Molecular Inner-Shell Spectroscopy: Electronic Structure and Intermolecular Interaction

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



KOSUGI, Nobuhiro HATSUI, Takaki NAGASAKA, Masanari KIMBERG, Victor NAKANE, Junko

Professor Assistant Professor Assistant Professor JSPS Post-Doctoral Fellow Secretary

To reveal electronic structure and intermolecular interaction of free molecules and molecular solids and clusters, we are developing and improving soft X-ray spectrometers for resonant photoelectron spectroscopy and inelastic soft X-ray emission spectroscopy optimized to an undulator beamline BL3U at the UVSOR facility. We are also developing and improving an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

1. High-Resolution Soft X-Ray Emission Spectroscopy with a Transmission Grating

We have recently reported our new design of a transmission-grating spectrometer (TGS) for high resolution soft X-ray emission studies.¹⁾ The high resolution spectrometer generally requires high light gathering capability without sacrificing the energy resolution. This requirement can be fulfilled by use of the Wolter type-I mirror and the transmission grating (TG). Our spectrometer incorporates the basic concept for x-ray imaging and spectroscopy telescopes²⁾ into a compact and easy-to-use layout.

The present optical layout is a modification of the Rowland torus mount with facet gratings. In the ideal Rowland torus mount, the facet TGs should be mounted onto Rowland torus with keeping their normal to point the focus of the incoming x-rays. In our spectrometer, the facet TGs are positioned onto a single Si wafer. Such simplification might degrade optical properties. However, we demonstrated by ray-tracing simulations that the aberration in our geometry is small enough to realize the energy resolving power better than 5000.



Figure 1. Layout of the present soft X-ray emission spectrometer.

Our TGS shown in Figure 1 is installed at the XES endstation of the undulator beamline BL3U. A soft x-ray emission spectrometer generally requires small beam size at the sample position, because a smaller opening of the spectrometer entrance slit is needed to achieve higher energy resolution. BL3U is designed to give small beam size of order of $10 \times 40 \ \mu m^2$. To check the stray light contamination, the profile of the 0th order diffraction was measured. The stray light intensity was less than 1% of the 1st diffraction order intensity. To check the energy resolution, diffuse scattering from aluminum samples illuminated by 60 eV soft x-rays was measured. Figure 2 shows the 1st order diffraction peak. The peak width was FWHM of 3 pixels, which corresponds to the energy resolving power of 4600. To our knowledge, the present resolving power is more than 4 times higher than the best record reported so far.



Emitted Photon Energy (eV)

Figure 2. 1^{st} order diffraction peak of the diffuse scattering from aluminum samples (hv = 60 eV), observed by using the present TGS.

2. X-Ray Natural Circular Dichroism of Amino Acids³⁾

X-ray absorption spectroscopy (XAS) is a powerful tool to study even large molecules. Due to the localized character of a core electron responsible for XAS, it is possible to correlate a specific XAS feature with a specific functional group or with an individual bond. In addition, even natural circular dichroism (NCD) is now observable in XAS of amino acids, though difference in XAS between the left and right circularly polarized X-rays proves to be tiny : $g = 2(I_L - I_R)/(I_L + I_R) \approx 10^{-3}$.

In the present work, we evaluate feasibility of different theoretical approaches for XNCD by using GSCF3 and other available *ab initio* codes. We describe the excited orbital set using the ground state Hartree-Fock (HF) orbital set employed in (i) RPA and (ii) static exchange approach (STEX) (unrelaxed), (iii) core-ionized state HF orbital set applied in STEX(relaxed) and (iv) HF excited state orbital set for each core-to-valence excited state. Furthermore in (i) the DFT-RPA method is compared with the RPA where the *ab initio* HF orbital set is used. In (iv), the oscillator and rotary strengths evaluated by different orbital sets for the initial and final states, namely, non-orthogonal ground-state and core-excited HF orbitals, are compared with those evaluated by using the coreexcited HF orbital set to describe the initial (ground) state.

The basis set dependence of XNCD spectra of some amino acids in different approaches is systematically investigated using Woon and Dunning basis sets up to aug-cc-pCV5Z. The RPA calculation shows most satisfactory and self-consistent results for the low-lying core-to-valence excitations near the O K-edge. A clear convergence of the oscillator strength for the basis sets larger than triple-zeta is found for the RPA approach. Use of extended quadruple-zeta or larger basis sets are required to obtain satisfactory results for the rotary strength on the O K-edge. The relative simplicity of the RPA technique using the same ground-state HF orbital set for any core-to-valence excitation makes it applicable to chiral centers in rather large compounds such as proteins.

3. Inner-Shell Ionized and Excited States of Molecular Pyridine Clusters⁴⁾

Photoionization of clusters containing aromatic molecules shows characteristic redshifts of the appearance energies in the regime of the first ionization energy.⁵⁾ These redshifts are rationalized with the polarization (PL) effect by molecules surrounding a positively-charged core-ionized molecule. On the other hand, photoexcitation of clusters containing aromatic molecules does not show such a PL effect, because the core excited states are neutral. Recently, we have investigated the C $1s-\pi^*$ excitation in variable size benzene clusters,⁶⁾ whose excited states undergo substantial redshifts up to 60 meV relative to the isolated molecule. On the other hand, the N $1s-\pi^*$ excitations in pyridine clusters show ca. 60 meV-blueshifts. The mechanism of the energy shift in inner-shell excitation of molecular clusters could be different from that in inner-shell ionization.

The most stable pyridine dimer structure is theoretically found to be an anti-parallel displaced structure with the N atoms opposing each other, where the positively charged H atom of one ring lies on top of the negatively charged nitrogen atom of the other ring. In the parallel displaced geometry of pyridine trimer, the middle pyridine is displaced with respect to the top and bottom pyridine rings, such as two anti-parallel displaced pyridine geometries. In contrast to less stable parallel displaced stacking interaction in benzene dimer, the stacking interaction in pyridine dimer and trimer is stabilized electrostatically with the permanent dipole moment.

In the anti-parallel displaced dimer structure the blueshift is calculated to be 42 meV by using GSCF3. In the antiparallel displaced trimer, the N 1s on the middle ring has the largest blueshift of 85 meV, whereas the top and bottom N 1s leads to the same blueshift of 42 meV as in the dimer. This means the second neighbor molecule is not contributive at all to the energy shift. We have also observed that the N 1s– π * excitation energy shift is oscillating against a horizontal sliding in the anti-parallel displaced pyridine dimer. This indicates covalent intermolecular interaction is important; that is, a small π – π orbital interaction is visible as a small energy shift in the 1s– π * excitation even in van der Waals clusters. In addition, this result indicates a possibility to know nearest neighbor molecular conformation by referring to the shift in core-to-valence excitation energy.

References

- T. Hatsui, E. Shigemasa and N. Kosugi, J. Electron Spectrosc. Relat. Phenom. 144, 1059 (2005).
- 2) K. P. Beuermann, H. Bräuninger and J. Trümper, *Appl. Opt.* **17**, 2304 (1978).
- 3) V. Kimberg and N. Kosugi, J. Chem. Phys. 126, 245101 (2007).
- 4) I. Bradeanu and N. Kosugi, AIP Conf. Proc. 882, 815 (2007).
- 5) E. Rühl, P. Bisling, B. Brutschy and H. Baumgärtel, *Chem. Phys. Lett.* **126**, 232 (1986).
- 6) I. L. Bradeanu, R. Flesch, N. Kosugi, A. Pavlychev and E. Rühl, *Phys. Chem. Chem. Phys.* 8, 1906 (2006).