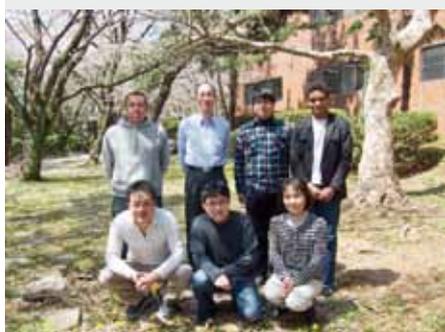# Molecular Inner-Shell Spectroscopy: Local Electronic Structure and Intermolecular Interaction

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In order to reveal local electronic structures and weak intermolecular interactions in molecular systems such as organic solids, liquids, aqueous solutions, and molecular clusters, we are developing and improving several kinds of soft X-ray spectroscopic techniques, such as X-ray photo-electron spectroscopy (X-ray PES, XPS), X-ray absorption spectroscopy (XAS), resonant Auger electron spectroscopy (RAS), X-ray emission spectroscopy (XES), resonant XES (RXES), and resonant inelastic X-ray scattering (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. Concentration Dependence of Local Structure in Methanol-Water Binary Liquid

A water molecule has two H(hydrogen)-accepting ('acceptor') and H-donating ('donor') sites, and the water liquid forms three dimensional (3D) hydrogen bonding (HB) networks. On the other hand, a methanol molecule with a hydrophobic methyl group has one H-donor and one or two H-acceptor sites, and the methanol liquid forms one and two dimensional (1D, 2D) HB networks, such as chains and rings of 6–8 methanol molecules. It is known that the methanol–water binary liquid has 3D cluster structures. However, the local structures of the methanol–water mixtures are still unknown. In this work, the local structure of the methanol–water binary liquid at different concentrations is studied by using carbon K-edge XAS.

The experiments were performed at soft X-ray undulator beam line BL3U at UVSOR-II facility. The liquid thin layer was sandwiched between two 100 nm-thick Si_3N_4 membranes. The photon energy was calibrated by the first peak (287.96 eV) of methanol gas filled in a He buffer space between the Si_3N_4 membrane and the detector in the liquid cell.

Figure 1 shows the carbon K-edge XAS spectra of the methanol–water binary liquids. The peak around 288.5 eV arises from the molecular orbital with a component of the hydroxyl group in the methanol molecule, and has a HB effect. On the other hand, the peak around 290 eV is mainly distributed at the methyl group. This peak is shifted to the higher photon energy by increasing the mixing ratio of water. It means that the methyl groups approach with each other in a dilute aqueous solution and the interaction between the methyl groups increase, contrary to liquid methanol, where the methyl groups are apart from each other.
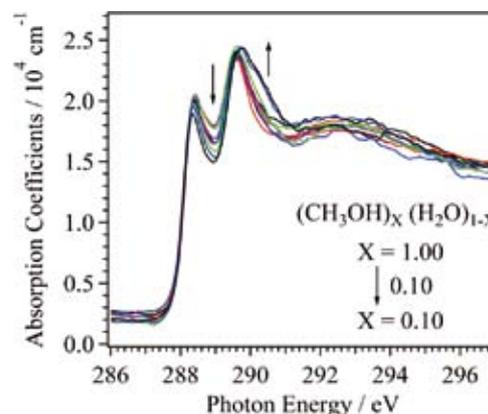

Figure 1. Carbon K-edge XAS spectra of the methanol-water binary liquid at different concentrations at 25 °C. The mixing ratio of water is increased along indicated arrows.

Figure 2 shows the intensities of the 289 eV region at different mixing ratios. The intensities are changed non-linearly, and indicate three different regions. The intensities are not changed so much in the methanol-rich region (I), indicating the local structure of pure methanol chain and ring clusters is preserved. On the other hand, in the region (II), the intensity is suddenly decreased at the methanol molar fraction $X \approx 0.7$, indicating a 1D/2D methanol–water mixed cluster is suddenly formed and this local structure is preserved down to $X \approx 0.3$. When $X < \sim 0.3$ (III), the intensity is going down, indicating a 3D methanol–water mixed cluster is almost proportionally formed.
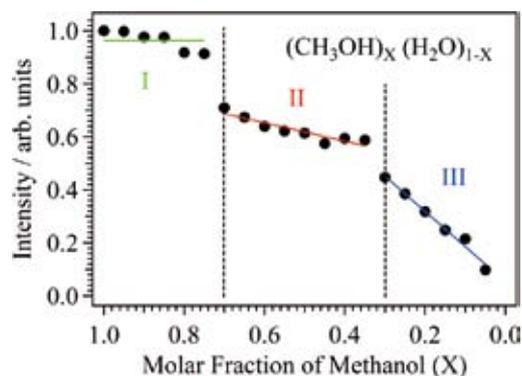

