

Ionization of C_3F_8 by electron and ion impact

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Abstract

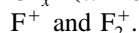
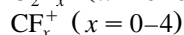
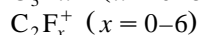
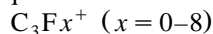
The dissociative ionization of perfluoropropane, C_3F_8 , by electron impact has been measured under single collision conditions using Fourier Transform Mass Spectrometry. The total ionization cross-section rises to a maximum value of $1.24 \pm 0.20 \times 10^{-15} \text{ cm}^2$ at 140 eV. CF_3^+ is the most prominent ion fragment at all energies, followed by $C_3F_7^+$, CF^+ , CF_2^+ , $C_2F_4^+$ and $C_2F_5^+$; $C_3F_8^+$ is not observed. The ratio of dissociative ionization to total dissociation increases from $25 \pm 8\%$ at 22 eV to no less than 70% from 70 to 200 eV. Among the ion fragments only $C_3F_7^+$ reacts at room temperature to produce $C_2F_5^+$. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Perfluoropropane, C_3F_8 , is used as a precursor for reactive ion etching of semiconductors, as a gaseous dielectric for insulation, and is a candidate for replacement of Halon fire suppressants. Earlier work on dissociative ionization of perfluoropropane includes magnetic sector measurements by Beran and Kevan [1] and quadrupole studies by Poll and Meischner [2]. A need for better quality C_3F_8 ionization cross-sections was recently noted in a review of its low energy electron transport characteristics by Christophorou and Olthoff [3].

The partitioning of fragments among plausible dissociation channels is of both practical and fundamental significance. Twenty-three of the 36 statisti-

cally possible fragment ions satisfy normal valence requirements:



Only six of these 23 ions are observed to form by low-energy electron impact:



Others among this list of 23 are observed to form by dissociative ionization from different precursors. For example, $C_3F_5^+$ and $C_3F_2^+$ are formed by dissociative ionization of perfluorocyclobutane, and are therefore thermodynamically stable species¹. The

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¹ See for example [4].

selection among fragment channels is a result of dynamical constraints on either the electronic states to which C_3F_8 is excited, or on the trajectory followed by nuclei during the fragmentation of the excited ion state.

While theoretical estimates of ionization by electron impact using ab initio molecular orbital theory and the Binary Encounter Bethe (BEB) model have provided insight into the total ionization cross-sections for some molecular species [5], there may be value in exploring whether these methods provide guidance on the number and relative importance of the partial ionization cross-sections as well. We will present a few observations and comments on this question for the case of C_3F_8 ionization below.

On a more practical note, the performance of plasma etch chemistries based on fluorocarbons generally – and C_3F_8 particularly – is constrained by ion kinetics. The partial ionization cross-sections can be integrated with the electron energy distribution of a gas discharge to evaluate the rates for production of each ion species. This initial ion species distribution may be modified by charge transfer collisions before or while the cations are extracted through a plasma sheath to the reactor boundaries. Combined with an understanding of the ion–molecule reaction rates for the plasma species, the partial ionization cross-sections permit estimates of the scaling of ion fluxes and composition with reactor pressure and gas mixture composition.

2. Experiment

Perfluoropropane C_3F_8 (Aldrich, 99%) is mixed with argon (99.999%, Matheson Research Grade) and admitted through a precision leak valve into a modified Fourier Transform Mass Spectrometry (FTMS) system that has been described in detail elsewhere [6,7]. Ions are formed by electron impact in a cubic ion cyclotron resonance (ICR) trap cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG-2, Wilton, NH) located 2 meters from the trap irradiates the gas with a short (2–6 ms) pulse of a few hundred picocoulombs of low-energy electrons. The motions of ions produced by electron impact are constrained radially by a

superconducting solenoidal magnetic field (≈ 2 T) and axially by a nominal electrostatic trapping potential (1–2 V) applied to the trap faces that are perpendicular to the magnetic field. Ions of all mass to charge ratios are simultaneously and coherently excited into cyclotron orbits using a stored voltage waveform [8]. The image currents induced on the two remaining trap faces are then digitized and Fourier analyzed to yield a mass spectrum.

