RESEARCH ACTIVITIES Photo-Molecular Science

Molecules respond to photon irradiation in a variety of ways, including photo-induced transitions and photochemical reactions. We have employed various light sources and experimental schemes to elucidate molecular structures and properties, and to control chemical reactions and molecular functions. We have also developed novel and advanced light sources for molecular science. Two of research facilities, the Laser Research Center for Molecular Science and the UVSOR Facility, conduct collaborative researches having intimate contacts with the Department of Photo-Molecular Science.

The main topics pursued in the Department include: Development of novel laser spectroscopic methods to reveal fundamental properties of molecules, development of high-resolution optical microscopic methods and application to nanomaterials, coherent control of molecules with ultrafast techniques, spectroscopy of inner-shell excited molecules and fundamental vacuum-UV photochemistry, investigation of the functionality of solid-state materials, developments of novel laser and synchrotron-orbit radiation sources, and so on.

Development of Advanced Near-Field Spectroscopy and Application to Nanometric Systems

Department of Photo-Molecular Science Division of Photo-Molecular Science I



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There is much demand for the study of local optical properties of molecular assemblies and materials, to understand mesoscopic phenomena and/or to construct optoelectronic devices in the nanometric scale. 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 offer a direct probe of dynamical processes in nanomaterials. It may provide essential and basic knowledge for analyzing origins of characteristic features and functionalities of the nanometric systems. We have constructed apparatuses of near-field spectroscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. They enable near-field measurements of twophoton induced emission and femtosecond transient transmission, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal behaviors of various metal-nanoparticle systems and molecular assemblies.

1. Visualization of Plasmon Wavefunctions and Enhanced Optical Fields Induced in Metal Nanoparticles

We recently reported that wavefunctions of localized plasmon resonances of chemically synthesized metal (Au and Ag) nanoparticles are visualized by near-field transmission or two-photon excitation measurements.^{1,2)} Figure 1 shows typical near-field transmission images of longitudinal plasmon modes on a Au nanorod, which correspond to the square moduli of the plasmon wavefunctions. We also visualized optical fields in Au nanoparticle assemblies by the near-field two-photon excitation imaging method.^{1,3)} It was revealed for the dimers that highly localized optical field is generated at the interstitial sites between the particles. In many-particle assemblies, the localized fields were especially intensified at the rim parts of the assemblies.



Figure 1. Near-field transmission images of a Au nanorod (diameter 20 nm, length 510 nm), observed at 678 nm (A) and 729 nm (B).

We are now extending the studies to metal nanostructures manufactured by the electron-beam lithography technique, in collaboration with researchers of other institution. Peculiar nano-optical characteristics and characteristic plasmon waves have been found for some metal nanostructures. Near-field properties of nano-void structures opened on thin gold metallic films on substrates have been also characterized, and the field distributions in the vicinities of the voids have been visualized. The detailed analyses of the characteristic optical fields are now under way. Such a study is essential as a basis for designing unique optical properties and functions of metal nanostructures, and their applications to highly sensitive spectroscopic methods and exotic photochemical fields.

2. Properties of Two-Photon Induced Photoluminescence from Au and Ag Nanoparticles

We investigated properties of photoluminescence from Au and Ag nanorods induced by near-field two-photon excitation. For Au nanorods,⁴⁾ photoluminescence spectrum showed two peaks around 550 and 650 nm regardless of the rod dimensions, whereas the intensity ratio of the two spectral compo-

nents varies from rod to rod. The observed spectral features were discussed based on electromagnetic calculations. We found that the spectral components were attributable to the interband transition of gold, and the intensity variation was explainable in terms of local field enhancement in the vicinity of the nanorod due to plasmon-mode excitation.

We also discussed the mechanism of the luminescence from Ag nanowires.⁵⁾ The luminescence was most probably attributed to emission from the oxidized surface layer of the nanowires, which was enhanced in resonance with plasmons on the wires. In a similar way to the Au case, we succeeded in visualization of enhanced electric fields and plasmon modes for Ag nanowires (Figure 2) by the near-field two-photon excitation imaging, by detecting the luminescence from silver.



Figure 2. Topography (left) and near-field two-photon excitation (right) images of a silver nanowire (diameter 25 nm, length 6 μ m).⁵⁾ © 2009 Royal Society of Chemistry.

3. Bioimaging with Two-Photon-Induced Luminescence from Triangular Nanoplates and Nanoparticle Aggregates of Gold

Two-photon laser scanning microscopy (TPLSM) has been widely used recently in the field of biological imaging because of its merit in z-axis resolution and in effective avoidance of photodamage. Since it is difficult to completely eliminate the photobleaching for ordinary fluorophores, ideal optical imaging agents for TPLSM still have to be found. Recently, our group and some others found that two-photon-induced photoluminescence (TPIPL) from Au nanoparticles in the visible region shows quite high efficiency upon femtosecond nearinfrared excitation. Based on detailed experimental and theoretical studies on the luminescence characteristics, we found that TPIPL from triangular Au nanoplates is especially efficient. Chemically stable (and as a consequence nontoxic) nature of Au is also beneficial in practical applications. Au nanoplates thus have the potential to be ideal agents for biosensing for microanlysis or bioimaging with TPIPL by TPLSM. In the present study we have demonstrated that Au nanoplate could be indeed a promising material for bioimaging studies by TPLSM.⁶⁾

Images of yeast cells conjugated to nanoplates were recorded by (far-field) TPLSM for biological use (Figure 3). We found that dried yeast as well as living cells in water can be clearly imaged by this method. We also found that cells



Figure 3. SEM (left) and far-field TPIPL (right) images of dried yeast cells conjugated to triangular Au nanoplates (base length ~300 nm) and some naked dried yeast cells.⁶⁾ Scale bar: 5 μ m. © 2009 Wiley-VCH Verlag.

conjugated with aggregated Au nanospheres give bright TPIPL, while isolated nanospheres were TPIPL-inactive.

4. Construction of Apparatuses for Nonlinear and Ultrafast Near-Field Spectroscopy

In previous studies we achieved ultrafast near-field imaging with a time resolution of ~100 fs.^{2,7)} To further extend the dynamical studies of plasmons, we are now developing basic technologies to achieve near-field time-resolved measurements with <20 fs time resolution. We are also constructing an apparatus for near-field/far-field microscopic nonlinear optical measurements based on the technique of atomic-force microscope.

5. Near-Field Imaging of Organic Molecular Assemblies and Hybrid Systems

We are studying nanometric structures and optical properties of organic molecular assemblies such as carbon nanotubes embedded in sugar polymer chains, LB films of functional conjugated molecules, and hybrid systems consist of metal nanoparticles and organic functional materials, mainly as collaborations with other research groups.

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Quantum-State Manupulation of Molecular Motions

Department of Photo-Molecular Science Division of Photo-Molecular Science I



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Molecules in gas phase undergo translational, rotational and vibrational motions in a random manner, and the total molecular system is a statistical ensemble that contains a number of molecules in many different states of motions. This research group aims to establish methods to manipulate the quantum-state distribution pertinent to molecular motions, by utilizing the coherent interaction with laser lights. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for manipulation of molecular motions.

1. Nonadiabatic Rotational Excitation of Molecules by Nonresonant Intense Femtosecond Laser Fields

When a gaseous molecular sample is irradiated by an intense nonresonant ultrafast laser pulse, the laser field exerts a torque that aligns the molecular axis along the laser polarization vector, due to the interaction with the molecular anisotropic polarizability. The process has now been termed commonly as "nonadiabatic molecular alignment," and has been attracting much attention because of interesting physics involved and possible broader applications.¹⁾ Here the field–molecule interaction only remains in much shorter duration than the characteristic time for molecular rotation, and thus the nonadiabatic rotational excitation (NAREX), where rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP), a non-stationary superposition of rotational eigenstates.

