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 ofmulticanonical 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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Theoretical Studies of Chemical Dynamics

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Various types of chemical dynamics have been studied analytically as well as numerically. In order to treat multi-dimensional non-adiabatic chemical dynamics by taking into account important quantum mechanical effects, we have developed a general TSH (trajectory surface hopping) method and a semiclassical frozen Gaussian wave packet propagation method by incorporating the Zhu-Nakamura theory.1),2),3) Furthermore, new formulations have been made for direct evaluation of thermal rate constant of electronically nonadiabatic chemical reactions by incorporating the Zhu-Nakamura theory. In order to take into account the tunneling effects in the dynamics, we have developed a general method to find caustics along classical trajectories in multi-dimensional system.4)

Our theory of tunneling splitting5) has been successfully appield to real polyatomic molecules such as malonaldehyde, vinyl radical, and formic acid dimer.6) The calculated results are in very good agreement with experiment and have proved the power of our theory.

As is well known, nonadiabatic transitions play crucial roles in various types of molecular functions such as photochromism and encapsulation of atoms in nanotubes. We have studied the transformation between cyclohexadiene and hexatriene by a high level of quantum chemical calculations and found a conical intersection important for the transformation. As a model of encapsulation, we have investigated the system composed of $C_{20}H_{10}$ and H quantum chemically and dynamically. The nonadiabatic transition is found to play crucial role and it is possible to transmit H through the ring molecule $C_{15}H_{10}B_5$ with high efficiency.

Laser control of molecular processes is another important subject of our activities. A numerically efficient new semiclassical optimal control theory (OCT) has been successfully formulated and is expected to be applicable to multi-dimensional systems.7) Electronic transition of wave packet is an important element of controlling chemical dynamics and is found to be controlled efficiently by using quadratically chirped pulses.[8)] Combination of this idea with the semiclassical OTC would enable us to treat realistic multi-dimensional chemical dynamics.

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Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

KOSUGI, Nobuhiro; HATSUI, Takaki

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 and radicals 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 non-radiative (photoelectron emission) and radiative (photon emission) deexcitation spectra. 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 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

Dynamics of molecular vibration in solution has been investigated based upon two simulation methods. The first one is an application of path integral influence functional theory assuming harmonic oscillations bath. The second is mixed quantum-classical molecular dynamics calculation with mean field approximation for the force on the classical solvent molecules.

Based upon the first method, dynamics of coherence between vibrational states of a solute molecule in the solution has been analysed. The formalism of the present method was compared with that of the Redfield theory. The method was applied to the vibrational relaxation of CN^- ion in water. The calculated $\mathrm{Re}\rho_{01}(t)$ showed an oscillatory behavior, whose amplitude was damped as a function of time. This is an annihilation of the coherence. Further, inhomogeneous environment for the system of interest clearly showed a dephasing when the function is averaged over a number of solute molecules.

Population decay mechanism in the fluid, *i.e.* collision or resonance, has also been analysed based upon mixed quantum-classical molecular dynamics calculation. It was clarified that it depends upon temperature, density, and transition frequency as well as the interaction, *i.e.* long-ranged coulombic one or short-ranged one of LJ type.

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 vibrational motions at surfaces coherently prepared by impulsive resonance Raman excitation. 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.

Fundamental Study on High Speed DNA Sequencing Method

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Fundamental study on high speed DNA sequencing method was carried out using field ion microscope (FIM), which has atomic-level resolution of the surface morphology. For the sample preparation of FIM observation, immobilization of DNA molecules on an electropolished Au wire serving as a high voltage electrode was studied. Optical microscopic observation of the fluorescently labeled DNA molecules showed that DNA molecules of which terminus was modified with -SH group were immobilized on the Au tip through specific reaction between Au and -SH groups. For the FIM observation, positive high voltage was applied to the Au tip on which DNA molecules were immobilized. As a result, FIM image was observed at lower applied voltage compared with the sample without DNA molecules. The difference in on-set voltage of the FIM images seems to be attributed to the difference in the surface morphology especially the difference in evenness; thin DNA molecules must have introduced atomically uneven surface to the Au tip.

Development of Molecular Frame (e,2e) Spectroscopy: Towards Complete Mapping of Molecular Orbitals

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Through the last three decades of studies of binary (e,2e) spectroscopy or electron momentum spectroscopy (EMS), it has been demonstrated that the ionization reaction near the Bethe ridge is a sensitive probe for electronic structure and electron correlation. Under the high-energy Bethe ridge conditions, where the collision kinematics most nearly corresponds to collision of two free electrons with the residual ion acting as a spectator, EMS allows us to measure individual orbital momentum densities or to look at individual molecular orbitals in momentum space. In spite of the remarkable feature of the technique, however, EMS has not yet reached the stage of full use of its ability for intensive investigation on electronic structure of molecules. The reason for this may have been twofold; (1) a more complete knowledge of the binary (e,2e) reaction mechanism is an ever-increasing necessity as sophistication of experiments increases, and (2) the present EMS experiments measure averages over all orientations of gaseous molecules, resulting in enormous loss of information on electronic structure, anisotropy of the target wavefunction in particular.

To resolve the historical issues, we have proposed a method for complete mapping of the electron momentum densities in the molecular frame.1),2) 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,2e) experiments with fixed-in-space molecules, which should be designated as (e,2e+M) spectroscopy. Our apparatus has already been used to explore the phenomena of H_2 and O_2 for which detailed theoretical explanations are eagerly awaited. We believe that these are the first observation of molecular frame (e,2e) cross sections, which visualize collision stereodynamics.

However, there is ample room for improvements mainly in collection efficiency, which could be achieved by detection of the outgoing electrons in the momentum dispersive plane around full 2π azimuth and detection of the fragment ion over the full 4π solid angle. With these further technical developments the method would exploit a new area for studies on collision dynamics and electronic structure in the molecular frame.

