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Electron impact ionization of CHF₃

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Abstract

Electron impact production of ions from CHF₃ has been studied by a crossed electron beam–molecular beam geometry under single collision conditions for electron incident energies ranging from threshold of ionization to 1000 eV. Ions of CF₃⁺, CHF₂⁺, CF₂⁺, CHF⁺, CF⁺, F⁺, CH⁺, and C⁺ are observed. Cross sections for their production have been measured by utilising the relative flow technique. At each impact energy, the cross sections for the production of individual ions have been summed up in order to yield total cross sections for the generation of all ions. These total cross sections are in good agreement with recent theoretical results of Kim [Proceedings of the 20th International Conference on the Physics of Electronic and Atomic Collisions, Vienna, Austria, July 1997, Vol. I, p. WE103] and experimental results of Jiao et al. [Chem. Phys. Lett. 269 (1997) 117] in the energy range where the comparison is made. However, there is a considerable disagreement between present results and previously published data and the recommended values of NIST. In addition, appearance energies for each ion have been measured and compared with previously published values. (Int J Mass Spectrom 208 (2001) 159–167) © 2001 Elsevier Science B.V.

1. Introduction

CHF₃, an atmospherically benign gas, is used by the semiconductor industry for plasma etching and cleaning of semi conductors. The plasmas employed for this purpose are termed as “low temperature plasmas” and operate under the conditions of non-local thermal equilibrium (non-LTE). In order to model these non-LTE plasmas for optimum performance of the reactors, an accurate knowledge of electron impact collision cross sections is needed. In particular, electron impact ionization cross sections, which determine the ionization balance of the plasma,

are the most important. Excellent review articles were recently published by Christophorou et al. [1] and Christophorou and Olthoff [2] which provide a survey of all data that are available on CHF₃.

Despite the important role played by CHF₃ in various areas of application, only limited measurements [3–6] of cross sections for the ionization of CHF₃ have been reported during the past 15 years. The differences between the previously measured values are large. Also the maximum electron impact energy in these measurements was restricted to 125 eV.

With these facts in mind, we undertook the measurement of the electron impact ionization cross sections for CHF₃. In the present work, we report the absolute values of partial ionization cross sections for the formation of fragments CF₃⁺, CHF₂⁺ + CF₂⁺, CHF⁺ + CF⁺, F⁺, and CH⁺ + C⁺ for electron–

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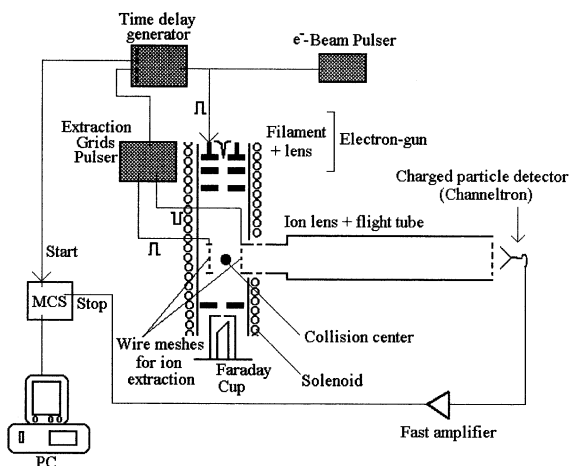


Fig. 1. Schematic diagram of the time-of-flight mass spectrometer (TOFMS).

CHF_3 interaction, as well as total ionization cross sections at impact energies ranging from threshold of ionization to 1000 eV. As will be made clear in Sec. 3, our data agree with a recent theoretical calculation of Kim et al. [7], which has been proven to predict accurate values of cross sections for a large number of molecules.

