RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. The UVSOR Synchrotron Facility, closely collaborates with the Department.

The core topics of the Department include ultrahigh-precision coherent control of gas- and condensed-phase atoms and molecules, high-resolution optical microscopy applied to nanomaterials, synchrotron-based spectroscopy of core-excited molecules and solid-state materials, vacuum-UV photochemistry, and the development of novel laser- and synchrotron-radiation sources.

Exploring Quantum-Classical Boundary

Department of Photo-Molecular Science
Division of Photo-Molecular Science II

OHMORI, Kenji
Professor
[ohmori@ims.ac.jp]

Education

1987	B. E. The University of Tokyo
1992	Ph.D. The University of Tokyo

Professional Employment

1992	Research Associate, Tohoku University
2001	Associate Professor, Tohoku University
2003	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2004	Visiting Professor, Tohoku University (–2005)
2007	Visiting Professor, Tokyo Institute of Technology (–2008)
2009	Visiting Professor, The University of Tokyo (–2011)
2012	Visiting Professor, University of Heidelberg
2014	Visiting Professor, University of Strasbourg (–2016)

Awards

1998	Award by Research Foundation for Opto-Science and Technology
2007	JSPS Prize
2007	Japan Academy Medal
2009	Fellow of the American Physical Society
2012	Humboldt Research Award

Member

Assistant Professor
- TAKEI, Nobuyuki
- TAKEDA, Shuntaro*

IMS Research Assistant Professor
- TANAKA, Akira

Post-Doctoral Fellow
- ZHANG, Yichi
- MENG, Zengming

Visiting Scientist
- TIRUMALASETTY PANDURANGA, Mahesh†

Graduate Student
- MIZOGUCHI, Michiteru
- CHEW, Yee Lai

Secretary
- INAGAKI, Itsuko
- KAWAMOTO, Minako
- YAMAGAMI, Yukiko

Keywords Quantum-Classical Boundary, Coherent Control, Attosecond

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.$^{1)}$ This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is a bulk solid composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as "collapse" in quantum mechanics, is often accepted as a discontinuous event, but a basic question arises: When and how the delocalized wave function becomes localized? Our dream is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this dream in mind, we have developed coherent control with precisions on the picometer spatial and attosecond temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems such as an ensemble of ultracold Rydberg atoms, as depicted schematically in Figure 1, and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

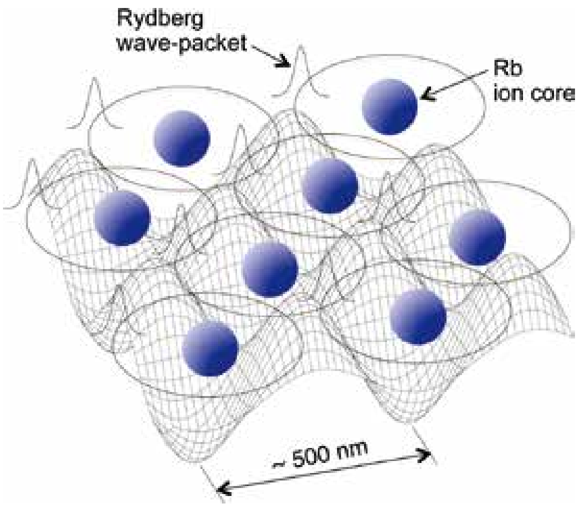


Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.$^{2)}$

Selected Publications

- H. Katsuki *et al.*, "Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference," *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, "Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales," *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, "Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule," *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, "Strong-Laser-Induced Quantum Interference," *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in a Strongly-Correlated Ultracold Rydberg Gas," *Nat. Commun.* **7**, 13449 (2016).

1. Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas[3]

Many-body correlations govern a variety of important quantum phenomena such as the emergence of superconductivity and magnetism. Understanding quantum many-body systems is thus one of the central goals of modern sciences. Here we demonstrate an experimental approach towards this goal by utilizing an ultracold Rydberg gas generated with a broadband picosecond laser pulse, as schematically depicted in Figure 2. We follow the ultrafast evolution of its electronic coherence by time-domain Ramsey interferometry with attosecond precision. The observed electronic coherence shows an ultrafast oscillation with a period of 1 femtosecond, whose phase shift on the attosecond timescale is consistent with many-body correlations among Rydberg atoms beyond mean-field approximations. This coherent and ultrafast many-body dynamics is actively controlled by tuning the orbital size and population of the Rydberg state, as well as the mean atomic distance. Our approach will offer a versatile platform to observe and manipulate non-equilibrium dynamics of quantum many-body systems on the ultrafast timescale.

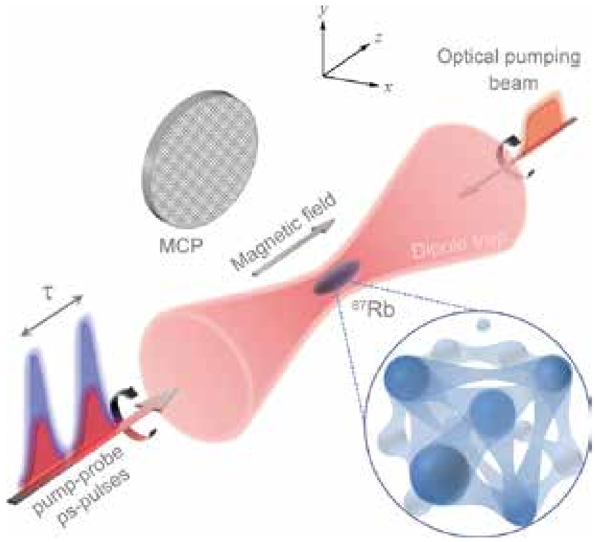


Figure 2. Schematic diagram of the experimental setup for the observation of ultrafast many-body electron dynamics in a strongly correlated ultracold Rydberg gas.[3]

References

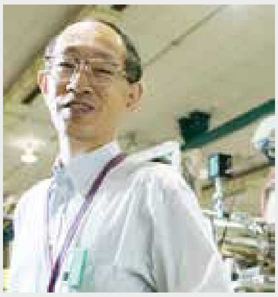
1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).

