

# Electron-impact dissociative ionization of fluoromethanes CHF<sub>3</sub> and CF<sub>4</sub>

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## Abstract

The electron-impact dissociative ionization of fluoromethanes CHF<sub>3</sub> and CF<sub>4</sub> has been investigated by probing their supersonic expansions with a beam of electrons of selected kinetic energy within a time-of-flight mass spectrometer system. Partial (absolute) ionization cross sections of all the nascent ions arising from electron impact, namely CF<sub>3</sub><sup>+</sup>, CHF<sub>2</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, CHF<sup>+</sup>, CF<sup>+</sup>, HF<sup>+</sup>, F<sup>+</sup>, CH<sup>+</sup>, C<sup>+</sup>, and H<sup>+</sup> from CHF<sub>3</sub> and CF<sub>2</sub><sup>+</sup>, CF<sub>2</sub><sup>2+</sup>, CF<sub>3</sub><sup>+</sup>, CF<sub>3</sub><sup>2+</sup>, CF<sup>+</sup>, C<sup>+</sup>, and F<sup>+</sup> from CF<sub>4</sub>, were measured for electron incident energies up to 100 eV (nominal). The kinetic energy distributions of the nascent ions were also characterized and the information that they supply combined with the appearance potentials (APs) provides an improved identification of the molecular dissociative ionization channels. The correlation between the channel AP and the character and energies of the precursor molecular orbitals is discussed.

## 1. Introduction

Inelastic collisions between electrons and molecules are dominated by channels yielding both electrons and positive ions (Märk 1995). Processes of this type occur in low-energy or cold-temperature plasmas, whose industrial and technological applications are of the utmost interest in semiconductor processing, atmospheric chemistry, etc (Becker 1991). A crucial requirement for modelling low-energy plasmas is the knowledge of the partial ionization cross section (ICS) distribution of the nascent ions as a function of the electron-impact kinetic energy. Besides the experimental determination of the partial and total ICSs, considerable effort has been focused on the development of theoretical approaches for computing the total ICS based on *ab initio* and semiempirical methods. Along these lines, we have recently compared the experimental total ICSs of the benchmark fluoromethanes CF<sub>4</sub>, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F (Torres *et al* 2001)

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with those computed by means of the binary-encounter–Bethe (BEB) theory, the modified additivity rule (MAR), the Deutsch–Märk (DM) formalism, and the polarizability correlation.

The title halomethanes  $\text{CF}_4$  and  $\text{CHF}_3$  are two of the most widely used gases for a variety of plasma-assisted material processing and other industrial applications. The actual ICS measurements are influenced by ions lost on their route to the detector, which may be significant for light-mass species, and, to a minor extent, by the background gas pressure, multichannel plate (MCP) voltage and ion-impact energy on the detector (Syage 1991, Bruce and Bonham 1993). It follows that reliable partial and total ICSs are hard to measure and in some cases are not settled. In fact, for  $\text{CF}_4$  and  $\text{CHF}_3$  some of today's accepted ICSs have been considerably lowered ( $>10\%$  at 100 eV) (Christophorou and Olthoff 1999) with respect to those 'recommended' only a few years ago (Christophorou *et al* 1996, 1997). Earlier total ICSs for  $\text{CF}_4$  (Bruce and Bonham 1993, Ma *et al* 1991) and for  $\text{CHF}_3$  (Beran and Kevan 1969, Poll and Meichsner 1987) thought to underestimate the true values have been reappraised. The last reported ICSs for the  $\text{CHF}_3$  molecule (Iga *et al* 2001) have significant differences from the computed total ICSs, and have played their role in all these re-examinations.

Measurements of partial ICSs of precursors  $\text{CF}_4$  and  $\text{CHF}_3$  reported to date have been carried out under low mass resolution, and ions with close mass-to-charge ratios are indistinguishable (e.g.  $\text{CHF}_2^+/\text{CF}_2^+$  measured by Poll and Meichsner (1987) and Iga *et al* (2001),  $\text{CF}^+/\text{CF}_3^{2+}$  by Sieglaff *et al* (2001), and  $\text{C}^+/\text{CH}^+$  and  $\text{CF}^+/\text{CHF}^+$  by Iga *et al* (2001)). In addition, ICSs for light ions such as  $\text{C}^+$  and  $\text{H}^+$  are sparse or not reported at all. In dissociative ionization, light-mass ions have high or very high nascent kinetic energy, the trajectories to the detector are difficult to control, and, consequently, the losses are difficult to estimate and in some cases severe.

This work reports the total and partial (counting) ICSs of the set of nascent ions produced by electron impact at nominal energies up to 100 eV on  $\text{CHF}_3$  and  $\text{CF}_4$  molecules. No  $\text{CHF}_3^+$  and  $\text{CF}_4^+$  parent ions have been observed, most probably due to their own fast predissociation. A discussion of the correlation between the ion appearance potentials (APs), their kinetic energies, and the molecular orbital energies calculated with the Gaussian 98W package is presented. The study leads to plausible identification of the ionization pathways chosen by the nascent ions produced.

## 2. Experimental procedure

The experimental set-up used to measure the partial ICSs has been described elsewhere (Torres *et al* 2000a) and only a succinct description is presented here. A mixture of the selected halomethane and the reference gas, at a stagnant pressure of 3 bar, was introduced into the chamber of a linear double-focusing time-of-flight apparatus through a nozzle controlled by a pulsed electromagnetic valve (Iota, General Valve). The supersonic molecular beam produced is crossed at right angles with a quasi-monoenergetic ( $\pm 0.5$  eV) electron beam pulse of 300 ns duration and variable energy of up to 100 eV. Following the electron–molecule collisions, a negative pulse is applied to the extraction grid in the ionization region, setting an electric field that drives the ions onto the ( $z$ -) axis of the 86.5 cm long flight tube, where a couple of  $x$ – $y$  plates focuses the ions onto a three-stage microchannel plate (MCP), (C-07001, diameter  $\phi = 18$  mm) detector. The detector electrical response is routed to a digital oscilloscope (Tektronix TDS360) and later to a computer for storage and further analysis.

Electron kinetic energies are varied from 0 to 100 eV (nominal) and calibrated with the  $\text{Ar}^+$  and  $\text{Ar}^{2+}$  APs at 15.75 and 27.62 eV respectively (Rosenstock *et al* 1977), to an accuracy better than  $\pm 0.7$  eV. The electron gun spread energy varies with the filament heating current and has been estimated to be 1 eV at 100  $\mu\text{A}$  electron intensity. In order to narrow the energy

spread, the AP measurements were conducted at only 1  $\mu$ A electron intensity, with an energy accuracy estimated to be  $\pm 0.5$  eV.

