

Molecular Inner-Shell Spectroscopy: Electronic Structure and Intermolecular Interaction

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In order to reveal electronic structure and intermolecular interaction of molecular solids, liquids, and clusters, we are developing and improving several kinds of soft X-ray spectroscopic techniques and also an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

1. Development of a Liquid Flow Cell to Measure Soft X-Ray Absorption in Transmission Mode¹⁾

We have developed a liquid flow cell for transmission measurement of soft X-ray absorption spectra of liquid samples. The liquid flow cell consists of four regions as shown in Figure 1; (I) vacuum region below 1.0×10^{-4} Pa, connected to the soft X-ray undulator beamline, (II) helium buffer region filled by 1-atm helium, (III) liquid layer and flow region, and (IV) photodiode region in the helium atmosphere. Each region is separated by a 100 nm-thick SiN_x membrane. The window size is $200 \times 200 \mu\text{m}^2$ in the region I/II and $2 \times 2 \text{mm}^2$ in the regions II/III and III/IV. The photon energy calibration is simply carried out by mixing a reference such as oxygen in the helium gas. Fresh liquid samples can be continually supplied to avoid the radiation damage. We have tested this cell for the measurement of O K-edge X-ray absorption spectra in absorbance of liquid water. Thickness of the liquid water layer (region III) is controlled to be $\sim 600 \text{nm}$ by optimizing a water flow speed in a tubing pump system. The present liquid flow cell may enable us to investigate electronic structure of liquid samples confined at a nano-scale space by increasing the helium pressure in the regions IV and II and/or by slowing down the liquid flow.

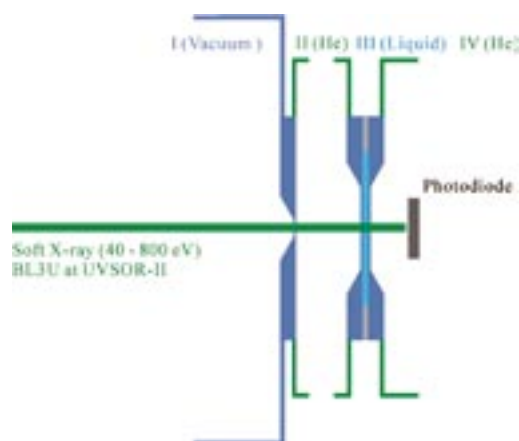


Figure 1. A schematic soft X-ray transmission liquid cell.

2. Strong Double Excitation Features in Soft X-Ray Absorption Spectra of Ferrocene and Ferrocenium Compounds²⁾

We measured the Fe 2p X-ray absorption spectra of decamethyl ferrocene ($\text{Fe } 3d^6$) and ferrocenium hexafluorophosphate ($\text{Fe } 3d^5$). The 2p-edge features of 3d transition metal compounds have been attributed, variably, to an atomic multiplet model or a covalent bonding model. A unique covalent bonding between Fe and the two cyclopentadienyl (Cp) rings, especially, the ligand π and out-of-plane $3d^*_{xz,yz}$ (e_{1g}) orbitals, suggests that covalent effects will be most important in the spectral features.

We found the Fe 2p excitation parallel to the π ($//z$) direction cannot be interpreted within a single excitation picture and is split into two strong features as shown in Figure

2. *Ab initio* CI calculations predict a significant role of the double excitation features in the Fe 2p spectra of both Fe^{II}(Cp)₂ and the [Fe^{III}(Cp)₂]⁺ ion. An additional low energy feature (W) observed in [Fe^{III}(Cp)₂]⁺ is attributed to a Fe 2p to SOMO excitation.

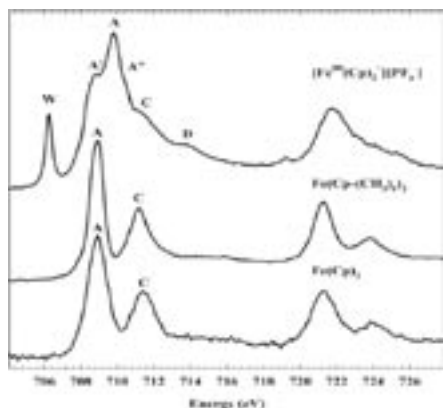


Figure 2. Fe 2p-edge spectra of [Fe^{III}(Cp)₂]⁺[PF₆]⁻, Fe^{II}(Cp-(CH₃)₅)₂ and Fe^{II}(Cp)₂.

