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.

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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Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

KOSUGI, Nobuhiro; HATSUI, Takaki; HIYAMA, Miyabi

This project is being carried out at the Beamlines 4B and 3U on the UVSOR-II ring. We have three subprojects: (A) spin-orbit, exchange, and molecular field splittings in S 2p and P 2p excited states, (B) molecules in free clusters, in condensed phase, and in rare gas matrix, and (C) ionic fragmentations following the inner-shell resonance excitation. In (A), we have found some spin-forbidden ionized and excited states in nonradiative (photoelectron emission) and radiative (photon emission) deexcitation spectra. We have succeeded in development of a next-generation soft X-ray emission spectrometer. In (B), we have discussed blueshift and redshift in inner-shell excitation energy by relating to exchange repulsion and polarization stabilization from surrounding molecules. In (C), we are concentrating on theoretical interpretation, based on the R-matrix/MQDT method, of our experimental data measured for recent several years.

Computational Study of Quantum Dynamics of a Solute in Solution

OKAZAKI, Susumu; MIURA, Shinichi; MIKAMI, Taiji; SATO, Masahiro

Vibrational relaxation mechanism in condensed phase has been investigated based upon a series of mixed quantum-classical molecular dynamics calculations for non-polar solute in non-polar solvent and polar solute in polar solvent.

First, relaxation mechanism of I_2 in Ar, where Lennard-Jones force is predominant in the interaction, is investigated as a function of density and temperature, focusing our attention on the isolated binary collision (IBC) model. The model was originally established for the relaxation in gas phase. A key question, here, is “Can we apply the IBC model to the relaxation in the high-density fluid?” Analysing the trajectory of solvent molecule as well as its interaction with the solute, we found that collisions between them may be defined clearly even in the high-density fluid. Change of the survival probability of the vibrationally first excited state on collision was traced. The change caused by collisions with a particular solvent molecule was also traced together with the interaction between them. Each collision makes a contribution to the relaxation by a stepwise change in the probability. The analysis clearly shows that the relaxation is caused by collisions even in the high-density fluid. Difference between stepwise relaxation and continuous one found for the total relaxation in the low-density fluid and in the high-density one, respectively, was clarified to come from just the difference in frequency of the collision. The stronger the intensity of the collision is, the greater the relaxation caused by the collision is. Further, the shorter the collision time is, the greater the resultant relaxation is.

Second, we found that molecular mechanism of the relaxation of a polar molecule in supercritical water is significantly different from that assumed in the IBC model despite that the density dependence of the relaxation rate showed a linear correlation with the local density of water around the solute, the linear correlation being apparently in good accordance with the IBC model. The puzzle has been solved by this project.

Chemical Reactions at Surfaces and Nano-Structured Materials Studied by Spatio-Temporally Resolved Spectroscopy

MATSUMOTO, Yoshiyasu; WATANABE, Kazuya; MATSUMOTO, Taketoshi

Chemical reactions on solid surfaces are typical heterogeneous reactions. Studies in the time domain such as kinetics are useful to understand reaction mechanisms, but these are not enough to have a full understanding of the reaction mechanisms because reactions depend on local environment of reactants. Therefore, it is necessary to perform studies both in the time and spatial domains. This project aims for developing spatio-temporally resolved methods to probe various processes at surfaces. In the time domain, we perform fs time-resolved nonlinear spectroscopy including multiphoton photoelectron spectroscopy (MPS), second harmonic generation (SHG), and sum frequency generation (SFG). MPS is very suitable to investigate the unoccupied states of adsorbates and how they decay. This method is applied to ultrafast electron transfer at surfaces and interfaces. SHG is used for monitoring the dephasing processes of coherent vibrational motions at surfaces. This is a first step toward coherent control of surface processes. SFG provides time-resolved vibrational spectra of adsobates, which is useful to detect reaction intermediates. On the other hand, in the spatial domain we perform scanning tunneling microscopy (STM) in ultrahigh vacuum conditions. Observations of temporal progresses in STM images while surface reactions take place make it possible to confirm active sites of the reactions. Furthermore, a variable temperature STM allows us to monitor changes in surface geometry with the atomic resolution during surface reactions. This capability is extremely useful to monitor spatial propagation of surface reactions, in particular, autocatalytic reactions.

Towards Complete Imaging of Molecular Orbital Patterns: Development of Molecular Frame (*e*,2*e*) Spectroscopy

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The use of the (*e*,2*e*) technique for measurement of electron momentum density in matter was first accomplished by Amaldi *et al.* on a thin carbon film in 1969.1) Since then, a number of studies were conducted and have established the attempts as so-called binary (*e*,2*e*) spectroscopy or electron momentum spectroscopy (EMS). The success of EMS with simple systems has led to its rapid expansion into various targets involving laser excited oriented atoms, biomolecules and solids. For molecules, however, EMS has long been plagued by the fact that the experiments measure averages over all orientations of gaseous targets. The spherical averaging results in enormous loss of versatile information on collision dynamics and target electronic structure; intrinsically anisotropic or three-dimensional character of the (*e*,2*e*) scattering deteriorates into the one-dimensional momentum distribution. If it were possible to fix a molecule in space, the experiment would remove ambiguities inherent in the spherically averaged (*e*,2*e*) cross sections.

To resolve the historical issue, we have proposed a method for complete imaging of electron momentum densities2); in the axial recoil limit of fragmentation of the residual ion measurements of vector correlations among the two outgoing electrons and the fragment ion are equivalent to (*e*,2*e*) experiments with fixed-in-space molecules, which should be designated as (*e*,2*e*+M) spectroscopy. Furthermore, we have observed, for the first time, transition-specific anisotropy of molecular frame (*e*,2*e*) cross section,3),4) a phenomenon for which detailed theoretical explanations are eagerly awaited. This project aims at establishing molecular frame (*e*,2*e*) spectroscopy by extending the pioneering work2)–4) with introduction and/or development of latest multichannel techniques. We believe that the project would exploit a new area for studies on stereodynamics of electron-molecule collisions as well as on bound electronic wavefunctions of molecules, directly providing information important to atomic physics and momentum space chemistry.

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(b) Molecular Photophysics and Science

Theoretical Studies of Quantum Many-Particle Dynamics in Open Systems

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This research project is aimed to develop new theoretical and numerical methods describing dynamics in quantum many-particle systems such as (i) electron dynamics (not explicitly taking account of spin degrees of freedom), (ii) exciton dynamics, (iii) spin dynamics, and also (iv) photon dynamics. For example, the electron dynamics in molecular systems is an intrinsic process related to a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. Very recently, we have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

Our goal of this project is to further elucidate the quantum dynamics even in open quantum systems where quantum dissipation is indispensable.

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Spatiotemporal Dynamics in Nanometric Molecular Assemblies by Near-Field Spectroscopy

OKAMOTO, Hiromi; IMURA, Kohei; NAGAHARA, Tetsuhiko; LIM, Jong Kuk; HORIMOTO, Noriko

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 pump-probe technique. With the apparatus, we have achieved ~50 nm spatial and ~100 fs temporal resolution at the same time. The continuum generation in photonic crystal fibers have enabled near-field pump-probe experiments in wide-range probe wavelengths. 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 physical and chemical processes in nanometric systems. Right now we have performed measurements to understand basic local optical properties of porphyrin nanoassemblies and metal nanoparticles. On porphyrin assemblies, we have obtained morphological information of thin films on substrates. On metal nanoparticles, we have succeeded in direct imaging of resonant plasmon modes. 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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Concerning "studies on laser cooling and trapping of metastable helium atoms," we have added small improvements to our cooling and trapping apparatus for He atoms. On the other hand, as for "laser spectroscopic studies of atoms and ions in liquid helium," emission and excitation spectra of the $3s^2\ {}^1S_0$–$3s3p\ {}^1P_1$ transition of Mg atom in pressurized liquid helium-4 and helium-3 have been measured. In the emission spectra we have found that their transition wavelengths, which are significantly red shifted, remain constant or slightly increase with increasing the liquid He pressure, whereas for other alkali-earth atoms the increase of the liquid pressure always shifts their emission spectra toward shorter wavelength. Our theoretical calculations based on a bubble model have successfully reproduced this unique spectral property, and have suggested the possibility of the formation of a $\mathrm{Mg}(3s3p\ {}^1P_1)\mathrm{He}_n$ exciplex in a bubble. (see II-B-1).

