SPECIAL RESEARCH PROJECTS

IMS has special research projects supported by national funds. Three projects in progress are:
(1) Development of microscopic environments with functionality and quantum steering for reactions
(2) Study of molecular solid toward molecular electronics
(3) Material control in multi-reaction centers

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.

(1) Development of Microscopic Environments with Functionality and Quantum Steering for Reactions

Structures, Reactions and Spectroscopies of Molecules and Clusters

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Ab initio molecular orbital methods were applied to various chemical and physical problems. The density functional theory were also used in some of the studies. Most of works were carried out under close collaboration with several experimental groups. In addition new theoretical techniques in molecular electronic calculations were developed. The followings are the titles the topics we have worked in the last year.

A. Development of New Theoretical and Numerical Techniques in the Study of Molecular Structure
B. Water Clusters and Their Complexes with Atomic Ions
C. Computational Chemistry of Atomic and Molecular Processes in Atmospheric Environment
D. Application of Ab Initio Molecular Orbital Methods to Experimentally Relevant Systems

Folding Mechanism of Protein Molecules Studied by Generalized-Ensemble Algorithms

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Proteins are the most complicated molecules that exist in nature. Since protein Structures are closely related to their biological functions, the understanding of their folding mechanism from the first principles is not only very challenging but also very important a problem in theoretical molecular science. To be more specific, it is widely believed that three-dimensional structure of proteins is determined by their amino-acidsequences. However, nobody has succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles.) There are two reasons for the difficulty. One reason is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be considered is very large.

The other reason for the difficulty is that there exist huge number of local minima in the energy function, and conventional simulation techniques necessarily get trapped in one of the local minima without ever finding the energy global minimum. Generalized-ensemble algorithms are new simulation algorithms that can alleviate this difficulty (for reviews, see References 1 and 2).

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

References

1) Y. Okamoto, *Recent Res. Dev. Pure Appl. Chem.* **2**, 1 (1998).
2) U. H. E. Hansmann and Y. Okamoto, *Curr. Opin. Struct. Biol.* **9**, 177 (1999).

Studies of Nonadiabatic Transitions, Chemical Reaction Dynamics, and Their Control

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Quantum mechanical studies of chemical reactions in heavy-light-heavy systems have been further pursued, and the reaction mechanisms have been clarified in terms of vibrationally adiabatic potential ridge lines and vibrationally nonadiabatic transitions. In addition to these numerical studies, the recently established analytical theory of the Landau-Zener-Stueckelberg type nonadiabatic transitions has been applied to the three-dimensional chemical reaction $O(^3P) + HCl \rightarrow OH + Cl$ and found to reproduce the cumulative reaction probability nicely. The computer code for the quantum reaction dynamics based on the hyperspherical elliptic coordinates has been extended so as to deal with electronically nonadiabatic chemical reactions and a work on the $D + H_2^+$ system is now going on.

The challenging trial is continued to try to formulate a unified theory of nonadiabatic transition which covers the Landau-Zener-Stueckelberg (LZS) and the Rosen-Zener-Demkov type of transitions. Quantum mechanical exact as well as semiclassical solutions have been successfully obtained for certain exponential potential models.

Controlling molecular processes based on our new idea has been pursued in three ways. One is to control molecular processes by periodically sweeping laser fields (frequency and/or intensity). Depending on the availability of lasers, we can recommend various types of control schemes. The second is to control molecular photodissociation by using the intriguing phenomenon of complete reflection. In this case a static laser field is used and the control is made by appropriately adjusting the laser frequency. The third is a trial to propose a new effective method in NMR by sweeping the magnetic field.

The 5th- and 7th-order 2D Raman Spectroscopy for Intramolecular Vibrational Modes

TANIMURA, Yoshitaka

We calculated the 3rd-, 5th-, and 7th-order Raman signals for an Iodine dimer in the condensed phase, which was modeled by a Morse potential coupled to a heat bath. It is shown that the 5th- and 7th-order signals are very sensitive to the anharmonicity of the potential and useful to study intramolecular vibrational modes. In the case of harmonic vibrational modes, the 5th- and 7th-order signals are the function of both the linear and nonlinear linear coordinate dependence of the polarizability, whereas the present case they are the function of the linear coordinate dependence of the polarizability. Thus, the signals in the present case are expected to be much stronger than in the harmonic case. We also showed that the 7th-order 2D signal for a harmonic system with a nonlinear system-bath interaction, which is a possible model of an inhomogeneously distributed molecular-vibrational system, depends in the lowest order on the nonlinear coordinate dependence of the polarizability and is useful to see the effects of the inhomogeneity, in cases where the 5th-order 2D signals were very weak.

Constructing Molecular Theory of Chemical Process in Solution

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([1]Kyoto Univ.)

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

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

1. Temperature dependence of autoionization of water or pK_w.
2. Self-consistent determination of electronic structure and liquid state properties of water.
3. Solvatochlomism of triiodide ion in solutions.
4. Solvent effect on keto-enol tautomers of formamide in aprotic solvents.
5. Type II S_N2 reaction (Menshutkin reaction).
6. Salt effect on solubility of nonpolar solute in water.
7. Solvation dynamics and thermodynamics of ions.
8. Stability of peptide and protein conformations in aqueous solution.
9. Non-equlibrium free energy surface related to electron transfer reactions
10. Dynamical coupling between intra- and inter molecular motions in liquids.
11. Description of collective excitation in liquds by interaction site model.
12. Microscopic characterization of metal-liquid interface.
13. Path integral theory of a hydrated electron.

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

MORITA, Norio; MORIWAKI, Yoshiki; KUMAKURA, Mitsutaka

In “studies on laser cooling and trapping of neutral atoms,” we have carried out precise theoretical calculations to investigate the cause of the isotopic difference in collisional ionization rate coefficients between cold ^{4}He($2s^3S_1$) + ^{4}He($2s^3S_1$) and ^{3}He($2s^3S_1$) + ^{3}He($2s^3S_1$) collisions at 0.5 mK, which is observed in our previous magneto-optical trap experiments on He atoms (see II-B-1). The design and construction of a new laser cooling and trapping apparatus, with which we expect to confine a much larger number of He atoms at much lower temperature, are now in progress. On the other hand, in “laser spectroscopic studies of atoms and ions in liquid helium,” we have measured some excitation and emission spectra of Mg and Ca in liquid ^{3}He in order to observe interesting phenomena which arise from quantum features differing between liquid ^{3}He and ^{4}He (see II-C-1). For this series of study, we have also been constructing a new spectrometer, which is equipped with an image-intensified CCD camera and will allow us to observe spectra with much higher sensitivity.

Time-Resolved Resonance Raman Study on Mechanisms of Oxygen Reduction by Cytochrome *c* Oxidase

KITAGAWA, Teizo

Reaction intermediates in the enzymatic reduction of O_2 by bovine cytochrome *c* oxidase (CcO) were investigated with time-resolved resonance Raman spectroscopy. Six oxygen-associated vibrations were identified in the $O_2 \rightarrow H_2O$ process. The isotopic shift of the Fe-O_2 stretching frequency for an asymmetrically labeled dioxygen, $^{16}O^{18}O$, has established that the primary intermediate of cytochrome a_3 is an end-on type O_2 adduct of Fe_{a3} with the Fe-O-O angle of ~120°. The subsequent intermediates appearing around 0.1–3 ms following the start of the reaction yielded Raman bands at 804/764, 785/751, and 356/342 cm^{-1} for $^{18}O_2/^{16}O_2$ derivatives, respectively, in H_2O at pH 7.4. While these frequencies were the same between the H_2O and D_2O solutions, the final intermediate appearing around 3 ms gave the Raman bands at 450/425 cm^{-1} in H_2O and 443/417 cm^{-1} in D_2O. The last bands are reasonably assigned to the Fe_{a3}-OH(D) stretching mode. The extended measurements at lower temperatures and longer delay times have demonstrated that the 804/764 cm^{-1} pair appears prior to the 785/751 cm^{-1} pair and that the conversion from the former to the latter species is significantly delayed in D_2O compared with in H_2O, suggesting that this step of electron transfer is tightly coupled with proton pumping. The experiments using $^{16}O^{18}O$ have established that all the 804/764, 785/751, and 356/342 cm^{-1} bands arise from the Fe=O heme, but definitely not from the Fe_{a3}-O-O-Cu_B the presence of which has been long postulated. The same three sets of oxygen-isotope sensitive bands have also been observed for the reaction intermediates of oxidized CcO with H_2O_2, indicating the identity of intermediates. IR Study of this enzyme revealed that ligand dissociation form the a_3 heme causes deprotonation of one carboxyl group, that does not perceive outside pH or has pK_a higher than 9.5.