Figure 2. Intensities of the 289 eV region as a function of molar fraction of methanol in the methanol–water mixtures. The intensities of methanol and water are normalized to one and zero, respectively

2. Intramolecular and Intermolecular Interactions in Crystalline Films of Zinc Phthalocyanine (ZnPc)

It has been theoretically predicted that local and nonlocal electron–phonon (e–ph) interactions play a crucial role in the charge transport mechanism in organic solids. Recently, we have succeeded in observation of a small energy *versus* wave-vector $[E(k)]$ relation for the crystalline film of an archetypal organic semiconductor of ZnPc on Au(111) by using the high-resolution angle-resolved UV photoemission spectroscopy (ARPES). Based on the precise $E(k)$ data, we have evaluated the e–ph interaction on the charge transport mechanism of the ZnPc crystalline film.

Figure 3(a) shows the $E(k)$ relation of the ZnPc crystalline film on Au(111), which is obtained from the photon energy dependence of the normal-emission ARPES spectra at 15 K. The highest occupied molecular orbital [HOMO (π, a_{1u})], Zn 3d (b_{1g}), and π's derived peaks show a dispersive shift with the same periodicity. This periodicity corresponds well with the

highly symmetric Γ and Y points, estimated from the lattice constant of 3.32 Å determined by the specular X-ray diffraction [Figure 3(b)].

In order to examine the e–ph coupling in crystalline ZnPc film, we measured the temperature dependence of ARPES at the Γ and Y points with the 60 and 90 eV incident photons, respectively. As seen in Figure 3(c), the Γ-point HOMO energy shifts depending on the temperature, while the Y-point HOMO energy seems independent on the temperature. From the lineshape analysis, we found that both the HOMO band-width (*i.e.*, energy difference between the Γ-HOMO and Y-HOMO) and the Γ-HOMO peakwidth are narrowed with increasing the temperature, which is an opposite behavior to the remanent Au(111) Fermi edge. This is distinct indication of the local/nonlocal e–ph interaction; that is, band narrowing due to the interaction with local phonons (*intra*molecular vibrations) and band widening due to the interaction with nonlocal phonons (*inter*molecular lattice vibrations). Judging from the temperature dependence of the HOMO bandwidth and peakwidth, it is considered that the temperature-dependent transition between the incoherent hopping transport associated with the local e–ph coupling and the coherent band transport associated with the nonlocal e–ph coupling occurs within the energy scale of 100 meV in the ZnPc crystalline film.
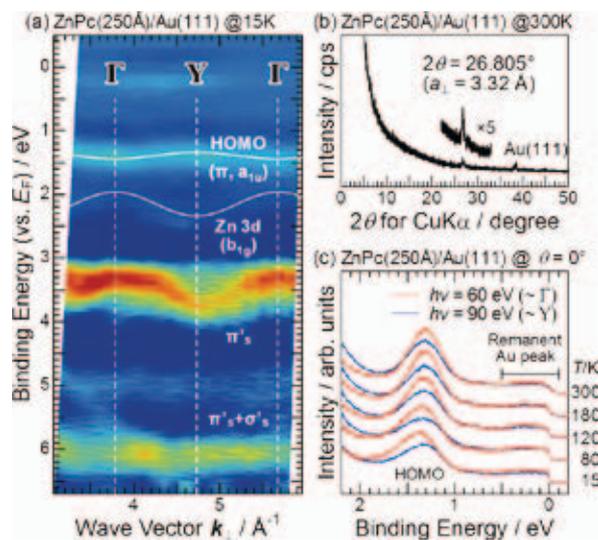

Figure 3. (a) Intermolecular $E(k)$ relation of the crystalline ZnPc film on Au(111) at 15 K, wherein the second derivative of the ARPES spectra were used for mapping out. White curves for the HOMO and Zn 3d derived bands are the best-fit results in the tight-binding model. (b) CuKα X-ray diffraction of the crystalline ZnPc film on Au(111) at 300 K. (c) Temperature dependence of ARPES in the HOMO-band region at the Γ and Y points, measured with 60 and 90 eV incident photons, respectively.

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