2. Experimental apparatus and measurement procedures

The experimental apparatus and the method used for the present measurements are similar as used in our previous studies [8]. However, in the present study, both a quadrupole mass spectrometer (QMS) and a time-of-flight mass spectrometer (TOFMS) [9,10] were used for mass/charge selection. Specifically, the QMS at Jet Propulsion Laboratory was used for obtaining the relative values of ionization cross sections from near thresholds to 200 eV whereas the TOFMS at the Universidade Federal de São Carlos (UFSCar) was used for the determination of these cross sections in the 150–1000 eV impact energy range. Fig. 1 shows a scheme of the experimental arrangement of UFSCar. The molecular beam was prepared by flowing the CHF_3 gas through a capillary array. This gas beam was crossed at 90° by a

magnetically collimated and energy selected beam of electrons generated by an electron gun of special design [11]. This electron gun possesses two properties: it produces very short pulses of electrons (pulse width ~ 100 ns) and the beam current is constant in the entire energy range (~ 0 –1000 eV). The first property is important for the operation of TOFMS and pulsed extraction of ions from the ion source and the second property is used to obtain accurate relative values of cross sections. In the pulsed mode and for a repetition rate of 5 kHz this gun provides currents typically in the 10^{-9} A range. The electron impact energy was calibrated by measuring appearance potentials of rare gases [12]. We have time and again verified in the past by utilizing the threshold energy data of rare gas atoms that the energy resolution of the electron beam is about 500 meV.

The overlap of the electron and the molecular beams forms a collision region which is approximately of the size of a cube of $1.5 \text{ mm} \times 1.5 \text{ mm} \times 1.5 \text{ mm}$. This collision region is the source of various ions of present interest. A pair of wire meshes is symmetrically placed on the sides of the collision region, separated by a distance of 6 mm, in such a way that the axis (perpendicular to the surfaces of the parallel wire meshes) is at 90° to both the electron and the molecular beam axes. Since the fragment ions can be created with appreciable kinetic energies [13] it is essential to extract them out of the collision region with a high extraction field, which is generated by applying high voltages to the wire meshes (Fig. 1). If the voltages are applied in a dc mode then they interfere with the electron beam and deflect it from its straight path. Therefore, a pulsed extraction method was devised in the past by Krishnakumar and Srivastava [8]. This method uses a pulsed electron beam. During the passage of this pulse of electrons through the collision region the voltage on the pair of grids is kept at 0 V. However, as soon as the electron pulse passes through the collision region within 100 ns a voltage of about 200 V is applied to the grids (+200 V on the repeller side and -200 V on the side facing TOFMS) by a fast pulse generator. This extraction field ensures a complete collection of ions with initial energies up to 20 eV [9].

The flight time of each ion varies according to its mass to charge ratio. This ion is detected by a charged particle detector, which is a “channeltron,” for the present measurements and is placed at the exit end of the flight path. The output pulse of the channeltron is directed to a fast amplifier. In order to record the time-of-flight (TOF) spectrum, output pulses from the amplifier are subsequently fed to the discriminator input of a multichannel scaler (EG&G Turbo-MCS). The start of this device is connected to the pulse generator employed for pulsing the electron gun. TOF mass spectra were recorded with temporal resolution of 5 ns per channel. Many spectra were obtained for e^- -CHF₃ interaction at electron energy of 200 eV to provide reproducible values of intensity ratios (commonly known as “cracking patterns”) of the following fragment ions: CF₃⁺, (CHF⁺ + CF⁺), F⁺, and (CH⁺ + C⁺) with respect to the intensity of (CHF₂⁺ + CF₂⁺) ions. Because, in general, the transmission efficiency of the mass spectrometers depends on mass to charge ratios, we calibrated our mass spectrometer system (including ion source, TOF tube and the charged particle detector) by utilising various rare gases and other gases for which the ionization cross sections are accurately known. It was found that the transmission efficiency of ions in our system was practically independent of mass to charge ratios of ions. In addition, the intensities of each fragment ion, or group of two adjacent ions (i.e. with masses differing by 1 u), seen in the TOF spectrum, were independently recorded in the multichannel scaler (MCS), as a function of the electron beam energy varying from threshold of ionization to 1000 eV.

