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

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

KOSUGI, Nobuhiro
Professor

YAMANE, Hiroyuki
Assistant Professor

NAGASAKA, Masanari
Assistant Professor

YUZAWA, Hayato	IMS Fellow
MOCHIZUKI, Kenji	Graduate Student
WANG, Yu-Fu	Graduate Student*
NAKANE, Junko	Secretary

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 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.

1. Electrochemical Reaction of Aqueous Iron Sulfate Solutions[1)]

The redox reactions of Fe ions are one of the most common electrochemical systems. Fe redox reactions have been mainly studied by voltammetric methods, but it is difficult to observe *in situ* change in valence of Fe ions in dilute electrolyte solutions. Recently, we have developed a liquid cell for soft X-ray absorption spectroscopy (XAS) in transmission mode. Furthermore, we have succeeded in development of an *in situ* XAS measurement system to study electrochemical reactions of electrolytes under realistic conditions by using a liquid cell with built-in electrodes. Change in valence of Fe ions in an aqueous iron sulfate solution at different potentials is investigated by Fe L-edge XAS.[1)]

Figure 1 shows the Fe L-edge XAS spectra of 0.5 M aqueous iron sulfate solutions at pH = 2.2 by variation of the potential at a gold electrode. Each XAS spectrum is measured at a constant potential. The XAS spectra reveal signals from Fe(II) and Fe(III) ions and show an isosbestic point, indicating only two species are involved. As seen in Figure 1(a), a nonlinear oxidation of Fe(II) to Fe(III) ions is observed when the potential is increased from 0.0 to 0.9 V. On the other hand, in Figure 1(b), the reduction of Fe(III) to Fe(II) ions shows linear dependence on the potential as decreased from 0.9 to –0.4 V.

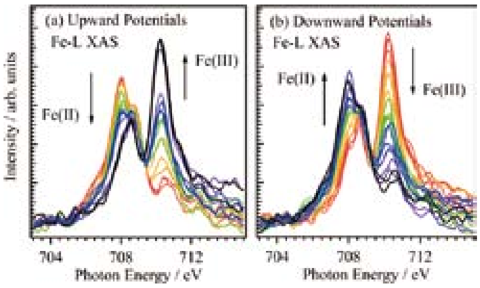

Figure 1. Fe L-edge XAS spectra of Fe ions in a 0.5 M aqueous iron sulfate at different potentials: (a) increasing from 0.00 to 0.90 V and (b) decreasing from 0.90 to –0.40 V.

Figure 2 shows the fraction of Fe(II) ions from total Fe ions as a function of potential and scanning direction, which is obtained from the XAS spectra. The fraction of Fe(II) ions decreases with increasing potential. Two processes are found in this oxidation process. The process at a high potential (0.72 V) is simple oxidation of Fe(II). The process at a low potential (0.34 V) involves the sulfate ions. The peak positions are dependent on the scanning rate because the rate of this process is dominantly influenced by the sulfate ions, which affect electrode kinetic parameters and diffusion coefficients. On the other hand, the formation of Fe(II) with decreasing potential is a simple reduction of Fe(III) ions. We have discussed the mechanism of these Fe redox processes by correlating the XAS results with cyclic voltammetry results at different scanning rates.

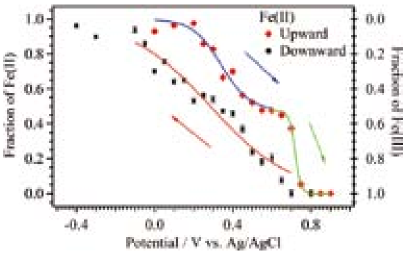

Figure 2. Fraction of Fe(II) ions as a function of potential and scanning direction versus Ag/AgCl with saturated KCl solutions.

2. Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band-Dispersion Measurements[2)]

The intermolecular band dispersion, originating from the periodicity of the molecular stacking structure, is essential to investigate the charge transport mechanism related to organic electronics. Recently, we have succeeded in observation of quite small intermolecular band dispersions for crystalline films of metal phthalocyanine (MPc, M = metal) by the precise angle-resolved photoemission spectroscopy (ARPES) experiments.[2)] These observations enable us to perform systematic study of the intermolecular interaction in terms of the intermolecular distance along the π-π stacking direction ($a_\perp$) by changing terminal groups or central metals in MPc.

