

# Cross sections for radicals from electron impact on methane and fluoroalkanes

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Molecular and atomic radicals from electron-impact dissociation of methane and a variety of fluoroalkanes are detected mass spectrometrically as organotellurides produced by the reaction of the radicals at the surface of a tellurium mirror. The radicals detected include  $\text{CH}_3$  from  $\text{CH}_4$ ;  $\text{CF}_3$  from  $\text{CF}_4$  and  $\text{CHF}_3$ ;  $\text{CHF}_2$  from  $\text{CHF}_3$  and  $\text{CH}_2\text{F}_2$ ;  $\text{CH}_2\text{F}$  from  $\text{CH}_3\text{F}$ ; and  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  from  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$  produced by electron impact at energies between 10 eV and 500 eV. Relative cross sections are measured. These are placed on an absolute scale by comparison with related measurements. For the collision energies relevant to processing plasmas, 10–30 eV, it is shown that dissociation into neutrals rather than dissociative ionization is mainly responsible for the production of molecular radicals. © 1998 American Institute of Physics. [S0021-9606(98)00626-6]

## INTRODUCTION

An electrical discharge in a low-pressure gas is the basis of a variety of technologies, the most important being plasma etching in the semiconductor industry. These so-called “cold plasmas” are far from equilibrium; their distinctive characteristic is the presence of high-energy chemical species in an environment that does not heat its container. Ions, radicals, and electronically excited molecules are examples of high-energy species that ordinarily would only be found at equilibrium at very high temperatures. In plasma processing, these species are used to initiate very aggressive chemical reactions on a substrate at temperatures sufficiently low that the substrate suffers no thermal damage.

Fluorinated alkanes are major feed gases in plasma reactors. Chief among these is  $\text{CF}_4$ , however, concerns about its potential as a greenhouse gas are leading to a consideration of other perfluorinated alkanes, as well as partially fluorinated methanes, as possible replacements. In the plasma, electron-molecule collisions lead to reactive chemical species via ionization, dissociative ionization, dissociative electron attachment, and direct dissociation into neutrals (so-called neutral dissociation). For example, in  $\text{CF}_4$ , neutral dissociation yields the radicals F and  $\text{CF}_3$  (and  $\text{CF}_2$ , CF, and C to a considerably lesser extent), while dissociative ionization leads to  $\text{CF}_3^+ + \text{F}$  and  $\text{F}^+ + \text{CF}_3$  (the former being the dominant channel). For  $\text{CF}_4$ , the electron attachment cross section is small and the parent ion is unstable so the production of radicals and negative ions ( $\text{F}^-$  or  $\text{CF}_3^-$ ) by dissociative electron attachment, and the parent ion ( $\text{CF}_4^+$ ) by direct ionization, need not be considered. To a greater or lesser extent, the same is true of other fluorinated alkanes. Within the plasma, radicals are the dominant species; typical radical concentrations are of the order of  $10^{14} \text{ cm}^{-3}$ , while ion concentrations are of the order of  $10^{10} \text{ cm}^{-3}$  owing to the relatively low surface-sticking coefficients of radicals compared to those of ions.<sup>1</sup>

The rational design of a plasma reactor requires cross sections for electron-molecule collision processes as a func-

tion of electron energy. A great deal of effort has gone into determining the cross sections for dissociation into neutrals and for dissociative ionization in fluorocarbons. Since one need only measure the rate of production of one of the fragments of a dissociation process to determine a cross section, the determination of dissociative ionization cross sections is the easier of the two cross section measurements to make mass spectrometrically: to get the dissociative ionization cross section one measures the rate of production of the charged fragment, whereas the neutral dissociation cross section requires the detection and identification of one or the other of the neutral radical fragments.

Total ionization cross sections and partial ionization cross sections (that is, cross sections for the production of a particular ionic fragment) have been reported for methane<sup>2–6</sup> and many of the fluorinated alkanes.<sup>7–10</sup> In comparison, reports of neutral dissociation cross sections are sparse. The difficulty stems from the fact that a radical and its parent molecule cannot generally be distinguished from one another by ordinary mass-spectrometric methods. For example, the  $\text{CF}_3^+$  peak at 69 amu is the main feature in the mass spectrum of both the  $\text{CF}_3$  radical and its parent  $\text{CF}_4$ . In an attempt to circumvent this difficulty, Sugai and co-workers<sup>11–14</sup> have employed threshold-ionization mass spectrometry to measure partial neutral dissociation cross sections for  $\text{CH}_4$ ,  $\text{CF}_4$ , and  $\text{CHF}_3$ . Winters and Inokuti<sup>15,16</sup> and Perrin and co-workers<sup>17</sup> determined total dissociation cross sections (dissociative ionization plus neutral dissociation) for  $\text{CH}_4$ ,  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$  from the pressure drop observed when a gas was irradiated with electrons in the presence of a getter that adsorbed all reactive fragments. From these, total neutral dissociation cross sections have been calculated for  $\text{CH}_4$ ,  $\text{CF}_4$ , and  $\text{C}_2\text{F}_6$  as the difference between the total dissociation and total ionization cross sections.<sup>7,9,18–24</sup> Recently, Mi and Bonham<sup>25</sup> have obtained the total neutral dissociation cross section for  $\text{CF}_4$  by taking the difference between total inelastic electron scattering and total ion production.

