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Absolute partial cross sections for electron-impact ionization of CF_4 from threshold to 1000 eV

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Abstract

Absolute partial cross sections for electron-impact ionization of CF_4 are reported for electron energies from threshold to 1000 eV. The product ions are mass-analysed using a time-of-flight mass spectrometer and detected with a position-sensitive detector whose output demonstrates that all product ions are collected with equal efficiency irrespective of their initial kinetic energies. Data are presented for the production of CF_3^+, CF_2^+, (CF^+ + CF_3^{2+}), C^+, F^+ and CF_2^{2+} and for the total cross section which is obtained as the sum of these partial cross sections. The overall uncertainties in the absolute cross section values are ±5% to ±8%. Data are also presented for formation of (CF^+, F^+) and ($CF_2{}^+$, F^+) ion pairs. Comparison is made with prior experiments and calculations.

1. Introduction

Plasma processing of materials is commonly employed in the semiconductor industry. As in many other areas of technology, accurate models of such plasmas require knowledge of the basic atomic physics processes involved. Cross sections for the production of reactive ions and neutrals by electron-impact on plasma processing feed gases are particularly important. This paper reports a study of electron-impact ionization of tetrafluoromethane, a widely used plasma processing gas.

There have been a number of prior experimental studies of CF_4, most of which have taken place over the past 15 years; however, considerable doubt remains as to the accuracy of much of this work. The earliest study in which partial cross sections were measured, Stephan *et al* (1985), was shown to discriminate strongly against energetic fragment ions by Poll *et al* (1992) who attempted to correct for these effects by utilizing a computer simulation of the apparatus employed by Stephan *et al* (1985). However, their corrections are very large, up to a factor of 7, and furthermore no uncertainty was assigned to the revised values. Cross sections for the production of the major fragment ions, CF_3^+, CF_2^+, and CF^+ at energies up to 130 eV, were also obtained by Poll and Meichsner (1987) using a quadrupole mass spectrometer, and were normalized with reference to the argon cross section of Rapp and Englander-Golden (1965).

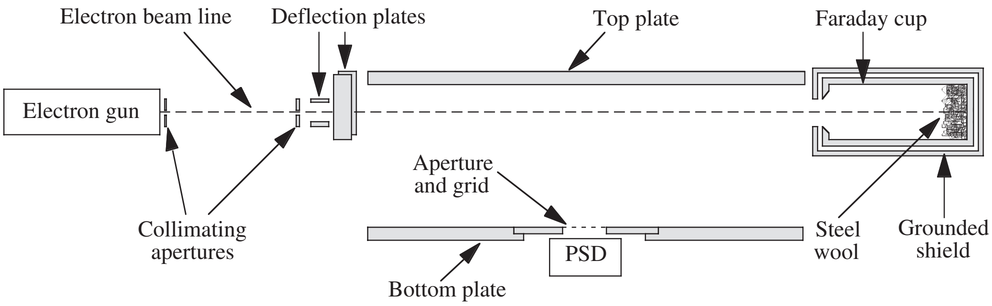

Figure 1. Schematic diagram of the apparatus.

However, neither these data nor those of Beran and Kevan (1969), who measured total cross sections at three specific energies, were assigned any uncertainty. Ma *et al* (1991) measured partial and total cross sections, which were later subject to a number of revisions (Ma *et al* 1992, Bruce and Bonham 1993, 1995). The data used for comparison with the present work are the updated values given by Bruce and Bonham (1993) multiplied by 1.18 as indicated in Bruce *et al* (1994). The determination of the 1.18 factor is described in Bruce and Bonham (1995). This group also reported measurements of the cross sections for production of positive ion pairs (Bruce *et al* 1992, 1994). Despite all this activity, the only published partial cross sections to which an uncertainty has been ascribed, and therefore to which a meaningful comparison may be made, are the latest data of Bonham's group (Bruce and Bonham 1993, Bruce *et al* 1994). Recently, total cross sections have been measured by Rao and Srivastava (1997)[1] and Nishimura *et al* (1999) and calculations have been performed by Nishimura *et al* (1999) and by Deutsch *et al* (2000). The available electron-impact ionization data for CF_4 have been reviewed by Bonham (1994) and by Christophorou and co-workers (Christophorou *et al* 1996, Christophorou and Olthoff 1999).