Laser Raman Beat Detection of Magnetic Resonance

KATO, Tatsuhisa; MATSUSHITA, Michio

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

There are some causes to hide the Raman beat signal, that is, the inhomogeneity of the circumstance of the molecule, the fluctuation of the applied field, and the interference by the crystal phonon. It is the key to success in the Raman beat detection to eliminate these cause of the incoherence. Then it is needed to prepare the sophisticated single crystal sample, the highly stabilized magnetic field, and a cryostat of liquid helium. It has been completed to set up the apparatus, and the Raman beat detection was applied to the study on the quadrupole transitions of ^{139}La nuclei around Pr^{3+} doped in LaF_3, and on the delocalized excitation in molecular crystals of 1,4-dibromonaphthalene, in Section II-J-1.

Environment Dependent Association of Acetic Acid in Liquid Phase

NISHI, Nobuyuki; NAKABAYASHI, Takakazu; KOSUGI, Kentaroh[1]; INOKUCHI, Yoshiya
([1]GUAS)

Acetic acid is known to form a stable cyclic dimer through two-site hydrogen-bonding in gas phase. Many of literatures describe the presence of such cyclic dimers in pure acetic acid or in aqueous solutions. Through the study of low frequency Raman spectra of various solution of acetic acid as well as the mass spectrometric studies of acetic acid aqueous solutions, we found that the cyclic dimer is not seen in polar solutions. The low frequency Raman spectrum of liquid acetic acid and its temperature dependence on the melting process of the crystalline acid suggest that the structure of the clusters in pure acetic acid is described as the fragments of crystalline acetic acids with chain-type 2-site hydrogen-bonds not only at the O–HO site but also at the O–HC site. Doubly coordination is characteristic of crystalline structure. In water, the situation is quite different. We know that the density of aqueous solution of acetic acid becomes maximum at 1:1 molar mixing ratio ($\chi_A = 0.5$). Apparently, at this concentration we have a closed packed structure of the acetic acid/water mixture. Spectroscopically, we have found that the clusters in this mixture are homogeneous associates of acetic acid. Water clusters are thought to fill the gap among the acetic acid clusters. This is called microphases of acid and water. The acetic acid clusters are thought to be composed of a side-on type dimer unit with a dipole moment of 4.0 Debye (in vacuum). Such a large dipole moment is expected to induce strong dipole-dipole interaction between the dimer units producing fairly large clusters of acetic acids.

Carbon tetrachloride (CCl_4) has a null dipole moment where acetic acids are found to generete aggregates with a structure similar to that of crystalline acetic acid at the concentration $\chi_A \geq 0.1$. The structure of acetic acid associates are thus so sensitive to the environment.

Higher Vibrational States of Molecules and Clusters as Studied by Nonresonant Ionization Detected IR Spectroscopy

FUJII, Masaaki

This special research project, started in April 1997 is planning to study spectroscopy and dynamics of molecules and clusters in higher vibrational state by the nonresonant ionization detected IR spectroscopy. The nonresonant ionization detected IR spectroscopy (shortly NID-IR) is a newly developed IR-UV double resonance spectroscopy which detects IR absorption by the selective ionization of a vibrationally excited molecule. Briefly, a jet-cooled molecule is excited to a vibrational level in the ground state by the IR laser. The vibrationally excited molecule is selectively ionized by the nonresonant two-photon process due to the UV laser. The simplest way of the selective ionization can be achieved by fixing the frequency of the UV laser to energy slightly less than a half of the ionization potential. Under this frequency condition, only the vibrationally excited molecule can be ionized by the two-photon process due to the UV laser. Therefore, the ion current is detected only when the IR laser is resonant to the vibrational level. This spectroscopy has an advantage in the sensitivity because of the weak background signal and the ionization detection. The experimental setup for the measurement of the non-resonant ionization detected IR spectroscopy has already been described elsewhere (*Annual Review* 1997-1998, *Chem. Phys. Lett.* **252**, 287 (1996) and *Chem. Phys. Lett.* **283**, 243 (1998)).

The nonresonant ionization detected IR spectroscopy has been applied to jet-cooled phenol and various deuterated phenols (C_6H_6OH, C_6H_6OD, C_6D_6OH and C_6D_6OD). Vibrational transitions of jet-cooled phenol have been detected by nonresonant two-photon ionization due to UV laser from 3400 cm^{-1} to 14000 cm^{-1}. The spectra show well-resolved structure due to the first to the fourth quantum of OH (OD) stretching vibrations, CH overtones and various combination vibrations. The vibrational frequency, anharmonisity and the dissociation energy of the OH stretching mode has been measured. The bandwidth of the OH (OD) overtone in C_6H_6OH and C_6D_6OD is found to decrease with increase in the vibrational quantum number. This change in bandwidth suggests that the intramolecular vibrational redistribution (IVR) in C_6H_6OH and C_6D_6OD is not statistical. On the other hand, partially deuterated phenols (C_6H_6OD and C_6D_6OH) show the opposite change that the bandwidth increases in going to the higher overtone, likely to the statistical limit case. The observed results has been explained by the existence of the door way state in IVR from OH overtones.

Imaging of Chemical Dynamics

SUZUKI, Toshinori; KOHGUCHI, Hiroshi

Femtosecond time-resolved photoelectron imaging method has been developed, for the first time. The scattering distributions of photoelectrons in [1+1’] REMPI of NO and [1+2’] REMPI of Pyrazine have been observed. In the latter case, ultrafast decay of optically-prepared S_1 character and corresponding build-up of triplet character were visualized. In addition, the results suggested the possibility that intersystem crossing is mediated by $T_2(\pi,\pi^*)$ state. Crossed beam ion imaging method has been applied to inelastic scattering of NO with Ar at the collision energy of 66 meV, and the differential cross sections were compared with scattering calculations by Millard Alexander using the newest *ab initio* surface.

Theoretical Study on the Electronic Structures of Atoms, Molecules, and Clusters

MIYOSHI, Eisaku; GHOSH, Tapas Kumar; SUMI, Tomonari

We have developped various types of model core potentials (MCPs) and applied the MCPs to investigate the electronic structures of atoms, molecules, and clusters. In particular, our research interests are concentrated upon the electronic structures of complexes with coordinate bond between metals, $(Me_3P)(OC)_4Os\text{-}W(CO)_5$, which was recently found in experiments and is interesting because of its potential of application to new materials.

In addition, the electronic structures of weakly bound molecules such as ArHF, $Fe(CO)_n$ (n = 1–3), C_3O_2, and $(C_6H_6)_3^+$ were investigated by using sophisticated methods for electron correlation. The methods contain the model core potential (MCP) method, and multi-reference coupled pair approximation. It has been shown that such methods are necessary to compute accurate potential energy surfaces of weakly bound molecules. We have also investigated electronic structues of TiCl, ZrCl, and MX_4: M = Ti, Zr, Hf and X = F, Cl, Br, I).

Using potential energy surfaces obtained by *ab initio* molecular orbital calculations, molecular dynamics calculations were also performed to investigate physical and chemical properties of liquid mercury and other systems.

