JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institute, IMS undertakes joint studies programs for which funds are available to cover research expenses as well as travel and living expenses of individuals. The proposals from domestic scientists are reviewed and controlled by an inter-university committee.

The programs are carried out under one of the following categories:

(1) Joint Studies on Special Projects (a special project of significant relevance to the advancement of molecular science can be carried out by a team of several groups of scientists).
(2) Research Symposia (a symposium on timely topics organized by collaboration between outside and IMS scientists).
(3) Cooperative Research (a research program carried out by outside scientists with collaboration from an IMS scientist).
(4) Use of Facility (a research program carried out by outside scientists at the research facilities of IMS except the UVSOR facility).
(5) Invited Research Project
(6) Joint Studies Programs using beam lines of UVSOR Facility.
(7) Use of Facility Program of the Computer Center (research programs carried out by outside scientists at research facilities in Computer Center).

In 2004 Oct.–2005 Sep., the numbers of joint studies programs accepted for the categories (1)–(7) were 5, 11, 94, 47, 0, 125, and 133, respectively.

(1) Special Projects

A. Exchange and Spin-Orbit Interactions in Molecular Inner-Shell Excitation

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In the orbital interaction theory,[1)] the electron-hole interaction between occupied and unoccupied orbitals is related to short-range interaction, delocalization or charge transfer, and long-range interaction, polarization (PL) or local excitation. On the other hand, the electron-electron interaction in two occupied orbitals is related to short-range exchange repulsion (EX) and long-range electrostatic interaction. The spin-orbit (SO) interaction is inherently of atomic character. EX and SO interactions involving core electrons of the first-row and second-row elements such as carbon 1s and sulfur 2p are relatively small in comparison with intra-valence EX and deep-core SO, but have been recently essential to understand fine structures newly found in high-resolution and sophisticated measurements of inner-shell phenomena using third-generation synchrotron radiation facilities.

There are some types of EX. EX in closed-shell electrons results in an *exclusion* effect on the electrons in the interacting region. This is completely different from electrons *sharing* in the interacting region and forming covalent bonds. The interatomic core-core and core-valance EX interactions[2)] are important in discussing core hole localization in the core ionization and resonant phenomena such as multi-atom resonant photoemission. The core excitation in the closed-shell system creates an open-shell valence and/or Rydberg electron. In this case, the intra-atomic core-valence and core-Rydberg EX result in large and small singlet-triplet (ST) exchange splittings, respectively, where the core electron is localized on an atom and the intra-atomic EX component is predominant. On the other hand, the Rydberg electron may have relatively large intermolecular EX interaction with surrounding molecules in cluster, liquid, solid, and adsorbate phases, because of its diffuse character. In the core excitation and ionization of the open-shell system, EX causes more complicated multiplet splittings (MS). The core-valence EX sometimes competes with the intra-valence EX in core excitations of open-shell molecules composed of first-row elements.[2–5)]

The SO splitting on the core electron is directly observed in X-ray photoelectron spectroscopy. Even in 2p photoabsorption spectroscopy, the 2p SO splitting of third-row and heavier elements is large and is easily distinguishable. The singlet and triplet (ST) 2p excited states are strongly and indistinguishably mixed with each other through SO or *jj* coupling. However, in second-row elements such as phosphor and sulfur, 2p SO is not satisfactorily analyzed due to a small and comparable splitting to the intra-atomic core-valence EX splitting. SO is still a major factor in the core-to-Rydberg excited state with a small ST (EX) splitting, but is only one of some important factors in the core-to-valence excited state with a large ST (EX) splitting.[6)] Recent high-resolution photoelectron spectroscopy is possible to reveal another small splitting in the $2p_{3/2}$ manifold due to the molecular filed (MF) effect.[7)]

Now we have to consider SO, MF, and EX splittings in interpreting 2p excitation spectra of molecules involving second-row elements. Furthermore, de-excitation or resonant inner-shell spectroscopy may indicate additional features *via* triplet components in intermediate core-excited states; that is, triplet valence excitation in resonant inelastic X-ray scattering and quartet valence ionization in resonant photoelectron or Auger electron emission. In the present special project, we have discussed various types of EX and intermediate

couplings between SO and EX to analyze experimental evidence in inner-shell spectra of some simple molecules.[8)]

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B. Integration of Bio-Molecular Recognition Reaction System on Solid Surfaces and the Structure Analysis

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Membrane protein biosensors and biochips are the most important research targets in the post-genome. However, their developments are surprisingly delayed. One of the reasons is due to the difficulty in integrating the membrane protein on solid surfaces without loosing their physiological activities. They express their physiological activity only when they are reconstructed in the lipid bilayers under the water. In this research project, we are going to develop elementary technologies of constructing membrane protein/lipid bilayer systems on Si surfaces and conduct the analysis of their structures by atomic force microscopy (AFM) and infrared reflection absorption spectroscopy using buried metal layer substrates (BML-IRRAS).