---

* Present Address: The University of Tokyo
† IMS International Internship Program

Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



KOSUGI, Nobuhiro
Professor
[kosugi@ims.ac.jp]

Education
1976 B.S. Kyoto University
1981 Ph.D. The University of Tokyo

Professional Employment
1981 JSPS Postdoctoral Fellow
1982 Research Associate, The University of Tokyo
1988 Lecturer, The University of Tokyo
1989 Associate Professor, Kyoto University
1993 Professor, Institute for Molecular Science
1993 Professor, The Graduate University for Advanced Studies

1996 Visiting Professor, McMaster University, Canada
2008 Visiting Professor, Université P&M Curie - Paris VI, France
2011 Visiting Professor, Université Paris-Sud - Paris XI, France
2013 Visiting Professor, Freie Universität Berlin, Germany

Award
2015 The 68th Chemical Society of Japan (CSJ) Award

Member
Assistant Professor
  NAGASAKA, Masanari
  YAMANE, Hiroyuki
Post-Dctoral Fellow
  YUZAWA, Hayato
Visiting Scientist
  JU, Huanxin
  CARLIER, Andy*
  BOUVIER, Mathilde*
Secretary
  INAGAKI, Itsuko
  SUGIYAMA, Kayoko

Keywords X-Ray Spectroscopy, Local Chemical State Analysis, Quantum Chemistry

This research group has strong international network in the field of soft X-ray molecular sciences using world-leading advanced synchrotron radiation facilities for more than 20 years.

Soft X-rays cannot pass through air or bulk water due to photoabsorption of N_2, O_2, and H_2O molecules. Such strong photoabsorption can be used in highly sensitive chemical state analysis of thin or dilute samples, because soft X-rays with photon energies of 100–700 eV excite 1s inner-shell (K-shell) electrons of chemically important light elements such as C, N, and O selectively to unoccupied states of molecules. The 1s electron is localized and bound by an atom in the system but is slightly affected by surrounding atoms and chemical bonds. Therefore, we can select a 1s electron in each atom in molecules by choosing different X-ray energies with 10–100 meV accuracy, and know each atomic component and chemical environment in the unoccupied state.

In order to realize *in situ* and *in operando* chemical state analysis revealing local electronic structures and weak intermolecular interactions in molecular systems such as organic solids, liquids, aqueous solutions, and molecular clusters, we are developing and improving several kinds of thin sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). We are also using resonant and non-resonant X-ray emission spectroscopy (XES) and angle-resolved photoelectron spectroscopy (ARPES).

Sample thickness should be optimized below 1 μm to get optimal absorbance in XAS. For inhomogeneous samples, the 10 nm-scale spatial resolution is necessary. It is also important to reduce the radiation damage of samples due to strong light-matter interaction in the soft X-ray region.

Highly brilliant soft X-rays for the chemical state analysis are available on our UVSOR-III Synchrotron in IMS. In addition to quite unique experimental and instrumental developments at UVSOR-III BL3U, BL4U and BL6U, we are developing an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

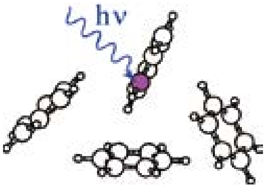


Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

- M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock and N. Kosugi, "Electrochemical Reaction of Aqueous Iron Sulfate Solutions Studied by Fe L-Edge Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. C* **117**, 16343–16348 (2013).
- M. Nagasaka, K. Mochizuki, V. Leloup and N. Kosugi, "Local Structures of Methanol-Water Binary Solutions Studied by Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. B* **118**, 4388–4396 (2014).
- H. Yamane and N. Kosugi, "Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band Dispersion Mesurements," *Phys. Rev. Lett.* **111**, 086602 (5 pages) (2013).

1. Liquid–Liquid Interfaces in Aqueous TEA Solution by Spatially-Resolved XAS

Aqueous triethylamine (TEA) solution shows a lower critical solution temperature (LCST) behavior,[1] in which two liquids are mixed at the lower temperature and are separated into two phases with the increase of temperature. This phase transition is contrary to normal and the mechanism of LCST has not yet been fully understood. We have observed local structures of liquid–liquid interfaces between TEA and water phases by spatially-resolved XAS with the resolution of 140 nm using a scanning transmission X-ray microscope (STXM) on UVSOR BL4U.[2] The liquid–liquid interfaces between TEA and water phases are formed from aqueous TEA solutions with the molar fraction of 0.4 at the temperature of 29.9 °C above LCST.

Figure 2(a) shows O K-edge XAS of water at different positions of the liquid–liquid interfaces. The inset shows the soft X-ray transmission image at 530 eV, in which the central part is a water phase and is surrounded by a TEA phase. We have estimated molar concentrations of water and TEA at different positions from the edge jumps of XAS in the O and C K-edges, respectively. It was confirmed that the mixing ratio of TEA and water determined in both the water and TEA phases are consistent with the phase diagram of TEA-water mixtures.[1]

Figure 2(b) shows the energy shift of the pre-edge peak (535 eV) in the O K-edge XAS at different positions. It is already known that the pre-edge peak is shifted to the lower photon energy when the hydrogen bond (HB) between water molecules is elongated/weakened. From the water to the TEA phase, the pre-edge peak is shifted to the lower energy. Because the amount of water is decreased with the direction of the TEA phase, the hydrophobic interaction of the ethyl group in TEA is dominant and the HB interaction of water molecules is decreased. Water and TEA molecules are coexisted in the TEA phase because the HB network of water is broken. The liquid–liquid interface between the water and TEA phases is formed with the balance of the hydrophobic interaction of TEA and the HB interaction of water molecules.

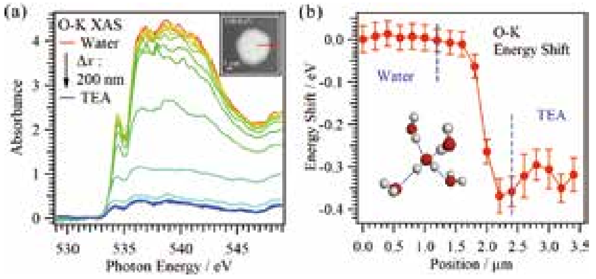


Figure 2. (a) O K-edge XAS of liquid–liquid interfaces at different positions. The inset shows soft X-ray transmission image at 530 eV. (b) Energy shift of the pre-edge peak as a function of position.