Supersonic Jet Submillimeter-Wave Absorption Spectrometer with Backward Wave Oscillator

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Molecular clusters have extremely low-frequency vibrations, so called van der Waals (vdW) Vibrations, which sometimes falls in the submillimeter wave region below 30 cm^{-1}. The backward wave oscillator (BWO) is an ideal light source in the submillimeter wave region for the detection of the vdW vibrations of the molecular cluster, and the oscillator is commercially available up to 1.2 THz. One tube covers about 200 GHz frequency region with output power of 1–50 mW. In the present study, we have set up the submillimeter wave spectrometer with the BWO as a light source for the detection of the vdW vibration of the molecular cluster.

The frequency region from 150 to 800 GHz are covered using three BWO tubes mounted inside of the permanent magnet of 10 kG. The frequency of BWO was phase-locked to the local oscillator with a harmonic mixer, while the frequency of the local oscillator was frequency modulated by applying 36 kHz sinewave. The magnetic enhanced InSb borometer was used for the detection, and the output of the detector was phase sensitively detected with the second harmonic of the modulation frequency as a reference. The transient absorption of the molecular cluster was phase sensitively detected with the time constant of 100 µs, transferred to the personal computer, and integrated in the computer system.

The sample gas of 1% HCN, 49% Ar, and 50% Ne was used for the detection of Ar-HCN. The sensitivity check was done by detecting the J = 3–2 rotational transition of $HC^{15}N$ on the sealed-off condition of the mixed gas. The detection sensitivity of the system was 4.2×10^{-8} cm^{-1} at the time constant of 180 ms with the path length of 42 cm. Figure 1 shows the R(5) line of the $\Pi_1\text{-}\Sigma_0$ vdW bending band of Ar-HCN generated in a supersonic expansion. The signal to noize ratio of 26 was obtained with the effective sampling time of 100 ms for each frequency point.

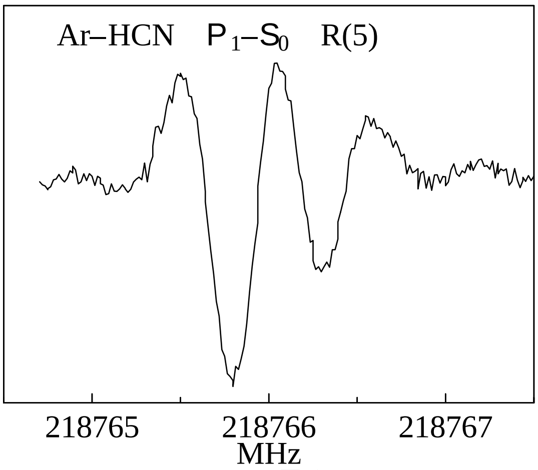

Figure 1. The R(5) line of the Π_1-Σ_0 vdW band of Ar-HCN observed with BWO.

Experimental Study of Ion-Induced Nucleation

NAGATO, Kenkichi

Ultrafine particle formation by ion-induced nucleation has recently gained attention both in atmospheric science and in material processing. However, experimental results of ion-induced nucleation to date show significant deviations from theoretical predictions. One of the reasons is that nucleation theories have not taken account of chemical nature of ions. In order to improve theories, experimental investigations about the influence of ion species on the nucleation process are necessary. For this purpose, we have developed a high-resolution ion mobility/mass spectrometer that is capable of simultaneous measurements of mobility and mass spectra of cluster ions generated by ion-molecule reactions under atmospheric pressure. We have tested the performance of this spectrometer using ions generated in the laboratory air. We are going to investigate the role of ions in ultrafine particle formation in $NH_3/SO_2/H_2O$/Air mixture using this spectrometer. The results will be of importance in developing the model of tropospheric aerosol formation. Experiments will be extended to the study on the nucleation by ion-ion recombination.

Time-Resolved Spectroscopic Study of Photochemical Dynamics in Condensed Phase

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

Time-resolved spectroscopy is one of the most powerful tools for the studies of chemical reactions. It enables us to directly observe the temporal changes occurring in the course of chemical reactions. Recent progress of time-resolved spectroscopy relies on the drastic advance of the laser technology, and we are now able to examine the dynamics of the primary chemical processes with pico/femtosecond time-resolution. The aims of this project are (1) development of new technique and method in time-resolved spectroscopy, and (2) application of pico/femtosecond spectroscopy to the study of dynamics of molecules in condensed phase.

Our research activity of this year consists of the following three. First, we constructed two optical setups to generate ultrashort optical pulses whose duration is in the range from ten to a few tens of femtoseconds. Secondly, with use of time-resolved fluorescence and absorption spectroscopy having a few hundreds femtoseconds time-resolution, we studied ultrafast proton transfer reactions and the relaxation process of the highly excited states of several fundamental molecules in solution. Thirdly, we applied picosecond time-resolved Raman spectroscopy to the study of trans-azobenzene that is a prototypical molecule showing fast cis-trans isomerization. We examined the electronic and vibrational relaxation processes as well as the structure of the S_1 state of this molecule. In addition, while doing time-resolved Raman work, we noticed that amplified picosecond pulses are suitable for the excitation of hyper-Raman scattering.

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

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Synchrotron radiation-laser combination techniques developed at UVSOR have been employed for probing ionic and neutral photofragments produced in the vacuum ultraviolet. First, N_2^+ ($X\ ^2\Sigma_g^+$, v_X = 0 and 1) resulting from direct ionization or autoionization of N_2 or N_2O is detected by laser induced fluorescence excitation spectroscopy in the wavelength region of the $B\ ^2\Sigma_u^+ \leftarrow X\ ^2\Sigma_g^+$ transition. The rotational distribution of N_2^+ is considered to be determined by the change in the rotational quantum number in photoionization and by the partitioning of the excess energy impulsively released in dissociation. Second, S($3s^23p^4\ ^3P_2$) produced by predissociation of Rydberg states of OCS is detected by resonance enhanced multiphoton ionization spectroscopy.

The combination technique has been also incorporated into an apparatus for two-dimensional photoelectron spectroscopy of atoms and molecules in order to investigate photoionization dynamics of polarized atoms. Ground state Ar atoms are excited with linearly polarized synchrotron radiation to Rydberg states lying below the first ionization potential. Aligned atoms thus formed are ionized by irradiation of laser which is also linearly polarized. Photoelectrons emitted in the direction of the electric vector of synchrotron radiation are sampled and energy-analyzed. Photoelectron angular distribution is measured with respect to the electric vector of the laser. Derivation is made on the expressions which correlate asymmetric coefficients for the angular distribution with theoretical dynamic parameters involving transition dipole matrix elements. The anisotropy of the present angular distribution can be reasonably explained, assuming that the matrix elements and phase shift differences are essentially independent of the total angular momentum quantum number of the final state and that the spin-orbit interaction in the continuous spectrum is small.

Vibrational Spectroscopy on Cryogenic Surfaces Using Synchrotron Radiation

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Vibrational Spectroscopy makes it possible to analyze dynamical aspects of molecules adsorbed on surfaces. Molecular layers on cryogenic surfaces show specific structures which depend on the interaction between molecules and substrate, and the vibrational spectra reveal the details of the interaction. Infrared reflection absorption spectroscopy (IRAS) and high-resolution electron energy loss spectroscopy (HREELS) are useful tools for vibrational spectroscopy on surfaces, and they have complemental characteristics, that is, IRAS is superior in resolution and stability whereas HREELS has higher sensitivity. Utilization of IRAS with HREELS in an identical vacuum system brings advantageous apparatus for researches of dynamical aspects of adsorbed molecules.

Under this project, we develop an apparatus for vibrational spectroscopy of molecules on cryogenic surfaces. The apparatus comprises both measurement systems (IRAS and HREELS), a cryogenic sample holder and tools for preparation and characterization of surface cleanliness. The IRAS system has optical system for inlet and outlet of synchrotron radiation in far-infrared (FIR) and infrared (IR) regions, since synchrotron radiation is brighter light source than conventional ones in these regions taking into account that the light source necessary for IRAS should have low emittance.