We have developed a specific and nearly universal tech-

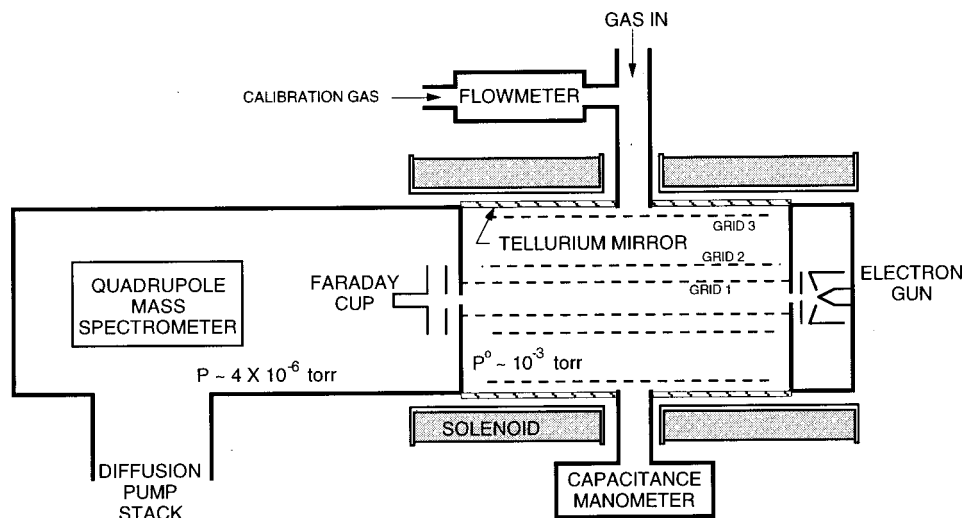


FIG. 1. Schematic diagram of the apparatus.

nique for the quantitative analysis of radicals and have employed our method in the measurement of partial neutral dissociation cross sections for  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$  under electron impact in the 10–500 eV range. The technique, based on the method by which radicals in the gas phase were first identified,<sup>26</sup> relies on the efficient reaction of radicals with tellurium to yield volatile and stable organotellurides. In our apparatus a beam of electrons passes through a target gas in a collision cell that has a tellurium mirror on its inner surface. With a mass spectrometer we measure the telluride partial pressure which in turn is related to the radical production rate. The virtue of this technique is that the tellurium surface does not react with the target gas. In addition, the portion of the mass spectrum under observation is displaced by more than 128 amu (the nominal tellurium mass) from the region displaying peaks characteristic of the parent gas.

## EXPERIMENT

The apparatus is divided into two compartments separated by a 4 mm aperture as shown schematically in Fig. 1; the first compartment is the dissociation region that contains the target gas, the electron gun, and the tellurium surface; the second is the analysis region containing the quadrupole mass spectrometer. The target gas is admitted to the dissociation region and evacuated from the analysis region so there is a significant pressure drop across the aperture separating the two compartments. The mass spectrometer requires pressures below  $10^{-5}$  Torr, while for these experiments the target gas pressure in the dissociation region was of the order of  $10^{-3}$  Torr. In operation, an electron beam is directed along the axis of the dissociation region. Radicals produced in electron-molecule collisions are converted to volatile tellurides at the tellurium surface. The partial pressures of tellurides in the dissociation region reflect the efficiency of conversion of radicals to tellurides as well as the cross section for radical production. The partial pressure of tellurides in the lower-pressure region is measured by the mass spectrometer and is proportional to the telluride partial pressure in the

higher-pressure region. Thus the cross section for the production of a radical by electron impact can be determined from the mass spectrometer signal rate if one knows the mass spectrometer sensitivity, the conductance of the aperture separating the high-pressure and low-pressure regions of the apparatus, the radical-to-telluride conversion efficiency, the target gas pressure, the electron beam current, and the length of the cell.

The electron gun consists of a resistively heated, tungsten-wire filament in a Pierce diode.<sup>27</sup> Electrons from the gun are accelerated into a beam that passes along the axis of the cylindrical dissociation region, out through its exit aperture, through a secondary electron suppressor, and into a “faraday cup” that captures the electrons in order to measure the beam current. A coaxial electromagnet outside the apparatus helps collimate the beam. Gas from the dissociation region that enters the gun through its output aperture is pumped away through a bypass to the diffusion pump. This minimizes the possibility of interference from radicals produced by thermal decomposition on the filament of the gun. Tellurium is evaporated onto the inside surface of the cylinder in a separate apparatus to avoid contaminating the cell and the mass spectrometer with tellurium. The glass cylinder has two side arms; the target gas is admitted through one arm and a capacitance manometer is attached to the other. The electron beam axis is surrounded by three, concentric, cylindrical, wire-mesh grids. The innermost grid defines a field-free region for the electron beam. The intermediate grid is biased to prevent ions from escaping the collision region and impinging on the tellurium surface, although we have evidence that ions do not react with tellurium to produce the tellurides of interest. The outermost grid is in contact with, and thus defines the electrical potential of, the tellurium surface.