The fast MCS is useful in acquiring the mass spectrum and for measuring accurate values of the ratios of intensities of various spectral features. However, in order to measure the variation of intensity of a particular ion such as CF₃⁺ as a function of electron impact energy we need to isolate this spectral feature from others. In the present form the fast MCS used in this experiment for acquiring TOF spectra does not have this capability. Therefore, we followed a method that we have used in the past [14]. More details on this method can be found in [14]. Here we will describe it briefly. It uses a time-to-pulse height converter

(TPHC). For TPHC the start pulse is the same one that pulses the electron gun. The ion of interest travels through the TOFMS and after a time ΔT later it arrives at the channeltron. The output of the channeltron is fed to the “stop” of the TPHC. The TPHC gives rise to a rectangular pulse whose amplitude is directly proportional to ΔT . The selected output pulses, corresponding to a specific mass to charge ratio, from TPHC are fed to the MCS. The intensity of that particular ion is recorded as a function of the electron beam energy by the MCS. The curve representing the variation of ion intensity as a function of electron beam energy is called “ionization efficiency curve” [15]. Since the intensity of a particular ion is directly proportional to the cross section for its formation by ionization or dissociative ionization of the parent molecule, the ionization efficiency curve also represents the variation of cross sections for the formation of that particular ion as a function of electron beam energy and, therefore, the curve provides relative values of cross sections. In order to convert these relative values into absolute values of cross sections we employed the relative flow technique [16], the most recent version of which is described by Krishnakumar and Srivastava [8] and/or by Srivastava [15]. Briefly, under the identical conditions, the method measures the intensities, I_x , of an ion x of the sample gas (S) under study and I_{std} of an ion of known cross sections which is used as a secondary standard (std) [17]. The partial ionization cross section σ_x can be related with known cross sections (σ_{std}), as

$$\sigma_x(E) = \sigma_{std}(E) \frac{I_x(E)}{I_{std}(E)} \frac{q_{std}}{q_s} \left(\frac{M_{std}}{M_s} \right)^{1/2} \quad (1)$$

where, I represents intensity of each ion, q the flow rate of individual gases, and M the molecular weight of each gas. Eq. (1) is valid if the beam profiles (density and velocity distribution) of both gases, S and std, are closely the same. The conditions for the validity of Eq. (1) are met when the gases are flowed through a capillary array with effusive flow conditions. According to Olander and Kruger [18], this requirement is fulfilled under two conditions: the

equal mean free paths (λ) of the gases behind the capillaries and the Knudsen number K_L defined as λ/L varying between $\gamma \leq K_L \leq 10$, where γ is the aspect ratio of capillaries ($\gamma = 0.01$ in present work). In the present measurements the absolute partial ionization cross section of Krishnakumar and Srivastava [8] for Ar^+ at 200 eV electron impact energy was used for σ_{std} . The collisional diameters of Ar and CHF_3 are 2.95 [19] and 3.70 Å, respectively. The latter was calculated using the van der Waals' constants published in the Handbook of Chemistry and Physics [12]. Thus the theoretical pressure ratio for equal Knudsen numbers will be 1.6:1. We used pressures of 0.50 Torr for Ar and 0.32 Torr for CHF_3 . This corresponds to the mean free path of 160 μm and $K_L = 0.03$ for both gases.

Flow rates for each gas were determined by measuring the pressure variation of the trapped gas in the space behind the capillary array versus time after the input of gases is closed. Simple exponential decay curves are used to fit this pressure variation. More details on the method of measuring small flow rates are given in several papers [17,20].

The normalization of cross sections by using the relative flow technique was applied to generate the absolute partial ionization cross section values for the production of $(\text{CHF}_2^+ + \text{CF}_2^+)$ ion since it is the most intense peak in the TOF spectra of CHF_3 . The values of absolute cross sections for CF_3^+ , $\text{CHF}^+ + \text{CF}^+$, F^+ , and $\text{CH}^+ + \text{C}^+$ were obtained from their intensity ratios with respect to the intensity of $(\text{CHF}_2^+ + \text{CF}_2^+)$.