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Efficient Generation of Potential Energy Surfaces

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We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and the modified Shepard interpolation proposed by Collins are employed to describe potential energy surfaces. This IMLS/Shepard scheme is applicable to do potential interpolation with quantum chemical results for which analytical derivatives are not available. We applied the scheme to a four atomic system $OH + H_2 \rightarrow H_2O + H$ reaction and H_4.

As for the former system, we compared the results with those based on the modified Shepard interpolation using second order Taylor expansions. An analytical surface is used to define the potential function so that errors in the interpolation function may accurately be determined. We found that the energy and gradient errors in the present scheme is comparable to those in the modified Shepard scheme. Note that the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does.

For H_4 system, in order to take advantage of the full symmetry of nuclear permutation of it, we generalized our code to handle the symmetry. This reduces the computational time as well as memory storage. In addition, we parallelized our code. We used an analytical surface by Boothroyd et al to test the IMLS/Shepard scheme. They employed a global function to fit their ab initio points with the error of several kcal/mol, but our scheme use all the points and there is no errors at least at the points.

The accuracy and convenience in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

(b) Molecular Photophysics and Science

Spatiotemporal Dynamics in Nanometric Molecular Assemblies by Near-Field Spectroscopy

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

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. Using continuum generation in a photonic crystal fiber, we have also succeeded in near-field pump-probe experiments in wide-range probe wavelength. 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 aggregates and metal nanoparticles. On porphyrin aggregates, we have obtained information on inhomogeneity of spectroscopic character and dynamic behavior. 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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In “studies on laser cooling and trapping of metastable helium atoms,” we have improved the vacuum system at the trapping section by introducing a non-evaporative getter pump in order to extend the lifetime of the trap. On the other hand, in “laser spectroscopic studies of atoms and ions in liquid helium,” we have measured emission spectra of Mg atoms in cold helium gas in order to confirm the inference presented in our previous work, in which the formation of Mg(3s3p ^{1}P)He$_{10}$ exciplex in liquid helium is inferred. The spectrum obtained in the present experiment has shown good agreement with a theoretical spectrum calculated based on the model of the exciplex formation, and this result strongly supports the previous inference (see II-B-1). In addition, we have also measured emission spectra of Eu atoms in liquid and solid helium over a wide pressure range across the solidification pressure. As a result, we have found that the behavior of the spectral intensity across the solidification pressure remarkably differs between ^{3}He and ^{4}He; while for ^{4}He the intensity drastically increases above the solidification pressure, no significant change is seen for ^{3}He across the solidification pressure. We have interpreted this difference as a manifestation of the difference between mobilities of Eu atoms in solid ^{3}He and ^{4}He, and have inferred that such a difference in mobility is caused by the difference in mass between the two helium species and also depends on whether the solid is a Bose condensate or not (see II-B-2).

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

FUJII, Masaaki

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

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 meter 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.

Probing Ultrafast Molecular Dynamics by Extremely Short Laser Pulses

TAKAHASHI, Eiji J.; HISHIKAWA, Akiyoshi

Highly excited molecules often undergo ultrafast nuclear dynamics with a time scale less than 100 fs as observed in intense laser fields (see VI-C). This special research project is aimed to trace in real time the evolution of such ultrafast nuclear motion by extremely short laser pulses with the duration less than 15 fs. For this purpose, a new Ti:Sapphire amplifier system has been introduced. The output from the Ti:Sapphire oscillator (800 nm, 20 fs, 600 mW) is amplified by a regenerative amplifier and a double path main amplifier. The typical output power is 2.5 W at the repetition frequency of 1 kHz. The pulse compression system of the amplifier output with the pulse duration of ~35 fs to deliver high power, sub-15fs laser pulses is under construction.

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

MITSUKE, Koichiro; KOU, Junkei; MORI, Takanori

One of our main interests is to elucidate the spectroscopy and dynamics of superexcited states of fundamental molecules. 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. Autoionization usually takes place in a very short period, but strong interactions caused by neighboring neutral states often lead the superexcited states to 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 synchrotron radiation-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 Development of Vibrational Sum Frequency Generation Spectroscopy

MORITA, Akihiro

The sum frequency generation (SFG) spectroscopy is a powerful technique for interface characterization, owing to a number of unique, useful features. It has a sufficient surface sensitivity in a molecular scale as a surface vibrational spectroscopy. It can be applied to surfaces in both vacuum and ambient conditions, and even to buried interfaces such as liquid-liquid or liquid-solid interfaces. By utilizing the time resolution of short-pulse lasers, this technique possesses high potential applicability to dynamics studies at interfaces.

Although SFG spectra involve rich structural information of interfaces in molecular level, their microscopic interpretation is often not straightforward to determine the interfacial structure. Theoretical calculations to help assign the experimental spectra are therefore greatly needed to fully exploit the potential of SFG spectroscopy. We proposed theories of SFG spectroscopy,1),2),3) which enable us to compute SFG spectra in non-empirical ways by molecular simulation.

The present project started this year after Dr. Morita moved to the IMS. This project develops our SFG theories toward general and practical use for experimental interpretation. We have two sub-projects in this category: (1) development of fundamental SFG theory toward quantitative interpretation of the experiments, and (2) application to other interfacial structures of interest using massive computation. This year we have developed a theory for bulk contribution to SFG spectra, which is readily implemented in molecular dynamics simulation. Numerical calculation of the bulk contribution is now in progress.

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Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; HIKOSAKA, Yasumasa

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 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. 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 “double toroidal” electron analyzer, which has been originally developed by a French group, has been constructed at UVSOR. The conical symmetry of the lens system limits the detection angle of electrons to 54.7° with respect to the cylindrical symmetry axis of the analyzer. The incident electrons are focused by the lens, and then dispersed in energy between the double toroidal deflectors, and reach a delay-line-type imaging detector mounted on the output plane. The imaging detection without any exit slit enables us to observe electrons within an energy range more than 10% of the pass energy. Recently the performance of the analyzer has been improved considerably after careful tuning, but an insulation failure on the detector has occurred and might be damaged beyond repair. The introduction of a new detector system will be seriously considered.