In this paper, absolute partial cross sections are reported for the production of CF_3^+, CF_2^+, $(CF^+ + CF_3^{2+})$, C^+, F^+ and CF_2^{2+} from threshold to 1000 eV. Only the sum of the CF^+ and CF_3^{2+} cross sections is presented since these ions could not be fully resolved by the mass spectrometer. The total ionization cross section is obtained as the sum of the measured partial cross sections. Electron-impact ionization of CF_4 may also result in the production of positive ion pairs and the cross sections for the two major positive ion pair production channels are reported here.

2. Apparatus and experimental method

The apparatus (see figure 1) consists of an electron gun, a time-of-flight mass spectrometer with a position-sensitive detector (PSD), and an absolute pressure gauge (not shown). It has been described in detail previously (Straub *et al* 1995, 1996). Briefly, during a cross-section measurement, the entire vacuum chamber is filled with CF_4 at a pressure of 4×10^{-6} Torr. The electron gun produces 20 ns long pulses at a repetition rate of approximately 2.5 kHz. These pulses are directed through an interaction region, located between two plates maintained at ground potential, and are collected in a Faraday cup. Approximately 250 ns after each electron pulse, a 3 kV pulse is applied to the top plate to drive any positive ions formed by electron impact toward the bottom plate. Some ions pass through a grid-covered aperture, of length 1.91 cm in the direction parallel to the electron beam, in the bottom plate. These ions are

[1] These workers also measured the partial cross sections, but no values have been reported in the literature.

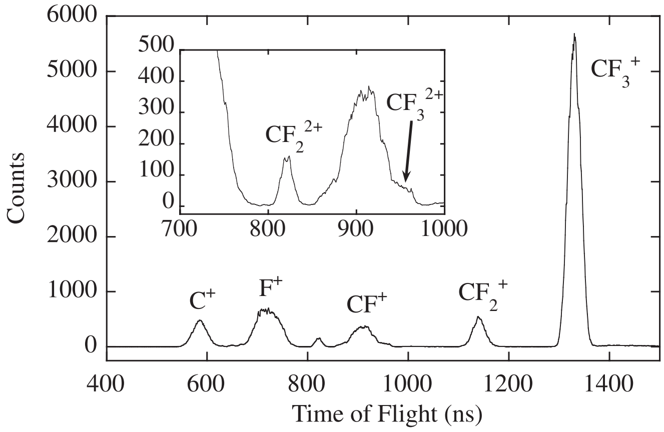

Figure 2. Time-of-flight spectrum for ions produced by 160 eV electron impact on CF_4.

then accelerated to an energy of 5.4 keV and subsequently impact a PSD, comprising a pair of 25 mm diameter microchannel plates and a resistive-encoded anode (Gao *et al* 1984), which records their arrival times and positions. The ion arrival times are used to identify their mass-to-charge ratios and the ion arrival positions are used to determine the effectiveness of product ion collection.

Under conditions in which very few of the incident electrons produce an ion, the partial cross section $\sigma(X)$ for production of ion species X is given by

