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# Site-selective ion pair production via normal Auger decay of free CH<sub>3</sub>F molecules studied by electron–ion–ion coincidence spectroscopy

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## Abstract

Site-specific fragmentation caused by C KVV and F KVV Auger decay of free CH<sub>3</sub>F molecules has been studied. Energy-resolved Auger electrons and pairs of mass-resolved ions were detected in coincidence. Strong enhancements for the production of CH<sub>3</sub><sup>+</sup>–F<sup>+</sup> and H<sup>+</sup>–CF<sup>+</sup> ion pairs were found for the F KVV and C KVV Auger decays, respectively.

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## 1. Introduction

To study molecular photodissociation in detail, it is highly advantageous to employ site-specific core ionization [1,2]. One of the most exciting findings in the dissociation of core-ionized molecules is site-specific fragmentation [3,4]. Bond breaking often takes place near the excited atomic site [5]. Between the site-specific core ionization and the ionic fragmentation, however, there is one more step: the system undergoes Auger decay and the electronic energies of its final states may be widely spread and each final state can lead to different ionic fragments. Thus a coincidence experiment detecting the energy-resolved Auger electron and the mass-resolved fragment ion is needed in order to specify the dissociation pathways and thus to determine the mechanism leading to site-specific fragmentation [1,6,7].

Recently, Liu et al. have investigated site-specific ion production via spectator Auger decay of core-excited fluoromethane (CH<sub>3</sub>F) molecules by electron–ion coincidence

measurements in the binding energy region of 26–36 eV [8]. They found a switching of the F<sup>+</sup> and CH<sup>+</sup> ion productions from the two-hole one-electron states populated via F KVV and C KVV Auger decay, respectively, due to nuclear dynamics. In the case of normal Auger decay, Auger final states are two-hole states which should produce ion pairs or doubly charged ions. In the present Letter, we have applied an energy-resolved electron–ion–ion triple coincidence technique to investigate the site-specific fragmentation via normal Auger decay following site-selective core-level photoionization of the CH<sub>3</sub>F molecule.

## 2. Experimental

The experiment was carried out at the c-branch of the high-resolution soft X-ray monochromator [9] installed in beamline 27SU [10] at SPring-8, the 8 GeV synchrotron radiation facility in Japan. The radiation source is a figure-8 undulator [11]. In the present experiment, we employed horizontal polarization.

The experimental setup and the data acquisition system are described elsewhere [12,13]. The setup consists of a hemispherical electron spectrometer (Gammadata-Scienta

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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  $\text{CH}_3\text{F}$  was introduced between the pusher and extractor electrodes of the ion spectrometer through a grounded copper needle. The electrons passed through 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 and the extractor, the high-voltage pulse delay, and the drift-tube voltage were adjusted to collect all ions ejected in  $4\pi$  sr except some protons with high energy. 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 subtracting random coincidences [14]. Ion pairs consisting of two ions with an identical mass-to-charge ratio, e.g. two protons, could not be detected as a pair because of the dead time of the ion detector.

### 3. Results

The  $\text{CH}_3\text{F}$  molecule in the ground state has a  $\text{C}_{3v}$  symmetry and its electronic configuration is written as

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^4 {}^1A_1$$

Here  $1a_1$  and  $2a_1$  correspond to F 1s and C 1s core orbitals, respectively. The vertical ionization potentials of the C 1s and F 1s levels in  $\text{CH}_3\text{F}$  are 293.557 and 692.4 eV, respectively [15,16].

A C KVV Auger electron spectrum was recorded at a photon energy of 370 eV and a F KVV Auger electron spectrum was recorded at 725 eV. They are shown in Fig. 1a and b, respectively. The spectrometer resolution was  $\sim 4$  eV. The horizontal axis of Fig. 1 is the double ionization potential (DIP) given by

$$\text{DIP} = \text{IP} - \text{KE}, \quad (1)$$

where IP is the ionization potential of C 1s or F 1s, and KE is the kinetic energy of the Auger electrons. Theoretical Auger spectra calculated by Liegener using a Green's function method [17] are also shown in Fig. 1a and b as vertical bars. The height of each vertical bar reflects the intensity of the Auger transition. The numbers relate the lines to the two-hole states in Table 1 where the calculated DIPs of these states and their dominant components are listed. The calculated C KVV Auger spectrum in Fig. 1a roughly agrees with the measured spectrum. Probably the main peak in the measured spectrum around DIP of 43 eV is