Calculation of the cross-section from the mass spectral intensities requires knowledge of the gas pressure, the electron beam current, and the number of ions produced. It is particularly important that the measurements are made during a time that is short enough to preclude perturbation of the species' distribution by charge transfer reactions. These calibration issues have been discussed elsewhere [6,7]. In the measurements reported here we calibrate the cross-sections using ratios of the ion signals to those of Argon, whose cross-section is known to $\pm 12\%$ from the crossed beam measurements of Wetzel and Freund [9].

The distribution of electron energies in the ion trap, based on the solution of Laplace's equation for the experimental geometry, is roughly Gaussian with a full-width-at-half-maximum of 0.5 eV due to the electrostatic trapping bias. The mean energy is accurate to ± 0.2 eV based on comparison of noble gas ionization thresholds with spectroscopic data.

It is important to note that the ions are not actually collected in the FTMS experiment; only their electromagnetic influence on the antenna is recorded. As a result, the spectrometer sensitivity is *neither mass nor species dependent* for the results described here. We estimate the accuracy in the partitioning among ionic channels relative to argon to be $\pm 4\%$. Combined with the precision of the crossed beam measurements on argon, $\pm 12\%$ [9], we estimate the magnitude of the cross-sections presented here to be accurate within $\pm 16\%$.

3. Results and discussion

The partial ionization cross-sections are displayed in Fig. 1a. Cleavage of a C–C bond to produce CF_3^+ has the lowest threshold and the highest yield at all