This research group has developed a method for exploring the NAREX process in a quantum-state resolved manner by using resonance-enhanced multiphoton ionization (REMPI), and reported state distributions after the impulsive excitation with a fundamental output of a femtosecond (fs) Ti:Sapphire laser.^{2,3)} It has been shown that the state distribution is a useful experimental source for verifying the excitation process, since population for each rotational level is proportional to the square of the probability amplitude of the corresponding eigenstate in the rotational WP thus created.

The state-resolved REMPI probe has also been coupled successfully with double-pulse fs excitation. The population for each rotational eigenstate changes oscillatory against the delay between the excitation pulses. When the population of the initial pure state is probed, the delay-time dependent signals provide the phases as well as amplitudes of the WP. Such an experimental reconstruction of WP has recently been demonstrated on the adiabatically cooled molecular sample of benzene by this research group.⁴⁾ The determined phases show a clear signature for impulsive rotational excitation in non-perturbative regime driven by the intense ultrashort pulse.

The double-pulse excitation study has been extended to probe population changes in various eigenstates with different rotational quantum numbers. For benzene molecules, states with *J* ranging from 0 to 4 with K = 0-3 have been examined. This systematic investigation experimentally verifies the *K* dependence of the excitation pathways in the NAREX process for symmetric-top molecules.

2. Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields

In a quantum-mechanical description, the anisotropy of molecular system is represented as a non-uniform distribution of projections, M, of angular momenta onto a space-fixed (Z) axis. In particular, the system is designated as being *oriented* when the populations for +M and -M are different, while it is *aligned* when the populations for $\pm M$ are the same, but those for different |M| differ from one another. In previous studies, the application of circularly polarized radiations had been exclusively considered for the realization of orientation, because it is regarded as being the only way to induce the required helical interaction that breaks the right/left-handed symmetry around the Z axis. The molecular-axis orientation has already been reported in several studies with intense nonresonant radiation, but all of them implemented linearly polarized light, and thus were related to the angular-momen-

tum alignment. Quite recently, this research group theoretically shows and experimentally verifies that a pair of linearly-polarized intense ultrafast pulses creates molecular ensembles with oriented rotational angular momentum in ultrafast time scale, when the delay and the mutual polarization between them are appropriately arranged (as shown in Figure 1). Asymmetric distribution for +M and -M sublevels relies on quantum interference between the rotational WPs created in the stimulated Raman excitation by the first and the second pulses. The present approach provides spatiotemporally propagating ensembles, of which classical perspective are molecules rotating in clockwise or counter-clockwise direction.



Figure 1. Experimental scheme to create and observe the angularmomentum orientation in molecular rotation.

3. Nonadiabatic Vibrational Excitation by Nonresonant Intense Ultrafast Laser Fields

Nonadiabatic interaction with a nonresonant intense ultrafast laser field can also coherently excite the vibration of molecules, because the molecular polarizability depends on vibrational coordinates. By adopting the similar method to the NAREX studies, nonadiabatic vibrational excitation (NAVEX) of intermolecular vibrations has been successfully realized for benzene clusters by this research group. Here, benzene clusters generated in a supersonic expansion were irradiated with laser pulses (~800 nm, 40–200 fs duration, up to 40 TW/cm² in intensity) from the fs Ti:Sapphire laser. Observed changes in intensities of vibronic bands of the benzene dimer indicated the population transfer pertinent to intermolecular vibrational excitation induced by impulsive Raman process. Double-pulse experiments have also been performed, to show that the populations in the ground and excited intermolecular vibrational states oscillatory changed against the delay between the two pulses (see Figure 2). The beat frequencies for the population changes match well with those of the intermolecular modes obtained by the previous ns stimulated Raman spectroscopic studies.⁵⁾ This fact confirms that quantum WPs pertinent to intermolecular vibrations in the ground state manifold were created via impulsive stimulated Raman process by a single fs laser pulse. The similar experiment has been performed to record the time-domain spectrum of benzene



Figure 2. Double-pulse NAVEX spectra of benzene dimer, recorded by probing cold (red) and hot (blue) band transitions.

trimer, which provides the first experimental information on its intermolecular vibrations.

4. New Experimental Setup for NAREX and NAVEX Studies

A new vacuum chamber and a high-reputation rate dye laser system have been installed for REMPI-probed studies on NAREX/NAVEX processes. The chamber is differentially pumped in two stages and equipped with a high-pressure pulsed valve, which can be operated up to 80 atm at 1 kHz. The laser system runs also at 1 kHz by pumping with a third harmonic of a Nd:YLF laser with the pulse duration of <10 ns, and affords the doubled output of ~50 μ J/pulse at 220–260 nm. High reputation in data acquisition will greatly improve the quality of REMPI spectra to be observed. The performance of the new setup is now examined in the investigation of the intermolecular vibrational excitation of NO–Ar.

5. Development of Coherent ns Pulsed Light Sources and Its Application to Adiabatic Population Transfer

Adiabatic interactions with coherent pulsed radiation can accomplish highly efficient population transfer between quantum states. For realizing such an adiabatic quantum-state manipulation, we are constructing laser systems which deriver single-longitudinal mode (SLM) ns pulses. Among various coherent population transfer methods, we are planning to mainly adopt chirped adiabatic Raman passage (CARP),⁶⁾ where one or both of the laser frequency to drive stimulated Raman transitions is swept so as to cross over the two-photon resonance. This method affords multiple advantages, e.g., robustness in transfer probability against variation in laser parameters and broader applicability without necessity for radiation in one-photon resonance to molecular transitions. The laser system for CARP experiments under construction is based on the optical parametric oscillation (OPO), which is injection-seeded by an extracavity cw diode laser to achieve the SLM operation. The seeding laser frequency is phase modulated at appropriate RF frequency to attain the frequency chirp to drive the CARP process. The OPO operates near the degenerate condition, so that its signal and idler waves can be used for pump and Stokes fields for stimulated Raman transitions. This design greatly reduces the complication in the setup and will provide much simpler and reliable operation for CARP experiments.

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Development of High-Precision Coherent Control and Its Applications

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



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Coherent control is based on manipulation of quantum phases of wave functions. It is a basic scheme of controlling a variety of quantum systems from simple atoms to nanostructures with possible applications to novel quantum technologies such as bond-selective chemistry and quantum computation. Coherent control is thus currently one of the principal subjects of various fields of science and technology such as atomic and molecular physics, solid-state physics, quantum electronics, and information science and technology. One promising strategy to carry out coherent control is to use coherent light to modulate a matter wave with its optical phase. We have so far developed a high-precision wave-packet interferometry by stabilizing the relative quantum phase of the two molecular wave packets generated by a pair of femtosecond laser pulses on the attosecond time scale. We will apply our high-precision quantum interferometry to gas, liquid, solid, and surface systems to explore and control various quantum phenomena.

1. Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales¹⁾

Interference fringes of quantum waves weave highly regular space-time images, which could be seen in various wave systems such as wave packets in atoms and molecules, Bose Einstein condensates, and Fermions in a box potential. We have experimentally designed and visualized spatiotemporal images of dynamical quantum interferences of two counterpropagating nuclear wave packets in the iodine molecule; the wave packets are generated with a pair of femtosecond laser pulses whose relative phase is locked within the attosecond time scale. The design of the image has picometer and femtosecond resolutions, and changes drastically as we change the relative phase of the laser pulses, providing a direct spatiotemporal control of quantum interferences.



Figure 1. Pump-control-probe scheme for tailoring and visualizing the quantum carpet in the iodine molecule. (Left) Three femtosecond laser pulses are employed. Two of them are phase-locked and used as the pump and control pulses, and the other one is not phase-locked and is used as the probe pulse. The fluorescence signal induced by the probe pulse is measured with a photomultiplier tube attached to a monochromator. (Right) The model simulation of the quantum interference of two wave packets created on the *B*-state potential curve of the iodine molecule by the pump and control pulses. The interference shows a highly regular space-time image that looks like a carpet.