The estimate of experimental uncertainties contributing to various steps of the measurements is described as follows. The uncertainties in the relative cross sections of each fragment ion originate mainly from the fluctuations of the intensity ratios relative to the most intense peak corresponding to the $(\text{CHF}_2^+ + \text{CF}_2^+)$ ions. In this work, at least six independent measurements of ratios were taken and the data fluctuations were calculated from them. The fluctuations of electron current and pressure in the vacuum chamber do not contribute to the error in the relative measurement of intensities since all the ions are measured at the same time. The resulting relative

uncertainties in the intensity ratios for the ions CF_3^+ , $\text{CHF}^+ + \text{CF}^+$, F^+ , and $\text{CH}^+ + \text{C}^+$ are 10%, 10%, 17%, and 10%, respectively. The larger error for the F^+ is due to the de-convolution procedure that was followed and will be described in Sec. 3. In determining the absolute cross sections, an additional error of 5% in the shape of the ionization efficiency curve [8] combined with the error of the flow rate measurements, estimated to be less than 2%, and the uncertainty of the cross sections of the reference gas (10%) are also considered. The resulting relative errors in the absolute partial ionization cross sections are, therefore, 13% for $(\text{CHF}_2^+ + \text{CF}_2^+)$ ions, 21% for F^+ and 16% for all other ions. The total ionization cross sections ($\sigma_{i,T}$) are obtained by summing up the cross sections of individual ions. Moreover, the relative standard uncertainty of $\sigma_{i,T}$ calculated according to the error-propagation formulae [21],

$$\frac{\Delta\sigma_{i,T}}{\sigma_{i,T}} = \frac{\sqrt{\sum_j (\Delta\sigma_j)^2}}{\sigma_{i,T}} \quad (2)$$

i,T is approximately 9% at impact energies covered in this work. In Eq. (2), $\Delta\sigma_j$ is the standard deviation of partial ionization cross section for a given ion j .

3. Results

The mass spectrum of CHF_3 at 200 eV electron impact energy is shown in Fig. 2. The ground state of the CHF_3^+ ion is unstable [22]. Therefore, it is absent in this spectrum. The most prominent mass peak is CHF_2^+ . However, on its shoulder toward the lower mass side there is a weak feature which we attribute to the presence of CF_2^+ . In the high mass range our TOF mass spectrometer has poor resolution and, therefore, we cannot resolve this feature from that corresponding to CHF_2^+ . However, we plotted this feature on an expanded scale. It is shown in Fig. 3. We then fitted the profiles of the two spectral features (i.e. CF_2^+ and CHF_2^+) by utilizing the fitting program contained in the software package ORIGIN 3.0 [23]. For the purpose of fitting we assumed a Gaussian profile for these

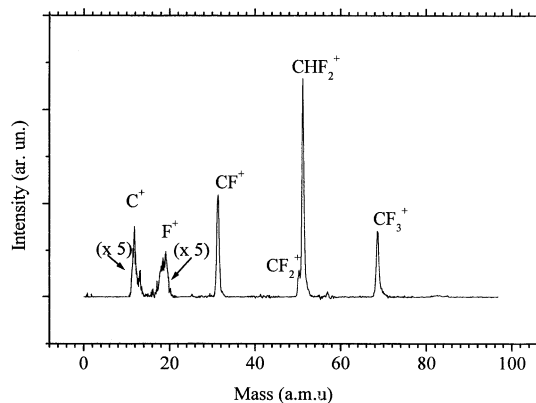


Fig. 2. Time-of-flight mass spectrum for ionization of CHF_3 by electron impact at 200 eV. The background contributions have been subtracted.

spectral features. A typical result for the deconvoluted features is shown in Fig. 3. From this procedure we obtained a ratio of 0.107 ± 0.013 at 200 eV electron impact energy for the intensities of $\text{CF}_2^+/\text{CHF}_2^+$. Although the intensity of any spectral feature is directly proportional to the ionization cross section (σ), the above ratio represents the factor ratio of two cross sections, i.e. $\sigma(\text{CF}_2^+)/\sigma(\text{CHF}_2^+)$ at 200 eV. Ion peaks corresponding to C^+ and CH^+ also could not be resolved from each other. Therefore, we followed the above procedure to obtain the ratio of cross sections for CH^+ and C^+ . This ratio at 200 eV is

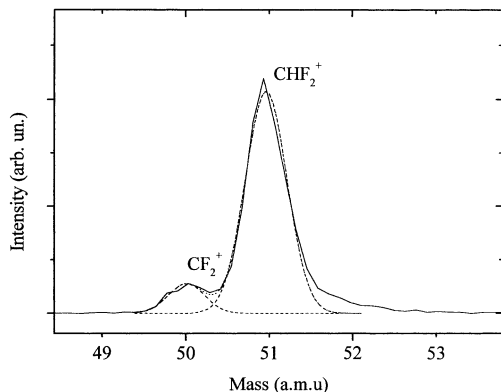


Fig. 3. Deconvolution of experimental intensity of the ions (CF_2^+ and CHF_2^+). Solid line, experimental intensity of the ions; dotted line, the fitted intensity of the ions; dashed line, individual contribution of the ions fitted by Gaussian profiles.

