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

UVSOR Facility
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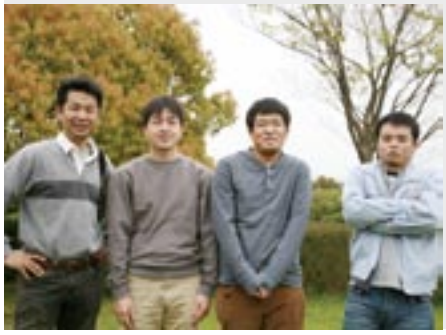

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The dynamics of the inner-shell photoexcitation, photoionization, and subsequent decay processes is much more complex, in comparison to outer-shell photo-processes. For instance, the inner-shell photoionization is concomitant with the excitation and 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. Dissociation Dynamics in Polyatomic Molecules Following Core Hole Creation

Auger electron-ion coincidence is a powerful method for studying the decay dynamics of core-excited/ionized molecules produced by soft x-ray irradiation. In order to exert the full potential of this method, the spectrometer should be equipped with a performance realizing analyses of vector correlations among the momenta of all the particles emitted. Coincidence imaging spectrometers, which enable us to measure three-dimensional momenta of both the electron and ions, have been widely used in the research field of atomic and molecular science. However it is difficult for such imaging technique to observe fast Auger electrons with a sufficient energy resolution. In this respect, a conventional electrostatic analyzer is suitable for observing the fast Auger electrons.

We have newly developed an Auger electron-ion coincidence spectrometer which consists of a double toroidal electron analyzer and a three-dimensional ion momentum spectrometer.[1)] The performance has been evaluated by measuring Auger electrons and photoions emitted after inner-shell photoionization of OCS.

2. One-Photon Multi-Electron Emission Processes Studied by Multi-Eelectron Coincidence Spectroscopy

The double photoionization (DPI) of atoms and molecules has attracted special attention for a long time because this process is due entirely to electron correlation and, consequently, investigations of DPI reveal fundamental aspects of atomic and molecular physics. Until now, most DPI studies have concentrated on the removal of two valence electrons. Direct experimental observations of core-valence or core-core DPI are limited to a few cases. This is because investigations using conventional photoelectron spectroscopy offer neither direct spectroscopy of the doubly-ionized states nor the detailed DPI dynamics. By contrast, coincidence detection between the two photoelectrons emitted in DPI processes provides direct spectroscopic information on DPI processes; however, a sophisticated coincidence method is required, because the DPI cross section is unfavorable as compared with the main inner-shell ionization processes and, consequently, the events associated with these DPI processes are easily hidden behind ordinary inner-shell photoionization events. We have introduced a very efficient coincidence technique, the magnetic bottle time-of-flight electron coincidence method, into an investigation of DPI associated with the removal of a core electron. The powerful capabilities of this coincidence method on electron coincidence observations have recently been described.[2–5)]

A multi-electron coincidence dataset for Xe was accumulated at a photon energy of 301.6 eV.[6)] Figure 1(a) shows the photoelectron spectrum in the kinetic energy range of 60–

250 eV, and Figure 1(b) displays a two-dimensional (2D) map showing coincidences between photoelectrons and slower electrons in the energy range 0–100 eV. Several diagonal stripes are observed on the 2D map. They are due to coincidences between two photoelectrons emitted through core-core or core-valence DPI. The intensity distributions along the diagonal stripes describe how the two photoelectrons produced from the DPI processes share the available energy. Resonance structures are discernable on the distributions: interactions and interference of the Xe^+ states with the DPI continua can be discussed from the resonance features.

