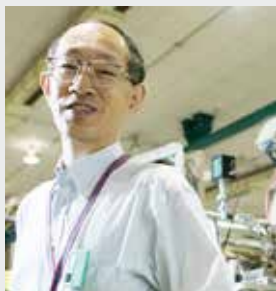


Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

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This research group has strong international network in the field of soft X-ray molecular sciences using world-leading advanced synchrotron radiation facilities for more than 20 years.

Soft X-rays cannot pass through air or bulk water due to photoabsorption of N₂, O₂, and H₂O molecules. Such strong photoabsorption can be used in highly sensitive chemical state analysis of thin or dilute samples, because soft X-rays with photon energies of 100–700 eV excite 1s inner-shell (K-shell) electrons of chemically important light elements such as C, N, and O selectively to unoccupied states of molecules. The 1s electron is localized and bound by an atom in the system but is slightly affected by surrounding atoms and chemical bonds. Therefore, we can select a 1s electron in each atom in molecules by choosing different X-ray energies with 10–100 meV accuracy, and know each atomic component and chemical environment in the unoccupied state.

In order to realize *in situ* and *in operando* chemical state analysis revealing 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 thin sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) and X-ray photo-

electron spectroscopy (XPS). We are also using resonant and non-resonant X-ray emission spectroscopy (XES) and angle-resolved photoelectron spectroscopy (ARPES).

Sample thickness should be optimized below 1 μm to get optimal absorbance in XAS. For inhomogeneous samples, the 10 nm-scale spatial resolution is necessary. It is also important to reduce the radiation damage of samples due to strong light-matter interaction in the soft X-ray region.

Highly brilliant soft X-rays for the chemical state analysis are available on our UVSOR-III Synchrotron in IMS. In addition to quite unique experimental and instrumental developments at UVSOR-III BL3U, BL4U and BL6U, we are developing an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

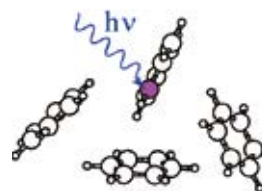


Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

- M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock and N. Kosugi, "Electrochemical Reaction of Aqueous Iron Sulfate Solutions Studied by Fe L-Edge Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. C* **117**, 16343–16348 (2013).
- M. Nagasaka, K. Mochizuki, V. Leloup and N. Kosugi, "Local Structures of Methanol-Water Binary Solutions Studied by Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. B* **118**, 4388–4396 (2014).
- H. Yamane and N. Kosugi, "Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band Dispersion Measurements," *Phys. Rev. Lett.* **111**, 086602 (5 pages) (2013).

1. Liquid–Liquid Interfaces in Aqueous TEA Solution by Spatially-Resolved XAS

Aqueous triethylamine (TEA) solution shows a lower critical solution temperature (LCST) behavior,¹⁾ in which two liquids are mixed at the lower temperature and are separated into two phases with the increase of temperature. This phase transition is contrary to normal and the mechanism of LCST has not yet been fully understood. We have observed local structures of liquid–liquid interfaces between TEA and water phases by spatially-resolved XAS with the resolution of 140 nm using a scanning transmission X-ray microscope (STXM) on UVSOR BL4U.²⁾ The liquid–liquid interfaces between TEA and water phases are formed from aqueous TEA solutions with the molar fraction of 0.4 at the temperature of 29.9 °C above LCST.

Figure 2(a) shows O K-edge XAS of water at different positions of the liquid–liquid interfaces. The inset shows the soft X-ray transmission image at 530 eV, in which the central part is a water phase and is surrounded by a TEA phase. We have estimated molar concentrations of water and TEA at different positions from the edge jumps of XAS in the O and C K-edges, respectively. It was confirmed that the mixing ratio of TEA and water determined in both the water and TEA phases are consistent with the phase diagram of TEA-water mixtures.¹⁾

Figure 2(b) shows the energy shift of the pre-edge peak (535 eV) in the O K-edge XAS at different positions. It is already known that the pre-edge peak is shifted to the lower photon energy when the hydrogen bond (HB) between water molecules is elongated/weakened. From the water to the TEA phase, the pre-edge peak is shifted to the lower energy. Because the amount of water is decreased with the direction of the TEA phase, the hydrophobic interaction of the ethyl group in TEA is dominant and the HB interaction of water molecules is decreased. Water and TEA molecules are coexisted in the TEA phase because the HB network of water is broken. The liquid–liquid interface between the water and TEA phases is formed with the balance of the hydrophobic interaction of TEA and the HB interaction of water molecules.