$$\sigma(X) = \frac{N_{\mathrm{i}}(X)}{N_{\mathrm{e}}nl} \tag{1}$$

where $N_{\mathrm{i}}(X)$ is the number of X ions produced by a number N_{e} of electrons passing a distance l through a uniform CF_4 target of number density n. Since the data-acquisition electronics only allow one ion to be detected following each electron pulse a small correction is applied to account for pulses in which more than one ionizing collision occurs (Straub *et al* 1995). Determination of an absolute cross section requires measurement of all four quantities on the right-hand side of equation (1) and has been previously described in detail (Straub *et al* 1995, 1996). Briefly, the number of electrons N_{e} is determined by collecting the electron beam in a Faraday cup and measuring the current with an electrometer operating in the charge collection mode. Measurement of $N_{\mathrm{i}}(X)$ is accomplished by recording the time-of-flight spectrum, counting the number of ions in an appropriate portion of the spectrum, and accounting for the detection efficiency of the PSD and the transparency of the grid. The overall detection efficiency was previously determined to be $(37.2 \pm 0.6)\%$ and to be independent of ion species by repetitively directing an ion beam of appropriate species and energy alternately onto the PSD and into a second Faraday cup (not shown in figure 1) (Straub *et al* 1999). The effective path length l from which detected ions originate is determined by the aperture directly in front of the PSD, although, due to slight non-uniformities in the pulsed electric field, l is 2% smaller than the actual length of this aperture. In the present measurements, a few of the energetic fragment ions that are created in the region directly above the aperture with components of velocity parallel to the electron-beam axis will escape detection. However, the translational symmetry of the apparatus along the electron-beam axis ensures that for every ion produced in the region directly above the PSD that escapes detection, one from outside this region will be detected. The target number density n is obtained from measurements of the gas pressure using a capacitance diaphragm gauge (Straub *et al* 1994).

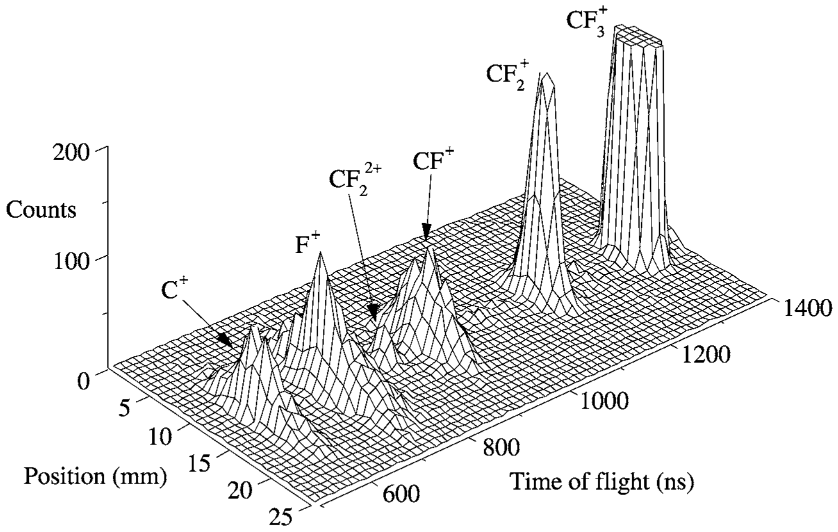

Figure 3. Position and time-of-flight distribution produced by 160 eV electron impact on CF_4. The position axis indicates the displacement of the ions perpendicular to the axis of the electron beam.

The CF_4 used in this work was obtained from Matheson Gas Products and has a specified purity of better than 99.9%. It is transported from the gas cylinder through stainless-steel tubing and introduced to the vacuum chamber through a leak valve. The effectiveness of these procedures in preventing contamination can be seen from the absence of spurious peaks in the time-of-flight spectrum shown in figure 2. As noted previously by other workers, no stable CF_4^+ ion is observed and as the figure shows it was not possible to completely resolve the CF^+ peak from the CF_3^{2+} peak which appears as a shoulder on the larger CF^+ peak.

Figure 3 shows a plot in which the product ions' transverse arrival positions at the PSD (i.e., the displacement of the ions perpendicular to the electron beam axis) have been combined with their flight times. The widths in both position and time of the various ion peaks are due to the ions' initial velocities perpendicular to the electron beam in addition to the transverse spatial extent of the electron beam itself. The width of the CF_3^+ peak is due primarily to the spatial extent of the electron beam, but the widths of the lightest ion peaks are determined largely by the energies with which these ions are formed. Complete collection of all product ions from the path length l is demonstrated by the arrival position distribution of the ions at the PSD.