Methods of Analysis for Protein Dynamics in Living Cells

OZAWA, Takeaki

Protein-protein interactions and protein localization have key roles in many essential biological processes in living cells. To investigate the biological processes, fluorescent and bioluminescent proteins, which are called reporters, are now being used as readout. One of the most useful reporters is a green fluorescent protein (GFP) derived from *Aequorea victoria* and its spectral variants. It is particularly valuable due to its structural stability and the fact that its chromophore is spontaneously formed in an autocatalytic cyclization that does not require any cofactors.

We have developed novel reporter proteins with general applicability for detecting protein-protein interactions and protein localization in living cells and animals. The principle is based on reconstitution of split reporter proteins by protein splicing, which involves a self-catalyzed excision of a protein splicing element, intein, from flanking polypeptide sequences, exteins, leading to ligation of the flanking exteins by a peptide bond. As the exteins, N- and C-terminal fragments of rationally-dissected GFP was used. The N- and C-terminal reporters connected respectively with a pair of interacting proteins worked as indicators for protein-protein interactions. The split-GFP reporter provided a genetic method for identifying mitochondrial proteins from large-scale cDNA libraries. This basic concept of split reporter reconstitution by protein splicing provides a wide variety of applications for fundamental biological studies.

This research project aims to develop novel fluorescent and bioluminescent reporters with various spectral properties based on protein splicing. Using the reporters, I will develop methods of analysis for the gene expression, intracellular protein dynamics, enzyme activities, and protein-protein interactions in living subjects. To identify a key molecule in the biological processes, I am also investigating analytical techniques such as cDNA library screenings with fluorescence-activated cell sorting.

Development of Attosecond Coherent Control and Its Application

OHMORI, Kenji

Coherent control is based on manipulation of quantum phases of wave functions. It is a basic scheme of controlling a variety of quantum systems from simple atoms to nanostructures with possible applications to novel quantum technologies such as bond-selective chemistry and quantum computation. Coherent control is also expected to serve as an effective tool for the fundamental test of quantum theory. We have developed an "attosecond phase modulator (APM)," which we have applied to vibrational wave packets in molecules to realize an unprecedented high-precision quantum interferometry. In this research project, we utilize our present APM as a sensitive decoherence detector for the fundamental test of quantum theory. Also the APM will be developed to a more fexible quantum-phase modulator. And they will be applied to (1) fundamental test and control of decoherence, (2) high-precision reaction control, (3) control of highly-nonlinear processes in intense laser fields, and (4) molecule-based quantum information processing.

Laser Manipulation of Molecular Motions and Its Application to Reaction Dynamics Studies

OHSHIMA, Yasuhiro; HASEGAWA, Hirokazu; MIYAZAKI, Mitsuhiko

This special research program aims to establish methods for manipulating molecular motions in a quantum mechanical manner by utilizing the coherent interaction with laser lights, and to exploit the methods to detailed studies in chemical reaction dynamics. Three complement approaches are adopted. The first one employs fs pump–probe techniques to create and detect vibrational and/or rotational wavepackets of molecules. Time-resolved fluorescence depletion and random phase interferometry in fs regime have been applied for the first time to jet-cooled polyatomic systems. Observation of wavepacket dynamics has demonstrated for over-all rotation of benzene and methyl internal rotation of *o*-fluorotoluene. The second method exploits an impulsive interaction with ultrafast intense laser light to transform the initial distribution into non-equilibrium one. New vacuum chamber system has been constructed for this purpose. The third one utilizes an adiabatic interaction to achieve the complete transfer in molecular quantum states, by which all the molecules are launched into states with high excitation of vibrations or rotation. A single-mode ns laser system is now under construction to realize the adiabatic interaction with coherent laser light. Along the instrumental development, an initial search for appropriate candidates for the quantum-state adiabatic manipulation has been started: energy-level structure of the intermolecular vibrations in the 1:1 benzene–water cluster is studied by mass-analyzed resonance enhanced two-photon ionization coupled with laser double-resonance technique.

Probing Ultrafast Molecular Dynamics by Extremely Short Laser Pulses

TAKAHASHI, Eiji J.; HISHIKAWA, Akiyoshi

Highly excited molecules formed in intense laser fields often undergo ultrafast nuclear dynamics with a time scale shorter than 100 fs. This special research project is aimed to trace the evolution of such ultrafast nuclear motion in real time by extremely short laser pulses with the duration less than 10 fs. For this purpose, a pulse compression system consisting of a hollow fiber filled with Ar gas and a chirp mirror compressor was developed. The duration of the output pulse is typically 9 fs with an energy of 0.4 mJ/pulse. The pump-and-probe experiments combined with the coincidence momentum imaging technique are under progress.

Photoionization and Photodissociation of Fullerenes and Metal Encapsulated Fullerenes, Their Mechanisms, Kinetics, and Dynamics

MITSUKE, Koichiro; KATAYANAGI, Hideki; KOU, Junkei; MORI, Takanori

Fullerenes are characterized by their unique geometric and electronic structures, and have attracted wide attention because they provide possibilities of applications toward materials of novel functionalities. Nevertheless, only a few experimental works have been made on photoabsorption spectroscopy of solitary fullerenes, particularly above their ionization thresholds. Hence, there is little information on their oscillator strength distributions, dielectric functions, and dynamics of highly-excited states.

We have observed for the first time the giant dipole resonance in the photoionization yield curves of isolated endohedral metallofullerenes. The yield curves for the singly- and doubly-charged parent ions from $Ce@C_{82}$ and $Pr@C_{82}$ were measured by using mass spectrometry. The curves of $Ce@C_{82}{}^{2+}$ and $Pr@C_{82}{}^{2+}$ exhibit broad resonances between $h\nu$ =120 and 150 eV which were ascribed to the shape resonance arising from the $4d \to 4f$ dipole transition in the encapsulated metal atom.

Analogous giant resonances are well known phenomena for the isolated atoms of Xe, Ba and various lanthanide metals. They are interpreted on the basis of favorable overlap between the wave functions of 4*d* and 4*f* atomic orbitals whose amplitudes are concentrated inside the associated centrifugal barriers generated on the effective potential that acts upon the ionized electron. Our results clearly show that such a resonance does not collapse even inside the fullerene cage, in a qualitative agreement with the theoretical prediction from previous *ab initio* TDLDA calculations made by Wendin and Wästberg in 1993.

Theoretical Development of Interfacial Sum Frequency Generation Spectroscopy

MORITA, Akihiro; ISHIDA, Tateki; ISHIYAMA, Tatsuya

The visible-infrared Sum Frequency Generation spectroscopy has a wide applicability for interface characterization, including surfaces in ambient conditions and various liquid (liquid-gas, liquid-liquid, liquid-solid) interfaces. Although the spectra provides intramolecular vibrational spectroscopy specific to the interface region, it is not straightforward to extract unique information on the interface structure in a molecular level. This project develops theoretical methods to compute the SFG spectra by molecular dynamics simulation.

To apply our computational methods to a variety of systems, a general scheme of molecular modeling is a key ingredient. The molecular model should be polarizable and flexible, and in addition it should be capable of describing dipole and polarizability as a function of molecular conformation. To meet these requirements we are developing a new molecular model based on the Charge Response Kernel theory, which was proposed by us in 1997. While the original theory was based on the Hartree-Fock wavefunction, it is extended to the density functional theory to take account of the electron correlation effects.

The non-empirical computation of SFG spectroscopy needs a large computational cost, and therefore effective computation by a large-scale massive parallel environment is also critical. We are trying to establish an efficient computational scheme for the SFG calculations by utilizing the supercomputer resources in the IMS computer center.

Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; HIKOSAKA, Yasumasa; KANEYASU, Tatsuo

Multielectron processes in inner-shell photoabsorption, in which more than two electrons are promoted by the absorption of a single photon, have long drawn special attention. This is because such processes are due entirely to correlation effects among the electrons in a system and consequently their investigation covers fundamental aspects of atomic and molecular physics. The ejection of a second electron into unoccupied bound and continuum states, accompanying the ionization of the inner-shell electron, are often observed as shake-up and shake-off satellite structures in the corresponding photoelectron spectra. Another important example for the multielectron processes is the formation of neutral states embedded in the ionization continuum, which is generally referred to as the multiple excitations. The multielectron 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.