Reference and target gases were mixed in an external stainless steel cylinder and their partial pressures measured to 1% accuracy with a capacitance manometer (MKS-baratron 750B). Partial ICSs were measured and later converted to absolute values by reference to Ar (40 amu) or Kr (84 amu), chosen for its closeness in mass to the fluoromethane fragments, in order to minimize the mass effect in the extraction and flight processes. The absolute partial ICS for the CF<sub>3</sub><sup>+</sup> ion produced by dissociative ionization of the CF<sub>4</sub> molecule, taken as an example, is computed as

$$\sigma_{\text{CF}_3^+}(E) = \frac{I_{\text{CF}_3^+} n_{\text{Kr}}}{I_{\text{Kr}^+} n_{\text{CF}_4}} \sigma_{\text{Kr}^+}(E) \quad (1)$$

where  $I_{\text{CF}_3^+}$  and  $I_{\text{Kr}^+}$  are the detector currents produced by the CF<sub>3</sub><sup>+</sup> and the Kr<sup>+</sup> ions respectively;  $n_{\text{CF}_4}$  and  $n_{\text{Kr}}$  stand for the precursor and the reference gas density. The ICSs for Ar<sup>+</sup> and Kr<sup>+</sup> reported by Stephan *et al* (1980) and Straub *et al* (1995) have been used to calibrate references on an absolute scale, following Syage (1988). Total ICSs (counting) were determined by adding up the partial ICSs.

In the dissociative ionization process, the ions are ejected with characteristic kinetic energy distributions (KEDs). For lighter ions the KEDs may have sizable contributions as large as 10 eV or more (Wiley and McLaren 1955, Torres *et al* 2000a, 2000b). Kinetic energies are crucial to evaluating the detection yield, since the ion mass and the high kinetic energy dictate the ion losses in the flight to the detector causing underestimation of the ICSs. We have used the SIMION-3D (1987) software to find the trajectories of the ions as a function of their kinetic energy, and to finally calculate the actual percentage of ions impinging on the detector.

The KED of ejected ions has been investigated by a number of experimental methods (Märk 1983), including: (i) retarding plates analysis; (ii) control of the focusing deflection plates on the detector current (e.g. Syage (1992), Muigg *et al* (1998)); and (iii) analysis of the ion time-of-flight profiles (e.g. Tian and Vidal (1998), Torres *et al* (2000a, 2000b)). In the electron-impact process the energy excess of the experimental AP over the thermodynamic onset is balanced by the kinetic energy of the fragments. Channel identification requires taking into account the kinetic energy of the ion studied and of its partner fragments. Assuming that the fragments have no internal energy, i.e. are produced in the ground state, the excess of the kinetic energy ( $W_{\text{exc}}$ ) is distributed between the neutral and ion fragments according to the momentum and energy conservation laws (Poll and Meichsner 1987):

$$W_{\text{kin}} = \left\{ 1 - \frac{M^+}{N} \right\} \beta W_{\text{exc}} \quad (2)$$

where  $M^+$  and  $N$  stand for the ion and the parent neutral molecular weights,  $W_{\text{kin}}$  for the kinetic energy of the ion, and  $\beta$  is the fraction of excess energy allocated to translation (Schiaivone *et al* 1977), a parameter hard to determine. Thereby, the knowledge of the energy  $W_{\text{kin}}$  allows the calculation of the total process energy,  $W_{\text{exc}}$ . It is also worth noting that the lighter the ion mass, the higher the kinetic energy, and vice versa. In consequence, heavy-ion-mass ionization energies are expected to be close to the APs of the parent ion, and correlate with the molecular orbital energies. In contrast, light-atom production channels are associated with complex processes such as dissociative ionization or Coulomb explosions.

The nascent KEDs have been worked out from the TOF band profiles (Schäfer *et al* 1991) and jointly with the APs provide a better and more accurate identification of the dissociative ionization channel. Uncertainties in the dissociative ICSs (equation (1)) basically stem from both the reference cross section uncertainties and the accuracy of the electron-impact energy,

**Table 1.** Partial (counting) and total ionization cross sections of the ions produced by electron impact on the CHF<sub>3</sub> molecule (in units of 10<sup>-20</sup> m<sup>2</sup>).

Energy (eV)	HF <sup>+</sup> × 10	C <sup>+</sup> × 10	CHF <sup>+</sup> × 10	CH <sup>+</sup> × 10	F <sup>+</sup> × 10	H <sup>+</sup>
20	0.001	0.002	0.010	0.002	0.000	0.004
25	0.003	0.004	0.040	0.006	0.002	0.011
30	0.007	0.019	0.150	0.026	0.004	0.022
35	0.015	0.031	0.214	0.108	0.023	0.028
40	0.027	0.031	0.255	0.237	0.104	0.046
45	0.031	0.062	0.294	0.369	0.236	0.062
50	0.035	0.059	0.326	0.438	0.365	0.086
55	0.042	0.070	0.347	0.474	0.485	0.093
60	0.046	0.051	0.340	0.494	0.606	0.113
65	0.046	0.062	0.383	0.518	0.72	0.114
70	0.047	0.083	0.406	0.572	0.826	0.132
75	0.059	0.047	0.397	0.572	0.913	0.139
80	0.05	0.064	0.389	0.594	0.965	0.150
85	0.058	0.065	0.400	0.577	1.082	0.149

