Electronic Structure and Decay Dynamics in Atoms and Molecules Following Core Hole Creation

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The dynamics of the inner-shell photoexcitation, photoionization, and subsequent decay processes is much more complex, in comparison to outer-shell photo-processes. For instance, the inner-shell photoionization is concomitant with the excitation and ionization of valence electrons, which reveal themselves as shake-up and shake-off satellite structures in the corresponding photoelectron spectrum. The one-photon multi-electron processes, which are entirely due to the electron correlation in the system, are known to happen not only in the primary inner-shell hole creation processes, but also in their relaxation processes. Our research project is focused on elucidating the electronic structures and decay dynamics in core-excited atoms and molecules, by utilizing various spectroscopic techniques together with monochromatized synchrotron radiation in the soft x-ray region.

1. Ultrafast Molecular Dissociation of Core-Excited HBr Studied by High-Resolution Electron Spectroscopy

Soft X-ray absorption spectra of molecules exhibit rich structures in the region below the ionization thresholds, which are due to the excitations of a core electron to unoccupied valence or Rydberg orbitals. The core excited states are predominantly relaxed via Auger electron emission, in the case of the molecules composed of light elements, and subsequently fragmentation follows. As demonstrated by Morin and Nenner, however, a fast neutral dissociation could precede the resonant Auger decay.1) In other words, the electronic decay of the core hole takes place after the constituent atoms come apart. Since then, many research works have been conducted to identify such ultrafast dissociation processes in various different systems. Recent works on high-resolution resonant Auger electron spectroscopy have revealed that the nuclear motion of the molecular core-excited states is promoted in competition with the Auger decay. Here, we revisit the first discovery of ultrafast dissociation following the Br 3d core excitation in HBr. High-resolution electron spectroscopy for the subsequent Auger decay has been applied.

The experiments were carried out on the soft X-ray beamline BL6U at UVSOR. The radiation from an undulator was monochromatized by a variable included angle varied line-spacing plane grazing monochromator. The exit slit opening was set to 300 µm, which corresponds to the photon energy resolution $E/\Delta E$ of ~1500 at 70 eV. The monochromatized radiation was introduced into a gas cell with sample gases. Kinetic energies of the emitted electrons were measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle relative to the photon beam direction. The degree of the linear polarization of the incident light was essentially 100%, and the direction of the electric vector was set to be parallel to the axis of the electrostatic lens of the analyzer. The energy resolution of the analyzer was set to ~12 meV. Under these experimental conditions, the full width at half maximum of the vibrational fine structure for the X state of HBr^+ was measured to be ~50 meV.

Figure 1 represents a resonant Auger spectrum taken at 70.4 eV, where the $3d_{5/2}$ core-hole states are mainly populated. The vertical scale of the red line spectrum is magnified by the five times. The most marked feature in Figure 1 is the numerous sharp peaks, due to the vibrational structures for the HBr^+ states and the atomic Auger lines from the Br fragments with a 3d core-hole. In the previous work,1) only five atomic lines indicated by the blue arrows in Figure 1 have been identified, owing to the limited resolution. In contrast, at least ten more atomic Auger peaks and some molecular peaks with vibrational structures are clearly resolved in the present work. The detailed analyses for the spectral features observed are just beginning to be performed.

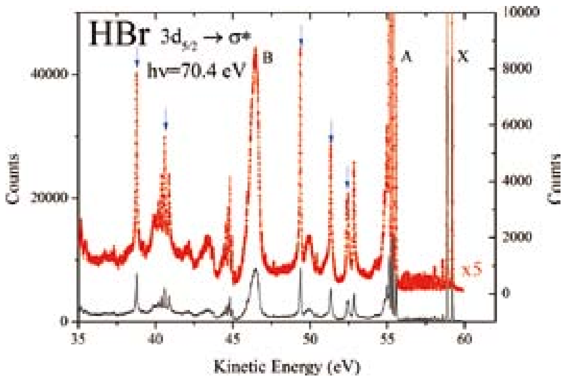

Figure 1. Resonant Auger spectrum taken at the Br $3d_{5/2} \rightarrow \sigma^*$ resonance of HBr.