The double toroidal analyzer (DTA) at UVSOR, which has been originally developed by a French group, has been under conditioning. The imaging detection without any exit slit enables us to observe electrons within an energy range more than 10% of the pass energy, and their angular distributions simultaneously. Recently it was confirmed that the performance of the analyzer has been improved considerably, after reassembling of DTA and its careful tuning. The introduction of an ion time-of-flight spectrometer with a two dimensional detector is in the planning stage, to perform energy-selected-electron–ion coincidence experiments.

Parallel to the research and development of new experimental setups, some trial experiments have been made for observing minor products, such as highly excited neutral species and anions after the molecular inner-shell excitations. A strong enhancement due to the N* formation has been observed around the 1s threshold of N_2 molecules. It has been found that the highly excited N_2^{+*} states leading to the N* formation are populated by spectator Auger decay from the core-excited states, as well as by the recapture of slow photoelectrons into the Rydberg orbitals. It turns out that the metastable observation is a new and sensitive tool to study the decay dynamics of core-excited states and the photoelectron recapture due to the post-collision interaction. Concerning the anion imaging detection after the molecular inner-shell excitations, we have confronted difficulty in eliminating a large background noise by electrons, which may be fixed by performing time-resolved experiments.

(c) Novel Materials Science

Quantum Chemistry Calculations of Large Molecular Systems

ISHIMURA, Kazuya; NAGASE, Shigeru

Density functional theory (DFT) is currently the most widely used method to calculate larger molecular systems. However, the generally used DFT methods fail to describe weak non-covalent interactions that play an important role in host-guest chemistry, molecular recognition, and self-assembly. An efficient method to calculate non-covalent interactions in a reliable way is second order Møller-Plesset perturbation theory (MP2). To make MP2 calculations applicable to large molecular systems, we have developed a new parallel algorithm with two-step parallelization and dynamic load-balancing. This developed algorithm has been implemented in the freely distributed quantum chemistry program package GAMESS. The parallel efficiency is tested for two relatively large molecules, taxol ($C_{47}H_{51}NO_{14}$) and luciferin ($C_{11}H_8N_2O_3S_2$), with the 6-311G(d,p) basis set (1484 basis functions and 164 correlated electrons) and the aug-cc-pVTZ basis set (1198 basis functions and 46 correlated electrons), respectively. The cost of MP2 calculations is comparable to that of Hartree-Fock SCF calculations. The CPU efficiency of the present algorithm is high; the elapsed time is only slightly longer than the CPU time. An MP2 energy calculation on a carbon nanotube, $C_{130}H_{10}$ (1970 basis functions), completes in less than 2 hours on 128 processors. Therefore, it is entirely practical to calculate the MP2 energies of relatively large molecular systems. We are now developing a parallel algorithm of MP2 energy gradient calculations to determine effectively the structures of large molecules.

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

YONEMITSU, Kenji; YAMASHITA, Yasufumi; MAESHIMA, Nobuya; MIYASHITA, Satoshi

In low-dimensional molecular materials, effects of different interactions appear not only in their equilibrium phases but also in their non-equilibrium states. i) Ambipolar field-effect characteristics are recently found by an experimental group in metal-insulator-semiconductor field-effect transistor device structures based on organic single crystals of the quasi-one-dimensional Mott insulator (BEDT-TTF)(F_2TCNQ). For coherent charge transport, the insulator-(source and drain) electrode interface barrier (Schottky barrier) potentials are important. In FET devices based on band insulators, the Schottky barriers govern the IV characteristics. When the work function of the electrodes is different from that of the channel, the IV characteristics are generally very asymmetric with respect to the polarity of the gate bias and therefore unipolar. The ambipolar characteristics of the organic Mott insulator imply very similar effects of insulator-electrode interface barrier potentials, when combined with electron correlation effects, for electron and hole injections. In order to understand its mechanism, we perform model calculations to show rather symmetric IV characteristics for Mott insulators only. Scalar potentials are included, which originate from the long-range Coulomb interaction and produce the Schottky barriers. The time-dependent Schrödinger equation is numerically solved for both the mean-field and many-body electronic wave functions to obtain the current density. We find ambipolar carrier injections in Mott insulators only, even if the work function of the crystal is quite different from that of the electrodes. They result from balancing the correlation effect with the barrier effect. For the gate-bias polarity with higher Schottky barriers, the correlation effect is weakened accordingly, owing to collective transport in the one-dimensional correlated electron systems. ii) Effects of interchain electron-electron interactions on the photoinduced ionic-to-neutral and neutral-to-ionic transition dynamics are studied in a quasi-one-dimensional extended Peierls-Hubbard model with alternating potentials for mixed-stack charge-transfer complexes. The ionic-to-neutral transition dynamics depend on the strengths of interchain couplings. For strong interchain couplings such as those corresponding to TTF-CA, once neutral domains are nucleated above an increased absorption threshold, they grow spontaneously and cooperatively till the whole system is converted. In contrast, interchain couplings slightly enhance nonlinearity of the otherwise uncooperative neutral-to-ionic transition dynamics. These results are consistent with the latest experimental results including coherent motion of the macroscopic neutral-ionic domain boundary during the photoinduced ionic-to-neutral transition.

UHV Systems for MOKE, MSHG, XMCD and STM Measurements

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

In order to investigate magnetic properties of ultrathin metal films, we have been so far constructing three ultrahigh vacuum chambers equipped with standard surface analysis apparatus and magnets. The first one is operated for the magneto-optical Kerr effect (MOKE) that is usually the most suitable method to characterize magnetic properties of ultrathin films. A UHV-compatible electromagnet (max. 3000 G, static) is installed. While information from the MOKE is basically attributed to the whole films, information only on surfaces and interfaces can be given by the magnetic second harmonic generation (MSHG) technique. We have installed a Ti:sapphire laser (800 nm) and the detection system in the same chamber. Both the MOKE and the MSHG data can now be taken with high quality. The second one is for X-ray magnetic circular dichroism (XMCD) that provides information on element-specific magnetization and on the orbital magnetic moment because of its importance for discussion on magnetic anisotropy. This experiment can usually be done at Beamline 4B in UVSOR-II. In order to measure XMCD a similar UHV-compatible electromagnet is installed. X-ray absorption fine structure (XAFS) spectra of adsorbates are also obtainable in the same chamber for the determination of the surface structure. Furthermore, we will reconstruct this chamber at the end of this year and install a superconducting magnet (up to 7 T) with a sample cryostat (down to ~2 K). The third one is for scanning tunneling microscopy (STM) to characterize surface structure. The chamber is now also being operated.

Development and Characterization of Metal/Carbon Hybrid Nano-Systems

NISHI, Nobuyuki; JUDAI, Ken; NISHIJO, Junichi

Nanometals, such as wires, dots, sheets, or wheels, are expected to show quantum electronic properties. When nanometals with countable numbers of metallic atoms are aligned with interfacial π electron spacers through d-π junctions, the electrons originally localized in metal atoms could transfer through π* orbitals of the carbon spacers. The probability of this tunneling process is a function of carbon spacer distances and the applied electric field strength. Magnetic field is also expected to work on the tunneling processes.

We are developing new metal/carbon systems with transition metal acetylides. The acetylides are composed of ionic bonds between metal cations and ethynyl anions. The low lying electronic excited states of the acetylides are characterized as metal-ethynyl charge transfer states and the excitation induces charge neutralization reaction of the cation-anion pairs resulting in the production of metal clusters bonded with π electron systems of conjugated carbons. In the case of iron acetylide, FeC_2, the produced iron nanocrytalline core wears graphitic skin with Fe–C direct chemical bonds.

We have succeeded to synthesize Cu_2C_2 nanowires with diameters of 10–20 nm and lengths of approximately 1 μm. The acetylide nanowires are converted to metallic copper nanowires with outside carbon layers by moderate heating or other excitations. The interface is composed of copper-carbon bonds, that is charge polarized in nature and forms Schottoky-barrier like Fe nanocrystals with graphitic skins (3.5 nm thick) controlling the electron transfer directions under appropriate conditions.

