

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

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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. Ultrafast Dynamics in C 1s Core-Excited CF<sub>4</sub> Studied by Two-Dimensional Resonant Auger Spectroscopy

Excitation of a core electron to the lowest unoccupied antibonding orbital weakens the molecular bonding and populates generally a dissociative state. Morin and Nenner demonstrated that the  $3d \rightarrow \sigma^*$  excitation in HBr leads to a fast neutral dissociation which can precede the Auger relaxation; in other words, one can observe 'atomic' 3d hole decays in the Br fragment.<sup>1)</sup> The CF<sub>4</sub> molecule, tetrafluoro methane, has been a benchmark for several spectroscopic studies, due to its high symmetry, same as methane, CH<sub>4</sub>. One of the most interesting observations deriving from the comparison between CH<sub>4</sub> and CF<sub>4</sub> is the relative intensity of below-threshold photoabsorption structures around the C 1s ionization thresh-

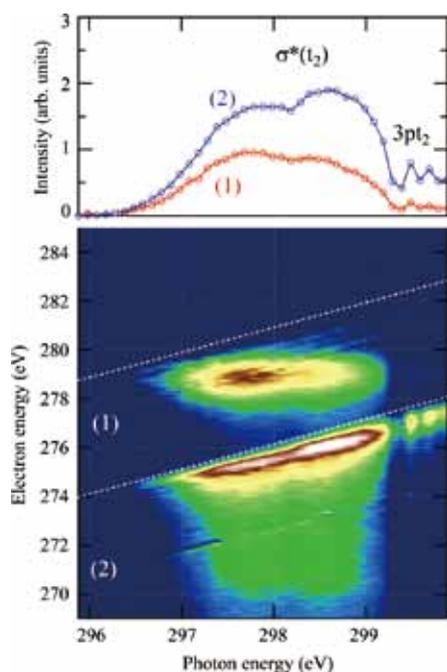
old associated with transitions to empty molecular orbitals versus Rydberg states. CF<sub>4</sub> is a good candidate to investigate the dynamical properties of core-excited states with an electron in the antibonding lowest-unoccupied molecular orbital (LUMO) in a highly symmetric system.

Here an investigation of ultrafast dissociation following C1s-to-LUMO core excitation in CF<sub>4</sub>, with high-resolution resonant Auger spectroscopy, is presented. The main novelty of this work is the use of two-dimensional (2D) maps to record resonant Auger spectra across the resonance as a function of photon energy with a small energy step and then to characterize ultrafast dynamics. This method allows one to follow in great detail the evolution of the resonant enhancement of spectral features corresponding to final ionic states while scanning the energy across the resonance, and to fully exploit the so-called detuning effects.

The experiment was performed on the soft X-ray beamline BL6U at UVSOR. The photon energy resolutions were set to 10000 and 4000 for total-ion yield and 2D map measurements, respectively. Kinetic energies of the emitted electrons were measured by a hemispherical electron energy analyzer (MBS-A1). The direction of the electric vector was set to be parallel to the axis of the electrostatic lens of the analyzer. The kinetic energy resolution of the analyzer was set to 60 meV. The 2D maps were obtained by taking decay spectra at regular photon energy intervals of 100 meV across the resonance.

Figure 1 shows the 2D map after subtraction of the non-resonant contributions, and with on-top two pseudo-absorption curves obtained by the CIS (Constant Ionic State) method, and namely plotting the integrated intensity of the two resonant features, the non-dispersive one related to the fragment and the dispersive one related to the  $3t_2$  state, as a function of photon energy. The double feature with maxima at 297.7 and 298.4

eV is assigned to the Jahn-Teller-split transition to the LUMO ( $\sigma^*$  of  $t_2$  symmetry), followed by the Rydberg series. It is seen that while the intensity of the molecular state closely mimics one of the absorption curve, the non-dispersive feature related to the fragment decreases in relative intensity across the resonance, and disappears in the photon energy region of the Rydberg states. Detailed calculations on the potential curves of the intermediate and final state would be needed to fully clarify this finding.