It was shown by Bruce *et al* (1992) that in electron collisions with CF_4 there is a significant probability that, in a single collision, an F^+ ion may be formed together with a CF_3^+, CF_2^+, CF^+ or C^+ ion. In that the instrumentation utilized here is capable of counting only one ion per electron pulse when two ions are created in the same collision, the first to arrive at the detector will, if detected, preclude detection of any subsequent ions and thus lead to underestimation of their cross sections. In order, therefore, to measure the cross sections for all ions other than F^+, a gate was applied to the timing signal to suppress detection of the F^+ ions. This ensures that the measured partial cross section $\sigma(X)$ is for production of the specified fragment ion X irrespective of whether an F^+ ion is also formed. The cross section for F^+ ions was obtained by suppressing detection of all other ions. However, this approach leads to a slight underestimation of the true F^+ cross section because, as shown by Bruce *et al* (1994), two

Table 1. Present absolute partial ionization cross sections for electron-impact ionization of CF_4. The uncertainties in the CF_3^+, CF_2^+, ($CF^+ + CF_3^{2+}$), C^+, F^+ and CF_2^{2+} cross sections are ±5%, ±5%, ±5%, ±5%, ±8% and ±6% respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CF_3^+)$ (10^{-16} cm^2)	$\sigma(CF_2^+)$ (10^{-17} cm^2)	$\sigma(CF^+ + CF_3^{2+})$ (10^{-17} cm^2)	$\sigma(C^+)$ (10^{-17} cm^2)	$\sigma(F^+)$ (10^{-17} cm^2)	$\sigma(CF_2^{2+})$ (10^{-18} cm^2)
18	0.041 ± 0.004					
20	0.16 ± 0.01					
23	0.40	0.021 ± 0.006				
27	0.82	0.22 ± 0.02				
30	1.20	0.53	0.023 ± 0.005			
35	1.65	1.26	0.14 ± 0.01	0.005 ± 0.002	0.018 ± 0.009	
40	1.97	1.42	0.56	0.089 ± 0.006	0.092	
45	2.26	1.57	1.08	0.41	0.30	0.02 ± 0.04
50	2.52	1.90	1.59	0.85	0.65	0.32 ± 0.03
60	2.84	2.25	1.97	1.29	1.37	0.91
70	3.03	2.48	2.57	1.67	2.22	1.86
80	3.14	2.67	2.93	1.95	3.08	2.76
90	3.23	2.88	3.20	2.18	3.76	3.35
100	3.26	2.98	3.56	2.43	4.66	3.93
120	3.29	3.07	3.91	2.72	5.86	4.64
140	3.25	3.02	3.89	2.83	6.52	5.01
160	3.19	3.02	4.03	2.93	7.06	5.02
200	3.09	2.85	3.79	2.87	7.36	4.97
250	2.92	2.72	3.58	2.70	6.89	4.49
300	2.74	2.53	3.23	2.50	6.44	4.41
400	2.47	2.20	2.59	2.08	5.31	3.52
500	2.22	1.97	2.20	1.80	4.50	2.91
600	2.03	1.75	1.94	1.55	3.80	2.69
800	1.72	1.46	1.52	1.26	2.89	2.10
1000	1.51	1.24	1.24	1.04	2.47	1.57

F^+ ions may occasionally be formed in the same collision. Based on their work, the F^+ cross section measured here has therefore been increased by up to 6%.