2. Delocalization of Charge-Transfer-Induced Valence Levels in Two-Dimensional Metal- Molecule Networks

Because of the large electron affinity, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) is well known as a strong electron accepter, and has been applied for the *p*-type doping of organic semiconductors and for the work-function control of metal electrodes. It is understood that the cyano group in the F_4TCNQ molecule plays a crucial role in the charge-transfer (CT) interaction. At the F_4TCNQ/Au(111) interface, in particular, the F_4TCNQ molecule forms a two-dimensional network via the cyano group with the segregated Au atom from the underlying Au(111) surface. In the present work, in order to investigate the electronic structure of the Au-F_4TCNQ network, we have studied the electronic structure of the F_4TCNQ/Au(111) interface by means of angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation at BL6U of the UVSOR Synchrotron.

From the low-energy electron diffraction (LEED), shown in Figure 3, it was found that the F_4TCNQ molecule on Au(111) forms a commensurate (5,2)(1,3) structure. Furthermore, the LEED image of F_4TCNQ/Au(111) does not show the 22×√3 herringbone pattern of Au(111) just around the (0,0) spot. This indicates the possibility of the Au-atom segregation from the Au(111) surface, which can introduce the formation of the Au-F_4TCNQ network.

Figure 3 shows the photoemission-angle (θ) dependence of ARPES for the clean Au(111) surface and the F_4TCNQ monolayer on Au(111) at 20 K using $h\nu = 45$ eV. Upon the deposition of F_4TCNQ, the Shockley-type surface state of Au(111) (labeled S) is almost quenched due to the presence of the strong chemical interaction, and the CT-induced electronic states are appeared at around 0.5 eV (labeled CT_1) and 1.5 eV (labeled CT_2) below the Fermi level. The CT_1 peak, which can be ascribed to LUMO (lowest-unoccupied molecular orbital) accepting a CT electron, shows a dispersive behavior with θ. The width of the dispersion of CT_1 is about 250 meV, and can be ascribed to the adatom-mediated intermolecular interaction in the Au-F_4TCNQ network, which was not observable at the physisorbed TCNQ/Au(111) interface.

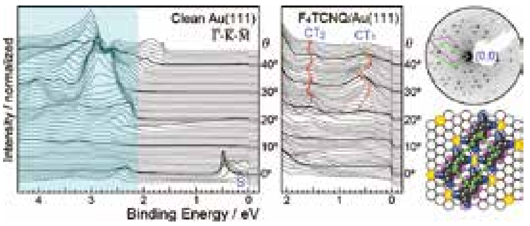


Figure 3. Photoemission-angle dependence of ARPES for the clean Au(111) and the F_4TCNQ monolayer on Au(111) at 20 K, measured at $h\nu = 45$ eV. The LEED image and the 2D ordering structure of the F_4TCNQ monolayer on Au(111) are shown in the right side.

References

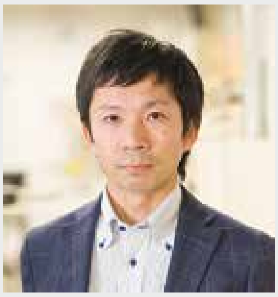
1) F. Kohler and O. K. Rice, *J. Chem. Phys.* **26**, 1614 (1957).
2) T. Ohigashi *et al.*, *AIP Conf. Proc.* **1741**, 050002 (2016).

---

* IMS International Internship Program

Electronic Property of Functional Organic Materials

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



KERA, Satoshi
Professor
[kera@ims.ac.jp]

Education

1996	B.E. Chiba University
1998	M.E. Chiba University
2001	Ph.D. Chiba University

Professional Employment

1998	JSPS Research Fellow
2001	Research Associate, Chiba University
2003	Research Associate, Institute for Molecular Science
2003	Postdoctoral Fellow, Wuerzburg University
2004	Assistant Professor, Chiba University
2007	Associate Professor, Chiba University
2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
2014	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting Professor, Chiba University

Member
Assistant Professor
UEBA, Takahiro
IMS Fellow
MEISSNER, Matthias
Visiting Scientist
SUN, Zhengyi
YANG, Jinpeng
Graduate Student
SHIRAISHI, Ryo
YAMAGUCHI, Takuma
Secretary
MASUDA, Michiko

Keywords Photoelectron Spectroscopy, Molecular Film, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However the mechanisms and its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to weak van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of photoelectron-emission fine features depending on adsorption and aggregation on the surface. By recent development in the instrumental we can assess hidden fine structures in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small gap-state DOS, weak band dispersion and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM at the interface upon weak interaction, an evaluation on the wave-function spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

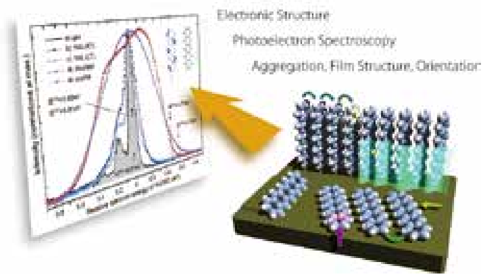


Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- F. Bussolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, "Gap States in Pentacene Thin Film Induced by Inert Gas Exposure," *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, "Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron Spectroscopy," *Adv. Mater.* **24**, 901–905 (2012).
- S. Kera, H. Yamane and N. Ueno, "First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films," *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Hole–Phonon Coupling Effect on the Band Dispersion of Organic Molecular Semiconductors1)

Understanding the mechanism of charge transfer in functional molecular solids, the electronic structure measurement, especially of the energy-band dispersion, is requested for molecular materials. However the electronic structure measurement has not been well achieved due to experimental difficulties for the molecular solids. More importantly, the dynamic interaction between the traveling charges and the molecular vibrations is critical for the charge transport in organic semiconductors. However, a direct evidence of the expected impact of the charge–phonon coupling on the band dispersion of organic semiconductors is yet to be provided. We reported on the electronic properties of rubrene single crystal as investigated by angle resolved ultraviolet photoelectron spectroscopy. A gap opening and kink-like features in the rubrene electronic band dispersion are observed. In particular, the latter results in a large enhancement of the hole effective mass, well above the limit of the theoretical estimations. The results are consistent with the expected modifications of the band structures in organic semiconductors as introduced by hole–phonon coupling effects and represent an important experimental step toward the understanding of the charge localization phenomena in organic materials.

