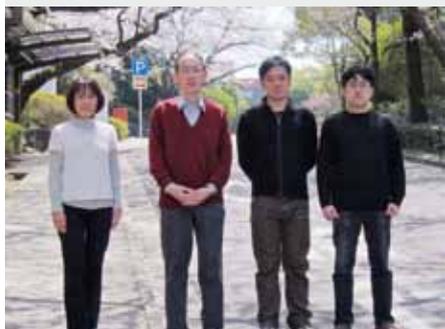


Molecular Inner-Shell Spectroscopy: Local Electronic Structure and Intermolecular Interaction

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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 X-ray photoelectron 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.

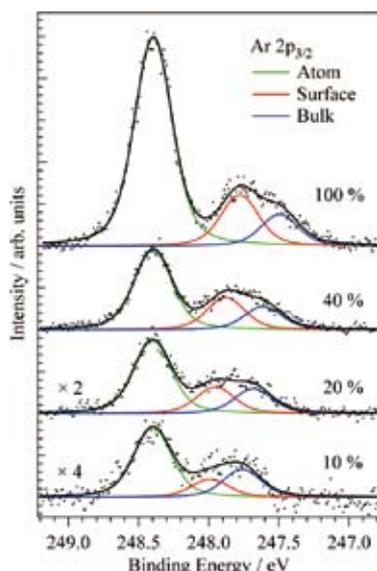


Figure 1. Ar $2p_{3/2}$ XPS spectra for mixed Ar- N_2 clusters prepared from different mixing ratio of Ar. The surface and bulk sites of the mixed clusters are separately obtained by a fitting procedures.

1. Structures of Small Mixed Ar- N_2 Clusters Studied by Soft X-Ray Photoelectron Spectroscopy¹⁾

Figure 1 shows Ar $2p_{3/2}$ XPS spectra for Ar and mixed Ar- N_2 clusters of different compositions. The surface and bulk sites of the clusters are distinguished by a fitting procedure. The cluster size of 200 corresponds to icosahedral multilayer structures with 4 or 5 layers. The intensity ratio of the surface and bulk sites observed for the Ar $2p_{3/2}$ XPS spectra of the pure (100%) Ar₂₀₀ cluster is consistent with such icosahedral multilayer structures. On the other hand, in 10% Ar, the intensity of the surface sites is smaller than that of the bulk sites. This intensity ratio suggests a core-shell structure, where the Ar aggregates are located in the bulk and are covered by a N_2 shell. We have roughly estimated the composition of N_2 bound in clusters from the partial pressure of N_2 , and confirmed that the surface-to-bulk ratio of Ar is consistent with a core-shell structure, where Ar is covered by N_2 . These core-shell structures are also observed in expansions containing 20 and 40% Ar.

2. Electronic Structure of Liquid Methanol Studied by Carbon K-Edge Soft X-Ray Absorption Spectroscopy²⁾

Figure 2 shows C K-edge XAS spectra of molecular (gas) and liquid methanol at 25 °C. Two peaks around 288 and 289.5 eV and several Rydberg states are observed in the molecular spectra. The 288 eV and 289.5 eV peaks contain O-H and C-H components, respectively, and the 292.5 eV peak contains a σ^* C-O component. Our C K-edge XAS spectrum of liquid methanol shows a simple structure with three contributions around 288.5, 290, and 293 eV as shown in

Figure 2(b).

The peak around 288.5 eV in liquid methanol is shifted to higher photon energy compared to that of methanol gas. The energy shift (0.53 eV) would be caused by the formation of the hydrogen bonding networks between methanol molecules. The peak around 290 eV in liquid methanol is also shifted to higher photon energy, but the energy shift (0.20 eV) is smaller than in the first band. This may be explained by a dominant contribution from the hydrophilic OH component in the first band. The peak around 293 eV does not show a noticeable difference between gas and liquid because the σ^* (C–O) orbital is not influenced by the hydrogen bonding network.