0.311 ± 0.037 . Also, the width of the Gaussian profile associated with the C^+ ion is significantly broader than the corresponding profiles of CF_2^+ and CHF_2^+ , etc, indicating that energetic C^+ ions are formed. Ion peaks corresponding to CF^+ and CHF^+ were also unresolved. They were also deconvoluted and the ratio, $\sigma(\text{CHF}^+)/\sigma(\text{CF}^+)$, was found to be 0.074 ± 0.015 at 200 eV electron impact energy.

Table 1 presents our partial and total ionization cross section data for electron impact energies ranging from thresholds to 1000 eV. Figs. 4–8 compare our data with previously published measurements. In the following we will discuss each data separately.

In Fig. 4 our combined cross section data for the fragments CF_2^+ and CHF_2^+ are presented. Since the intensity of CF_2^+ is small in comparison of the intensity of CHF_2^+ our data, as shown in this figure, basically correspond to cross sections for the production of CHF_2^+ . As is clear from Fig. 4, the previous two measurements [3,4] which were confined to an electron impact energy range of 0–125 eV, are very different from each other (about a factor of ~ 4). The present measurements lie approximately in midway. However, the energies for the maximum ion yield are very similar. Results of a recent measurement by Jiao et al. [5] are also presented in this Fig. 4. Their results, confined to 60 eV maximum, are in good agreement with our values. Fig. 5 presents cross section data for the production of $\text{CF}^+ + \text{CHF}^+$. Again, the differences between the results of the previous two measurements [3,4] and our data are too large and are irreconcilable. However, the most recent data of Jiao et al. is in better agreement with the present results.

Fig. 6 presents our data along with previous three measurements [3–5] for the production of CF_3^+ . As noted before, the differences between the present results and the data of Poll and Meischner [3] and Goto et al. [4] are irreconcilable. According to our measurements, the maximum of the ionization cross sections for the production of CF_3^+ is located at around 60 eV. Our cross sections are in good agreement with those reported by Jiao et al. [5] up to 50 eV but are much lower at higher energies.

Cross-section data for the production of F^+ are plotted in Fig. 7 along with the only previously

Table 1

Absolute total and partial ionization cross sections in 10^{-20} m^2 for CHF_3 as a function of electron energy in eV

Electron energy (eV)	$\sigma_{i,T}$	$\sigma_{i,\text{part.}}^+(\text{CF}_3^+)$	$\sigma_{i,\text{part.}}^+(\text{CHF}_2^+ + \text{CF}_2^+)$	$\sigma_{i,\text{part.}}^+(\text{CF}^+ + \text{CHF}^+)$	$\sigma_{i,\text{part.}}^+(\text{F}^+)$	$\sigma_{i,\text{part.}}^+(\text{C}^+ + \text{CH}^+)$
20	0.452	0.152	0.239	0.061		
30	1.99	0.435	1.16	0.397		
40	2.88	0.616	1.57	0.621	0.029	0.048
50	3.52	0.702	1.86	0.779	0.078	0.101
60	3.89	0.726	2.03	0.876	0.119	0.141
70	4.08	0.732	2.11	0.916	0.152	0.168
80	4.20	0.731	2.15	0.947	0.179	0.192
90	4.26	0.730	2.16	0.962	0.201	0.208
100	4.28	0.725	2.15	0.967	0.218	0.218
110	4.29	0.725	2.15	0.967	0.231	0.219
120	4.29	0.717	2.15	0.967	0.239	0.219
130	4.28	0.711	2.14	0.962	0.245	0.220
140	4.27	0.709	2.13	0.962	0.248	0.219
150	4.24	0.707	2.11	0.951	0.249	0.220
160	4.22	0.703	2.10	0.945	0.250	0.219
170	4.19	0.701	2.09	0.935	0.250	0.218
180	4.16	0.693	2.07	0.928	0.249	0.216
190	4.10	0.682	2.05	0.914	0.245	0.213
200	4.07	0.679	2.03	0.906	0.241	0.211
250	3.79	0.640	1.89	0.843	0.223	0.190
300	3.53	0.603	1.76	0.792	0.201	0.171
350	3.30	0.578	1.68	0.711	0.185	0.151
400	3.14	0.548	1.58	0.707	0.171	0.137
450	2.98	0.259	1.50	0.667	0.157	0.125
500	2.83	0.508	1.43	0.625	0.147	0.116
550	2.66	0.486	1.35	0.585	0.135	0.106
600	2.55	0.474	1.30	0.554	0.127	0.097
650	2.46	0.455	1.26	0.532	0.118	0.090
700	2.35	0.437	1.21	0.511	0.111	0.085
750	2.27	0.418	1.18	0.498	0.102	0.080
800	2.18	0.394	1.14	0.476	0.099	0.075
850	2.11	0.375	1.11	0.460	0.092	0.072
900	2.03	0.357	1.07	0.445	0.089	0.068
950	1.96	0.338	1.04	0.428	0.085	0.067
1000	1.92	0.326	1.03	0.414	0.083	0.065