3. Inner Electronic States beneath Electrodes: Fluorescence-Yield X-Ray Absorption of Pentacene Derivative Films³⁾

The electronic states of inner organic thin films were investigated by X-ray absorption spectroscopy in a bulk-sensitive fluorescence yield (FY) mode. The thin films of the synthesized pentacene derivative (HAPn), 6,13-dihydrodiazapentacene (C₂₀N₂H₁₄), on SiO₂-covered Si substrates were

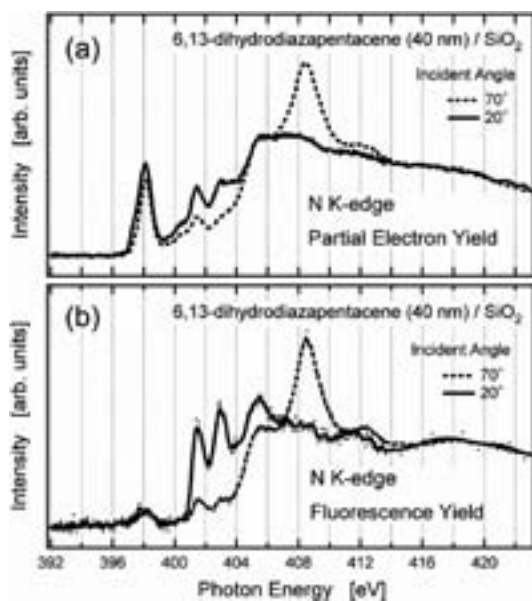


Figure 3. N K-edge X-ray absorption spectra of the HAPn thin film (40 nm thick) deposited on the oxidized Si substrate: Detected in (a) PEY mode and (b) FY mode. The incident angle of X-rays is defined from the surface normal. The spectra are normalized by the signal height at around 420 eV. The sample was stored for 2 weeks in a desiccator at room temperature.

fabricated and their morphology and crystallinity were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis, respectively. The observed N K-edge FY spectra were different from the surface-sensitive spectra measured in a partial-electron-yield (PEY) mode as shown in Figure 3. The incident angle dependence of the FY spectra was consistent with the expected molecular orientation in the thin films. As a result, we successfully obtained the N and C K-edge FY spectra of the inner HAPn thin films, even beneath the Au electrodes.

4. Origin of Fine Structures on the Dissociative 1s-σ* Resonance in X-Ray Absorption Spectra of O₂⁴⁾

We attempted to explain a puzzling long-tailed peak shape of the X-ray absorption spectrum of the oxygen molecule in the energy region around 539 eV by taking into account the Rydberg-valence and vibronic couplings. The long-tailed feature is found to arise from two dissociative σ* states and the sudden drop in intensity is related to decrease in transition dipole near the crossing point between the repulsive σ* and weak 3s Rydberg states with the quartet ion core. This is supported by numerical wave-packet simulations allowing for all inter-channel couplings between the Rydberg and valence manifolds with the quartet (Q) and doublet (D) ion cores in a diabatic representation of the core-excited states as shown in Figure 4.

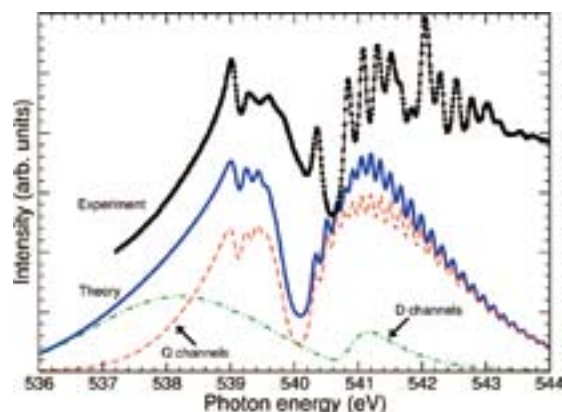


Figure 4. Theoretical X-ray absorption spectra obtained for the excitation to all the channels (solid line), and Q (dashed red line) and D (dash-dotted green line) channels.

References

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