The vacuum system has been constructed and punped down to UHV region. Spectral distribution of primary light from a conventional light source in an FTIR spectrometer through the whole optical system including the reflection at the clean surface of Ag(111) was measured after the alignment of the optical system.

Similarity Transformed Preconditioners for Green Function Evaluation in Cumulative Reaction Probability Calculations

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The micro-canonical rate constant of interest for unimolecular reaction is given in terms of the cumulative reaction probability $N(E)$, $k(E) = N(E)/\{h\rho_r(E)\}$, where $\rho_r(E)$ is the density of reactant states per unit energy. The calculation of $N(E)$ is based on a discrete variable representation (DVR) of Hamiltonian and the use of absorbing boundary conditions (ABC). Recently Seidemann, Manthe and Miller showed that $N(E)$ was given as the eigenvalue sum of the probability operator $P(E)$. $P(E)$ is expressed in terms of the ABC Green function $G^{(\varepsilon)}(E)$,

$$P(E) = 4\varepsilon_r^{1/2}\, G^{(\varepsilon)}(E)\, \varepsilon_p\, G^{(\varepsilon)}(E)\, \varepsilon_r^{1/2}.$$

The use of ABC provides the well-behaved representation of the Green function without having to include information regarding the asymptotic region. Since it is difficult to reproduce a global structures of the potential energy surface for a many-atom molecule with an analytic function, this feature is efficient for realistic applications.

We employ iterative methods for diagonalizing $P(E)$ and for evaluating $G^{(\varepsilon)}(E)$. Since the ill-conditioned linear problem of this kind cannot be solved with ordinary iterations, we proposed Kyrlov subspace methods with numerical preconditioning in order to reach a convergence. The resulting iterative expansion with the preconditioner corresponds to the distorted-wave Born expansion of the Green's function.

$$G = G_0 + G_0\,\Delta\,G_0\,G_0 + G_0\,\Delta\,G_0\,\Delta\,G_0 + \cdots$$

The acceleration with the preconditioning is most effective when the preconditioner is closest to the Green's function. We found that the banded matrix extracted from E-H-$i\varepsilon$ effectively accelerate the convergence, and GMRES and Davidson method can get a convergence even when the bandwidth is only 3% of the matrix size. The LU decomposition of this banded preconditioner, however, needs extremely large amount of memory when the molecule has many degrees of freedom. We overcome this difficulty by employing the similarity transformed preconditioner.

$$M = U\,\text{Band}\,(U^{+}\,(E\text{-}H\text{-}i\varepsilon)\,U)\,U^{+},$$

where U is prepared for block-diagonalizing the Hamiltonian to reduce the memory requirement. We showed that this kind of preconditioner is as effective as the 'fat' preconditioner.

Developments of Advanced Lasers for Chemical Reaction Controls

SATO, Shin-ichiro; WATANABE, Kazuo

The chemical reaction controls with laser lights are one of the most important subjects of chemistry. The coherence of laser lights has not been considered seriously in the old fashion of the laser controls of chemical reactions. Recent theoretical studies have shown that the more sophisticated controls of chemical reactions. As a first step, we are trying to maximize efficiency of the quantum transition with a chirped ultra short pulsed laser. This technique is based on an adiabatic passage theory of quantum transitions. We are developing a photo waveform shaper of ultra short laser pulses to make an arbitrary shaped pulse, including chirped ones. The spectral components of the incident pulse are spatially dispersed with a grating, modulated or retarded with a liquid crystal array on the Fourier plane and recombined with an another grating.

Developments and Researches of New Laser Materials

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

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

Development and Research of Advanced Tunable Solid State Lasers

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

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

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

In this projects we research and develop new diode-pumped-solid-sate lasers and new frequency conversion devices. Especially, we will focus on the combination of Yb-doped lasers and QPM devices. These kinds of advanced tunable solid-state light sources which based on microchip lasers will be powerful tools in the research of molecular science.

UHV Tribometer

KONDOH, Takuhiko; ASAKA, Shuji; WATANABE, Michio

For actuators with sliding surfaces to operate smoothly in ultra-vacuum (UHV) it is important to obtain a surface treatment which is excellent in antigalling.

This year we have newly built an UHV tribometer to enable evaluation of sixteen kinds of surface treatment. We have found that among the samples tested MoS_2 coatings formed by sputtering method has had the best performance both in antigalling and in low coefficient of friction. Among the six kinds of coatings formed by electroplating Sn plating showed the best performance. All of the samples coated by five kinds of electroless plating have produced a poor result to show a high coefficient of friction in early stages of the test.

Investigation of Dynamics on photo-excited Solids and Surfaces by Using Synchrotron Radiation

KAMADA, Masao; TANAKA, Shin-ichiro

Dynamics on solids and surfaces excited by photons has attracted much interest from both of basic and application sides. We have carried out photoelectron spectroscopic studies on semiconductor surfaces using synchrotron radiation and lasers. Core-level shifts observed on GaAs (100) can be interpreted in terms of surface photo-voltage effects induced by laser. Dynamics of the Cs and Oxygen on GaAs surfaces is one of interesting subjects and may be useful to understand the mechanism to produce the negative-electron affinity on GaAs surfaces. We have investigated the formation processes of the negative-electron affinity GaAs surfaces using photoelectron spectroscopy.

It is also important subject to investigate decay dynamics of the core-exciton using resonant photo-electron spectroscopy. The probability of the non-radiative decay of the core-excitons has been estimated on BaF2 and CsCl, providing idea which explain the missing of the core-exciton peaks in the excitation spectra of the Auger-free luminescence. Moreover, two-photon excited spectroscopy has been applied to investigate the valence-exciton and core-exciton in CaF2 and BaF2.

We have been investigating the photon-stimulated desorption (PSD) in recent years, since PSD is interesting and promising field from a point of view from the application to micro-fabrication and the basic surface science. The photoelectron and ion coincidence technique and the laser-induced fluorescence method are powerful to understand the PSD dynamics on semiconductor and insulator surfaces, respectively.

Non-Linear Phenomena and Related Beam Physics in Storage Ring Free Electron Lasers

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([1]SPring-8)

[*Nucl. Instrum. Methods Phys. Res. A* **431**, 396 (1999)]

We provide a perturbative formulation of nonlinear dispersion for particle motion in storage rings without linearizing the kinematic term and give recursion expressions for higher-order terms up to the fourth order. As an example, the nonlinear dispersion function of the SPring-8 storage ring is numerically calculated. The numerical calculation shows that the higher-order terms up to third order are not significantly modulated by magnetic error if the dispersion of the linear optics is sufficiently small. An experimental study of the nonlinear dispersion was also carried out and it was found that the agreement between the theory and the measurement was fairly good up to second order.

Photoelectron Spectroscopy Studies of Solids, Surfaces and Interfaces

KINOSHITA, Toyohiko[1]; NATH, Krishna G.[2]; HARUYAMA, Yuichi[3]
([1]Univ. Tokyo; [2]NTT; [3]Himeji Inst. Tech.)

The construction of the photoelectron spectromicroscopy equipment (the modified VG ESCALAB 220i-XL) has been completed. Some of the photoelectron spectroscopy and spectromicroscopy studies have been performed as described in this issue; (see, research activities). The combination with the laser annealing system allows us to measure the electronic structures of high temperature phase of solids and surfaces. All the members of the group have been removed from the IMS already. The group of associate professor Dr. K. Fukui may mainly use the system from 1999.

