RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction between molecules and optical fields with its possible applications to active control of molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Laser Research Center for Molecular Science and the UVSOR, closely collaborate with the Department.

The core topics of the Department include ultrahigh-precision coherent control of gas- and condensed-phase 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.

Development of Advanced Near-Field Spectroscopy Imaging and Application to Nanomaterials

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Keywords Near-Field Optical Microscopy, Plasmons, Excited States of Nanomaterials

There is much demand for the studies of local optical properties of molecular assemblies and materials, to understand nanoscale physical and chemical phenomena and/or to construct nanoscale optoelectronic devices. Scanning near-field optical microscopy (SNOM) is an imaging method that enables spatial resolution beyond the diffraction limit of light. Combination of this technique with various advanced spectroscopic methods may provide direct probing methods for dynamics in nanomaterials and nanoscale functionalities. It may yield essential and basic knowledge to analyze origins of characteristic features of the nanomaterial systems. We have constructed apparatuses of near-field spectroscopy and microscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable near-field measurements of two-photon induced emission, femtosecond time-resolved signals, and circular dichroism, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are given in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies, and so forth.

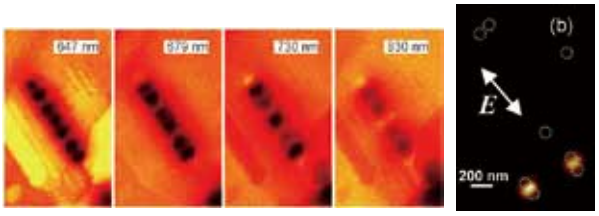

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).
- H. Okamoto, "Nanooptical Studies on Physical and Chemical Characteristics of Noble Metal Nanostructures," *Bull. Chem. Soc. Jpn.* **86**, 397–413 (2013).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Plasmon-Mode Analysis of Gold Nanodisks[1)]

Spatial and spectral properties of plasmons in noble metal nanoparticles are strongly influenced by the geometry of the particles. We previously demonstrated that standing wave functions of plasmon modes of gold nanorods (1-dimensional system) could be visualized by near-field microscopy. In the present study we visualized plasmon-modes for gold nanodisks (2-dimensional system) fabricated by the electron-beam lithography lift-off method. Near-field transmission spectrum of a single nanodisk exhibited multiple plasmon resonances in the visible to near-infrared region. Near-field transmission images observed at these resonance wavelengths show wavy spatial features depending on the wavelength of observation, which are much more complicated than those of the 1-dimensional rods. Theoretical analysis is indispensable to clarify the origins of the spatial features of the modes. For this purpose, numerical simulations with a novel theoretical formalism based on spatial correlation between electromagnetic fundamental modes inside and outside of the disc were performed. Simulated images reproduced the observed spatial structures excited in the disc.

Compared with other electromagnetic simulation methods frequently used for the analysis of plasmons, such as finite-difference time-domain (FDTD) method, the present method is advantageous in its capability of mode-based analysis of the electromagnetic fields. Mode-analysis of the simulated images indicates that the spatial features observed in the transmission images originate mainly from a few fundamental modes of the disc. The relative phases of the collective oscillation of electrons in the lobes observed near-field images were also clarified by this analysis.

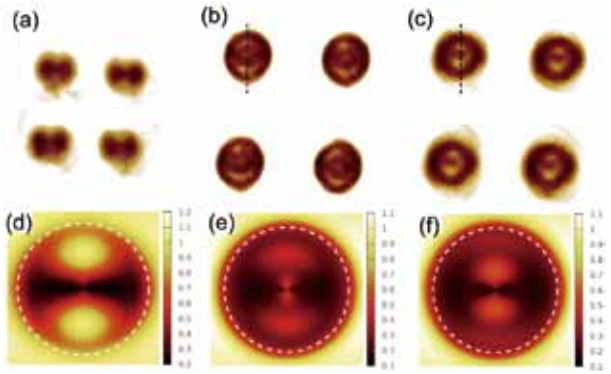

Figure 2. Observed (a–c) and simulated (d–f) near-field transmission images of gold nanodisks (thickness 35 nm).[1)] The diameters of the disks were 400 nm (a,d) and 800 nm (b,c,e,f). The wavelengths of observation and calculation were 780 nm (a,d), 710 nm (b), 790 nm (c), 705 nm (e), and 765 nm (f).

2. Strong Nanoscale Local Optical Activity in 2-D Chiral Metal Nanostructures

Nanostructures with chiral shapes show optical activity. Chiral metal nanostructures are expected to yield particularly strong optical activity arising from plasmon resonances. We recently developed a near-field circular dichroism (CD) imaging system with 100-nm-scale spatial resolution.

In the present work, we measured near-field CD images of S-shaped gold nanostructures and compared the results with the macroscopically obtained CD spectrum.[2)] Local CD signals of both handedness coexisted in the individual nanostructures, and the spatial distribution of the CD reflected the chiral symmetry of the nanostructure (Figure 3). When integrated over the entire nanostructure, the local CD signal was approximately 1% of the maximum of the local CD signal, which approximately coincided with the macroscopic CD signal. This indicates that there are possibly prominent nanoscale local CD signals even if only a tiny CD signal is observed macroscopically. We also studied developing optical activity with increasing chirality.[3)] We measured 2-D nanostructures composed of two symmetrically arranged C-shaped partial structures with various distances between them, which formed an "S" structure when the two partial structures were contacted. The chirality formed with the two partial structures caused an enhanced local optical activity when the partial structures were close enough to each other, even without a physical contact between them.

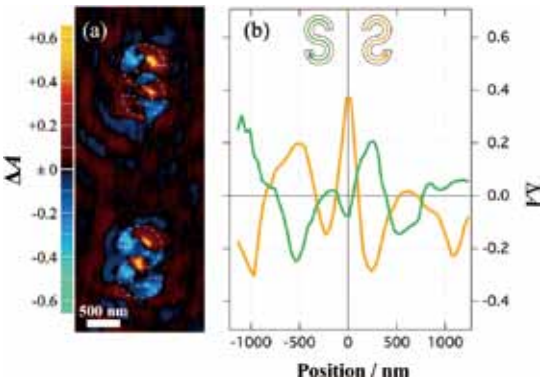

Figure 3. Near-field CD images of "S" shaped gold nanostructures (thickness 35 nm) observed at 785 nm (a) and the line profiles along the curves of the structures (b).[2)]

References

1) K. Imura, K. Ueno, H. Misawa, H. Okamoto, D. McArthur, B. Hourahine and F. Papoff, *Opt. Express* **22**, 12189–12199 (2014).
2) T. Narushima and H. Okamoto, *J. Phys. Chem. C* **117**, 23964–23969 (2013).
3) T. Narushima, S. Hashiyada and H. Okamoto, *ACS Photonics* **1**, 732–738 (2014).

Awards

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Design and Reconstruction of Molecular Quantum States of Motion

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Keywords Molecular Spectroscopy, Ultrafast Laser Science, Coherent Control

Molecules are vital existence. In a gas-phase ensemble at room temperature, they are, in an average, flying away by a few hundred meters, making turns almost reaching to 10^{11} times, and shaking themselves more than 10^{13} times within the duration of only one second. The ultimate goal this research group has been aiming to is to capture the lively figures of molecules moving in such a dynamic manner and to have a perfect command over the molecular motions. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for this purpose.

When a gaseous molecular sample is irradiated by an intense nonresonant ultrashort laser pulse, the rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP). We developed a method to explore the nonadiabatic excitation in a quantum-state resolved manner and applied it to diatomic and symmetric-top molecules. It has been shown that the state distribution is a useful experimental source for verifying the excitation process. When a pair of excitation pulses is implemented, partial control of rotational-state distribution has been achieved. In a favorable case, the double-pulse excitation has enabled us to reconstruct experimentally a rotational WP thus created. The sense of rotation can also be controlled, yielding to a rotational WP exhibiting angular-momentum orientation.

Nonadiabatic interaction with an intense ultrashort laser field can also coherently excite vibration of molecule. We have succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their vibronic ground states.

In the course of the control over molecular motion with high-resolution lasers, we constructed an optical parametric amplifier (OPA), to realize rapid adiabatic passage (RAP), which drives coherent population transfer from an initial quantum state to a target state with 100% efficiency. The laser system is consisted with BiBO crystals, which are seeded by a phase-modulated cw beam in the 1,040–1,070 nm region. Two-stage pre-amplification by Yb-doped fibers are implemented for stable injection to the OPA. The frequency chirp in the OPA pulse was actively controlled. Down/up chirps with up to 500 MHz shift were demonstrated. The output pulse energy was ~40 mJ, which is sufficient for two-photon RAP.