Vacuum ultraviolet (VUV) fluorescence may be a unique probe for identifying the multielectron processes, because it is expected that such processes may lead to highly-excited molecular ions, fragment ions, and neutral fragments produced after Auger decays. We have constructed a 0.3-m Seya-Namioka-type fluorescence spectrometer, for observing the VUV fluorescence following the molecular inner-shell excitation. The dispersed fluorescence is detected by a position sensitive detector composed of three microchannel plates and a resistive anode encoder, where the front microchannel plate is coated by CsI. The position sensitive detector installed enables us to observe the fluorescence spectrum with its spectral range about 300 Å simultaneously. Preliminary results for some simple molecules such as N_2, O_2, and N_2O have been gained at BL4B.

Parallel to the developments of the apparatus mentioned above, several trial experimental setups have been made for observing minor products, such as highly excited neutral species and anions after the molecular inner-shell excitations and their performance tests have been conducted with success. However, due to the insufficient intensity of the monochromatized soft X-rays at BL4B, it is difficult to obtain the reliable data for the minor products including the VUV fluorescence. The utilization of the new undulator beamline BL3U is highly desired, in order to overcome such a situation.

(c) Novel Materials Science

Quantum Chemistry Calculations of Large Molecules

ISHIMURA, Kazuya; NAGASE, Shigeru

In order to make reliable quantum chemistry calculations possible for large molecular systems, we have developed a new program code that is suitable for the high-speed parallel treatments of two-electron integrals as well as the generation and diagonalization of Fock matrices, these being essential for molecular orbital and density functional theory calculations. By using this code, test calculations are performed using Pentinum 4 3.0GHz PC clusters, for example, for a taxol molecule ($C_{47}H_{51}NO_{14}$) without symmetry at the HF/6-31G level (a total of 660 contracted functions). The speedup ratios are 2.0, 4.2, 10.2, and 32.7 for 2, 4, 8, and 16 CPUs, respectively. As the number of CPUs increases, it is evident that the speedup is highly enhanced and a super-linear parallelization is achieved. To incorporate effects of electron correlation, we are now developing a program code of second-order Møller-Plesset perturbation (MP2) calculations that are applicable to non-covalent interactions playing an important role in host-guest chemistry, molecular recognition, and sele-assembly.

Statistical Mechanics of Interfacial Fluids: Electric Double-Layer in Carbon Nano-Pore and Super-Capacitor

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Materials with randomly distributed pores such as charcoal are attracting much attention as “new materials” for industrial applications. In fact, so called ‘super capacitor’ or ‘electric-double-layer capacitor (ELC),’ which consists of a porous carbon and an electrolyte solution, has been among latest targets of industrial research due to its high capability of storing charges; million to 10 million time greater than traditional capacitor using metal electrodes. Theoretical investigation of such materials, however, has been largely limited simply by the difficulty of describing or modeling randomly distributed pores, electrolyte solutions, and their interface.

Recently, we have devised a new theory for modeling the interface of solution and materials with randomly distributed pores based on the RISM theory and the replica method developed in the field of the spin glass: the liquid phase is described by the RISM theory and the disordered porous material is modeled by branched polymeric chains of nano-spheres, which are quenched into a matrix spatial configurations. The averaging of the free energy of solution over the matrix configurations is carried out by the replica trick.

Using the method, we could have successfully accounted the liquid-vapor phase transition of water and methanol sorbed in nanoporous carbons. The theory is also successful to predict the large capacity exhibited by the electric-double-layer capacitor. A research is in progress to figure out possible factors which produce such high capability of storing charges: electrolyte concentrations, ionic species, shape of pores, and so on.

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

YONEMITSU, Kenji; YAMASHITA, Yasufumi; OTSUKA, Yuichi; INOUE, Hitoshi; MAESHIMA, Nobuya

In low-dimensional molecular materials, effects of different interactions appear not only in their equilibrium phases but also in their non-equilibrium time-evolution. i) Mixed-stack organic charge-transfer complexes show neutral-ionic and dimerization-induced ferroelectric phase transitions. In the most famous TTF-CA complex, they occur simultaneously at ambient pressure but at different temperatures under high pressure. Thus we treat both the ionicity and the dimerization using the Blume-Emery-Griffiths model. Long-time evolution is studied by solving the master equation during and after photoirradiation of the complex. As a first step, we use the mean-field approximation that does not distinguish the intra- and inter-chain couplings. We find photoinduced breaking of the inversion symmetry and spontaneous ordering of electric polarizations leading to the ferroelectric ionic phase after the neutral phase is photoexcited and converted into the paraelectric ionic phase. This would explain the recent experimental findings with intra-molecular excitations. ii) Recent experimental data on photoinduced phase transitions of the materials with strong electron-lattice coupling show different degrees of coherence. In the TTF-CA complex also, the coherent oscillation of neutral-ionic domain walls is observed. In order to study the effect of coherence in the ionic-to-neutral transition, we use the one-dimensional extended Peierls-Hubbard model with alternating potentials. A double pulse of oscillating electric field is introduced in the time-dependent Schrödinger equation. The two pulses constructively interfere with each other if the interval is a multiple of the period of the optical lattice vibration, while they destructively interfere if the interval is a half-odd integer times the period, in the processes toward the neutral phase. The interference is strong especially when the pulse is strong and short because the coherence is also strong. Here we have observed the coherence in domino-like photoinduced phenomena for the first time, *i.e.*, in photoinduced phenomena which spontaneously proceed once triggered. iii) Some spin-crossover complexes show two-step transitions by changing temperature between high-spin and low-spin phases in equilibrium. In [Fe(2-pic)$_3$]Cl$_2$·EtOH, high-spin-low-spin ordering is recently observed on the 50% plateau of high-spin fraction at intermediate temperatures. However, the time evolution of this material under continuous photoirradiation does not clearly show the high-spin-low-spin-ordered phase even transiently. We employ a two-sublattice classical-spin model, where an intra-dimer inter-sublattice antiferroic coupling prefers the intermediate phase while an inter-dimer intra-sublattice ferroic coupling the uniformly high-spin or low-spin phase. Although an inter-dimer inter-sublattice coupling plays the same role with the intra-dimer inter-sublattice coupling at the mean-field level, we find by Monte Carlo simulations that their effects are different especially when the material is under photoirradiation. This fact can explain why the high-spin-low-spin-ordered phase is hardly realized under photoirradiation.

