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

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The dynamics of the inner-shell photoexcitation, photo-ionization, 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 spectro-scopic techniques together with monochromatized synchrotron radiation in the soft x-ray region.

1. Doppler Effect in Fragment Autoionization Following Core-to-Valence Excitations

The Doppler effect is known to occur when the source and observer are in motion relative to each other, leading to an apparent change in the observed frequency of the propagating wave. This effect has a wide variety of applications in many fields, relating to the sensing of movement. In the research field of molecular science, the sensing of nuclear motion has long been an attractive issue. Gel'mukhanov and co-workers predicted in 1998[1] that the nuclear motion in 'ultrafast disso-ciation' following molecular core-level photoexcitation can be probed by the Doppler effect in emitted Auger electron. Ultrafast dissociation is a process where the molecular dis-sociation at the core-excited state precedes the Auger decay and then an atomic fragment emits an Auger electron. This atomic Auger electron can possess the opposite Doppler shift

depending on the direction approaching the detector (label (A) in Figure 1(a)) or moving away from it (label (B) in Figure 1(a)). This electron Doppler shift in kinetic energy can be expressed as $\mathbf{p}\cdot\mathbf{v}$, where $\mathbf{p}$ is the momentum of the electron and $\mathbf{v}$ is the velocity vector of the emitting fragment, and thus it becomes maximum when both vectors are parallel. Although molecules in the gas phase are randomly oriented, molecular photoabsorption is known to be highly anisotropic relative to the polarization vector of the incident radiation. Therefore, detection of the emitted Auger electron along the preferred direction of emission of the fragment makes the measurement of the Doppler shift possible experimentally.

In our recent works,[2] it has been disclosed that the Doppler effect can be utilized as a unique tool to investigate the molecular dynamics at singly-charged ion states produced by resonant Auger decay. Special attention is paid to detecting slow electrons. In cascade Auger decay, two electrons are ejected sequentially with distinct kinetic energies depending on the energy levels of the initial, intermediate, and final electronic states involved. One of the two emitted electrons is often slow (typically less than 5 eV). Singly-charged molecu-lar ion states populated by the first electron emission can undergo competition between second electron emission and molecular dissociation. If one of the dissociating fragments is excited it may subsequently autoionize; the autoionizing atomic fragment can act as an electron emitter which can exhibit a Doppler splitting if the kinetic energy of the atomic fragment is sufficiently large and the initial photoabsorption anisotropy is substantially maintained in the angular distri-bution of fragments.

As an example, the O* autoionizing electron spectrum following the O1s $\rightarrow$ σ^* excitation in O_2 is denoted in Figure 1(b). Clear Doppler profiles, depending on the fragment-ion directions as labeled in (A) or (B), are discernable in the atomic oxygen autoionization peaks. The corresponding Doppler

profiles, as a counterpart of the fragmentation process, are also seen in the atomic Auger electron peak. It is clarified that femtosecond dissociation dynamics of singly-charged ion states produced by resonant Auger decay can be deduced from the information obtained by analyzing the Doppler profiles. In the cascade Auger decay following the O1s → σ* excitation in O_2, it is concluded that the slow Auger electrons are produced by autoionization of valence-excited atomic fragments created simultaneously to the core-excited atomic fragments during ultrafast dissociation of the oxygen molecule.
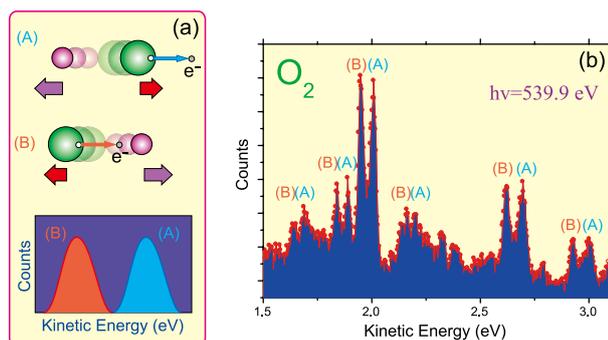
Figure 1. (a) Schematic representations for explaining a source of the electron Doppler splittings in kinetic energy, and (b) Doppler splittings observed in the autoionizing electron spectrum from an atomic oxygen following the O1s → σ* excitation in O_2.