**Figure 1.** Top: CIS spectra of the fragment (1) and of the  $3t_2$  (2) final states. Bottom: resonant Auger 2-D map showing only the resonant contributions: (1) the non-dispersive state and (2) the  $3t_2$  spectral line.

## 2. High-Resolution Electron Spectroscopy for Ethyl Trifluoroacetate

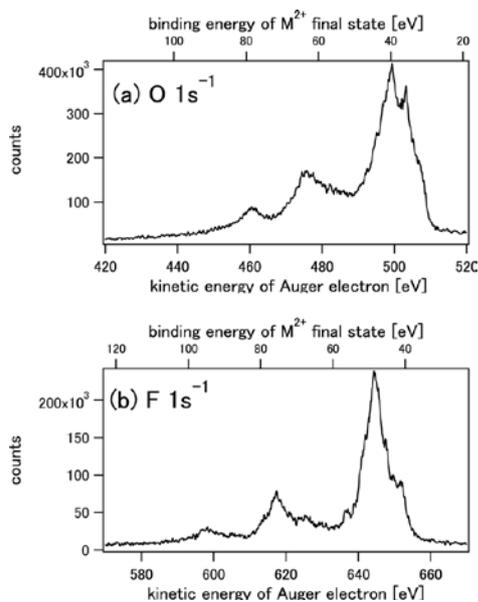
Inner-shell photoionization of light elements is mostly relaxed via an Auger decay process, causing the emission of another electron from an outer-shell. Auger electron spectroscopy (AES) is thus an element-sensitive method with various analytical applications. Since a core hole can be regarded as being strongly localized at a particular atom, it can be expected that the Auger final dicationic state has two valence holes which are also localized near the inner-shell ionized atom. According to this simple atomic picture, the binding energies of the molecular Auger final states would also show chemical shifts. Owing to a hole-hole repulsion, the chemical shift in Auger electron spectra reflects any localization character of the two valence holes.

The interpretation of molecular Auger spectra is complex and the difficulties increase with increasing the number of atoms in a molecule. The Auger spectra become much more complicated in the case where a molecule is composed of several atoms of the same element. While well-defined photoelectron peaks reflecting the chemical shifts can be observed in photoelectron spectra, direct observations of the corre-

sponding chemical shifts in molecular Auger spectra are practically impossible without using a coincidence technique. In order to stabilize the interpretation on the site-specific Auger spectra obtained by such coincidence experiments, however, high-resolution Auger electron spectra as well as theoretical calculations are indispensable. We have carried out high-resolution electron spectroscopic measurements on ethyl trifluoroacetate ( $C_4H_5F_3O_2$ ).

The experiment was performed on the soft X-ray beamline BL6U at UVSOR. The radiation from an undulator was monochromatized by a variable included angle varied line-spacing plane grazing monochromator. The monochromatized radiation was introduced into a cell with sample gases. Kinetic energies of the emitted electrons were measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle with respect to the photon beam direction. The direction of the electric vector was set to be parallel to the axis of the electrostatic lens of the analyzer. The energy resolution of the analyzer was set to 20 meV.

The oxygen and fluorine Auger electron spectra are displayed in Figure 2 (a) and (b), respectively. It is seen that the populations of the Auger final states strongly depend on which core electron is ionized. No fine structure is found in every Auger electron spectrum, in spite of the high-resolution. The Auger spectra have been simulated using a statistical approach. It is found that all Auger decays populate mainly localized dicationic states, with the two holes located either on the same fluorine atom or on adjacent fluorine atoms. While the decay of the F 1s hole populates exclusively the former states, the latter class of states is also populated by the decay of the C and O 1s holes.



**Figure 2.** (a) Oxygen and (b) fluorine Auger electron spectra of  $C_4H_5F_3O_2$ .

## References

- 1) P. Morin and I. Nenner, *Phys. Rev. Lett.* **56**, 1913–1916 (1986).
- 2) M. N. Piancastelli *et al.*, *J. Chem. Phys.* **138**, 234305 (2013).
- 3) H. Iwayama *et al.*, *J. Chem. Phys.* **138**, 024306 (2013).