

Partial ionization cross-sections of C_2F_6

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Abstract

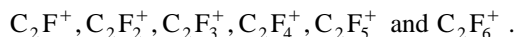
The dissociative ionization of perfluoroethane, C_2F_6 , by electron impact has been measured under single-collision conditions using Fourier transform mass spectrometry. The total ionization cross-section rises to a maximum value of $8.9 \pm 1.3 \times 10^{-16} \text{ cm}^2$ at 70 eV. CF_3^+ is the most prominent ion fragment at all energies, followed by $C_2F_5^+$, CF^+ , and CF_2^+ . $C_2F_6^+$ is not observed. The ratio of dissociative ionization to total dissociation increases from $27 \pm 5\%$ at 22 eV to $89 \pm 11\%$ at 70 eV. The total cross-section and the partitioning among the dissociative channels is examined in the context of the binary encounter Bethe (BEB) molecular orbital model. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Perfluoroethane, C_2F_6 , is used as a precursor for reactive ion etching of semiconductors and as a gaseous dielectric for insulation. Earlier work on dissociative ionization of perfluoroethane includes magnetic sector measurements by Beran and Kevan [1] and quadrupole studies by Poll and Meischner [2]. A need for better quality C_2F_6 ionization cross-sections was recently noted in a review of its low-energy electron transport characteristics by Olthoff and Christophorou [3].

The partitioning of fragments among plausible dissociation channels is of both practical and fundamental significance. Fourteen of the 18 statistically

possible fragment ions satisfy normal valence requirements:



Only four of these ions are observed to form by low-energy electron impact: CF_3^+ , $C_2F_5^+$, CF^+ and CF_2^+ .

Others among this list of 14 are observed to form by dissociative ionization from different precursors. For example, $C_2F_3^+$ and $C_2F_4^+$, are formed by dissociative ionization of $c\text{-C}_4\text{F}_8$, and are therefore thermodynamically stable species (see, e.g., Ref. [4]). The selection among fragment channels is a result of dynamical constraints on either the electronic states to which C_2F_6 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

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and the binary encounter Bethe (BEB) model have provided insight into the total ionization cross-sections for some molecular species [5], there is 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_2F_6 ionization below.

On a more practical note, the performance of plasma etch chemistries based on fluorocarbons generally – and C_2F_6 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 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

Perfluoroethane C_2F_6 (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 m 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 (FWHM) 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 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. 1. CF_3^+ is formed with the lowest threshold and in the highest yield at all energies out to 70 eV. The yields of CF_3^+ and $C_2F_5^+$ rise from threshold to 25 eV at similar rates, but the yield of carbon–carbon bond scission product increases more rapidly from 25 to 70 eV than that of carbon–fluorine cleavage. The present results are in plausible agreement with the early quadrupole measurements of Poll and

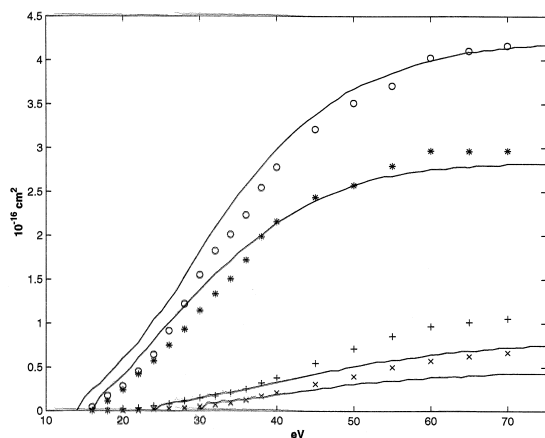
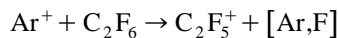
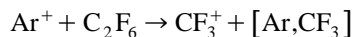


Fig. 1. Partial ionization cross-sections of C_2F_6 ; \circ , CF_3^+ ; $*$, $C_2F_5^+$; $+$, CF^+ ; \times , CF_2^+ . Solid lines are digitized quadrupole data from Ref. [2].

Meichsner as illustrated by the solid lines in Fig. 1 [2]. We find higher yields of CF^+ (20 eV) and CF_2^+ above 40 eV and a more gradual increase of cross-section with energy near threshold for CF_3^+ and $C_2F_5^+$.