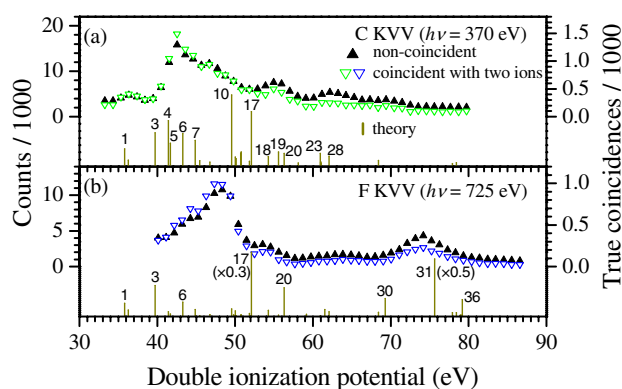


Fig. 1. (a) The C KVV Auger electron spectrum (filled upward triangles) and the spectrum of electrons detected in coincidence with any two ions (open downward triangles) recorded at a photon energy of 370 eV. The intensities refer to the scales at the left and right axes, respectively. The vertical lines show calculated Auger spectra by Liegener [17] in arbitrary units. (b) Corresponding electron spectra for the F KVV Auger electrons measured at a photon energy of 725 eV. The statistical uncertainties are within the size of the data points.

mainly due to two-hole states labeled 3–7. In contrast, the calculated F KVV Auger spectrum in Fig. 1b disagrees with the measured spectrum. This discrepancy may, at least partly, be due to nuclear relaxation of the F core-ionized molecule as we discuss below.

The Auger final states considered in this study are two-hole states. The dominant decay processes lead to ion pair formation. Thus let us consider the production of ion pairs. The Auger electron spectra detected in coincidence with any two ions are also shown in Fig. 1a and b. These spectra are similar in shape to the corresponding non-coincident spectra. This similarity confirms that the dominant decay pathways of Auger final states lead to the formation of the ion pairs. The ratio between the scales of the non-coincident spectra and the spectra measured in coincidence with two ions is determined to obtain overall agreement. The square root of this ratio is the single ion detection efficiency. It is 29%. Let us estimate the contribution of the doubly charged ions using this detection efficiency. Assuming the same detection efficiency of 29% for a singly charged and a doubly charged ion, the chance to detect both ions of an ion pair is 0.29 times the chance to detect a doubly charged ion. Based on this assumption the ratios of  $\text{C}^{2+}$  and  $\text{F}^{2+}$  yields to any ion pair yield are plotted versus the DIP in Fig. 2a and b, respectively. The ratio of doubly charged ion yield to ion pair yield is estimated to be lower than 5% for most kinetic energies and lower than 9% at its maximum.

The ion pairs observed in this study are  $\text{H}^+\text{-C}^+$ ,  $\text{H}^+\text{-CH}^+$ ,  $\text{H}^+\text{-CH}_2^+$ ,  $\text{H}^+\text{-F}^+$ ,  $\text{H}^+\text{-CF}^+$ ,  $\text{H}^+\text{-CHF}^+$ ,  $\text{H}_2^+\text{-CH}_2\text{F}^+$ ,  $\text{H}_2^+\text{-CH}^+$ ,  $\text{H}_2^+\text{-CF}^+$ ,  $\text{H}_2^+\text{-CHF}^+$ ,  $\text{C}^+\text{-F}^+$ ,  $\text{CH}^+\text{-F}^+$ ,  $\text{CH}_2^+\text{-F}^+$  and  $\text{CH}_3^+\text{-F}^+$ . The C KVV and F KVV Auger electron spectra in coincidence with these ion pairs are shown in Fig. 3. The ratio between the scale of the C and F KVV spectra is equal to the ratio of the numbers

Table 1

The calculated double ionization potentials (DIP) of two-hole states and their dominant components [17]