Dissolving organometallic clusters in organic solvents allow us to make films as thin as 10 nm or less. A copper 24-mer with *t*-butyl-ethynyl groups, $(t\text{-butyl–C}\equiv\text{C–Cu})_{24}$, is soluble in *n*-hexane and can provide thin films on various plates. We have succeeded to prepare metallic copper nano-films sandwiched in conjugated organic polymer thin layers just like nano-pies by photo-segregation of the original films. On the other hand, heating of the films provides nano-dots of metallic Cu particles embedded in organic polymers. Electronic properties of these new materials, such as conductivity and quantum tunneling effect, are now in progress.

Charge ordering in Organic Conductors

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

The charge ordering is originated from the localization of charge driven by the on-site and inter-site Coulomb interaction which is slightly stronger than the kinetic energy gain. In organic conductors, these competing energies are comparable with each other. Therefore, many organic conductors are situated in the boundary between delocalized and localized states. Organic conductors exhibits various electronic ground states such as charge-density wave (CDW), spin-density wave (SCW), 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) is recognized as the new ground state, and drawing attention. For example, the CO state shows ferroelectric property in some organic compounds, and the superconducting state neighbored on a CO state is considered to have a charge-fluctuation-mediated superconducting mechanism. We are investigating the CO system in organic conductors employing the technique of infrared and Raman spectroscopy, and obtained the following achievements. (1) We have examined more precisely the relationship between the charge on ET molecule and the frequency shift of ν_{27} and ν_2. Based on the isotope substituted ET compounds (^{13}C and ^{2}H) and DFT calculation, we obtained the linear relationship, $\nu_{27}(\rho) = 1398 + 140(1–\rho)$ cm^{-1}, for the flat ET molecule. The frequency shift due to oxidation is remarkably larger than reported in previous studies. The fractional charges of several ET salts in a charge-ordered state can be successfully estimated by applying this relationship. Similarly, the linear relationship for the ν_2 mode was obtained as $\nu_2(\rho) = 1447 + 120(1–\rho)$ in the region of $0 < \rho < 0.8$. (IV-A-1) (2) We examined the electronic states of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ and the high-temperature and frozen states of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$. The charge distribution is inhomogeneous with a large amplitude in the high-temperature and frozen states of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, whereas the amplitude of charge-density wave in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ is very small. Although the charge distribution of the latter compound is nearly homogeneous, the indication of the weakly localized nature is found in the Raman spectrum and optical conductivity spectrum. This weakly localized nature is frozen below 20 K, which may be related to the non-linear conductivity. (IV-A-2) (3) In some compounds, the CO phase is considered to be neighbored on superconducting phase. We examined the Raman spectrum of β”-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$, wherein the electrical resistivity increases on lowering temperature and shows superconductivity at 5 K. We found a clear splitting in the ν_2 mode of this compound below 50 K. This observation suggests the possibility of a superconducting ground state with a charge-fluctuation-mediated superconductivity mechanism rather than the spin-fluctuation mechanism. (IV-A-3) (4) The CO state of some compound shows ferroelectricity. We discovered second harmonic generation (SHG) in α-(BEDT-TTF)$_2$ I$_3$, which has a CO ground state. A strong SHG signal at 700 nm appears just below the CO phase transition temperature (136 K). We consider that SHG is related to the ferroelectric property, and that the CO system will become new non-linear optical materials in the near infrared region. (IV-A-5) (5) We examined the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I, and β-(BEDT-TTF)$_2$I$_3$ to find the relation between the Raman shift and linewidth and the structural and electronic anomalies. (IV-A-4) and (IV-A-6) We reasonably determined the site-charge distribution of (EDO-TTF)$_2$X (X = ReO$_4$ and GaCl$_4$) and TEA (TCNQ)$_2$ employing the infrared and Raman spectroscopy. (IV-A-7) and (IV-A-8). (6) We found a phase separation in the temperature region of 160 K–100 K in biferrocenium (F$_1$TCNQ)$_3$, through the x-ray diffraction experiment, infrared and Raman experiments. In the phase-separation region, nonovalent (D$^+$A^{3-}) and divalent (D^{2+}A$_3$$^{2-}$) ionic states coexist. A rough mapping of the monovalent and divalent domains was conducted using micro Raman spectroscopy. The domain size was macroscopic and the domain boundary may involve mesoscopic or microscopic domain structure. (IV-A-9) and (IV-A-10).

Multi-Frequency and Pulsed ESR Investigation for Molecular-Based Materials

FURUKAWA, Ko; MATSUOKA, Hideto; HARA, Toshifumi; TANATAR, Makariy; MAEDA, Keisuke; NAKAMURA, Toshikazu

In general, high frequency (high field) ESR measurements are advantageous because they are high sensitive and high resolution spectroscopy. So we can get ESR signals even for very tiny samples. Moreover, as for the solid compounds, *i.e.* conducting and/or magnetic materials, multi-frequency measurements give us information about frequency (magnetic field) dependent ESR parameters. For example, the frequency dependence of the *g*-values tells us the development of the short-range order for the paramagnetic states. In the magnetic long-range order phases, we can estimate the dispersion of their collective mode. From the frequency dependence of the linewidth, we can estimate the characteristic time of the spin diffusive motion, the development of the spin-spin correlation time for the paramagnetic phases. Such kind of information is very important to understand the electronic interaction in functional materials.

Moreover pulsed ESR measurements are advantageous since we can directly obtain the spin-lattice (T_1) and spin-spin (T_2) relaxation times. From these parameters, we can understand detail of electronic phases.

We performed the multi-frequency (X-, Q-, and W-band) and pulsed-ESR measurements for several molecular-based materials in order to clarify low-temperature electronic phase. The following studies are now going on.

[1] Multi-frequency ESR measurements for charge-ordering phases in (TMTTF)$_2X$

[2] Pulsed ESR investigation of the spin-Peierls phases in (TMTTF)$_2X$

[3] ESR study of Mn-cluster in the S-0 and S-2 states of Cyanobacterial single crystals

[4] ESR study on low-dimensional antiferromagnet (BEDT-TTF)$_2$PF$_6$

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

NAKAMURA, Toshikazu; TANATAR, Makariy

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 following investigations are now underway.

[1] NMR Investigation of Charge-Ordering Phenomena in (TMTTF)$_2X$

^{13}C NMR measurements were performed for one-dimensional organic conductors, (TMTTF)$_2$ReO$_4$. We firstly clarified the existence of an intermediate charge-ordering (CO) phase for a TMTTF salt with a Td-symmetry counter anion by ^{13}C NMR absorption line and spin-lattice relaxation rate, ^{13}C $T_1{}^{-1}$: The NMR spectra, which are characteristic of nuclei in equivalent molecules at room temperature, indicate two inequivalent molecules with unequal electron densities below 225 K. Moreover, the spin-singlet transition associated with the ReO$_4$ anion ordering was confirmed at around 158 K by ^{13}C NMR. The drastic change of NMR lines at 158 K also indicates a redistribution of the electronic charge at the anion ordering temperature. The existence of the two independent transitions suggests the possible origin of the charge-ordering phenomena is purely electronic.

[2] Low temperature electronic state of κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]I

Although κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X = Cl, Br, I) salts have almost same crystal structures, their low-temperature ground states are quite different. κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is the well-known high-T_c superconductors, and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br undergoes an antiferromagnetic transition. On the other hand, preparation of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I single crystal is very difficult, and the electronic structure of it is not clarified so far. The resistivity of κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]I shows weak temperature dependence with a minimum around 100 K. However, this resistivity behavior indicates crucial sample dependence which is due to formation of super-lattice probably originated from conformations of the ethylene located at the end of BEDT-TTF molecules. To understand the low temperature electronic state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I, we are performing ^{13}C and ^{1}H NMR measurements for the same crystal. We can understand the detail of electronic state from the ^{13}C NMR analyses, and the ^{1}H NMR lineshape gives us the information of the ethylene conformation.