UHV Systems for MOKE, MSHG, XMCD and STM Measurements

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

The magneto-optical Kerr effect (MOKE) is usually the most suitable method to characterize magnetic properties of ultrathin films. We have constructed an ultrahigh vacuum (UHV) MOKE system equipped with an UHV-compatible electromagnet (max. 3000 G, static). 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, and the preliminary MSHG data have been recorded.

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. We have constructed another UHV chamber that is installed 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.

In order to characterize surface structure, we are also now constructing a new surface analysis system based on UHV scanning tunneling microscopy (STM). The performance test was completed and we observed good STM images of graphite at ~10 K as well as at room temperature.

Some experimental results concerning MOKE and XMCD have already been obtained and are described in the section of Research Activities. Using the MOKE, MSHG, XMCD and STM techniques, we will investigate surface magnetism that can be controlled by surface chemical adsorption and reactions.

Advanced Use of Electron Spin Resonance Spectyroscopy

KATO, Tatsuhisa; FURUKAWA, Ko

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of ESR spectroscopy enables us to investigate the transient phenomena in detail as well as the high spin state. 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 combined use of the different frequency ESR spectrometers, *i.e.* X-band (9 GHz), Q-band (35 GHz) and W-band (95 GHz) spectrometers, gave the detail information of the high spin state. The advanced ESR method was applied to the study on the high spin state of Ce@C$_{82}$ described in section II-G-1, of La@C$_{82}$ derivatives described in section II-G-2. And the high-field high-frequency ESR method was also applied to the biological system, the manganese cluster in oxygen evolving complex of photosystem II in the S$_2$-state, described in section II-H-1.

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 driven by 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 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) 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) We have investigated the infrared and Raman properties of all θ-type ET salts, θ-(ET)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$, θ$_m$-(ET)$_2$TlZn(SCN)$_4$, θ$_o$-(ET)$_2$TlZn(SCN)$_4$, θ-(ET)$_2$RbZn(SCN)$_4$, θ-(ET)$_2$CsZn(SCN)$_4$, and θ-(ET)$_2$I$_3$ in the sequence of the bandwidth. All of these compounds showed a metal-insulator transition except θ-(ET)$_2$I$_3$. The metal-insulator transitions are accompanied by charge order and structural change except for θ-$(ET)_2CsZn(SCN)_4$ We characterized the CO pattern of θ-$(ET)_2RbZn(SCN)_4$, $θ_o$-$(ET)_2$ $TlZn(SCN)_4$, and θ-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ as a horizontal stripe and that of $θ_m$-$(ET)_2TlZn(SCN)_4$ as a diagonal stripe. The Raman spectra of these θ-type ET compounds show a systematic change depending upon the bandwidth. (2) We found a precursory phenomenon of charge ordering above the CO transition temperature in the θ-type ET compounds which show the CO phase transition. The electronic state of this unusual high-temperature phase is not well understood. (3) We found a similar phenomenon at room temperature in the metallic phase of β”-(BEDT-TTF)(TCNQ) last year. To verify that this compound is located near the boundary between delocalized and localized states, we applied hydrostatic pressure to contract the crystal lattice. We found that the hydrostatic pressure worked in the same way as the temperature lowering. (4) We examined the β”-type ET salts, β”-$(ET)_3X_2$ (X = ReO_4, HSO_4, ClO_4), and found that the metal-insulator phase transitions of all these compounds were accompanied by charge ordering. The difference in the CO pattern between X = ReO_4 and X = HSO_4, ClO_4 was reasonably explained from the structural point of view. (5) 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. This theoretical work succeeded to explain the dip structures in the electronic absorption band in the frequency range of 2000–3000 cm^{-1}, which have been universally observed in various organic charge-transfer compounds. Another important result of this theoretical work is that the Raman-active vibronic band is insensitive to the site charge when the EMV coupling constant is large, even if this mode is very sensitive to the molecular ionicity in the free molecule. (6) We have detected the charge disproportionation in $(DI\text{-}DCNQI)_2Ag$ through the measurement of infrared-active b_u molecular vibrations. Combining with the selection rule of the infrared- and Raman-active modes of a_g molecular vibration, we proposed the CO pattern as 0110 that is different from the 0101 pattern proposed based on NMR experiment.

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.

TMTTF family salts are now attracted attention by the observation of the charge ordering (CO) phenomena. We investigated the ESR linewidth anisotropy at low temperatures for a series of $(TMTTF)_2X$, and proposed that the variation of ESR behaviors have their origins in the variation of the charge-ordering patterns at low temperatures, such as –O–O–o–o– and –O–o–O–o– along the stacking axes. In order to clarify the CO mechanisms of the TMTTF salts, we synthesized perdeuterio-TMTTF, TMTTF-d_{12}. It is well known that deuteration often gives a great influence on the electronic states of organic conductors as a chemical pressure. We found that the deuteration does not affect the anion ordering transition temperature. However, the CO transition temperatures show large increases with the deuteration. It is likely negative pressure effects with deuteration for TMTTF salts. To check the possibility of the anion effect through the hydrogen bonds between proton on donors and fluorine, we performed ^{19}F and ^{13}C NMR. According to the experimental results, we found that the CO phenomena are independent from the counter anion motion.

