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Chemical Physics Letters 431 (2006) 253–256

**CHEMICAL
PHYSICS
LETTERS**
www.elsevier.com/locate/cplett

Site-specific fragmentation following F 1s photoionization of free CF₃SF₅ molecules studied by electron–ion coincidence spectroscopy

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Received 12 August 2006; in final form 25 September 2006

Available online 5 October 2006

Abstract

We have studied site-specific fragmentation caused by F 1s photoionization of free CF₃SF₅ molecules. Energy-resolved electrons and mass-resolved ions were detected in coincidence. We found an enhancement of the CF₃⁺ ion production in coincidence with photoelectrons emitted from F atoms in the SF₅ group due to a reaction path leading to CF₃⁺–SF⁺ pair production. We found an enhancement of the CF⁺ and C⁺ ions due to F 1s electron emission from the CF₃ group. Site-selectivity was also observed for the CF⁺–SF⁺, CF⁺–SF₂⁺, CF⁺–SF₃⁺, C⁺–F⁺, C⁺–S⁺ and C⁺–SF⁺ ion pair production.

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1. Introduction

To study molecular photodissociation in detail, it is highly advantageous to employ site-specific core ionization [1]. One of the most exciting findings in the dissociation of core-ionized molecules is site-specific fragmentation. Bond breaking often takes place near the excited atomic site [2]. A core electron of an atom inside a molecule is localized very close to the nucleus, and the chemical shift seen in the electron spectrum depends on the chemical environment of the atomic site. Atoms of the same element in different chemical environments thus show different chemical shifts. These properties have been used to study site-specific fragmentation [3,4], which is potentially useful for controlling chemical reactions through selective bond dissociation.

A study of the dependence of reaction pathways on the ionized atomic site requires a coincidence technique, which combines energy-resolved photoelectron detection and mass-resolved ion (pair) detection [1]. In the present work,

we have applied energy-resolved photoelectron-ion(-ion) coincidence technique to investigation of site-specific fragmentation following site-selective F 1s photoionization of the CF₃SF₅ molecule. CF₃SF₅ has F atoms in two different sites, i.e., those inside the CF₃ and SF₅ groups. Therefore, one can expect to observe site-specific fragmentation following site-selective F 1s photoionization. Previously, Ibuki et al. investigated X-ray absorption of CF₃SF₅ [5] and ionic fragmentation of CF₃SF₅ following promotion of a core electron to unoccupied orbitals [6]. They discussed site-selectivity of the fragmentation in relation to the character of the antibonding orbital in which the core electron is promoted. In the present work, we investigate core-ionized state specified ion (pair) production following normal Auger transitions and discuss the site-selectivity of the fragmentation in relation to the character of the two-hole states.

2. Experimental

The experiment was carried out at the c-branch of the high-resolution soft X-ray monochromator [7] installed in beamline 27SU [8] at SPring-8, the 8 GeV synchrotron

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radiation facility in Japan. The radiation source is a figure-8 undulator [9]. With this undulator, one can switch the direction of polarization between horizontal (using first-order harmonic) and vertical (using the so-called 0.5th-order harmonic), by only adjusting the gap of the undulator. In the present experiment, we employed the horizontal polarization.

The experimental setup and the data acquisition system are described elsewhere [10,11]. The setup consisted of a hemispherical electron spectrometer (Gammadata-Scienta SES-2002) and an ion time-of-flight (TOF) spectrometer mounted inside a vacuum chamber on opposite sides along the horizontal axis. The sample gas CF_3SF_5 was introduced between the pusher and extractor electrodes of the ion spectrometer through a grounded copper needle. Electrons passed the pusher electrode and enter the electron spectrometer equipped with a delay-line detector (Roentdek DLD40). During the coincidence experiment, all voltages of the electron spectrometer were fixed. Triggered by the electron detection, rectangular high-voltage pulses with opposite signs were generated by a pulse generator (GPTA HVC-1000) and applied to the pusher and extractor electrodes. The ions were detected by another delay-line detector with an active diameter of 80 mm (Roentdek DLD80) mounted at the end of the TOF drift-tube. The voltages applied to the pusher, the extractor and the drift-tube were adjusted to collect all ions ejected in 4π sr. All data were recorded by multichannel time-to-digital converters (Roentdek TDC-8) and stored in the list mode for off-line analysis. The method of data analysis was modified to extract electron–ion–ion triple coincidences [12]. Ion pairs consisting of two ions with an identical mass-to-charge ratio, e.g. two singly charged F ions, could not be detected as a pair because of dead time effects of the ion detector.