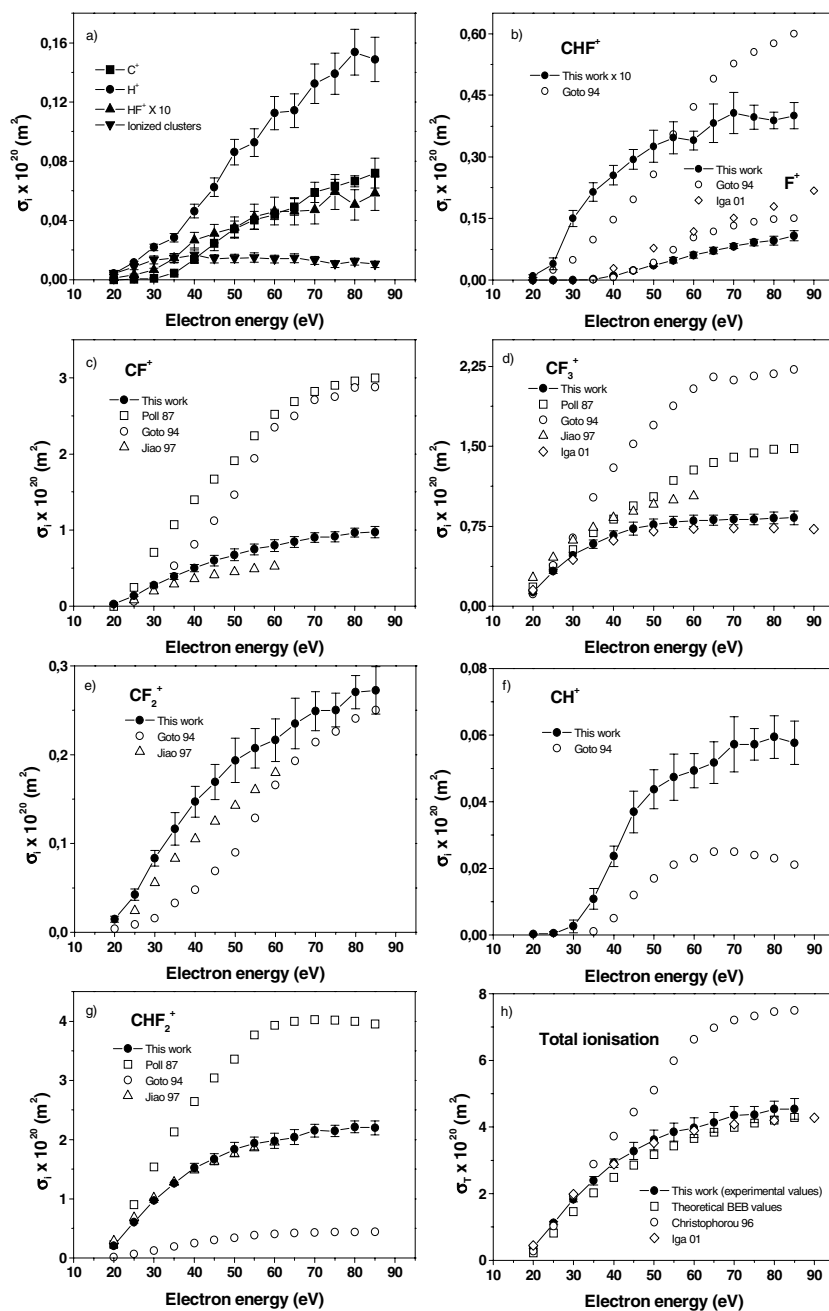
Energy (eV)	CF <sub>2</sub> <sup>+</sup>	CF <sub>3</sub> <sup>+</sup>	CF <sup>+</sup>	CHF <sub>2</sub> <sup>+</sup>	Total
20	0.015	0.132	0.028	0.209	0.389
25	0.043	0.327	0.138	0.606	1.130
30	0.083	0.476	0.278	0.969	1.849
35	0.116	0.583	0.392	1.258	2.416
40	0.147	0.667	0.502	1.527	2.954
45	0.169	0.728	0.598	1.671	3.327
50	0.194	0.766	0.676	1.834	3.678
55	0.207	0.791	0.746	1.938	3.917
60	0.217	0.801	0.797	1.979	3.990
65	0.235	0.808	0.844	2.042	4.216
70	0.249	0.813	0.903	2.151	4.441
75	0.250	0.813	0.915	2.145	4.454
80	0.270	0.829	0.965	2.215	4.635
85	0.272	0.829	0.972	2.195	4.634

estimated to be 3.5% (Straub *et al* 1995) and  $\pm 1$  eV, once the system has been calibrated with the Ar<sup>+</sup> AP. Pressure, measured to a 1% accuracy, is a minor error source. Overall, uncertainties are estimated to be <10% for ions with a mass similar to that of the reference, increasing to 15–20% for light fragments.

### 3. Experimental results and discussion

#### 3.1. CHF<sub>3</sub>

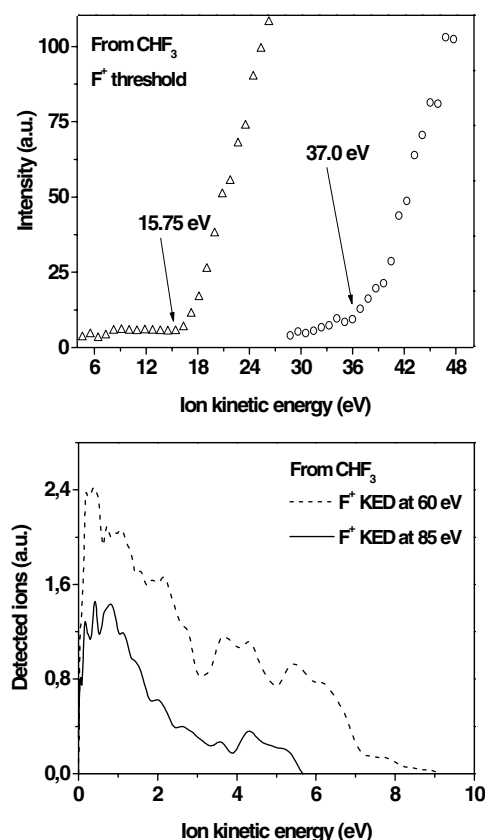
Nascent ions observed following electron impact on the CHF<sub>3</sub> molecule include CF<sub>3</sub><sup>+</sup>, CHF<sub>2</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, CHF<sup>+</sup>, CF<sup>+</sup>, HF<sup>+</sup>, F<sup>+</sup>, CH<sup>+</sup>, C<sup>+</sup>, and H<sup>+</sup>. Partial and the total ICSs have been measured up to electron incident energies of 100 eV (nominal), and their profiles, along with some significant reported profiles, are shown for comparison purposes in figure 1 and in more detail in table 1. The total ICS plotted in figure 1(h) includes the computed BEB results (Torres *et al* 2001), those ‘recommended’ by Christophorou *et al* (1997), and those reported by Iga *et al* (2001) and in this work. The partial ICSs reported to date (Poll and Meichsner 1987, Goto *et al* 1994, Jiao *et al* 1997) include ions of heavy and medium mass, but not ones of light



**Figure 1.** Profiles of the partial (counting) ionization cross sections (ICSs) of the  $\text{C}^+$ ,  $\text{H}^+$ ,  $\text{HF}^+$ ,  $\text{CHF}^+$ ,  $\text{CF}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}_2^+$ ,  $\text{CH}^+$  and  $\text{CHF}_2^+$  ions (a)–(g) and total ICS (h) as a function of the electron-impact energy on the  $\text{CHF}_3$  molecule. References within the plot are abbreviated as follows: Poll 87: Poll and Meichsner (1987); Goto 94: Goto *et al* (1994); Jiao 97: Jiao *et al* (1997); Christophorou 97: Christophorou *et al* (1997); Iga 01: Iga *et al* (2001).