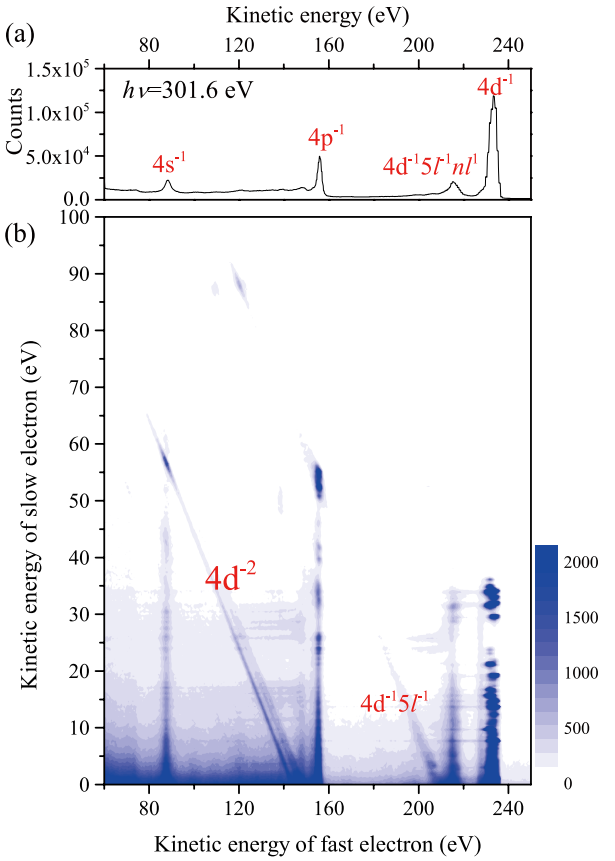

Figure 1. (a) Photoelectron spectrum of Xe obtained at a photon energy of 301.6 eV. (b) Two dimensional map of all coincidence pairs, represented as a function of the kinetic energies of fast and slow electrons.

3. Electronic Structures and Decay Dynamics in Multiply Excited States of Simple Molecules

Excitation of a core-electron in molecules can be accompanied by promotion of one or several valence electrons, due to the electron relaxation (valence polarization) and correlation effect. Such core-valence doubly or multiply excited states usually lie above the corresponding core ionization thresholds. The doubly excited states of N_2 are exhibited on the photoabsorption spectrum in the photon energy range of 413–416 eV. We have performed an inner-shell photoelectron spectroscopic study of the autoionization of the core-valence doubly excited states.[7] The principal concern is the interplay between the autoionization from the doubly excited states and the femtosecond nuclear motion. The vibrational structure of the $N_2^+(1\sigma_{g/u}^{-1})$ states in photoelectron spectra manifests the relative rates for autoionization and nuclear motion.

In order to investigate all the autoionization features of the doubly excited states, we measured photoelectron spectra in the region of 412.5–417.3 eV with the photon energy intervals of 50 meV, at both 0° and 90° with respect to the electric vector. For an effective presentation of the obtained photoelectron spectra, 2D maps were used (Figures 2 (a) and (b)). The 2D maps show clearly that the vibrational features of the $N_2^+(1\sigma_{g/u}^{-1})$ states depends strongly on both photon energy and detection angle.

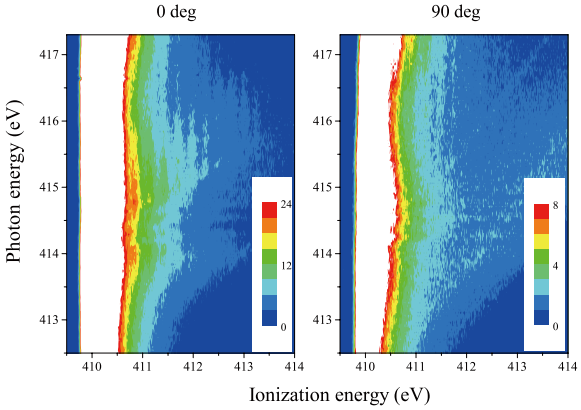

Figure 2. Two-dimensional maps of the inner-shell photoelectron yields from N_2 as a function of photon energy and ionization energy, measured in the photon energy region of 412.5–417.3 eV at (a) 0° and (b) 90° with respect to the electric vector.

References

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