published result of Goto et al. [4]. Because the mass of fluorine ion is 19 it is very close to the mass of water, which is always present in the vacuum chamber in spite of the fact that background pressures in the range of 10^{-8} Torr are achieved. Therefore by assuming the Gaussian line profiles we fitted the spectral profiles of H_2O^+ and F^+ following the procedure described above for the deconvolution of line profiles of CHF_2^+ and CF_2^+ . In addition, the width of deconvoluted profiles indicates that the F^+ ions are also energetic.

Cross section data for the production of C^+ and CH^+ are shown in Fig. 8. The only other data found (Goto et al. [4]) are also shown. Again the differences are great.

4. Discussion

In view of the fact that our results for partial ionization cross sections are very different from the two previous measurements [3,4], we need to examine

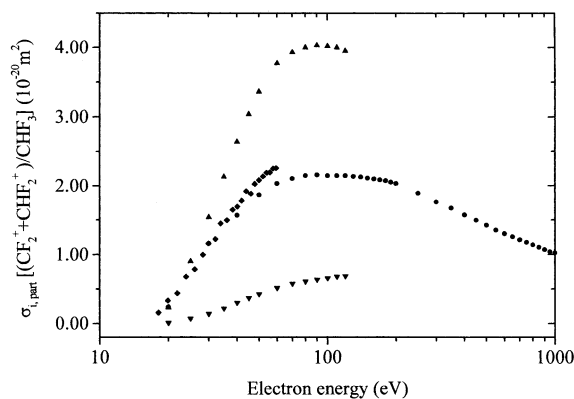


Fig. 4. Partial ionization cross sections, $\sigma_{i,\text{part}}(E)$ for $(\text{CF}_2^+ + \text{CHF}_2^+)$ produced by electron-impact ionization of CHF_3 in the 0–1000 eV energy range: circles, present experimental results, upright triangles the measured results of Poll and Meischner [3]; inverted triangles, the experimental results of Goto et al. [4], diamonds, experimental results of Jiao et al. [5].

them critically and explain why we believe that our results are more accurate than theirs. We will compare these results in a chronological order.

First results on the partial ionization cross sections were published in 1987 by Poll and Meischner [3]. The experimental procedure is very poorly described in their paper. No care has been taken to explain the possible sources of error. The article presents results on nine fluorinated compounds. CHF_3 is one of them. Their results for CHF_2^+ are about a factor of 2 higher than ours and are presented only for an electron impact energy range of 0–125 eV. At low energies the

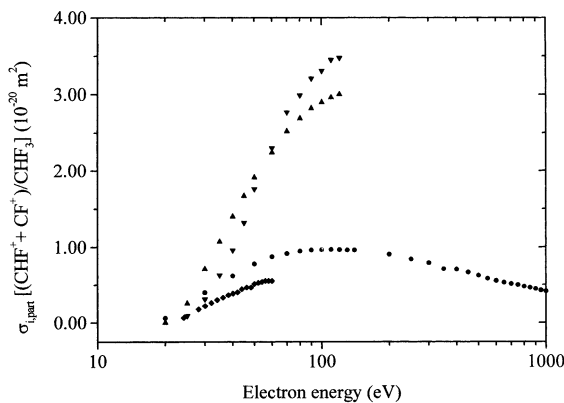


Fig. 5. Same as Fig. 4 but for $(\text{CF}^+ + \text{CHF}^+)$.

