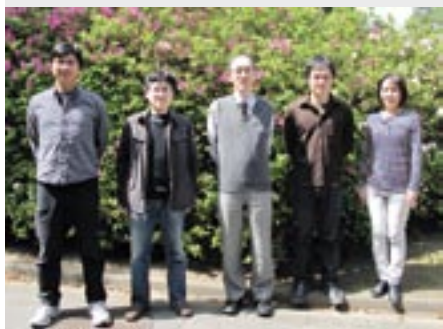


Molecular Inner-Shell Spectroscopy: Local Electronic Structure and Intermolecular Interaction

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In order to reveal local electronic structures and weak intermolecular interactions in molecular solids, liquids, and clusters, we are developing and improving several kinds of soft X-ray spectroscopic techniques such as XPS, XAS, RAS, XES, RXES, and RIXS at UVSOR in-vacuum undulator beamlines BL-3U and BL-6U with some international collaboration programs, and also an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

1. Inner-Shell Spectroscopy and Exchange Interaction of Rydberg Electrons Bound by Singly and Doubly Charged Kr and Xe Atoms in Small Clusters¹⁾

Surface-site resolved Kr $3d_{5/2}$ and Xe $4d_{5/2}$ ionized states and Kr $3d_{5/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ and Xe $4d_{5/2}^{-1}6p$ and $4d_{5/2}^{-1}7p$ Rydberg excited states in small van der Waals Kr and Xe clusters with a mean size of $\langle N \rangle = 15$ are investigated by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). Furthermore, surface-site resolved Kr $4s^{-2}5p$, $4s^{-2}6p$, and $4s^{-1}4p^{-1}5p$ shakeup-like Rydberg states in small Kr clusters are investigated by resonant Auger electron spectroscopy (RAS). As shown in Figure 1, the exchange interaction (EX) of the Rydberg electron with the surrounding atoms and the induced polarization (iPL) of the surrounding atoms in the singly and doubly ionized atoms are deduced from the experimental spectra to analyze different surface site contributions in small clusters. The induced polarization and exchange repulsion energies are almost proportional to the number of the nearest neighbor atoms. The present analysis indicates that small Kr and Xe clusters with $\langle N \rangle = 15$ have an average or mixture structure between the fcc-like cubic and icosahedron-like spherical structures.

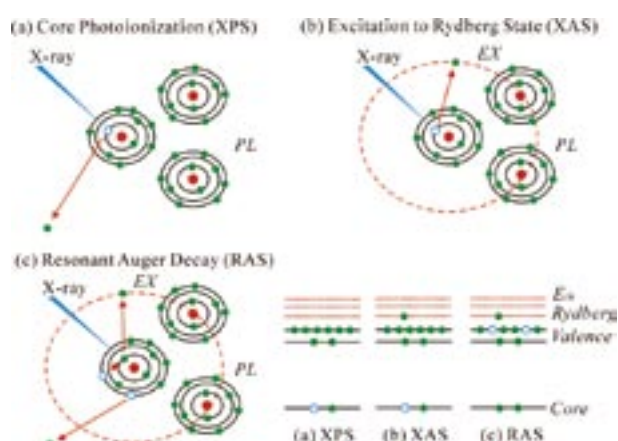


Figure 1. The final state in (a) XPS is stabilized by the induced polarization in clusters. The final states in (b) XAS and (c) spectator-like RAS are also stabilized by the induced polarization but are destabilized by the exchange interaction of the Rydberg electron with the surrounding atoms.

2. Vibrational Scattering Anisotropy Generated by Multichannel Quantum Interference in C1s- π^* Resonance Auger Spectra of Acetylene²⁾

We measured the Fe 2p X-ray absorption spectra of decamethane. Based on angularly and vibrationally resolved electron spectroscopy measurements in acetylene, we report the first observation of anomalously strong vibrational anisotropy of RAS via the C1s- π^* excited state with the strong Renner-Teller effect. We provide a model explaining this new phenomenon by three coexisting interference effects: (i) interference between resonant and direct photoionization channels, (ii) interference of the scattering channels through the core-

excited bending states with orthogonal orientation of the molecular orbitals, (iii) scattering through two wells of the double-well bending mode potential. The interplay of nuclear and electronic motions offers in this case a new type of nuclear wave packet interferometry sensitive to the anisotropy of nuclear dynamics: Whether which-path information is available or not depends on the final vibrational state serving for path selection.

