

ULTRAFAST FRAGMENTATION PROCESSES OF CF₄ STUDIED BY ELECTRON-ION MOMENTUM COINCIDENCE SPECTROSCOPY

While purely spectroscopic methods like XPS yield information about the electronic and geometrical structure of materials, dynamic phenomena like chemical reactions can only be investigated using time-resolved or coincidence methods. One class of model reactions is ultrafast fragmentation of core excited small molecules. In the pre-edge region soft X-ray absorption spectra show a rich structure due to the excitation of a core electron to unoccupied molecular orbitals. This excitation leads to well defined initial states which can be considered a model of an intermediate state of a chemical reaction, even though the excitation energy involved is much higher than those in typical chemical reactions. Nuclear relaxation of the core-excited state takes place on a femtosecond time scale, in competition with the electronic relaxation. This femtosecond nuclear motion can be studied using an electron-ion momentum correlation measurement.

In the present work we focus on a specific Auger electron emission that belongs to atomic like Auger transition from the core excited F atom produced via ultrafast dissociation of a core excited CF₄ molecule [1]. We consider the following sequence of reactions:

- (1) $\text{CF}_4 + h\nu \rightarrow \text{CF}_4^* (\text{F } 1s^{-1}) a_1^*$
- (2) $\text{CF}_4^* \rightarrow \text{CF}_3 + \text{F}^* (1s 2p^6 \ ^2S)$
- (3) $\text{F}^* (1s 2p^6 \ ^2S) \rightarrow \text{F}^+ + e^-$

In step (1), a F(1s) electron in the CF₄ molecule is promoted into the lowest unoccupied antibonding molecular orbital. In step (2), the core-excited molecule dissociates into a core-excited F atom and a CF₃ fragment. We do not analyze the neutral molecular fragments. Thus, in the present work, CF₃ may be considered a symbol summarizing all possible excited or fragmented states involving an C atom and three F atoms. We will show that this part of the system absorbs most of the excess energy. In step (3), the F* atom emits an Auger electron with a kinetic energy close to 656.5 eV. The time scale of this decay is about 3 fs.

The experimental setup and the data acquisition system are described in detail elsewhere [2,3]. Briefly, the setup consists of a hemispherical electron spectrometer (Gamdata-Scienta SES-2002) and an ion time-of-flight (TOF) spectrometer mounted inside a vacuum chamber. The CF₄ is introduced as an effusive beam. Electrons that are emitted in the direction of

the electron spectrometer are detected by a delay-line detector. Triggered by the electron detection, rectangular high voltage pulses are applied to the pusher and extractor electrodes. The ions are detected by another delay-line detector. All data are recorded in a TDC module and stored in the list-mode for off-line analysis. The experiment has been carried out on the c-branch of the high resolution photochemistry beamline BL27SU. The radiation source is a figure-8 undulator. We used first-order harmonic light generated by this undulator which has horizontal linear polarization (Fig. 1).

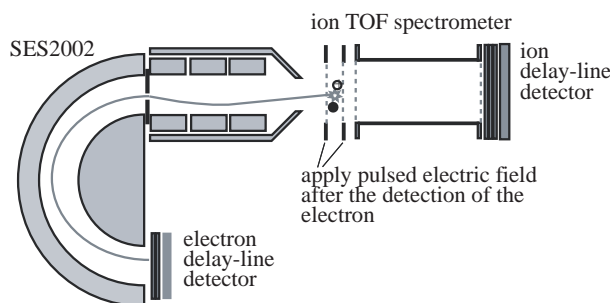


Fig. 1. Experimental setup for electron-ion momentum correlation measurements.

Figure 2 shows an example data set of the coincidence experiment belonging to the reactions (1),(2) and (3). Each point in the map corresponds to one electron-F⁺ ion event. Below the Auger peak two clusters of points can be seen. They occur due to the fact that the Auger electron is emitted by a fast core excited F-atom and thus gets additional momentum compared with an emission from an F-atom at rest. The corresponding energy shift is termed Doppler shift. By analyzing the momentum distribution of the F⁺ ions coincident with the atomic Auger line, the kinetic energy release of the F CF₃ fragmentation is determined.