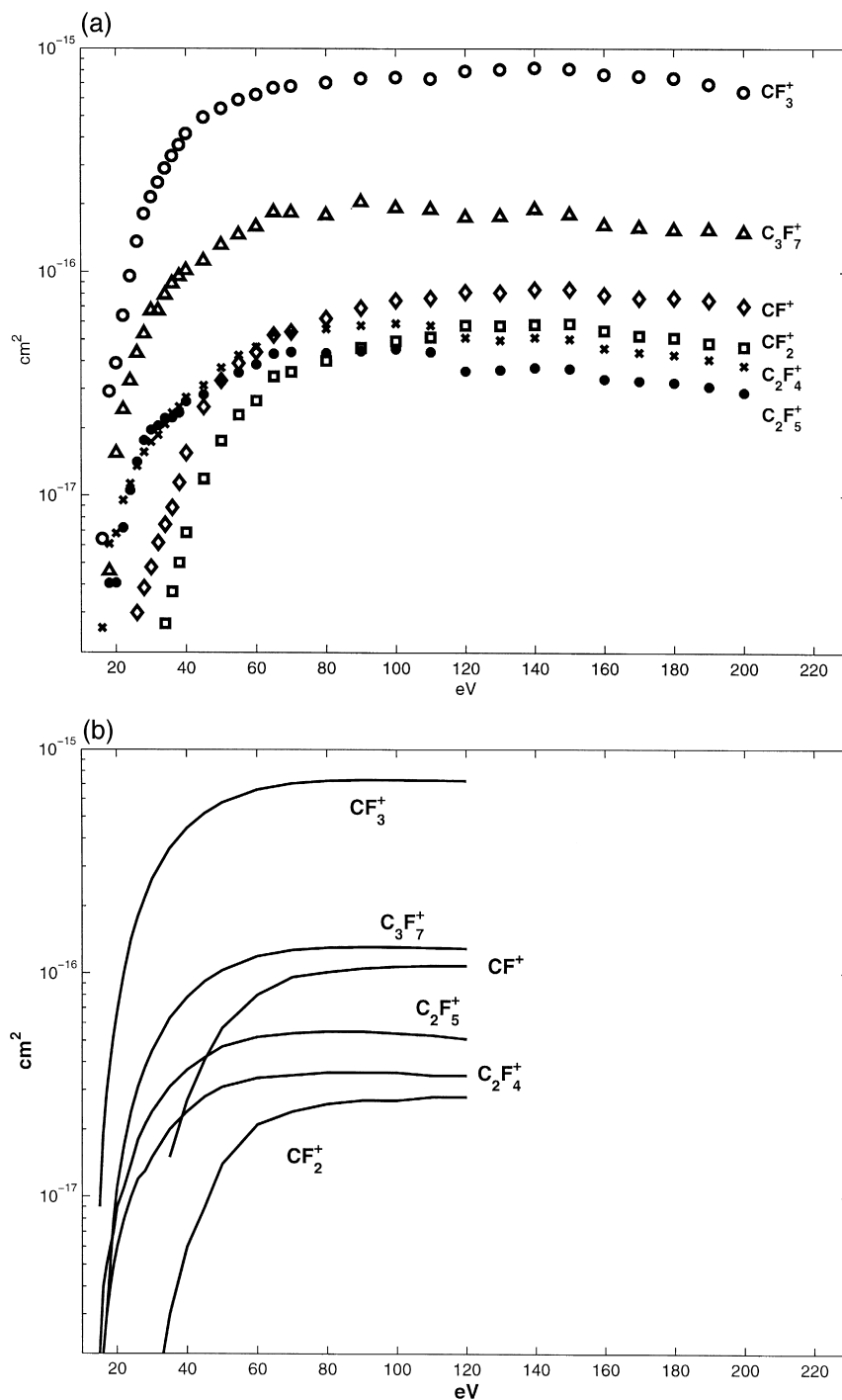


Fig. 1. Partial ionization cross-sections of perfluoropropane by (a) FTMS: \circ , CF_3^+ ; \triangle , C_3F_7^+ ; \diamond , CF^+ ; \square , CF_2^+ ; \times , C_2F_4^+ ; \bullet , C_2F_5^+ ; and (b) quadrupole mass spectrometry reported in Ref. [2].

Table 1

Comparison of cross-sections for electron impact dissociation (σ_d) and dissociative ionization (σ_i) of C_3F_8

Energy (eV)	σ_d (10^{-16} cm 2)	Error (10^{-16} cm 2)	σ_i (10^{-16} cm 2)	Error (10^{-16} cm 2)	σ_i/σ_d	min σ_i/σ_d	max σ_i/σ_d
22	4.39	± 0.87	1.06	± 0.17	0.25	0.17	0.35
72	11.0	± 2.2	10.5	± 1.7	0.95	0.67	1.38
100	11.6	± 2.3	11.6	± 1.9	1.00	0.70	1.45
125	11.8	± 2.4	11.9	± 1.9	1.00	0.70	1.47
200	10.0	± 2.0	9.8	± 1.6	0.98	0.68	1.42

The values in the min and max columns are computed presuming one sigma variation of the reported total and ionic dissociation cross-sections. The fact that all ionization is dissociative implies that values of $\sigma_i/\sigma_d > 1$ in the max σ_i/σ_d column are unphysical.

energies up to 200 eV. The next most abundant ion, $C_3F_7^+$, is the result of C–F bond scission and is formed in approximately 15% yield above 40 eV. This pattern is similar to that seen in dissociative ionization of perfluorethane, where CF_3^+ and $C_2F_5^+$ are the most abundant products [10]. $C_2F_4^+$ and $C_2F_5^+$ are formed with thresholds below 20 eV, while CF^+ and CF_2^+ have higher thresholds and larger cross-sections above 100 eV. The present

results for CF_3^+ formation are in excellent agreement with the early quadrupole measurements of Poll and Meichsner as illustrated by the solid curves in Fig. 1b [2]. The total ionization cross-section reported by these authors is also in good agreement with the FTMS data. However, the partitioning among the remaining five dissociative pathways observed by FTMS differs from prior results, as can be seen in a detailed comparison of Fig. 1a and b. There