(2) Study of Molecular Solid toward Molecular Electronics

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

YONEMITSU, Kenji; KISHINE, Jun-ichiro; MORI, Michiyasu; KUWABARA, Makoto; SUN, Xin[1]; IMAMURA, Yutaka[2]
([1]Fudan Univ.; [2]GUAS)

Electron correlation in low dimensions brings about variety of electronic phases. i) In quasi-one-dimensional organic conductors $(TMTCF)_2X$, commensurability of the average electron-electron distance with the lattice spacing causes umklapp processes that are responsible for the Mott insulator phase. When the interchain hopping is small and the charge gap due to the umklapp processes is large, interchain one-particle hopping correlation is suppressed even if the antiferromagnetic long-range order is well developed. Otherwise, the nesting of the Fermi surface leads to instability toward a spin density wave. Such dimensional crossover is studied from high to low temperatures and for the ground states. When random potential exists, the electronic phases compete with the Anderson localization phase, as realized, *e.g.*, in $(DCNQI)_2Ag_{1-x}Cu_x$. ii) In one-dimensional metal complexes, M_2L_4X, strong electron-lattice coupling and electron-electron interaction bring about variety of charge and lattice ordering states. The electronic phases are reproduced when we consider up to the next-nearest-neighbor repulsion. Overall features are explained from the atomic (*i.e.*, vanishing transfer integrals) limit and the adiabatic/antiadiabatic (*i.e.*, zero/infinite phonon frequencies) limits. Reasonable change of parameters qualitatively reproduces general tendency for the dependence of the electronic state on the interdimer distance and on the presence/absence of counter ions. iii) In two-dimensional metal-assembled complexes $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$, the presence of two bands with different characters makes the phase diagram richer than that of κ-$(BEDT\text{-}TTF)_2X$. Dimensionality and frustration control the magnetic and transport properties of $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$, while correlation strength controls the electronic phase of κ-$(BEDT\text{-}TTF)_2X$.

π-d Interaction in Molecular Metals

YAKUSHI, Kyuya; YONEHARA, Yukako; DING, Yuqin; SIMONYAN, Mkhital; NAKANO, Chikako

We have undertaken a systematic study on the solid molecular systems in which transition metals are embedded in a π-conjugated system from the viewpoint of the future design of the superconducting material. The highly conductive phthalocyanine salts such as $CoPc(AsF_6)_{0.5}$ and $NiPc(AsF_6)_{0.5}$ are the prototype of the one-dimensional conductors in which the d- and π-orbitals form a double-chain and two-band system. Subsequently to the high-pressure optical experiment, we performed the high-pressure resistivity measurement in 0.25–0.95 GPa range. The resistivity minimum continuously shifted to higher temperature as we increased the pressure, reaching up to 283 K at 0.95 GPa. This result is in accord with the prediction of the metal-insulator transition derived from the analysis of the optical spectrum under high pressure. (*See IV-A-2*) This year we expanded our attention to the mixed crystals of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ to elucidate the role of the unpaired 3d electron on Co. First the X-ray diffraction and EPMA proved that the mixed crystals were formed in a wide range. Second we found a hyperfine structure in the ESR signal of $Ni_{0.99}Co_{0.01}Pc(AsF_6)_{0.5}$. The temperature dependence undoubtedly shows the exchange interaction between the localized 3d-electron and itinerant π-electron. (*See IV-A-1*) Third we found new Raman bands only in the mixed crystals $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$. This observation gives an information of the electronically excited state inherent in mixed crystal. (*See IV-A-3*) From this year we started a new π-d system, DMTSA-$FeCl_4$, which showed an antiferromagnetic phase transition at 12 K.

Search for Negative-*U* Materials in Molecular Solid

YAKUSHI, Kyuya; URUICHI, Mikio; OUYANG, Jianyong; YAMASHITA, Yoshiro; NAKANO, Chikako

The negative-*U* material comprises the molecule that has a negative on-site Coulomb energy or, in other words, an attractive force between two electrons within the molecule. We are looking for such compounds from the two directions: (1) a strong electron-molecular vibration coupling and (2) a strong nearest neighbor Coulomb repulsion. (1) A strong electron-molecular vibration interaction may overcome the repulsive force within the molecule and stabilize an on-site bipolaron state. The similar state has been found in the insulating compound, Cs_2SbCl_6, superconducting compound, $BaPb_{1-x}Bi_xO_3$, and conducting polymer, poly-pyrrole, but never been in an organic charge-transfer compound. (2) The molecular distance between the neighboring molecules is about 3.4 Å, whereas recently synthesized long conjugated molecule has more than 15 Å. If we use the long conjugated molecule which is stacked in an eclipsed overlapping mode, the on-site Coulomb repulsion energy happens to be smaller than the nearest neighbor Coulomb repulsion occasionally.

To look for such molecules, multi-step-oxidation properties of electron donors are one of the key parameters. Generally, the difference (ΔE) between the first and second oxidation potentials is thought to be a measure of the on-site Coulomb energy in the organic conductor. BEDT-ATD has a small difference (90 meV) in the first and second oxidation potentials. Subsequently to the study of $(BEDT\text{-}ATD)_2PF_6(THF)$ that shows a metal-insulator transition, we conducted the low-temperature structural study of $(BEDT\text{-}ATD)_2X$(solvent) ($X = PF_6$, AsF_6, BF_4; solvent = THF, DHF, DO). The most interesting point is the ferroelectric order of the solvent molecules in the insulator phase, which might show ferroelectricity near the phase transition. The experiment to examine this possibility is now in progress. (*See IV-B-5*)

We examined the band structure of new organic metals based on a long conjugated molecule BDT-TTP. Subsequently to the band structure study of (BDT-TTP)$_2$-X (X = SbF$_6$, AsF$_6$), we expanded our attention to analogous compounds (BDT-TTP)$_2$X (X = ClO$_4$, ReO$_4$), (ST-TTP)$_2$AsF$_6$, and (BDS-TTP)$_2$AsF$_6$. All of these compounds exhibit very similar reflection spectra, which means similar band structure. The correlation effect seems to be weak along the stacking direction in these compounds. However, we found a weak correlation effect in the spectra polarized along the inter-chain direction according to the analysis of the generalized Drude model. We still have no information on the sign of U.

The negative-U state is a dynamic state of the charge disproportionation: the paired charge is moving coherently. Contrary to this state, some charge-transfer salts in a mixed-valent state show a static charge disproportionation state. The Raman spectroscopy is an efficient method to detect this kind of charge distribution. From this viewpoint, we examined θ-(BDT-TTP)$_2$-Cu(NCS)$_2$ (*See I-B-4*) and (Et$_4$N)(DMe-TCNQ)$_2$ (*See IV-B-6*), and evaluated the electrostatic energy with counter anion/cation using the Ewald method.

Investigation of Novel Electronic Phases in Molecular-Based Conductors

NAKAMURA, Toshikazu; NAKAZAWA, Yasuhiro; TSUKADA, Hiroshi

The aims of this project are to study the electronic structure and to explore novel electronic phases in molecular-based conductors by microscopic and thermodynamical measurements. Molecular-based conductors are very advantageous because of several features as follows: (1) low-dimensional and simple Fermi surfaces, (2) clean system, (3) various ground states, and (4) molecular internal-freedom. We will perform the investigation with the following procedure: firstly we will understand the fundamental electronic properties by static magnetic susceptibility, EPR and transport measurements. Secondly we study the detailed electronic structure and mechanism of the phase transition by means of (a) EPR, (b) NMR and (c) specific heats measurements. We also try to carry out experiments with new devices under unconventional circumstance.

We start to study on these topics.

[1] Microscopic Investigation of the charge localized states in a quarter-filled system: (EDT-TTF)$_2$AuBr$_2$, is a quarter-filled system with uniform stacked. It undergoes a metal-insulator transition around 20 K. This system has very simple structure but its electronic state is not clarified. We started magnetic investigation of the low-temperature insulating phase.

[2] Competition between local and itinerant electrons in charge-transfer salts: (CPDT-STF)-TCNQ is a two-band system where the conduction and localized electrons coexist. We investigate possible interaction between them.

[3] Understanding of the electronic structure of conducting metal complex from a microscopic point of view: NMR measurements are performed for ^{13}C substituted Pd(dmit)$_2$ families.