For alkanes the production of a radical by electron impact proceeds via dissociative ionization or neutral dissociation; dissociative electron attachment occurs only for electron energies below about 20 eV and, in any event, the cross section for this channel is vanishingly small. In our experi-

ment, the cross sections for neutral dissociation,  $\sigma_n$  (cm<sup>2</sup>), and dissociative ionization,  $\sigma_{di}$  (cm<sup>2</sup>), are determined from the mass spectrometer signal rate,  $S_{\text{TeR}_2}$  (Hz), for the diradical telluride  $\text{TeR}_2$  arising from the production of the radical  $R$  by electron impact on the parent  $\text{XR}$ . The signal rate is proportional to the rate  $R_{\text{TeR}_2}$  at which the telluride is produced:

$$S_{\text{TeR}_2} = s_{\text{TeR}_2} R_{\text{TeR}_2}.$$

The proportionality constant,  $s_{\text{TeR}_2}$ , reflects the transmission of the mass spectrometer for the  $\text{TeR}_2^+$  ion, the ionization efficiency and fragmentation pattern for  $\text{TeR}_2$ , and the conductance rate for  $\text{TeR}_2$  from the collision region into the low-pressure region where the mass spectrometer is located. The first two factors are difficult to assess and, in the analysis that follows, we are obliged to assume they remain constant for the series  $\text{Te}(\text{CF}_3)_2$ ,  $\text{Te}(\text{CHF}_2)_2$ ,  $\text{Te}(\text{CH}_2\text{F})_2$ . The assumption of constant transmission over the range from 190 amu to 266 amu is quite reasonable since we operate the spectrometer in a low-resolution mode. The electronic structure of these three tellurides is so similar that the assumption of similar ionization efficiencies and fragmentation patterns is also reasonable. The conductance varies as the inverse of the square root of the molecular weight. The telluride production rate is proportional to the rate at which radicals are produced:

$$R_{\text{TeR}_2} = \epsilon R,$$

where  $\epsilon$  is the radical-to-telluride conversion efficiency at the tellurium mirror surface; as will be shown below,  $\epsilon$  is of the order of 0.1. Finally the rate of radical production is, to first order, proportional to the sum of the cross sections:

$$R_R = \left(\frac{I}{e}\right) \left(\frac{P_{\text{XR}} N_A}{10^3 RT}\right) l (\sigma_n + \sigma_{di}),$$

where  $I(A)$  is the incident electron beam current;  $l$  (cm) the path length of the electron beam through the parent gas;  $P_{\text{XR}}$  (Torr) the pressure of target gas in the dissociation region; the elementary charge  $e = 1.60 \times 10^{-19}$  C; the gas constant  $R = 62.4$  Torr L K<sup>-1</sup> mol<sup>-1</sup>; Avogadro's constant  $N_A = 6.02 \times 10^{23}$  mol<sup>-1</sup>; and  $10^3$  converts L to cm<sup>3</sup>. Combining these three equations and solving for the cross section sum gives

$$\sigma_n + \sigma_{di} = \left(\frac{10^3 e RT}{N_A}\right) \left(\frac{S_{\text{TeR}_2}}{I l P_{\text{XR}}}\right) \left(\frac{1}{s_{\text{TeR}_2} \epsilon}\right).$$

With our apparatus, the quantities  $S_{\text{TeR}_2}$ ,  $I$ ,  $l$ , and  $P_{\text{XR}}$  are measured directly with sufficient accuracy and precision that the uncertainty in the quantity  $S_{\text{TeR}_2}/I l P_{\text{XR}}$  is less than 10%. The determination of the product  $s_{\text{TeR}_2} \epsilon$  is much less certain. We estimate the accuracy of our cross sections to be about 30%; however, since the product  $s_{\text{TeR}_2} \epsilon$  does not vary with incident electron energy, the precision of our cross sections as a function of electron energy is determined by the precision of the directly measured quantities. We have taken two approaches to finding the overall mass spectrometer sensitivity and the radical-to-telluride conversion efficiency or,