The cross sections for ion pair production were determined by taking advantage of the fact that the counting electronics used can only process one event at a time. Thus, if a light ion Y and a heavier ion X are formed in the same collision and the timing electronics is limited to recording only the first ion detected, then the apparent cross section for production of the heavier ion X, $\sigma_{app}(X)$, is given by

$$\sigma_{app}(X) = \sigma(X) - \varepsilon\sigma(X, Y) \qquad (2)$$

where $\sigma(X)$ is the true cross section for production of X ions, $\sigma(X, Y)$ is the cross section for production of both an X and a Y ion in the same event, and ε is the detection efficiency of the system. By measuring both the true and the apparent cross sections for production of ($CF^+ + CF_3^{2+}$) and CF_2^+ ions and then applying equation (2) it is therefore possible to determine the cross sections for production of (CF^+, F^+) and (CF_2^+, F^+) ion pairs. It should be noted that this analysis assumes relatively few ionization events result in the formation of three positive ions, which is almost certainly warranted within the accuracy of the reported measurements; and that the presence of CF_3^{2+} ions has no effect on the analysis as they appear on both sides of equation (2).

A detailed analysis of the experimental uncertainties has been given previously (Straub *et al* 1995, 1996). However, in the light of experience gained with this apparatus over a number

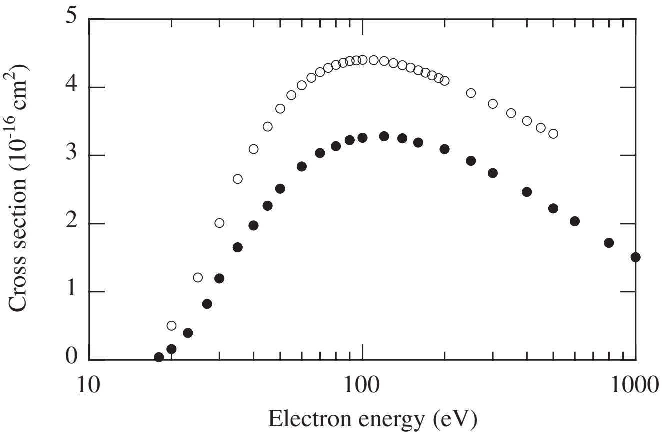

Figure 4. CF_3^+ cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

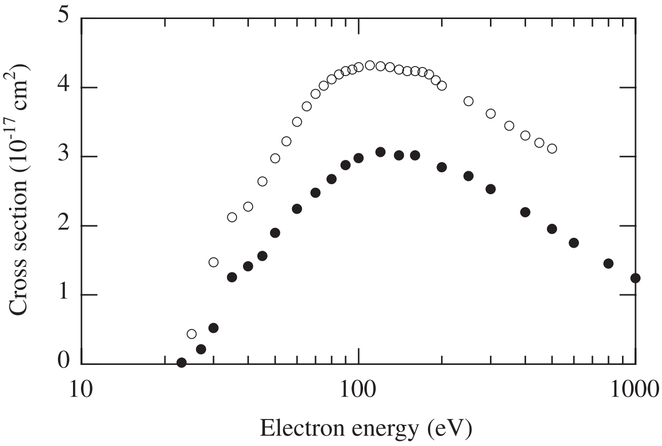

Figure 5. CF_2^+ cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

of years the uncertainty in the absolute cross section for ions, such as CF_3^+ (where the counting statistics are ±1% or better), is now considered to be ±5%. The uncertainties in the CF_2^+, ($CF^+ + CF_3^{2+}$) and C^+ cross sections are also ±5%, and that in the CF_2^{2+} cross section is ±7%. The uncertainty in the F^+ cross section, ±8%, is somewhat greater than that for the other major partial cross sections because of the above-described experimental difficulties related to ion pair production. The uncertainties in the (CF^+, F^+) and (CF_2^+, F^+) ion pair production cross sections are due primarily to counting statistics and are ±20% and ±30% respectively. The mean energy of the electron beam was established to within ±0.5 eV by observing the threshold for He^+ formation.