The relatively high thresholds and small cross-sections for production of CF^+ (20 eV) and CF_2^+ (23 eV) imply that the rates of their formation from C_2F_6 in a plasma will be much less than those for CF_3^+ and $C_2F_5^+$ formation. One can also probe the evolution of ion composition due to charge transfer reactions by introducing a delay between ion formation and mass spectral evaluation in the FTMS experiment. In this way, we find that CF_3^+ , $C_2F_5^+$ and CF^+ do not react with C_2F_6 . However, CF_2^+ reacts with perfluoroethane to yield $C_2F_5^+$ with a rate coefficient of about $1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This coefficient is estimated by presuming charge transfer from argon [10]:



occurs at the Langevin limiting value of $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for the measured polarizability of $6.2 \times 10^{-24} \text{ cm}^3$ [11]. The product $C_2F_5^+$ is unreactive, so that the ion composition of a glow discharge that contains C_2F_6 should be primarily CF_3^+ , $C_2F_5^+$, and CF^+ . The observation of other ion species in a plasma reactor can be thereby ascribed to alternate

processes such as ionization of neutral radicals or the products of gas-phase neutral reactions.

The absence of the parent molecular ions, $C_2F_6^+$, implies that ionization of perfluoroethane by electrons is exclusively dissociative. The total dissociation cross-section has been reported by Winters and Inokuti to be $3.2 \pm 0.6 \times 10^{-16} \text{ cm}^2$ at 22 eV and $8.1 \pm 1.6 \times 10^{-16} \text{ cm}^2$ at 72 eV [12]. The total ionization cross-sections reported here are $0.9 \pm 0.13 \times 10^{-16} \text{ cm}^2$ and $8.9 \pm 1.3 \times 10^{-16} \text{ cm}^2$ at the same energies. At 22 eV, which is still well above the ionization thresholds, approximately $73 \pm 5\%$ of the total dissociation yields only neutral fragments. At 72 eV the dissociation is predominantly ionic within the combined uncertainties of the experimental measurements. (The upper bound for the neutral fraction is 22%.) Neutral species are also produced by dissociative ionization; for example F is a neutral product of the process that forms $C_2F_5^+$.

Fig. 2 displays the total experimental cross-sections recently reported by Nishimura [13] 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.

Beran and Kevan [1] reported total cross-sections for a range of halocarbons at 20, 35, and 70 eV in

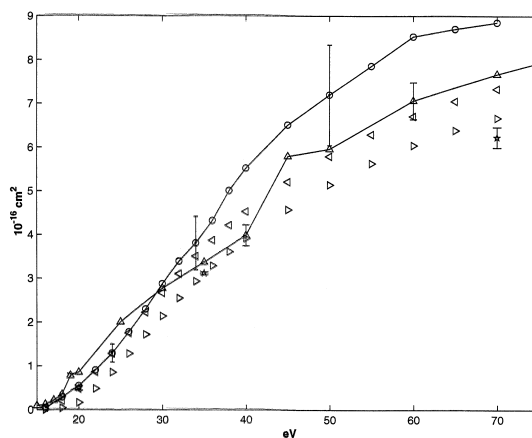


Fig. 2. Comparison of the present FTMS total ionization cross-section (\circ), the ionization tube experimental values of Nishimura (Δ) [13] and of Beran and Kevan (\star) [1], and two BEB estimates using orbital energies of Kim (\triangleleft) [13] and energies of Winstead (\triangleright) [17].

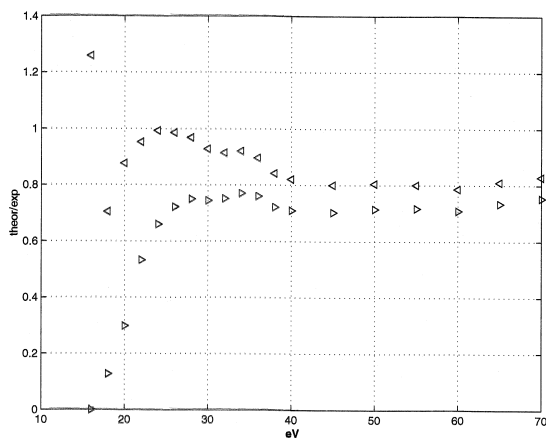


Fig. 3. Ratio of BEB cross-section estimates to the sum of the partial ionization cross-sections measured by FTMS. Calculations used RHF energies (\triangleright) and empirically adjusted CASSCF energies (\triangleleft).