Figure 2. Comparisons of the quantum carpets measured (left) and simulated (right) at the pump-control relative phases $\theta_{pc} = (a) 0^{\circ}$, (b) 90°, (c) 180°, and (d) 270°. The color scaling is common within each set of measured or simulated carpets; the maxima of those two sets have the same color. The origin $\tau_{probe} = 0$ of the simulated carpet denotes a position of the top of the first oscillation around the outer turning point. The simulations include the interactions with the pump, control, and probe pulses. The parameter $\tau_{control}$, used for the simulation of $\theta_{pc} = 0^{\circ}$, was 468.920 fs.

2. Optical Control and Mode Selective Excitation of Coherent Phonons in $YBa_2Cu_3O_{7-\delta}{}^{2)}$

Femtosecond time-resolved reflectivity measurement is performed on YBa₂Cu₃O_{7- δ} films. Coherent phonons of both the Ba–O and Cu–O modes are observed at frequencies of 3.4 and 4.3 THz, respectively. Amplitudes of both Ba–O and Cu– O modes are optically manipulated by using a pair of femtosecond pulses, the separation time of which is controlled. Coherent phonons of the Ba–O and Cu–O modes are completely suppressed at the double-pulse separation times of 135.0 and 108.5 fs and those amplitudes are enhanced at 217 and 270 fs, respectively.

Award KATSUKI, Hiroyuki; PCCP Prize.



Figure 3. Time-resolved reflectivity of a photo-excited YBa₂Cu₃O_{7- δ} thin film by irradiation of a pair of femtosecond laser pulses at double-pulse separation time of 0 (a), 108.5 (b), 135 (c), 217 (c), and 270 fs (e).



Figure 4. Fourier transformation of the transient relectivity change of a photo-excited $YBa_2Cu_3O_{7-\delta}$ thin film by irradiation of a pair of femtosecond laser pulses at double-pulse separation time of 0 (a), 108.5 (b), 135 (c), 217 (d), and 270 fs (e).

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Molecular Inner-Shell Spectroscopy: Electronic Structure and Intermolecular Interaction

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



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In order to reveal electronic structure and intermolecular interaction of molecular solids, liquids, and clusters, we are developing and improving several kinds of soft X-ray spectroscopic techniques and also an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

1. Development of a Liquid Flow Cell to Measure Soft X-Ray Absorption in Transmission Mode¹⁾

We have developed a liquid flow cell for transmission measurement of soft X-ray absorption spectra of liquid samples. The liquid flow cell consists of four regions as shown in Figure 1; (I) vacuum region below 1.0×10^{-4} Pa, connected to the soft X-ray undulator beamline, (II) helium buffer region filled by 1-atm helium, (III) liquid layer and flow region, and (IV) photodiode region in the helium atmosphere. Each region is separated by a 100 nm-thick SiN_x membrane. The window size is $200 \times 200 \ \mu\text{m}^2$ in the region I/II and $2 \times 2 \ \text{mm}^2$ in the regions II/III and III/IV. The photon energy calibration is simply carried out by mixing a reference such as oxygen in the helium gas. Fresh liquid samples can be continually supplied to avoid the radiation damage. We have tested this cell for the measurement of O K-edge X-ray absorption spectra in absorbance of liquid water. Thickness of the liquid water layer (region III) is controlled to be ~600 nm by optimizing a water flow speed in a tubing pump system. The present liquid flow cell may enable us to investigate electronic structure of liquid samples confined at a nano-scale space by increasing the helium pressure in the regions IV and II and/or by slowing down the liquid flow.



Figure 1. A schematic soft X-ray transmission liquid cell.

2. Strong Double Excitation Features in Soft X-Ray Absorption Spectra of Ferrocene and Ferrocenium Compounds²⁾

We measured the Fe 2p X-ray absorption spectra of decamethyl ferrocene (Fe 3d⁶) and ferrocenium hexafluorophosphate (Fe 3d⁵). The 2p-edge features of 3d transition metal compounds have been attributed, variably, to an atomic multiplet model or a covalent bonding model. A unique covalent bonding between Fe and the two cyclopentadienyl (Cp) rings, especially, the ligand π and out-of-plane 3d*_{*x*Z,*y*Z} (e_{1g}) orbitals, suggests that covalent effects will be most important in the spectral features.

We found the Fe 2p excitation parallel to the π (//z) direction cannot be interpreted within a single excitation picture and is split into two strong features as shown in Figure

2. *Ab initio* CI calculations predict a significant role of the double excitation features in the Fe 2p spectra of both Fe^{II} (Cp)₂ and the $[Fe^{III}(Cp)_2]^+$ ion. An additional low energy feature (W) observed in $[Fe^{III}(Cp)_2]^+$ is attributed to a Fe 2p to SOMO excitation.



Figure 2. Fe 2p-edge spectra of $[Fe^{II}(Cp)_2^+][PF_6^-]$, $Fe^{II}(Cp-(CH_3)_5)_2$ and $Fe^{II}(Cp)_2$.

3. Inner Electronic States beneath Electrodes: Fluorescence-Yield X-Ray Absorption of Pentacene Derivative Films³⁾

The electronic states of inner organic thin films were investigated by X-ray absorption spectroscopy in a bulksensitive fluorescence yield (FY) mode. The thin films of the synthesized pentacene derivative (HAPn), 6,13-dihydrodiazapentacence ($C_{20}N_2H_{14}$), on SiO₂-covered Si substrates were



Figure 3. N K-edge X-ray absorption spectra of the HAPn thin film (40 nm thick) deposited on the oxidized Si substrate: Detected in (a) PEY mode and (b) FY mode. The incident angle of X-rays is defined from the surface normal. The spectra are normalized by the signal height at around 420 eV. The sample was stored for 2 weeks in a desiccator at room temperature.

fabricated and their morphology and crystallinity were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis, respectively. The observed N K-edge FY spectra were different from the surface-sensitive spectra measured in a partial-electron-yield (PEY) mode as shown in Figure 3. The incident angle dependence of the FY spectra was consistent with the expected molecular orientation in the thin films. As a result, we successfully obtained the N and C Kedge FY spectra of the inner HAPn thin films, even beneath the Au electrodes.

4. Origin of Fine Structures on the Dissociative $1s-\sigma^*$ Resonance in X-Ray Absorption Spectra of $O_2^{4)}$

We attempted to explain a puzzling long-tailed peak shape of the X-ray absorption spectrum of the oxygen molecule in the energy region around 539 eV by taking into account the Rydberg-valence and vibronic couplings. The long-tailed feature is found to arise from two dissociative σ^* states and the sudden drop in intensity is related to decrease in transition dipole near the crossing point between the repulsive σ^* and weak 3s Rydberg states with the quartet ion core. This is supported by numerical wave-packet simulations allowing for all inter-channel couplings between the Rydberg and valence manifolds with the quartet (Q) and doublet (D) ion cores in a diabatic representation of the core-excited states as shown in Figure 4.



Figure 4. Theoretical X-ray absorption spectra obtained for the excitation to all the channels (solid line), and Q (dashed red line) and D (dash-dotted green line) channels.

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Photoabsorption and Photoionization Studies of Fullerenes and Development of High-Efficiency Organic Solar Cells

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



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The total photoabsorption cross section curves of C_{60} and C_{70} at hv = 1.3 to 42 eV were determinined by using photon attenuation method in the UVSOR facility. Moreover, the yield curves of singly- and multiply-charged photoions from fulle-renes were measured at hv = 25 to 200 eV. We have thus studied the mechanisms and kinetics of sequential C_2 -release reactions on the basis of (i) the yield curves for the fragments $C_{60(70)-2n}^{z+}$ as a function of the primary internal energy of the parent $C_{60(70)}^{z+}$ and (ii) the 3D velocity distributions (velocity map imaging) of the fragments.

In the second topic we have fabricated dye-sensitized solar cells (DSCs) containing Ru dye and iodide electrolyte and measured their short-circuit current density and the intensity of the transmitted light to estimate the wavelength dependence of the incidence photon-to-current conversion efficiency (IPCE) and photoabsorbance (ABS) in the range of 300 to 1000 nm. In addition, we evaluated the quantum yield (APCE) of DSCs for the electron injection from the excited orbital of Ru dye to the conduction band of TiO₂ nano particles. Our final goal is to develop DSCs with high performance and long lifetime by improving ABS and APCE mainly in the near infrared region.