Selected Publications

- H. Hasegawa and Y. Ohshima, "Decoding the State Distribution in a Nonadiabatic Rotational Excitation by a Nonresonant Intense Laser Field," *Phys. Rev. A* **74**, 061401 (4 pages) (R) (2006).
- H. Hasegawa and Y. Ohshima, "Quantum State Reconstruction of a Rotational Wave Packet Created by a Nonresonant Intense Femto-Second Laser Field," *Phys. Rev. Lett.* **101**, 053002 (4 pages) (2008).
- K. Kitano, H. Hasegawa and Y. Ohshima, "Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields," *Phys. Rev. Lett.* **103**, 223002 (4 pages) (2009).
- Y. Ohshima and H. Hasegawa, "Coherent Rotational Excitation by Intense Nonresonant Laser Fields," *Int. Rev. Phys. Chem.* **29**, 619–663 (2010).
- S. Miyake and Y. Ohshima, "Injection-Seeded Optical Parametric Amplifier for Generating Chirped Nanosecond Pulses," *Opt. Express* **21**, 5269–5274 (2013).

1. New Ion-Imaging Apparatus for Molecular Wave-Packet Dynamics Studies

To characterize the rotational wave-packet dynamics, ion imaging is one of the direct and powerful methods. In a conventional 2D ion imaging with a typical camera-based technique, only a 2D projection of the 3D particle distribution is observed. When the particle distribution is cylindrically symmetric, the original 3D distribution can be reconstructed from the 2D projection by utilizing a mathematical procedure (*e.g.*, inverse Abel transformation). However, we sometimes encounter non-Abel-invertable cases, such as unidirectional molecular rotation. Although 3D imaging techniques could be successfully applied for such a case, a 2D detector has many advantages over a 3D detector: Higher multi-hit capability, lower cost, and simpler setup.

In this study, we designed and built up a new 2D ion imaging apparatus. We installed a 2D imaging unit (MCP/screen/camera) and a repeller plate electrode in the middle of the flight tube of a typical imaging apparatus. A jet-cooled gaseous molecular sample was irradiated by the output of a Ti:Sapphire laser. The molecules were multiply ionized and then exploded within the laser duration (Coulomb explosion). The ion fragments were first accelerated perpendicularly to the laser propagation direction. At the time when the ions of interest arrived at the repeller, a fast high voltage pulse was applied to the repeller to push the ions perpendicularly to the imaging unit.

For dynamics studies, we carried out time-resolved pump–probe experiments on N_2 molecules by using circularly polarized light as a probe to explode molecules of all orientation angles. Pump pulse used was a linearly polarized light (800 nm, 120 fs, ~50 TW/cm^2), which induced rotational wave-packet dynamics. Figure 1 shows selected 2D polar plots for the Coulomb exploded fragment distribution of N^{3+}, recorded at various delay time between the linearly polarized pump and the circularly polarized probe pulses. This delay-dependent anisotropic distribution of the fragments directly correlates to the 2D slice of the molecular-axis probability distribution in the 3D laboratory frame, and the clear manifestation of spatio-temporal propagation of the rotational wave packet created by an impulsive strong laser field.

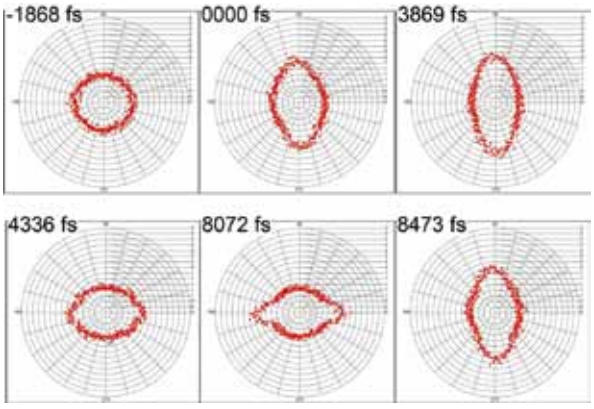

Figure 1. Delay-time dependent 2D distribution of Coulomb exploded N^{3+} fragments.

Owing to the multi-hit counting (*ca.* up to 150 events) for a single camera shot in the present imaging setup, we could record the snapshots with the time increment as small as 66.7 fs, within reasonable total data accusation time of 5 hours for 20 ps duration

2. Consideration of Coherent Population Transfer by Actively Phase-Controlled Nanosecond Laser Pulses

We have considered possible application of the newly developed ns OPA to advanced coherent population transfer and coherent control including chiral discrimination.

The constructed OPA is designed to produce the chirped signal and idler waves, of which energy difference is in the range of 0–400 cm^{-1}. Thus, by using the two beams as pump and Stokes pulses for stimulated Raman excitation, we will realize coherent population transfer in low-frequency Raman transitions. We numerically verified the robustness in the population transfer efficiency against the change of pulse intensity.

The amplification bandwidth of the constructed OPA is *ca.* 20 cm^{-1}. Multiple seeding beams can be amplified if their frequencies are covered in the OPA bandwidth, and multiple signal and idler waves with frequency chirp can be derived. This affords us to realize multiple chirped adiabatic Raman passage (CARP) within a single ns pulse operation. We numerically examined a ladder climbing coherent population transfer, $J = 0 \rightarrow 2 \rightarrow 4 \rightarrow 6 \rightarrow 8$, via CARP (Figure 2). As shown in the right panel, almost 90% of the initial population can be transferred to the final target state by setting the chirp rate and the seeding frequencies appropriately.

The seeding beam can be phase-modulated at up to 40 GHz. The relative optical phase between the carrier (ω_1) and the side band (ω_2) is precisely adjusted to that of the modulating microwave (MW) frequency (ω_3). Then, we can interfere constructively or destructively the stimulated Raman excitation pathway driven by ω_1 and ω_2 with the dipole transition pathway by ω_3. Among such quantum-control scenarios, the most interesting may be the realization of chiral discrimination. Here we numerically examined CARP excitation coupled with a resonant MW field and confirmed almost perfect enatio-selective population control.

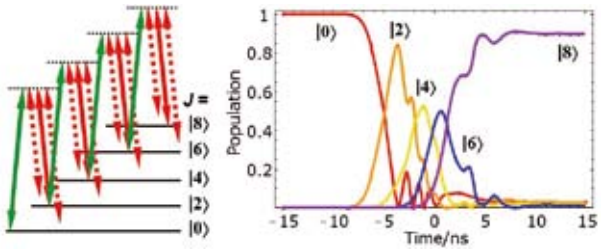

Figure 2. Rotational ladder climbing by multiple CARP process within a single-pulse OPA operation. (Light): Schematic energy levels and CARP transitions. (Right): Population change for five rotational levels involved.

Exploring Quantum-Classical Boundary

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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 and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

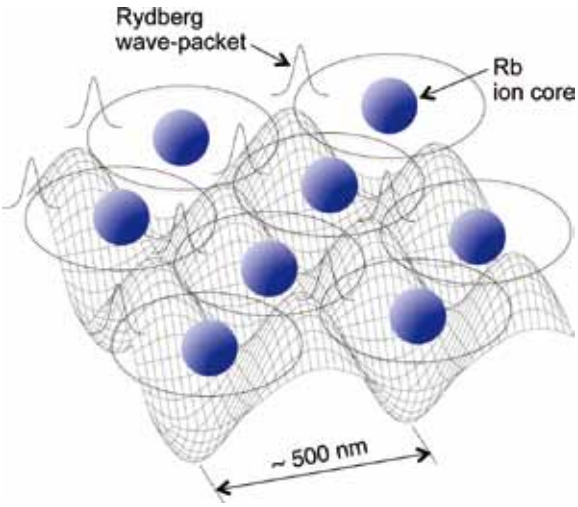

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.[2]

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. Hosak *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).

1. All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth[3)]

In a bulk solid, optical control of atomic motion provides a better understanding of its physical properties and functionalities. Such studies would benefit from active control and visualization of atomic motions in arbitrary directions, yet, so far, mostly only one-dimensional control has been shown. Here we demonstrate a novel method to optically control and visualize two-dimensional atomic motions in a bulk solid. We use a femtosecond laser pulse to coherently superpose two orthogonal atomic motions in crystalline bismuth. The relative amplitudes of those two motions are manipulated by modulating the intensity profile of the laser pulse, and these controlled motions are quantitatively visualized by density functional theory calculations. Our control-visualization scheme is based on the simple, robust and universal concept that in any physical system, two-dimensional particle motion is decomposed into two orthogonal one-dimensional motions, and thus it is applicable to a variety of condensed matter systems.

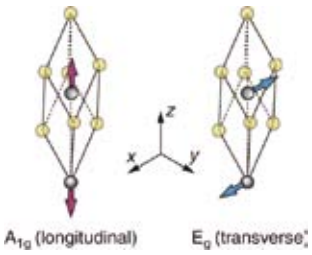

Figure 2. Crystal unit cell structure of Bi and the orientation of the A_{1g} (longitudinal) and E_g (transverse) phonon motions.