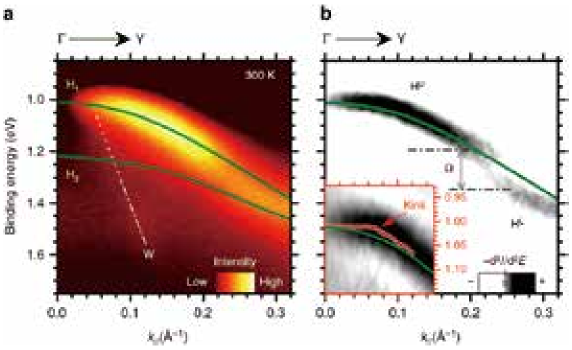


Figure 2. Renormalization of the energy-band dispersion of HOMO band of rubrene single crystal at 300 K. a) The photoelectron-emission intensity map by ARUPS. Binding energy vs. $k_{//}$ along the ΓY direction of the single crystal. Theoretical HOMO band dispersions are plotted as continuous green lines. The secondary-electron emission feature of W is overlapping (dashed line). b) Second derivative of ARUPS intensity map as obtained from data in a). The splitting of the HOMO band in two subband H^U and H^L is evidenced as separated by gap Ω. Inset: Magnification of second derivative map close to Γ point. Experimental H peak positions are also indicated by red circles and compared with theoretical band dispersion (continuous green line) to highlight the kink-like distortion.

2. Metal-Organic Interface Functionalization via Acceptor End Groups2)

The presence of functional groups in π-conjugated molecules not only determines the specific electronic and geometrical properties of the molecule, but also impacts the molecule–substrate and the molecule–molecule interactions. We reported a comprehensive study of the complex interface between perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) and the (111) surfaces of the three coinage metals. The specific structural, electronic, and chemical properties of the interface rendered by the different substrate reactivities are monitored with low-energy electron diffraction (LEED), x-ray standing waves (XSW), and ultraviolet and x-ray photelectron spectroscopy (UPS and XPS). In particular, the balance between molecule–substrate and molecule–molecule interactions is considered when interpreting the core-level spectra of the different interfaces. By presenting additional adsorption distances of the unsubstituted perylene, we show that the molecular functionalization via end groups with acceptor character facilitates the charge transfer from the substrate but it is not directly responsible for the associated short adsorption distances, demonstrating that this frequently assumed correlation is not necessarily correct.

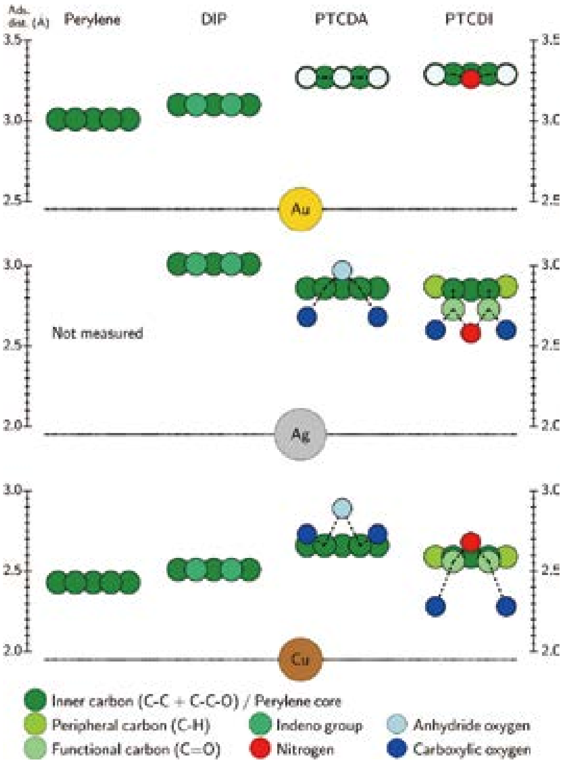


Figure 3. Adsorption distances extracted from XSW measurements for different perylene derivatives. Together with the data for perylene, DIP and PTCDA on Au(111), Ag(111) and on Cu(111). The adsorption distances on Au(111) have been corrected taking into account the surface reconstruction.

References

1) F. Bussolotti, J. Yang, T. Yamaguchi, Y. Nakayama, M. Matsunami, H. Ishii, N. Ueno and S. Kera, *Nat. Commun.* **8**, 173–179 (2017).

2) A. F.-Canellas, Q. Wang, K. Broch, D. A. Duncan, P. Kumar Thakur, L. Liu, S. Kera, A. Gerlach, S. Duhm and F. Schreiber, *Phys. Rev. Mater. (Rapid)* **1**, 013001 (6 pages) (2017).

Light Source Developments by Using Relativistic Electron Beams

UVSOR Synchrotron Facility
Division of Advanced Accelerator Research

KATOH, Masahiro
Professor
[mkatoh@ims.ac.jp]

Education

1982	B.S. Tohoku University
1997	Ph.D. Tohoku University

Professional Employment

1986	Reseach Associate, National Laboratory for High Energy Physics
2000	Assistant Professor, Institute for Molecular Science
2004	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
FUJIMOTO, Masaki
Graduate Student
HASEGAWA, Jun*
IMAO, Kenta*

Keywords Accelerator, Beam Physics, Astrobiology

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz wave to soft X-rays. Although it was constructed about 30 years ago, its performance is still in the world top level. This is the result of the continuous effort on improving the machine. Our research group has been developing accelerator technologies toward producing bright and stable synchrotron light, such as high brightness electron beam optics, novel insertion devices or state-of-the-art beam injection technique. We have been also developing novel light source technologies toward producing photons with excellent properties, such as free electron laser, coherent synchrotron radiation and laser Compton gamma-rays. We are also investigating beam physics which would be the basis of the novel light source technologies. We are exploring a future plan for the facility, such as a diffraction-limited storage ring or a free electron laser facility.

Figure 1. UVSOR-III Electron Storage Ring and Synchrotron Radiation Beamlines.