1. Photoabsorption Cross Section of C₇₀ Thin Films from the Visible to Vacuum Ultraviolet¹⁾

Absolute photoabsorption cross sections of C_{70} thin films were determined for *hv* values from 1.3 to 42 eV using photon attenuation. The spectrum showed a prominent peak of 1320 Mb at 21.4 eV with several fine structures mostly due to $\sigma \rightarrow \sigma^*$ single-electron excitation. The complex refractive index and complex dielectric function were calculated up to 42 eV with Kramers-Kronig analyses. From the present data of C_{70} thin films, the cross section curve of molecular C_{70} was calculated using the standard Clausius-Mossotti relation dealing with



Figure 1. Absolute photoabsorption cross sections of a single C_{70} molecule.

correction of the local electromagnetic field, with a plausible assumption that the anisotropy in molecular structure of C_{70} was smeared out by molecular rotation at room temperature.

2. Potential-Switch Mass Gate Incorporated into a TOM Spectrometer²⁾

A photoionization spectrometer for velocity map imaging (VMI) has been developed for measuring the scattering distribution of fragment ions from polyatomic molecules. The mass gate and an ion reflector in the spectrometer are capable of discriminating ions with a particular mass-to-charge ratio m/z. The basic functions and feasibility of these devices were tested experimentally. The photoions from SF₆ were extracted into a time-of-flight (TOF) mass spectrometer by pulsed electrostatic fields. Mass resolution of the fragments was very poor in Figure 2a, because the stationary reverse electric field exists at the ionization region in the absence of the extraction pulses. When the pulse-application timing on the mass gate was tuned to a specific m/z, an exclusive peak of the selected ions was present on a TOF spectrum (Figure 2b).



Figure 2. (a) TOF mass spectrum of photofragments from SF₆ at hv = 100 eV. (b) Peak of SF₃⁺ selected by applying a 5-V pulsed voltage to the mass gate at an appropriate timing.

3. Mass-Selected Velocity Map Imaging of Fullerenes

The performance of the mass gate in the VMI spectrometer was investigated by the computer simulations of the ion trajectories of photofragments from C_{60} . The initial three-dimensional velocity distribution of C_{58}^+ was projected onto the image plane with an energy resolution better than 10 meV. The C_{58}^+ image was free from the contamination of other ions such as C_{60}^+ and C_{56}^+ . We have also tried to deconvolute the effect of the initial beam temperature with the aid of a low pass filter.³⁾

4. Measurements of IPCE and Photo-Absorbance of Dye-Sensitized Solar Cells

The IPCE curve a in Figure 3 calculated from the density of the output short-circuit current J_{SC} and the number of the incident photons on the cell I_P agrees with the curve b that was obtained using a laboratory instrument fitting a Xe lamp. An IPCE value was improved to be 0.7 when the layer of TiO₂ film is thicker than 16 µm. Two APCE curves in Figure 4 were calculated in different ways of estimation of ΔI_P , according as whether the scattered SR in the TiO₂ film is partly absorbed by dye (curve b) or not (curve a). It is clear that such multiple absorption may favorably take place in shorter wavelengths and contributes to electron injection from the dye. The quantum yield of the electron injection is expected to be more than 0.8 at shorter wavelengths, whereas it gradually decreases at longer wavelengths.

5. Transient Fluorescence Spectroscopy of DSCs

We observed fluorescence decay by time-resolved single photon counting using free electron laser (FEL) of ~580 nm. Figure 5 shows the dependence of the decay curves of the DSCs on the fluorescence wavelength. The fluorescence lifetime appears to increase with increasing wavelength. This



Figure 3. IPCE curves obtained using (a) the SR source and (b) an exclusive IPCE spectrometer.



Figure 4. APCE curves calculated in different ways of estimation of $\Delta I_{\rm P}$.



Figure 5. Fluorescence decay curves of DSSC and photovoltaic electrodes, obtained by FEL photolysis.

suggests that the conversion rates to other electronic states are comparable to those of the electron injection and fluorescing emission. The decay curves were monitored at 720 nm for a complete DSC and a photovoltaic electrode of TiO_2 film covered with Ru dye. The apparent fluorescence lifetime of the complete DSC is longer than those of the photovoltaic electrode, due to either slower electron injection induced by one of the additives in the electrolyte or aggregation of the dye molecules at the surface of TiO_2 .

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Atoms & Molecules in Intense Laser Fields

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



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Intense laser fields, comparable in magnitude with the Coulomb field within atoms and molecules, can be generated by focussing high-energy and ultrashort laser pulses. When exposed to such a strongly perturbing field, molecules exhibit various exotic features that cannot be observed in weak laser fields. We are seeking a deeper understanding of the behavior of molecules in intense laser fields, to elucidate how molecules interact with light, as well as to apply the new features they exhibit to the real-time visualization of ultrafast chemical reactions and their control. In particular, we focus on the following research themes:

(1) Understanding of atomic and molecular dynamics in intense laser fields and the control

(2) Ultrafast reaction imaging by laser Coulomb explosion imaging

(3) Generation and application of ultrashort soft-X-ray pulses by laser high-order harmonics.

1. Electron-Ion Coincidence Momentum Imaging of Molecular Dissociative Ionization in Intense Laser Fields: Application to $CS_2^{(1)}$

Molecules in intense laser fields show characteristic reaction processes, such as above-threshold dissociation (ATD), bond softening/hardening and deformation of the geometrical structures, associated with rearrangement of the electron distribution. Here, we performed photoelectron spectroscopy of the dissociative ionization of CS_2 to clarify the electron dynamics in intense laser fields. We developed a new electronion coincidence imaging system to label each photoelectron with the counterpart ion, so that the electron dynamics for different pathways can be discussed separately from the corresponding photoelectron images.

Photoelectron images of CS₂ in 35 fs intense laser fields (2

 \times 10¹³ W/cm², 800 nm, linearly polarized) recorded in coincidence with the parent ion, CS₂⁺, show clear concentric ring patterns due to the above-threshold ionization (ATI) process. On the other hand, broad structure-less distributions elongated along the direction of the laser polarization are observed in the coincidence electron images for the CS⁺ and S⁺ fragment ions. The difference in the electron images indicates that the dissociative ionization does not proceed sequentially by the formation and photodissociation of CS₂⁺ in intense laser fields. The origin of the difference in the spectra was discussed in terms of the direct ionization to the dissociative state and of the (multiple) electron recollision process.



Figure 1. Photoelectron images of CS_2 recorded at a field intensity of 2.1×10^{13} W/cm² (800 nm, 35 fs) (a) and those recorded in coincidence with CS_2^+ (b), CS^+ (c) and S^+ (d). The concentric ring patterns appearing in (a) are the ATI peaks. The laser pulses are linearly polarized. The total electron-ion coincidence count rate is less than 0.03 per laser shot.

2. Multiple Explosion Pathways of the Deuterated Benzene Trication in 9-fs Intense Laser Fields²⁾

The formation and fragmentation of multiply charged molecular ions are commonly observed as the responses of molecules exposed to intense laser fields. The fragmentation dynamics in these interactions have been extensively studied in recent years as they provide insight into the interplay between the electron and nuclear dynamics with large degrees of nuclear freedom in the presence of strong alternating electric fields. Here we employ the coincidence momentum imaging technique to clarify the fragmentation process of benzene in 9 fs intense laser fields (1×10^{15} W/cm²). By using this technique we can unambiguously identify the Coulomb explosion pathways from one particular charge state of interest and determine the momenta of the fragment ions in the laboratory frame.