B-1 Development of New Infrared Reflection Absorption Spectroscopy and Application to Bio Materials

We have been developing BML-IRRAS, which shows characteristics of the surface top layer chemically, and shows characteristics of buried metal for the incident electromagnetic wave. We have investigated the surface chemical reactions for relatively simple molecules on the BML substrate to understand basic performance of this technique. An application to biomaterials is another important target of this subproject. We have designed and constructed a special sample holder and IR beam optics for BML-IRRAS measurements of the biomaterials under water (D_2O).

B-2 Chemical Modification of Si Surfaces and Formation of Supported Lipid Bilayers

Chemical modification of Si surfaces is one of the important elementary processes of the membrane protein biosensor fabrications. In this sub-project, we are developing Si surface chemical modification techniques. Avidin molecules were immobilized on COOH-modified SiO_2/Si(100) surfaces with subnano-level flatness (R_a < 0.1 nm) forming covalent bonds between COOH groups on the substrate surface and NH_2 groups of the avidin molecules. The avidin-immobilized surfaces were characterized by AFM, BML-IRRAS, transmission infrared absorption spectroscopy (TIRAS), and elipsometry. It is concluded from these data that the avidin molecules are immobilized with the symmetry axis of the tetramer almost perpendicular to the substrate surface.

The effect of the electrostatic attractive force between vesicles and the substrate surface on Ca^{2+} free supported lipid bilayer formation has been investigated by using atomic force microscopy and fluorescence microscopy. When negative-charged giant vesicles were incubated without Ca^{2+}, the surface coverage of lipid bilayer was extremely low on the SiO_2 surface. On the other hand, in case of the positive-charged surface modified by aminopropyldimethylethoxysilane, the highcoverage of the lipid bilayer was obtained without Ca^{2+}. The attractive force between the negative-charged giant vesicles and the positive-charged surface is essentially useful to induce the vesicle fusion without addition of Ca^{2+}.

Fluorescence recovery after photobleaching (FRAP) method has become an important tool for investigating the lateral mobility and dynamics of biomembranes in living cells and mimicking membranes. Some groups have reported the fabrication of FRAP apparatus. While for those, fluorescence intensities were estimated by some complicated calibrations. In the present study, we successfully fabricated a new FRAP machine. There are two excitations for new FRAP apparatus. One is UV lamp, which is for fluorescence microscope observations. Another is the second harmonic of the 1120 nm semiconductor laser for photobleaching and quantitative high speed monoitoring. On the optical pathway, two neutral density filters with different transmission coefficients can be inserted to the filter holder to attenuate the powers of the UV lamp and the laser. Two recording devices are equipped which can continuously record fluorescence recovery resulting in acquisition of images at CCD and the photomultiplier tube (PMT) joined with an oscillograph and computer by which the curve representing the time dependence of fluorescence intensity can be obtained.

B-3 Membrane Protein Biosensor Fabrications

High resistance lipid bilayer formation is the most important first step of the supported membrane single ion channel biosensors. In this sub-project, we have recently succeeded in the fabrication of gigaohm seals on the Si subatrate with microelectrodes and the guard ring consisted of self assembled monolayer of alkyl silane compounds to reduce the edge leak currents.

Furthermore, we have also started the new subject of integrating the membrane protein biosensor to the micro-fluidic circuit

We have developed a technique to fabricate the hole (well) with about 1 μm diameter for the microelectrode on the surface of SiO_2/Si substrate. The circle pattern was made on the Co thin film by using the femto-second laser ablation, and the hole was made by the succeeding synchrotron radiation etching using this Co pattern as the mask. This process enabled the fabrication of the electrode hole with keeping the original nano-level flatness (R_a ~ 0.8 nm) of the substrate. A single planar lipid bilayer, deposited on these microelectrodes by the rapture of giant unilamellar vesicles, showed a high resistance (1.2 GΩ) necessary for the single channel recordings.