**Table 2.** Reaction channel numbering, standard reaction enthalpies, experimental thresholds, average translational energy, and energy excess at threshold of the ions produced by electron-impact dissociative ionization on CHF<sub>3</sub>. Data labelled <sup>a</sup> were reported by Fiegele *et al* (2000), <sup>b</sup> by Goto *et al* (1994), <sup>c</sup> by Hobrock and Kiser (1964), <sup>d</sup> by Former *et al* (1956) and <sup>e</sup> by Lifshitz and Long (1965).

Channel No	$\Delta H^0$ (eV)	Experimental threshold and other measurements	Observed translational energy (eV)	Excess energy at threshold (eV) (column 3 – column 2)
1. CHF <sub>3</sub> → CF <sub>3</sub> <sup>+</sup> + H	13.85	13.9 ± 0.6 (14.43 <sup>a</sup> , 15.2 <sup>b</sup> , 14.67 <sup>c</sup> , 14.53 <sup>d</sup> , 14.42 <sup>e</sup> )	Very small < 0.1	—
2. CHF <sub>3</sub> → CHF <sub>2</sub> <sup>+</sup> + F	14.18	15.7 ± 0.5 (15.23 <sup>a</sup> , 16.8 <sup>b</sup> , 16.4 <sup>c</sup> , 15.75 <sup>e</sup> )	0–1.0	1–2
3. CHF <sub>3</sub> → CF <sub>2</sub> <sup>+</sup> + HF	14.16			
4. CF <sub>2</sub> <sup>+</sup> + H + F	19.59	19.5 ± 0.5 (15.04 <sup>a</sup> , 17.6 <sup>b</sup> , 17.5 <sup>c</sup> , 20.2 <sup>e</sup> )	Very small, extending to 1.0	0–0.5
5. CHF <sub>3</sub> → CHF <sup>+</sup> + F <sub>2</sub>	18.83			
6. CHF <sup>+</sup> + 2F	20.47	20.7 ± 0.5 (19.8 <sup>a</sup> )	0.1 extending to 0.8	0–0.8
7. CHF <sub>3</sub> → CF <sup>+</sup> + HF + F	16.95			
8. CF <sup>+</sup> + H + F <sub>2</sub>	21.22	20.9 ± 0.5 (17.89 <sup>a</sup> , 20.9 <sup>b</sup> , 20.2 <sup>c</sup> , 20.75 <sup>e</sup> )	0.2 extending to 2.5	0–0.2
9. CF <sup>+</sup> + H + 2F	23.04			
10. CHF <sub>3</sub> → HF <sup>+</sup> + CF <sub>2</sub>	18.2		0–0.5	
11. HF <sup>+</sup> + CF + F	23.60		0.5–2	
12. HF <sup>+</sup> + C + F <sub>2</sub>	27.86	28.8 ± 0.5		0.5–1.5
13. HF <sup>+</sup> + C + 2F	29.51			
14. CHF <sub>3</sub> → CH <sup>+</sup> + F + F <sub>2</sub>	24.85			
15. CH <sup>+</sup> + 3F	26.49	29.9 ± 0.5 (33.5 <sup>b</sup> )	0.5–4 (at threshold) 2–8 (energy > 50 eV)	3–5
16. CHF <sub>3</sub> → C <sup>+</sup> + HF + F <sub>2</sub>	23.06			
17. C <sup>+</sup> + HF + 2F	24.71			
18. C <sup>+</sup> + H + F + F <sub>2</sub>	28.98			
19. C <sup>+</sup> + H + 3F	30.62	33.8 ± 0.5	0–4 (at threshold) 0–10 (energy > 50 eV)	2.7–3.8
20. CHF <sub>3</sub> → F <sup>+</sup> + CHF <sub>2</sub>	22.97			
21. F <sup>+</sup> + CF + HF	25.35			
22. F <sup>+</sup> + CHF + F	27.66			
23. F <sup>+</sup> + C + HF + F	30.87			
24. F <sup>+</sup> + CF + H + F	31.26			
25. F <sup>+</sup> + CH + F <sub>2</sub>	31.62			
26. F <sup>+</sup> + CH + 2F	33.34			3.2–4.2
27. F <sup>+</sup> + C + H + F <sub>2</sub>	35.22	37.0 ± 0.5 (37.0 <sup>b</sup> )	0–6 (at threshold) 0–9 (energy > 60 eV)	1.3–2.3
28. F <sup>+</sup> + C + H + 2F	36.78			0–1



**Figure 2.** The AP and nascent KED of the  $\text{F}^+$  ion as produced by electron impact on  $\text{CHF}_3$ . The  $\text{Ar}^+$  signal at 15.75 eV is used as an internal standard to calibrate the electron energy. A list of the APs of the ions produced by electron impact on the  $\text{CHF}_3$  molecule is presented in table 2.

mass:  $\text{C}^+$ ,  $\text{H}^+$ , and  $\text{HF}^+$ . Furthermore, ions with  $<1$  amu difference, such as  $\text{CHF}_2^+$  and  $\text{CF}_2^+$  or  $\text{CHF}^+$  and  $\text{CF}^+$ , are indistinguishable (Poll and Meichsner 1987). Our measured partial ICSs are consistently slightly lower than those reported by Goto *et al* (1994) except for  $\text{CH}^+$  and  $\text{CHF}_2^+$ , but in good agreement with those reported by Jiao *et al* (1997) and for  $\text{CF}_3^+$  by Iga *et al* (2001).