3. Electric Field Effect on Electronic States in Organic Thin Films Studied by Fluorescence-Yield Soft X-Ray Absorption³⁾

In order to detect *in situ* electronic states of organic field effect transistor (OFET) in operation, we have utilized X-ray absorption spectroscopy (XAS) in the fluorescence yield (FY) mode. FY-XAS is a promising bulk-sensitive method for detection of inner electronic states of organic devices. To our best of knowledge, this is the first successful FY-XAS study on characterization of the organic devices under operating condition. Poly- and oligo-thiophenes are known to show high p-type-like performance. We fabricated 17nm-thick α,ω -dihexylsexithiophene (DH6T) films on the 500 nm-thick SiO₂ pre-covered Si substrates (highly B-doped, 0.5 mm-thick), and confirmed clear step-and-terrace morphology on the films by atomic force microscope. For the measurements of bias dependence, full-covered top-contact 25 nm-thick Au electrode was deposited on the DH6T thin films with cooling the substrate below 20 °C. The applied retarding bias exceeded -1 kV to shut out the photoelectrons excited by not only the fundamental X-rays but also the false second-order X-rays generated from gratings.

4. Site-Specific Intermolecular Interaction in α -Crystalline Films of Phthalocyanines Studied by Soft X-Ray Emission⁴⁾

The local electronic structures of crystalline and amorphous films of zinc phthalocyanine (ZnPc, C₃₂H₁₆N₈Zn) and metal-free phthalocyanine (H₂Pc, C₃₂H₁₈N₈) have been studied using photon-in-photon-out type resonant X-ray emission spectroscopy (RXES) with a novel optical design based on a Wolter type I mirror, a transmission grating, and a back-illuminated charge couples device detector, which enables a high light-gathering capability without sacrificing the energy resolution. We found a clear crystalline structure dependence of the elastic-peak lineshape in RXES. As shown in Figure 2, the elastic peak observed for the crystalline films of ZnPc and H₂Pc shows an asymmetric lineshape with resonant inelastic scattering (RIXS) structures, which cannot be observed for the amorphous films. The observed structure can be ascribed to the interplay of the intermolecular charge transfer excitation and the vibronic excitation that accompanies a direct recombination emission due to the Raman-active intermolecular interaction in crystalline phthalocyanine films.

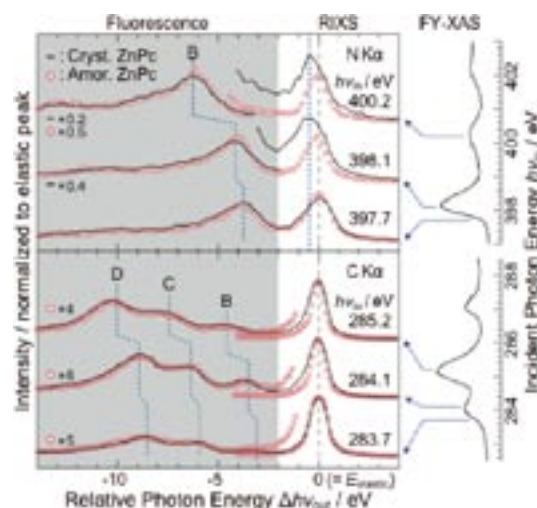


Figure 2. C and N K α RXES and RIXS spectra for the crystalline and amorphous ZnPc films. The abscissa is the energy difference between emitted and incident photons $\Delta h\nu_{out}$ ($= h\nu_{out} - h\nu_{in}$). All the spectra are normalized to the elastic peak intensity. The spectra for the crystalline and amorphous ZnPc films are shown using solid curves (black) and opened circles (red), respectively. The C and N K-edge FY-XAS spectra for the crystalline ZnPc film are shown in the right panel.

5. Orientation of *n*-Alkane in Thin Films on Graphite (0001) Studied by Soft X-Ray Absorption⁵⁾

We observed soft X-ray absorption spectra at the carbon K-edge of *n*-C₁₂H₂₆ films grown on graphite (0001). The C1s-to- σ^*_{CH} +Rydberg resonance directed along the CH bond was observed at 286.9 eV for the first layer of the *n*-C₁₂H₂₆ film on graphite. This indicates that the CCC plane of the molecule is parallel to the surface (flat-on orientation). As the film thickness increases, the C1s-to- σ^*_{CH} +Rydberg resonance directed perpendicular to the CH bond grows at 288.0 eV, suggesting an increase in the number of molecules with the CCC plane perpendicular to the surface in a multilayer film.

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