Five two-body and eight three-body Coulomb explosion pathways from the trication ($C_6D_6^{3+}$), associated with the deprotonation and ring-opening reactions, are identified. It is found from the fragment momentum correlation that all the observed three-body explosion processes proceed sequentially via the two-body Coulomb explosion forming molecular dications, $C_mD_n^{2+}$, with (m,n) = (6,5), (5,5), (5,4), (4,4), (4,3)and (3,3), which further dissociate into pairs of monocations (see Figure 2). The branching ratios of the observed Coulomb explosion pathways, estimated from the number of the corresponding coincidence events, largely deviate from the previous RRKM prediction, showing that the dissociation processes are not fully statistical.



Figure 2. Three-dimensional momentum correlation map, plotting all the coincidence events identified for the three-body Coulomb explosion pathway, $C_6D_6^{3+} \rightarrow C_3D_2^+ + C_2D_2^+ + CD_2^+$, in intense laser fields (9 fs, 1×10^{15} W/cm²). The results of simulations based on the free-rotor model for the sequential three-body explosion are shown by the red solid lines.

3. Development of Time-Resolved Reaction Imaging System with Laser High-Order Harmonics³⁾

Laser high-order harmonics have novel features such as i) photon energy higher than several 100 eV, ii) extremely short pulse duration in the sub-fs regime, iii) high-quality spatiotemporal coherence, iv) high photon flux comparable to synchrotron radiation and v) simple and precise synchronization with other laser light sources. Because of these aspects, the laser high-order harmonic pulses are of great interest as a potential light source for time-resolved spectroscopy of ultrafast dynamics that could not be elucidated in real time by conventional techniques.

Figure 3 shows the schematic of new time-resolved reaction imaging system developed in our group. It consists of a laser high-order harmonics source, a soft X-ray spectrograph, a beam line equipped with a time delay line as well as a pair of dielectric mirrors to select one of the harmonic orders, and an electron-ion coincidence imaging chamber. The photoelectron spectra recorded for Xe with the 59 th harmonics (~92 eV) show the 4d inner-core photoelectron and the associated Auger electron peaks. Real-time probing of chemical reaction dynamics using this system is in progress.



Figure 3. Schematic of time-resolved reaction imaging system developed at IMS, consisting of (i) a high-order harmonics source, (ii) a soft X-ray spectrograph, (iii) a beam line and (iv) a coincidence momentum imaging chamber.

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Light Source Developments by Using Relativistic Electron Beams

UVSOR Facility Division of Advanced Accelerator Research



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This project involves researches and developments on synchrotron light source, free electron laser, beam physics and related technologies. Most of these works are performed at the UVSOR-II electron storage ring and its injector.

1. Developments on UVSOR-II Accelerators

After the major upgrade in 2003,¹⁾ the UVSOR-II electron storage ring has been operated with a small emittance of 27 nm-rad, that enables four undulators to produce highly brilliant synchrotron radiation in the VUV region. This small emittance, on the other hand, makes the beam lifetime short through the intra-beam scattering, so called Touschek effect. To solve this lifetime problem eternally, we have been preparing for top-up injection. In this operation scheme, electron beam is re-filled with a short interval, typically one minute, to keep the beam current almost constant.

In 2008, we have started test operation with the top-up injection on every Thursday night. The electron beam is kept at 300 mA for 12 hours, as shown in Figure 1. We have observed instability on the injection efficiency, which causes gradual reduction of the beam current. We have found that the instability is mainly caused by some drifts of the electron energy from the linear accelerator and also of the high voltage of the injection septum electrode of the booster synchrotron. A feedback system is being developed. It has been demonstrated that this system could stabilize the injection efficiency.

In 2009, we have successfully demonstrated a top-up operation in single bunch mode. Short electron pulse produced



Figure 1. Beam current history in the top-up test operation. After operated for 12 hours in the ordinary operation mode, the ring was operated for about 12 hours in the top-up mode as keeping the beam current at 300 mA.

by the electron gun was successfully accelerated and transferred to the storage ring. This new operation scheme drastically improves not only the performances of the single bunch users' runs but also the free electron laser and other coherent light sources as described below.

2. Storage Ring Free Electron Laser

The low emittance and the high peak current of UVSOR-II

enable the free electron laser to oscillate in the deep UV region with high output power exceeding 1W.²⁾ During the high power operation of the free electron laser, a rapid change of the output power was observed, which was partly due to the decrease of the electron beam intensity and partly due to the thermal deformation of the mirrors of the optical cavity. To solve this problem, a feedback system has been developed, which control the mirror alignment as monitoring the FEL output power. It was successfully demonstrated to stabilize the output power.³⁾ In adding to this, FEL operation with top-up injection was tried. We have succeeded in lazing for several hours as keeping the output power almost constant.

3. Coherent Synchrotron Radiation by Laser-Electron Interaction

We have developed a system to create micro-density structure on electron bunches circulating in the storage ring.⁴) By controlling the laser pulse shape, we can create various density structures such as a short dip structure or periodic structure. In the former case, broadband coherent terahertz radiation was produced.⁴) In the latter case, quasi-mono-chromatic coherent terahertz radiation was produced.⁵)

Coherent harmonic generation is a method to produce coherent harmonics of laser light by using relativistic electron beam. The laser-electron interaction in an undulator produces density modulation of a period of the laser wavelength. When the energy modulation is sufficiently larger than the natural energy spread, a density modulation is created which contains higher harmonic component of the laser wavelength. Such an electron bunch emits coherent harmonics of the injected laser. We have successfully observed the coherent third harmonics of Ti:Sa laser.⁶⁾ We have demonstrated a generation of variable polarization coherent harmonics using a variable polarization undulator.⁷⁾

The coherent radiation experiments using laser has come into a new phase as supported by the Quantum Beam Technology Program of JST/MEXT. In the new research project, a part of the storage ring was reconstructed. By moving the injection point to anther short straight section, we will have a new long straight section dedicated for the coherent radiation experiments. A new undulator system is under designing. The laser system is being upgraded. A VUV diagnostic system is under preparation.

4. Developments of Accelerator Technologies

The stabilization of the electron orbit of the storage ring is important to provide stable synchrotron radiation to users. At UVSOR-II, a drift of the orbit in a time scale of minutes to hours has been observed. An orbit feedback system has been developed which observes the orbit drift and control the orbit steering magnets in the ring. It was successfully demonstrated that the system can suppress the orbit drift of a few hundred of microns to a few tens of microns.⁸⁾

A 5T super-conducting bending magnet has been designed for a 1.2 GeV synchrotron light source to produce hard X-rays planned at Nagoya University. The bending angle is 12 degree and the peak magnetic field is above 5T. The pole shape was optimized by using a 3D simulation to provide X-rays to three beam-lines separated by a few degrees.

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Synchrotron Radiation Spectroscopy on Strongly Correlated Electron Systems

UVSOR Facility Division of Advanced Solid State Physics



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Solids with strong electron–electron interaction, so-called strongly correlated electron systems (SCES), have a various physical properties, such as non-BCS superconducting, colossal magneto-resistance, heavy fermion and so on, which cannot be predicted by first-principle band structure calculation. Thanks to the physical properties, the materials are the candidates of the next generation functional materials. We are investigating the mechanism of the physical properties of SCES, especially rare-earth compounds, organic superconductors and transition-metal compounds, by infrared/THz spectroscopy and angle-resolved photoemission spectroscopy using synchrotron radiation. Since experimental techniques using synchrotron radiation are evolved rapidly, the development of the synchrotron radiation instruments is also one of our research subjects.