Changing the excitation energy from 688.80 to 690.90 eV increases the excess energy of the excited CF₄ molecule. As we consider reactions where the Auger decay takes place in the atomic regime the excess energy can distribute among the fragmentation energy and the excitation of the CF₃ fragment. The slope of the curve in Fig. 3(a) indicates that more than half of the excess energy goes into excitation of the

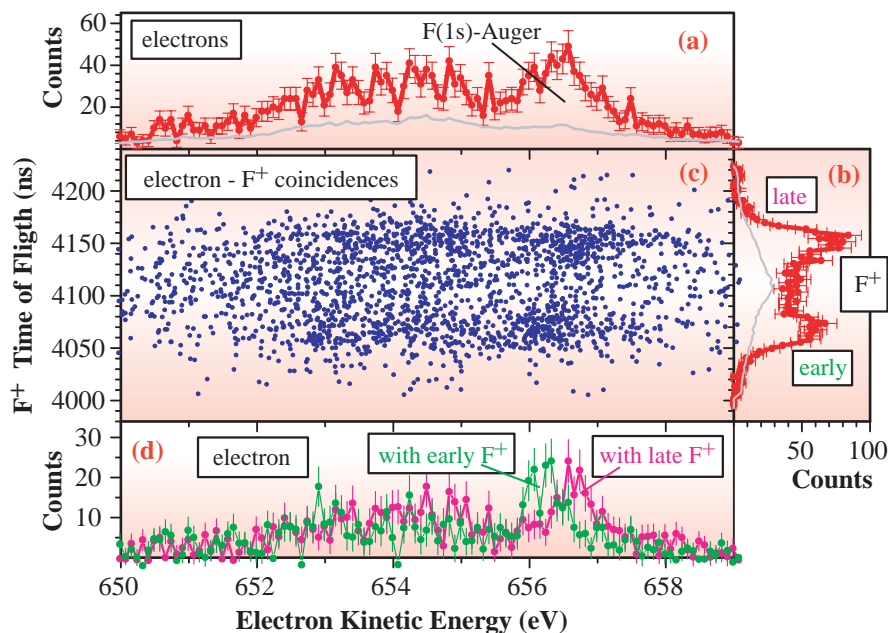


Fig. 2. The electron (a) and ion (b) spectrum of the coincidence events, together with the coincidence map (c). Each dot represents one event. The grey lines in (a) and (b) are the contributions from the random coincidences. The two curves in (d) are the electron spectra that belong to a F⁺ emission towards and away from the ion detector.

CF₃ fragment. The most probable channel for this excitation is the vibrational motion of CF₃, as the CF₃ remainder originates from a tetrahedral configuration it will vibrate around its almost planar ground state. Additionally the momentum analysis of the F⁺ ions yields the amount of back-scattering at the CF₃ fragment. For the photon energies considered here we found an average molecular back scattering of 4.7 ± 1.7 percent. Our estimate for the C-F separation is an almost constant value of 1.5×10^{-10} m for all photon energies considered.

We have shown that electron-ion momentum correlation measurements combined with detuning from the excitation is a versatile tool to study the femtoseconds nuclear relaxation processes of core excited molecules. Our data provides a consistent picture of the time scales and magnitudes of the involved processes. Further systematic studies involving other molecules and electron-ion-ion coincidence are in progress.

Georg Prümper^{a,*}, Kiyoshi Ueda^a and Yusuke Tamenori^b

(a) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
 (b) SPring-8 / JASRI

*E-mail: pruemper@tagen.tohoku.ac.jp

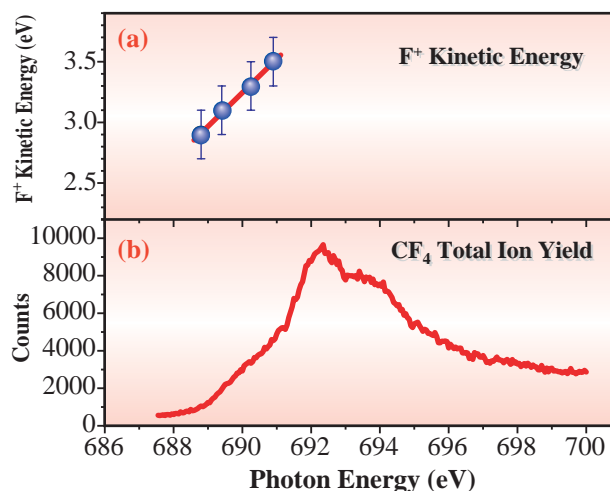


Fig. 3. Total ion yield and the kinetic energy of the F⁺ ion as a function of the photon energy.

References

- [1] G. Prümper, K. Ueda, Y. Tamenori, M. Kitajima, N. Kuze, H. Tanaka, C. Makochekanwa, M. Hoshino and M. Oura: *Phys. Rev. A* **71** (2005) 052704, (also available at: June 1, 2005 issue of *Virtual J. of Ultrafast Science*).
- [2] G. Prümper, Y. Tamenori, A. De Fanis, U. Hergenbahn, M. Kitajima, M. Hoshino, H. Tanaka and K. Ueda: *J. Phys. B* **38** (2005) 1.
- [3] G. Prümper, K. Ueda, U. Hergenbahn, A. De Fanis, Y. Tamenori, M. Kitajima, M. Hoshino and H. Tanaka: *J. Elec. Spectrosc.* **144-146** (2005) 227.