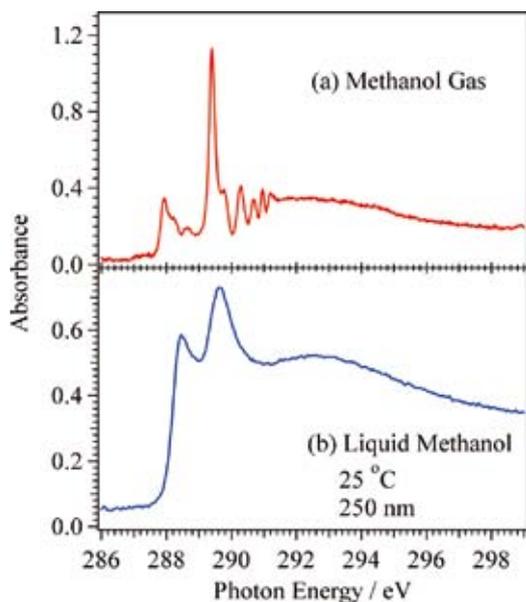


Figure 2. Carbon K-edge XAS spectra for (a) methanol gas and (b) liquid methanol at 25 °C. The thickness of liquid methanol layer is estimated to be 250 nm.

3. Very Narrow Intermolecular Electronic Band Dispersion in a Crystalline Film of Zn-Phthalocyanine³⁾

The electronic band dispersion, energy *versus* wave vector: $E(k)$, is a fundamental parameter to understand electric properties of solids such as hole mobility (μ_h). In the field of organic semiconductors, study of the intermolecular $E(k)$ shows a rapid progress due to the needs of the interpretation of the charge transport mechanism in molecular electronic devices. However, due to very weak intermolecular interaction and difficulty in preparing crystallized films appropriate for the $E(k)$ measurement, the observation of the intermolecular $E(k)$ has been limited in the case of high- μ_h materials. In order to elucidate and control the functionality of organic semiconductors, a systematic and quantitative experiment on the intermolecular interaction is essential. In this work, we have succeeded to observe a very narrow intermolecular $E(k)$ in crystalline films of Zn-phthalocyanine (ZnPc), which is one of

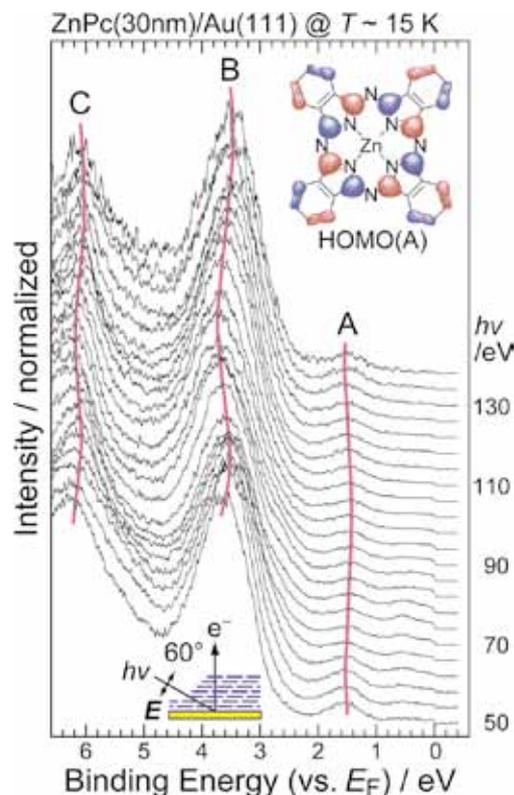


Figure 3. The $h\nu$ dependent angle-resolved PES spectra (4 eV step) at the normal emission for the crystalline ZnPc films on Au(111) at 15K.

the promising materials in the field of organic electronics.

Figure 3 shows $h\nu$ dependent angle-resolved PES (ARPES) spectra at the normal emission for the ZnPc crystalline film on Au(111) at 15 K. Since the ZnPc crystalline film on Au(111) shows a Stranski-Krastanov growth mode, there are the remnant substrate signal such as a Fermi edge, which we can use for the fine $h\nu$ calibration. For the ZnPc-derived peaks A, B, and C, we have observed a clear dispersive behavior with $h\nu$, wherein (i) the periodicities of A–C are the same in the k space and (ii) the bandwidth of peak A, originating from the highest occupied molecular orbital (HOMO), is 120 meV.

The present observation clearly indicates that the band-like transport is realized in the phthalocyanine films by the control of the geometric film structure. Moreover, the present result can be a benchmark for the systematic study on the intermolecular interaction, *e.g.*, intermolecular $E(k)$ as a function of the central metal atom in the phthalocyanine molecule, which enables to discuss experimentally the intermolecular interaction in terms of the intermolecular distance and the molecular orbital symmetry.

References

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