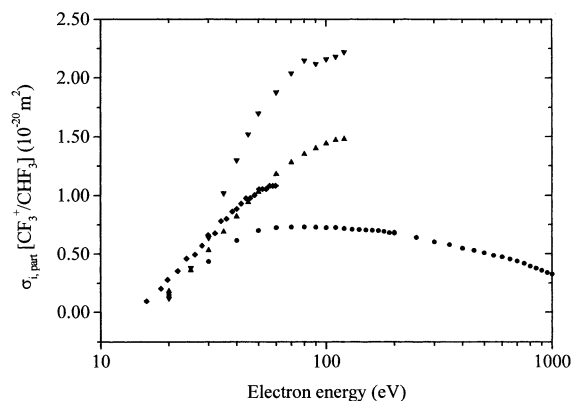


Fig. 6. Same as Fig. 4 but for (CF_3^+) .

values of cross sections vary rapidly with energy. Therefore, an accurate calibration of energy is crucial. Poll and Meischner did not explain how their electron beam energy was calibrated. The visual agreement (Fig. 4) at low electron impact energies of their results with ours is good but differences increase with increasing incident energies. Similar is our criticism of their data for $\text{CF}^+ + \text{CHF}^+$ and CF_3^+ .

Subsequently, partial cross sections for the production of various ions were published by Goto et al. [4]. The apparatus used by them for the measurement of cross sections was primarily designed to measure cross sections for the production of neutral fragments by electron impact on CHF_3 . However, using the same experimental arrangement partial ionization cross sections were also measured. The experimental

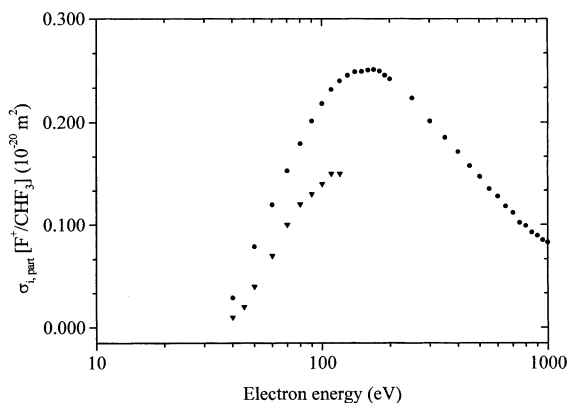


Fig. 7. Same as Fig. 4 but for (F^+) .

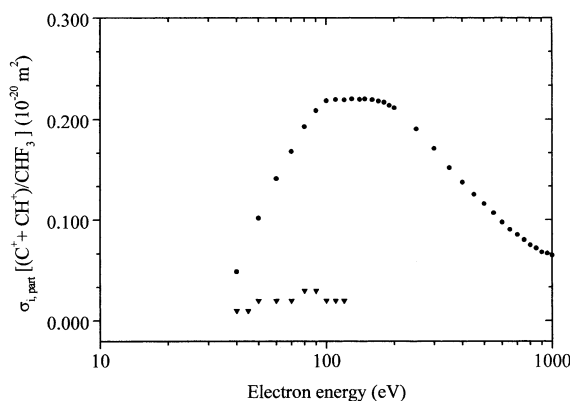


Fig. 8. Same as Fig. 4 but for $(\text{C}^+ + \text{CH}^+)$.

arrangement was basically a “static gas collision geometry” where three collision chambers were filled by the gas under investigation. Their measured intensity ratios for various ionic species are very different from all others and their data of partial ionization cross sections also disagree strongly with others [3,5]. Nevertheless, it is very difficult to speculate the origin leading to such disagreement. The experimental procedure was very briefly described in their paper. Goto et al. stated that the QMS sensitivity for ions with different masses was overcome by comparing the production of ionic fragments generated by electron impact on CHF_3 with that of the same ions produced from CF_4 and CH_4 with known cross sections. However, it is expected that the same ionic fragments generated from different gases via electron impact processes may have different kinetic energies. No discussion on the kinetic energy dependence for ion detection in their experimental apparatus was provided in their publication. The loss of energetic ions could be one of the sources of errors in their experiments.