Multi-Frequency ESR Investigation for Molecular-Based Materials

FURUKAWA, Ko; HARA, Toshifumi; 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.

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

[1] Charge Configurations and Spin Dynamics of $(TMTTF)_2X$
[2] ESR study on low-dimensional antiferromagnet α-$(BEDT\text{-}TTF)_2PF_6$ and ζ-$(BEDT\text{-}TTF)_2PF_6$ (THF)
[3] Charge and spin dynamics in molecular based compounds.

Development of New Functional Molecular Systems

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

Since the discovery of the first organic superconductors about a quarter century ago, extremely large progress has been made not only in the field of physics of organic conductors but also in the chemistry of molecular conductors. We have recently discovered antiferromagnetic organic superconductors, field-induced organic superconductors and single-component molecular metals. Though the development of Bechgaard-type organic conductors, D_2X (D = TTF-like π donor, X = inorganic anion) is still actively pursued especially in Japan, the renewal of the chemistry of conducting molecular materials seems to be highly desired. The main results of our group in the last year are as follows. (1) In the last two years we have tried to observe the de Haas van Alphen oscillation of the first single-component molecular metal $Ni(tmdt)_2$ by using piezoresistive cantilever technique. The angle dependence of the oscillation frequencies agrees well with the results of band structure calculations base on the local density approximation (LDA) and *ab initio* plane-wave norm-conserved pseudo potential method. Thus, the existence of the molecular crystal where the metal electrons are automatically produced by self-assembling the identical molecules was finally proved in the most rigorous sense. (2) We have developed various single-component molecular conductors based on the transition metal complex molecules with extended-TTF ligands. The antiferromagnetic transition of $Au(tmdt)_2$ previously observed by ESR and SQUID measurement around 100 K was confirmed by NMR experiments ($T_N \approx 85$ K), which revealed another magnetic transition at lower temperature. (3) We are continuing to try to prepare various magnetic organic conductors based on the π donor molecules with stable organic radical parts. (4) We are also going to try to develop new molecular systems with tailored dielectric properties by using the porous molecular systems based on transition metal complexes.

Lipid Membrane Formation by Vesicle Fusion on Silicon Dioxide Surfaces Modified with Alkyl Self-Assembled-Monolayer Islands

TERO, Ryugo; TAKIZAWA, Morio; LI, Yanjun; YAMAZAKI, Masakazu[1]; URISU, Tsuneo
([1]Shizuoka Univ.)

[*Langmuir* **20**, 7526–7531 (2004)]

We have investigated the formation of the dipalmitoylphosphatidylcholine (DPPC) membrane by the vesicle fusion method on SiO_2 surfaces modified with self-assembled monolayer (SAM) islands of octadecyltrichlorosilane (OTS) with sizes comparable to those of the vesicles by means of atomic force microscopy. OTS-SAM islands with various size and coverage can be constructed on the SiO_2 surfaces prepared by thermal oxidation followed by partial hydroxylation in a H_2O_2/H_2SO_4 solution (Figure 1. a, b). When vesicles are sufficiently smaller than the SiO_2 domains, DPPC bilayers and DPPC/OTS layers form on the SiO_2 and OTS domains, respectively (Figure 1. c). However, the adhesion of larger vesicles onto SiO_2 is prevented by the OTS islands, therefore only DPPC/OTS layers form without formation of DPPC bilayers on the SiO_2 domains (Figure 1. d). On surfaces with domains in tens to hundreds nanometer scale, the relative size between the hydrophilic domains and the vesicles becomes important factor in the membrane formation by the fusion of vesicles.

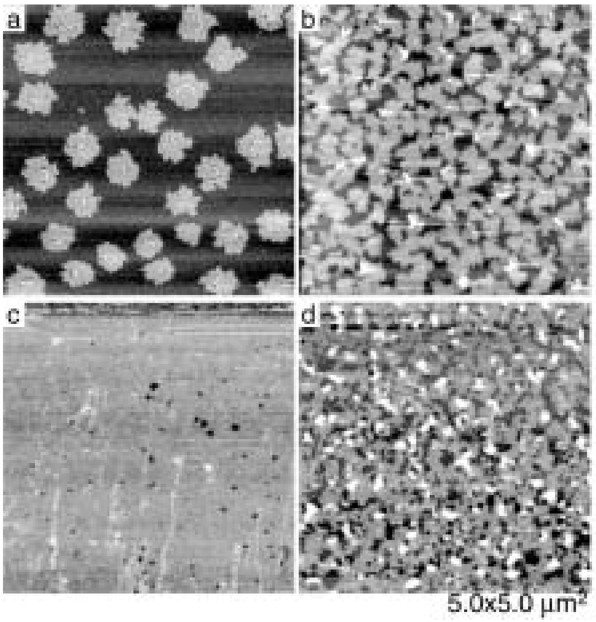

Figure 1. (a, b) AFM images of OTS-SAM islands on chemically oxidized SiO_2 surfaces with different treatment times in a H_2O_2/H_2SO_4 solution. Observed in air. (c, d) OTS/SiO_2 surfaces prepared the same as (b) were incubated in the suspensions of sonicated (c) and 200-nm-filtered (d) vesicles. Observed in a buffer solution.