Development and Solid State Properties of New Organic Conductors

KOBAYASHI, Hayao; FUJIWARA, Hideki; SATO, Akane; OJIMA, Emiko; ADACHI, Takafumi; NARYMBETOV, Bakhyt; TANAKA, Hisashi[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have tried to develop new organic superconductors. The main results obtained in the last one year are as follows: (1) we have found the antiferromagnetic metal phase and superconductivity in λ-BETS$_2$FeCl$_4$ at high pressure. To our knowledge. this is the first observation of the coexistence of magnetic order and π metal electrons in organic conducting systems. (2) The first antiferromagnetic organic metal exhibiting superconducting transition, κ-BETS$_2$FeBr$_4$ was discovered. From the thermodynamic viewpoint, it will be hardly imagined that the antiferromagnetic ordering of Fe^{3+} (S = 5/2) spins developed around 2.5 K is broken by the onset of the superconductivity of the π electron system at 1 K. Therefore, it is highly possible that this system is the first antiferromagnetic organic superconductor, which is one of the final targets in the recent studies on the development of the new organic conductors. (3) A new organic superconductor κ-BETS$_2$GaBr$_4$, which is isostructural to the recently discovered magnetic superconductor κ-BETS$_2$FeBr$_4$, was found out.

We have studied the low temperature structure of C$_{60}$ ferromagnets. We have successfully analysed the 7 K structure of unannealed TDAE*C$_{60}$ crystals. Whereas the annealed crystal exhibiting ferromagnetism below 16 K contains structural disorder even below 10 K. We have recently obtained a reasonable structural model for this disordered ferromagnetic crystal, which will be very important for the studies on the ferromagnetism of this salient system.

In the course of the trials on the establishment of the four-probe high-pressure resistivity technique using diamond anvil cell, we have recently succeeded to measure the resistivity of thin needle organic crystals up to 100 kbar, which will be an important step for the development of the solid state chemistry at high pressure.

NMR Studies of Liquid Crystals

OISHI, Osamu; NAKAI, Toshihito[1]; MIYAJIMA, Seiichi
([1]Tokyo Univ. Agric. Tech.)

Extensive high resolution NMR studies were conducted to investigate the dynamics and the microscopic mechanism of antiferroelectric ordering in liquid crystal MHPOBC. (1) Pulsed field gradient spin echo (PGSE) NMR study revealed that MHPOBC molecules are confined in the smectic layers, and therefore the self-diffusion takes place mainly within the layer. (2) Deuterium NMR for the specifically deuterated samples revealed unusual nature of the chiral chain; the chain is bent from the molecular long axis, and its motion is asymmetrically hindered.

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

INOUE, Katsuya; KUMAGAI, Hitoshi

The design of molecular materials with interesting magnetic and optical or electrical properties is one of the major challenges in the last few years. We have introduced a strategy of using π-conjugated high-spin oligonitroxide radicals which can be used as bridging ligands for paramagnetic transition metal ions in order to assemble and align the electron spins on a macroscopic scale. The synthesis and study of chiral molecular-based magnetic materials which are transparent for light are of great interest. Novel magneto-optical phenomena have been theoretically predicted and observed in chiral paramagnetic materials in 1997. Although novel properties are expected for such compounds, few examples of chiral molecular-based magnetic materials are still known. To get more insight in their properties it is therefore important to construct such chiral molecule-based magnets in a systematic way. We designed and synthesized a chiral organic radical which was can be employed to construct chiral molecular-based magnets. By this strategy, we have made chiral metamagnet of **1**·Mn(hfac)$_2$ and ferrimagnet of **2**·Mn(hfac)$_2$ (see V-F). The observation of MChD effect of this complex is now underway.

Studies on Electronic States of Organic Thin Films by Angle-Resolved UPS

UENO, Nobuo[1]; HASEGAWA, Shinji; AZUMA, Yasushi[1,2]; OKUDAIRA, Koji K.[1]; ISHII, Hisao[3]; YOSHIMURA, Daisuke[2,3]; SEKI, Kazuhiko[3]
([1]Chiba Univ.; [2]IMS; [3]Nagoya Univ.)

The archetypal organic semiconductor, perylene-3,4,9,10-tetracarboxylicdianhydride (PTCDA), has recently gained increasing interest as a promising material for organic electroluminescence devices. Furthermore, it was reported that a thin film of PTCDA provides a new state in the PTCDA band gap due to the reaction between the film and the substrate or overlayer materials such as GaAs,$^{1)}$ In, Al, Ti, and Sn.$^{2)}$ This result is very important because the new band is located very close to the Fermi level, and therefore it is expected that it plays an important role in the organic-device properties. However, there is little information on the origin of the band-gap state.

We performed ARUPS measurements of In/PTCDA interface on a cleaved MoS$_2$ surface in order to study of the new band-gap state.

Figure 1 shows the take-off-angle (θ) dependencies of the ARUPS of a 3-Å-thick PTCDA [panel (a)] and an In/PTCDA interface [panel (b)] which was prepared by evaporating the In onto the 3-Å-thick PTCDA film. The thickness of the In overlayer was 1 Å.When we compare Figure 2(a) and Figure 2(b), some spectral changes can be clearly seen. Firstly, a new band X appears at E_B = 0.8 eV in the PTCDA band gap after the In deposition. Secondly, at the region of E_B = 1.5–5 eV, some new features arise in the spectra and they are broader than the spectral features of the pristine PTCDA thin film in Figure 2(a). These results are consistent with those obtained by Hirose *et al.*$^{2)}$ Furthermore, the n_o// (oxygen nonbonding orbital with 2px and 2py atomic orbitals) band of PTCDA [band C in Figure 2(a)] was not resolved after the In deposition, while new band X' (E_B = 3.6 eV) is observed at $\theta \cong 62°$. These spectral changes originate from a chemical reaction between the PTCDA and the In. The disappearance of the n_o// band in Figure 2(b) suggests that the chemical reaction between the PTCDA and the In atoms takes place at the C=O parts to change the n_o// states. It is expected that the band X' originates from the AO which is distributed parallel to the surface, since the band X' observed at a large value of θ.

On the other hand, we measured high-resolution electron energy loss spectra (HREELS) for the In/PTCDA on the MoS$_2$ in order to clarify the chemical site of the reaction. The HREELS results showed that the intensities due to the excitation of C=O stretching mode [ν(C=O)] becomes weak relative to that of C-C stretching mode [ν(C-C)] and COC stretching mode [ν(COC)], and only the peak position of the ν(C=O) shifts to lower wave-number side. These findings indicate that a strong interaction between the PTCDA molecules and the In atoms exists only at the C=O parts. Furthermore, our recent Penning ionization electron spectroscopy (PIES) measurements on the In/PTCDA interface on the MoS$_2$ surface showed that four In atoms react with the one PTCDA molecule.

In Figure 2, the observed θ dependence of the band X intensity is compared with calculated one, where the calculations were performed using ab initio (STO-6G) and SS/MO methods[3-5] for an expected reaction product, In$_4$PTCDA. The calculated results were obtained by assuming random azimuthal orientation of the molecules for β = 0, 10 and 20° with the short molecular-axis being parallel to the surface. The calculated θ pattern for $\beta \approx 10°$ agrees better with the observed one in the value of θ max and the width of the angular distribution. This result indicates that the In$_4$PTCDA are oriented tilt at $\beta \approx 10°$ as shown in Figure 2.

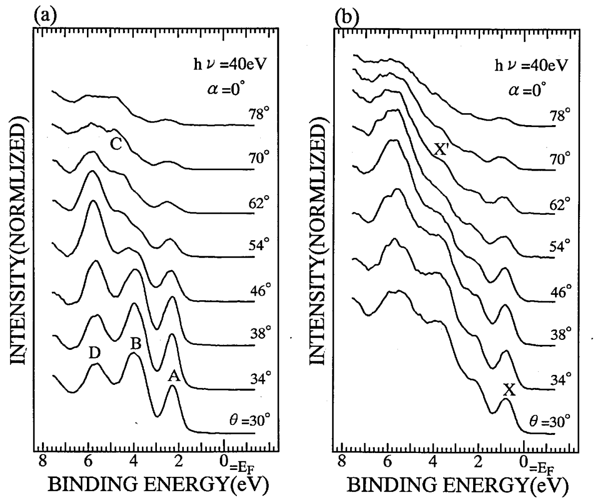


Figure 1. The take-off angle θ dependencies of ARUPS spectra of a 3-Å-thick PTCDA film on MoS$_2$ before (a) and after 1-Å-thick In overlayer deposition (b). The incidence angle of photon (α) is 0° and $h\nu$ = 40 eV. The intensity is normalized to the incidence photon flux.