We only measured a subset of events where the F 1s electron was emitted along the electric vector. We questioned whether the site-specific fragmentation could depend on the emission direction of the photoelectron. By use of the two-step picture of photoemission and Auger decay, angular correlation can only be caused by alignment or polarization of the hole, which is of course zero for pure 1s holes. Therefore, we claim that the results are independent of the direction of electron emission.

CF_3SF_5 with a purity of over 99% (SynQuest Lab.) was used without further purification.

3. Results and discussion

The F 1s ionization potentials of the SF_5 and CF_3 groups inside the CF_3SF_5 molecule are 694.95 and 695.64 eV, respectively [5].

Fig. 1 shows the F 1s photoelectron spectrum of CF_3SF_5 at a photon energy of 746.95 eV. All electrons were counted, whether ions were detected in coincidence or not. The binding energy scale was established by putting the peak center to 695.30 eV. The difference in the F 1s chemical shift between the SF_5 and CF_3 groups is

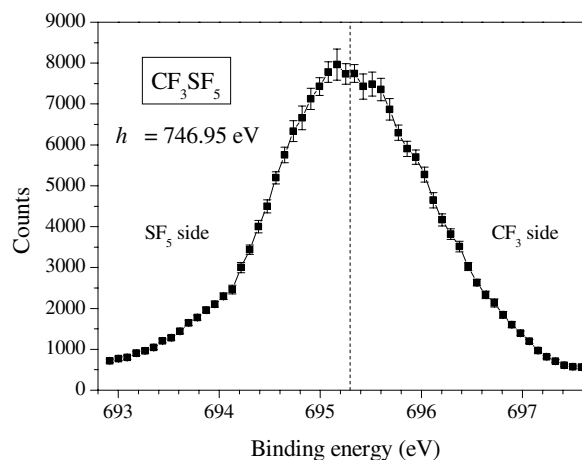


Fig. 1. The F 1s photoelectron spectrum of CF_3SF_5 free molecules at a photon energy of 746.95 eV. The vertical broken line marks the binding energy of 695.30 eV, which we chose as the limit to distinguish the SF_5 -side from the CF_3 -side in this work.

0.69 eV. Two distinct photoelectron peaks were not resolved because of the many vibrational modes that contribute to the peak width. The spectrometer resolution was ~ 80 meV. The peak width and shape in the electron spectra are affected by vibrational excitations. Although contributions of the photoelectrons emitted from the F atoms from the two sites cannot be resolved, the left and right halves of the peak in Fig. 1 should include preferentially electrons emitted from the F atoms in the SF_5 and CF_3 groups, respectively. Thus, we call the left and right halves the SF_5 and CF_3 sides, respectively. As a reference we put a vertical line at 695.30 eV in Figs. 1, 3 and 4.

Fig. 2 shows the TOF mass spectra of the ions measured in coincidence with the photoelectrons of the (a) CF_3 and

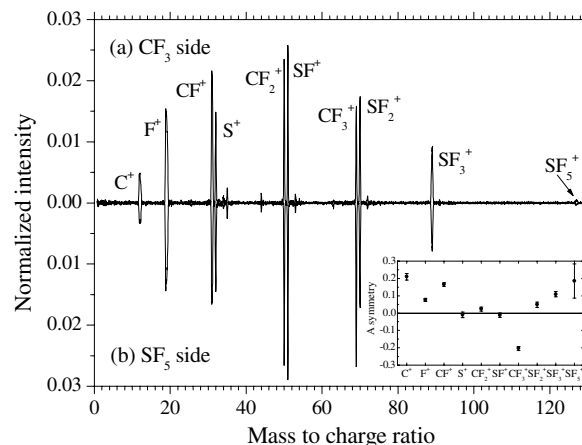


Fig. 2. The TOF mass spectra of fragment ions of free CF_3SF_5 molecules at a photon energy of 746.95 eV detected in coincidence with F 1s photoelectrons from the SF_5 -group (a), or the CF_3 -group (b). The total area of each mass spectrum was normalized to unity. The small inlay graph shows the corresponding asymmetry of the dominant ions. Positive and negative asymmetry mean site-specific ion production due to F 1s-ionization of the CF_3 -group or the SF_5 -group, respectively.

