

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

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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 in the system. The excited electron 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 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 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.

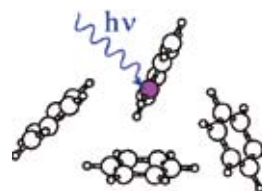


Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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. *In Operando* Soft X-Ray Absorption Spectroscopy with Potential Modulation Applied to Electrochemical Reaction

In order to investigate local structures of electrolytes in electrochemical reactions under the same scan rate as a typical value 100 mV/s in cyclic voltammetry (CV), we have developed an *in operando* observation system for electrochemical reactions by soft X-ray absorption spectroscopy (XAS) with a potential modulation method. XAS spectra of electrolytes are measured by using a transmission-type liquid flow cell with built-in electrodes. The electrode potential is swept with a scan rate of 100 mV/s at a fixed photon energy, and soft X-ray absorption coefficients at different potentials are measured at the same time. By repeating the potential modulation at each fixed photon energy, it is possible to measure XAS of electrochemical reaction at the same scan rate as in CV. As shown in Figure 2, we have successfully measured the Fe 2p (L-edge) XAS spectra of aqueous iron sulfate solutions and the change in valence of Fe ions at different potentials in the Fe redox reaction.

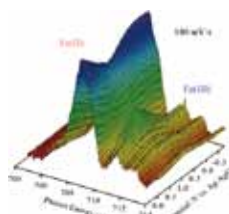


Figure 2. 3D plots of Fe 2p XAS spectra in the electrochemical reaction of aqueous iron sulfate solution under CV (100 mV/s scan).

2. *In Situ* Soft X-Ray Absorption Spectroscopy Applied to Hydration Reaction of Cyanopyrazine on Titanium Oxide Catalyst

In situ observation of liquid substrate conversion in solid-liquid heterogeneous catalytic reactions is difficult due to disturbance of the solvent and substrate itself. In this work, the hydration reaction of cyanopyrazine to produce pyrazinamide on TiO₂ catalyst ($\text{PzCN} + \text{H}_2\text{O} \rightarrow \text{PzCONH}_2$) has been successfully measured by the C K-edge and N K-edge XAS in transmission mode. Spectral change in both the C K-edge and N K-edge XAS, due to decreasing reactants PzCN and increasing products PzCONH₂, is clearly observed in spite of the coexistence of bulk liquid components PzCN, H₂O and solvent EtOH. The time dependence indicates that the hydration is the first order reaction. This result is also consistent with the linear relationship found in the Arrhenius plot, which is obtained from temperature dependent XAS measurements.

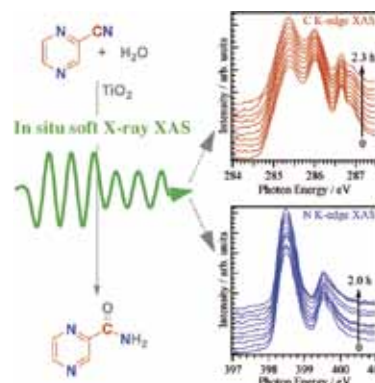


Figure 3. C K-edge (red) and N K-edge (blue) XAS spectra for the catalytic hydration reaction from cyanopyrazine to pyrazinamide.

3. Orbital-Specific Valence-Band Dispersion in α -Phase Crystalline Films of Cobalt Phthalocyanine

The valence band structure of α -crystalline cobalt phthalocyanine (CoPc) films grown on Au(111) is investigated by using angle-resolved photoemission spectroscopy (ARPES). The time-dependent photo-induced change in the ARPES peaks is noticed in shape and energy of the highest occupied molecular orbital (HOMO, C 2p) and HOMO-1 (Co 3d) of CoPc, and is misleading the interpretation of the electronic properties of CoPc films. By successfully avoiding such serious radiation damage, the clear valence-band dispersion has been first observed, showing that orbital-specific behaviors are attributable to the interplay of the intermolecular π - π and π -d interactions. The HOMO band dispersion by 0.1 eV gives the lower limit of the hole mobility for α -CoPc of 28.9 cm² V⁻¹s⁻¹ at 15 K. The non-dispersive character of the splitted HOMO-1 bands indicates that the localization of the spin state is a possible origin of the antiferromagnetism.

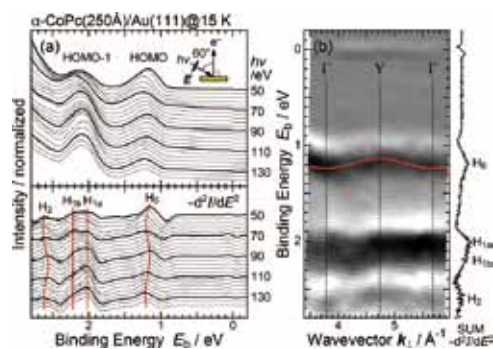


Figure 4. Intermolecular $E(k_1)$ in the α -CoPc film on Au(111) at 15 K. (a) $h\nu$ -dependent normal-emission ARPES spectra. (b) $E(k_1)$ map with the tight-binding fitting for the HOMO-band dispersion (red curve).

Awards

NAGASAKA, Masanari; The 2014 JSSRR Scientific Award (Japanese Society for Synchrotron Radiation Research).

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

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