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, "Tunable Narrowband Terahertz Emission from Mastered Laser–Eelectron Beam Interaction," *Nat. Phys.* **4**, 390–393 (2008).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, "Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing," *Phys. Rev. Lett.* **103**, 144802 (2009).
- E. Roussel, C. Evain, C. Szwaj, S. Bielawski, J. Raasch, P. Thoma, A. Scheuring, M. Hofherr, K. Ilin, S. Wünsch, M. Siegel, M. Hosaka, N. Yamamoto, Y. Takashima, H. Zen, T. Konomi, M. Adachi, S. Kimura and M. Katoh, "Microbunching Instability in Relativistic Electron Bunches: Direct Observations of the Microstructures Using Ultrafast YBCO Detectors," *Phys. Rev. Lett.* **113**, 094801 (2014).
- M. Katoh, M. Fujimoto, H. Kawaguchi, K. Tsuchiya, K. Ohmi, T. Kaneyasu, Y. Taira, M. Hosaka, A. Mochihashi and Y. Takashima, "Angular Momentum of Twisted Radiation from an Electron in Spiral Motion," *Phys. Rev. Lett.* **118**, 094801 (2017).
- M. Katoh, M. Fujimoto, N. S. Mirian, T. Konomi, Y. Taira, T. Kaneyasu, M. Hosaka, N. Yamamoto, A. Mochihashi, Y. Takashima, K. Kuroda, A. Miyamoto, K. Miyamoto and S. Sasaki, "Helical Phase Structure of Radiation from an Electron in Circular Motion," *Sci. Rep.* **7**, 6130 (2017).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have developed novel light source technologies using UVSOR-III electron storage ring and a dedicated experimental station BL1U which was constructed under the support of Quantum Beam Technology Program of JST/MEXT, for developing novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beam-line. The generation of coherent synchrotron radiation based on our original method was successfully demonstrated in collaboration with Lille Univ. and Nagoya Univ. Its application is under preparation, in collaborating with Osaka Univ. Optical vortex beam from undulators are intensively investigated in collaboration with Hiroshima Univ., Nagoya Univ., AIST and so on.

Laser Compton scattering is a method to produce monochromatic and energy-tunable gamma-ray pulses. Laser pulses are injected to the storage ring and are scattered by the relativistic electrons circulating in the ring. We developed a unique method to produce ultra-short gamma-ray pulses in pico- and femtosecond range for the first time and demonstrated its potential as a powerful tool for material sciences by a photon-induced positron annihilation lifetime spectroscopy experiment, in collaboration with AIST. We have started developing an imaging technology for isotopes based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and JAEA. We have started reconstructing the resonator free electron laser on UVSOR-III, which will be used to produce intense gamma-rays through intra-cavity inverse Compton scattering.

Figure 2. Twin Polarization-variable Undulators/Optical Klystron at UVSOR-III.

2. Accelerator Technology Developments for Synchrotron Light Source and Free Electron Laser

We proposed several upgrade plans and have carried out all of them successfully. We designed a special electron beam optics intended to higher brightness. We designed necessary accelerator components, remodeled the machine and commissioned. We have designed six undulators and have successfully installed and commissioned all of them. We have succeeded in introducing a novel operation mode called Top-up operation, in which the electron beam intensity is kept quasi-constant at a high beam current, 300 mA. As the result of all these efforts, now, the machine is the brightest synchrotron light sources among the low energy machines below 1 GeV in the world.

We continue the efforts to improve the machine performance by introducing new technologies such as pulsed sextupole injection scheme. We are planning to replace some of the undulators to fit the changes of the users' requirements. Also, we are designing new accelerators for future project of the facility, such as linear accelerator based free electron laser or diffraction limited storage ring light source.

We are collaborating with Nagoya University Synchrotron Radiation Research Center (NUSR) for the accelerator developments at Aichi-SR. Accelerator magnets based on permanent magnets are being developed. Various high brightness electron sources are being developed and tested. New beam diagnostic technologies toward beam stabilization are being tested. Several PhD students from the University are involved. We are also collaborating with Accelerator Research Laboratory at KEK for the compact Energy Recovery Linac (cERL) project.

Figure 3. Optical Cavity for Resonator Free Electron Laser is under reconstruction at UVSOR-III.

---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics

TANAKA, Kiyohisa
Associate Professor
[k-tanaka@ims.ac.jp]

Education

2000	B.S. The University of Tokyo
2005	Ph.D. The University of Tokyo

Professional Employment

2005	Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
2008	Assistant Professor, Osaka University
2013	Associate Professor, Osaka University
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Member

Assistant Professor
  IDETA, Shin-Ichiro
Graduate Student
  KUSUNOKI, Naohiro*
  VINCINI, Giulio†

Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has attracted more attentions in the last few decades because of their unusual and fascinating properties such as high-T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES), a powerful tool in studying the electronic structure of complex materials, based on synchrotron radiation.

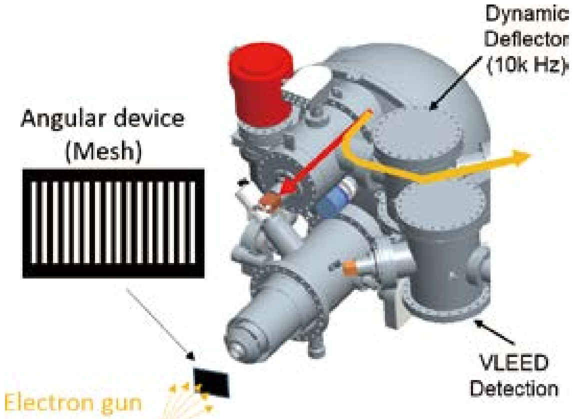


Figure 1. Schematic view of current spun-resolved ARPES system. Red and yellow arrows indicate the electron trajectory of conventional ARPES and spin-resolved ARPES, respectively.

Selected Publications

- K. Tanaka, T. Yoshida, A. Fujimori, D. H. Lu, Z.-X. Shen, X.-J. Zhou, H. Eisaki, Z. Hussain, S. Uchida, Y. Aiura, K. Ono, T. Sugaya, T. Mizuno and I. Terasaki, "Effects of Next-Nearest-Neighbor Hopping *t*' on the Electronic Structure of Cuprates," *Phys. Rev. B* **70**, 092503 (4 pages) (2004).
- K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- E. Uykur, K. Tanaka, T. Masui, S. Miyasaka and S. Tajima, "Coexistence of the Pseudogap and the Superconducting Gap Revealed by the *c*-Axis Optical Study of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$," *J. Phys. Soc. Jpn.* **82**, 033701 (4 pages) (2013).

