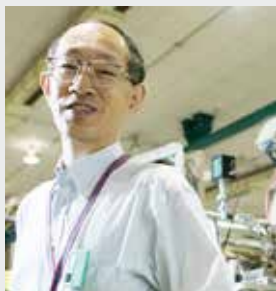


Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

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

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.

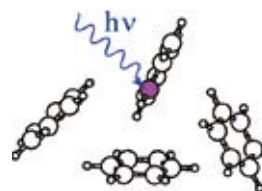


Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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. Temperature Dependent Structural Changes in Liquid Benzene

Benzene is the simplest aromatic molecule with a possibility of several kinds of intermolecular π - π interactions. Since ordered liquids are key structures to study chemical and biological phenomena in the liquid state, ordered structures of benzene confined in nanopores have been extensively studied, whereas those in the liquid state are still unknown. In this study, we address fundamental questions whether ordered structures of benzene are formed in the liquid state by using carbon K-edge X-ray absorption spectroscopy (XAS) as a sensitive local probe.

The experiments were performed at soft X-ray undulator beamline BL3U at UVSOR-III Synchrotron. Figure 2(a) shows C K-edge XAS of liquid benzene at different temperatures. The energy shifts of the solid at -193 °C¹⁾ and clusters²⁾ from the gas peak are -55 meV and -70 meV, respectively. The energy shift of liquid benzene is between the gas and the solid at -193 °C. Figure 2(b) shows the energy shift of the π^* peak of liquid benzene relative to benzene gas as a function of temperature. The π^* peak of liquid benzene shows a lower energy shift with increasing temperature. Although the π^* peak of liquid benzene should be approaching that of gaseous benzene with increasing temperature, the experimentally observed energy shift of the π^* peak goes into the opposite direction.

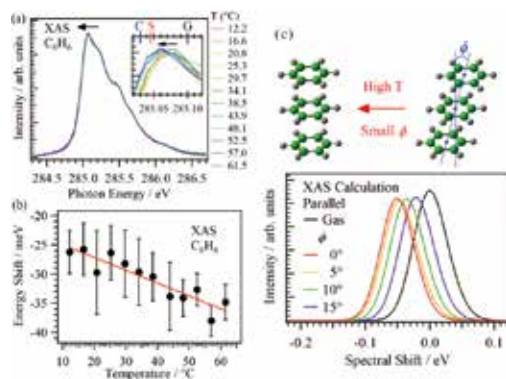


Figure 2. (a) C K-edge XAS of liquid benzene at different temperatures. (G), (S), and (C) are the peaks of gas, solid, and clusters, respectively. (b) Energy shifts of the π^* peak as a function of temperature. (c) Calculated spectral shifts of parallel structures at the different angles ϕ , which become smaller at higher temperatures (T).

For understanding the characteristic temperature behavior of the π^* peak shift in C K-edge XAS of liquid benzene, we have performed molecular dynamics simulation and inner-shell calculation based on quantum chemistry. In radial distribution functions of parallel structures in liquid benzene, the components of small intermolecular distance become abundant by increasing temperature. Figure 2(c) shows inner-shell spectra of benzene trimers at different angle ϕ in parallel structures. The π^* peaks show lower energy shifts with decreasing the tilt angle ϕ of the

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parallel displaced structures. Since the angle ϕ in the parallel displaced structure becomes smaller by increasing temperature, these spectral shifts suggest that parallel displaced structures in liquid benzene are changed to sandwich (parallel non-displaced) structures for the higher temperature.

2. Microfluidics of Liquid Mixtures Observed by Spatially-Resolved XAS

Microfluidics is a technique for efficient chemical reactions, interfaces, and transport processes in the liquid phase.³⁾ Although XAS is an element specific method to reveal structures of liquids by microfluidics, the application of XAS to microfluidics is difficult since soft X-rays cannot deeply penetrate a microfluidic cell. In this study, we have developed a microfluidic cell, where a T-shape microfluidic setup with the width and thickness of 50 μm is made of PDMS resin and is covered by a 100 nm thick Si_3N_4 membrane.

Figure 3(a) shows a soft X-ray fluorescence image of the T-shape microfluidic cell excited by soft X-rays at 550 eV. The spatial resolution of this image is 30×30 μm^2 . The fluorescence shows high intensity at the water part and low intensity at the pyridine part. A laminar flow of pyridine and water is observed in the mixed part of the microfluidic cell. As shown in Figure 3(b), the π^* peak of pyridine in N K-edge XAS shows a higher energy shift from the pyridine to water part across the mixed part due to the formation of hydrogen bond between pyridine and water.⁴⁾ This energy shift indicates that the phase separation in the laminar flow is clearly observed by spatially resolved XAS. This spectroscopic technique will be applicable to only to liquid mixtures but also to chemical and biological reactions.

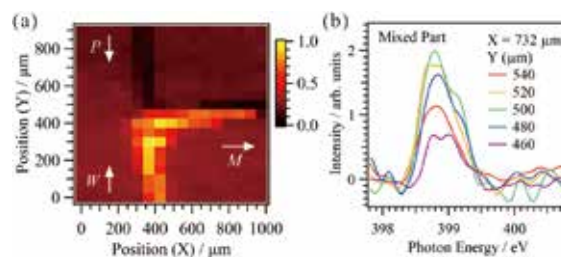


Figure 3. Soft X-ray fluorescence image of a T-shaped microfluidic cell excited by soft X-rays at 550 eV. Pyridine (P) and water (W) flow in the upper and lower sides, respectively, and the laminar flow is observed in the mixed part (M). (b) N K-edge XAS at different positions in the mixed part shown in (a). The horizontal position is fixed to $X = 732$ μm , and the vertical position is scanned.

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