

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

UVSOR Facility  
Division of Advanced Photochemistry



SHIGEMASA, Eiji  
HIKOSAKA, Yasumasa

Associate Professor  
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. Dissociation Dynamics in Polyatomic Molecules Following Core Hole Creation

The acetylene dication is one of the smallest metastable polyatomic dications, whose dissociation and isomerization from the acetylene (HCCH) into the vinylidene (H<sub>2</sub>CC) configurations have been extensively investigated. By using the PEPIICO technique, it was found that the acetylene dications dissociate from excited states above 34 eV, where five three-body reactions and three two-body reactions including the dissociation channel via the vinylidene form (CH<sub>2</sub><sup>+</sup> + C<sup>+</sup>; V-channel) have been identified. The isomerization time of the acetylene dication produced following the Auger decay was estimated to proceed within 60 fs. Very lately, the visualization of ultrafast hydrogen migration in deuterated acetylene dication, which occurs in a recurrent manner, was nicely demonstrated by using intense ultrashort laser pulses.<sup>1)</sup>

In the previous work, in addition to the V-channel, the other two channels in the two-body reactions, such as the acetylene channel (CH<sup>+</sup> + CH<sup>+</sup>; A-channel) and deprotonation

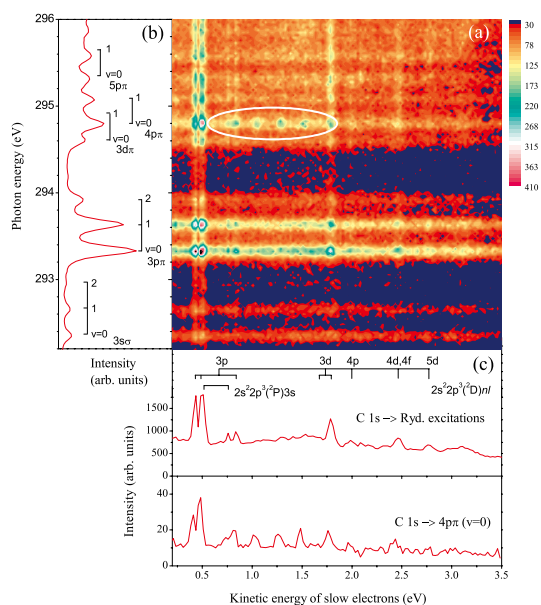
channels (C<sub>2</sub>H<sup>+</sup> + H<sup>+</sup>; P-channel), were correlated with some Auger final states. In order to gain a further insight into the dissociation mechanism of the Auger final states, we have performed an Auger-electron-ion coincidence study on fragmentations of deuterated acetylene dication, C<sub>2</sub>D<sub>2</sub><sup>2+</sup>, formed via Auger decay. With the use of our Auger-electron-ion coincidence spectrometer,<sup>2)</sup> we have identified Auger final states relevant to the individual fragmentations including the three-body reaction, as well as to the formation of metastable C<sub>2</sub>D<sub>2</sub><sup>2+</sup>.

It is found that the atomic fragment ions tend to be produced in the entire region of Auger electrons, while the molecular ions except for CD<sup>+</sup> exhibit specific productions for certain Auger final states. The parent dications are mainly observed at the lowest band, which shows a clear maximum around 33.3 eV. The CD<sub>2</sub><sup>+</sup> fragments related to the V-channel, as well as the atomic fragments C<sup>+</sup> and D<sup>+</sup> yield the highest energy peak in the 1π<sub>u</sub><sup>-2</sup> band at 35.0 eV. The highest binding energy band centered at 50 eV enhances violent fragmentation leading to the productions of C<sup>+</sup>, D<sup>+</sup>, CD<sup>+</sup>, and C<sub>2</sub><sup>+</sup>.

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

Neutral core-excited states of low-Z atoms relax mainly by electron emission, which has been investigated intensively in rare gases. It leads predominantly to singly-charged ions, but formation of doubly-charged ions by emission of two Auger electrons also makes up a considerable fraction of the total decay. Both direct and indirect processes can contribute to resonant double Auger decay. In the direct process, two electrons are simultaneously ejected and the available energy is continuously shared between the two electrons. In the indirect process, two electrons are emitted sequentially with distinct kinetic energies depending on the energy levels of the initial,

intermediate, and final electronic states involved. Resonant double Auger decay of molecules is indeed known to exist from mass spectroscopic studies of ions. However, the molecular process is much more complicated than the atomic one, because it can be influenced by nuclear motions at any stage of the decay. In order to clarify the resonant double Auger process in molecules, we have used high-resolution electron spectroscopy and electron-electron coincidence spectroscopy.