1. Development of New Spin-Resolved ARPES

Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is one of the most powerful experimental techniques to investigate the magnetic properties of such materials, where one can know the "complete" information; energy, momentum, and spin, on electronic states of materials. Recent development of high energy- and angle-resolution photoelectron analyzer as well as the contemporary light sources such as third generation synchrotron radiation make it possible for the photoemission spectroscopy to investigate not only precise band structures but many body interactions of electrons in solids. However, appending the spin resolution is quite difficult because of an extremely low efficiency (10^{-4}) of Mott-type spin detections, and has not been established. Recently, very-low-energy-electron-diffraction (VLEED-type) spin detector with 100 times higher efficiency than that of conventional Mott-type one has been developed and spin-resolved ARPES has been started to be realized. So far, all the spin-resolved ARPES system in the world is using the single-channel detector and efficiency is still a problem. UVSOR Facility in Institute for Molecular Science equipped two public undulator-beamlines for ARPES, one was BL5U in the photon energy $h\nu$ region of 20–200 eV and the other BL7U of $h\nu$ = 6–40eV. Since the monochromator of BL5U was an old-style spherical grating type SGMTRAIN constructed in 1990s and the throughput intensity and energy resolution were poor, the whole beamline has been replaced to state-of-the-art monochromator and end station. The new beamline has been opened to users as high resolution and high flux ARPES beamline from FY2016. The newly developed electron lens system successfully achieved ~100 times better momentum resolution perpendicular to slit direction compared to the conventional ARPES. As a new function for this beamline, we have started high-efficient spin-resolved ARPES project with multi-channel detection as shown in Figure 1 (we call "image-spin" detection). Currently we successfully introduce electrons to the VLEED target position with maintaining the angle information emitted from the sample (Figure 2). If this new image-spin ARPES is realized, efficiency will be better than 100 times and the momentum resolution will be 10 times better than the current spin-resolved ARPES system in the world, which can be a breakthrough in this field.

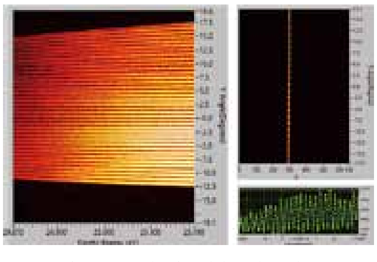


Figure 2. Detector images obtained by the electron trajectory with conventional ARPES (left) and spin-resolved ARPES (right).

2. Triple-Layer Splitting in Slightly-Overdoped $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ Observed by ARPES

It has been known that one of the most efficient ways to increase the critical temperature (T_c) of high-T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO_2 planes (n). T_c generally increases from single-layer (n = 1), double-layer (n = 2), to tri-layer (n = 3) and then decreases for $n \geq 4$. Although several mechanisms have been proposed to explain the n dependence of T_c, it is still not clear because of the lack of detailed knowledge about the electronic structure of the multi-layer ($n \geq 3$) cuprates. We performed detailed low-photon-energy dependent ARPES study of slightly-overdoped tri-layer $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223, T_c = 110 K) in the superconducting states at UVSOR BL7U, and successfully observed the third band dispersion originated from the band splitting caused by hybridization between the CuO_2 planes. This is the first observation of three bands in Bi2223.[1,2] Surprisingly, each band shows different superconducting gaps as shown in Figure 3. We are performing temperature dependent study of those gaps to clarify which superconducting gap governs the T_c of this system.

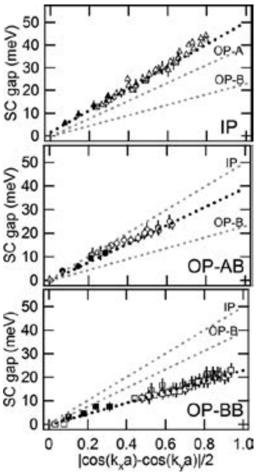


Figure 3. Superconducting gap of each band along the Fermi surface against *d*-wave form. The dashed lines are guides to the eye indicating the expected momentum dependence of a simple *d*-wave form.

References

1) K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, *Science* **314**, 1910–1913 (2006).

2) S. Ideta, K. Takashima, M. Hashimoto, T. Yoshida, A. Fujimori, H. Anzai, T. Fujita, Y. Nakashima, A. Ino, M. Arita, H. Namatame, M. Taniguchi, K. Ono, M. Kubota, D. H. Lu, Z.-X. Shen, K. M. Kojima and S. Uchida, *Phys. Rev. Lett.* **104**, 227001 (2010).

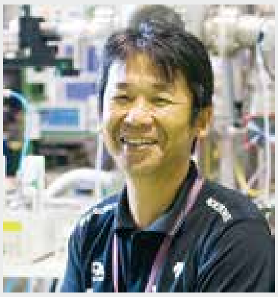
---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

† carrying out graduate research on Cooperative Education Program of IMS with Osaka University

Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

UVSOR Synchrotron Facility
Division of Advanced Photochemistry



SHIGEMASA, Eiji
Associate Professor
[sigemasa@ims.ac.jp]

Education

1986	B.S. Hiroshima University
1988	M.S. Osaka University
1997	Ph.D. The University of Tokyo

Professional Employment

1990	Research Associate, National Laboratory for High Energy Physics
1997	CEA Researcher, LURE, Université de Paris-Sud
1999	Associate Professor, Institute for Molecular Science
2007	Associate Professor, The Graduate University for Advanced Studies

Member

Assistant Professor
IWAYAMA, Hiroshi

Graduate Student
FUJISE, Hikaru

Keywords Soft X-Ray Spectroscopy, Inner-Shell Excitation, Photodissociation Dynamics

The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals. The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.

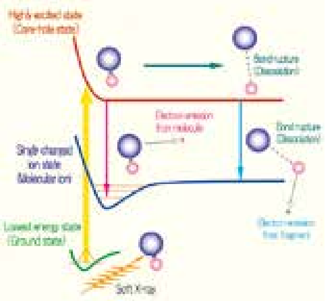


Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

- E. Shigemasa and N. Kosugi, “Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications,” in *Advances in Chemical Physics*, S. A. Rice and A. Dinner, Eds., Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- H. Iwayama, T. Kaneyasu, Y. Hikosaka and E. Shigemasa, “Stability and Dissociation Dynamics of N_2^{++} Ions Following Core Ionization Studied by an Auger-Electron–Photoion Coincidence Method,” *J. Chem. Phys.* **145**, 034305 (8 pages) (2016).