2. Two-Dimensional Electron Spectroscopy on BL6U

A new project for constructing the undulator beamline BL6U has been initiated since 2007. A Monk-Gillieson mounting with a variable-included-angle mechanism has been chosen, in order to cover a wide photon energy region (30–500 eV) with one single grating. It has been confirmed through its performance tests that the monochromator designed can cover the photon energy ranging from 40 to 400 eV with the resolving power higher than 5000 and the photon flux more than 10^{11} photons/sec, when the storage ring is operated in the top-up mode.

A new electron spectrometer, MBS-A1, for gas phase spectroscopy has successfully been installed, in parallel with the construction program of BL6U. High-resolution electron spectroscopy is a powerful method to study electronic structures of atoms and molecules, especially when high-resolution electron spectra and their polarization dependences are measured as a function of photon energy. The ability of this two dimensional (2D) electron spectroscopy has been proved in our recent work at SPring-8.[2,4] In order to apply high-resolution 2D electron spectroscopy to the investigation of the L-shell excitations of the second row elements, a new experimental setup for BL6U has been designed and constructed.

For realizing 2D electron spectroscopy with high resolution, software development for controlling both the beamline monochromator and MBS-A1 analyzer has been performed. For the beamline monochromator, not only its output but the gap of the undulator should be controlled. After careful optimizations for the undulator gaps, 2D electron spectroscopy on BL6U has become feasible, thanks to the stable operation of the UVSOR-II storage ring.

Figure 2 demonstrates the 2D maps for the de-excitation spectra following the double excitations near the carbon 1s photoionization threshold in CO, measured in (a) horizontal, and (b) vertical directions, respectively, as an example of successful measurements. The exit slit opening of the monochromator was set at 30 μm, which corresponds to the photon energy resolution of about 60 meV. The pass energy and slit width of the MBS-A1 analyzer were set to 100 eV and 0.2 mm, which results in the electron energy resolution of about 60 meV. The straight lines with a slope of 1 in the high kinetic energy (KE) region in each 2D map are due to the valence photoelectrons with vibrational structures. The vertical lines around KE of 275 eV in Figure 2(b) are assigned to the atomic Auger line from oxygen atoms after the dissociation of CO molecules. Some island-like structures are seen in the KE range of 267–270 eV in Figure 2(a) and Figure 2(b), which seem to be specific to the decay processes of the double excitations. The complicated photon energy dependences of the structures may suggest that the de-excitation processes of the doubly excited states of CO are not so simple.
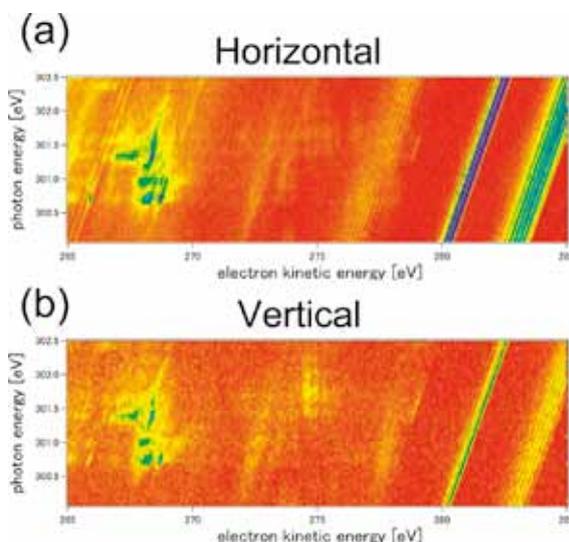
Figure 2. 2D map of de-excitation spectra following the double excitations around the carbon K-edge of CO, measured in (a) horizontal, and (b) vertical directions, respectively.

References

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