Most recent data published by Jiao et al. [5] measured cross sections for the production of CF_3^+ , CHF_2^+ , CF_2^+ , and CF^+ using a modified Fourier transform mass spectrometer (FTMS) in the 0–60 eV electron impact energy range. The agreement of their data with the present results is, in general, very good. In principle, the measured data of Jiao et al. should be more reliable than the two previously reported exper-

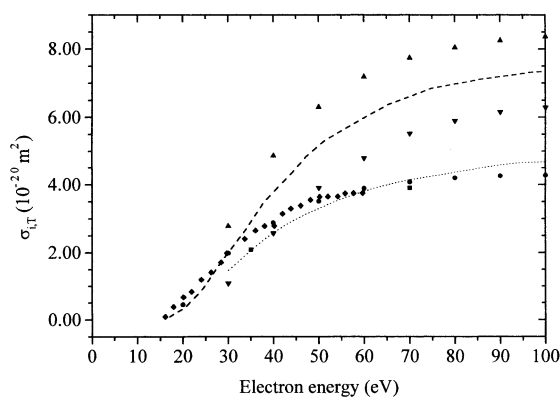


Fig. 9. Total cross sections, $\sigma_{i,T}(E)$ for electron-impact ionization of CHF_3 in the 0–1000 eV energy range. The symbols used are the same as Fig. 4 except, squares, experimental results of Beran and Kevan [6]; dotted line, calculated results of Kim et al. [7], dashed line, recommended data [1].

imental data [3,4], as stated by the authors [5], the sensitivity of FTMS is independent of ion mass and chemical composition in contrast to the quadrupole-based experiments of Poll and Meischner [3] and Goto et al. [4]. Moreover, due to the characteristics of the FTMS, no calibrations associated to ion optics, collection efficiency and multiplier gain are required. Thus, the good agreement with the results of Jiao et al. [5] reinforces our confidence on our data.

As described previously, total ionization cross sections can be obtained by summing up all partial ionization cross sections. These cross sections, derived from the present measurements, shown in Table 1, are also compared in Fig. 9 with the available experimental results [3–6] as well as with the calculated results of Kim et al. [7]. In order to better illustrate the comparison at lower energies, Fig. 10 presents total ionization cross sections in the 0 to 100 eV impact energy. From these figures it is clear that at low electron impact energies the various results agree very well with each other. However, at energies near the maximum of ion yield, the differences are very large and are irreconcilable. On the other hand, the recent calculations of Kim et al. [7] are in perfect agreement with our data. In 1999, Christophorou and Olthoff [2] published a survey on the following molecules: CF_4 , CHF_3 , C_2F_6 , and C_3F_8 . Their recom-

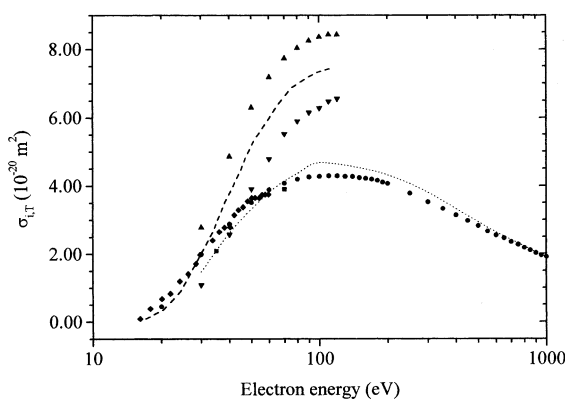


Fig. 10. Same as Fig. 9, but in the 0–100 eV range.

mended values for the total ionization cross sections are also shown in Fig. 9. These values were simply an average of the results of Poll and Meischner [3] and Goto et al. [4]. In our opinion these recommended values should be revised in view of the recent results of Jiao et al. and our new results.

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