3. Results and discussion

The present cross sections for production of CF_3^+, CF_2^+, ($CF^+ + CF_3^{2+}$), C^+, F^+ and CF_2^{2+} are given in table 1 and are shown in figures 4–9 together with the data of Bruce and Bonham (1993) which have been multiplied by 1.18 as indicated in Bruce *et al* (1994). It should be noted

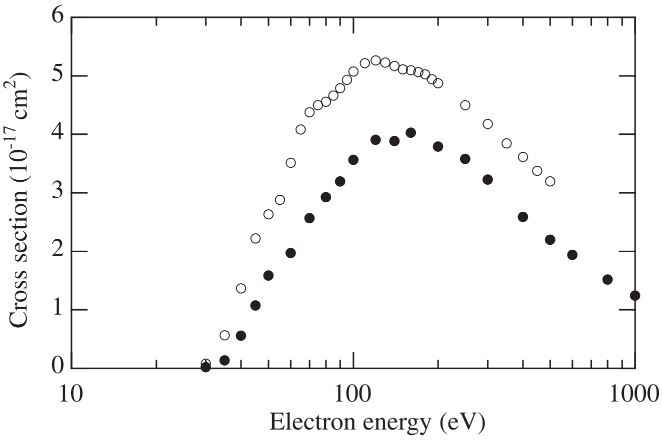

Figure 6. ($CF^+ + CF_3^{2+}$) cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

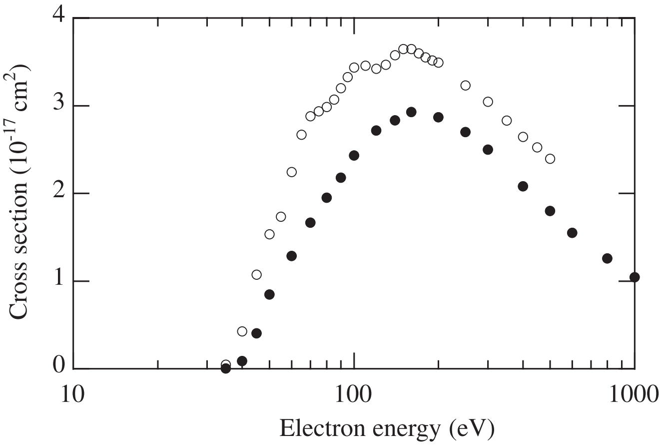

Figure 7. C^+ cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

that the cross sections shown are for production of the specified fragment ion, irrespective of whether another ion is produced in the same event. The uncertainty in the original data of Bonham and co-workers is given as ±15%; the uncertainty in their revised data is probably somewhat larger due to the additional uncertainties involved in the various corrections applied. In every case, except for the F^+ cross section (figure 8), the partial cross sections reported by Bruce and Bonham (1993) are larger than the present data. The apparent agreement in the case of F^+, however, is somewhat misleading, as the F^+ cross section of Bruce and Bonham (1993) is only reported as a lower bound to the true F^+ cross section (Ma *et al* 1992). Interestingly, the cross sections originally reported by Ma *et al* (1991) are in much better agreement with the present measurements than their revised values.

The present CF_4 total electron-impact ionization cross section is shown in figure 10 together with the absolute cross section of Bruce and Bonham (1993) and that of Nishimura *et al* (1999), whose uncertainties are ±15% and ±6% respectively. It should be noted that the data of Nishimura *et al* (1999) are for total charge production whereas the present data and