DIP (eV)	Dominant component(s)	No. <sup>a</sup>	DIP (eV)	Dominant component(s)	No. <sup>a</sup>
35.79	$2e^{-2}$	1	55.56	$4a_1^{-2}$	19
36.27	$2e^{-2}$	2	56.31	$4a_1^{-1}5a_1^{-1}$	20
39.73	$5a_1^{-1}2e^{-1}$	3	58.11	$4a_1^{-2}$	21
41.41	$1e^{-1}2e^{-1}$	4	59.18	$3a_1^{-1}1e^{-1}$	22
41.67	$1e^{-1}2e^{-1}$	5	60.94	$4a_1^{-2}$	23
43.28	$5a_1^{-1}1e^{-1}$	6	60.98	$4a_1^{-2}$	24
44.89	$5a_1^{-2}$	7	61.03	$4a_1^{-2}$	25
45.45	$5a_1^{-2}$	8	61.07	$4a_1^{-2}$	26
46.75	$5a_1^{-1}1e^{-1}$	9	61.51	$3a_1^{-1}2e^{-1}$	27
49.54	$1e^{-2}$	10	62.08	$3a_1^{-1}2e^{-1}$	28
49.80	$5a_1^{-1}1e^{-1}, 4a_1^{-1}2e^{-1}$	11	68.42	$3a_1^{-1}5a_1^{-1}$	29
50.03	$4a_1^{-1}1e^{-1}$	12	69.27	$3a_1^{-1}1e^{-1}$	30
50.13	$1e^{-2}$	13	75.65	$3a_1^{-1}1e^{-1}$	31
50.73	$1e^{-2}$	14	77.92	$3a_1^{-1}4a_1^{-1}$	32
50.80	$1e^{-2}$	15	78.43	$3a_1^{-1}4a_1^{-1}$	33
51.82	$4a_1^{-1}1e^{-1}$	16	78.88	$3a_1^{-1}4a_1^{-1}$	34
52.11	$4a_1^{-1}2e^{-1}$	17	79.00	$3a_1^{-1}4a_1^{-1}$	35
54.26	$4a_1^{-1}1e^{-1}$	18	79.19	$3a_1^{-1}4a_1^{-1}$	36
			96.83	$3a_1^{-2}$	37

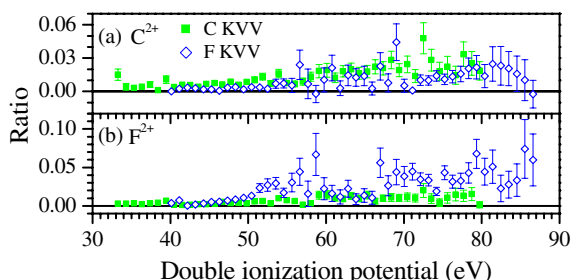
<sup>a</sup> The numbers are used to identify the theoretical Auger spectra in Fig. 1.

Fig. 2. (a) The ratios of the  $C^{2+}$  yield multiplied by the single ion detection efficiency 0.29 to the total ion pair yield. C KVV Auger decays (filled squares) and F (open diamonds) KVV Auger decays versus the double ionization potential. (b) The corresponding ratios for the  $F^{2+}$  yield. The statistical uncertainties are within the size of the data points, or represented if they are larger than the marks.

of the detected C and F KVV Auger electrons in the DIP region of 40–80 eV.

#### 4. Discussion

In order to discuss which ion pairs are site-selectively produced via C KVV or F KVV Auger decay, the branching ratios of these ion pair yields are plotted versus the DIP in Fig. 4. The branching ratios are determined by dividing the spectra in Fig. 3 by the spectra in coincidence with any two ions in Fig. 1. If the two-hole states were completely resolved in the Auger electron spectra, and if the nuclear dynamics did not play a role, the branching ratios at a specific two-hole state at a specific DIP should be identical both for the C KVV and F KVV Auger decays. The resolution of the electron spectrometer was, however, not sufficient to resolve the individual two-hole states. Even with ultimate instrumental resolution, the individual two-hole states may not be resolved in the Auger spectrum because

the Auger line width is limited by the core-hole lifetime broadening and furthermore the Auger bands decaying to dissociative two-hole states may overlap. Thus, the measured value of the branching ratios in Fig. 4 at a specific value of DIP cannot be correlated to a specific two-hole state but should be considered as the value ‘averaged’ over different two-hole states overlapping in the Auger spectra.

One can see the site-selectivity of fragmentation in the branching ratio when one goes from the C KVV to F KVV Auger decay. The largest site-selectivity is seen in the  $CH_3^+-F^+$  ion pair production (Fig. 4n). This ion pair is a major product in the F KVV Auger decay in the DIP region of 40–50 eV, but a minor product in the C KVV Auger decay. Especially, in the region of 40–45 eV,  $CH_3^+-F^+$  is solely produced by the F KVV Auger decay, even though the C KVV Auger decay has significant intensity in this region. In case of direct double-photoionization, this ion pair production is also a minor channel [18,19]. This means that only two-hole states produced via F KVV Auger transitions leave the  $CH_3^+$  intact.