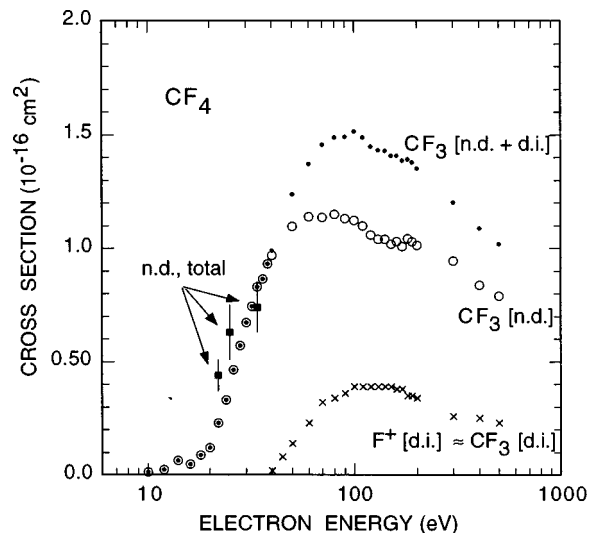


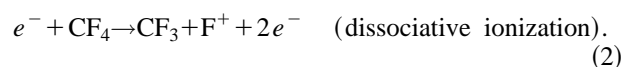
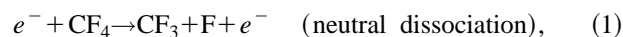
FIG. 2. The cross section for the production of  $\text{CF}_3$  by neutral dissociation (n.d.) and dissociative ionization (d.i.) from electron impact on  $\text{CF}_4$  (●) normalized to the total neutral dissociation cross section reported in Ref. 25 (■); the cross section for production of  $\text{CF}_3$  by dissociative ionization taken as equal to the cross section for production of  $\text{F}^+$  by dissociative ionization as reported in Ref. 7 (×); and the cross section for the production of  $\text{CF}_3$  by neutral dissociation taken as the difference between the normalized cross section for production of  $\text{CF}_3$  by neutral dissociation and dissociative ionization and the cross section for the production of  $\text{CF}_3$  by dissociative ionization (○).

alternatively, the product  $s_{\text{TeR}_2} \epsilon$ . For  $\text{CF}_4$  the total neutral dissociation cross section for electrons in the range 22–34 eV has recently been reported.<sup>25</sup> We normalize our relative measurements to these data; the result is entirely consistent with the plethora of data for all other dissociation processes in  $\text{CF}_4$ . The value of the product  $s_{\text{TeR}_2} \epsilon$  calculated from the normalized  $\text{CF}_4$  cross section is used to place all the fluoroalkane measurements on an approximate absolute scale. For  $\text{CH}_4$  we determine  $s_{\text{TeR}_2}$  by calibration with  $\text{Te}(\text{CH}_3)_2$ . We then determine  $\epsilon$  through an indirect comparison with existing data.

## RESULTS

### Tetrafluoromethane

We measured the relative cross section for the production of  $\text{CF}_3$  from electron impact on  $\text{CF}_4$  by monitoring the intensity of the  $\text{Te}(\text{CF}_3)_2^+$  peak in the mass spectrum and the cross section for the production of  $\text{F}$  from  $\text{CF}_4$  by monitoring the intensity of the  $\text{TeF}_2^+$  peak. The two processes contributing to  $\text{CF}_3$  production are



Cross sections for the production of  $\text{F}^+$  have been measured by Ma, Bruce, and Bonham<sup>28,29</sup> and by Poll, Winkler, Margreiter, Grill, and Mark.<sup>30</sup> These data are in excellent agreement with one another. The recommended average<sup>7</sup> (following various corrections<sup>29,31</sup>) of these two data sets is shown in Fig. 2 along with our measurements and the recently reported total neutral dissociation cross sections of Mi and

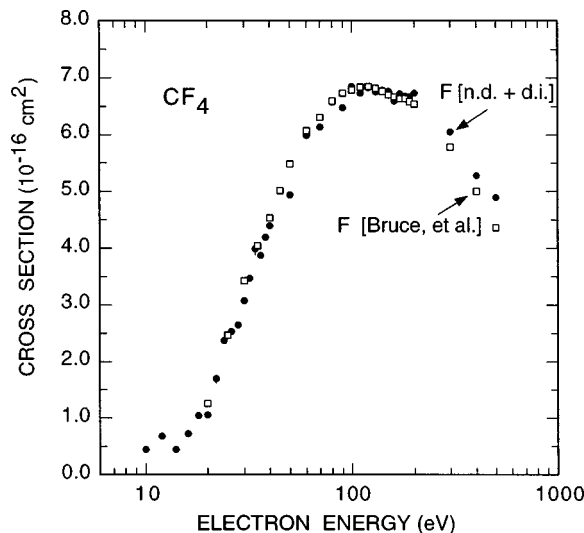


FIG. 3. The cross section for the production of F by neutral dissociation (n.d.) and dissociative ionization (d.i.) from electron impact on  $\text{CF}_4$  (●) normalized to the total F production cross section (□) reported in the analysis of Ref. 31.

Bonham.<sup>25</sup> The total neutral dissociation measurements fall in the energy range below that for dissociative ionization yielding  $\text{F}^+$ , and almost certainly below the thresholds for all neutral dissociation processes apart from that described by reaction (1) above. We have therefore employed a least squares procedure to fit our data to that of Mi and Bonham in order to place our measurements on an absolute scale. The result gives a cross section for the sum of reactions (1) and (2) that is considerably greater than reaction (2) alone. Owing to the relatively larger cross section for reaction (1), it is not surprising that the onset of channel (2) does not appear as a break in the slope of the cross section for the sum.

