

Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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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.

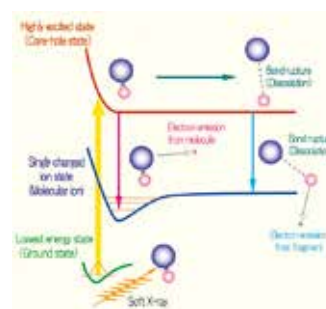


Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, S. A. Rice and A. Dinner, Eds., Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- H. Iwayama, T. Kaneyasu, Y. Hikosaka and E. Shigemasa, "Stability and Dissociation Dynamics of N_2^{2+} Ions Following Core Ionization Studied by an Auger-Electron-Photoion Coincidence Method," *J. Chem. Phys.* **145**, 034305 (8 pages) (2016).

1. Anisotropic Angular Distributions of CF_3^+ Fragment Ions Following Ultrafast Dissociation of CF_4

Following inner-shell excitation, the relaxation pathway of a molecular system involves complex fragmentation patterns, depending on the nature of the core-excited state (bound or dissociative), and/or of the final states reached after the whole relaxation process. In particular, elongation and breaking of chemical bonds can occur in many molecular systems during the lifetime of the excited state: In this case, the dissociation is defined as ultrafast, since typical lifetimes of core-excited states in molecules containing light atoms are of the order of few femtoseconds (see e.g. ref. 1)). Molecular fragmentation can also occur in a final state reached after resonant Auger decay, if such final state is unstable. In this case, the time scale for the breaking of the chemical bond is much longer. In this work, we performed resonant Auger-electron-ion coincidence measurements, which allowed us to enlighten the angular distributions of the fragments.

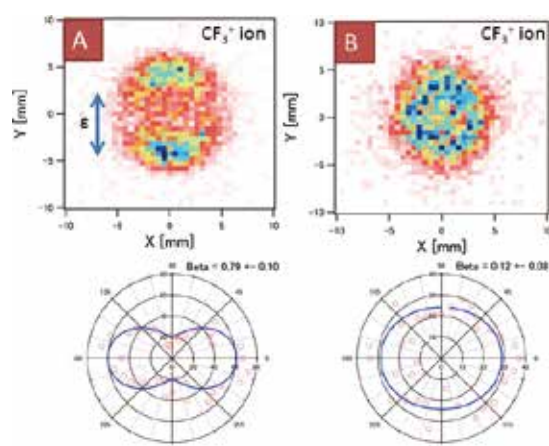


Figure 2. Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after $\text{C } 1s \rightarrow \text{LUMO}$ excitation: (A) the lowest binding energy peak related to the ultrafast dissociation and (B) the second lowest peak corresponding to $3t_2^{-1}$ final states. The lower figures represent the results of the fitting procedures.

Figure 2 shows Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after $\text{C } 1s \rightarrow \text{LUMO}$ excitation. The coincidence resonant Auger spectrum exhibits two broad peaks. The lower binding energy peak corresponds to the resonant Auger decay of the CF_3^* fragment originated from ultrafast dissociation, while the higher is related to the molecular CF_4^+ final states ($3t_2^{-1}$).²⁾ The angular distributions of CF_3^+ ions in panels (A) and (B) of Figure 2 have been taken in coincidence with the former and the latter peaks, respectively. The electric vector e is vertical in both cases. It can immediately be seen that in the case of ultrafast fragmentation (A) the angular distribution of the CF_3^+ ions is quite asymmetric and peaked along the e vector, while in the case of (B) the angular distribution is much more isotropic. These observations strongly suggest that the time scales of the two dissociation channels are different:

For the ultrafast dissociation, the molecule has no time to rotate and the fragments are emitted according to the maintained orientation of the core-excited species, while for the dissociation after the resonant Auger decay, the molecule still keeps some memory of the excitation process before re-assuming random orientation.

2. Limitations in Photoionization of Helium atoms by Extreme Ultraviolet Vortex

A circularly polarized extreme ultraviolet vortex (XUV) beam can be produced by a helical undulator. The XUV vortex beam carries not only spin angular momentum but also orbital angular momentum (OAM) with a helical wavefront. It is known that the n th harmonic off-axis radiation from a helical undulator carries OAM of $(n-1)\hbar$ per photon. According to recent theoretical works, it is predicted that a violation of the so-called electric dipole selection rules can be observed as a result of the transference of the OAM to the system. In order to investigate vortex-matter interactions in the short wavelength region experimentally, photoionization of helium atoms by the circularly polarized XUV vortex beam has been studied.

Figure 3 shows the angular distributions of photoelectrons measured for (A) the first, (B) second, and third harmonics, which correspond to plane-wave photons ($l = 0$), and the XUV vortices ($l = 1$ and $l = 2$), respectively. As seen in Figure 3, the angular distributions of photoelectrons are well reproduced by the dipole components alone, in contrast to the theoretical predictions. It is found that non-dipole transitions by vortex are hardly observable in conventional gas phase experiments.

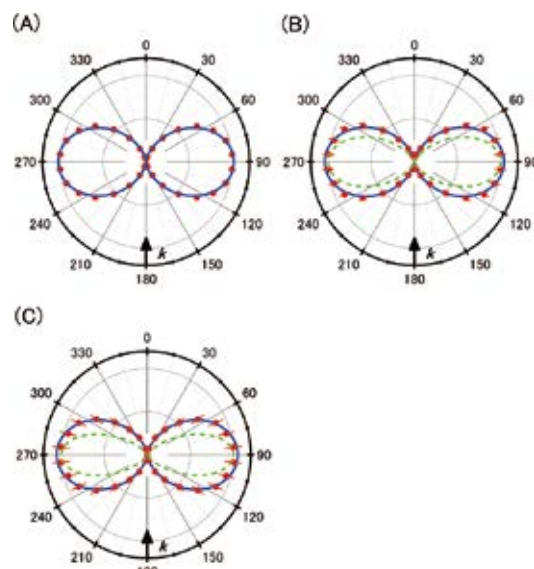


Figure 3. Angular distributions of $1s$ photoelectrons from helium atoms measured for (A) the first, (B) second, and (C) third harmonics from a helical undulator.

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