To explain such site-selectivity, one might expect that only electrons in molecular orbitals which overlap with the core-hole participate in the Auger decay and thus chemical bond dissociation tends to take place near the core-ionized atom. Indeed such a model is valid in many cases (see, for example [4]). Looking at the result of ab initio calculations by Liegener shown in Fig. 1a and b, however, we cannot find F site-specific Auger-final electronic states in the DIP region of 40–45 eV. On the contrary, most of the two-hole states are populated by the C KVV Auger decay in this DIP region. So, if one would attribute the  $CH_3^+-F^+$  formation to the state corresponding to line 3 or 6 of the F KVV Auger decay in Fig. 1b, then  $CH_3^+-F^+$  should also appear from the final state 3 or 6 of the C KVV Auger decay; this contradicts the observation

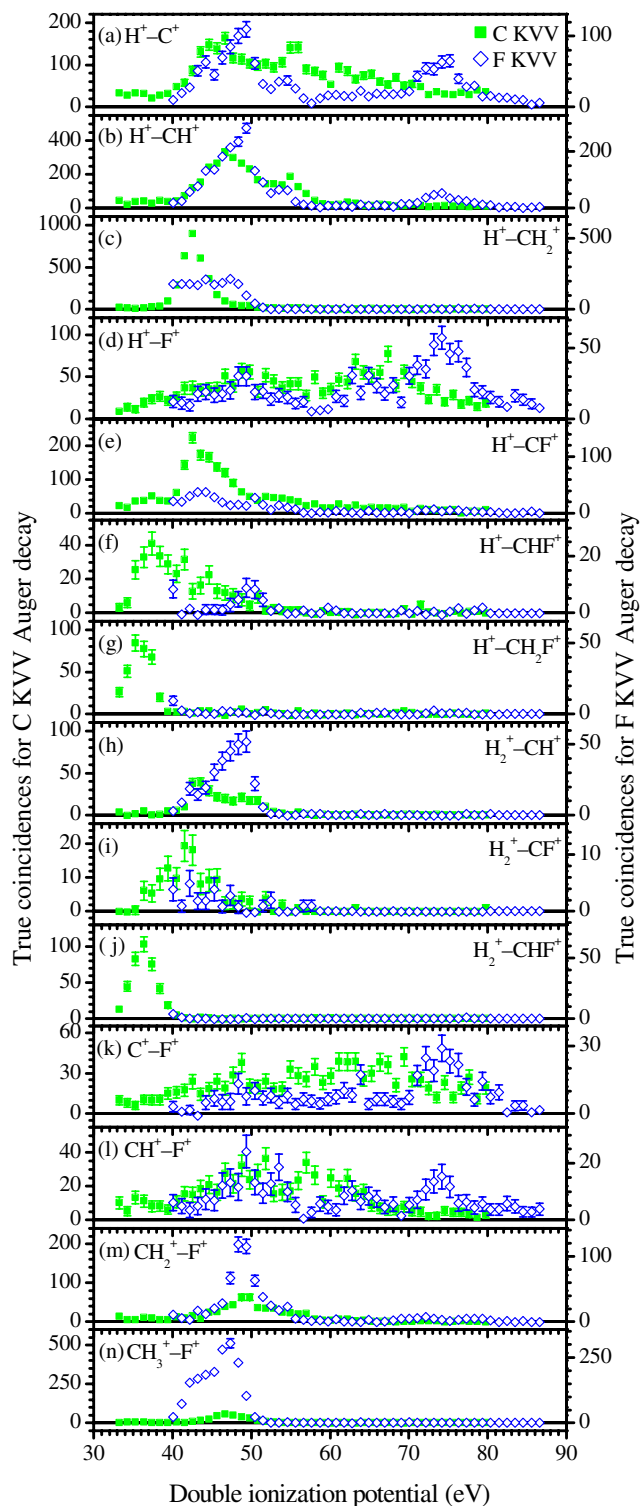


Fig. 3. The Auger electron spectra in coincidence with specific ion pairs for the C (filled squares) and F (open diamonds) KVV Auger decays. The intensities refer to the scales at the left and right axes, respectively. The statistical uncertainties are within the size of the data points, or represented if they are larger than the marks.

and thus implies that one cannot explain the observed site-specific fragmentation in terms of the selectivity of the two-hole electronic states in the Auger decay. Instead, the