Synchrotron X-Ray Diffraction Experiments and MEM Analyses for Single Crystals of Organic Conductors

HARA, Toshifumi; FURUKAWA, Ko; NAKAMURA, Toshikazu

MEM (The Maximum Entropy Method) analyses for synchrotron X-ray diffraction are powerful method to understand local electric charge distribution on each atom for crystalline samples. We performed these techniques for single crystals of organic conductors to study whether there is a change of symmetry of frontier orbitals (electric charge distribution in molecules), which is believed to be rigid so far, at phase transitions, and to investigate possible relation between the detailed electric charge distribution in molecules and the electronic phases. It is believed that most of physics phenomena can be explained within the framework that the frontier orbital can be treated as if one rigid atomic orbital in an alkaline metal. However, there are several experimental results which suggest a change of electric charge distribution in the molecule in some systems.

Possibility of inter-molecular electric charge redistribution has been ignored so far also for charge-ordering phenomena, Hence, we performed synchrotron X-ray diffraction measurements and MEM analyses to investigate the electric charge distribution of molecules on (TMTTF)$_2$PF$_6$. Detailed MEM analyses are now going on.

Development of New Functional Molecular Systems

KOBAYASHI, Hayao; TAKAHASHI, Kazuyuki; CUI, HengBo; OKANO, Yoshinori; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

The molecules are usually assembled by relatively weak intermolecular interactions and tend to retain their intrinsic properties even in the crystalline states. Consequently, it might be easily imagined that the different molecular functions can be accumulated in the same crystal by assembling different building blocks with different characters. In these systems, the multi-functional properties will be realized due to the synergetic actions of different building blocks. The magnetic conductor based on π donors conveying electron conduction and magnetic anions with localized magnetic moments may be a good example. We have recently discovered unprecedented magnetic organic conductors such as the conductors showing superconductor-to-insulator transition, antiferromagnetic organic superconductors and field-induced organic superconductors. We are trying to develop various types of molecular systems with new electronic functions. The main results of our group in the last year are as follows. (1) We have recently found the possibility of unprecedented "constant resistivity state" below T_c, in λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($x \approx 0.35$) exhibiting superconductor-to-insulator transition where the resistivity was independent of temperature and magnetic field applied parallel to the π conduction plane. (2) We are trying to develop photo-controllable magnetic molecular conductors by using Ni(dmit)$_2$ molecules and spin-crossover complex cations. (3) By the improvement of the crystal quality, the antiferromagnetic transition temperature of single-component molecular metal Au(tmdt)$_2$ was enhanced up to 110 K. This is the first molecular metal where π metal electrons and magnetic order coexist above 100 K. (4) We are developing new molecular systems with unprecedentedly high dielectric constant by combining porous molecular crystals and polar guest molecules. Very recently, we have succeeded to obtain molecular systems with dielectric constants one or two orders of magnitude larger than those of usual organic and inorganic compounds.

Synthesis and Properties of Novel Chiral Organic-Inorganic Molecule-Based Magnets

AKITA, Motoko; INOUE, Katsuya

The design and synthesis of molecular materials with interesting electrical and/or optical and magnetic properties has been one of the major challenges of the last few years. The aim of this project is synthesis and characterization of new chiral magnetic materials. Novel properties are expected for The MChD (magneto-chiral dichroism) effect dipends on the magunitude of the optical activity and the magnetic moment. The chiral ferro/ferrimagnets are expected to exhibit a strong MChD effect.

Organic radicals like aminoxyl radicals have been used to construct molecule-based magnets. A strategy of using π-conjugated high-spin oligonitroxide radicals as bridging ligands for transition metal ions in order to assemble and align the electron spins on a macroscopic scale has been established. The crystal structures and magnetic structures of these complexes are well investigated and can be tuned by using appropriately designed ligands. We have been synthesized new chiral organic radicals as ligands in order to introduce chirality to molecule-based magnets constructed with aminoxyl radicals and magnetic metals.

Chiral organic radical 2-{4'-((*S*)-2"-methylbutoxy) phenyl}-4,4,5,5-tetrametylimidazoline-1-oxyl-3-oxide (**1**) and its metal complex **1**·M(II)(hfac)$_2$ (M = Mn, Co, Cu) were synthesized and characterized. The radical **1** crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with a = 11.494(3), b = 25.328(3), c = 6.1281(5) Å. **1**·Mn(II)(hfac)$_2$ crystallized in the same space group with a = 14.081(1), b = 15.940(1), c = 16.075(1) Å. X-ray crystal structure analysis of the **1**·Mn(II)(hfac)$_2$ revealed the formation of a helical chain strucuture. The temperature dependence of the magnetization and the magnetization curve revealed that **1**·Mn(II)(hfac)$_2$ behaves as a ferrimagnet below T_c = 4.3 K.

Design and Functions of Novel Soft Nanomaterials Based on Molecular Programming

JIANG, Donglin

In this special project, we focus on creation of novel soft nanomaterials based on molecular programming. By developing new self-assembling protocols, we target at synthesis of soft nanomaterials with highly controlled structures and well-defined morphologies that lead to the discovery of novel functions. In detail, molecular components bearing photoactive, conductive, and/or spin-active moieties are integrated as building blocks for programmed hierarchical fabrication of nanomaterials. Especially, creation of novel nanomaterials for highly efficient photoinduced energy and electron transfers, construction of functional nanomaterials for future-generation spin-based devices, and realization of high efficiency room-temperature light-induced spin transition are important missions.

Giant Vesicle Fusion on Microelectrodes Fabricated by Femtosecond Laser Ablation Followed by Synchrotron Radiation Etching

RAHMAN, Md. Mashiur; NONOGAKI, Youichi; TERO, Ryugo; KIM, Yong-Hoon; UNO, Hidetaka; ZHANG, Zhen-Long; YANO, Takayuki; AOYAMA, Masaki; URISU, Tsuneo

[*Jpn. J. Appl. Phys.* **44**, L1207–1210 (2005)]

Figure 1 shows the fabrication process for the well structures with microelectrodes. A Co thin film (10 nm thick) was sputter deposited on a mirror-polished Si (100) surface after conventional wet cleaning and Co (10 nm thick) and Ag (100 nm thick) films on the rough back surface [Figure 1(b)]. After that, a SiO_2 thin film consisting of SOG (400 nm thickness) and sputtered SiO_2 (200 nm thickness) were deposited [Figure 1(c)], then the sample was annealed at 540 °C for 10 min. The Co layer was changed to $CoSi_2$ and the Co/Si interface became ohmic [Figure 1(d)]. The sample was then annealed by SR irradiation to remove gas from SOG [Figure 1(e)]. A Co layer as an etching contact-mask was deposited on the SOG surface by sputtering [Figure 1(f)], and electrode hole mask patterns were made using a femtosecond laser (λ = 560 nm, average power = 250 mW, frequency = 258 kHz, pulse width = 900 fs, and irradiation time = 4 ms) [Figure 1(g)]. The diameter of an electrode hole was about 1 mm. SR etching of the SiO_2 layer for making the well on the electrode was carried out at beam line 4A2 of the SR facility (UVSOR) at the Institute for Molecular Science, using a mixture of SF_6 (0.05 Torr) and O_2 (0.002 Torr) as the etching gas [Figure 1(h)]. The SR etching gives a vertical side wall and completely stops at the $CoSi_2$ surface. The Co contact-mask was successfully removed without damaging the substrate by immersion into 0.1M HNO_3 *aq*. [Figure 1(i)]. Ag (50 nm thickness) was deposited on $CoSi_2$ electrode surfaces by electroplating [Figure 1(j)]. Then, AgCl/Ag was formed also by electroplating [Figure 1(k)]. Unilamellar giant vesicles of DPPC : POPS : Rb (89:5 : 10 : 0:5) were prepared as follows; a chloroform solution of a lipid mixture (10 mg/ml) was dried under N_2 flow using a rotary evaporator for about 30 min and subsequently vacuum-dried for 10 h to clearly remove the solvent; then a buffer solution (10 mM KCl) was added to the obtained lipid thin film and gently agitated. The lipid concentration of the obtained suspension was 0.1 mg/ml. All the processes were carried out at room temperature (RT). Then, after incubation at 48 °C for 10 h, dialysis was carried out for the suspension of giant vesicles by using a 5 μm filter for 1 h in the buffer solution (10 mM KCl, pH = 6.6) at RT. For the deposition of lipid bilayer membranes, the substrate was incubated for 1 h at 50 °C under a buffer solution formed by mixing 200 ml of the vesicle suspension and 50 ml of $CaCl_2$ 50 mM solution. Then the sample was washed five times at room temperature (RT) with the buffer solution [Figure 1(l)]. Atomic force microscope (AFM) observations were performed using a SPI3800 scanning probe microscopy system (Seiko Instruments) in the dynamic-force mode (tapping mode) using a Si cantilever. The spring constant of the cantilever for measuring the surface roughness of the substrate in air was 43 N/m, and 1.5 N/m for the in situ characterization of the lipid bilayer.