The AP onsets and the average excess KE of the ions have also been measured and are summarized in table 2. As an example, figure 2 shows the AP profiles and the KEDs for the  $\text{F}^+$  ion at electron incident energies of 60 and 85 eV respectively. In general it may be stated that the KEDs of the light-mass ions, such as  $\text{HF}^+$ ,  $\text{CH}^+$ ,  $\text{C}^+$ , and  $\text{F}^+$ , are weighed at relatively high kinetic energies (a few eV), the heavier-mass ions, such as  $\text{CF}_3^+$ ,  $\text{CF}_2^+$ , and  $\text{CHF}_2^+$ , at low energies ( $\ll 1$  eV), and the medium-size  $\text{CHF}^+$  and  $\text{CF}^+$  ions at intermediate energies (about 1 eV). The comparison between the thermodynamic heat of formation (JANAF 1985), the APs and the fragment KEDs provides an improved method for identifying the channel pathway of ion formation.

Dissociative ionization channels are precisely identified if the KE excess of the ions at threshold is well characterized. In these processes, the channel partners of the ions are usually neutral ground-state atoms (Becker 1991) and in the case of haloalkanes, the partners may be halogen-ion pairs (Martínez *et al* 1998, Torres *et al* 1999). Examples of the latter mechanisms

**Table 3.** Molecular orbital labelling, *ab initio* calculated orbital energies (Gaussian 98W at the RHF/6-311G\*\* level), corrected Koopmans ionization potentials, and experimental adiabatic and vertical ionization potentials (Brundle *et al* 1970) (in eV) for the CHF<sub>3</sub> and CF<sub>4</sub> molecules.

	Molecular orbital	Orbital energy (eV)	Calculated IP $\times 0.85$	Adiabatic IP (eV)	Vertical IP (eV)
CHF <sub>3</sub>	6a <sub>1</sub>	−16.17	13.74	$\geq 13.8$	14.80
	1a <sub>2</sub>	−17.66	15.01	—	15.5
	5e	−18.18	15.45	—	16.2
	4e	−19.45	16.53	17.11	17.24
	3e	22.74	19.33	20.6	19.84
	5a <sub>1</sub>	23.37	19.86		
	4a <sub>1</sub>	−27.04	22.98	$\geq 24.34$	24.44
	2e	−44.79	38.07	—	—
CF <sub>4</sub>	1t <sub>1</sub>	−18.52	15.74	$\geq 15.35$	16.20
	4t <sub>2</sub>	−19.42	16.51	17.1	17.40
	1e	−20.94	17.80	18.3	18.50
	3t <sub>2</sub>	−24.54	20.86	21.70	22.12
	4a <sub>1</sub>	−27.63	23.49	25.12	25.12

are given in channels 8 and 12 of table 2. The formation of F<sup>+</sup> ions (channels 20–28) is characterized by a broad KED (cf figure 2), with an average energy of about 1 eV (to balance the energy of channel 28) and extended up to 5 eV, explaining the participation of channels 26 and 27. For comparison purposes, table 3 depicts the computed precursor orbital energies as well as the adiabatic and vertical ionization potentials (IPs).

The correlation between the precursor orbital energies (and its bonding character) and the dissociation pathways helps us to understand the dissociative ionization collisional processes. The outer electron structure of the CHF<sub>3</sub> molecule in the electron-independent model is ... (2e)<sup>4</sup>(4a<sub>1</sub>)<sup>2</sup>(5a<sub>1</sub>)<sup>2</sup>(3e)<sup>4</sup>(4e)<sup>4</sup>(5e)<sup>4</sup>(1a<sub>2</sub>)<sup>2</sup>(6a<sub>1</sub>)<sup>2</sup>. Although low-resolution photoelectron spectroscopy is unable to distinguish the adiabatic IPs of the molecular orbitals (Brundle *et al* 1970, Harshbarger *et al* 1972/1973), the vertical IPs have been measured for all the precursor orbitals. It should also be noted that neither the parent ion itself, CHF<sub>3</sub><sup>+</sup>, nor its optical emissions have been observed (Martínez 1992), presumably due to fast predissociation or some other dissociative process. The adiabatic IP of the outer 6a<sub>1</sub> orbital ( $\geq 13.8$  eV, Brundle *et al* (1970)) matches very well with the  $13.9 \pm 0.6$  eV for the CF<sub>3</sub><sup>+</sup>-ion formation (channel 1). The 6a<sub>1</sub> orbital has a strong C–H bonding character and the removal of one of its electrons leads to an unstable CHF<sub>3</sub><sup>+</sup> ion that finally evolves to CF<sub>3</sub><sup>+</sup>.

The AP for yielding the CHF<sub>2</sub><sup>+</sup> ion has been measured to be  $15.7 \pm 0.5$  eV and this energy compares well with that of the vertical IPs of 1a<sub>2</sub> and 5e orbitals (15.5 and 16.2 eV). The 5e orbital has a weak C–F bonding character and its energy is not high enough to produce CHF<sub>2</sub><sup>+</sup> ions with an average KE in the range 0–1.0 eV (cf table 2). Further, the 1a<sub>2</sub> orbital has a nonbonding character and its adiabatic IP is not accurately known, though presumably it lies below 15.5 eV. As the kinetic energy of the CHF<sub>2</sub><sup>+</sup> fragment is small, the adiabatic IP ought to be close to 15.0 eV, and, therefore, the (1a<sub>2</sub>)<sup>−1</sup> configuration plays a fundamental role in the channel yielding the CHF<sub>2</sub><sup>+</sup> ion.

The upper nearby AP onset is at  $19.5 \pm 0.5$  eV and correlates with the formation of the CF<sub>2</sub><sup>+</sup> ion of channel 4 (table 2). This AP is close to the heat of formation and consequently the kinetic energy of the ejected CF<sub>2</sub><sup>+</sup> is expected to be low. The electron involved in the process is likely to be in the 3e orbital for which, although in photoelectron spectroscopy it overlaps with 5a<sub>1</sub> at 20.6 eV, the computations suggest an adiabatic IP of 20.05 eV (Pullen *et al* 1970)—in