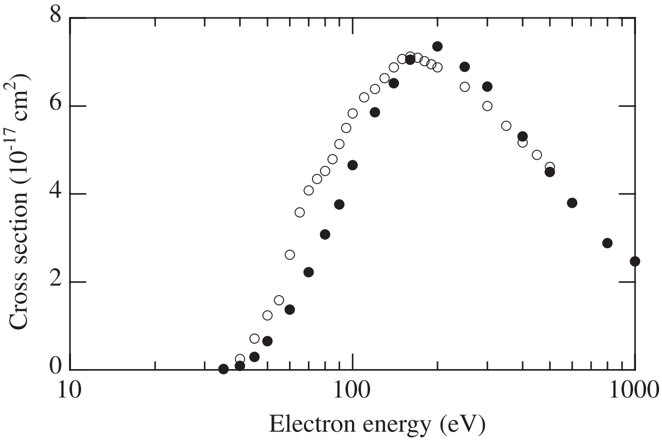

Figure 8. F^+ cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

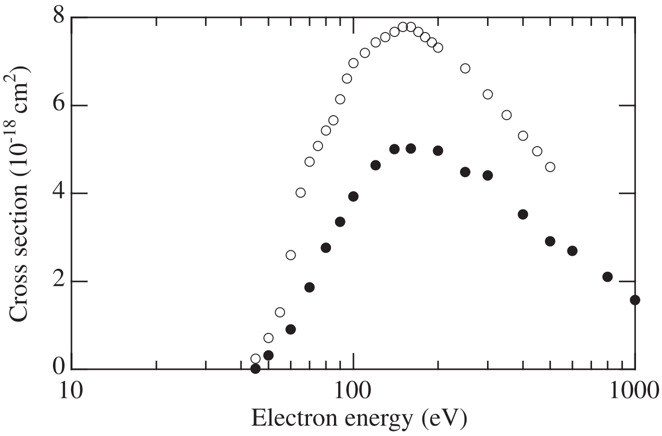

Figure 9. CF_2^{2+} cross section: present results (●); revised data of Bruce and Bonham (1993) (○).

those of Bruce and Bonham (1993) are the sums of the partial cross sections. These data are nonetheless directly comparable because of the very small number of multiply charged ions observed. The present total cross section is in excellent agreement with the measurements of Nishimura *et al* (1999), and also with the normalized data of Rao and Srivastava (1997) (not shown). The data of Bruce and Bonham (1993), however, lie considerably higher than the present measurements.

Figure 10 also shows the recent calculations of Nishimura *et al* (1999), and Deutsch *et al* (2000). The total electron-impact ionization cross section of Nishimura *et al* (1999), obtained by use of the binary-encounter-Bethe model (BEB) and using molecular wavefunctions based on the restricted Hartree–Fock (RHF) method, is in very good agreement with the present measurements. It should, however, be noted that BEB calculations using a different set of molecular wavefunctions are not in as good an agreement (Nishimura *et al* 1999). The calculations of Deutsch *et al* (2000) obtained using the semiclassical Deutsch–Märk (DM) formalism are also in reasonably good agreement with the present work.

The cross sections for production of (CF^+, F^+) and (CF_2^+, F^+) ion pairs are shown in

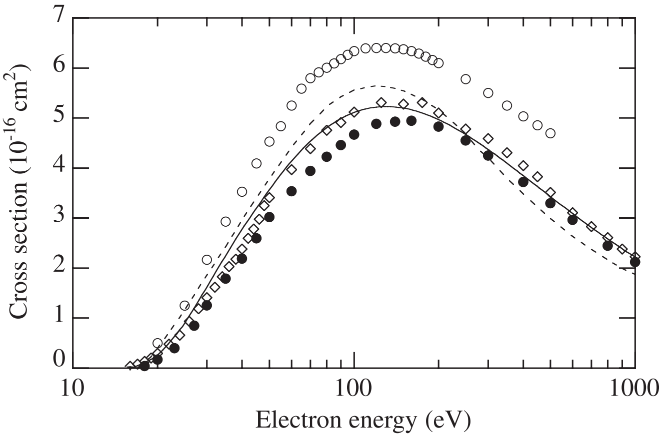

Figure 10. Total cross section: present results (●); Nishimura *et al* (1999) (◇); revised data of Bruce and Bonham (1993) (○); BEB-RHF theory from Nishimura *et al* (1999) (——); DM theory from Deutsch *et al* (2000) (- - - -).