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 [14]. This value, $3.62 \times 10^{-16} \text{ cm}^2$, is substantially higher than that reported by Rapp and Englander-Golden $2.77 \times 10^{-16} \text{ cm}^2$ [15] in a total ionization tube, as well as more recent magnetic sector $2.80 \times 10^{-16} \text{ cm}^2$ [16] 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 eV but underestimate the total cross-section at 45 and 70 eV as depicted in Fig. 2.

The total ionization cross-section can be estimated using the 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

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

a_o 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.

We also show in Fig. 2 two BEB estimates using different sets of molecular orbital energies. The first set are results of Hartree–Fock calculations at the RHF/6-311 + g* level of theory (\diamond) provided by Winstead and McKoy [17]. The second set (\square) is derived from correlated wavefunctions with semi-empirical corrections to the binding energies as reported by Nishimura et al. [13]. The BEB method with no empirical corrections to the HF wavefunctions is about 70% of the measured value above 25 eV. The BEB estimate is poor near threshold since its value drops to zero when the energy is less than the Koopman's theorem ionization potential. The BEB estimate accounts for over 80% of the measured cross-section using the correlated and empirically adjusted orbital energies. This behavior is illustrated in Fig. 3.

Motivated in part by this encouraging agreement we explored correlations between the orbital-by-orbital contributions and the measured partial ioniza-

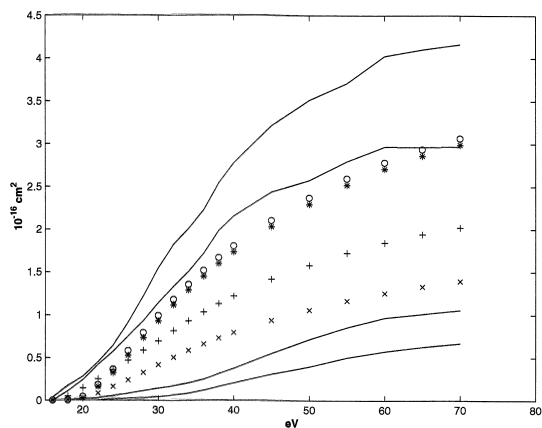


Fig. 4. Contributions to the BEB cross-section from orbitals of each symmetry scaled (by 1.4) to match the total cross-section at 70 eV. \circ , e_g ; $*$, e_u , $+$, a_{1g} , and \times , a_{2u} . Solid lines are FTMS cross-sections.

tion cross-sections. The 33 filled molecular orbitals of C_2F_6 transform in four symmetry groups: $5e_g$, $5e_u$, $7a_{1g}$, and $6a_{2u}$. Twenty-five of these orbitals contribute to the BEB cross-sections below 70 eV. There are four pairs each of symmetry e_g and e_u , $5a_{1g}$, and $4a_{1u}$ filled orbitals. Summing the Hartree–Fock [17] contributions over each symmetry and scaling to match the measured total cross-sections yields the partial ionization estimates shown in Fig. 4. Although the numbers of symmetry groups and observed fragments are both four, the thresholds, shape, and relative magnitude of the cross-sections have only qualitative similarities. This hint of a correlation between orbital symmetry and partial ionization may be worthy of further investigation.

4. Conclusions

The partial ionization cross-sections of perfluoroethane C_2F_6 have been measured under single-collision conditions using FTMS. The results are consistent with the most recently published data for the total ionization cross-section, and the details of partitioning among the four charged products, CF_3^+ , $C_2F_5^+$, CF^+ , and CF_2^+ are quantified. Of these ions, only CF_2^+ reacts with the parent molecule at room temperature yielding $C_2F_5^+$, presumably by F^- transfer. The observation of ion species other than CF_3^+ , $C_2F_5^+$, CF^+ , and CF_2^+ in glow discharges can be ascribed to alternate processes such as ionization of neutral radicals or the products of gas-phase neutral 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 proportion of neutral dissociation decreases from 73% at 22 eV to less than 22% at 70 eV.

The BEB model provides reasonable estimates of the total ionization cross-section and, perhaps coinci-

dentally, suggests qualitative features that correlate the symmetry of the molecular orbitals to the partial ionization cross-sections.

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