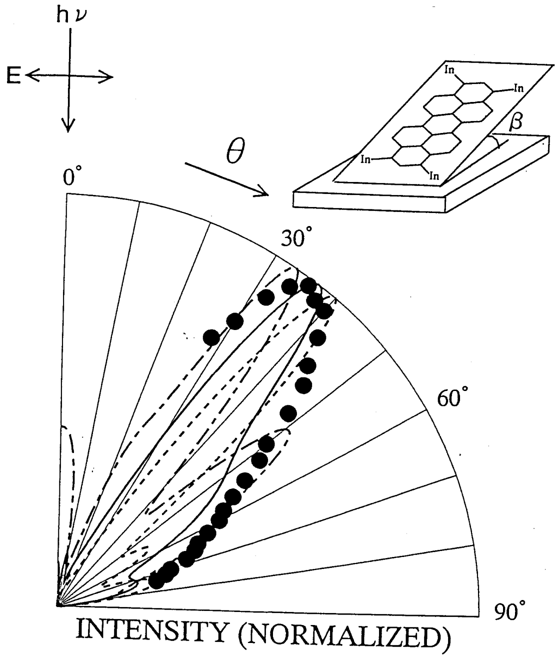


Figure 2. The comparison between the observed and calculated θ dependencies of the photoelectron intensities for the band-gap state. The SS/MO results at $h\nu$ = 40 eV and α = 0° are shown for β = 0° (------), 10° (———) and 20° (–—–). The calculation was made by assuming azimuthal disorder of the reaction product, In$_4$PTCDA.The tilt direction of the molecule is also shown.

References

1) Y. Hirose, W. Chen, E. I. Haskal and A. Kahn, *Appl. Phys. Lett.* **64**, 3482 (1994).

2) Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic and S. R. Forrest, Phys. Rev. B54, 13728 (1996).

3) N. Ueno, A. Kitamura, K. K. Okudaira, T. Miyamae, Y. Harada, S. Hasegawa, H. Ishii, H. Inokuchi, T. Fujikawa, T. Miyazaki and K. Seki, *J. Chem. Phys.* **107**, 2079 (1997).

4) S. Hasegawa, T. Miyamae, K. Yakushi, H. Inokuchi, K. Seki and N. Ueno, *Phys. Rev. B* **58**, 4927 (1998)

5) K. K. Okudaira, S. Hasegawa, H. Ishii, K. Seki, Y. Harada and N. Ueno, *J. Appl. Phys.* **85**, 6453 (1999).

New Advanced Organic Materials Based on Novel Heterocyclic Compounds

YAMASHITA, Yoshiro; TANAKA, Shoji; TOMURA, Masaaki

We have succeeded in preparing new electron donors and acceptors with extended π-conjugation. For example, TTF vinylogues bearing various substituents at the vinyl positions have been prepared using an oxidative dimerization reaction of 1,4-dithiafulvenes. In the derivatives with *o*-substituted phenyl groups the TTF vinylogue skeleton is planar when the aryl part is twisted. We have now found that TTF vinylogues containing one halogen atom at the ortho position afford cation radical salts with Au(CN)$_2$ anion as single crystals. The unique crystal structures were revealed by the X-ray structure analysis. We have also prepared non-planar BEDT-TTF derivatives fused with tetrahydrofuran (THF) rings. The donor molecule afforded the cation radical salts whose crystal structures are unusual due to the sterically hindered THF rings. On the other hand, bithiophene-TCNQ derivative and a tetracyanodiphenoquinodimethane derivative containing 1,2,5-thiadiazole rings have been newly synthesized as electron acceptors. X-ray analyses revealed the interesting crystal structures where intermolecular networks are formed by short S···N contacts. A new type of hydrogen-bonding system has been developed by using bipyridine and bispyridylethylene as proton acceptor and chloranilic acid as proton donor. The component molecules are combined via three-center hydrogen bonded interactions. Furthermore, we have prepared thiophene oligomers as promising molecular-scale electronic wire which have small energy gaps with a rigid and coplanar main chain. Details of these works are described in VIII-E section.

Design and Synthesis of New Tellurium-Containing Donors

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

In the field of molecular conductors, systems based on tellurium-containing donor molecules have not received as much attention as systems based on sulfur- or selenium-containing donors. By incorporating heavy chalcogen atoms such as tellurium into donor molecules, a new metallic system with a wider bandwidth and a higher dimensionality is expected to appear. We have designed dimeric donor molecules containing two HM-TTeF moiety and been trying to synthesize them. After obtaining these molecules, we are planning to study their crystal structures and physical properties of both neutral and oxidized states.

(3) Material Control in Multi-Reaction Centers

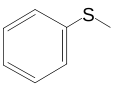
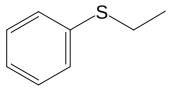
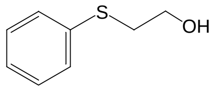
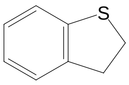
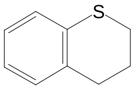
Asymmetric Oxidation Catalyzed by Myoglobin Mutants

OZAKI, Shin-ichi; YANG, Hui-Jun; MATSUI, Toshitaka; GOTO, Yoshio; WATANABE, Yoshihito

[*Tetrahedron: Asymmetry* **10**, 183 (1999)]

The sperm whale myoglobin active site mutants (L29H/H64L and F43H/H64L Mb) have been shown to catalyze the asymmetric oxidation of sulfides and olefins. Thioanisole, ethyl phenyl sulfide, and *cis*-β-methylstyrene are oxidized by L29H/H64L Mb with more than 95% enantiomeric excess (% ee). On the other hand, the F43H/H64L mutant transforms *trans*-β-methylstyrene into *trans*-epoxide with 96% ee. The dominant sulfoxide product in the incubation of alkyl phenyl thioethers is the *R* isomer; however, the mutants afford dominantly the *S* isomer of aromatic bicyclic sulfoxides. The results help us for the rationalization of the difference in the preferred stereochemistry of the Mb mutants-catalyzed reactions. Furthermore, the Mb mutants exhibit the improvement of the oxidation rate up to 300-fold with respect to wild type.

Table 1. Enantiospecific Sulfoxidation of Cyclic and Acyclic Thioethers.

		wild type Mb		L29H/H64L Mb		F43H/H64L Mb	
		rate[a]	ee (%)	rate[a]	ee (%)	rate[a]	ee(%)
1[b]		0.25	25 (R)	5.5	97 (R)	47	85 (R)
2		0.46	7.6 (R)	6.5	95 (R)	26	54 (R)
3		0.65	27 (R)[c]	1.6	71 (R)[c]	3.2	27 (R)[c]
4		2.2	0.2 (R)	24	67 (S)	95	17 (S)
5		0.8	5.4 (R)	3.2	66 (S)	50	34 (S)

(a) The unit for rate is turnover/min.
(b) The results are taken from reference 7f and 8a.
(c) The *R* configuration was assigned by comparison of CD spectra of (*S*)-methyl phenyl sulfoxide and synthetic sulfoxide of **3**.

Bio-Inspired Molecular Architecture

SHIONOYA, Mitsuhiko; TANAKA, Kentaro; TASAKA, Motoyuki[1]; SHIGEMORI, Kazuki[1]; HATANO, Akihiko[1]; MORISHITA, Hiromasa[1]; CAO, Honghua[1]; BU, Xian-He[2]
([1]GUAS; [2]Nankai Univ.)