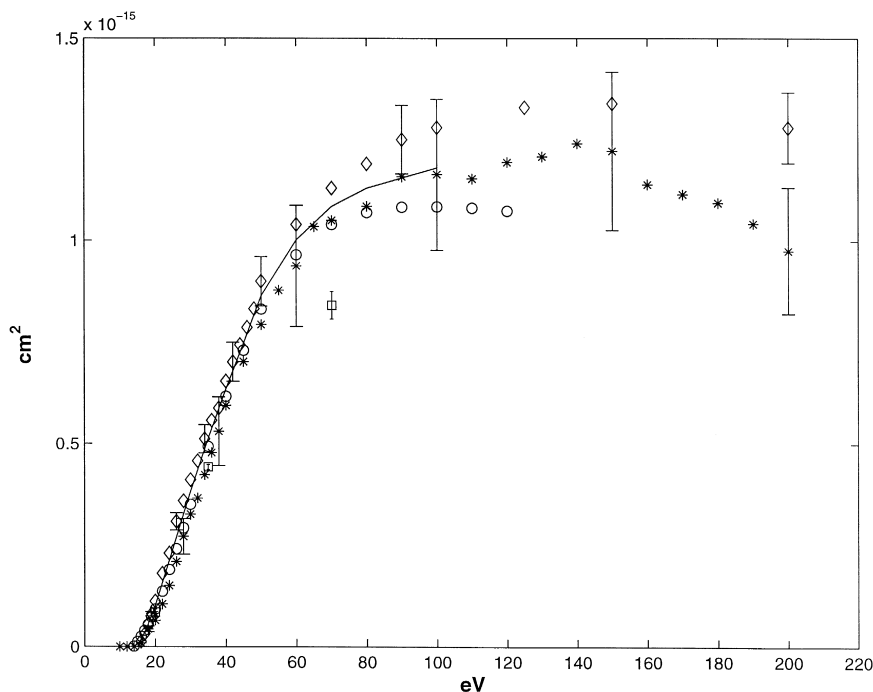


Fig. 2. Total ionization cross-sections for perfluoropropane. *, FTMS; ○, Poll [2]; ◇, Nishimura [12]; solid line, Christophorou and Olthoff [3]; □, Beran and Kevan [1].

are three arguments in favor of accepting the partitioning inferred by the FTMS measurements

- All ions are measured simultaneously, so that pressure or electron beam current fluctuations do not influence the relative ion yields.
- The ions are not collected as a current; only their electrostatic influence is recorded and this is independent of ion mass or chemical composition.
- The measurements are made at pressures and times that preclude charge transfer reactions from altering the measured species distribution.

The relatively high thresholds and small cross-sections for production of CF^+ (21 eV) and CF_2^+ (27 eV) imply that the rates of their formation from C_3F_8 in a plasma will be much less than those for CF_3^+ and C_3F_7^+ formation.

The absence of the parent molecular ions, C_3F_8^+ , implies that ionization of perfluoropropane by electrons is exclusively dissociative. The total dissociation cross-section has been reported by Winters and Inokuti and is summarized in Table 1 [11]. At 22 eV,

the lowest energy reported by Winters, the total dissociation cross-section is four times that for dissociative ionization. In other words, $25 \pm 8\%$ of the dissociation produces a positively charged fragment. The balance of dissociation is, by inference, into uncharged products. At energies between 72 and 200 eV, the total dissociation and dissociative ionization cross-sections are equal within the combined uncertainties of Winters' measurements and the present FTMS results. This dramatic increase in the ionic proportion of total dissociation with electron energy was also observed with perfluoroethane [10]. Note that neutral radicals are also produced even when $\sigma_i = \sigma_d$; for example F is a neutral product of the dissociative ionization process that forms C_3F_7^+ .

Fig. 2 displays the total experimental cross-sections recently reported by Nishimura [12] and the sum of the partial cross-sections presented here. These total ionization cross-sections are in quantitative agreement within the combined experimental uncertainties of the measurements. Fig. 2 also shows