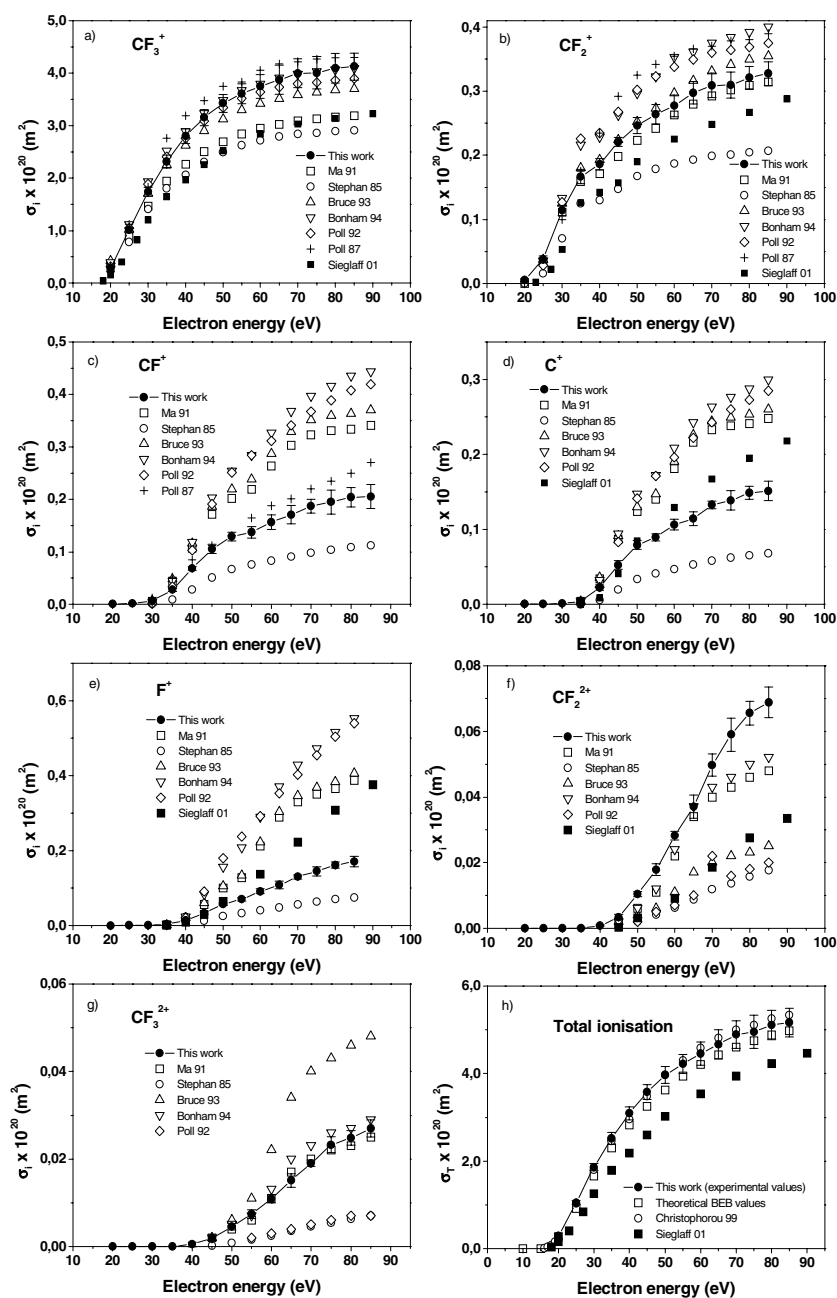
preference to the nonbonding 4e orbital with an adiabatic IP close to 17.11 eV. Henceforth, the partial C–F bond character of the 3e orbital is taken to explain the dissociative ionization of the (3e)<sup>−1</sup> configuration to yield CF<sub>2</sub><sup>+</sup>.

CHF<sup>+</sup> and CF<sup>+</sup> ions have very close APs, namely 20.7±0.5 and 20.9±0.5 eV respectively, and their formation is plausibly related to the withdrawal of one electron from either the 3e or the 5a<sub>1</sub> orbital. The average KED at threshold of the nascent CHF<sup>+</sup> ion is a few tenths of an eV, whereas that of CF<sup>+</sup> is about 1.0 eV. Therefore, the formation of both ions correlates with the ion precursor (5a<sub>1</sub>)<sup>−1</sup> and the (3e)<sup>−1</sup> electronic structure. The 5a<sub>1</sub> orbital has a mixture of C–F and C–H bond characters and, in consequence, is the favoured candidate for being involved in the production of CF<sup>+</sup>.

The APs of the HF<sup>+</sup> and CH<sup>+</sup> ions are both larger than the IP of the 4a<sub>1</sub> orbital (24.34 eV, Brundle *et al* 1970) and, hence, the expected KE is high. Indeed, even at threshold, both ions are released with a broad-profile KED extending up to 4 eV. Further, the C–H bond character of the 4a<sub>1</sub> orbital is in accord with the assignment proposed. Other medium-size-mass ions, such as C<sup>+</sup> and F<sup>+</sup>, are observed at APs of 33.8±0.5 and 37.0±0.5 eV, respectively, lower than the IP of the 2e orbital (44.79 eV, computed at the HF/6-311G\*\* level). Its IP is close to 39 eV, much higher than the 24.34 eV of the nearby 4a<sub>1</sub> orbital, and therefore the overall energy balance requires nascent ions with a significant KE. In these cases the mechanisms are presumably more complex and production of atomic ions may be related to multiple ionization of the parent molecule, which is unstable and produces high-KE nascent atomic ions by Coulomb explosions (Torres *et al* 2000b).

