes in Nanometer Scale

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New materials based on fullerenes with novel physical properties were studied in various scales from bulk to nanometer size. The structures for the isomer-separated Dy@C_{82} and Ce@C_{82} crystals have been studied by powder X-ray diffraction with synchrotron radiation, and the electronic properties have also been clarified from the resistivity and Raman of their thin films. The crystals of these metallofullerenes exhibited simple cubic structures with space groups of $Pa\overline{3}$. The temperature dependence of resistivity showed a narrow-gap semiconducting behavior for these metallofulleres. The gap energies were 0.2–0.5 eV. These experimental studies led to new stage of solid state physics and chemistry of metallofullerenes.

The field effect transistors (FETs) have been fabricated with thin films of C_{60}, C_{70}, C_{84} and Dy@C_{82}. The C_{60} and C_{70} FETs showed normally-off enhancement-type properties, while the C_{84} and Dy@C_{82} FETs showed normally-on depletion-type properties. The C_{84} FET exhibited the highest mobility ($\sim 10^{-3}$ $cm^2V^{-1}s^{-1}$) among normally-on fullerene FETs. This will open a way to practical devices such as logic gate circuits for computing and memory.

The STM/STS has been studied for metallofullerenes deposited on Si(111)-7×7 surface, and the adsorption pattern of Dy@C_{82} has been clarified. The Dy@C_{82} molecule preferred an adsorption site surrounded by three Si adatoms. This origin is an ability to form strong Si–C interaction in this site. Further, the high-resolution STM image showed a charge distribution ascribable to the fullerene cage in Dy@C_{82}. These STM/STS studies opened the first step of nanoscale materials-science based on metallofullerene.

Effects of Vertical Magnetic Field in Material Science

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Magnetic control of chemical processes has been one of the most interesting and hot topics in material science. This is partly because a superconducting magnet, which generates a high magnetic field, is now commercially available and partly because new phenomena, which can not be observed in a low magnetic field, emerge in a high magnetic field. We have studied the effect of vertical magnetic field (up to 15 T and 1500 T^2/m) on various processes. It is shown that we can control natural convection of aqueous solution and levitate various materials using a vertical magnetic field. It is considered that vertical magnetic field can provide us a novel composite environment useful in material science where influence of gravity is negligibly small and various mechanisms of magnetic field effects are operative.

Many chemical reactions occur at the solid-liquid interface. In order to examine the influence of microgravity created by a strong magnetic field, the following chemical reactions are examined in a vertical magnetic field.

$$\mathrm{Cu} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{Ag}\downarrow \qquad (1)$$

$$\mathrm{Zn} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{Ag}\downarrow \qquad (2)$$

The reaction was carried out in a plastic plates (2 mm × 20 mm × 55 mm) between which a thin metal plate (0.1 mm × 20 mm × 5 mm) was placed and silver nitrate aqueous solution was charged in the space between them. The 2D-dendrite grows at the upper and lower sides of the plate. The plates are placed in a vertical magnetic field. At zero field, the dendrite grows at the upper side of the copper plate more efficiently than that at the lower one for both reactions. In the presence of a magnetic field, the yield at the lower side of the plate is larger than that at the upper one. The efficiency is reversed. At zero field natural convection of the solution due to gravity determines the efficiency of the dendrite yield, whereas in the presence of a magnetic field it is controlled by the magnetic field-induced convection. Furthermore, the dendrites grown by the reaction (2) are tilted by *ca*. 30° in a magnetic field. This could be ascribed to the magnetic anisotropy due to its shape.

It is capable to levitate diamagnetic materials by using an intense vertical magnetic field when the magnetic force (F_{mag}) is equal to gravity,

$$F_{\mathrm{mag}} = mg \qquad (3)$$

where m is the mass, and g is gravity. Furthermore, F_{mag} is given,

$$F_{\mathrm{mag}} = (1/\mu_0)\chi B dB/dz \qquad (4)$$

where μ_0 is the magnetic permeability of vacuum, χ is the magnetic susceptibility of a material, B is the magnetic intensity, and dB/dz is its gradient in the vertical direction.

In case of water, this condition will be satisfied when $F_{\mathrm{mag}} = 1360$ T^2/m. Since our magnet can generate the intense magnetic force of 1500 T^2/m, magnetic levitation of several materials were attempted. As expected, we succeeded to levitate water droplet, cherry tomato, nylon ball, polyethylene chip, polystyrene chip, and frog. Furthermore it is succeeded to separate polyethylene chip and polystyrene chip simply by levitating them by the magnetic force. It is clearly shown that magnetic levitation is a useful technique for processing various materials without vessel.

Development of “Entropy-Saving” Nano-Materials

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Integration of molecular devices has been of much interest for miniaturization in the field of electronics and photonics. For global, sustainable development, in our opinion, such future materials should also be “entropy-saving”: reusable, repairable, and bio-degradable. By utilizing a cytoskeleton, “microtubule” (MT), we fabricated an artificial photosynthetic system as a prototype of such nano-devices. Because formation and maintenance of MT require hydrolysis of GTP, MT is not in an equilibrium but in a dissipative process called dynamic instability: our functionalized MT is the first artificial system that functions in a dissipative process. In view that self-fabrication, self-healing, adaptation and learning, that are characteristics of living organisms, may occur in dissipative processes, utilization or functionalization of the dynamic instability may afford, *e.g.*, self-healing artificial nano-device. We now examine this possibility in addition to further characterization of the functionalized MT and improvement of efficiencies of excitation energy transfer and charge separation (see VIII-DD).