1. Anisotropic Angular Distributions of CF_3^+ Fragment Ions Following Ultrafast Dissociation of CF_4

Following inner-shell excitation, the relaxation pathway of a molecular system involves complex fragmentation patterns, depending on the nature of the core-excited state (bound or dissociative), and/or of the final states reached after the whole relaxation process. In particular, elongation and breaking of chemical bonds can occur in many molecular systems during the lifetime of the excited state: In this case, the dissociation is defined as ultrafast, since typical lifetimes of core-excited states in molecules containing light atoms are of the order of few femtoseconds (see e.g. ref. 1)). Molecular fragmentation can also occur in a final state reached after resonant Auger decay, if such final state is unstable. In this case, the time scale for the breaking of the chemical bond is much longer. In this work, we performed resonant Auger-electron–ion coincidence measurements, which allowed us to enlighten the angular distributions of the fragments.

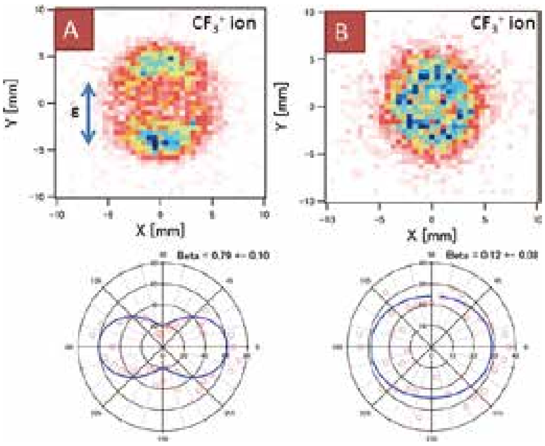


Figure 2. Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after C 1s → LUMO excitation: (A) the lowest binding energy peak related to the ultrafast dissociation and (B) the second lowest peak corresponding to $3t_2^{-1}$ final states. The lower figures represent the results of the fitting procedures.

Figure 2 shows Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after C 1s → LUMO excitation. The coincidence resonant Auger spectrum exhibits two broad peaks. The lower binding energy peak corresponds to the resonant Auger decay of the CF_3^* fragment originated from ultrafast dissociation, while the higher is related to the molecular CF_4^+ final states ($3t_2^{-1}$).[2] The angular distributions of CF_3^+ ions in panels (A) and (B) of Figure 2 have been taken in coincidence with the former and the latter peaks, respectively. The electric vector ε is vertical in both cases. It can immediately be seen that in the case of ultrafast fragmentation (A) the angular distribution of the CF_3^+ ions is quite asymmetric and peaked along the ε vector, while in the case of (B) the angular distribution is much more isotropic. These observations strongly suggest that the time scales of the two dissociation channels are different: For the ultrafast dissociation, the molecule has no time to rotate and the fragments are emitted according to the maintained orientation of the core-excited species, while for the dissociation after the resonant Auger decay, the molecule still keeps some memory of the excitation process before reassuming random orientation.

2. Limitations in Photoionization of Helium atoms by Extreme Ultraviolet Vortex

A circularly polarized extreme ultraviolet vortex (XUV) beam can be produced by a helical undulator. The XUV vortex beam carries not only spin angular momentum but also orbital angular momentum (OAM) with a helical wavefront. It is known that the nth harmonic off-axis radiation from a helical undulator carries OAM of $(n-1)\hbar$ per photon. According to recent theoretical works, it is predicted that a violation of the so-called electric dipole selection rules can be observed as a result of the transference of the OAM to the system. In order to investigate vortex-matter interactions in the short wavelength region experimentally, photoionization of helium atoms by the circularly polarized XUV vortex beam has been studied.

Figure 3 shows the angular distributions of photoelectrons measured for (A) the first, (B) second, and third harmonics, which correspond to plane-wave photons ($l = 0$), and the XUV vortices ($l = 1$ and $l = 2$), respectively. As seen in Figure 3, the angular distributions of photoelectrons are well reproduced by the dipole components alone, in contrast to the theoretical predictions. It is found that non-dipole transitions by vortex are hardly observable in conventional gas phase experiments.

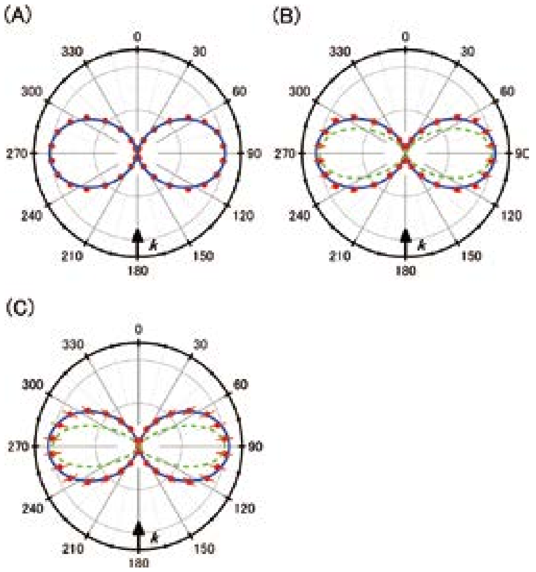


Figure 3. Angular distributions of 1s photoelectrons from helium atoms measured for (A) the first, (B) second, and (C) third harmonics from a helical undulator.

References
1) O. Björneholm *et al.*, *Phys. Rev. Lett.* **68**, 1892 (1992).
2) M. N. Piancastelli *et al.*, *J. Chem. Phys.* **138**, 234305 (2013).
3) T. Kaneyasu *et al.*, *Phys.Rev. A* **95**, 023413 (2017).

Photoelectron Spectroscopy of Ionic Liquids and Thin Films Made of Fullerenes and Their Application to Photoelectrochemistry

Department of Photo-Molecular Science
Division of Photo-Molecular Science III

KATAYANAGI, Hideki
Assistant Professor

Electrodes made of fullerenes and their derivatives and electrolytes containing ionic liquids (ILs) are used in the photovoltaic devices such as dye-sensitized solar cells (DSSCs) to make a breakthrough in the field of renewable energy sources. Both electronic structures and mesoscopic mixing schemes of the materials are key issues which affect their efficiency and lifetime. These structures can be investigated using a combined study of spectroscopic and thermodynamic measurements.