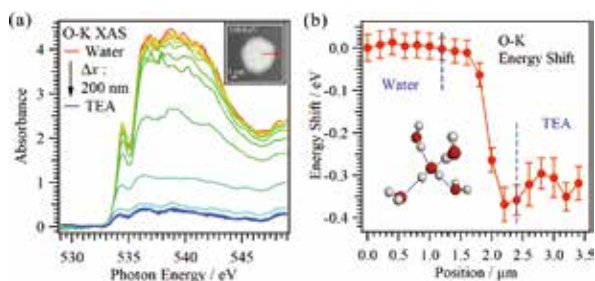


Figure 2. (a) O K-edge XAS of liquid–liquid interfaces at different positions. The inset shows soft X-ray transmission image at 530 eV. (b) Energy shift of the pre-edge peak as a function of position.

2. Delocalization of Charge-Transfer-Induced Valence Levels in Two-Dimensional Metal- Molecule Networks

Because of the large electron affinity, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) is well known as a strong electron acceptor, and has been applied for the *p*-type doping of organic semiconductors and for the work-function control of metal electrodes. It is understood that the cyano group in the F_4TCNQ molecule plays a crucial role in the charge-transfer (CT) interaction. At the $F_4TCNQ/Au(111)$ interface, in particular, the F_4TCNQ molecule forms a two-dimensional network via the cyano group with the segregated Au atom from the underlying Au(111) surface. In the present work, in order to investigate the electronic structure of the Au- F_4TCNQ network, we have studied the electronic structure of the $F_4TCNQ/Au(111)$ interface by means of angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation at BL6U of the UVSOR Synchrotron.

From the low-energy electron diffraction (LEED), shown in Figure 3, it was found that the F_4TCNQ molecule on Au(111) forms a commensurate (5,2)(1,3) structure. Furthermore, the LEED image of $F_4TCNQ/Au(111)$ does not show the $22\times\sqrt{3}$ herringbone pattern of Au(111) just around the (0,0) spot. This indicates the possibility of the Au-atom segregation from the Au(111) surface, which can introduce the formation of the Au- F_4TCNQ network.

Figure 3 shows the photoemission-angle (θ) dependence of ARPES for the clean Au(111) surface and the F_4TCNQ monolayer on Au(111) at 20 K using $h\nu = 45$ eV. Upon the deposition of F_4TCNQ , the Shockley-type surface state of Au(111) (labeled S) is almost quenched due to the presence of the strong chemical interaction, and the CT-induced electronic states are appeared at around 0.5 eV (labeled CT_1) and 1.5 eV (labeled CT_2) below the Fermi level. The CT_1 peak, which can be ascribed to LUMO (lowest-unoccupied molecular orbital) accepting a CT electron, shows a dispersive behavior with θ . The width of the dispersion of CT_1 is about 250 meV, and can be ascribed to the adatom-mediated intermolecular interaction in the Au- F_4TCNQ network, which was not observable at the physisorbed $TCNQ/Au(111)$ interface.

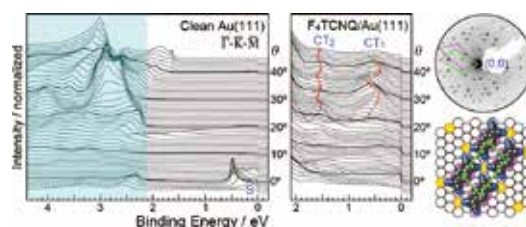


Figure 3. Photoemission-angle dependence of ARPES for the clean Au(111) and the F_4TCNQ monolayer on Au(111) at 20 K, measured at $h\nu = 45$ eV. The LEED image and the 2D ordering structure of the F_4TCNQ monolayer on Au(111) are shown in the right side.

References

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- 2) T. Ohgashi *et al.*, *AIP Conf. Proc.* **1741**, 050002 (2016).