2. Angle-Resolved Metastable Fragment Yields Spectra

Multi-electron processes, where more than two electrons are excited simultaneously, have usually been observed in absorption and photoelectron spectra of inner-shell excited molecules. Double excitations, one of the typical multielectron processes involving two electrons, are often observed above the ionization threshold energy region in photoabsorption spectra. Shake-up excitations in ions, where one of two electrons is excited into the continuum, are often observed in the energy region close to resonance features in photoelectron spectra. These processes occur mainly due to correlation effects among the electrons in a system and are fundamental aspects of atomic and molecular physics.

Recently, we demonstrated that "metastable" fragments spectroscopy, in which highly excited neutral fragments are observed, is quite useful as a spectroscopic technique for the investigation of multi-electron processes.[2)] Metastable photofragment spectroscopy can also be used for investigating shake-up satellites at the threshold excitation energy, because neutral photofragments can be detected wherever the scanning photon energies match the threshold energies of the ionic states. In addition, if one measures the angular distribution of the fragment emission with respect to the polarization direction of the synchrotron radiation, the symmetries of the inner-shell excited states can be deduced from this information. The angular distribution of fragments emitted after core-hole creation is related to the molecular orientation upon photoabsorption, because the lifetime of the core-hole ($\tau \sim 10^{-14}$ s) is dominated by Auger decay leading to dissociative states and is much shorter than the molecular rotational period ($\tau \sim 10^{-10}$ s). Thus, symmetry-resolved, namely, angle-resolved metastable spectroscopy provides complete symmetry resolution between the $\Delta\Lambda = 0$ (parallel) and $\Delta\Lambda = \pm 1$ (perpendicular) transitions in the *K*-shell photoabsorption of diatomic molecules. As a result, the Σ- or Π-symmetry character of transition states can be detected.[3)]

Figure 2 demonstrates a zero kinetic energy electron (ZEKE) spectrum, and angle-resolved metastable yield spectra of CO in the C *K*-edge region, measured at 0° (Σ-symmetry) and 90° (Π-symmetry), respectively, as an example of successful measurements. The photon energy range shown in Figure 2 corresponds to double and triple excitation regions, where shake-up satellite states also lie. Several peaks are clearly separated by Π-symmetry and Σ-symmetry spectra. We observed new peaks at 310.2 eV, 313.2 eV, and 313.9 eV. These should be double/triple excitation peaks since angle-resolved photoion yield spectra show small peaks at the same energy positions and these peaks have not been observed by conventional photoelectron spectroscopy. We successfully showed that all peaks in angle-resolved metastable fragment yields spectra of CO in the C 1*s* ionization threshold region can be assigned as either satellite states or double/triple excitation states.

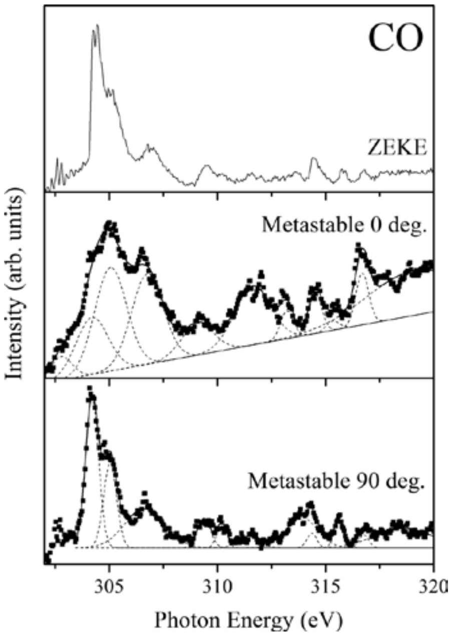

Figure 2. ZEKE spectrum, and angle-resolved metastable yield spectra, measured at 0° (Σ-symmetry) and 90° (Π-symmetry), in the satellite and double/triple excitation regions of CO in the C *K*-edge region.

References

1) P. Morin and I. Nenner, *Phys. Rev. Lett.* **56**, 1913–1916 (1986).
2) Y. Hikosaka *et al.*, *J. Phys. B* **40**, 2091–2097 (2007).
3) E. Shigemasa and N. Kosugi, *Adv. Chem. Phys.* **147**, 75–126 (2012).