Figure 3(a) shows the photon energy ($h\nu$) dependence of normal-emission ARPES for the crystalline MnPc film on Au(111) at 15 K. The highest occupied molecular orbital (HOMO, Mn 3d) and HOMO-1 (C 2p) derived peaks of MnPc show a clear periodic shift. Moreover, we have found that the Mn 3d derived peak consists of two components with the different dispersion, indicating the relatively strong interaction at the Mn site. Figure 3(b) shows the valence band map for the crystalline MnPc film on Au(111), wherein the symmetric Γ and Y points are estimated from the lattice constant of 3.27 Å from the X-ray diffraction. The agreement between the periodicity of C 2p peak and the symmetric points indicates that the observed dispersion is ascribed to the intermolecular interaction. For the Mn 3d peak, the peak split and its dispersion are clearly seen in the band map. Furthermore, the periodicity of the Mn 3d dispersion is 1/2 times of that of the C 2p dispersion as labeled Y_{2a}. A possible origin of the Mn 3d dispersion is dimerization of the Mn d_π state.

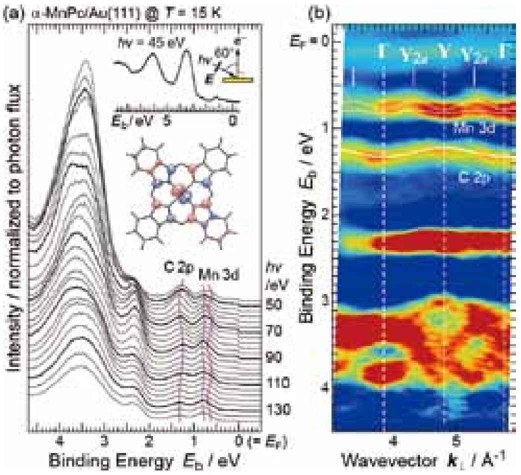

Figure 3. (a) $h\nu$-dependent normal-emission ARPES spectra ($h\nu$ step = 4 eV) of the MnPc crystalline film on Au(111) at 15 K. Inset shows the experimental geometry, wide valence-band spectrum at $h\nu$ = 45 eV, and the spatial distribution of the HOMO of MnPc. (b) Valence band map obtained from the second derivative of the ARPES spectra, with the tight-binding fitting (white curve).

From the observed band dispersions of the C-2p-derived band for crystalline films of various MPc molecules, the intermolecular transfer integral ($t_\perp$) can be evaluated with respect to the intermolecular distance ($a_\perp$) as shown in Figure 4. From the $t_\perp$-vs.-$a_\perp$ relation, we have found that (i) the $t_\perp$ value is getting large with decreasing the $a_\perp$ value due to the stronger intermolecular electronic coupling and that (ii) the $t_\perp$-vs.-$a_\perp$ relation seems to be fitted by a linear function in the present narrow $a_\perp$ range. From the least-squares fitting, the slope parameter of $t_\perp/a_\perp$ is determined to be 75±5 meV/Å for the C-2p-derived band of α-crystalline MPc films.

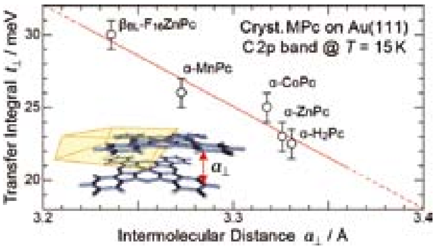

Figure 4. The $t_\perp$-versus-$a_\perp$ relation for the C 2p band in MPc crystals at 15 K obtained from the band dispersion measurement. The least-square fitting gives a slope parameter of $t_\perp/a_\perp$ = 75±5 meV/Å.

References

1) M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock and N. Kosugi, *J. Phys. Chem. C* **117**, 16343–16348 (2013).
2) H. Yamane and N. Kosugi, *Phys. Rev. Lett.* **111**, 086602 (2013).

Award

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* carrying out graduate research on Cooperative Education Program of IMS with Tamkang University, Taiwan