We show in Fig. 2 the difference between our cross section for the production of  $\text{CF}_3$  and the cross section for dissociative ionization yielding  $\text{F}^+$ . Strictly speaking this difference is the cross section for the production of  $\text{CF}_3$  by neutral dissociation, however, since this process probably represents the great majority of the neutral dissociation, the difference shown is a reasonable approximation to the total neutral dissociation cross section and, as such, compares favorably with the result of the analysis of Bruce, Ma, and Bonham.<sup>31</sup>

The analysis of Bruce *et al.*<sup>31</sup> predicts the cross section for F atom production as a properly weighted sum of previously measured cross sections for dissociative ionization leading to F (i.e.,  $\text{CF}_3^+ + \text{F}$ ,  $\text{CF}_2^+ + 2\text{F}$ , and so on) and the neutral dissociation cross section. Our measurement of the relative cross section for F production provides a test of this analysis and, as shown in Fig. 3, the shapes as a function of energy of the two results are in excellent agreement.

### Methane

We measured the relative cross section for the production of  $\text{CH}_3$  from electron impact on  $\text{CH}_4$  by monitoring the intensity of the  $\text{Te}(\text{CH}_3)_2^+$  peak in the mass spectrum. The two processes contributing to methyl radical production are

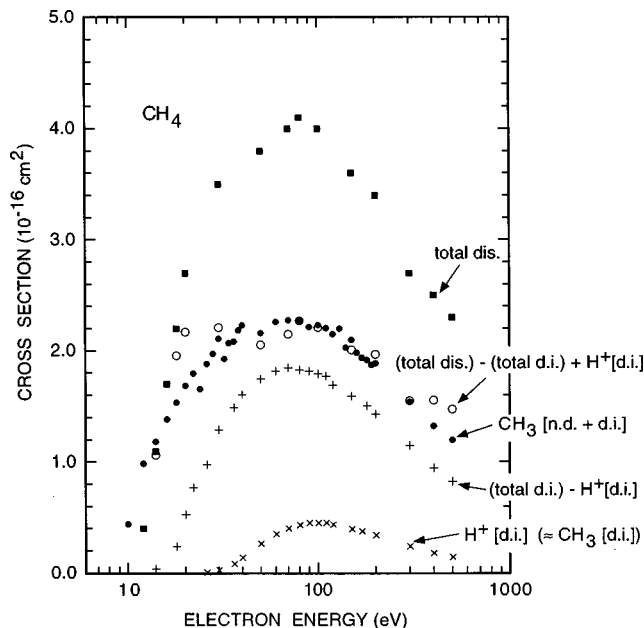
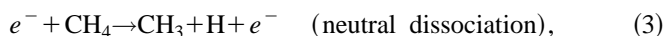
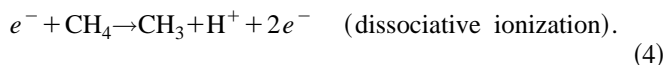
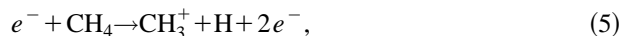


FIG. 4. The cross section for the production of  $\text{CH}_3$  by neutral dissociation (n.d.) and dissociative ionization (d.i.) from electron impact on  $\text{CH}_4$  (●) normalized to the difference between the total dissociation cross section (Ref. 15) (■) and the total dissociative ionization cross section apart from the contribution of dissociative ionization to  $\text{CH}_3$  production (Ref. 3) (+). The cross section for production of  $\text{CH}_3$  by dissociative ionization is taken equal to the cross section for the production of  $\text{H}^+$  by dissociative ionization (×).



The cross section for the production of  $\text{H}^+$  has been measured by Straub *et al.*<sup>3</sup> To place our measurement on an absolute scale, we assume that essentially all of the electron-impact dissociation of methane is accounted for by the two processes above along with the major dissociative ionization channels represented by



It then follows that our cross section for the sum of reactions (3) and (4),  $(\sigma_3 + \sigma_4)$ , corresponds approximately to the difference between the total dissociation cross section,  $\sigma_{d,t}$ , and those for the latter three dissociative ionization channels:

$$(\sigma_3 + \sigma_4) \approx \sigma_{d,t} - (\sigma_5 + \sigma_6 + \sigma_7).$$

In Fig. 4 we show the total dissociation cross section reported by Winters;<sup>15</sup> these data are labeled "total dis." The sum  $(\sigma_5 + \sigma_6 + \sigma_7)$  is taken from the partial ionization cross section measurements of Straub *et al.*;<sup>3</sup> this sum accounts for essentially all the dissociative ionization apart from that leading to  $\text{H}^+$  and is labeled "(total d.i.) -  $\text{H}^+$  [d.i.]" in the figure. Dissociative ionization leading to  $\text{H}^+$  also yields  $\text{CH}_3$ ; the cross section<sup>3</sup> is labeled " $\text{H}^+$  [d.i.] ( $\approx \text{CH}_3$  [d.i.])" in Fig. 4. The data labeled "(total d.i.) -  $\text{H}^+$  [d.i.]" thus account for essentially all the dissociation that does not lead to  $\text{CH}_3$  and the difference between the total

TABLE I. Radicals from electron impact dissociation of methane and the fluoromethanes, and the telluride ion observed in the mass spectrum.