Nature has produced a limited number of molecular modules such as nucleosides and nucleotides, amino acids, and lipids. However, the chemical diversity of these biomolecules and the different ways they can be polymerized or assembled into precisely-defined three-dimensional shapes provide a wide range of possible forms and functions. Furthermore, owing to advances in chemical synthesis and biotechnology we can combine or chemically modify these molecular building blocks, almost at will, to produce new functional molecules that have not yet been made in Nature. Based on these concepts, we have been working on the following research projects. Our research programs also consciously focus on structures and functions that have been unknown in living, biological systems.

1. Coordination-based artificial DNAs: metal-assisted base pairing.
2. Cyclic metallopeptides: efficient cyclization of oligopeptides linked to functional metal complexes.
3. Molecular recognition of ss-DNA sequences by self-assembling metal complexes.
4. An engineering-up approach to highly controlled hierarchical structures of metal complexes.

Activation of Carbon Dioxide Directed Toward Carbon-Carbon Bond Formation and Energy Conversion from Proton Gradients to Electricity

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A variety of metal complexes have proved to be aactive as catalysts precursors for the reduction of CO_2, though the reduction products are usually limited to CO and/or HCOOH. The difficulty of multi-electron reduction of CO_2 results from reductive cleavage of metal-CO bond derived from CO_2. We have found that Ru-CO bonds derived from CO_2 are successively activated without the bond-cleavage by utilizing redox reactions of monodentate 1,8-naphthyridine (napy). The ligand localized one- and two-electron reductions greatly enhanced the basicity of the free nitrogen. As a result, intramolecular nucleophilic attack of the free nitrogen to the carbonyl carbon takes place to form metallacyclic rings, where two-electrons are transferred to the carbonyl carbon from the reduced napy without through the central metal. The resultant Ru-CO bonds are activated enough to undergo mild electrophiles such as tera-alkyl ammonium salts. We have also achieved the first catalytic formation of ketones, α-keto acids and α-diketones under the electrochemical reduction of CO_2.

ATP synthesis utilized proton gradient is the key reaction for maintenance of biological activity. The proton gradient (Δp) between inside and outside of a cell is depicted as the sum of electric activity ($\Delta\psi$) and chemical activity (ΔpH) components. $\Delta p = \Delta\psi - Z\Delta\mathrm{pH}$ ($Z = 2.303RT/F$) Artificial energy conversion from proton gradients to other energy forms except for thermal energy has not been established so far. Biological system creates various valuable energies from the proton gradients, that is the neutralization energy. Basically, neutralization energy is originated from the binding energy of acid and base, namely is one of the chemical energies, which are expected to be converted directly to valuable chemical, electric or mechanical energy in 100% efficiency in principal. Along this line, we tried to convert the neutral energy to electronic energy by using metal complexes. The purpose of the two projects is to develop new methodology for utilization of CO_2 as a Cl resource and to generate reactive species for oxidation of hydrocarbons.

Self-Assembling Molecular Systems

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We have been studying the self-assembly of finite and infinite structures based on coordination chemistry, where metal-coordination induces the generation of defined structures. Our studies are focused on the self-assembly of finite structures such as macrocycles, catenanes (interlocked molecules), cages, tubes, and capsules as well as infinite network structures. In the construction of the discrete structure, our strategy may be characterized by the use of palladium's 90 degree coordination. Based on this concept, we have obtained the following results during 1999.

- Encapsulation of Large, Neutral Molecules in a Self-assembled Nanocage Incorporating Six Palladium(II) Ions: It is shown that self-assembled M_6L_4 type cage can hold as many as four adamantane molecules or *o*-carborane (8 Å in diameter) inside its nanosized cavity.
- "Ship-in-a-bottle" Formation of Stable Hydrophobic Dimers of *cis*-Azobenzene and -Stilbene Derivatives in a Self-assembled Coordination Nanocage: "C-shaped" molecules such as *cis*-azobenzene and -stilbene are enclathrated in the cavity of a nano-sized M_6L_4 type cage complex through "ship-in-a-bottle assembly" into a hydrophobically interacted dimer.
- A Nanometre-Sized Hexahedral Coordination Capsule Assembled from 24 Components: The transition metal-induced assembly of a stable, nanometer sized coordination capsule are achieved from twenty-four small components; eighteen metals and six triangular organic ligands.
- Spontaneous Assembly of Ten Components into a Two Interlocked, Identical Coordination Cages: Two cage complexes efficiently bind each other through giving rise to a ten-component self-assembly into a three-dimensionally interlocked molecule.
- Quantitative Formation of Coordination Nanotubes Templated by Rod-like Guests
- Guest-Selected Formation of Pd(II)-Linked Cages from a Prototypical Dynamic Library
- Quantitative and Spontaneous Formation of a Doubly Interlocking [2]Catenane using Copper(I) and Palladium(II) as Templating and Assembling Centers
- Flexible Coordination Networks with Fluorinated Backbones. Remarkable Ability for Made-to-order Enclathration of Organic Molecules
- Kinetic and Thermodynamic Aspects in the Substrate-Induced Assembly of Optimal Receptors from a Dynamic Library: Pyridine functionalized C2v ligand gives symmetric and asymmetric M_3L_2 receptors and their dimeric M_6L_4 cage; each of them is selected upon the addition of thier optimal guests.
- Dynamic Behavior of Rod-like Guest Accomodated in Coordination Nanotubes: Guest molecules are found to shuttle in the coordination nanotube in a one-way direction as revealed by NMR studies.
- Wacher Oxidation in an Aqueous Phase Through the Reversed Phase-transfer Catalysis of a Self-assembled Nanocage: Coordination nanocage shows reversed phase-transfer catalysis toward Wacker oxidation of olefins which is a typical Pd(II)-promoted catalytic reaction.
- Hydrophobic Assembling of a Coordination Nano-bowl into a Dimeric Capsule Which can Accommodate upto Six Large Organic Molecules: M_6L_4 coordination nanobowl assembles in aqueous media into a dimeric capsule accommodating as many as six neutral organic molecules.
- Porous Coordination Polytubes: Upon treatment with a transition metal (CuI), a panel-like oligo 3,5-pyridine ligand assembles into polytube structures which accomodate organic guests in the tubuler

cavities with the accessibleporosity of *ca.* 30–50%.

- X-Ray And NMR Observation of Encapsulated Molecules in a Self-assembled Coordination Nanocage: Encapsulation of tetrabenzylsilane and di(p-methoxybenzoyl) was confiermed by X-ray and NMR studies.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

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Metalloenzymes are a class of biologically important macromolecules which have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloenzymes have been thought to depend on the coordination structure of the reaction intermediate formed 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 stereoselectivity. In this project, we are studying the molecular mechanism of activation of molecular oxygen mediated by metalloenzymes.

(1) High valent iron-oxo species have been suggested as the active intermediates for catalytic oxygenation reactions by iron-containing oxygenases. In order to gain insight into the active intermediates, we try to synthesize iron complexes with bulky schiff-base ligands as biomimetic models of mononuclear non-heme iron active sites.

(2) Copper-dioxygen complexes are suggested as key reaction intermediates in many enzymatic reactions. To investigate the relationship between electronic structure and reactivity of copper-dioxygen complex, we have examined ^{17}O-NMR spectroscopies for several copper-dioxygen complexes.

(3) Heme oxygenase catalyzes the regiospecific oxidative degradation of iron protoporphyrin IX (heme) to biliverdin, CO and Fe, utilizing molecular oxygen and electrons donated from the NADPH-cytochrome P450 reductase. We have studied the reaction mechanism by using synthetic reaction intermediates and the enzyme obtained from bacterial expression.

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

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

A. Development of new binary (terpyridine-catechol) ligands that allow control over the metal coordination environment. This should enable us to design a series of redox catalysts with various electronic demand.

B. Synthesis and photoreaction of a porphyrin/metal-complex dyad molecule, which exhibits photoinduced electron transfer followed by cleavage of a metal-ligand bond.

C. Application of photoinduced electron transfer as a synthetic tool, where photoexcited molecules are considered from a synthetic point of view as short-lived reducing/oxidizing reagents.