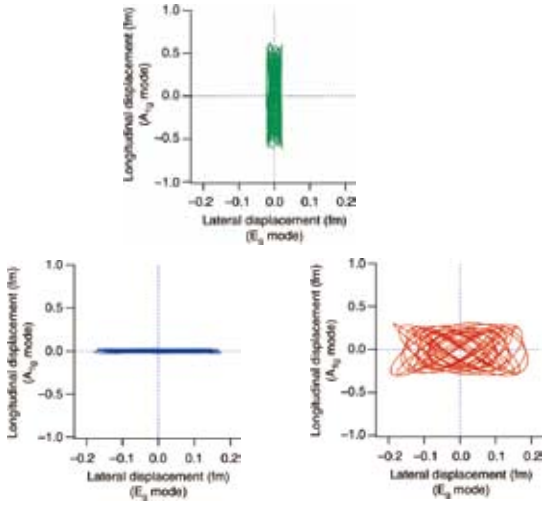

Figure 3. Traces of the atomic motions within a unit cell of Bi. Each trace represents the trajectory within the time window from 0.82 to 10.48 ps.

2. Ultrafast Coherent Control of an Ultracold Rydberg Gas[2)]

We employ an ensemble of ultracold Rb atoms as a model system to mimic a bulk solid. The model system offers longer coherence lifetime and more tunable parameters such as interatomic distance and interactions than a bulk solid. Since the interatomic distance is not shorter than submicrometers in this model system, longer than that of a bulk solid by more than three orders of magnitude, we generate Rydberg electronic wave-packets in those Rb atoms to induce interatomic interactions. Moreover these interactions can be actively tuned by changing the principal quantum numbers of Rydberg levels to be excited; the higher quantum numbers give larger diameters of Rydberg orbitals and hence stronger interactions. Briefly, a picosecond laser pulse produces Rydberg electronic wave-packets in laser-cooled Rb atoms. We measure the temporal evolution of those Rydberg wave-packets. We also measure the interferogram of two Rydberg wave-packets generated in each atom with a phased pair of picosecond laser pulses, whose delay is scanned in steps of attoseconds. Those temporal evolutions and interferograms of Rydberg wave-packets are measured as a function of the atom density, which can be converted to an atom–atom distance. We have observed that the interferogram is phase-shifted when we change the atom density. This observation suggests that the interatomic interactions have been induced by Rydberg wave-packets in Rb atoms. We plan to load these ultracold Rydberg atoms into an optical lattice to have better-defined interatomic configurations, as shown in Figure 1. Our ultrafast coherent control of an ultracold Rydberg gas could lead to the development of a novel simulator of quantum many-body dynamics.

3. Theoretical/Numerical Study on Strong-Laser-Induced Interference in the B State of I_2[4)]

In the B state of I_2, strong-laser-induced interference (SLI) was recently observed in the population of each vibrational eigenstate within a wave packet, which was initially prepared by a pump pulse and then strongly modulated by an intense femtosecond near-infrared (NIR) laser pulse. It was suggested that the interference as a function of the time delay occurs between the eigenstate reached by Rayleigh scattering and that by Raman scattering. To verify this mechanism and further discuss its characteristics, we theoretically/numerically study the SLI by adopting a two-electronic-state model of I_2. Numerical simulation reasonably reproduces the experimental signals and confirms the theoretical consequences, which include the π-phase shifts between Stokes and anti-Stokes transitions and (practically) no contribution from the energy shifts induced by the NIR pulse.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) H. Katsuki *et al.*, *Nat. Commun.* **4**, 2801 (2013).
4) Y. Ohtsuki *et al.*, *Phys. Chem. Chem. Phys.* **16**, 5689 (2014).

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

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

Soft X-rays cannot pass through air or through liquid water due to photoabsorption processes of N_2, O_2, and H_2O molecules. Such strong interaction of soft X-rays can be used in highly sensitive chemical state analysis of thin samples by X-ray absorption spectroscopy (XAS).

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 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, and know each atomic component in the unoccupied state in the system. The excited electron in the unoccupied state is also affected by chemical environments. The intermolecular interaction effect is often less than 0.1 eV; therefore, a highly resolved soft X-ray spectrometer is necessary.

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 sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) for resonant excitation, and resonant and non-resonant 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 as synchrotron radiation from in-vacuum undulator-type insertion devices even on low-energy electron storage rings; *e.g.* 0.75 GeV UVSOR in IMS. In addition to 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.

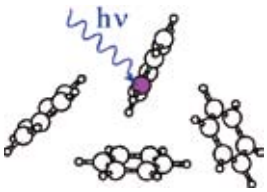

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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. *In Operando* Soft X-Ray Absorption Spectroscopy with Potential Modulation Applied to Electrochemical Reaction

In order to investigate local structures of electrolytes in electrochemical reactions under the same scan rate as a typical value 100 mV/s in cyclic voltammetry (CV), we have developed an *in operando* observation system for electrochemical reactions by soft X-ray absorption spectroscopy (XAS) with a potential modulation method. XAS spectra of electrolytes are measured by using a transmission-type liquid flow cell with built-in electrodes. The electrode potential is swept with a scan rate of 100 mV/s at a fixed photon energy, and soft X-ray absorption coefficients at different potentials are measured at the same time. By repeating the potential modulation at each fixed photon energy, it is possible to measure XAS of electrochemical reaction at the same scan rate as in CV. As shown in Figure 2, we have successfully measured the Fe 2p (L-edge) XAS spectra of aqueous iron sulfate solutions and the change in valence of Fe ions at different potentials in the Fe redox reaction.

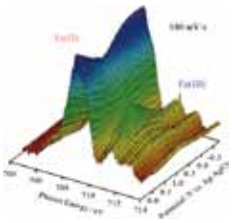

Figure 2. 3D plots of Fe 2p XAS spectra in the electrochemical reaction of aqueous iron sulfate solution under CV (100 mV/s scan).

2. *In Situ* Soft X-Ray Absorption Spectroscopy Applied to Hydration Reaction of Cyanopyrazine on Titanium Oxide Catalyst

In situ observation of liquid substrate conversion in solid–liquid heterogeneous catalytic reactions is difficult due to disturbance of the solvent and substrate itself. In this work, the hydration reaction of cyanopyrazine to produce pyrazinamide on TiO_2 catalyst ($PzCN + H_2O \rightarrow PzCONH_2$) has been successfully measured by the C K-edge and N K-edge XAS in transmission mode. Spectral change in both the C K-edge and N K-edge XAS, due to decreasing reactants PzCN and increasing products $PzCONH_2$, is clearly observed in spite of the coexistence of bulk liquid components PzCN, H_2O and solvent EtOH. The time dependence indicates that the hydration is the first order reaction. This result is also consistent with the linear relationship found in the Arrhenius plot, which is obtained from temperature dependent XAS measurements.

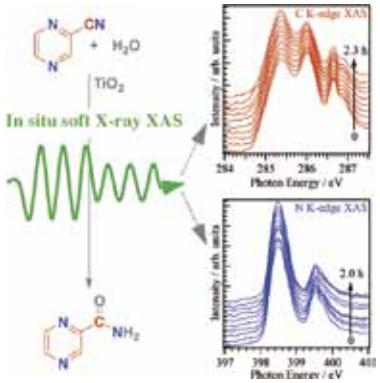

Figure 3. C K-edge (red) and N K-edge (blue) XAS spectra for the catalytic hydration reaction from cyanopyrazine to pyrazinamide.

3. Orbital-Specific Valence-Band Dispersion in α-Phase Crystalline Films of Cobalt Phthalocyanine

The valence band structure of α-crystalline cobalt phthalocyanine (CoPc) films grown on Au(111) is investigated by using angle-resolved photoemission spectroscopy (ARPES). The time-dependent photo-induced change in the ARPES peaks is noticed in shape and energy of the highest occupied molecular orbital (HOMO, C 2p) and HOMO-1 (Co 3d) of CoPc, and is misleading the interpretation of the electronic properties of CoPc films. By successfully avoiding such serious radiation damage, the clear valence-band dispersion has been first observed, showing that orbital-specific behaviors are attributable to the interplay of the intermolecular π–π and π–d interactions. The HOMO band dispersion by 0.1 eV gives the lower limit of the hole mobility for α-CoPc of 28.9 $cm^2 V^{-1}s^{-1}$ at 15 K. The non-dispersive character of the splitted HOMO-1 bands indicates that the localization of the spin state is a possible origin of the antiferromagnetism.