(b) SF₅ sides in Fig. 1. Each TOF spectrum was normalized by scaling the total area of the spectrum to unity. Dominant peaks at 12, 19, 31, 32, 50, 51, 69, 70, and 89 u belong to C⁺, F⁺, CF⁺, S⁺, CF₂⁺, SF⁺, CF₃⁺, SF₂⁺, and SF₃⁺, respectively. The fragmentation patterns are similar in both spectra, but the CF₃⁺ peak is enhanced in the mass spectrum of the SF₅ side, and the CF⁺ and C⁺ peaks are enhanced at the CF₃ side. This is more clearly seen in the diagram showing the corresponding asymmetry.

$$\text{asymmetry} = \frac{a-b}{a+b}, \quad a = \frac{A}{AN}, \quad b = \frac{B}{BN}. \quad (1)$$

A and *B* are the numbers of (mass-selected) ions detected in coincidence with F 1s electrons above and below a binding energy of 695.30 eV, respectively. *AN* and *BN* are the numbers of electrons detected above and below a binding energy of 695.30 eV, respectively, i.e. *AN* and *BN* are the areas of the two halves of the peak shown in Fig. 1. This definition ensures that if two ionized states lead to the same pattern of fragmentation, the asymmetry of all ionic fragments is zero.

The spectra of the photoelectron measured in coincidence with the CF₃⁺, CF⁺ or C⁺ ions are shown in Fig. 3. Compared to the total electron signal, shown in Fig. 1, these three coincident spectra are shifted towards lower (CF₃⁺) or higher (CF⁺ and C⁺) binding energy, respectively. This shows that CF₃⁺ is produced site-selectively in the F 1s photoionization of the SF₅ group, and the CF⁺ and C⁺ ions are produced site-selectively for the CF₃ group. This site-selectivity is consistent with the self-imaging nature of the Auger decay. Namely, the electrons in molecular orbitals that have the atomic populations with the atom in which core electron is removed participate in the Auger decay and thus the Auger spectrum reflects the self-convoluted local density of states [13]. In case of F 1s

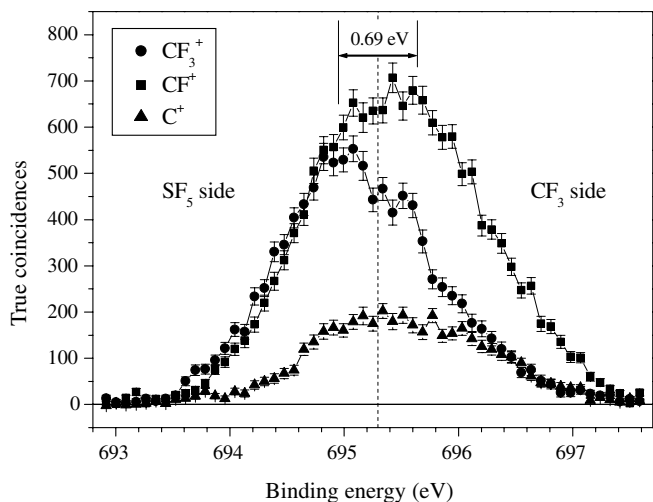


Fig. 3. The spectrum of F 1s photoelectrons of free CF₃SF₅ molecules detected in coincidence with CF₃⁺, CF⁺ or C⁺ ions at a photon energy of 746.95 eV. The vertical broken line marks 695.30 eV, the limit between the SF₅-side and the CF₃-side. For comparison, the arrow shows the chemical shift between the F 1s levels of the SF₅ and CF₃ group.

ionization, the subsequent Auger process tends to remove two electrons from ‘lone-pair’-like orbitals relatively localized to the F site in which a core hole is created and thus chemical bond break tends to take place near the core ionized atom. As a result, the C–S bond dissociation leaving the CF₃⁺ fragment intact occurs preferentially after the creation of a core hole in the SF₅ group, whereas additional break-up inside the CF₃ fragment, possibly producing CF⁺ or C⁺, occurs preferentially after the creation of a core hole in the CF₃ group. In the same way, SF₅⁺ (127 u) is produced preferentially after the creation of a core hole in the CF₃ group. SF⁺ and S⁺, however, show no asymmetry. This implies that they are produced with equal probabilities after the creation of a core hole in either of the two groups (see Fig. 2).