Commissioning of In-Vacuum Undulators at UVSOR

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In-vacuum undulators have been installed in the UVSOR-BL3U and BL7U. Due to the improvement of the UVSOR, the insertion devices with narrow magnetic gaps such as the in-vacuum undulators have become available. The undulators have the period length of 36/38mm and the minimum gap of 15 mm, which results in wide tunability in VUV and soft X-ray region. Influence on the stored beam, especially for the resistive wall instability, has been estimated and it has found that the disturbance for the stored beam can be negligible even in the minimum gap height.

Optical and Photoelectrical Studies on Fermiology of Strongly Correlated Electron Systems

KIMURA, Shin-ichi; ITO, Takahiro; NISHI, Tatsuhiko

Strongly correlated electron systems attract much attention because of their various physical properties. Since the origin is the interaction between the carriers and the localized magnetic moments, we are investigating the electronic structure near the Fermi level (fermiology) by infrared and photoemission spectroscopies using synchrotron radiation. In this year, we measured optical reflectivity spectra of $Ce_{1-x}La_xPd_3$, $YbRh_2Si_2$ and Ba_6Ge_{25}, infrared magneto-optical spectra of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ and angle-resolved photoemission spectrum of CeSb. A new high-energy-resolution angle-resolved photoemission instrument has been fixed and will be installed at BL5U of UVSOR in the autumn of 2003. The apparatus combined with UVSOR is useful for the three dimensional fermiology of strongly correlated electron systems including organic conductors.

Regulation of Biological Function by the Heme-Based Gas-Molecule Sensor Proteins

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A variety of gas molecules serve as substrates and/or reaction products in many enzymatic reactions including oxygen respiration, denitrification, nitrogen fixation and methanogenesis. Recently, a novel physiological function of gas molecules, that act as a signaling molecules, has been elucidated and studied extensively. For example, ethylene, O_2, NO, and CO are known to act as physiological effectors in the control of various biological functions. The corresponding receptor (sensor) proteins are required for these gas molecules to act in this way. The external signal is sensed by a sensor domain and then an intramolecular signal transduction proceed to express a physiological function of the sensor protein. A gas molecule that plays the role of the input signal is sensed by an active site of a sensor domain. An intramolecular signal transduction is induced following the detection of the gas molecule, which controls the functional activity in response to the input signal. Generally, a conformational change in the sensor protein facilitates this intramolecular signal transduction.

All of the gas sensor proteins so far reported have a metal-containing prosthetic group at the sensor active site. Specific interactions between protein and gas, for which the metal-containing prosthetic group is used, are required for the gas sensor protein to detect its physiological effector gas. Heme groups have been widely found at the active sites of the O_2, NO, and CO gas sensor proteins. This is not surprising as heme can bind O_2, NO, and CO reversibly.

In this project, we elucidate the structure and function relationships of the heme-based CO and O_2 sensor proteins, CooA and HemAT-Bs, respectively.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

FUJII, Hiroshi; KURAHASHI, Takuya; KUJIME, Masato

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

(1) High-valent iron-oxo species are proposed to be the key reactive intermediate in oxidation reactions catalyzed by the oxygen-activating iron enzyme. In the case of heme enzymes, porphyrin model complexes have been extensively investigated. However, an insight

into the nonheme oxidizing intermediate is still limited. We have been attempting to prepare the nonheme Compound I analog from a salen iron complex. To model the monomeric iron center of enzymes, bulky mesityl substituents are introduced to the salen iron complex. We found that a blue-green intermediate is formed at –80 °C by the oxidation of the ferric aqua complex of the salen with mCPBA.

(2) Copper is an essential trace element that plays an important role in a variety of biological functions. We have been studying coordination chemistry of copper complexes ligated by various tridentate ligands as synthetic models for the active site of copper protein which has three imidazolyl groups involved in the histidine residues. The results in this study show that $\delta(^{63}\mathrm{Cu})$ is the sensitive sensor of the extent of back-donation of the Cu-*d* electrons to the antibonding C≡O orbitals, *i.e.*, electron density at the metal center affected by the tridentate ligands. This study also shows the possibility that ^{63}Cu NMR can be the useful tool for the investigation of copper proteins.

(3) Heme oxygenase catalyzes the regiospecific oxidation of hemin to biliverdin IXα with concomitant liberation of CO and iron by three sequential mono-oxygenase reactions. We investigated the stereo-selectivity of each of the two reaction steps from *meso*-hydroxyhemin to verdoheme and verdoheme to biliverdin, by using a truncated form of rat heme oxygenase-1 and the chemically synthesized four isomers of *meso*-hydroxyhemin and verdoheme. Heme oxygenase-1 converted all four isomers of *meso*-hydroxyhemin to the corresponding isomers of verdoheme. In contrast, only verdoheme IXα was converted to the corresponding biliverdin IXα. We conclude that the third step, but not the second, is stereoselective for the α-isomer substrate. The present findings on regioselectivities of the second and the third steps have been discussed on the basis of the oxygen activation mechanisms of these steps.