1. Fabrication of LB Film Electrodes of Sulfonated Fullerenes and Evaluation of Their Feasibility for the DSSCs

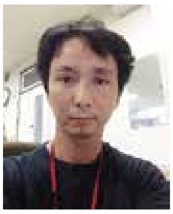
In the DSSCs, counter electrodes consist of Pt. The Pt electrode has some disadvantages such as cost and stability. Electrodes made of carbonaceous materials are candidates of substitutes for the Pt electrodes. To produce the carbon electrodes, we utilize the Langmuir-Blodgett (LB) technique. We have fabricated the LB films using fullerenes and their amphiphilic derivatives. We succeeded in producing homogeneous films on ITO glass substrates. The produced LB film electrodes were diagnosed by electrochemical methods. We found that the LB film electrodes exhibit the ionic charge- selective electron transfer (ICSET). The emergence of ICSET gives clue to utilize reactant selectivity of electrodes for suppressing side reactions which do not contribute to the efficiency of the cell.

2. Combined Study of Photoelectron Spectroscopy and Thermodynamic Measurements of ILs and Their Mixtures

We have started a research subject to apply the combined study of spectroscopic and thermodynamic measurements to the ILs. This combined study will allow us to understand the extraordinary characteristics of the ILs and their mixtures.

Observation of 3-Dimensional Nano-Structures of a Cell Nucleus

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Computed tomography (CT) is a powerful technique for X-ray microscopy to observe 3-dimensional internal structure of a sample without any destructive process. Additionally, by scanning the energy of X-rays, reconstructed image of CT can contain quantitative photoabsorption data to realize 3-dimensional spectroscopy. We have been developing CT for a scanning transmission X-ray microscopy (STXM) in UVSOR by designing a sample rotation cell and adjusting parameters of the optical system.[1]

We tried 3-dimensional structural analysis of an isolated cell nucleus of HeLaS$_3$ cell. The cell nucleus was fixed by glutaraldehyde and critical point drying to maintain its morphology. 50 STXM images of the nucleus on a tungsten needle were acquired with rotating the sample 3.6° each. In data acquisition, the X-ray energy of 280 eV, below C K-edge, was used for high transmission. The dwell time was 2 ms per a point and it took ~3 hours for measurement in total. A reconstructed cross sectional image and a 3-dimensional projection image are shown in Figure 1, where a voxel size is 80×80×80 nm^3. Network of actin filaments and nucleolus, round objects with high density, observed.

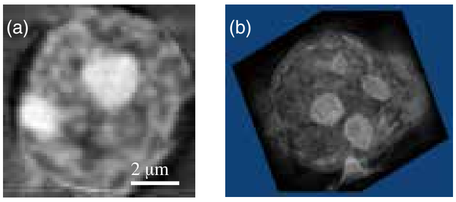


Figure 1. (a) Reconstructed cross sectional image and (b) 3-dimensional projection image of a cell nucleus.

Reference

1) T. Ohigashi *et al.*, *J. Phys.: Conf. Ser.*, in press.

Visiting Professors

Visiting Professor

KANAI, Kaname *(from Tokyo University of Science)*

Electronic Structure of Organic Molecules/Metal Interface

Fundamental questions about the adsorption of organic molecules on metal have gained importance also in applied research because the electronic structure at the interface between organic semiconductors and electrode metals (organic/metal interface) has a direct effect on the electric properties of various organic semiconductor devices. We have investigated how the electronic structure at the organic/metal interface is formed upon the adsorption of organic molecules by monitoring the modification of metal surface state (SS) induced by the adsorption of organic molecules using angle-resolved photoemission spectroscopy. Recently, we have focused on the interface between a well-ordered *n*-alkane monolayer and an Au(111) as an example of physisorption of organic molecule. We observed the shrinkage of quasi-free electron-like Fermi surface and enhancement of Rashba splitting of the SS upon the adsorption of the molecules. This substantial change in the metal SS directly shows that there is a certain amount of orbital interaction even in this ideal physisorption system. We have just started to investigate the other molecular systems.

Visiting Associate Professor

HIRAHARA, Toru *(from Tokyo Institute of Technology)*

Spin-Split States at the Surface/Interface of Nonmagnetic Ultrathin Films/Topological Materials

Recently there has been growing interest in utilizing the spin degree of freedom in electronic devices, the so-called *spintronics*. The conventional way is to use magnetic materials and manipulate the spin using a magnetic field. However, it is sometimes troublesome to apply a magnetic field to nano-scale materials and it is much easier to control the spin properties of materials using an electric field. By making use of the Rashba effect in which electrons become spin polarized in k-space due to spin–orbit coupling effects at the surface, such manipulation of electron spin with an electric field becomes possible, *i.e.*, a spin field effect transistor can be realized in such materials. We are developing a high-resolution spin- and angle- resolved photoemission spectroscopy measurement system equipped with *in situ* surface sample preparation facilities at BL-5U and characterize the novel spin property at the Rashba-split surface/interface states of nonmagnetic ultrathin films. We will also try to grow thin films of novel topological materials such as Dirac/Weyl/line-nodal semimetals. Furthermore, we will try to study the interplay between magnetism and the Rashba effect.

Visiting Associate Professor

KISHIMOTO, Tetsuo *(from University of Electro-Communications)*

Development towards Continuous Production of Bose-Einstein Condensates

Our goal is to realize continuous production of Bose-Einstein Condensates (BEC) based on all-optical techniques. By using sympathetic cooling techniques, this can further extend the possibility of realizing CW BECs for many other different atomic species or even molecules that are not eligible for direct evaporative cooling. So far we have explored the possibility of using the narrow $5S_{1/2}$–$6P_{3/2}$ cooling transition, however continuous loading of atoms into an optical dipole trap with this transition has not been successful so far. We have tuned this dipole trap to a special wavelength but the hyperfine states in the excited state experiences some vector light-shift, which may be the cause of insufficient cooling during the continuous loading. To avoid such vector shifts, currently we are moving toward the next approach of using a so called gray-molasses (GM) cooling with the $5S_{1/2}$–$6P_{1/2}$ transition. There has been no report of GM-cooling so far using such transitions with different principle quantum numbers.