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

UVSOR Facility
Division of Advanced Photochemistry

SHIGEMASA, Eiji — Associate Professor
HIKOSAKA, Yasumasa — Assistant Professor*
IWAYAMA, Hiroshi — Assistant Professor

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. PCI Effects in Double Auger Decay Probed by Multi-Electron Coincidence Spectroscopy

An inner atomic vacancy created by photoionization can decay by emission of radiation or by Auger decay. For L shells, the Auger decay is generally more probable and can occur with emission of one electron (single Auger decay) or of a few electrons (multiple Auger decay). The probability of multiple Auger decay is usually lower than the probability of single Auger decay but can be high enough to allow experimental observations. Recent progress in coincidence measurements opened the path to a deeper search of the double Auger (DA) decays. DA implies that the filling of the inner-shell vacancy by an outer electron can cause the ejection of two electrons. This process is in its turn divided into the direct double Auger decay (DDA) when the two electrons are emitted simultaneously and cascade double Auger decay (CDA) when the electrons emission occurs in two steps through the creation and decay of an intermediate quasi stationary state.

PCI is known as a special kind of electron correlation associated to the interaction between the charged particles of a resonant process, through the creation and decay of an intermediate quasi stationary state. In the case of inner shell photoionization, PCI reduces to the interaction of the emitted photoelectron with the Auger electrons and with the ion field which varies during the Auger decay. PCI in single Auger decay following inner-shell photoionization is quite well documented both experimentally and theoretically, but PCI in the DA processes has been much less studied.

In the present study, we reveal and investigate the PCI effects in DA processes, using Ar 2p inner-shell ionization as an example.[1)] We present a systematic investigation of photoelectron spectra measured in coincidence with two Auger electrons. The PCI distortion of the photoelectron and Auger lines is shown to be important both for DDA and CDA processes. Our measurements are supported by calculations based on an eikonal approach of PCI. The results of calculations are in good agreement with the experimental data thus demonstrating the adequacy of the theoretical model to the phenomenon considered. The analysis of the experimental and theoretical results shows that the photoelectron line shape depends both on the variation of the ionic field and on the interaction with the slow Auger electron. Moreover since the line shapes for DDA and CDA processes are slightly different, their analysis allows us to extract properties of the associated DA decays.

2. Doppler Effect in Fragment Autoionization Following Core-to-Rydberg 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 physics, the sensing of nuclear motion has long been an important issue. Gel'mukhanov and co-workers predicted in 1997[2] that the nuclear motion in 'ultrafast dissociation' following molecular core-level photoexcitation can be probed by the Doppler effect in emitted Auger electron. Ultrafast dissociation is a process in which the molecular dissociation at the core-excited state precedes the Auger decay and then an atomic fragment emits an Auger electron. The atomic Auger electron can possess the opposite Doppler shift depending on the direction approaching the detector or moving away from it.

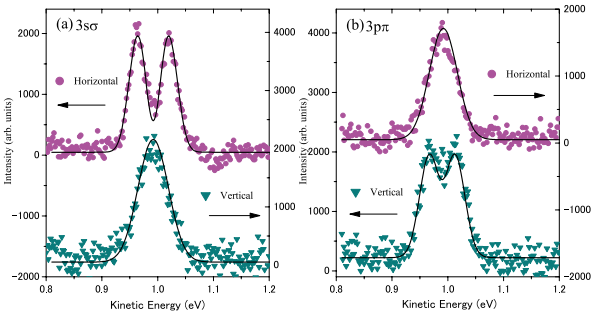

Figure 1. Doppler splitting observed in autoionizing electron spectra from an atomic nitrogen following the N1s to (a) 3sσ and (b) 3pπ Rydberg excitations of N_2.

In the current work, it is demonstrated that the Doppler effect can be utilized as a new tool to study 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 molecular 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 show Doppler splitting if the kinetic energy of the atomic fragment is sufficiently large and the initial photoabsorption anisotropy is substantially maintained in the angular distribution of fragments. Since anisotropic angular distributions of fragment-ions have clearly been observed in core-to-Rydberg excitations for simple linear molecules, the core-to-Rydberg excitations can be suitable precursors for observing Doppler shifts in the second step electron emissions.

As an example, the polarization dependences of the N*(4d $^2F^e$) autoionization peak following the 3sσ and 3pπ Rydberg excitations are shown in Figure 1. Clear Doppler profiles are observed in the atomic autoionization peaks, which also display clear polarization dependences on the symmetries of the excited states. It is demonstrated that femtosecond dissociation dynamics of singly-charged ion states produced by resonant Auger decay can be deduced from the information obtained by analysis of the Doppler profiles.

3. Construction of a New Experimental Setup for Gas Phase Electron Spectroscopy on BL6U

Parallel to the construction program of BL6U, the installation of a new electron spectrometer for gas phase spectroscopy has been initiated. High-resolution electron spectroscopy is a powerful tool to investigate electronic structures of atoms and molecules, especially when high-resolution electron spectra and their polarization dependences are measured as a function of photon energy in high-resolution mode. The ability of this two dimensional (2D) electron spectroscopy has been demonstrated in our recent work at SPring-8,[3] where a special attention is paid for detecting slow electrons following core excitations.

Figure 2 shows a photograph of the experimental setup, which is roughly composed of a vacuum chamber, a rotational mechanism, an MBS-A1 analyzer, a gas cell, and a double layer mu-metal screen. The analyzer is rotatable around the photon beam axis. The vacuum chamber and the rotational mechanism have been designed at UVSOR, and fabricated by TOYAMA Co., Ltd. The practical utilization of the new experimental setup has begun since October 2009.

Figure 2. A side view of the newly constructed experimental setup for gas phase electron spectroscopy on BL6U.

References

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* Present Address; Department of Environmental Science, Niigata University, Niigata 950-2181