Reduction of CO_2 and Oxidation of Organic Molecules Aiming at Energy Conversion between Chemical Energy and Electricity

TANAKA, Koji

Electro- and photochemical reduction of CO_2 affording methanol has become crucial issue in line with the progress of fuel energy cells using methanol. Carbon dioxide easily forms η^1- and η^2-CO_2 adducts by the reaction with coordinatively unsaturated low-valent metal complexes. Metal complexes with η^1-CO_2 in protic media are smoothly converted to the corresponding metal–CO ones, which undergo reductive cleavages of the M–CO bonds by accumulation of electrons at the metal centers under electrolysis conditions. A number of metal complexes have proven to catalyze reduction of CO_2 to CO, but the process prevents the CO ligand from hydrogenation leading to methanol formation. To achieve electrochemical reduction of the carbonyl ligand derived from CO_2, we are designing new types of metal complexes that can provide electrons to carbonyl carbon through redox active ligands without increasing electron densities in the metal centers.

Metal complexes that have an ability to oxidize organic molecules at potentials more negative than the reduction potential of dioxygen enable the direct conversion from chemical energy of organic molecules to electricity. Metal-oxo complexes are possible candidates for the smooth oxidation of organic molecules, 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 are limited because of the difficulty of selective formation of reactive M–O frameworks in artificial systems. On the other hand, high valent Ru=O complexes can be obtained by sequential electron and proton loss of the corresponding Ru-OH_2 ones, and have proven to work as oxidants of organic molecules. We have succeeded smooth and reversible conversion between aqua and oxo ligands on Ru-dioxolene frameworks without using any oxidants by taking advantage of dioxolene as a redox active ligand. Along this line, we have been preparing a variety of metal-aqua complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal-oxo forms.

Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

The chelate effect in coordination and organometallic chemistry has most pronounced kinetic and thermodynamic consequences. Complexes supported by multidentate ligands are known to have intriguing coordination and reactivity compared to metals supported by monodentate ligands, because the presence of the bridging units imposes a strong geometry constraint to the coordination groups. In this context, we have begun to study the coordination chemistry of multidentate ligands derived from aryloxides and arylthiolates. Our recent work concentrate on the synthesis, structural characterization, and reactivity of hydride Group 4 and 5 metal complexes supported by multidentate aryloxide (arylthiolate) ligands. According to preliminary results, the use of multidentate aryloxide(arylthiolate) ligands with constrained geometry has led to some highly unusual chemistry not seen in previously reported transition metal aryloxide(arylthiolate) complexes or in related metallocene hydrides. Further studies of these and hybrid ligand systems are in progress,

Developments and Researches of New Laser Materials

SARUKURA, Nobuhiko; ONO, Shingo; GOTO, Masahiro; QUEMA, Alex; MURAKAMI, Hidetoshi; DIWA, Girbert; KAMEI, Takayuki[1]
([1]Tokyo Univ. Sci.)

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; SHOJI, Ichiro; PAVEL, Nicolaie; TSUNEKANE, Masaki; DASCALU, Traian; ISHIZUKI, Hideki; SATO, Yoichi; SAIKAWA, Jiro

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

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 essential parts of the machine will be furnished within the end of December 2004.

The following molecules or molecular composites have been designed and synthesized.

(a) Sub-micro meter long fully conjugated porphyrin wires, which were designed to work as the basic framework of more elaborated nano-scale molecular structures. Those molecules were designed to have high solubility toward ordinal organic solvents despite the high molecular weights, and can be deposited on a variety of substrate surfaces without making the agglomeration, thus the individual molecules were clearly observed by AFM.

(b) Supramolecular sub-micro meter long porphyrin wires were prepared by utilizing LB trough and detergent. These molecules were designed to have more rigid structure than those described above, which enables easier measurement of individual molecules by scanning probe techniques and/or nano-gap electrodes method.

(c) One dimensional aggregates of gold nano-particles were prepared by utilizing structures of porphyrin molecules.

These newly prepared molecular wires and one dimensional nano structures are now elucidated their electronic and photonic properties by SPM and/or nano-gap electrodes.

Synthesis of Iridium Complexes with Ethylphenylcarbazole Dendrons and Applications for Organic Light-Emitting Diodes

SHIRASAWA, Nobuhiko; SUZUKI, Toshiyasu

We have synthesized novel iridium complexes with ethylphenylcarbazole dendrons up to the second generation. These dendrimers are soluble in common organic solvents and form good amorphous films. Light-emitting diodes using these complexes as the emitting material show high external quantum efficiencies up to 8%.

Visible Light Emission from Polymer-Based Field-Effect Transistors

SAKANOUE, Tomo[1]; FUJIWARA, Eiichi; YAMADA, Ryo; TADA, Hirokazu
([1]GUAS)

[*Appl. Phys. Lett.* **84**, 3037–3039 (2004)]

Field-effect transistors (FETs) based on poly [2-methoxy, 5-(2’-ethyl-hexoxy)-1, 4-phenylenevinylene] (MEH-PPV) were prepared with bottom-contact type interdigital electrodes of Cr/Au and Al/Au on the SiO_2/Si substrates. MEH-PPV exhibited a *p*-type semiconducting behavior and orange light emission was observed when the devices were operated in vacuum. It was found that the luminescence efficiency of the FETs with Al/Au electrodes was higher than that of Cr/Au electrodes, as shown in Figure 1. The simultaneous injection of holes and electrons into MEH-PPV occurred efficiently with the application of Al/Au heteroelectrodes.

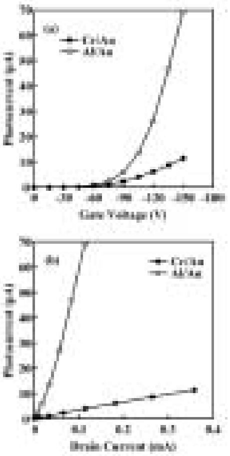

Figure 1. Luminescence intensity detected with a Si photodiode as a function of the gate voltage (a) and the drain current (b). The drain voltage was set at –150 V.