Target	Radical	Telluride ion
CH <sub>4</sub>	CH <sub>3</sub>	Te(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
CH <sub>3</sub> F	CH <sub>2</sub> F	Te(CH <sub>2</sub> F) <sub>2</sub> <sup>+</sup>
CH <sub>2</sub> F <sub>2</sub>	CHF <sub>2</sub>	Te(CHF <sub>2</sub> ) <sub>2</sub> <sup>+</sup>
CHF <sub>3</sub>	CHF <sub>2</sub>	Te(CHF <sub>2</sub> ) <sub>2</sub> <sup>+</sup>
CHF <sub>3</sub>	CF <sub>3</sub>	Te(CF <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
CHF <sub>3</sub>	F	TeF <sub>2</sub> <sup>+</sup>
CF <sub>4</sub>	CF <sub>3</sub>	Te(CF <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
CF <sub>4</sub>	F	TeF <sub>2</sub> <sup>+</sup>

dissociation cross sections and these data accounts for both neutral dissociation and dissociative ionization leading to CH<sub>3</sub>; the difference is labeled “(total dis.)–(total d.i.)+H<sup>+</sup> [d.i.]” We normalize our measurements to this difference; the result is labeled “CH<sub>3</sub> [n.d.+d.i.]” The dissociative ionization component CH<sub>3</sub> [d.i.] is small by comparison. Apparently neutral dissociation is the major contributor to our cross section. This observation reinforces Winters’ conclusion that, for electron-impact dissociation of methane, neutral dissociation [mainly reaction (3) above] accounts for about half the total dissociation.<sup>15</sup>

A sample of Te(CH<sub>3</sub>)<sub>2</sub> was available to calibrate the mass spectrometer sensitivity,  $s_{\text{Te}(\text{CH}_3)_2}$ , for these experiments. With this calibration and the normalization described above we calculate the methyl radical-to-dimethyl telluride efficiency

$$\epsilon = \frac{10^3 eRT s_{\text{Te}(\text{CH}_3)_2}}{N_A I P_{\text{CH}_4} s_{\text{Te}(\text{CH}_3)_2} (\sigma_3 + \sigma_4)} = 0.05.$$

The conversion is remarkably efficient considering that only about half the glass surface was coated with tellurium and no special effort was made to protect the surface from contamination. In fact, the same surface was used throughout these experiments in spite of repeated exposures to air. Samples of di(fluoroalkyl) tellurides are not available; however, assuming that the mass spectrometer sensitivity is about the same for these as for dimethyl telluride we estimate  $\epsilon \approx 0.1$  for CF<sub>3</sub>-to-Te(CF<sub>3</sub>)<sub>2</sub> conversion.

### Hydrofluoromethanes

Radicals from electron impact on the hydrofluoromethanes that could be detected by observation of the appropriate ditelluride molecular ion peak in the mass spectrum are indicated in Table I. The measurement of the cross section for each radical is placed on an absolute scale making use of the calibration factor,  $s_{\text{Te}(\text{CF}_3)_2} \epsilon$ , derived from the observation of CF<sub>3</sub> from CF<sub>4</sub>. As described above, the calibration factor for the other fluoromethyl radicals,  $\text{Te}(\text{CH}_x\text{F}_y)_2$ , is taken to be

$$s_{\text{Te}(\text{CH}_x\text{F}_y)_2} \epsilon = s_{\text{Te}(\text{CF}_3)_2} \epsilon \sqrt{\frac{M_{\text{Te}(\text{CF}_3)_2}}{M_{\text{Te}(\text{CH}_x\text{F}_y)_2}}},$$

where  $M_{\text{Te}(\text{CH}_x\text{F}_y)_2}$  is the molecular weight of the radical in question. This approximation was not extended to include F