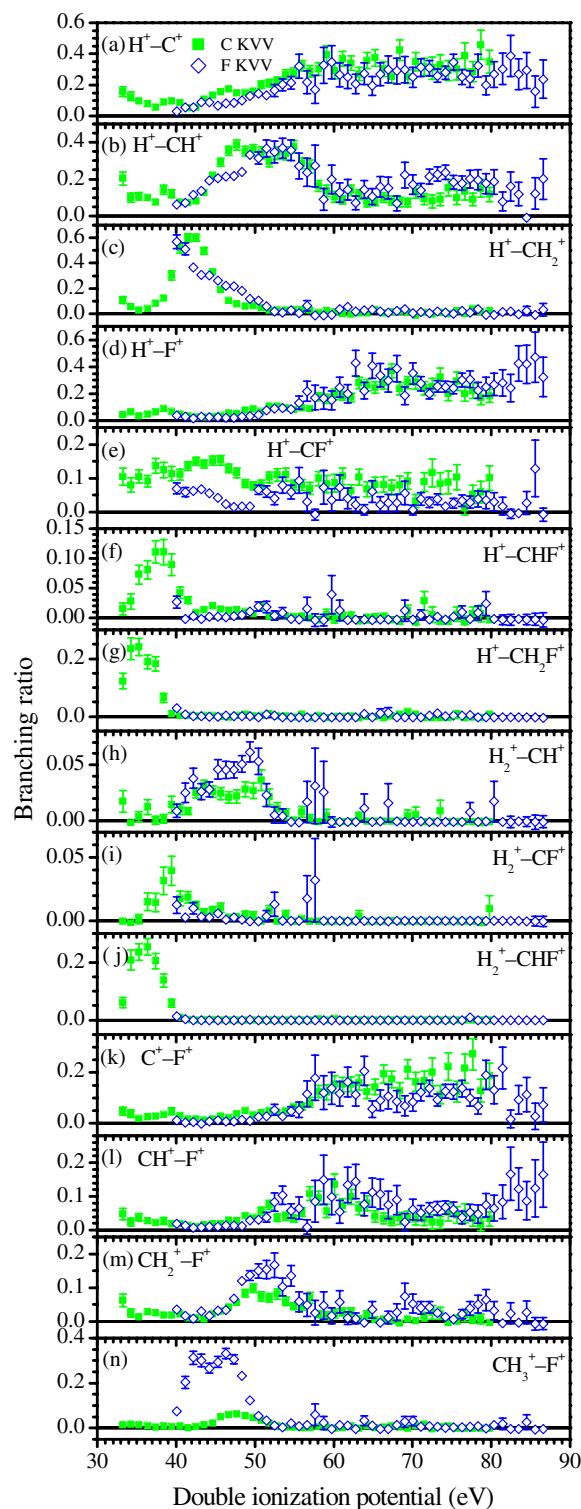


Fig. 4. The branching ratios of specific ion pair yields for the C KVV Auger decays (filled squares) and F (open diamonds) KVV Auger decays versus the double ionization potential. The statistical uncertainties are within the size of the data points, or represented if they are larger than the marks.

nuclear motion seems to play a role. The F core-ionized  $\text{CH}_3\text{F}$  can be approximated by  $(\text{CH}_3\text{Ne})^+$  within the equivalent core model:  $(\text{CH}_3\text{Ne})^+$  dissociates into  $\text{CH}_3^+$  and Ne

[20]. Thus, one can expect that the  $\text{CH}_3^+-\text{F}^*$  dissociation starts just after the F 1s ionization. Due to this strong nuclear relaxation within the core-hole life time of a few femtoseconds, the Auger decay can occur outside the Franck–Condon region defined by the zero-point vibrational wave function of the ground state, though the displacement of the C–F distance is still very small. Generally, one assumes that the nuclear relaxation of the core ionized state is negligible within the core-hole lifetime. However, the present observation implies that this is not the case. The calculation by Liegener did not take account of the nuclear dynamics. This may be the reason of disagreement between the experimental and theoretical F KVV Auger spectra.