1. Direct Observation of Momentum-Dependent Exchange Interaction in a Heisenberg Ferromagnet¹⁾

Local magnetism is generally believed to originate from the direct interaction among isolated electron spins described by the Heisenberg model, in which the electronic states with local magnetic moments are perfectly localized. In rare-earth compounds, instead of direct exchange interaction, superexchange interaction mediated by ligand valence electrons and indirect exchange interaction by conduction electrons among rare-earth ions are dominant because the 4f state in rare-earth ions is spatially localized. In the case of the superexchange and indirect exchange interactions, hybridization between the 4f electrons with local magnetic moments and the valence/ conduction electrons is important. Then we measured the temperature-dependent three-dimensional angle-resolved photoemission spectra of EuO(100) thin film, a typical Heisenberg ferromagnetic semiconductor, to investigate the essential origin of the ferromagnetic transition. We observed sizable



Figure 1. Energy distribution curves (EDCs, thick lines) and their second-derivative EDCs (thin lines) of EuO(100) thin film in the paramagnetic phase (PM) at 120 K and in the ferromagnetic phase (FM) at 5 K at the Γ (g1) and X (x1) points. The dashed lines indicate the peaks in the second-derivative EDCs that correspond to the peaks and shoulders in the EDCs. The 3D ARPES images were derived from the second-derivative EDCs in the paramagnetic phase at 120 K and in the ferromagnetic phase at 5 K near the Γ [(g2), (g3)] and X [(x2), (x3)] points. The open circles in (g2), (g3), (x2), and (x3) indicate the peaks and shoulders in the 3D ARPES images. The band structures calculated by the LSDA+U (U = 7 eV) method are shown near the Γ (g4) and X (x4) points. The solid and dashed lines in (g4) and (x4) denote the majority (\uparrow) and minority (\downarrow) spin states, respectively.

energy dispersion and large binding-energy shift of the Eu 4*f* state below the Curie temperature only near the Γ and X points, despite the expected Heisenberg-type local magnetism. The band dispersion and temperature dependence of the Eu 4*f* state indicates that the indirect exchange and superexchange interactions have strong momentum dependence. The observed temperature-dependent energy shift of the 4*f* state is the essential origin of the magnetism of EuO.



2. Origin of Infrared Peaks in the Optical Conductivity of Cerium and Ytterbium Compounds^{2,3)}

We have demonstrated that the middle-infrared (mid-IR) peaks commonly appearing in the optical conductivity $[\sigma(\omega)]$ spectra of CeX₃ (X = Pd, Sn, In) and ytterbium compounds

Awards

KIMURA, Shin-ichi; Morita Memorial Award, The Alumni Association of Physics Department "Senshu-kai," Tohoku University. MIYAZAKI, Hidetoshi; Best Presentation Award, PF Workshop on Recent Research Activities and Future Prospect of Angle-Resolved Photoemission Spectroscopy.

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Figure 2. Calculated optical conductivity $[\sigma(\omega)]$ spectra compared with experimental spectra of YbAl₃, YbAl₂, YbCu₂Si₂, YbNi₂Ge₂, YbInCu₄, YbRh₂Si₂, YbIr₂Si₂, and YbB₁₂. The $\sigma(\omega)$ spectra of YbCu₂Si₂, YbNi₂Ge₂, YbRh₂Si₂, and YbIr₂Si₂ were calculated along the *a*-axis, in the same way as the experimental spectra. The horizontal scales of the experimental and calculated spectra are located at the top and bottom, respectively. Note that the horizontal scale of the calculated $\sigma(\omega)$ spectra is reduced by a factor of 0.42 (= 0.5/1.2) compared with that of the experimental spectra. The vertical scales of the calculated and experimental $\sigma(\omega)$ spectra are identical except in the case of YbInCu₄, in which the experimental spectrum is three times as large as the calculated spectrum. The mid-IR peaks and far-IR shoulders of the experimental and calculated spectra are marked by open triangles and open circles, respectively.

(YbAl₃, YbAl₂, YbCu₂Si₂, YbNi₂Ge₂, YbInCu₄, YbRh₂Si₂, YbIr₂Si₂, and YbB₁₂) can be explained by first-principle band structure calculation with the spin-orbit interaction from the comparison with the results with the experimentally obtained $\sigma(\omega)$ spectra. On CeX₃, the mid-IR peak shapes are not identical to one another: CePd₃, CeSn₃, and CeIn₃ have a triplepeak structure, a double-peak structure, and a broad singlepeak structure, respectively. These peaks can be theoretically explained by the optical transition from the occupied state to the spin-orbit splitted Ce 4f state. On the other hand, in Yb compounds, the spectral feature of a peak in the middleinfrared (IR) region (mid-IR peak) and a shoulder structure in the far-infrared region (far-IR shoulder) in the experimental $\sigma(\omega)$ spectra can be described by the band calculation with a common renormalization factor of z = 0.42. These results suggested that the infrared spectra of Ce and Yb compounds originate from the own band structure but that the Yb 4f state shifts to the Fermi level with strong electron correlation.

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

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The dynamics of the inner-shell photoexcitation, photoionization, and subsequent decay processes is much more complex, in comparison to outer-shell photo-processes. For instance, the inner-shell photoionization is concomitant with the excitation and ionization of valence electrons, which reveal themselves as shake-up and shake-off satellite structures in the corresponding photoelectron spectrum. The one-photon multielectron processes, which are entirely due to the electron correlation in the system, are known to happen not only in the primary inner-shell hole creation processes, but also in their relaxation processes. Our research project is focused on elucidating the electronic structures and decay dynamics in core-excited atoms and molecules, by utilizing various spectroscopic techniques together with monochromatized synchrotron radiation in the soft x-ray region.

1. Dissociation Dynamics in Polyatomic Molecules Following Core Hole Creation

The acetylene dication is one of the smallest metastable polyatomic dications, whose dissociation and isomarization from the acetylene (HCCH) into the vinylidene (H₂CC) configurations have been extensively investigated. By using the PEPIPICO technique, it was found that the acetylene dications dissociate from excited states above 34 eV, where five threebody reactions and three two-body reactions including the dissociation channel via the vinylidene form (CH₂⁺ + C⁺: Vchannel) have been identified. The isomarization time of the acetylene decation produced following the Auger decay was estimated to proceed within 60 fs. Very lately, the visualization of ultrafast hydrogen migration in deuterated acetylene dication, which occurs in a recurrent manner, was nicely demonstrated by using intense ultrashort laser pulses.¹⁾

In the previous work, in addition to the V-channel, the other two channels in the two-body reactions, such as the acetylene channel ($CH^+ + CH^+$: A-channel) and deprotonation

channels (C_2H^+ + H⁺: P-channel), were correlated with some Auger final states. In order to gain a further insight into the dissociation mechanism of the Auger final states, we have performed an Auger-electron–ion coincidence study on fragmentations of deuterated acetylene dication, $C_2D_2^{2+}$, formed via Auger decay. With the use of our Auger-electron–ion coincidence spectrometer,²⁾ we have identified Auger final states relevant to the individual fragmentations including the three-body reaction, as well as to the formation of metastable $C_2D_2^{2+}$.

It is found that the atomic fragment ions tend to be produced in the entire region of Auger electrons, while the molecular ions except for CD⁺ exhibit specific productions for certain Auger final states. The parent dications are mainly observed at the lowest band, which shows a clear maximum around 33.3 eV. The CD₂⁺ fragments related to the V-channel, as well as the atomic fragments C⁺ and D⁺ yield the highest energy peak in the $1\pi_u^{-2}$ band at 35.0 eV. The highest binding energy band centered at 50 eV enhances violent fragmentation leading to the productions of C⁺, D⁺, CD⁺, and C₂⁺.

2. One-Photon Multi-Electron Emission Processes Studied by Multi-Eelectron Coincidence Spectroscopy

Neutral core-excited states of low-Z atoms relax mainly by electron emission, which has been investigated intensively in rare gases. It leads predominantly to singly-charged ions, but formation of doubly-charged ions by emission of two Auger electrons also makes up a considerable fraction of the total decay. Both direct and indirect processes can contribute to resonant double Auger decay. In the direct process, two electrons are simultaneously ejected and the available energy is continuously shared between the two electrons. In the indirect process, two electrons are emitted sequentially with distinct kinetic energies depending on the energy levels of the initial, intermediate, and final electronic states involved. Resonant double Auger decay of molecules is indeed known to exist from mass spectroscopic studies of ions. However, the molecular process is much more complicated than the atomic one, because it can be influenced by nuclear motions at any stage of the decay. In order to clarify the resonant double Auger process in molecules, we have used high-resolution electron spectroscopy and electron-electron coincidence spectroscopy.