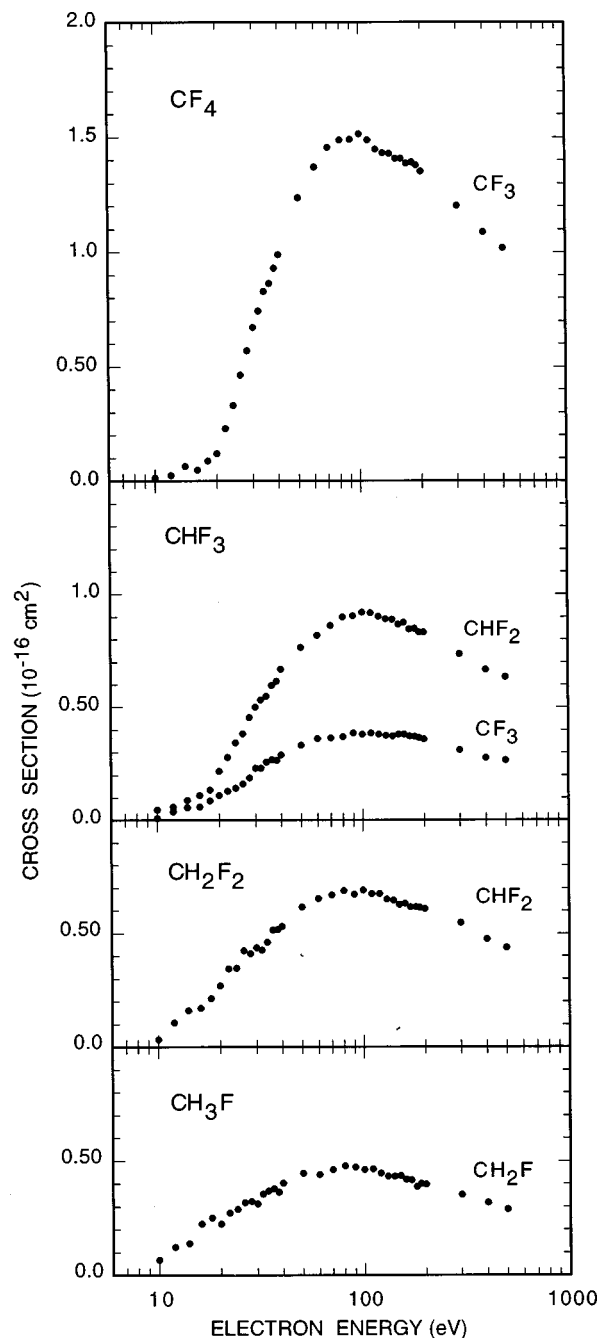
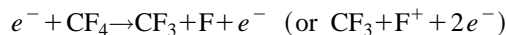


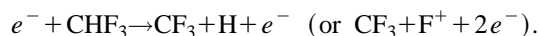
FIG. 5. Cross sections for the production of fluoromethyl radicals by neutral dissociation (n.d.) and dissociative ionization (d.i.) from electron impact on fluoromethanes.

atoms. The cross sections for fluoromethyl radical production by electron impact on the fluoromethanes are assembled in Fig. 5.

In general, the magnitude of the cross sections shown in Fig. 5 are consistent with the anticipated statistical distribution among fragmentation pathways. For example there are four identical paths for dissociation of CF<sub>4</sub> to yield CF<sub>3</sub>,



(i.e., any one of four C–F bonds might be broken), while there is only one pathway for CHF<sub>3</sub> leading to CF<sub>3</sub>,



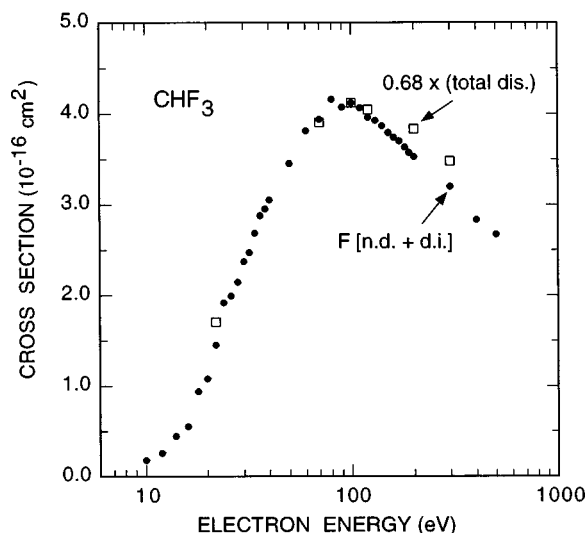
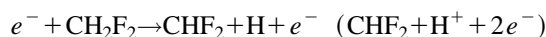
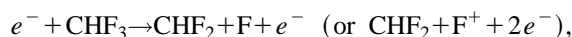


FIG. 6. The cross section for the production of F by neutral dissociation (n.d.) and dissociative ionization (d.i.) from electron impact on CHF<sub>3</sub> (●) normalized to our estimate of the portion of the total cross section for dissociation (Ref. 16) that accounts for F production (□).

The corresponding cross sections are approximately in a four-to-one ratio. Similarly the cross sections for the pathways leading to CHF<sub>2</sub> from CHF<sub>3</sub> or CH<sub>2</sub>F<sub>2</sub>,



are in the anticipated three-to-two ratio.