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

TANAKA, Shoji

In this project we have been trying to establish general architecture for “planar and multi-function integrated” π-conjugated macromolecules, which will be the key components for the fabrication of ultra-dense molecular-scale circuits. 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.” Recent progress in fabricating technologies has enabled us to obtain “flat nano-gap electrodes buried within insulating substrates” optimized for planar molecular-metal junctions. Charge transport at planar junctions will be controlled by the degree of the “face-to-face interactions” between π-system of conjugated molecules and electrode substrate. Therefore, to define exactly the positions and areas of the interactions, we have designed “partially insulated” oligothiophenes consisting of non-insulated chain moiety as “charge-transfer interface” and insulated chain moiety as “charge-retention site.” We have prepared a series of 3–6 nm long partially insulated oligothiophenes and investigated the redox features by electrochemical methods.

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. A variety of 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 identified to be effective for various palladium-catalyzed asymmetric transformations. Thus, for example, catalytic asymmetric allylic amination of cycloalkenyl carbonates (methyl cyclohexen-2-yl carbonate, methyl cyclohepten-2-yl carbonate, methyl 5-methoxycarbonylcyclohexen-2-yl carbonate, methyl cyclohexenyl carbonate, *t*-butyl 5-methoxycarbonyloxy-1,2,5,6-tetrahydropyridine-dicarboxylate) with dibenzylamines ($(C_6H_5CH_2)_2NH$, $(C_6H_5CH_2)(4\text{-}CH_3OC_6H_4CH_2)NH$, $(4\text{-}CH_3OC_6H_4CH_2)_2NH$) was achieved in water under heterogeneous conditions by use of a palladium complex of (3*R*,9a*S*)-3-[2-(diphenylphosphino)phenyl]-2-phenyltetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one anchored on polystyrene-poly(ethylene glycol) copolymer resin to give the corresponding cycloalkenylamines with high enantiomeric selectivity (90–98% *ee*). Novel pincer palladium complexes having chiral hexahydro-1*H*-pyrrolo[1,2-*c*]imidazolone groups were also designed and prepared. Catalytic asymmetric Michael addition of isopropyl 2-cyanopropionate to ethyl vinyl ketone was catalyzed by the chiral pincer palladium complex to give isopropyl 2-cyano-2-methyl-5-oxoheptanoate with high enantioselectivity (up to 83% *ee*).

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; HOSOKAWA, Youichi; 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 construction of unimolecular redox pools by use of our newly developed dendrimers. 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 and quinone groups inside the dendrimer, and examined photochemistry of the porphyrin moiety attached at the core of the dendrimer.

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.

Toward Tailor-Made Synthesis of Monolayer-Protected Metal Clusters

NEGISHI, Yuichi; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya

Monolayer-protected clusters (MPCs) have been potential candidates for building blocks for novel nanostructured material. In order to fabricate tailor-made materials with the MPCs, it is important to understand how the basic properties evolve as functions of the core size and ligation numbers of thiolates. We have developed a large-scale synthesis of small gold clusters protected by carboxylated thiolates, high-resolution separation by polyacrylamide gel electrophoresis (PAGE), and compositional analysis by electrospray ionization (ESI) mass spectrometry. The most remarkable finding throughout these efforts is that the magic core sizes do not always take the same value but vary according to the structures of the thiolates. This result indicates that the core sizes of the gold MPCs are not determined solely by intrinsic stability of the gold cores themselves but also affected by thiolate ligation. The optical measurements of isolated clusters reveal that the thiolate structure has nontrivial effect on the electronic structure of the MPCs, probably due to thiolate-induced core deformation. These finding offer helpful guidelines for further experimental and theoretical studies on structures, stabilities and optical properties of small gold MPCs and a strategy toward fine-tuning of the fundamental properties of the MPCs.

Effects of Vertical Magnetic Field in Material Science

DUAN, Wenyong; FUJIWARA, Masao; TANIMOTO, Yoshifumi

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Magnetic control of chemical processes has been one of the most interesting and hot topics in material science. A 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.

In order to examine the effects of high vertical magnetic fields on the reaction in liquid solution, we have carried out *in situ* observation of laser-induced convection of benzene solution of a photochromic compound, 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene (CMTE), in vertical high magnetic fields (up to 15 T and 1500 T^2/m). When a CMTE solution is irradiated by a 308-nm laser from the bottom of a vessel (10 mm × 10 mm × 40 mm), CMTE undergoes photoisomerization reaction to its photo-isomer (PI) and the color of the solution changes from pale yellow to red. At zero field the PI solution formed on the bottom surface of the vessel removes at a 5 s delay after laser excitation and then moves upward. At –1300 T^{2}m^{-1} it removes at a 9 s delay and moves upwards, whereas at +1000 T^{2}m^{-1} it dose at a 3 s delay, moves upward and then finally moves downward.

The removal of the PI solution from the bottom surface will be explained by taking into account of the pressure in solution. The pressure difference of the bulk CMTE solution and the PI solution can be calculated by the following equation.

$$\Delta P = (\Delta\rho_{\text{solution}})gh + (\Delta\chi_{\text{benzene}})(1/\mu_0)hB\partial B/\partial z + (\chi_{\text{PI}} - \chi_{\text{CMTE}})c(1/\mu_0)hB\partial B/\partial z \qquad (1)$$

The first term of the right-hand side of eq. 1 is the density change of the solution induced by photoirradiation, the second is the magnetic susceptibility change of benzene due to temperature change and the third is the magnetic susceptibility change of solute due to photoisomerization. It is estimated that at –1300 T^{2}m^{-1} ΔP is about one order of magnitude smaller than that at zero field, whereas at +1000 T^{2}m^{-1} it is about 1.7 times larger than that at zero field. This is why the departure time of the PI solution is different in three cases.

The downward movement of the PI solution at +1000 T^2/m is attributed to the smaller magnetic susceptibility of PI than that of CMTE.

In conclusion, vertical high magnetic fields are a useful tool to control convection in solution. The fact suggests that we can use high vertical magnetic fields to control chemical yield and morphology of functional materials formed in solution.

