RESEARCH ACTIVITIES VI
Department of Vacuum UV Photoscience

VI-A Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

In this project, we have two major subjects: (a) resonant photoelectron spectroscopy and (b) resonant inelastic soft X-ray emission spectroscopy following inner-shell excitations of simple molecules and clusters. We have recently succeeded in development of a next-generation soft X-ray emission spectrometer.

VI-A-1 Improvement of the Energy Resolution of Transmission Grating Soft X-Ray Emission Spectrometer

HATSUI, Takaki; HORIGOME, Toshio; KOSUGI, Nobuhiro

Last year we reported the first results on the performance of a transmission-grating spectrometer (TGS) for high-resolution soft X-ray emission studies. The obtained energy resolution ($E/\Delta E$) was about 3100 at the photon energy of 110 eV, which was limited by the source size on the sample. In order to obtain higher energy resolution, an UHV-compatible entrance slit with the slit opening of 1–30 µm has been developed. The slit blades are mounted on a flexure guided stage in combination with a piezo actuator. The slit opening is feedback controlled by monitoring a capacitance sensor attached to the frame. The performance of the TGS was evaluated by introducing the new entrance slit. The elastic x-ray scattering from aluminum sample irradiated by the monochromatic x-rays (Figure 1) indicates that the overall energy resolution is now 4500 at the photon energy of 114 eV. The resolution is limited by the energy resolving power of the beamline BL3U for the incident soft x-ray, not by the TGS.

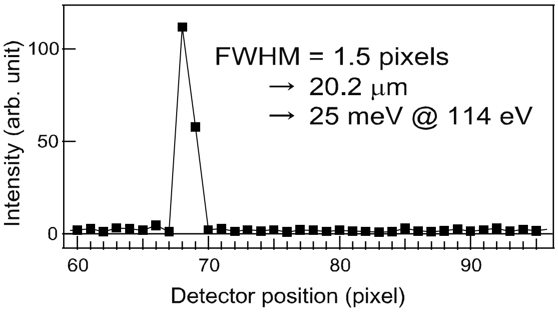

Figure 1. Line profile along dispersion direction of the CCD detector image. Full width at half maximum (FWHM) is 20.2 µm, corresponding to energy resolution of 25 meV ($E/\Delta E$ = 4500).

VI-A-2 Development of a Sub-Pixel Resolution CCD for High Resolution Soft X-Ray Emission Spectrometer

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Last year we reported the performance of a transmission-grating spectrometer (TGS) for high-resolution soft X-ray emission studies. The TGS equipped with a conventional charge coupled device (CCD) detector with the pixel size of 13 µm realized an energy resolution $E/\Delta E$ up to 4500 at the photon energy of 114 eV. The observed peak has the full width at half maximum (FWHM) of 1.5 pixels under this high energy-resolution condition. The performance is hence limited dominantly by the spatial resolution of the CCD detector. In order to improve the spatial resolution of the detector, we have developed an electron multiplying CCD detection system with the pixel size of 16 µm for photon-counting detection of the soft x-rays. By amplifying the charge generated by soft x-ray photon prior to on-chip MOSFET, which is the dominant source of the readout noise, the noise is reduced less than 1 electron rms/pixel at the readout rate as high as 400 kHz/pixel. The obtained signals are analyzed to obtain the centroid of the charge, or the position of the x-ray absorption. By examining the image of a slit with a width of 10 µm (Figure 1) and assuming Gaussian profile of the point spread function (PSF) of the detector, the PSF is estimated to have FWHM of 3.0 µm. The results indicate that this new detection technique improves the special resolution by a factor of 10 compared with the conventional CCD detector without degrading the quantum efficiency.

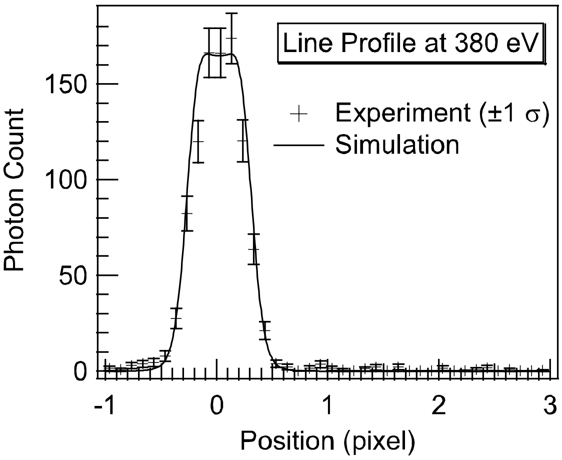

Figure 1. Line profile measured for the image of the slit and simulated profile, based on the diffraction theory assuming the detector PSF with FWHM of 3.0 µm.