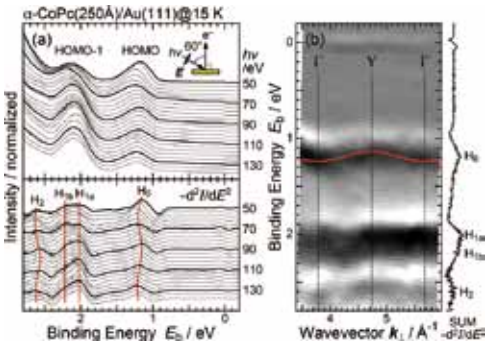

Figure 4. Intermolecular $E(\boldsymbol{k}_\perp)$ in the α-CoPc film on Au(111) at 15 K. (a) $h\nu$-dependent normal-emission ARPES spectra. (b) $E(\boldsymbol{k}_\perp)$ map with the tight-binding fitting for the HOMO-band dispersion (red curve).

Awards

NAGASAKA, Masanari; The 2014 JSSRR Scientific Award (Japanese Society for Synchrotron Radiation Research).
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Electronic Property of Functional Organic Materials

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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 for solid phases due to 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 photoemission 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, weak band dispersion and dynamic electronic polarization. To elucidate what really happens for 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).

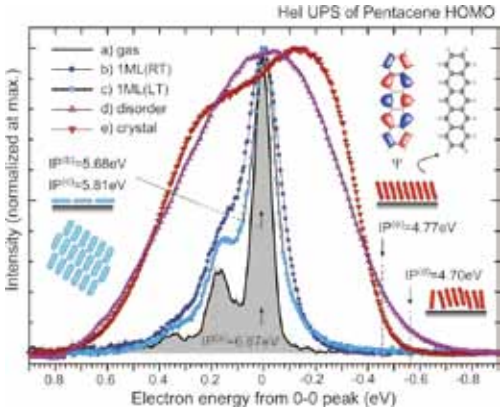

Figure 1. Wide variety in the feature of ultraviolet photoelectron spectra (UPS) for the HOMO band region taken for pentacene molecule in various aggregations (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- Q. Xin, S. Duhm, F. Bussolotti, K. Akaike, Y. Kubozono, H. Aoki, T. Kosugi, S. Kera and N. Ueno, "Accessing Surface Brillouin Zone and Band Structure of Picene Single Crystals," *Phys. Rev. Lett.* **108**, 226401 (5 pages) (2012).
- 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. Impact of Intermolecular Interaction on the Reorganization Energy of Molecules[1)]

Organic semiconductors are molecular solids with specific charge transport properties due to weak intermolecular interaction. The transport properties of organic single crystals and organic thin films are far from being adequately understood. Important subjects still to be understood are related to molecular and lattice vibrations (phonons) and their coupling to a charge carrier. The electron–phonon interaction depends on the molecular structure and their packing motif and therefore it can impact both molecular site energies and transfer integrals. The overall strength of local electron–phonon coupling observed in highly-resolved UPS is given by the relaxation energy between neutral and ionized states, and the reorganization energy associated.

We investigated the impacts of perfluorination on the electronic structure of pentacene (PEN) monolayer on graphite and hole–vibration coupling, which is specified by the reorganization energy and the binding energy of molecular polaron. We demonstrate that electron-withdrawing property of F atom mediates increase in spatial spread of highest-occupied molecular orbital (HOMO), which contributes significantly to increase in the vibronic-satellite intensity, and then leads to significant increase in reorganization energy. This contribution is much larger than an opposite contribution by lowering of vibration energies by perfluorination of PEN.

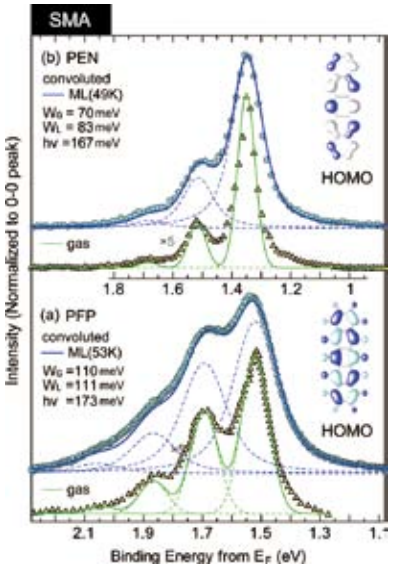

Figure 2. Comparison of HOMO band between gaseous HeI UPS (triangles) and angle-integrated UPS (circles) for the monolayer of perfluoropentacene (PFP) (a) and PEN (b), compared with convoluted curves by the single mode analysis of vibration coupling.

2. Mechanism of Energy-Level Alignment: Gap States Induced by Inert Gas Exposure[2)]

Energy level alignment (ELA) at organic-substrate and organic–organic interfaces is a crucial issue for any organic-based device, given that the interface electronic structure controls the charge injection process in the organic semiconductor. Despite considerable effort, however, there still remains a mystery why some organic semiconductors, such as PEN, always show p-type charge transport property while some others, such as C_{60}, show n-type property without heavy intentional doping, that is the transport property seems to be determined by molecule itself. Therefore, a consensus on ELA mechanism has yet to be reached.

We examined the energy distribution of density-of-gap state (DOGS) of the order of 10^{16} states $eV^{-1}cm^{-3}$, which is comparable to DOGS detected by electrical measurements, in an organic layer by means of ultralow background, high sensitivity UPS technique. We investigate PEN deposited on SiO_2/Si(100) and Au(111) substrates at 295 K. The impact of exposure to 1-atm of inert N_2 atmosphere on the PEN electronic properties is evaluated. Despite the absence of chemical interaction between N_2 and PEN molecules, the DOGS and ELA at the PEN/SiO_2 interface are strongly modified by the exposure to N_2 gas. This effect is ascribed to the structural disorder caused by N_2 molecules penetrating into the PEN film. A similar effect is observed upon exposure to Ar, while in case of O_2 exposure, the DOGS formation is accelerated, presumably because of the difference in the chemical properties of the gas molecules.

The present results demonstrate that structural disorder has a significant impact on the electronic properties and interfacial ELA. This is related to the nature of organic semiconductor crystals, which consists of low-symmetry molecules held together by weak intermolecular forces. The results also have great practical significance, as they show that organic layer processing in inert atmosphere does affect the electronic structure of the organic semiconductor, a point which had not been understood so far.

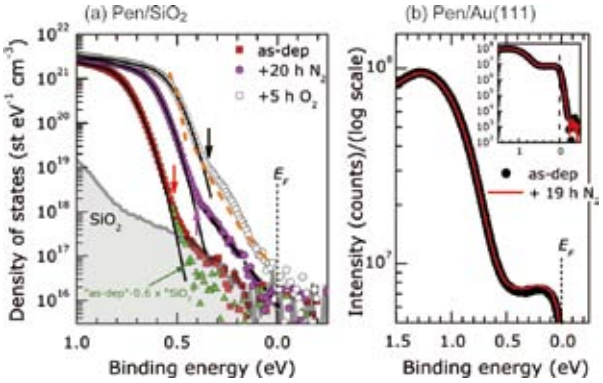

Figure 3. (a) DOS (log scale plot) of as-deposited, N_2-exposed, and O_2-exposed PEN film on SiO_2 by XeI-UPS. (b) XeI-UPS of as-deposited PEN film on Au(111) before and after N_2 exposure.

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Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Synchrotron Radiation, Free Electron Laser

UVSOR is a synchrotron light source to provide 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 have 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 synchrotron radiation with various characteristics such as free electron laser, coherent synchrotron radiation and laser Compton gamma-rays. We are also investigating future light sources for the facility, such as a diffraction limited light source or a linac-based free electron laser source.

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).
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- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultrashort-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696–700 (2011).
- I. Katayama, H. Shimosato, M. Bito, K. Furusawa, M. Adachi, M. Shimada, H. Zen, S. Kimura, N. Yamamoto, M. Hosaka, M. Katoh and M. Ashida, "Electric Field Detection of Coherent Synchrotron Radiation in a Storage Ring Generated Using Laser Bunch Slicing," *Appl. Phys. Lett.* **100**, 111112 (2012).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, "Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses," *Rev. Sci. Instrum.* **84**, 053305 (2013).

1. Light Source Technology Developments Based on Laser and Synchrotron and Their Applications to Molecular Science

We have demonstrated that coherent synchrotron radiation of various properties could be generated in an electron storage ring by using an external laser source. This research was supported by the Quantum Beam Technology Program of JST/MEXT. Under this support, a new experimental station has been constructed. The generation of coherent synchrotron radiation at the new site was successfully demonstrated in collaboration with Lille Univ. and Nagoya Univ. Some basic researches on coherent synchrotron radiation have been conducted with an ultrafast terahertz detector in collaboration with Karlsruhe Institute of Technology, Lille Univ., Nagoya Univ. and Kyoto Univ. Applications using coherent synchrotron radiation are under preparation. Some basic researches on the optical vortex beam have been started in collaboration with Hiroshima Univ.

Figure 2. Twin Polarization-variable Undulators for Coherent Synchrotorn Radiation generation.