In many cases, core-ionized molecules dissociate into two or more fragment ions. In the present case, the production

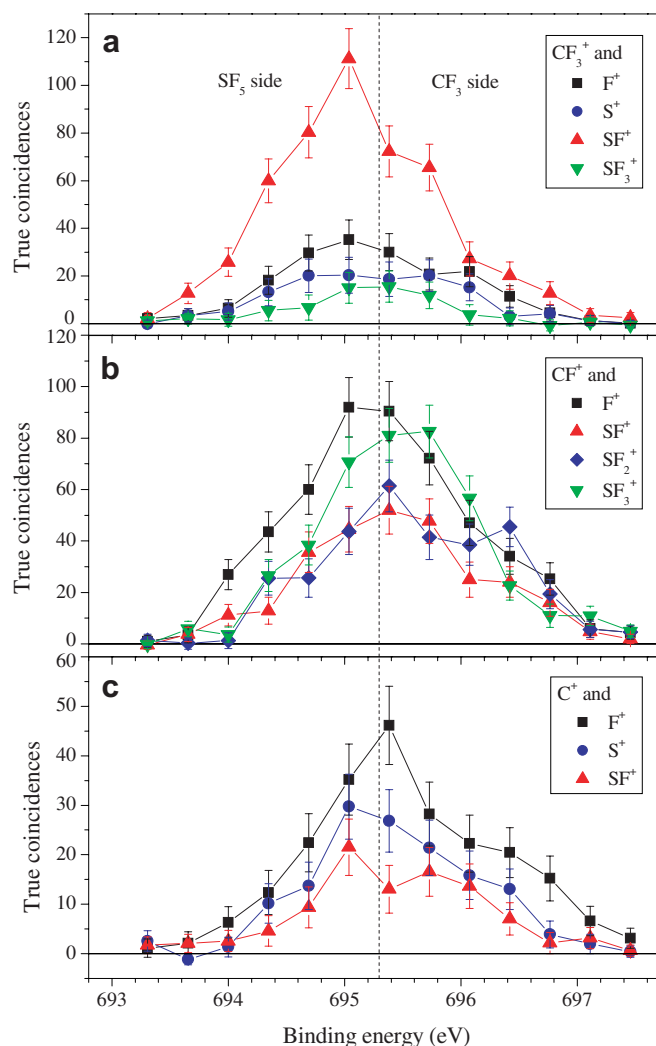


Fig. 4. The spectra of F 1s photoelectrons of free CF₃SF₅ molecules at a photon energy of 746.95 eV, detected in coincidence with CF₃⁺–F⁺, CF₃⁺–S⁺, CF₃⁺–SF⁺ or CF₃⁺–SF₃⁺ ion pairs (a). (b) In coincidence with CF⁺–F⁺, CF⁺–SF⁺, CF⁺–SF₂⁺ or CF⁺–SF₃⁺ ion pairs. (c) In coincidence with C⁺–F⁺, C⁺–S⁺ or C⁺–SF⁺ ion pairs. The vertical broken line marks 695.30 eV, the limit between the SF₅-side and the CF₃-side.

of doubly charged final states should be the dominating electronic decay process. Therefore, we have also extracted the most abundant partners found in coincidence with CF_3^+ , CF^+ or C^+ . These ion pairs are CF_3^+-F^+ , CF_3^+-S^+ , $\text{CF}_3^+-\text{SF}^+$, $\text{CF}_3^+-\text{SF}_2^+$, $\text{CF}_3^+-\text{SF}_3^+$, CF^+-F^+ , CF^+-SF^+ , $\text{CF}^+-\text{SF}_2^+$, $\text{CF}^+-\text{SF}_3^+$ and C^+-F^+ , C^+-S^+ , C^+-SF^+ . Fig. 4 shows the photoelectron spectra recorded in coincidence with these ion pairs. Apparently the site-selectivity found in the CF_3^+ ion coincidences is due to a specific reaction path leading to production of the $\text{CF}_3^+-\text{SF}^+$ ion pair. The site-selectivity found in the CF^+ ion production is also found in three different ion pair productions: the CF^+-SF^+ , $\text{CF}^+-\text{SF}_2^+$, and $\text{CF}^+-\text{SF}_3^+$. The site-selectivity in the production of C^+ is similar to that of all ion pairs C^+-F^+ , C^+-S^+ , C^+-SF^+ .

4. Summary

We have studied site-specific fragmentation of free CF_3SF_5 molecules following F 1s photoionization. We found that the photoionization leading to a F 1s core hole in the SF_5 group enhances CF_3^+ ion production mainly through a reaction path leading to $\text{CF}_3^+-\text{SF}^+$ pair production. The F 1s core holes in the CF_3 group enhance CF^+ and C^+ ion production through a number of pathways leading to CF^+-SF^+ , $\text{CF}^+-\text{SF}_2^+$, $\text{CF}^+-\text{SF}_3^+$, C^+-F^+ , C^+-S^+ , and C^+-SF^+ pairs.

Acknowledgements

The experiment was performed at SPring-8 with the approval of the Program Review Committee. The work was partly supported by Grants-in-Aid for Scientific Research from the Japan Society for Promotion of Science (JSPS). XJL is grateful to the COE program of Tohoku University and JSPS for financial support.

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