Figure 1. (a) Two-dimensional (2D) map of the slow electron yields in the C1s-to-Rydberg range. (b) Total ion yield spectrum. (c) Top: Sum of the slow electron yields in the Rydberg excitation region which is derived by projecting the electron yields in the 2D map onto the horizontal axis. Bottom: slow electron spectrum at the C $1s \rightarrow 4p\pi$ (v = 0) resonance.

Figure 1 shows a two-dimensional (2D) map of slow electron yields as a function of the photon energy in the C 1s Rydberg excitation region of CO, with the total ion yield spectrum measured together with the slow electron yields. The 2D map exhibits horizontal stripes in the Rydberg resonances. Knots of enhancement are discernable in each stripe on the 2D map. The locations of some of these knots are common to all different C1s-to-Rydberg excitations. The observation implies that dissociation of CO⁺ states formed by first-step Auger decay and subsequent fragment O* atom autoionization constitute a major path for the double Auger decay of the C1s-to-Rydberg states. It is also found that additional spots appearing only on the $4p\pi$ (v = 0) resonance. These spots are spaced at 0.24 eV intervals, as clearly seen in the horizontal cut of the 2D map on this resonance [bottom panel of Figure 1(c)]. The constant intervals suggest that the peaks correspond to vibrational levels of CO^+ or CO_2^+ , and are therefore associated with molecular autoionization of CO⁺ into CO₂⁺. The mechanisms of the complicated molecular double Auger decay has nicely been clarified by the combined use of the two different spectroscopic methods.

3. Construction of New Soft X-Ray Spectroscopy Beamline BL6U

A new project for constructing the undulator beamline BL6U has been initiated. We have decided to choose the entrance slit-less configuration for the monochromator. A varied-line-spacing (VLS) plane grating monochromator (PGM) seems to be one of the most trustworthy ones to realizing high resolution in the soft x-ray range. In order to cover a wide photon energy region (30–500 eV) with one single grating, a variable-included-angle Monk-Gillieson mounting VLS-PGM has been selected.

The monochromator has been designed to cover the photon energy ranging from 30 to 500 eV, with the resolving power higher than 10000 and the photon flux more than 10^{10} photons/ sec. The practical construction of BL6U has begun from the summer shutdown in 2008. The first light has been observed in December 2008 and then precise tunings of the monochromator have been continued.

The installation of a new electron spectrometer to BL6U, which can be rotated around the photon beam axis, has been finished in August 2009, and its performance test has begun.



Figure 2. A top view of the newly constructed soft X-ray spectroscopy beamline BL6U.

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Micro Solid-State Photonics

Laser Research Center for Molecular Science **Division of Advanced Laser Development**



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Spark plug

The artistic optical devices should be compact, reliable, efficient and high power light sources. With the approaches of domain structures and boundaries engineering, it is possible to bring the new interaction in their coherent radiation. The highbrightness nature of Yb or Nd doped single crystal or ceramic microchip lasers can realize efficient nonlinear wavelength conversion. In addition, designed nonlinear polarization under coherent length level allows us new function, such as the quasi phase matching (QPM). The development of "Micro Solid-State Photonics," which is based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science.

1. High Peak Power, Passively Q-Switched Cr:YAG/Nd:YAG Micro-Laser for Ignition of Engines

Our high peak power, micro-laser igniter was first applied for a real automobile engine. A commercial engine of 1AZ-FSE (TOYOTA Motor Corp.) which is a 2.0 L, straight-4 piston engine with a gasoline direct injection system was prepared. The ignition point of a laser is set to be the same point as a spark plug. In this experiment, three of four cylinders (from #1 to #3) were ignited by conventional spark plugs and a #4 cylinder was ignited by our laser. Each ignition timing was carefully controlled and optimized. The repletion rates of the igniters are 13.3 Hz corresponding to an engine speed of 1600 rpm. Schlieren photographies of the early stage of ignition and subsequent combustion in a real engine are shown in Figure 1. The left figure shows the image of a conventional spark plug ignition and the right shows the laser ignition. The A/F is 14.5 which is a stoichiometric mixture of gasoline and air. It should be emphasized that a single laser pulse with an energy of 2mJ can successfully ignite a real engine. We think it will be the lowest energy ever reported for laser ignition of a real automobile engine. High brightness, passively Q-switched micro-laser could reduce the ignition energy dramatically compared to previous ignition lasers and also a spark plug. We further demonstrated the first prototype micro-laser module which had the same dimension as a spark plug as shown in Figure 2.



Figure 1. Schlieren photographs of the flame kernel ignited by a spark plug (a) and the micro-laser (b) in a constant volume combustion chamber at 6 ms after ignition trigger.



Figure 2. First prototype micro-laser module (right), which has the same dimension as a spark plug (left).

2. Spectroscopic Characteristics of Nd³⁺⁻ Doped Photo-Thermo-Refractive Glass

Considering recent spreading of laser resonator control that uses volume Bragg diffraction grating (VBG), it is convenient for VBG to have an ability of laser action. VBG is made of photo-thermo-refractive (PTR) glass, therefore we have evaluated the spectroscopic properties of Nd^{3+} -doped photo-thermo-refractive glass (Nd:PTR). From absorption characteristics we can estimate radiative lifetime of Nd:PTR by Judd-Ofelt analysis to be 861 µs while quantum efficiency of 0.8at.% Nd:PTR is considered to be 57.6%. Authors assures that Nd:PTR is the promised laser medium due to wide absorption and emission bandwidth, long fluorescent lifetime.



Figure 3. Emission cross section of Nd:PTR. Center wavelength of fluorescence is 1058 nm with a very wide emission bandwidth of 28nm that is useful for tuning by Bragg grating.

3. Broadly and Continuously Tunable, High-Energy Optical Parametric System by Angular Tuning of Tilted QPM Structures

We proposed a broadly and continuously tunable highenergy colinear optical parametric systems by using a periodically poled Mg-dpoped LiNbO₃ (MgLN) device with tilted quasi-phase matching (QPM) structures as shown in Figure 4, and experimentally demonstrated expanded tuning characteristics of the tilted QPM devices. The resulting tuning ranges of signal wave were 0.22 μ m (1.50 μ m ~ 1.72 μ m), 0.13 μ m (1.45 μ m ~ 1.58 μ m), for tilted QPM device with QPM period $\Lambda_0 = 28.0, 29.0 \ \mu$ m, in device-rotation angle θ_1 from -10° to +10°. Combination of angular rotation and tilted QPM structure is effective for compact and broadband-tunable coherent light source, especially for high refractive index crystals, as MgLN.



Figure 4. Broad and continuous tuning of optical parametric system by angular tuning of tilted QPM device.

4. Formation of Anisotropic Laser Ceramics

Rare-earth doped transparent ceramics (polycrystalline materials) have attracted considerable attentions as the next generation laser gain media due to their capability for engineered structure and improved mechanical properties. In this study, we have newly established "Rare-earth assisted electromagnetic material processing" which is a precise grain orientation controlling method for transparent *anisotropic* laser ceramics. We applied it for fabrication of rare-earth doped FAP (Ca₁₀(PO₄)₆F₂) materials and successfully obtained the uniaxially oriented laser grade Nd³⁺:FAP ceramics as shown in Figure 5 by imposition of a feeble (1.4 tesla) static magnetic field during slip-casting process.



Figure 5. Macro photograph of Nd³⁺ doped transparent FAP ceramics.

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Photo-Induced Dynamics and Reactions at Solid Surfaces

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Solid surfaces provide an interesting environment where two completely different electronic systems meet to each other: Localized electronic system, *i.e.*, atoms and molecules and delocalized one, *i.e.*, solid bulk surfaces. Charge transfer at surfaces is fundamental to adsorbate-metal interactions and reactions. Moreover, dynamic processes including chemical reactions on surfaces, particularly metal surfaces, are associated with continuous nonadiabatic transitions. This research program aims for understanding electron and nuclear dynamics at surfaces. Photo-induced processes including photochemistry at surfaces are the major focus in this program. Photons are used for not only exciting electronic states of adsorbate and substrate, but also for probing those states with various types of nonlinear optical spectroscopy.