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 have developed a method to produce ultra-short gamma-ray pulses and have demonstrated a photon-induced positron annihilation lifetime spectroscopy experiment, in collaboration with AIST. We have started constructing a system to produce intense gamma-rays by using an optical cavity, in collaboration with Kyoto Univ.

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

The UVSOR facility has been operational as a national synchrotron light source for lower energy photons from the terahertz wave to the soft X-rays. The machine was born as a low energy second generation light source and now it is 30 years old. However, the accelerators have been upgraded continuously. We have succeeded in introducing a specially designed electron beam optics intended to higher brightness. We have succeeded in commissioning six undulators. 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.

We continue upgrading the machine, year by year. In 2014, one old undulator at BL5U was remodeled. Now it has become capable of producing any polarization, such as horizontal and vertical linear polarizations and left and right circular polarizations. The non-linear focusing forces produced by such undulators make significant effects on the beam injection and storage. We are developing correction scheme for these non-linear effects.

Figure 3. Remodeling of Variable Polarization Undulator at BL5U.

Award

INAGAKI, Toshiki; 2013 Annual Meeting Award of the Particle Accelerator Society of Japan.

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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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.

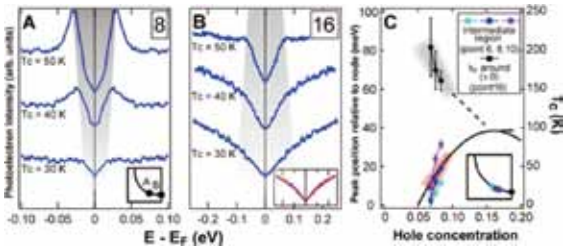

Figure 1. The symmetrized ARPES spectra of heavily underdoped Bi2212 at (A) the tip of the Fermi Arc region and (B) the antinodal region. Their corresponding locations on the Fermi surface are shown in the inset of (A).

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).
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- 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. ARPES Study on High-T_c Cuprate Superconductors

Two decades after the discovery of first high temperature superconductors, the microscopic mechanism of high-T_c superconductivity remains elusive. In conventional superconductors, it has been well established that electrons form so-called Cooper pairs to give rise to superconductivity. The pair binding manifests itself as an energy gap in many spectroscopic measurements. This energy gap, known as superconducting gap, appears at the superconducting transition temperature T_c where the resistance also vanishes. For high temperature superconductors, the story is more complicated. Over a wide region of compositions and temperatures, there exists an energy gap well above T_c. This energy gap is called "pseudogap," because there is no direct correlation to the superconducting transition. The origin of this pseudogap and its relation to the superconducting gap are believed to hold the key for understanding the mechanism of high-T_c superconductivity—one of the outstanding problems in condensed matter physics. In this regard, we performed ARPES measurements on the highly underdoped cuprate superconductor $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (Bi2212) to clarify the doping dependence of the gap structure. Through a systematic study of heavily underdoped Bi2212 samples with T_c = 30, 40, and 50K, two distinct energy gaps along the Fermi surface were identified in different parts of the momentum space: A small gap along with a sharp coherence peak near the nodal region and a relatively large gap near the antinodal region. Remarkably, these two energy gaps exhibit opposite trends with doping as shown in Figure 1A and 1B. Panel A displays the data taken at the tip of the "Fermi-Arc"—the region along the Fermi surface where a coherence peak is observed, while panel B shows the data from the antinodal region. As indicated by the shaded area, the gap associated with the Fermi Arc region is reduced as the doping level and T_c decrease, while the gap in the antinodal region increases. The complete doping evolution of these two energy gaps is summarized in panel C. The doping dependence of the gap magnitude in the antinodal region (black circles and dashed line) is consistent with the well-studied pseudogap behavior. The unexpected doping evolution of the gap in the Fermi Arc region (colored symbols and solid line), on the other hand, is the new discovery of this work. Based on these observations, we proposes a picture of two energy gaps coexisting in different regions of the momentum space. The gap associated with the Fermi Arc region is most likely the superconducting gap as evidenced by the existence of a coherence peak in ARPES spectra and a positive correlation between the gap magnitude and T_c. The pseudogap in the antinodal region may, however, arise from another mechanism such as Umklapp scattering by the antiferromagnetic correlations or competing states, such as stripes, polaronic behavior, or a charge-density-wave. This two-gap scenario not only provides natural explanation of the new ARPES results, but also resolves the contradictory results on the superconducting gap deduced from different experimental techniques.

This two-gap scenario has two important implications that could be important for developing a microscopic theory of high-T_c superconductivity. First, the pseudogap near the antinodal region in these deeply underdoped samples is unlikely a precursor state of the superconducting state, as had been suggested previously. Instead, it is more likely a state that competes with the superconducting state. Second, these data suggest that the weakened superconductivity in the underdoped regime arises not only from the loss of phase coherence associated with the decrease in the superfluid density but also due to the weakening of the pairing amplitude. In this case, a mechanism for the superconducting gap reduction could be related to the shrinkage of the coherent Fermi surface with less doping, leading to a smaller phase space for pairing.

2. Development of New Spin-Resolved ARPES

UVSOR Facility in Institute for Molecular Science equips two public undulator-beamlines for ARPES, one is BL5U in the photon energy $h\nu$ region of 20–200 eV and the other BL7U of $h\nu$ = 6–40 eV. Since the monochromator of BL5U is an old-style spherical grating type SGMTRAIN constructed in 1990s and the throughput intensity and energy resolution are poor, the beamline was planned to be replaced to state-of-the-art monochromator and end station. Then we designed a new spin and angle-resolved photoemission spectroscopy instrument with variable photon energy and polarization. We employed a Monk-Gillieson-type variableline-spacing plane-grating monochromator covering the photon energy of 20–200 eV. The end station shown in Figure 2 will equip a VLEED spin detector for spin-resolved ARPES. The beamline is constructed in FY2013–FY2014 and will be opened to users from FY2015.

Figure 2. Picture of the new spin-resolved ARPES end station of BL5U, UVSOR-III.

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2) W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, *Nature* **450**, 81–84 (2007).

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Electronic Structure and Decay Dynamics in Following Core Hole Creation in Molecules

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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.

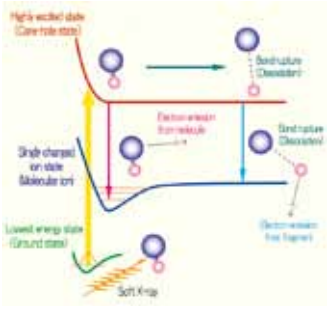

Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, Eds., S.A. Rice and A. Dinner, Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, "Ultrafast Dynamics in C 1s Core-Excited CF_4 Revealed by Two-Dimensional Resonant Auger Spectroscopy," *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).

1. Decay Processes Following Sulfur 2p Photoexcitation in OCS Studied by High-Resolution Two-Dimensional Electron Spectroscopy

In the current study, angle-resolved two dimensional (2D) electron spectroscopy,[1] where resonant Auger-electron spectra are recorded as a function of the photon energy, has been applied to the de-excitation processes in the S 2p excitation region of OCS, with previously unprecedented resolution.

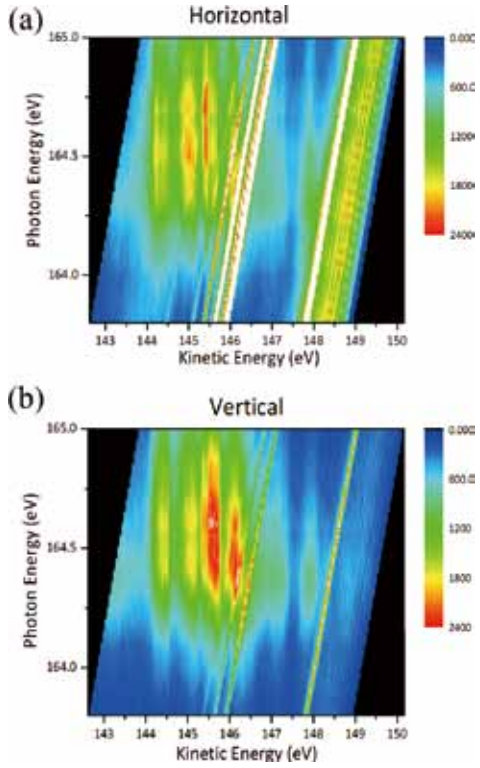

Figure 2. 2D maps of resonant Auger electron spectra after the S $2p_{3/2} \rightarrow \pi^*$ excitation of OCS, measured at horizontal (a) and vertical (b) directions relative to the electric vector of the incident radiation.

The 2D measurements were performed on the soft x-ray beam line BL6U at UVSOR. The undulator radiation was monochromatized by a variable included angle, varied line-spacing plane grating monochromator. For 2D electron spectroscopy, the monochromator bandwidth was set to ΔE_{Ph} ~20 meV at $h\nu$ = 165 eV. The kinetic energy of the emitted electrons was measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle with respect to the incident photon beam direction. The direction of the electric vector was set to be either parallel (horizontal) or perpendicular (vertical) to the axis of the electrostatic lens of the analyzer. The energy resolution of the analyzer was set to ΔE_k ~15 meV.