C. Development and Application of Short Wave Length Free Electron Laser

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As the result of the upgrade of the UVSOR-II electron storage ring in 2003, the ring can be operated with a small beam emittance of 17 nm-rad. This small emittance enables high power oscillation of the UVSOR free electron laser (FEL) in deep UV region. We tried the FEL oscillation at the wavelength of 250 nm and achieved a high power oscillation with several hundred mW. This circular polarized laser at 250 nm was used for the experiment on absolute asymmetric photo-reactions of amino acids. We have confirmed the progress of the photoreactions.

We have constructed a feed back system to stabilize the FEL output power. The system observes the change of the out-coupled laser power and control the synchronization between the laser pulse and the electron pulses. The test operation was successful. Even under the operating condition in which the laser was very unstable, the out-coupled power was stabilized sufficiently.

(2) Research Symposia

(From 2004 Oct. to 2005 Sep.)

1. Studies of Life Science from a Viepoint of Physical Chemistry—From Molecular Organizations to Living Cells—
   (Dec. 20–21, 2004)
   Chair: **TERAZIMA, Masahide**

2. Perspective of Biometal Molecular Science
   (Oct. 1–3, 2004)
   Chair: **SHIRO, Yoshitsugu**

3. Recent Developments of the Studies on Surface Magnetism
   (Nov. 5–6, 2004)
   Chair: **OHTA, Toshiaki**

4. Surface and Interface in Nano-Bioelectronics (Biotronics 2005)
   (March 3–7, 2005)
   Chair: **URISU, Tsuneo**

5. Symposium on Conductive and Photoconductive Organic Solids and Related Phenomena
   (Nov. 12–14, 2004)
   Chair: **YAKUSHI, Kyuya**

6. Frontiers in Biospectroscopy and Molecular Imaging
   (Jan. 17–18, 2005)
   Chair: **TAMURA, Mamoru**

7. Molecular Science of Heterogeneous Systems Observed in Atmospheric Sciences
   (Jan. 20–22, 2005)
   Chair: **TAKAMI, Akinori**

8. Progresses of Molecular Science and Related Fields
   (June 4–5, 2005)
   Chair: **NAKAJIMA, Atsushi**

9. Structure and Function of Retinal Proteins and GPCRs
   (June 15–17, 2005)
   Chair: **TSUDA, Motoyuki**

10. Various Hydrogen-Bonded Systems and Quantum Effects
    (July 8–9, 2005)
    Chair: **SEKIYA, Hiroshi**

11. Physical Chemistry Symposium for Young Researchers
    (June 8, 2005)
    Chair: **MASUHARA, Hiroshi**

(3) Cooperative Research

This is one of the most important categories that IMS undertakes for conducting its own research of the common interest to both outside and IMS scientists by using the facilities at IMS. In 2004 Oct.–2005 Mar., 118 outside scientists from 48 research groups joined the Cooperative Research programs, and 103 outside scientists from 46 research groups in 2005 Apr.–2005 Sep. The names and affiliations of those collaborations are found in the Research Activities sections in this Review.

(4) Use of Facility

The number of projects accepted for the Use of Facility in 2004 Oct.–2005 Mar. amounted 1, 23, and 0 for the Laser Research Center for Molecular Science (LRCMS), for the Research Center for Molecular-scale Nanoscience (RCMN) and for the Equipment Development Center (EDC), respectively. In 2005 Apr.–2005 Sep., the number of projects accepted amounted 2, 20, and 1 for LRCMS, for RCMN, and for EDC, respectively.

(5) Invited Research

Under this joint-study program, several scientists were invited from other institutions of help for construction and improvement of instruments in IMS. The total number of the projects in this category was 0.

(6) Use of UVSOR Projects

In the UVSOR Facility with the 750 MeV electron storage ring, there are sixteen beam lines available for synchrotron radiation research (see UVSOR ACTIVITY REPORT 2004). Under the Use of UVSOR Projects, many synchrotron radiation experiments have been carried out by outside scientists on eight beam lines in close cooperation with the UVSOR staff. The total number of the projects in this category was 125 (64 in 2004 Oct.–2005 Mar., and 61 in 2005 Apr.–2005 Sep.).

(7) Use of Facility Program of the Computer Center

Computer Center provides three types of research programs for outside scientists: (a) Use-of-Facility Program; (b) Cooperative Research Program; (c) Advanced Research Program. The numbers of projects accepted for each programs during the fiscal year of 2004 were (a) 126 with 501 users, (b) 6 with 12 users and (c) 1 with 3 users. Computer time distributed for these projects amounted to 85% of the total annual CPU time available.