1. Ultrafast Coherent Phonon Dynamics at Well-Defined Surfaces¹⁾

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We have demonstrated the real-time observations of surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces. We have focused on the excitation mechanism of coherent surface phonons at K-covered Cu(111) surfaces in comparison with Na adsorbates.

Professor*

At the coverages from 0.22 to 0.35 monolayer (ML), TRSHG traces show the oscillatory component with a frequency of 3.05 ± 0.05 THz. The amplitude of this component decreases as coverage increases higher than ~0.35 ML, whereas another oscillating component with a frequency of 1.26 ± 0.03 THz grows. Both components are ascribed to K–Cu stretching motion. The spectral changes with coverage suggest that the overlayer structure varies with lateral compression.

The fast transient peak in TRSHG traces at around zero delay changes its sign from negative to positive when coverage exceeds ~0.22 ML. Since the quantum-well state (QWS) is partly filled at around this coverage, electrons in the QWS are principally responsible for the transition of the electronic response. Furthermore, the excitation photon energy dependence of TRSHG traces indicates that the excitation of substrate d-band electrons, giving rise to rapid charge fluctuations in the QWS, generates the coherent K–Cu stretching vibration. Consequently, the QWS plays a major role in the electronic and nuclear dynamics induced by pump pulses at hv = 2.2 eV.

2. Ultrafast Vibrational Energy Transfer in Thin Layers on Pt(111) Surfaces²⁾

Ultrafast dynamics of vibrational energy transfer in overlayers of D_2O and CO on Pt(111) have been investigated by

femtosecond time-resolved (TR) IR-visible sum-frequencygeneration (SFG) spectroscopy under ultrahigh-vacuum conditions. About 10 layers of D₂O ice were epitaxially grown on $c(4\times2)$ -CO/Pt(111). The surface was excited by subpicosecond laser pulses, and subsequent energy transfer through lowfrequency modes of adsorbates was monitored in terms of peak shifts and broadenings of C-O and O-D stretching bands in SFG spectra as a function of the pump-probe delay. Because D₂O ice forms islands, there are two types of CO: one interacting with D₂O and the other free from D₂O. Simulations of the TR-SFG spectra by using a phenomenological model for the energy-transfer dynamics indicate that the coupling rate of perturbed CO is larger than that of free CO by a factor of 1.7; this is probably because CO $2\pi^*$ states shift toward the Fermi level due to interaction with D₂O. Two isolated bands at 2668 and 2713 cm⁻¹ were assignable to the OD stretching bands of D₂O directly interacting with CO at the D₂O/CO interface and D₂O at the vacuum/ice interface, respectively. Analysis of the temporal spectral changes of free D₂O by using a diffusive thermal transport model indicates that heat transfer through low-frequency phonons of the ice layers occurs within 3 ps; this is substantially faster than the pulsed laser-induced melting of thin ice films reported previously.

3. Spectroscopy of Molecules at Interfaces in Organic Field Effect Transistors by a Sum Frequency Generation Microscope

Organic field effect transistors (OFETs) have gained substantial attentions recently. In order to understand the efficiency of the device and the mechanism of charge transport, it is important to know carriers at the interface between a gate electrode and an organic semiconductor thin film. Since the interface is buried in the device, there are a few methods to investigate what is really happening at the interface. Sum frequency generation (SFG) is one of promising methods to realize it, since this is sensitive to the molecules at interfaces. SFG is a nonlinear optical process and, in particular, when visible and infrared beams are used, SFG is a powerful means for vibrational spectroscopy. We have developed a SFG microscope and applied it to the interface between pentacene and silicon oxide at the gate electrode. SFG signals generated at the interface are spatially resolved by the SFG microscope.

We observed clear SFG microscopic images of source and drain electrodes and the channel regions between them of the OFET devices. Upon application of a gate voltage of -50 V while keeping the voltage between the drain and source electrodes zero, the SFG signal intensity homogeneously increased only in the channel region about ten times and clear peak structures emerged in the SFG spectra. The observed peak structures are attributed to poly vinylphenol (PVP) used as a gate insulating layer of this devise; they are enhanced by the local electric field induced by carriers injected into the semiconductor/dielectric interface. Thus, the spatial distributions of carriers in the channel region at the interface were sensitively mapped by use of the vibrational resonance of PVP in the SFG images.

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Visiting Professors



Visiting Professor MIDORIKAWA, Katsumi (from RIKEN)

XUV Nonlinear Optics and Attosecond Dynamics in Atoms and Molecules

Nonlinear optical process in the XUV region is of paramount importance not only in the field of quantum electronic but also in ultrafast optics. From the viewpoint of quantum electronics, new features of the interaction between intense XUV photons and matters are expected to be revealed through observation of those nonlinear phenomena. On the other hand, those nonlinear processes in the XUV region is

indispensable for progress of attosecond science including attosecond atomic/molecular physics and chemistry, because it is very useful for investigating ultrafast phenomena directly in attosecond time scale. Using high harmonic generation by intense femtosecond lasers, we are pursuing extreme optical science including XUV nonlinear optics and attosecond physics/chemistry.



Visiting Professor TOMINAGA, Keisuke (from Kobe University)

Molecular Dynamics in Condensed Phases Studied by Ultrafast Laser Spectroscopy

Molecules in liquids interact with each other in a complex manner, and this complicated interaction yields a variety of aspects in the dynamical behaviors of liquids. We have investigated fluctuations of vibrational frequencies of solute in aqueous solutions by infrared three-pulse photon echo experiments. The time-correlation function of the frequency fluctuation can be expressed by a bi-exponential function with a

time constant of about 100 fs and that of 1 ps. The temperature dependence experiment shows that the picosecond component is very weakly temperature dependent. In order to compare the vibrational fluctuation with the fluctuation of the electronic state, we have also performed fluorescence dynamic Stokes shift experiment in aqueous solutions. It is found that the different dynamics and interactions are important for the fluctuations of the vibrational and electronic states.



Visiting Associate Professor AMEMIYA, Kenta (from High Energy Accelerator Research Organization)

Development of Soft X-Ray Optics and X-Ray Absorption Techniques

We have developed a high-resolution soft X-ray beamline in UVSOR, where the X-ray absorption spectroscopy (XAS) technique is available in order to investigate the atomic and electronic structures. Since the soft X-ray region includes the K edge of light elements such as carbon, nitrogen and oxygen, as well as the L edges of 3d transition metals, one can study various materials such as organic molecules and

complexes by using this new beamline. We are also trying to develop a novel experimental technique, three-dimensional XAS, by combining the soft X-ray microbeam with the depth-resolved XAS technique, in which the probing depth of the electron-yield XAS spectrum is controlled by the electron emission angle. The lateral and depth profiles of the atomic and electronic structures can be determined with lateral and depth resolution of several micron and sub nanometer, respectively.



Visiting Associate Professor KERA, Satoshi (from Chiba University)

Electronic Structure of π -Conjugated Organic Thin Film by Photoelectron Spectroscopy

To clarify the charge transport and injection mechanism in weakly-interacting organic molecular solids, ultraviolet photoelectron spectroscopy (UPS) is considered a conventional and novel powerful technique. Hole-vibronic coupling as well as intermolecular energy-band dispersion is important fundamental properties to reveal mysterious electric properties of organic molecular solids. Moreover, a quantitative

analysis of the intensity distribution from angle-resolved UPS using photoelectron scattering theory gives us information on the molecular orbital character as well as bonding nature, leading important aspects on intermolecular and molecule–substrate interaction to electronic/spin configuration. Photoemission related phenomena, *e.g.* scattering, interference and lifetime effect of photogenerated hole on a discrete and delocalized state of molecular orbital, are hot issues.