### 3.2. CF<sub>4</sub>

Electron impact on full fluorinated methane yields observable CF<sub>2</sub><sup>+</sup>, CF<sub>2</sub><sup>2+</sup>, CF<sub>3</sub><sup>+</sup>, CF<sub>3</sub><sup>2+</sup>, CF<sup>+</sup>, C<sup>+</sup>, and F<sup>+</sup> ions. The measured partial ICSs of the whole set of ions and the total ICSs at electron-impact energies up to nominal 100 eV are depicted in figures 3(a)–(g) and (h) respectively, along with a few previously reported measurements. In order to simplify the plot of the figure 3(h), only the total ICSs ‘recommended’ by Christophorou and Olthoff (1999), those reported by Sieglaff *et al* (2001) (and in this work) and the computed BEB profile (Torres *et al* 2001) are shown. The absolute partial ICSs for a number of electron-impact energies in the 0–100 eV range are presented in table 4. It is worth remembering that Bonham’s (1994) ICSs are versions corrected for multiple ionization and ion-mass detector efficiency of the results previously reported by Bruce and Bonham (1993) and Ma *et al* (1991). In our study, the detector efficiency lost has been assumed to be equal to the escape of ions on their route to the detector, and hence corrected by modelling the ion trajectories with the SIMION code. The correction factors of the low-mass ions may be readily estimated from figure 3 where it should be noted that the lighter the ion, the higher the ICS difference with respect to the commonly accepted ICSs. Heavier fragments such as CF<sub>3</sub><sup>+</sup> and CF<sub>2</sub><sup>+</sup> are produced with negligible kinetic energies, in agreement with Bonham (1994), Ma *et al* (1991) and Bruce and Bonham (1993). The lightest ions such as CF<sup>+</sup>, C<sup>+</sup>, and F<sup>+</sup> have characteristic KEDs in accordance with the measurements reported by Stephan *et al* (1985). The reported ICSs of the observed CF<sub>3</sub><sup>2+</sup> and CF<sub>2</sub><sup>2+</sup> dications are in good agreement with those of Ma *et al* (1991) and Bonham (1994). Sieglaff *et al* (2001) have recently reported the partial ICSs obtained in a TOF mass spectrometer with a position-sensitive detector. The mass resolution was not high enough to separate CF<sup>+</sup> and CF<sub>3</sub><sup>2+</sup> ions, but the method was recommended as efficient for collecting ions irrespective of their initial kinetic energies. The partial ICSs for all ions studied, except for the lighter C<sup>+</sup> and F<sup>+</sup>, are smaller than ours and other reported values. Although the lighter-ion ICS uncertainties are high, their contribution to the total ICS is small



**Figure 3.** Partial counting ICSs of the  $\text{CF}_3^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}^+$ ,  $\text{C}^+$ ,  $\text{F}^+$ ,  $\text{CF}_2^{2+}$  and  $\text{CF}_3^{2+}$  ions (a)–(g) and total ICS (h) produced by electron impact on the  $\text{CF}_4$  molecule, as a function of the electron incident energy. References within the plot have been abbreviated as follows: Ma 91: Ma *et al* (1991); Stephan 85: Stephan *et al* (1985); Bruce 93: Bruce and Bonham (1993); Bonham 94: Bonham (1994); Poll 92: Poll *et al* (1992); Poll 87: Poll and Meichsner (1987); Christophorou 99: Christophorou and Olthoff (1999); Sieglaff 01: Sieglaff *et al* (2001).

**Table 4.** Partial (counting) and total ionization cross sections of the ions produced by electron impact on the CF<sub>4</sub> molecule (in units of 10<sup>-20</sup> m<sup>2</sup>).

Energy (eV)	CF <sub>3</sub> <sup>2+</sup> × 10	CF <sub>2</sub> <sup>2+</sup> × 10	C <sup>+</sup> × 10	F <sup>+</sup> × 10
20	—	—	0.005	0
25	—	—	0.007	0.007
30	—	—	0.009	0.011
35	—	—	0.043	0.032
40	0.005	0.008	0.227	0.135
45	0.019	0.034	0.525	0.334
50	0.045	0.104	0.792	0.573
55	0.074	0.179	0.893	0.704
60	0.109	0.281	1.064	0.916
65	0.151	0.371	1.143	1.082
70	0.190	0.497	1.326	1.299
75	0.233	0.590	1.386	1.453
80	0.248	0.656	1.489	1.615
85	0.270	0.688	1.513	1.703

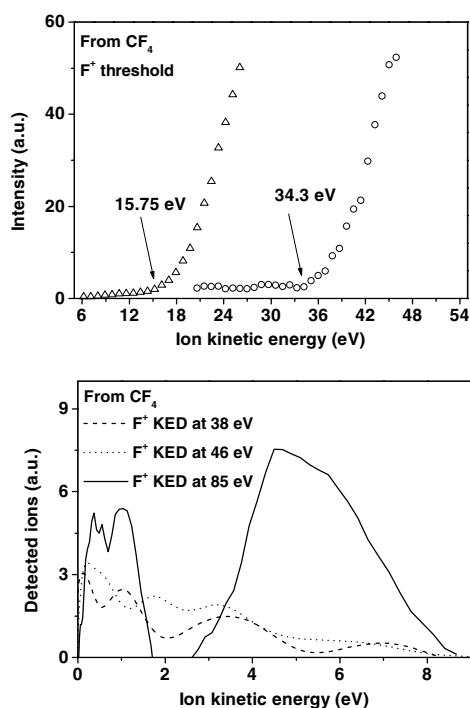
  

Energy (eV)	CF <sup>+</sup> × 10	CF <sub>2</sub> <sup>+</sup>	CF <sub>3</sub> <sup>+</sup>	Total
20	0.006	0.005	0.280	0.286
25	0.017	0.038	1.011	1.052
30	0.064	0.114	1.741	1.863
35	0.277	0.167	2.317	2.519
40	0.683	0.186	2.802	3.095
45	1.056	0.221	3.152	3.575
50	1.292	0.246	3.423	3.950
55	1.372	0.264	3.606	4.193
60	1.562	0.277	3.746	4.416
65	1.709	0.297	3.875	4.618
70	1.871	0.309	3.998	4.825
75	1.949	0.31	4.004	4.875
80	2.042	0.321	4.095	5.021
85	2.055	0.327	4.124	5.080

or negligible, explaining the excellent agreement between the BEB calculations (Nishimura *et al* 1999, Torres *et al* 2001) (figure 3(*h*)) and the total ICSS (Christophorou and Olthoff 1999).

Experimental APs and average KEs for the set of ions produced by electron impact on CF<sub>4</sub> are shown in table 5. In more detail and as an example, figure 4 depicts the AP profiles and the KEDs for the nascent F<sup>+</sup> ion where the distribution broadening with the increase of the electron impinging energy should be noted. It is also worth noting that the channel partners of CF<sub>2</sub><sup>+</sup>, CF<sup>+</sup>, and C<sup>+</sup> ions are ground-state atoms, in contrast to the F<sup>+</sup>-ion partner, the CF diatom and either two F atoms or one fluorine diatom. Nevertheless, ion atoms are unlikely to be associated with a particular channel, since they are often produced by multiple ionization of the parent molecule or by positive ion-pair formation, as has been shown for the F<sup>+</sup> ion, detected by coincidences with CF<sub>3</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, CF<sup>+</sup>, and C<sup>+</sup> ions (Bruce *et al* 1992, Sieglaff *et al* 2001).