The surface around the electrode well is very flat (R_a < 0.8 nm). To obtain such a flat surface, it was important to control the irradiation power of the femtosecond laser such that only the Co film is removed while causing negligible damage to the SiO_2 layer beneath. The electric characteristics were determined using a patch clamp amplifier (CEZ-2400, Nihon-Koden, Japan) through the AgCl/Ag electrode in conjunction with the eCell (ver 2.12) software. The diameter of the bilayer was typically about 200–300 μm, large enough to cover the electrode area (10–30 μm diameter).

The lipid bilayer covering the electrode well was formed by giant vesicle fusion. A fluorescence microscopy image after lipid bilayer formation on the microelectrode area clearly shows the existence of the homogeneous lipid thin film. From the current-voltage characteristics of the system measured after the lipid bilayer formation, the resistance of the lipid bilayer was estimated to be 1.2 GΩ.

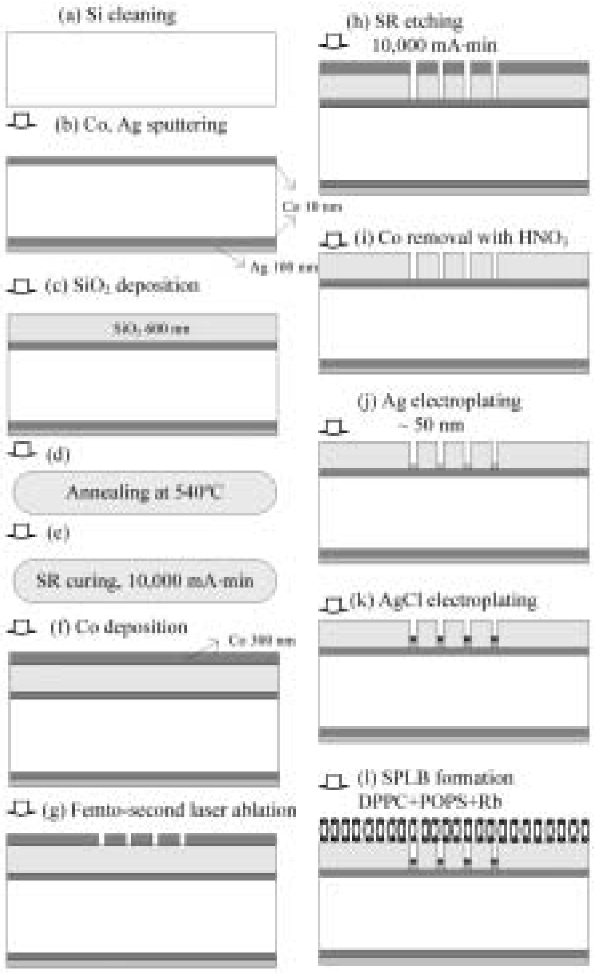

Figure 1.

Reduction of CO_2 and Oxidation of Organic Molecules Aiming at Reversible Conversion between Chemical and Electrical Energies

TANAKA, Koji

Electro- and photochemical reduction of CO_2 affording methanol has become the crucial issue in line with the progress of fuel energy cells using methanol. Carbon dioxide reacts with coordinatively unsaturated low-valent metal complexes to form η^1-CO_2 adducts, which can be converted to the corresponding metal-CO ones in protic media. Electrochemical reduction of metal-CO complexes usually results in the M–CO bonds cleavages due to accumulation of too much electrons on the central metals. Such reductive cleavage of metal–CO bonds plays the key role in the formation of CO in the electrochemical reduction of CO_2. On the other hand, the process prevents electrochemical hydrogenation of the CO ligand that would lead to four- and six-electron reduction affording formaldehyde and methanol. To achieve the six-electron reduction of CO_2, we are designing new types of metal complexes with redox active ligands, which can provide hydrides to carbonyl carbon without increasing electron densities in the metal centers.

Metal complexes that have an ability to oxidize methanol at potentials more negative than the reduction potential of dioxygen may be applied for electrocatalysts used in methanol fuel cells. Metal-oxo complexes are possible candidates for the oxidation of methanol, since metal-oxo species are believed to work as active centers in various metal enzymes, which oxidize various biological substrates under very mild conditions. Mechanistic understandings of the reactivity of metal-oxo species, however, are limited due to the difficulty of preparation of reactive M-O frameworks in artificial systems. Accordingly, reactivity of high valent Ru=O complexes prepared by sequential electron and proton loss of the corresponding Ru–OH_2 ones have been extensively studied and proven to work as oxidants of organic molecules to some extent. We have succeeded reversible conversion between aqua and oxo ligands on Ru-dioxolene frameworks without using any oxidants by taking advantage of the charge distribution between the metal center and the ligand. Along this line, we have been preparing a variety of metal–aqua and –amine complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal–oxo and –imido complexes.

Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

The introduction of substituents onto the two *ortho* positions of *para*-substituted phenol can be readily achieved by electrophilic substitution reactions. The availability of these two substituent positions at the phenol allows its ligand systems of podant and linear (or macrocyclic) linkage. This not only leads to a well defined relative orientation of the ligating atoms but opens up manifold possibilities of steric control. In addition, phenoxide functions may be combined with other functionalities which possess differences in formal charge and their interaction with the metal center. In this context, we are studying the coordination chemistry of multidentate ligands derived from phenoxides. Our recent work concentrate on the synthesis, structural characterization, and reactivity of early transition metal complexes supported by multidentate phenoxide ligands. Our main efforts have been directed toward activation of small molecules.

Studies on Development of Molecules and the Device Fabrications for Molecular Scale Electronics

OGAWA, Takuji; TANAKA, Hirofumi

The aim of this special project is to study the electric and photonic properties of individual single molecules, and to establish the fundamental of molecular nanoscience. The project is composed of two parts; (1) design and synthesis of novel molecules which are important in molecular nano-science and (2) construction of a “molecular tester” which is comprised of double probe conductive AFM. The “molecular tester” is capable of measuring the electric properties of individual molecules by using two conductive cantilevers like proves of conventional electric testers. The machine can be extended to include SNOM-type cantilever as the third prove, which will be used to measure the photonic properties of the individual molecules. The construction diagram was shown in Figure 1. In many cases multi probe SPMs do not have atomic resolutions because of the complexity of the system. However, our two probe STM has atomic images and 7×7 structure of Si(111) surface can be obtained successfully as shown in Figure 2. Figure 3 shows the cooling characteristics of the system. With this setup the sample can be cooled to less than 70 K within three hours.

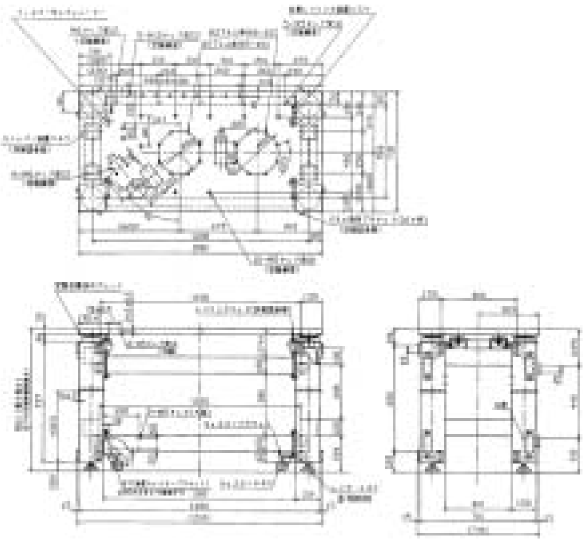

Figure 1.

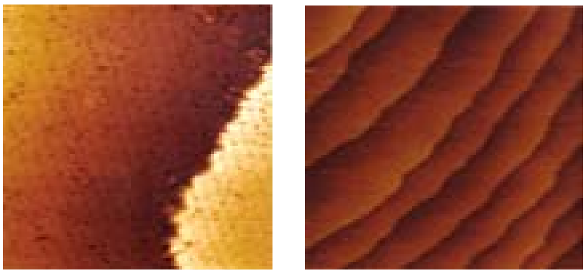

Figure 2.