Figure 2 shows 2D maps of resonant Auger electron spectra following the S $2p_{3/2} \rightarrow \pi^*$ resonant excitation of OCS measured in the horizontal (a) and vertical (b) directions. The diagonal lines can be attributed to valence photoelectron lines, and clearly show vibrational side bands indicating that the net energy resolution is much better than 50 meV.

Clear island-like structures elongated in the vertical direction can be seen in both Figure 2(a) and Figure 2(b) in the kinetic energy region from 144 to 148 eV. In sharp contrast to the valence photoelectron lines, these structures do not show strong anisotropic angular distributions. To our knowledge, no detailed assignments have previously been given to them. In order to understand the origins of the structures, sophisticated theoretical calculations are highly desired.

2. Lifetime Broadening of Atomic Lines Produced upon Ultrafast Dissociation of HCl and HBr[2]

The excitation of a core electron to the lowest unoccupied antibonding orbital in a molecule reduces the molecular bond strength and in general populates a dissociative state. When the timescales of the nuclear motion and of the core–hole relaxation are similar, this leads to a peculiar situation which has been named 'ultrafast dissociation.' Here, the excited state starts to dissociate, and electronic decay can occur at any point during the dissociation, up to the point where dissociation can be considered as completed. The first evidence for such a process was reported in 1986 by Morin and Nenner.[3]

In the present study we revisit ultrafast dissociation following Cl $2p_{3/2}$ excitation in HCl and Br $3d_{5/2}$ excitation in HBr. The improved experimental resolution allows us to observe in detail the line-widths of both the atomic and molecular peaks. The atomic peaks are observed to be broader than the molecular vibrational peaks which are due to direct photoionization. We suggest that this broadening is due to the lifetime of the neutral, core-excited Cl* or Br* atomic fragment and can be retrieved from our experimental data.

The experiments were carried out at BL6U. The kinetic energies of electrons emitted perpendicular to the photon beam direction were measured by the MBS-A1. The energy resolution was set to ~12 meV or ~6 meV. The degree of linear polarization of the incident light was calibrated by measurements with rare gazes and found to amount to 90–100%. The direction of the electric vector was set to be either parallel or perpendicular to the axis of the electrostatic lens of the analyzer.

After careful analysis of the experimental data, the Lorentzian broadenings of the atomic peaks in HCl and HBr were found to be 96±5 meV and 91±5 meV, respectively. We suggest that these values correspond in good approximation to the lifetimes of the $2p_{3/2}$ hole in the Cl* atom and the $3d_{5/2}$ hole in the Br* atom.

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1) M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).
2) P. Lablanquie, H. Iwayama, F. Penent, K. Soejima and E. Shigemasa, *J. Electron Spectrosc. Relat. Phenom.* **195**, 96–100 (2014).
3) P. Morin and I. Nenner, *Phys. Rev. Lett.* **56**, 1913–1916 (1986).

Micro Solid-State Photonics

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1983 B.A. Fukui University
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Professional Employment
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1989 Research Associate, Fukui University
1993 Visiting Researcher, Stanford University (–1994)
1998 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

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2010 OSA Fellow Award, The Optical Society (OSA)
2012 SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014 IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)

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ZHENG, Lihe
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KONG, Weipeng*
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ONO, Yoko
INAGAKI, Yayoi

Keywords Solid-State Lasers, Nonlinear Optics, Micro Solid-State Photonics

"*Micro Solid-State Photonics*," based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion, UV to THz wave generation. Moreover, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. The future may herald new photonics.

Giant pulse > 10 MW was obtained in 1064nm microchip lasers using micro-domain controlled materials. The world first laser ignited gasoline engine vehicle, giant-pulse UV (355 nm, 266 nm) and efficient VUV (118 nm) pulse generations have been successfully demonstrated. Also, few cycle mid-IR pulses for atto-second pulses are demonstrated by LA-PPMgLN. We have developed new theoretical models for the micro-domain control of anisotropic laser ceramics. These functional micro-domain based highly brightness/brightness-temperature compact lasers and nonlinear optics, so to speak "Giant Micro-photonics," are promising. Moreover, the new generation of micro and/or microchip lasers by using orientation-controlled advanced ceramics can provide extreme high performances in photonics.

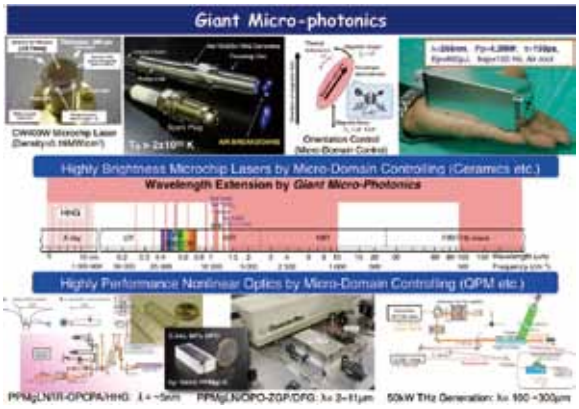

Figure 1. Giant micro-photonics.

Selected Publications

- H. Sakai, H. Kan and T. Taira, ">1 MW Peak Power Single-Mode High-Brightness Passively Q-Switched Nd^{3+}:YAG Microchip Laser," *Opt. Express* **16**, 19891–19899 (2008).
- M. Tsunekane, T. Inohara, A. Ando, N. Kido, K. Kanehara and T. Taira, "High Peak Power, Passively Q-Switched Microlaser for Ignition of Engines," *IEEE J. Quantum Electron.* **46**, 277–284 (2010).
- T. Taira, "Domain-Controlled Laser Ceramics toward Giant Micro-Photonics," *Opt. Mater. Express* **1**, 1040–1050 (2011).
- H. Ishizuki and T. Taira, "Half-Joule Output Optical-Parametric Oscillation by Using 10-mm-Thick Periodically Poled Mg-Doped Congruent $LiNbO_3$," *Opt. Express*, **20**, 20002–20010 (2012).
- R. Bhandari, N. Tsuji, T. Suzuki, M. Nishifuji and T. Taira, "Efficient Second to Ninth Harmonic Generation Using Megawatt Peak Power Microchip Laser," *Opt. Express* **21**, 28849–28855 (2013).

1. Timing Jitter Control of a Passively Q-Switched Nd:YVO_4/Cr^{4+}:YAG Laser by the Use of a Coupled Cavity

Timing jitter was measured in Nd:YVO_4/Cr:YAG passively Q-switched laser. Primary results with coupled cavity as shown in Figure 2 showed reduction of timing jitter by one order of magnitude down to 450 ns (2σ value), 40 μJ pulse energy and 2.5 ns pulse duration.

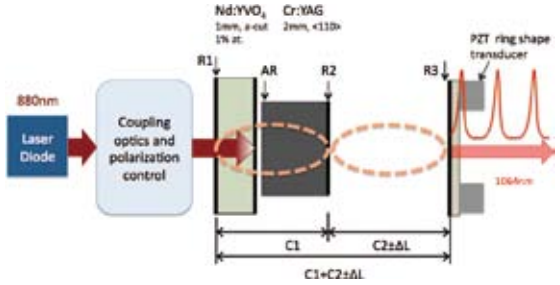

Figure 2. Schematic view of the Nd:YVO_4/Cr^{4+}:YAG passively Q-switched laser.

2. Highly Accurate Interferometric Evaluation of Thermal Expansion and *dn/dT* of Optical Materials

Thermo-mechanical and -optical properties of $Y_3Al_5O_{12}$ (YAG), YVO_4, and $GdVO_4$ were evaluated with high accuracy. Evaluation procedure that was established by authors enabled to suppress evaluation errors less than 2%, by means of the detection of temperature deviations in interferometric fringes on transmittance as shown in Figure 3.

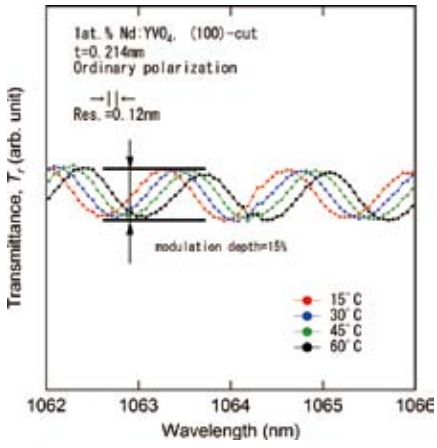

Figure 3. Temperature dependence of interferometric fringes in Nd:YVO_4.