As in the dissociative ionization of CHF<sub>3</sub>, the rationalization of the dissociation pathways according to their correlation with the precursor molecular orbital energies (table 3) is appealing. The outer valence shell configuration of the ground-state CF<sub>4</sub> is ... (4a<sub>1</sub>)<sup>2</sup>(3t<sub>2</sub>)<sup>6</sup>(1e)<sup>4</sup>(4t<sub>2</sub>)<sup>6</sup>(1t<sub>1</sub>)<sup>6</sup> with adiabatic IPs of 25.12, 21.70, 18.3, 17.1, and ≥15.35 eV (Brundle *et al* 1970). In the electron energy-loss spectrum it is observed that incident electron energies above 12.56 eV excite neutral species that are in competition with the dissociation of



**Figure 4.** The AP and nascent KED of the  $F^+$  ion as produced by electron impact on  $CF_4$ . The  $Ar^+$  signal at 15.75 eV is used as an internal standard to calibrate the electron energy. A list of the APs of the ions produced by electron impact on the  $CF_4$  molecule is presented in table 5.

$CF_4$  in neutral or ion fragments (Kuroki *et al* 1992). Most  $CF_4$  electronic excited states lead to dissociation or predissociation and, in fact, no optical emission from  $CF_4^*$  has been observed (Martínez 1992). The mass spectrum shows no traces of the  $CF_4^+$  ion, a significant additional clue to its instability.

The AP onset of the  $CF_3^+$  ion comes out at  $15.0 \pm 0.5$  eV and is plausibly correlated with the removal of one electron from the  $1t_1$  orbital, with an adiabatic IP  $\geq 15.35$  eV (Brundle *et al* 1970). The proximity of the two energies suggests nascent  $CF_3^+$  ions with little kinetic energy. In the case of the  $CF_2^+$  ions, the energy of the nearest orbital for yielding  $CF_2^+$  ions is the  $1e$  orbital with an adiabatic IP of 18.3 eV. Again, the similarity of the IP and thermodynamic threshold suggest a  $CF_2^+$  ion with minute kinetic energy. Autoionizing transitions may result in non-Franck–Condon populations of  $(1t_1)^{-1}$ ,  $(4t_2)^{-1}$  and  $(1e)^{-1}$  fragments with high vibrational levels modifying the  $CF_3^+ : CF_2^+$ -ion ratio at impact energies over 21.2 eV (Carlson *et al* 1984).

The  $CF^+$  fragment has an AP threshold of  $27.5 \pm 0.6$  eV and the orbital with closest energy is the  $4a_1$ , with an adiabatic IP of 25.12 eV. However, removal of one electron from the  $4a_1$  orbital leads to an ion with high kinetic energy, in agreement with experiments (table 5). The APs of the  $C^+$  and  $F^+$  ions are at  $34.1 \pm 0.5$  and  $34.3 \pm 0.5$  eV respectively, far from that of  $(4a_1)^{-1}$  state of the parent ion, and lower than the adiabatic IP of the  $2t_2$  state at about 40 eV (binding energy of 45.92 eV at the HF/6-311G\*\* level). If the ions correlate with the  $(4a_1)^{-1}$  structure, the high-kinetic-energy release of the process would be explained. Nevertheless, atomic ion formation is very difficult to explain if we bear in mind that Coulomb explosions produced in multiple ionizations are often associated with the production of high-KE atomic ions.

**Table 5.** Reaction channel numbering, standard reaction enthalpies, experimental thresholds, average translational energies, and energy excesses at threshold for the ions produced by electron-impact dissociative ionization on CF<sub>4</sub>. Data labelled as <sup>a</sup> were reported by Fiegele *et al* (2000), <sup>b</sup> by Bonham and Bruce (1991), <sup>c</sup> by Ma *et al* (1991), and <sup>d</sup> by Poll and Meichsner (1987).

Channel No	$\Delta H^0$ (eV)	Experimental threshold and other measurements	Observed translational energy (eV)	Excess energy at threshold (eV) (column 3 – column 2)
1. CF <sub>4</sub> → CF <sub>3</sub> <sup>+</sup> + F	14.63	15.0 ± 0.5 (15.72 <sup>a</sup> , 15.9 <sup>c,d</sup> )	< 0.5 (at threshold) 1.2 ± 0.5 <sup>c</sup> (at 20 eV)	0–1
2. CF <sub>4</sub> → CF <sub>2</sub> <sup>+</sup> + F <sub>2</sub>	18.97			
3. CF <sub>2</sub> <sup>+</sup> + 2F	20.62	20.5 ± 0.5 (21.45 <sup>a</sup> , 22 <sup>b</sup> , 22.4 <sup>d</sup> )	0.1 (at threshold)	0–0.5
4. CF <sub>4</sub> → CF <sup>+</sup> + F <sub>2</sub> + F	22.25			
5. CF <sup>+</sup> + 3F	23.90	27.5 ± 0.6 (29.15 <sup>a</sup> , 27 <sup>b</sup> , 28.7 <sup>d</sup> )	0–4, 10 (at threshold) 1–4 (energy > 60 eV)	3–4.2
6. CF <sub>4</sub> → C <sup>+</sup> + 2F <sub>2</sub>	28.36			
7. C <sup>+</sup> + F <sub>2</sub> + 2F	30.01			
8. C <sup>+</sup> + 4F	31.65	34.1 ± 0.5 (34.76 <sup>a</sup> , 34.5 <sup>b</sup> )	1–4 (at threshold) 1–6 (energy > 50 eV)	2–3
9. CF <sub>4</sub> → F <sup>+</sup> + CF <sub>3</sub>	23.13			
10. F <sup>+</sup> + CF <sub>2</sub> + F	26.92			
11. F <sup>+</sup> + CF + F <sub>2</sub>	30.63			
12. F <sup>+</sup> + CF + 2F	32.27	34.3 ± 0.5 (34.5 <sup>b</sup> )	0–5 (at threshold) 4–8 (energy > 80 eV)	0–2, 3–4 1.5–2.5
13. F <sup>+</sup> + C + F + F <sub>2</sub>	36.23			
14. F <sup>+</sup> + C + 3F	37.88			

The contributions of the Coulomb explosion are hard to estimate. Production of electronic excited neutral atoms has been reported previously (Martínez *et al* 1995) and the KEDs measured by the Doppler width method (cf Donohue *et al* (1977)). Such measurements show that neutral atoms are produced with KED maxima in the 1–3 eV range, an energy close to but lower than that observed in the production of atomic ions.

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