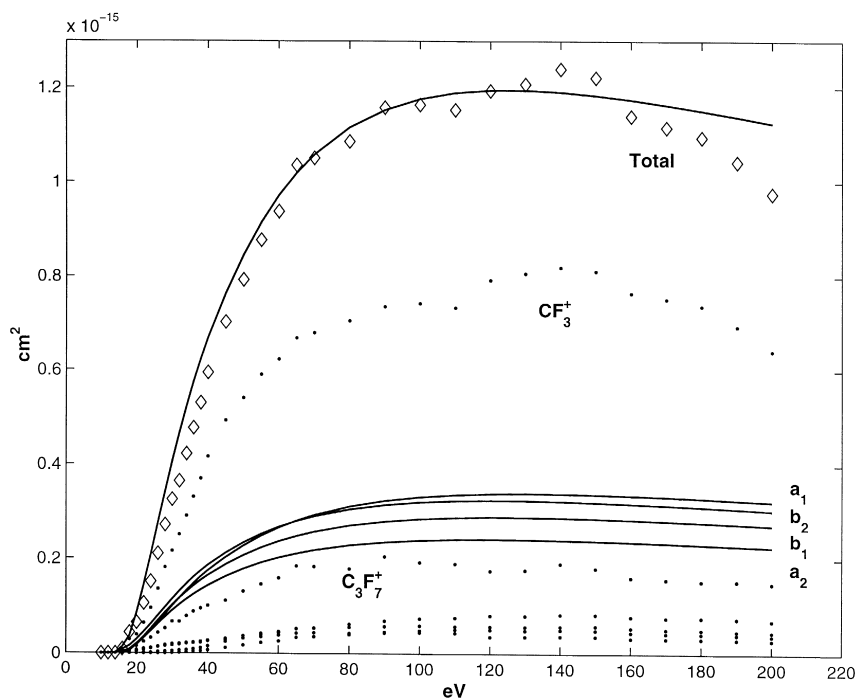


Fig. 3. BEB estimated cross-sections (solid lines) and FTMS results for total (\diamond) and partial (\cdot) ionization. The measured values for CF_3^+ and C_3F_7^+ are labeled; other partial ionization cross-sections are more clearly discerned in Fig. 1. The contributions to the BEB cross-section for each of the four orbital symmetries are shown as solid lines.

the values recommended in the recent review by Christophorou [3].

Beran and Kevan [1] reported total cross-sections for a range of halocarbons at 20, 35 and 70 eV in 1969. All of the cross-sections presented in their paper were based on the magnitude of the argon ionization cross-section at 70 eV reported by Asundi and Kurepa in 1963 [13]. This value, $3.62 \times 10^{-16} \text{ cm}^2$, is substantially higher than that reported by Rapp and Englander-Golden $2.77 \times 10^{-16} \text{ cm}^2$ [14] in a total ionization tube, as well as more recent magnetic sector $2.80 \times 10^{-16} \text{ cm}^2$ [15] and crossed beam $2.91 \times 10^{-16} \text{ cm}^2$ [9] results. When the data of Beran and Kevan are scaled to the correct argon ionization cross-section [9] they are consistent with the present results at 20 and 35 eV but underestimate the total cross-section by about 20% at 70 eV.

The total ionization cross-section can be calculated using the Binary Encounter Bethe (BEB) model [5]. Briefly, this model sums contributions to the total cross-section σ using ab initio estimates of the molecular orbital occupation numbers N , binding

energies B , orbital U , and incident T kinetic energies according to the formula:

$$\sigma_{\text{BEB}} = \frac{S}{t + u + 1} \left[\frac{Q \ln t}{2} \left(1 - \frac{1}{t^2} \right) + (2 - Q) \left(1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right) \right]$$

where

$$t = \frac{T}{B}, \quad u = \frac{U}{B}, \quad S = 4\pi a_0^2 N R^2 / B^2,$$

a_0 is the Bohr radius, R is the Rydberg constant, and Q is a weighted integral of the target's continuum dipole oscillator strength that is routinely set equal to unity in the BEB method.

Fig. 3 shows the results of BEB cross-sections estimates using CAS/SCF wavefunctions with semiempirical corrections to the binding energies as reported by Nishimura et al. [12]. The agreement between the FTMS total cross-sections (\diamond) and the calculated values is impressive. Motivated in part by

