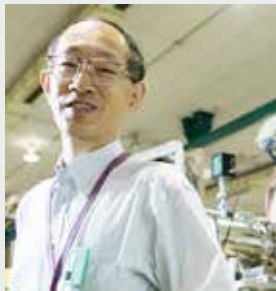# Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

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Division of Photo-Molecular Science III

Education
1976   B.S. Kyoto University
1981   Ph.D. The University of Tokyo
Professional Employment
1981   JSPS Postdoctoral Fellow
1982   Research Associate, The University of Tokyo
1988   Lecturer, The University of Tokyo
1989   Associate Professor, Kyoto University
1993   Professor, Institute for Molecular Science
1993   Professor, The Graduate University for Advanced Studies

1996   Visiting Professor, McMaster University, Canada
2008   Visiting Professor, Université P&M Curie - Paris VI, France
2011   Visiting Professor, Université Paris-Sud - Paris XI, France
2013   Visiting Professor, Freie Universität Berlin, Germany
Awards
2015   The 68th Chemical Society of Japan (CSJ) Award

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Keywords   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 N_2, O_2, and H_2O 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.
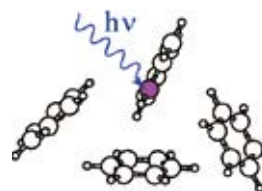

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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

1. Local Structures of Liquid Benzene Studied by C K-Edge Soft X-Ray Absorption Spectroscopy at Different Temperatures

Recently, we reported C K-edge X-ray absorption spectroscopy (XAS) of benzene in gas, cluster and solid phases.[1,2] Although solid benzene mainly shows T-shaped structures, liquid benzene shows both T-shaped and parallel structures. In this work, we have measured C K-edge XAS of liquid benzene at different temperatures by using a transmission-type liquid flow cell,[3] and studied the temperature effect of the molecular interaction.

Figure 2(a) shows C K-edge XAS of liquid benzene at different temperatures. The C 1s → π* peak shows adiabatic (0, 0) transition and vibrational fine structures at the higher photon energy. Figure 2(b) shows the energy shifts of (0, 0) transition peaks of liquid benzene from gas as a function of temperature. The π* peak shows a shift to the lower photon energy by increasing the temperature. The energy shift of liquid benzene relative to the gas phase is 29.4 meV at 25.3 °C. This shift is smaller than in solid benzene and clusters, which is 55 meV[2] and 70 meV,[1] respectively.

The lower energy shift of the π* peak is caused by induced polarization with surrounding molecules. Because the molecular distance in solid phase is smaller than that in liquid phase, the π* peak in solid phase shows lower photon energy shifts than that in liquid phase. We have performed molecular dynamics simulations of liquid benzene at different temperatures. The molecular distance in the T-shaped structure shows longer distances at higher temperatures. On the other hand, we found that the molecules in the parallel structure are getting close to each other by increasing the temperature. The lower energy shifts of the π* peak at higher temperatures would be derived from this parallel structure. In the near future, we will discuss the molecular interaction in liquid benzene by correlating C K-edge XAS results with infrared spectroscopy and molecular dynamics simulations.
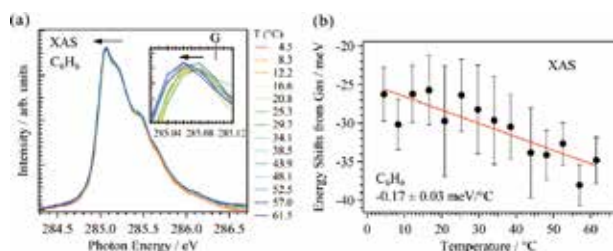

Figure 2. (a) C K-edge XAS of liquid benzene at different temperatures. The inset shows the maximum of the C 1s → π* transition in greater detail. (b) Energy shifts of C 1s → π* (0, 0) transition peak of liquid benzene relative to gaseous benzene as a function of temperature.

2. Site-Specific Organic/Metal Interaction Revealed from Shockley-Type Interface State

The Shockley state is a well-known surface state associated with the breakdown of the bulk-crystal periodicity at the surface, and can be observed by using angle-resolved photoemission spectroscopy (ARPES). In the present work, we have applied the Shockley-state measurement to the well-ordered monolayer of Co phthalocyanine (CoPc) on Au(111), in order to study the site-specific organic/metal interfacial interaction quantitatively.

The Shockley state of CoPc/Au(111) is compared with that of H_2Pc/Au(111) and that of the clean Au(111) at 23 K in Figure 3. The observed Shockley state of both CoPc/Au(111) and H_2Pc/Au(111), labeled S', shows the energy shift of about 120 meV towards the Fermi level (E_F) from that of the clean Au(111) surface. The observed upshift of the Shockley state upon adsorption originates from the exchange interaction of surface electron systems by CoPc. Furthermore, one more dispersive band just below E_F is observed for CoPc/Au(111), labeled X, which is not observable for H_2Pc/Au(111).

We found from the temperature dependence of ARPES for CoPc/Au(111) that peaks S' and X can be ascribed to the Shockley state modified by the site-specific interfacial interaction at the Pc-ligand site and the central-metal Co site in the molecule, respectively. Using the relation of $E_a = 0.106\ \Delta E_{SS}$, where E_a and ΔE_{SS} are the adsorption energy and the shift in the Shockley state, respectively,[4] we determined the site-specific interfacial bonding strength in CoPc/Au(111) at 23 K as $E_a = 13.0$ meV/$Å^2$ at the Pc-ligand site and $E_a = 45.9$ meV/$Å^2$ at the central-metal Co site.
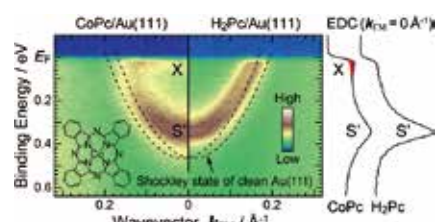

Figure 3. The $E–k$ map around the Shockley state for CoPc/Au(111) and H_2Pc/Au(111) at 23 K, together with the best-fit curve of the Shockley state for the clean Au(111) at 23 K (black dashed curve).

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