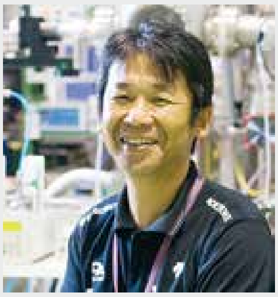
Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

UVSOR Facility
Division of Advanced Photochemistry



SHIGEMASA, Eiji
Associate Professor
[sigemasa@ims.ac.jp]

Education
1986 B.S. Hiroshima University
1988 M.S. Osaka University
1997 Ph.D. The University of Tokyo

Professional Employment
1990 Research Associate, National Laboratory for High Energy Physics
1997 CEA Researcher, LURE, Université de Paris-Sud
1999 Associate Professor, Institute for Molecular Science
2007 Associate Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
IWAYAMA, Hiroshi

Keywords Soft X-Ray Spectroscopy, Inner-Shell Excitation, Photodissociation Dynamics

The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals. The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.

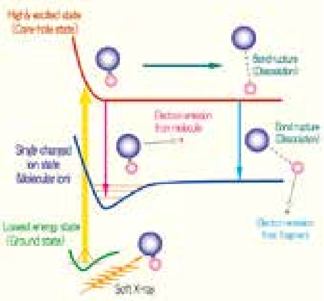


Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, Eds., S.A. Rice and A. Dinner, Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, "Ultrafast Dynamics in C 1s Core-Excited CF_4 Revealed by Two-Dimensional Resonant Auger Spectroscopy," *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).

1. Ultrafast Dissociation of Inner-Shell Excited CF_4 Molecules Studied by an Auger-Electron–Ion Coincidence Method

Recently, we found a signature of ultrafast dissociation following C 1s → $\sigma^*(t_2)$ core excitation in CF_4 by using two dimensional electron spectroscopy.[1] We observed Auger electrons from both CF_3^* fragment and CF_4^* parent molecule. This means that the Auger decay and dissociation processes take place on the same time scale and significantly compete with each other. In the current study, we have investigated anisotropic angular distributions of ejected CF_3^+ ions by using an Auger-electron–ion coincidence method. Since the CF bond involved in the C 1s → $\sigma^*(t_2)$ core excitation is immediately broken due to the ultrafast dissociation, anisotropic angular distributions of ejected the CF_3^+ ions are expected.

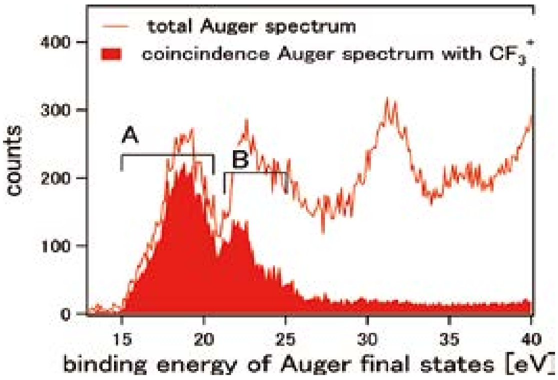


Figure 2. Non-coincident and coincident Auger electron spectra with CF_3^+ ions.

The Auger-electron–ion coincidence measurements were carried out on the undulator beamline BL6U at UVSOR. The radiation from an undulator was monochromatized by a variable included angle varied line-spacing plane grating monochromator. The electrons ejected at 54.7° with respect to the electric vector of the incident radiation were analyzed in energy by a double toroidal analyzer (DTA), while ions were extracted from the interaction region into a momentum spectrometer by a pulsed electric field according to the electron detection. Arrival position on the detector and time-of-flights of ions were recorded for every event. The pass energy of the DTA was set to 200 eV for observing the Auger electrons. The energy resolution was about 1.9 eV.

Figure 2 shows non-coincident and coincidence Auger spectra with CF_3^+ ions. It is seen that the CF_3^+ ions are coincident with electrons at the binding energy of 15 ~ 25 eV, where two peaks A and B are detected. For higher binding energies, we observed smaller fragment ions such as CF_2^+, CF^+ and C^+ (not shown here). From the previous work,[1] the peaks A and B are attributable to the Auger electrons from the CF_3^* fragment and CF_4^* parent molecules, respectively.

Figures 3(a) and 3(b) show ion images of CF_3^+ fragments, which were taken in coincident with electrons at the peaks A and B, respectively. The angular distribution of CF_3^+ ions is considerably anisotropic in Figure 3(a), while almost isotropic angular distributions are seen in Figure 3(b). Two island-like structures along the polarization vector are clearly observed in Figure 3(a). This means that the core-excited CF_4 molecules lead to immediate CF bond breaking, which is the direct evidence of the ultrafast dissociation for the peak A. The detailed data analyses are now in progress.

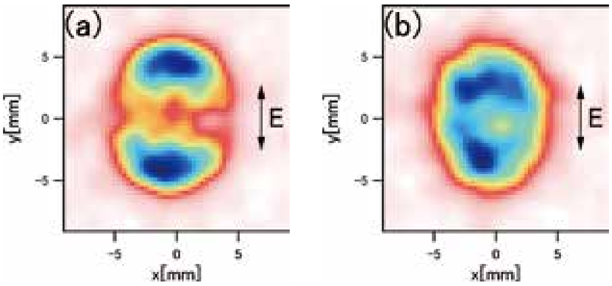


Figure 3. Ion images of CF_3^+ ions taken in coincident with Auger electrons at (a) peak A and (b) peak B.

2. Photoionization of Helium Atoms by Higher Harmonic Radiation from a Helical Undulator

The n_{th} harmonic radiation from a helical undulator carries orbital angular momentum (OAM) of $(n-1)\hbar$ per photon.[2,3] This accelerator-based method efficiently generates the OAM photon beam in a wide wavelength range. As a first step of the application study of the OAM photon beam, we have investigated the interaction of the OAM photon and gas-phase atoms in which violation of the dipole selection rules is predicted.[4]

The experiments were performed at the undulator beamline BL1U during the machine study operations. We observed the angular distributions of the He 1s photoelectrons by using an imaging spectrometer. The downstream part of the tandem APPLE-II undulators was used with horizontal and circular polarization modes. The OAM photon beams were obtained as the 2nd and 3rd harmonic radiation in the circular polarization mode.

Concerning the horizontal polarization and the fundamental radiation with circular polarization, the photoelectron angular distributions measured are fairly in agreement with those calculated by assuming the normal dipole transition. This confirms the validity of the analyzing procedure in the present study. The analysis of the photoionization by the OAM photon is in progress. Although preliminary result indicates the slight deviation from the dipole selection rule in the OAM photoionization, it is required to perform more precise measurements for unveiling the influence of the OAM photon.

References

1) M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).
2) S. Sasaki and I. McNulty, *Phys. Rev. Lett.* **100**, 124801 (2008).
3) J. Bahrdt *et al.*, *Phys. Rev. Lett.* **111**, 034801 (2013).
4) A. Picón *et al.*, *New J. Phys.* **12**, 083053 (2010).