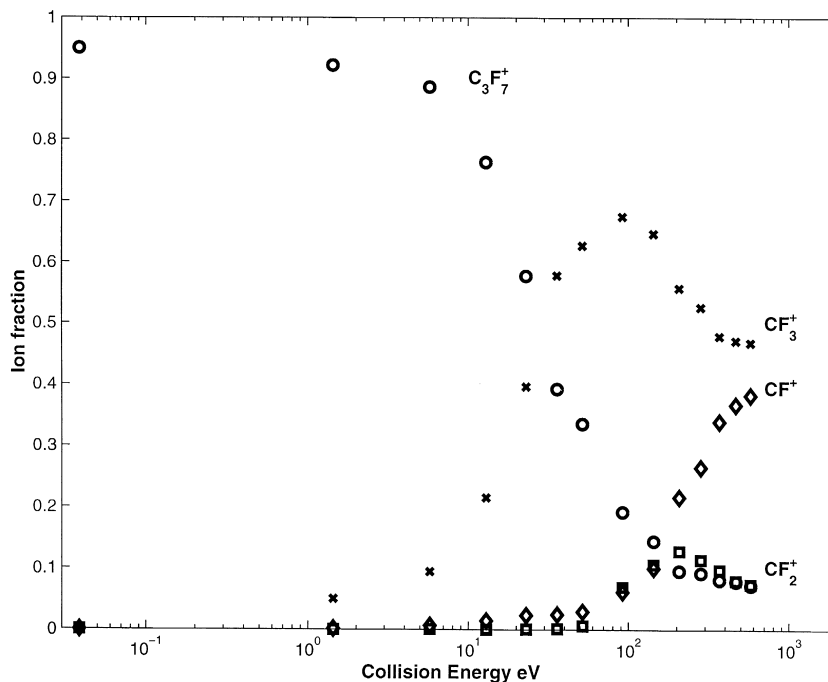


Fig. 4. Fate of translationally excited C_3F_7^+ (\circ) as a function of the center-of-mass kinetic energy to which the ion is excited. CF_3^+ (\times) is formed at all energies above 1.5 eV, with CF^+ (\diamond) and CF_2^+ (\square) being formed above 80 eV. Reactions occur at many collision energies as the ions' velocities cascade down following momentum transfer collisions.

this agreement and similar results obtained for perfluoroethane [10] we explored correlations between the orbital-by-orbital contributions and the measured partial ionization cross-sections. The 45 filled molecular orbitals of C_3F_8 transform in four symmetry groups: $16a_1$, $7a_2$, $10b_1$ and $12b_2$. Thirty-four of these orbitals, $11a_1$, $6a_2$, $8b_1$ and $9b_2$, contribute to the BEB cross-sections below 200 eV. Summing the CAS Hartree–Fock contributions over each symmetry yields the partial ionization estimates also shown in Fig. 3. The contributions from each symmetry group shown as solid lines are approximately the same. However, the measured partial cross-sections shown as dotted lines on the linear y-scale of Fig. 3 bear no correlation to the symmetry-grouped BEB values. One might sum the a_1 and b_2 contributions to match the CF_3^+ cross-section and split the b_1 cross-section into four contributions to account for CF_2^+ , $C_2F_4^+$, $C_2F_5^+$ and CF^+ while leaving the b_2 orbitals to account for $C_3F_7^+$, but these would be arbitrary assignments. None of the contributions grouped by symmetry have thresholds over 20 eV as observed for $C_2F_4^+$ and $C_2F_5^+$. We conclude that, although the

BEB model provides a good estimate of the total ionization cross-section for C_3F_8 , the partitioning among dissociative channels is not captured by grouping contributions of like orbital symmetry.

One can also probe the evolution of ion composition due to room-temperature charge transfer reactions by introducing a delay between ion formation and mass spectral evaluation in the FTMS experiment. In this way we find that the most abundant CF_3^+ ion does not react with C_3F_8 . The next most abundant ion, $C_3F_7^+$, reacts with perfluoropropane to yield $C_2F_5^+$ and neutral products with a rate coefficient of approximately $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. $C_2F_5^+$, CF_2^+ , CF^+ and $C_2F_4^+$ do not react at room temperature with perfluoropropane.

$C_3F_7^+$ was isolated in the trap by resonantly ejecting all of the other ions produced from 50 eV electron impact. 5% of these $C_3F_7^+$ ions yield CF_3^+ in the room-temperature trap within 300 ms. The remaining 95% of the $C_3F_7^+$ ions collide with perfluoropropane to produce $C_2F_5^+$. FTMS experiments do not resolve whether the excess energy in $C_3F_7^+$ that leads to CF_3^+ is electronic, vibrational, or rotational.