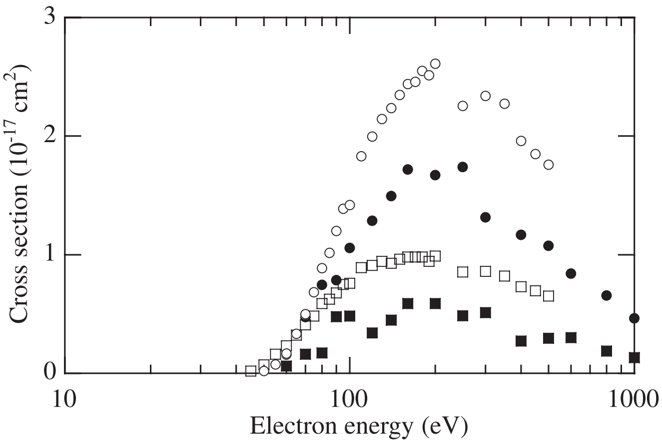

Figure 11. Cross section for production of (CF^+, F^+) ion pairs: present results (●); Bruce *et al* (1994) (○), and for production of (CF_2^+, F^+) ion pairs: present results (■); Bruce *et al* (1994) (□).

figure 11 together with the data of Bruce *et al* (1994) which have an uncertainty of ±20%. Note that the data points at 100, 200, 300, 400, and 500 eV are taken directly from Bruce *et al* (1994); data at other energies are from Bruce *et al* (1992) but have been renormalized to the more recent work of Bruce *et al* (1994). The values reported by Bruce *et al* (1994) are clearly much higher that the present (CF^+, F^+) and (CF_2^+, F^+) pair production cross sections. This is, however, consistent with the fact that Bruce *et al* (1994) normalized their data to the CF_3^+ cross section of Bruce and Bonham (1993), which is higher than the present cross section. When the data of Bruce *et al* (1994) are renormalized to the present CF_3^+ cross section they agree with the present pair production cross sections.

Table 2. Present absolute cross sections for production of (CF^+, F^+) and (CF_2^+, F^+) ion pairs by electron-impact ionization of CF_4. The uncertainties in $\sigma(CF^+, F^+)$ and $\sigma(CF_2^+, F^+)$ are ±20% and ±30% respectively.

Energy (eV)	$\sigma(CF^+, F^+)$ (10^{-17} cm^2)	$\sigma(CF_2^+, F^+)$ (10^{-17} cm^2)
60	0.16	0.061
70	0.47	0.16
80	0.75	0.17
90	0.79	0.48
100	1.06	0.48
120	1.29	0.34
140	1.50	0.45
160	1.72	0.59
200	1.67	0.59
250	1.74	0.49
300	1.32	0.51
400	1.17	0.27
500	1.08	0.30
600	0.84	0.30
800	0.66	0.19
1000	0.46	0.13

4. Conclusion

Absolute partial cross sections for the production of CF_3^+, CF_2^+, ($CF^+ + CF_3^{2+}$), C^+, F^+ and CF_2^{2+} from electron-impact ionization of CF_4 are reported for energies from threshold to 1000 eV. Data are also presented for the formation of (CF^+, F^+) and (CF_2^+, F^+) ion pairs. The apparatus geometry is of simple design, embodying a short-pathlength time-of-flight mass spectrometer and position-sensitive detection of the product ions, which unequivocally demonstrates that all fragment ion species are collected with equal efficiency irrespective of their initial kinetic energy. The previously published partial cross section data (Bruce and Bonham 1993) are generally higher than those reported here. The present total cross section is, however, in excellent agreement with the most precise previous measurement (Nishimura *et al* 1999). Agreement with the most recent theoretical calculations is quite good. Previous measurements of the (CF^+, F^+) and (CF_2^+, F^+) positive ion pair production cross sections by Bruce *et al* (1994) are higher than the present values. However, the data of Bruce *et al* (1994) agree with the present measurements when renormalized to the present CF_3^+ cross section.

Acknowledgments

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