VI-B Soft X-Ray Photoelectron-Photoabsorption Spectroscopy and Electronic Structure of Molecular Solids and Clusters

This project has been carried out in international collaboration. We have two subprojects: (a) molecules and radicals in condensed phase and in rare gas matrix, and (b) ionic fragmentation and photoelectron emission of atomic and molecular clusters following the inner-shell resonance excitation. In (a), we have measured excitation spectra in some matrix phases at the bending-magnet beamline BL4B of the UVSOR facility. In (b), we have measured soft X-ray photoelectron spectra of some atomic and molecular clusters on the undulator beamline BL3U.

VI-B-1 Orbital-Dependent Stabilization in the Valence Ionization of CS_2 Cluster

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Van der Waals clusters have been interested since they give opportunities to investigate the connection between isolated and condensed phases. Cluster formation is known to give the decrease or red shift in adiabatic and vertical ionization (binding) energies, which is commonly interpreted in terms of final-state polarization stabilization. The polarization stabilization is dependent on the distance to the surrounding atoms/molecules and their polarizabilities and numbers.

In the present work, we have investigated red shift dependent on the ionized state of CS_2. Figure 1 shows the spectrum measured by using the He I source, as plotted in relative energy scale, where zero energy is chosen to be the vertical energy of each ionized state of a single molecule. The band profile of the cluster spectrum indicates the abundance or size of the cluster. In the case of larger cluster size with increased stagnation pressure, the peak tops of the cluster bands show larger red shifts. The peak position can be regarded as the vertical binding energy at an average cluster size. We can assume that the vibrational progression of each ionized states does not change upon the cluster formation and is mainly determined by the intra-molecular potentials.

Figure 1 and Table 1 show that the relative binding energies are increased in order of X, A, B, and C. Charge distributions determined by a least-square fitting of the electrostatic potential evaluated by an ab initio MR-SDCI solution for each ionized state of a molecule explain different red shifts. The theoretical charge distribution of a single molecule reasonably predicts that the higher ionized state should have larger polarization stabilization by the surrounding molecules in the cluster.

Table 1. Charge Distribution of a CS_2 molecule in ground and ionized states.

State	Charge O	Charge S	Binding Energy (eV) Theory	Binding Energy (eV) Exp.
Ground state	–0.258	+0.129		
X $^2\Pi_g$	–0.228	+0.614	9.65	10.06
A $^2\Pi_u$	+0.048	+0.476	12.99	12.83
B $^2\Sigma_u^+$	–0.598	+0.799	14.45	14.42
C $^2\Sigma_g^+$	–0.552	+0.776	16.56	16.19

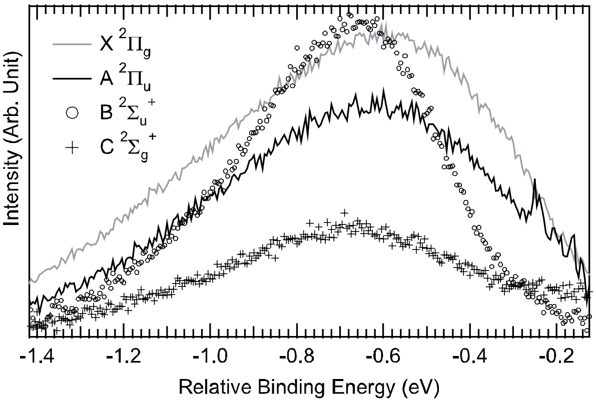

Figure 1. Valence bands for CS_2 clusters relative to the vertical binding energy of the corresponding state in a molecule.

VI-B-2 Absence of Symmetry Breaking Observed for O 1s Core-Excited SO_2 Molecule

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Electron-ion-ion coincidence measurements of sulphur dioxide at discrete resonances near the O 1*s* ionization edge were carried out. The spectra are analyzed using a dynamic model based upon molecular symmetry and on the geometry of the molecule. We have found clear evidence for molecular alignment which can be ascribed to symmetry properties of the ground and core excited states. Ab initio MR-SDCI calculations indicate geometry changes in accord with the analysis of the measured coincidence spectra. For the SO_2 molecule, however, we have found that the core-hole does not produce measurable evidence for localization, in contrast to the case of ozone, O_3. The dissociation behavior calculated using symmetry-adapted orbitals is equivalent to the behavior derived using symmetry-broken orbitals.

VI-B-3 Radiation Damage Effects on the Electronic Structure of Glycine

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The emerging field of molecular electronics has focused research on the electronic structures of biomaterials. Soft X-ray absorption and emission spectroscopy are synchrotron-based experimental probes of the electronic states of a material. These techniques can be used to determine structural, electronic and magnetic properties. However, large biological molecules such as proteins and DNA are prone to radiation damage and understanding the mechanisms that lead to the damage is essential. Amino acids are the building blocks of proteins and their simplicity makes them ideal candidates to study the effects of radiation. Radiation damage can cause organic molecules to undergo both structural changes and chemical modifications. Ab initio STEX calculation has been carried out to gain insight into the spectral changes that occur after amino acids are irradiated. It is found that deprotonation is a possible change occurring during the irradiation of glycine with soft X-rays.