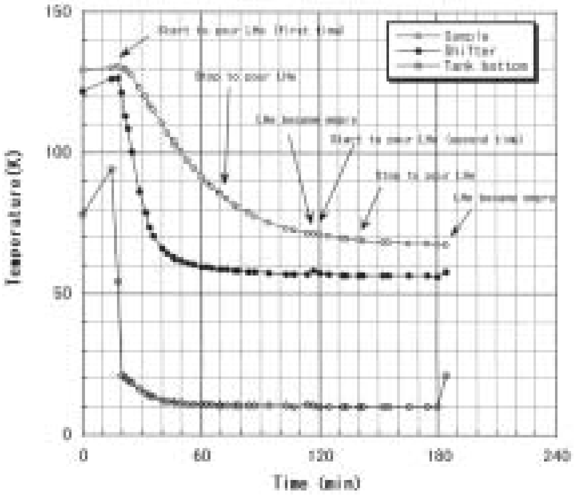

Figure 3.

Synthesis of Perfluorinated Fluorene Oligomers and Applications for Organic Light-Emitting Diodes

OKUBO, Kimitaka; SUZUKI, Toshiyasu

We have synthesized novel perfluorinated fluorene oligomers up to the tetramer. These oligomers form good amorphous films. Light-emitting diodes using these oligomers as the hole-blocking and electron-transport layers show high quantum efficiencies.

Novel Pincer Complexes and Their Catalytic Properties

UOZUMI, Yasuhiro

A wide range of NCN pincer palladium complexes, [4-*tert*-2,6-bis(*N*-alkylimino)phenyl]chloropalladium (alkyl = n-butyl, benzyl, cyclohexyl, t-butyl, adamantyl, phenyl, 4-methoxyphenyl), were readily prepared from *trans*-(4-*tert*-butyl-2,6-diformyl-phenyl)chlorobis(triphenylphosphine)palladium *via* dehydrative introduction of the corresponding alkylimino ligand groups (ligand introduction route) in excellent yields (71–98%). NMR studies on this route for forming pincer complexes revealed the intermediacy of [4-*tert*-2,6-bis(*N*-alkylimino)phenyl]chlorobis(triphenylphosphine)palladi um which is in equilibrium with the corresponding NCN pincer complexes *via* coordination/dissociation of the intramolecular imino groups and triphenylphosphine ligands. A series of chiral NCN pincer complexes bearing pyrroloimidazolone units as the trans-chelating donor groups, [4-*tert*-butyl-2,6-bis{(3*R*,7a*S*)-2-phenyl-hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-on-3-yl}phenyl]chloropalladium, were also prepared from the same precursor via condensation with proline anilides in high yields. The catalytic properties of the NCN imino and the NCN pyrroloimidazolone pincer palladium complexes were examined in the Heck reaction and the asymmetric Michael reaction to demonstrate their high catalytic activity and high enantioselectivity.

Asymmetric Aquacatalysis with Polymeric Palladium Complexes

UOZUMI, Yasuhiro

Catalytic asymmetric organic transformations performed in aqueous media with immobilized chiral palladium and rhodium complexes were developed. Amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin-supported MOP, boxax, BINAP, and an imidazoindole phosphine ligands were designed and prepared with a view to use them in asymmetric catalysis under aqueous and heterogeneous conditions. Several carbon–hydrogen, carbon–carbon, carbon–nitrogen, and carbon–oxygen bond forming reactions were achieved in water with high stereoselectivity and recyclability to meet the green chemical requirements.

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

NAGATA, Toshi; KIKUZAWA, Yoshihiro; NAGASAWA, Takayuki; MAKI, Suguru

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 chemical transformation by using light energy via photoinduced electron transfer. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, transition metal complexes, and metal nanoparticles.

During the last year, we have made progresses on the following three areas: (1) application of molecular dynamic simulations to the composite material of organic molecules and gold nanoparticles in organic solvents, which gives us better understanding of the solution behavior of these composites, (2) electrochemical examination of ferrocene-dendrimer-porphyrin molecules, which gives us some insights about the dynamic feature of these multiple redox-active molecules, and (3) synthesis and characterization of a series of cobalt complexes as candidates of new electrocatalysts.

Synthesis of Buckybowls and Heterobuckybowls

SAKURAI, Hidehiro; HIGASHIBAYASHI, Shuhei

Bowl-shaped π-conjugated compounds including partial structures of the fullerenes, which are called "buckybowls," are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, heterobuckybowls, some of whose carbon atoms in the framework are substituted to the appropriate heteroatoms such as N, O, S, Se, Si, B *etc.*, have been expected to exhibit unique physical characters based on the heteroatom induced effects.

However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure. In addition, most of thus-reported procedures are performed under severe reaction conditions, limiting the sort of the introducible atoms/functional groups. In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls using the organic synthesis approach. Targets of this year are as follows:

A. Novel and versatile route to C_5 symmetric corannulene and its derivatives.

B. Synthesis of C_2 symmetric C_{60} and C_{70} fragments.

C. Synthesis of nitrogen-containing heterobuckybowls.

D. Synthetic route to silicon-containing aromatic compounds.

Tuning Catalytic Activities of Gold Clusters *via* Hybrization of Functional Molecules

NEGISHI, Yuichi; TSUNOYAMA, Hironori; YANAGIMOTO, Yasushi; TSUKUDA, Tatsuya

We have recently demonstrated that the polymer-stabilized gold clusters dispersed in water exhibit inherent catalytic activities against aerobic oxidation. This finding shows that the small gold clusters are inherently catalytic active and are promising candidates for environmentally benign catalysts. In the present project, the gold clusters were hybridized with various types of functional organic molecules in order to add new and higher-ordered catalysis, such as catalytic activity, substrate selectivity and enantioselectivity. The molecules we used so fat include thiolated cyclodextrine, dendrimers, and chiral phosphines. The catalyses of these gold clusters have been compared with those of the gold clusters stabilized by linear polymers.

Structural Analyses of Multi-Domain Proteins by Use of Ultra-High Field NMR Spectroscopy Measured at 920 MHz ^{1}H Resonance Frequency

KATO, Koichi

Recent advances in NMR structural biology have made possible the high throughput structural determination of small simple proteins and protein domains. However, structural analyses of multi-domain proteins, natively unfolded proteins, and glycoproteins remain as tasks with more challenge. Although NMR structural biology of these troublesome proteins is still at a preliminary stage, the ultra-high field NMR spectrometer will be a powerful tool to cope with the difficulty in dealing with them. In the present study, we apply ultra-high field NMR spectroscopy to determination of the relative orientation of individual domains in multi-domain proteins using protein disulfide isomerase (PDI) as a model molecule.

PDI is a folding assistant operating in the endoplasmic reticulum, and catalyzes the formation, breakage and rearrangement of disulfide bonds of its substrate proteins. PDI has a modular structure with four globular domains, *a*, *b*, *b*' and *a*' plus a C-terminal acidic extension. The homologous *a* and *a*' domains contain a cysteine pair in a WCGHCK active site sequence motif directly involved in thiol-disulfide exchange reactions. So far the solution structures of the *a* and *b* domains have been reported to be thioredoxin folds. We have shown that substrate binding site of PDI is primarily composed of the *b*' and *a*' domains.

We performed structural analyses of three-dimensional structures, substrate recognition, and domain-domain interactions of the *b*' and *a*' domains of thermophilic fungal PDI. Isotopically labeled *b*' and *a*' domains as well as the fragments composed of these two domains were expressed in *E. coli*. Inspection of NOE, chemical shift, and residual dipolar coupling (RDC) data revealed that 1) the *b*' and *a*' domain assume typical thioredoxin folds, 2) substrate analogs, *e.g.* somatostatin and mastoparan, bind a hydrophobic area spanning the *b*' and *a*' domains in their oxidized form, and 3) reduction of the active site of the *a*' domain results in its increased contact with the *b*' domain, rendering the hydrophobic area less accessible. On the basis of these data, we conclude that this conformational rearrangement causes redox-dependent interaction of PDI with its substrates. In the NMR analyses, the 920 MHz NMR spectrometer plays a crucial role in observation of RDC because the alignment of macromolecules in the presence of liquid crystal media is more enhanced at higher magnetic fields. This study demonstrates that 920 MHz NMR spectroscopy provides us with invaluable information for structural determination of multi-domain proteins in the absence of crystal packing forces.