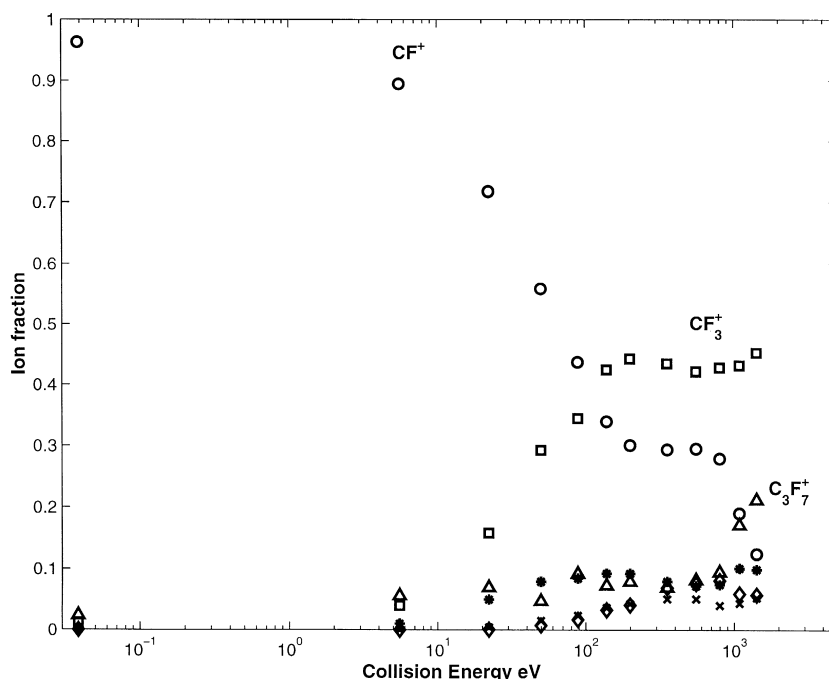


Fig. 5. Fate of translationally excited CF^+ (\circ) as a function of the center-of-mass kinetic energy to which the ion is excited. The most prominent products CF_3^+ (\square) and $C_3F_7^+$ (\triangle) are labeled. Low yields of CF_2^+ (\diamond), $C_2F_4^+$ (\times) and $C_2F_5^+$ ($*$) are also shown.

However, it is clear that internally excited $C_3F_7^+$ with enhanced reactivity is formed by 50 eV electron impact. This collisional decomposition of excited $C_3F_7^+$ may account in part for its smaller partial ionization cross-section reported by Poll and Meichsner [2].

Ionization of perfluoropropane by charge transfer was probed by selectively sweeping all but one ion species from the trap and exciting its cyclotron motion to larger orbits, then monitoring the fragmentation. We find that CF_3^+ is the predominant product of kinetically excited charge transfer whether the reactant ion is CF^+ , CF_2^+ , $C_2F_4^+$, $C_2F_5^+$, Ar^+ or $C_3F_7^+$. Typical results for the reactions of translationally excited $C_3F_7^+$ and CF^+ in Figs. 4 and 5. At room temperature 5% of the $C_3F_7^+$ ion is internally excited and has decomposed on the timescale of the measurements. The remaining, thermodynamically stable ion is converted to CF_3^+ starting at center-of-mass kinetic energies of 1.5 eV, with the dissociation or charge transfer half complete at 27 eV and maximized when the $C_3F_7^+$: C_3F_8 collision energy has been raised to 95 eV. As the energy increases above 90 eV new channels that produce CF^+ and CF_2^+ are opened at the expense of CF_3^+ production. Translationally hot CF^+ also produces CF_3^+ with a similar kinetic energy dependence as shown in Fig. 5. A $C_3F_7^+$ product channel opens at about 1 keV collision energy.

The low threshold and large cross-section for production of CF_3^+ and its failure to react further with perfluoropropane leads one to conclude that this species should dominate the reactive flux in a plasma that contains C_3F_8 . This prediction is strengthened by the fact that conversion of the other five ion species to CF_3^+ occurs at kinetic energies comparable to those expected from the electrostatic sheath in typical plasma reactors. If the sheath is collisional, in other words if the collisional mean-free path is less than the sheath thickness, one expects further enhancement of the CF_3^+ flux by charge transfer.

4. Conclusions

The partial ionization cross-sections of perfluoropropane C_3F_8 have been measured under single collision conditions using Fourier Transform Mass

Spectrometry. The results are consistent with the most recently published data for the total ionization cross-section, and the details of partitioning among the six charged products, CF_3^+ , $C_3F_7^+$, CF^+ , CF_2^+ , $C_2F_4^+$ and $C_2F_5^+$ are quantified. Of these ions only $C_3F_7^+$ reacts with the parent molecule at room temperature, yielding $C_2F_5^+$. Translationally excited ion fragments do react with perfluoropropane yielding CF_3^+ as the principal product. The observation of ion species other than CF_3^+ , $C_3F_7^+$, CF^+ , CF_2^+ , $C_2F_4^+$ and $C_2F_5^+$ in plasmas must therefore be ascribed to alternate processes such as ionization of neutral radicals, the products of gas-phase neutral reactions, or ion–radical reactions.

The ionization is also seen to be exclusively dissociative. Based on the published values of the total dissociation cross-section the present results allow us to conclude that the contribution of neutral dissociation to total dissociation decreases from 75% at 22 eV to less than 30% from 75 to 200 eV.

The Binary Encounter Bethe model provides a reasonable estimate of the total ionization cross-section, but partitioning the contributions among orbitals of like symmetry does not reproduce the observed fragmentation pattern.

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