Measured thermal expansion coefficient for YAG, [100]-YVO_4, [001]-YVO_4, [001]-$GdVO_4$, and [001]-$GdVO_4$ were 6.13, 1.76, 8.24, 1.19, and 7.26×10^{-6}/K at room temperature. Temperature coefficients of refractive index for YAG, YVO_4 in ordinary and extraordinary polarization, and $GdVO_4$ in ordinary and extraordinary polarization at room temperature for the wavelength of 1.06 μm were 12.1, 15.5, 8.41, 15.2, and 9.92×10^{-6}/K, respectively.

This work was ranked the fourth place in TOP-10 downloaded articles in June 2014 from OSA's Optical Materials Express.

3. Improvement of Laser-Beam Distortion in Large-Aperture PPMgLN Device by Using *X*-Axis Czochralski-Grown Crystal

Large-aperture periodically poled Mg-doped $LiNbO_3$ device using *X*-axis Czochralski-grown MgLN crystal was proposed to avoid a laser-beam distortion problem, as shown in Figure 4. Availability of periodic poling in 5-mm-thick MgLN and compatibility of wavelength-conversion characteristics in QPM-OPO were evaluated by comparing with conventional arrangement using *Z*-axis-grown crystal.

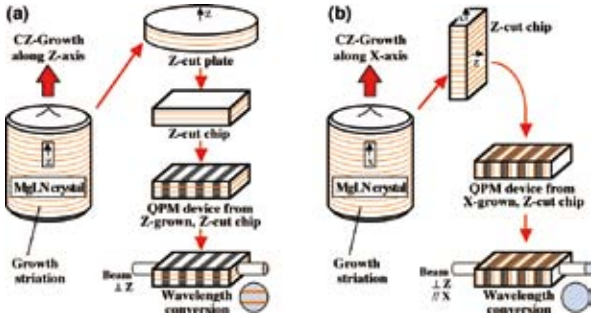

Figure 4. PPMgLN device fabricated from (a) *Z*-axis CZ-grown crystal, and (b) *X*-axis CZ-grown crystal.

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3) H. Ishizuki and T. Taira, *Opt. Express* **22**, 19668 (2014).

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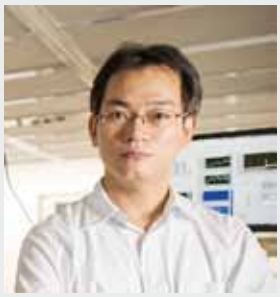
Ultrafast Laser Science

Laser Research Center for Molecular Science
Division of Advanced Laser Development



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Education
1994 B.S. University of Tsukuba
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Professional Employment
1999 Assistant Professor, The University of Tokyo
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2004 Guest Researcher, Max-Planck-Insitute of Quantum Optics
2006 Research Scientist, RIKEN
2008 Senior Scientist, RIKEN
2010 Associate Professor, Institute for Molecular Science
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MASUDA, Michiko

Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

Light is very common in daily life, on the other hand, light has many interesting physical properties, for example, constancy of velocity, wave-particle duality, *etc*. The study of light is still important in modern physics.

Light is electro-magnetic field, same as radio wave, however, the measurement of the waveform of light is not easy task even in the 21st century. The difficulty comes from the extremely fast oscillation of the light wave. The oscillation frequency of light wave is the order of hundred terahertz (THz = 10^{12} Hz), in other words, the oscillation period of light wave is the order of femtosecond (fs = 10^{-15} s).

In 2013, we have developed a new method for the measurement of light wave. It is called FROG-CEP, frequency-resolved optical gating capable of carrier-envelope phase determination. Our method does not need attosecond pulses, even self-referencing is possible. The electric field oscillation of infrared light with the period of several femtoseconds were clearly measured with the method as is shown in Figure 1.

Currently, amplitude modulation and phase modulation are common encoding techniques in optical communication. If we can encode information in the shape of the light wave itself, the communication speed becomes 3 orders of magnitude faster. We believe that our method, FROG-CEP, becomes very important to realize such communication technology.

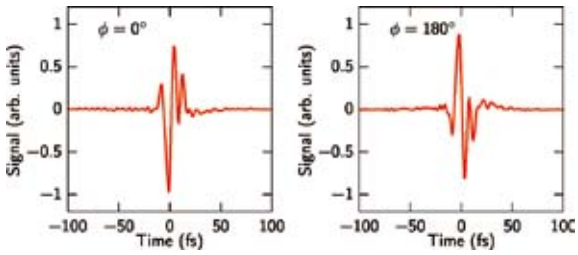

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

Other than FROG-CEP, ultrabroadband mid-infrared continuum generation through filamentation and single-shot detection of ultrabroadband mid-infrared spectra have been realized in our laboratory. We are developing such cutting edge technologies for ultrafast laser science.

Selected Publications

- Y. Nomura, H. Shirai, K. Ishii, N. Tsurumachi, A. A. Voronin, A. M. Zheltikov and T. Fuji, "Phase-Stable Sub-Cycle Mid-Infrared Conical Emission from Filamentation in Gases," *Opt. Express* **20**, 24741–24747 (2012).
- T. Fuji and Y. Nomura, "Generation of Phase-Stable Sub-Cycle Mid-Infrared Pulses from Filamentation in Nitrogen," *Appl. Sci.* **3**, 122–138 (2013).
- Y. Nomura, Y. T. Wang, T. Kozai, H. Shirai, A. Yabushita, C. W. Luo, S. Nakanishi and T. Fuji, "Single-Shot Detection of Mid-Infrared Spectra by Chirped-Pulse Upconversion with Four-Wave Difference Frequency Generation in Gases," *Opt. Express* **21**, 18249–18254 (2013).
- T. Fuji, "Single-Shot Broadband Mid-Ir Spectra Measured in the Visible via Upconversion," *Laser Focus World* **49**, 9 (1 page) (2013).
- Y. Nomura, H. Shirai and T. Fuji, "Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination," *Nat. Commun.* **4**, 2820 (11 pages) (2013).

1. Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination (FROG-CEP)[1,2)]

Recent progress of the coherent light synthesis technology has brought the generation of single-cycle pulses within our reach. To exploit the full potential of such a single-cycle pulse in any applications, it is highly important to obtain the full information of its electric field.

There has been a method to measure the oscillation of light wave using attosecond (as = 10^{-18} s) pulses (attosecond streaking, [*Science* **305**, 1257]), however, a huge high vacuum system is necessary for the measurement since attosecond pulses, which are in XUV region, are absorbed in air.

Here, we propose a novel pulse characterization scheme, which enables us to determine not only the intensity and phase profiles of ultrashort pulses but also their absolute carrier-envelope phase values without using attosecond pulses. The method is based on a combination of frequency-resolved optical gating and electro-optic sampling.

We have demonstrated the method by characterizing phase-stable sub-single-cycle 7 fs infrared pulses generated through filamentation[3,4)] by using a 30 fs reference pulse, which is much longer than the period of the carrier-wavelength of the characterized pulse. We have also demonstrated that the method has the capability of single-shot measurements. The self-referencing possibility of the method has been also discussed with numerical simulations. The results of our numerical simulations have clearly shown that it is possible to retrieve few-cycle 800 nm pulses with the absolute CEP information by self-referencing. It has turned out that approximately one octave spectrum and reasonable compression quality are necessary for the self-referencing, which is rather reasonable requirement for the waveform characterization of few-cycle pulses whose CEP becomes important. In principle, the concept has no limitation to characterize few-cycle pulses on measurable pulse duration or applicable wavelength regions thanks to the self-referencing possibility.

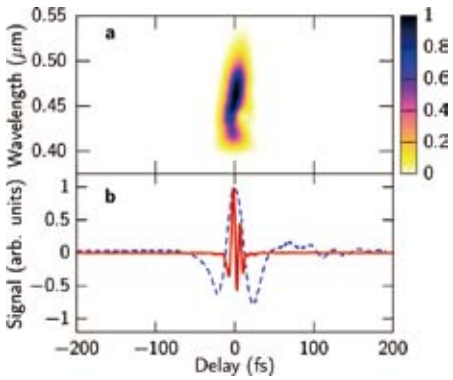

Figure 2. Experimental results of FROG-CEP. (a) The XFROG trace and (b) EOS signal measured in the experiment (blue dashed curve). The red solid curve shows the electric field reconstructed from the experimental data.

2. Sub-50-fs Pulse Generation from Thulium-Doped ZBLAN Fiber Laser Oscillator[5)]

Passively mode-locked fiber lasers operating around 1 μm and 1.5 μm have been extensively studied over the past decades. In recent years, thulium-doped fiber lasers have attracted significant attention because they extend the operating wavelength toward 2 μm region, which will be useful for various fields such as medical applications, remote sensing, micromachining, high harmonic generation, and mid-infrared generation. In particular, broad emission spectra of thulium-doped fibers make them ideal candidates for ultrashort pulse sources in this wavelength region. However, it is not trivial to obtain ultrashort pulses from fiber lasers where the effect of the dispersion from long fibers is quite significant.

