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

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



Keywords

X-Ray Spectroscopy, Local Chemical State Analysis, Quantum Chemistry

Soft X-rays cannot pass through air or through liquid water due to photoabsorption processes of  $N_2$ ,  $O_2$ , and  $H_2O$  molecules. Such strong interaction of soft X-rays can be used in highly sensitive chemical state analysis of thin samples by X-ray absorption spectroscopy (XAS).

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 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, and know each atomic component in the unoccupied state is also affected by chemical environments. The intermolecular interaction effect is often less than 0.1 eV; therefore, a highly resolved soft X-ray spectrometer is necessary.

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 sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) for resonant excitation, and resonant and non-resonant X-ray photoelectron spectros-

## 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

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

Member Visiting Professor

Sample thickness should be optimized below 1  $\mu$ m 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 as synchrotron radiation from in-vacuum undulator-type insertion devices even on low-energy electron storage rings; *e.g.* 0.75 GeV UVSOR in IMS. In addition to 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.

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 Mesurements," *Phys. Rev. Lett.* 111, 086602 (5 pages) (2013).

# 1. Optimization of Thin Liquid Layer Samples for Soft X-Ray Absorption Spectroscopy in Transmission Mode

In order to measure soft X-ray absorption spectroscopy (XAS) of liquid samples in transmission mode, it is necessary to optimize thickness of thin liquid layers and reduce non-uniformity of sample thickness in the X-ray absorbed/transmitted region. Recently, we have developed a liquid flow cell, in which the thin liquid layer is sandwiched between two Si<sub>3</sub>N<sub>4</sub> or SiC membranes with Teflon spacers and is pressed by O-rings outside the membranes.<sup>1)</sup> Although the liquid layer is easily assembled by our method, the thickness of liquid layer is not uniform at different positions due to the large window size  $(2 \times 2 \text{ mm}^2)$ . To find the region of the uniform sample thickness in the X-ray absorbed/transmitted region of 200 µm  $\times$  200 µm (determined by our using orifice), we have developed a chamber-type XAS measurement system that is able to scan the sample position, and investigated the influence of the spectral shapes caused by the non-uniform thickness in the O K-edge XAS of liquid water at different sample positions.



**Figure 2.** (a) O K-edge XAS of liquid water at different sample positions. The pre-edge at 535 eV and the main-edge at 538 eV are shown in the spectra. (b) Thickness of liquid water and Pre/Main ratio of XAS spectra as a function of sample positions. Inset shows the 2D images of the soft X-ray transmission at 550 eV, where the sample positions are scanned as indicated. The size of the present soft X-ray beam is 200  $\mu$ m × 200  $\mu$ m.

Figure 2(a) shows O K-edge XAS spectra of water at different positions of the liquid layer. The liquid thickness at different positions was estimated from the edge-jump of the XAS spectrum. It is also important to determine the intensity ratio of pre-edge at 535 eV to main-edge at 538 eV for the evaluation of the XAS spectra. Figure 2(b) shows the Pre/Main ratio and thickness at different sample positions. The thickness is constant when the sample position is within 300  $\mu$ m from the center, and is increased when the position exceeds 300  $\mu$ m. The Pre/Main ratio is nearly constant between 0.36 and 0.40 when the sample thickness is constant, but the Pre/Main ratio is increased at the larger and non-uniform thickness region. This behavior in the Pre/Main ratio is in agreement with the simulated behavior by using the absorbance of water for the non-uniform sample thickness.

# 2. Lateral Intermolecular Interaction in Two-Dimensional Superstructure of Organic Monolayers

The intermolecular interaction is a key issue in molecular electronic properties. In the present work, in order to examine the lateral intermolecular interaction in flat-lying molecular layers, we investigated the electronic structure of hexa-*peri*-hexabenzocoronene (HBC) monolayers on Au(111), which forms various superstructures, *e.g.*,  $(5\times5)R0^\circ$ ,  $(3\sqrt{3}\times3\sqrt{3})R30^\circ$ , and their mixture, depending on the preparation condition.

Figure 3 shows the low-energy electron diffraction (LEED) image, the surface Brillouin zone (SBZ), and the energy-vs.-momentum E(k) map of the R0 and R30 phases of the HBC monolayer on Au(111) at 15 K, obtained by angleresolved photoemission spectroscopy (ARPES). In the R0 phase, the highest occupied molecular orbital (HOMO, H<sub>0</sub>) disperses in a narrow width by 20 meV only along the  $k_{\Gamma K}$ direction, and the HOMO-1 (H1) disperses by 25 meV only along the  $k_{\Gamma M}$  direction. The opposite trend is observed in the R30 phase; that is, the HOMO disperses by 20 meV along the  $k_{\Gamma M}$  direction, and the HOMO-1 disperses by 25 meV along the  $k_{\Gamma K}$  direction. The observed dispersion and its k periodicity is dependent not on the substrate SBZ but on the molecular SBZ; therefore, the observed lateral band dispersion rationally arises from a long-range (direct or indirect) intermolecular  $\pi$ - $\pi$  interaction.



**Figure 3.** LEED, SBZ [black hexagon for Au(111) and blue hexagon for HBC], wherein the red line indicates the scanned region in ARPES, and the  $E(\mathbf{k})$  map of HBC/Au(111) of the R0 and R30 phases at 15 K.

### Reference

 M. Nagasaka et al., J. Electron Spectrosc. Relat. Phenom. 177, 130–134 (2010).

### Award

YAMANE, Hiroyuki; The 2014 Young Scientist Award of the Japan Society for Molecular Science.