

## Photofragmentation dynamics of the inner-shell excited 3,3,3-trifluoropropene by an ion–ion coincidence momentum imaging technique

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### Introduction

Molecules with a hole in the inner-shell orbitals decay in the order of femtosecond through Auger process, and multiply-charged molecular ions are formed in frequent cases. The molecular ions undergo Coulomb explosion due to strong repulsion between the charges. The momenta of resultant fragment ions reflect the dynamics of the explosion. The technology of position-sensitive detectors (PSDs) allows us to obtain both the energy and angle of the ejected ions from the positions on the detectors. From the information one can evaluate the structure of the molecular ions immediately before the dissociation.

It is known for a variety of hydrocarbon that hydrogen atom migration takes place within a photoexcited molecular ion (for example, see Ref. [1]). Such hydrogen migration induces deformation of molecular structure and dissociation. The purpose of this study is to obtain information on intramolecular migration of the atoms in the 3,3,3-trifluoropropene molecule and its dissociation pathways, by measuring the flight-time and momentum angular correlation of the fragment ion pairs produced in coincidence from the doubly-charged molecular ions.

### Experimental

The experiments were performed on the soft X-ray undulator beamline BL-2C using a multi-coincidence velocity-map imaging spectrometer (CO-VIS) [2]. Photoelectrons and ions produced by photoabsorption were extracted by a uniform electrostatic field towards the opposite directions. They were detected in coincidence by microchannel plate detectors equipped with delay-line readout (RoentDek, HEX80). A time reference signal from the detectors and delayed signals from both ends of each delay-line were amplified and discriminated to record their time information using time-to-digital converters. The ion positions were determined from the difference in the arrival time at the ends of each line. Momentum vectors of the ions were computed from the flight time and the impact positions on the ion detector. The coincidence signals were acquired as list-mode data at the photon energies of 296.4, 314.5, 688.7, 691.6, and 715.3 eV. The position data for the electrons were not analyzed in this study. For calibrating the photon energy, we used the photoabsorption peaks of CO<sub>2</sub> for the C 1s edge and of SF<sub>6</sub> for the F 1s edge.

The sample gas for this study was obtained from SynQuest Laboratories, Inc. and used as provided. The pressure in the main chamber was typically at  $7 \times 10^{-8}$  Torr during the measurements.

### Results and discussion

The total ion yield spectra near the C 1s and F 1s ionization thresholds of 3,3,3-trifluoropropene contain a variety of pronounced peaks. The peaks at 284.8 and 688.7 eV are assigned to the  $\pi_{C=C}^* \leftarrow C_1 1s$  and  $\pi_{C=C}^* \leftarrow F 1s$  transitions, respectively, where C<sub>1</sub> means the carbon at the 1-position. The other peaks are assigned reasonably as well, referring to the assignments for compounds with similar structure [3,4].

From the obtained photoelectron–photoion–photoion coincidence spectra, various fragment ion pairs are formed such as CH<sub>j</sub><sup>+</sup>/CF<sub>k</sub><sup>+</sup>, F<sup>+</sup>/C<sub>2</sub>H<sub>l</sub><sup>+</sup>, C<sub>2</sub>H<sup>+</sup>/CF<sub>k</sub><sup>+</sup> ( $j = 0-2, k = 1-3, l = 0-3$ ) at both the C 1s and F 1s edges. The ion pairs of C<sub>2</sub>H<sub>k</sub>F<sup>+</sup>/CF<sub>2</sub><sup>+</sup> and CF<sup>+</sup>/C<sub>2</sub>H<sub>l</sub>F<sup>+</sup> are also detected, exhibiting the existence of a fluorine atom migration. Relative yield of the latter two sets of ion pairs are higher in the C 1s region than in the F 1s region. The result can be reasonably explained in such a way that the F K-shell excited/ionized molecular ion undergoes fragmentation rather than the migration due to the high energy supplied at the fluorine site.

The plot of momentum vector correlation between the C<sub>2</sub>H<sub>3</sub><sup>+</sup> and CF<sub>2</sub><sup>+</sup> ions gives a distribution with a maximum at around 160°. The deviation from the 180° angles reflects the momentum of the eliminating F atom. This indicates that the fragmentation proceeds by secondary decay mechanism and that the angle  $\angle C-C_F-F$  is about 81°, illustrating the mobility of the fluorine atom.

### References

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