An interesting approach would be using fibers made of materials with less dispersion. Fluoride glass known as ZBLAN (ZrF_4–BaF_2-LaF_3-AlF_3-NaF) has high transmittance in the mid-infrared region. The property of low absorption suggests that it also has low dispersion in the mid-infrared region. However, the property has been overlooked and no previous work has utilized ZBLAN fibers for developing ultrafast laser oscillators.

In this work, we have developed a passively mode-locked laser oscillator based on thulium-doped ZBLAN fibers pumped by a cw Ti:sapphire laser. Output pulses with the average power of 13 mW are obtained at the repetition rate of 67.5 MHz with the pump power of 140 mW. Thanks to low dispersion of ZBLAN, the spectra of the output beam was as broad as 300 nm at 30 dB below the peak. The generated pulses was compressed down to 45 fs, which is the shortest pulses generated from laser oscillators operating around 2 μm wavelength region to the best of our knowledge.

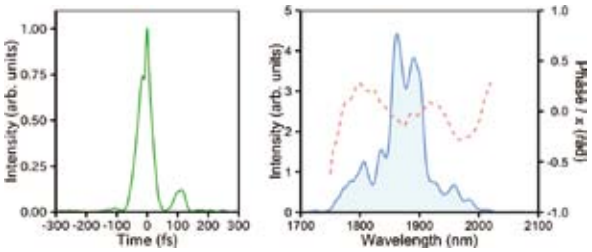

Figure 3. Measured pulse shape (Left). Measured spectral profile (Right, filled blue curve) and phase (Right, dashed red curve).

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3) Y. Nomura, H. Shirai, K. Ishii, N. Tsurumachi, A. A. Voronin, A. M. Zheltikov and T. Fuji, *Opt. Express* **20**, 24741–24747 (2012).
4) T. Fuji and Y. Nomura, *Appl. Sci.* **3**, 122–138 (2013).
5) Y. Nomura and T. Fuji, *Opt. Express* **22**, 12461–12466 (2014).

* EXODASS Program

† IMS International Internship Program

Dissociative Photoionization Studies of Fullerenes and Carbon Nanotubes and Their Application to Dye-Sensitized Solar Cells

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

KATAYANAGI, Hideki
Assistant Professor

We have observed the dissociative photoionization of the fullerenes. We studied the mechanisms and kinetics of C_2 release reactions from the fullerenes on the basis of the yield curves and the scattering velocity distributions of the fragments. We now intend to apply the above gas phase spectroscopy to functional materials such as carbon nanotubes (CNTs). Additionally we utilize the CNT to a catalytic counter electrode in dye-sensitized solar cells (DSSCs). This research aims at understanding the electron transfer phenomena from CNTs both in gas phase and in condensed phase.

1. Mass Resolved Velocity Map Imaging of Doubly Charged Photofragments from C_{60} and C_{70}

We have obtained 2D velocity images of the fragments from C_{60} and C_{70}. The 2D velocity images of fragments were found to be convolutions of isotropic center-of-mass velocity acquired by the C_2 emission and anisotropic velocity of C_{60} in the parent molecular beam.

2. Gas Phase Spectroscopy of CNTs

We have started to build a vacuum apparatus for the gas phase spectroscopy of CNTs. With the apparatus we will first perform experiments using the fullerenes and then improve the apparatus to achieve experiments using CNTs.

3. Development and Evaluation of CNT Catalytic Counter Electrodes for DSSCs

To improve photovoltaic energy conversion efficiency of the DSSC, the rate of charge transfer reaction on the counter electrode is important. We prepared the counter electrodes using commercial CNT aqueous dispersions. We have started the impedance spectroscopy of the CNT electrodes in order to elucidate the effect of series resistance of the electrodes on the performance of DSSC.

In-situ Soft X-Ray Spectromicroscopic Study of Chemical and Biological Systems

UVSOR Facility
Division of Beam Physics and Diagnostics Research

OHIGASHI, Takuji
Assistant Professor

We have constructed a scanning transmission X-ray microscope (STXM) beamline in the soft X-ray region at BL4U in the UVSOR-III facility.[1,2] One of the advantages of the STXM is a high tolerance for environments of samples. For example, vacuum is not required for samples and even the samples in water can be observed by using soft X-rays in the water window region (282 ~ 539 eV). This advantage enables the STXM to perform *in-situ* observation easily combined with a long working distance. Hence, we have been developing *in-situ* sample cells for the STXM measurement.

A schematic image of cross section of a liquid flow sample cell is shown in Figure 1. This sample cell uses two silicon nitride membranes of 100 nm thick as windows sealed by two O-rings. Liquid flows between a gap of the two membranes by using a tubing pump. Then, the gap width (*i.e.* thickness of the liquid) can be tuned by the pressure of helium gas in a main STXM chamber. As a test measurement, by changing the liquid from pure water to ethanol simply, their absorption spectra around oxygen 1s were measured (Figure 2). Recently, a window membrane with gold electrodes pettern was developed and *in-situ* measurement of electro-chemistry was performed.

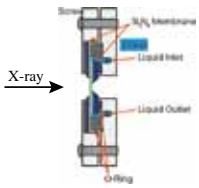

Figure 1. A liquid flow cell in section.

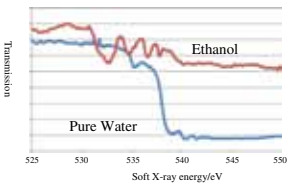

Figure 2. Transmission spectra of pure water and ethanol.

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Visiting Professors

Visiting Professor
NODA, Susumu *(from Kyoto University)*

Strong Coupling of Single Atoms to Photonic Crystal Cavity Field

We have investigated photonic crystal structures which enable modification of propagation properties of an electromagnetic field and also tight confinement of the field to a tiny resonator. Accordingly the field strength inside the resonator is much enhanced and therefore the field can be strongly coupled to a quantum emitter such as a quantum dot even at a single photon level. Such a nanostructure device would be suitable for applications in optical communication and future quantum information processing in terms of its scalability. We have studied the strong coupling of the cavity field with a quantum dot and also the Purcell effect. Recently we have been interested in adopting a single cold atom as a quantum emitter, which shows much longer coherence time and therefore would be desirable for future application. Cold atoms are first loaded into a magneto-optical trap and then one of them is captured in tightly-focused optical tweezers. A movable lens-positioner can translate the position of the focal point, thereby transferring the trapped atom to the vicinity of the photonic crystal cavity. With this technique, the strong coupling of the single atom with the cavity field will be studied.

Visiting Professor
ITO, Atsushi *(from Tokai University)*

X-Ray Spectromicroscopy of Biomedical Specimens

Soft X-ray microscopy has a great advantage over other microscopies in the mapping of light elements or molecules containing such elements at high resolution. The mapping is realized with soft X-ray scanning microscope (STXM) using an unique imaging method X-ray spectromicroscopy which utilizes distinctive spectral features of elements and molecules, that is, absorption edges and XANES profiles observed in the vicinity of the absorption edge. To apply to biomedical specimens, XANES profiles have been surveyed for a variety of biomolecules such as DNA, proteins (histone and albumin), sulfur-containing amino acids, calcium-containing biomolecules and iron-containing proteins at the C-K, N-K, O-K, S-L, Ca-L and Fe-L absorption edges in the soft X-ray region. One of the most interesting and useful results obtained in this survey is that DNA and histone, a nuclear protein, exhibited significantly different spectra at the N-K edge, suggesting the possibility to image DNA and proteins in cellular nuclei separately. We are now interested in the time dependence of distribution pattern of DNA and proteins in nuclei that undergo apoptosis.

Visiting Associate Professor
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Atomistic Dynamics in Metal-Semiconductor-Oxide (MOS) Transistor

This year, we have investigated on the static behavior of MOS transistors. MOS transistors are widely used in semiconductor industry. One of the bottlenecks in achieving the lower power consumption is random telegraph noise. In order to avoid the malfunctioning arising from the noise, the supply voltages should be higher than the optimal condition, resulting higher power consumption. The noise behavior in this study was investigated by manufacturing a transistor-element group of a fully-depleted silicon-on-insulator (FD-SOI) MOS transistors at a technology node equivalent to 350 nm node. The FD-SOI CMOS transistors haves a substrate terminal where we can externally control the vertical field in MOS channel. The low frequency drain-source noise around 100 Hz was measured at different substrate voltages. For a transistor (L = 0.4 μm/W = 1.0 μm) with high RTS noise was selected. At the substrate voltage of 0 V, the transistor shows prominent RTS noise; current shows two distinct levels with a difference of 1×10^{-8} A. At lower substrate voltage of –5 V, the RTS noise completely disappeared. Traditionally, this phenomenon was explained in terms of a defect in channel and channel depth within a classical band theory. In this study, this phenomenon was interpreted within an atomistic model based on quantum mechanics.