Observation of Intense Bursts of Terahertz Synchrotron Radiation at UVSOR-II

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We have detected very intense bursts of terahertz synchrotron radiation at the UVSOR-II electron storage ring operated in single bunch mode. The bursts were observed in the wavelength range from 0.2 to 3.0 mm by using a liquid-helium-cooled InSb hot-electron bolometer. The typical duration and interval of the bursts were about 200 μs and 10–15 ms, respectively. Each burst shows the quasi-periodic structure of about 30 μs. The peak intensity of the bursts was about 10000 times larger than that of ordinary synchrotron radiation in the same wavelength region. The extremely high intensity strongly suggests that the bursts are coherent synchrotron radiation, although the radiation wavelength was much shorter than the electron bunch length.

We have prepared a TiSa laser which is synchronized with the RF acceleration of the UVSOR-II electron storage ring. By using this laser, we can produce local density modulation in the electron pulses. Such electron pulses are expected to emit intense terahertz radiation. The laser has been successfully commissioned. A preliminary result indicated the successful production of coherent terahertz radiation.

Optical and Photoelectrical Studies on Fermiology of Strongly Correlated Electron Systems

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Strongly correlated electron systems attract much attention because of their various physical properties. To reveal the origin of the physical properties from microscopical viewpoints, we investigate the electronic structure near the Fermi level (Fermiology) by infrared and photoemission spectroscopies using synchrotron radiation. In this year, we investigated the electronic structure near the quantum critical point of rare-earth compounds $\mathrm{CeNi}_{1-x}\mathrm{Co}_x\mathrm{Ge}_2$ ($0 \le x \le 1$). The phase separation between the metallic and insulating states of partially-deuterated κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N(CN)}_2]\mathrm{Br}$ was directly observed by using infrared magneto-optical imaging spectroscopy and was concluded to originate from the inhomogenity of the sample itself. Infrared spectroscopy of CeSb under multi-extreme conditions of low-temperature, high-field and high-pressure was successfully performed and the pseudogap formation and its collapse due to magnetic fields were observed.

Developments and Researches of New Laser Materials

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

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

Development and Research of Advanced Tunable Solid State Lasers

TAIRA, Takunori; ISHIZUKI, Hideki; TSUNEKANE, Masaki; DASCALU, Traian; SATO, Yoichi; SAIKAWA, Jiro; PAVEL, Nicolaie

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 neodymium and ytterbium ion doped materials. 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. Recently developed transparent ceramic material enhances the flexibility of the solid-state laser, for example, the doping ions and host structures for the advanced laser systems.

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.

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

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The heme-based sensor proteins reveal a novel function of hemeproteins, in which the heme acts as the active site for sensing the external environmental signals such as diatomic gas molecules and redox change. As the heme-based sensor protein, O_2, NO, and CO sensor proteins are reported so far. In this project, we are working on CO sensor protein (CooA), O_2 sensor protein (HemAT), and a novel redox sensor protein (DcrA) to elucidate their structure-function relationships.

Elucidating the heme environmental structure is important to understand the structure-function relationships of the heme-based sensor proteins, because the heme is the active site for sensing the physiological effector molecules. Therefore, we have characterized the heme-based sensor proteins by UV/VIS, EPR, NMR, and resonance Raman spectroscopies along with mutagenesis studies. Electrochemical redox titration is also used to determine the redox properties of the heme-based sensor proteins. To determine the molecular structures of the heme-based sensor proteins by X-ray crystallography, screening the condition has been tried for crystallization of sensor proteins.

We are also trying to find novel heme-based sensor proteins by searching DNA data bases, and find a possible candidate so far. It is a Htr8 protein from *Halobacterium salinarum*, which would be a membrane-bound chemotaxis signal transducer protein. Based on the amino acid sequence deduced from the DNA sequence, Htr8 will consist of at least two domains, the N-terminal sensor domain and C-terminal signaling domain. The amino acid sequence of the sensor domain shows a homology to that of cytochrome *c* oxidase α subunit that contains hemes and copper ions as the active site for respiration. We are now constructing expression systems of Htr8 to obtain and characterize the recombinant Htr8.

Molecular Mechanism of Metalloenzymes Related to Oxygen Activation and Denitrification Processes

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. In this project, we are studying the molecular mechanism of metalloenzymes related to oxygen activation and denitrification.

(1) Oxidizing intermediates are generated from nonheme iron(III) complexes to investigate the electronic structure and the reactivity, in comparison with the oxoiron(IV) porphyrin π-cation radical (compound I) as a heme enzyme model. The present study explains unique properties of mononuclear nonheme enzymes with Tyr residues, and also a poor epoxidation activity of Fe salen compared to Mn and Cr salens.

(2) In non-heme metalloenzymes, imidazole rings of histidine residues often form part of the metal-binding site. For examples, in the active sites of hemocyanin (Cu), nitrite reductase (Cu), and carbonic anhydrase (Zn), three imidazoles coordinate to one metal ion. We report the synthesis of tris(4-imidazolyl)carbinol ligands having chemically stable methyl group as the NH protective group and bulky substituent (isopropyl or phenyl) for stabilizing reactive species bound to metal center.

(3) Heme oxygenase (HO) catalyzes catabolism of heme to biliverdin, CO and a free iron through three successive oxygenation steps. The third oxygenation, oxidative degradation of verdoheme to biliverdin, has been the least understood step in spite of its importance to regulate the HO activity. We have thoroughly examined degradation of a synthetic verdoheme IXa complexed with rat HO-1. We propose that the HO enzyme activates O_2 and H_2O_2 on the verdoheme iron with the aid of a nearby water molecule linked with Asp140.

(4) Reduction of nitrite (NO_2^-) to gaseous nitric oxide (NO) is one of key processes in the global nitrogen cycle and carried out by bacterial copper-containing nitrite reductases (NiR). We report detection and characterization of new reaction intermediates in the nitrite reduction. This study shows that two protons required for the reaction are not provided to the copper bound nitrite simultaneously but stepwise and that the intramolecular electron transfer from the copper(I) ion to the copper bound nitrite occurs in the second protonation step.

Molecular Science of Proteins Based on Vibrational Spectroscoy

KITAGAWA, Teizo

Proteins have an average structure as determined by x-ray crystallographic analysis. The higher order structure, details of which are not always clarified by x-ray crystallography and are easily altered by small energy, is directly related to a function of the molecule. Vibrational spectroscopy can provide some essential information on the higher order structure of proteins and its dynamics. It is the purpose of this group to apply resonance Raman and IR spectroscopy to observe vibrational spectra of proteins in aqueous solutions and to elucidate the structure-function relation in a level of molecular science.

In resonance Raman spectroscopy, various sensory proteins have been treated with visible and UV excitations. The visible excitation explored the structure of the heme site and UV excitation revealed what part of the protein is involved in the signal transduction *via* vibrational spectra of Trp and Tyr residues. For gas sensor proteins, sGC for NO, CooA and NPAS2 for CO and HemAT and Dos for O_2 are examined extensively. In addition, heme Raman spectra of new proteins including SOUL in mouse eyes, a maturation protein of cytochrome *c* (CcmE), and aldoxime dehydratase are also examined. Some basic features of Mb and Hb are also investigated in combination of UV and visible resonance Raman. We have been invited to contribute a mini-review paper on the gas sensory proteins by several international journals (*Acc. Chem. Res.*, *Inorg. Chem.* and *J. Inorg. Biochem.*).

As a very unique study, anti-stokes Raman spectra of dendrimer porphyrins are investigated in the presence and absence of IR irradiation, by which capturing of IR photons through antennae is confirmed. The Raman studies are extended to DNA-photolyse, various oxygen activating enzymes and their model compounds. On the other hand, our IR study is focused on an amyloid fibril. IR microscope technique is applied to several amyloid fibrils derived from fragment peptides of β_2 microglobulin. IR spectroscopy will also be used to reveal the coupling mechanism of proton and electron transfers by terminal oxidases.