Another ion pair that shows large site-selectivity is  $\text{H}^+-\text{CF}^+$  (Fig. 4e). This ion pair shows the opposite site-selectivity. It is a major product in the C KVV Auger decay coincidentally in the same DIP region of 40–50 eV. In case of the C 1s ionized state, however, the nuclear relaxation is small [15] and thus likely plays no role. Thus, the site-selectivity may be attributed to the two-hole electronic states populated by the C KVV Auger decay. From Fig. 1a, the two-hole states concerned here seems to be the ones corresponding to the lines 4, 5, 6 and/or 7. The states 4 and 5 have the major configuration  $1e^{-1}2e^{-1}$ , the state 6 has the major configuration  $1e^{-1}5a_1^{-1}$ , while the state 7 has the major configuration  $5a_1^{-2}$  (see Table 1). It is considered that the  $2e$  orbital is the C–H bonding, the  $5a_1$  orbital is the C–F bonding, and the  $1e$  orbital is the F lone-pair [21]. However, these orbitals have C (and H) atomic population to a certain amount [21] and participate in the C KVV Auger decay. Depletion of these electrons can be expected to weaken the C–H bonds. In this connection, we note that line 10 in Fig. 1a, which nearly disappears in the F KVV spectrum in Fig. 1b, has a dominant component  $1e^{-2}$  (see Table 1). The  $1e$  orbital has definitely large F atomic population. The disappearance of line 10 in the theoretical F KVV spectrum casts some doubts in the assignments given by Liegener.

The  $\text{H}^+-\text{CH}_2^+$  ion pair production (Fig. 4c) shows different Auger electron spectral distributions for C and F core holes, again in the same DIP region of 40–50 eV, although the relative ion yields are almost equal. In the case of the C KVV Auger decay, the contribution localizes around a DIP of 43 eV, but in the case of the F KVV Auger decay, it spreads over a broader DIP region. This may imply that  $\text{H}^+-\text{CH}_2^+$  production via the F KVV Auger decay involves the nuclear relaxation described above.

Some ion pairs show high intensity in the DIP region of 32–40 eV. Unfortunately only the C KVV Auger electrons were measured in this DIP region because the kinetic energy window of the electron analyzer was adjusted to have the peak in the non-coincident spectrum at the same position. This turned out to be an underestimate of the differences of the C and F KVV Auger spectrum. The  $\text{H}^+-\text{CH}_2\text{F}^+$  (g) and  $\text{H}_2^+-\text{CHF}^+$  (j) ion pairs have strong contributions around DIP of 35 eV.  $\text{CH}_3\text{F}^{2+}$  in its lowest

two-hole state  $2e^{-2}$  preferentially dissociates into  $\text{H}^+-\text{CH}_2\text{F}^+$  or  $\text{H}_2^+-\text{CHF}^+$ . The contributions of the  $\text{H}^+-\text{CHF}^+$  (f) and  $\text{H}_2^+-\text{CF}^+$  (i) ion pairs are located a few eV above those of the  $\text{H}^+-\text{CH}_2\text{F}^+$  (g) and  $\text{H}_2^+-\text{CHF}^+$  (j) ion pairs because an additional C–H bond breaking needs more energy. Similar trends are visible among the  $\text{H}^+-\text{CH}_2^+$  (c),  $\text{H}^+-\text{CH}^+$  (b) and  $\text{H}^+-\text{C}^+$  (a), and the  $\text{CH}_3^+-\text{F}^+$  (n),  $\text{CH}_2^+-\text{F}^+$  (m),  $\text{CH}^+-\text{F}^+$  (l) and  $\text{C}^+-\text{F}^+$  (k) ion pair productions in the higher DIP region.

Although the relative yields of the doubly charged ions are small, site-selectivity is also seen for  $\text{F}^{2+}$ . In Fig. 2b, the contribution of the  $\text{F}^{2+}$  via the F KVV Auger decay is certainly larger than that of the C KVV. This indicates that  $\text{F}^{2+}$  is also site-selectively produced via the F KVV Auger decay.

## 5. Summary

We have studied site-specific ion pair production of free  $\text{CH}_3\text{F}$  molecules following normal Auger decay. We found a strong enhancement of the  $\text{CH}_3^+-\text{F}^+$  ion pair formation in the F KVV Auger decay compared to the C KVV Auger decay and tentatively explained it in terms of the  $\text{CH}_3-\text{F}$  dissociative nature of the F core-ionized state. We also found an enhancement of the  $\text{H}^+-\text{CF}^+$  ion pair production in the C KVV Auger decay and tentatively attributed it to the depletion of the C–H bonding electron. To draw a decisive conclusion, however, further theoretical investigations of the Auger decay rate and of potential surfaces of the Auger final two-hole states are indispensable. We hope that the present results invoke such theoretical studies.

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