**Figure 1.** (a) Two-dimensional (2D) map of the slow electron yields in the C1s-to-Rydberg range. (b) Total ion yield spectrum. (c) Top: Sum of the slow electron yields in the Rydberg excitation region which is derived by projecting the electron yields in the 2D map onto the horizontal axis. Bottom: slow electron spectrum at the C 1s → 4pπ ( $\nu = 0$ ) resonance.

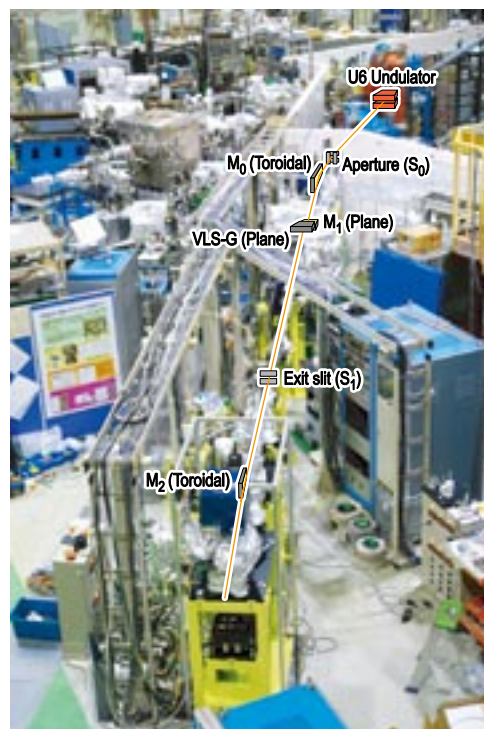
Figure 1 shows a two-dimensional (2D) map of slow electron yields as a function of the photon energy in the C 1s Rydberg excitation region of CO, with the total ion yield spectrum measured together with the slow electron yields. The 2D map exhibits horizontal stripes in the Rydberg resonances. Knots of enhancement are discernible in each stripe on the 2D map. The locations of some of these knots are common to all different C1s-to-Rydberg excitations. The observation implies that dissociation of CO<sup>+</sup> states formed by first-step Auger decay and subsequent fragment O\* atom autoionization constitute a major path for the double Auger decay of the C1s-to-Rydberg states. It is also found that additional spots appearing only on the 4pπ ( $\nu = 0$ ) resonance. These spots are spaced at 0.24 eV intervals, as clearly seen in the horizontal cut of the 2D map on this resonance [bottom panel of Figure 1(c)]. The constant intervals suggest that the peaks correspond to vibrational levels of CO<sup>+</sup> or CO<sub>2</sub><sup>+</sup>, and are therefore associated with molecular autoionization of CO<sup>+</sup> into CO<sub>2</sub><sup>+</sup>. The mechanisms of the complicated molecular double Auger decay has nicely been clarified by the combined use of the two different spectroscopic methods.

### 3. Construction of New Soft X-Ray Spectroscopy Beamline BL6U

A new project for constructing the undulator beamline BL6U has been initiated. We have decided to choose the entrance slit-less configuration for the monochromator. A varied-line-spacing (VLS) plane grating monochromator (PGM) seems to be one of the most trustworthy ones to realizing high resolution in the soft x-ray range. In order to cover a wide photon energy region (30–500 eV) with one single grating, a variable-included-angle Monk-Gillieson mounting VLS-PGM has been selected.

The monochromator has been designed to cover the photon energy ranging from 30 to 500 eV, with the resolving power higher than 10000 and the photon flux more than 10<sup>10</sup> photons/sec. The practical construction of BL6U has begun from the summer shutdown in 2008. The first light has been observed in December 2008 and then precise tunings of the monochromator have been continued.

The installation of a new electron spectrometer to BL6U, which can be rotated around the photon beam axis, has been finished in August 2009, and its performance test has begun.



**Figure 2.** A top view of the newly constructed soft X-ray spectroscopy beamline BL6U.

#### References

- 1) A. Hishikawa, A. Matsuda, M. Fushitani and E. Takahashi, *Phys. Rev. Lett.* **99**, 258302 (4 pages) (2007).
- 2) T. Kaneyasu, Y. Hikosaka and E. Shigemasa, *J. Electron Spectrosc. Relat. Phenom.* **156-158**, 279–282 (2007).
- 3) T. Kaneyasu, Y. Hikosaka, P. Lablanquie, F. Penent, L. Andric, G. Gamblin, J. H. D. Eland, Y. Tamenori, T. Matsushita and E. Shigemasa, *Phys. Rev. Lett.* **101**, 183003 (4 pages) (2008).