Development of Self-Healing Nano-Materials

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[*Photosynthesis: Fundamental Aspects to Global Perspectives* in press]

For development of elaborate nano-devices, we utilized naturally occurring nano-tube, ‘microtubule’ (MT), formed by self-assembly of the component protein, tubulin (Tub), to integrate functional molecules into a nano ordered structure (Figure 1). Tub/MT system is not in a simple equilibrium, because the Tub-assembly requires hydrolysis of GTP bound to each Tub. GTP hydrolysis in the MT lattice weakens protein-protein interactions between Tubs, which facilitates release of Tubs from the end of the MT. Bulk, undamaged Tubs exchange their nucleotides, then reassemble again to form and elongate MTs. All Tubs in a MT lattice are, thus, exchanged constantly with free Tubs in this cycle regardless of whether their structures are damaged or undamaged. For this metabolism-like behavior, the functionalized MT can be regarded as a prototype of self-healing devices. Future works to refine the system by using Tub and/or other nano-particles would give unique supramolecular systems (see also IX-Z).

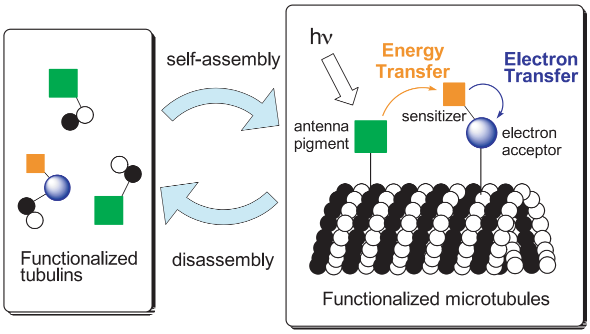

Figure 1. A concept of the on-demand nano-devices. The device possessing an ordered nano-structure is formed by self-assembly of nano building blocks conjugated with various functional molecules. The device functions only in the assembled form. The device can easily be decomposed into the component functional blocks on demand (loss of function), and the blocks can readily be reconstituted on demand (gain of function).

Observation of Coherent Synchrotron Radiation at UVSOR-II

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At a 750MeV electron storage ring, UVSOR-II, possible coherent synchrotron radiation was observed in the wavelength region between 0.2 and 3.0 mm. Bursts of far infrared emission were detected when the ring was operated in single bunch mode and the beam current exceeded a certain threshold current, typically around 100 mA. Typical duration and interval of the bursts are about 200 µsec and 10–15 msec, respectively. Each burst contains many peaks and shows quasi-periodicity of about 30 µsec. The peak intensities of the bursts are 10000 times higher than that of normal synchrotron radiation in the same wavelength region. The threshold current depends on the operation condition of the storage ring, especially that of the RF system.

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 investigate 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 rare-earth compounds $CeNi_{1-x}Co_xGe_2$ (x = 0, 0.3, 0.6 1), alkali-metal and alkali-earth skutterudites, AFe_4Sb_{12} (A = Na, K, Ca, Ba) and a clathrate, $Sr_6Ga_{16}Ge_{30}$, and the 4d-4f and 3d-4f resonant photoemission spectra of $CeNi_{1-x}Co_xGe_2$. Infrared spectroscopy under multi-extreme conditions of low-temperature, high-field and high-pressure has been also started in this year.

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. So far, 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. 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.

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, by molecular biological and spectroscopic techniques.

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 both heme and non-heme iron enzymes. We employ the salen ligand as a non-heme iron model complex, and attempt to isolate a transient oxidizing intermediate.

(2) Cu-containing nitrite reductase (NiR) contains a pair of Cu, a type1 Cu ion and a type2 Cu ion, which catalyze the reduction of NO_2^- to NO. In the catalytic reduction, the type 2 Cu site receives one electron from the type 1 Cu site and reduce Cu-bound NO_2^- ion to NO with addition of two protons. In this study, we synthesized Cu(I)-nitrite complexes with various tridentate ligands as a model for a reaction intermediate of NiR.

(3) Heme oxygenase (HO), an amphipathic microsomal protein, catalyzes the oxygen-dependent degradation of heme (iron-protoporphyrinIX) to α-biliverdin, CO, and free iron ion. Recently, an interesting example has been found in HO (PigA) of the Gram-negative bacterium Pseudomonas aeruginosa, which does not produce α-biliverdin at all, but forms the mixture of β- and δ-biliverdins at a ratio of 3:7. We show that Lys34 and Lys132 are essential amino acid residues to hold the rotated heme in the active site of PigA *via* hydrogen-bonding interaction with the heme propionate and that Phe189 controls the product ratio of β- and δ-biliverdins via steric interaction with heme substituents. These interactions place the β- or δ-meso position of the heme at the oxidation site of PigA, leading to the unique regioselectivity.

Molecular Science of Proteins Based on Vibrational Spectroscopy

KITAGAWA, Teizo

Proteins have a static structure as determined by x-ray crystallographic analysis, but its higher order structure, which is easily altered by small energy, is directly related with a function of the molecule. Vibrational spectroscopy can provide essential information on the higher order structure of proteins and its dynamics. It is the purpose of this study 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 the visible resonance Raman spectroscopy, we intend to explore the relation between the structure of chromophore and its reactivity by observing time-resolved spectra. In the UV resonance Raman spectroscopy, we focus on the structure of aromatic side chains like Trp and Tyr as well as a polypeptide skeleton. The two techniques will be combined to elucidate the allosteric effects in gas-sensing heme proteins as well as in hemoglobin and myoglobin. The study will be extended to DNA-photolyse and ogygenase enzymes and their model compounds. We are going to develop IR microscopy to reveal structural chemistry involved in amyloid formation of β_2-microglobulin. IR spectroscopy will also be used to reveal the coupling mechanism of proton and electron transfers by terminal oxidases.