There is a systematic increase in the threshold energy with increasing numbers of fluorine substituents for the dissociation processes observed in our measurements. For CHF<sub>3</sub> and CF<sub>4</sub>, a weak threshold is observed near 10 eV with an abrupt increase in cross section several eV higher. We hesitate to place any significance on this since the magnitude of the cross section in this region near 10 eV is of the order of the precision of the measurement. Apart from this, it can be seen that the threshold for neutral dissociation increases from about 8 eV for CH<sub>4</sub> to about 18 eV for CF<sub>4</sub>.

About 90% of all electron-impact dissociation channels in CF<sub>4</sub> yield F atoms.<sup>7</sup> By analogy and considering a statistical distribution of dissociation pathways, one expects about 3/4 of 90% of electron-impact dissociation channels in CHF<sub>3</sub> to yield F atoms. Following this rather crude line of reasoning, we show in Fig. 6 our measurement of F atom production from CHF<sub>3</sub> normalized to 68% of the total dissociation cross section reported by Winters and Inokuti.<sup>16</sup>

### Hexafluoroethane and octafluoropropane

The intensity of the 266 amu ion peak was measured as a function of electron energy for C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>. The implication of these measurements is ambiguous since both Te(CF<sub>3</sub>)<sub>2</sub><sup>+</sup> and FTe(C<sub>2</sub>F<sub>5</sub>)<sup>+</sup> contribute to the intensity at 266 amu. Roughly speaking, the signal from C<sub>2</sub>F<sub>6</sub> is proportional to a sum of cross sections for radical production by the reactions

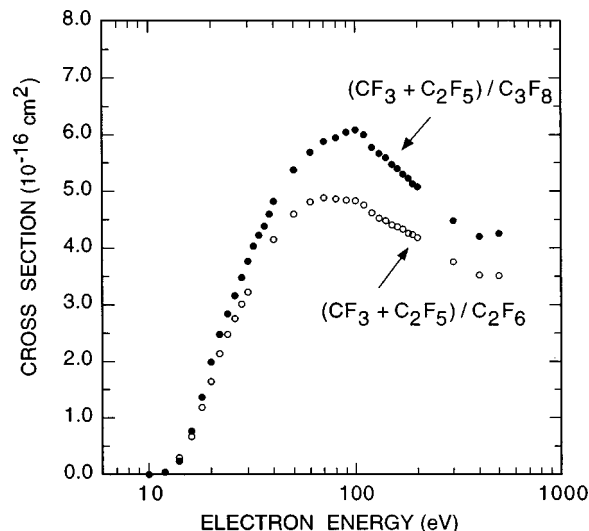
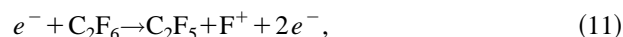
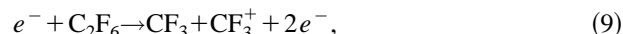


FIG. 7. Estimated cross sections for the production of CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub> by neutral dissociation and dissociative ionization from electron impact on C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>.



where the first of these reactions counts twice; it is assumed that the total cross section for processes yielding F atoms far exceeds those for dissociation to C<sub>2</sub>F<sub>5</sub> so the latter controls the rate of production of FTe(C<sub>2</sub>F<sub>5</sub>)<sup>+</sup>. Using the same normalization procedure as for the fluoromethanes, we estimate the cross section sum in Fig. 7. The cross section for F<sup>+</sup> production is small for the fluoromethanes and we assume the cross section for reaction (11) is similarly quite small. The CF<sub>3</sub><sup>+</sup> partial ionization cross section [reaction (9)] has been measured by Poll and Meichsner<sup>32</sup> and accounts for about 80% of our cross section sum. Most of the remaining fragmentation is neutral dissociation [reactions (8) and (10)]. This implies a neutral dissociation cross section of about  $1 \times 10^{-16} \text{ cm}^2$  at the maximum, consistent with the estimate of Christophorou and Olthoff.<sup>9</sup>

The threshold for producing molecular radicals by electron impact on C<sub>2</sub>F<sub>6</sub> lies about 5 eV lower than the threshold for CF<sub>4</sub>. Presumably this is mostly a result of the CF<sub>3</sub><sup>+</sup> dissociative ionization channel [reaction (9)]. In Fig. 7 we also show our approximation for the cross section for the dissociation of C<sub>3</sub>F<sub>8</sub> into CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub>. The threshold is the same as that for C<sub>2</sub>F<sub>6</sub>.

### CONCLUSION

We have developed a sensitive method for the detection of radicals and employed this technique for the observation of electron-impact fragmentation of methane and a series of fluoroalkanes to yield methyl and fluoroalkyl radicals. The interpretation of these measurements as absolute partial cross sections for a variety of neutral dissociation and dissociative ionization processes involved normalization to a small number of absolute measurements reported in the literature and

the results are shown to be consistent with measurements of cross sections for related dissociation processes. Our cross sections do not agree in magnitude or shape with the results of Sugai and co-workers.<sup>11–14</sup>

The gases studied were chosen because they are used in processing plasmas. Dissociation cross sections were measured for electron energies in the 10 eV to 500 eV range, however, it is only at the bottom of the range that our measurements have real applicability since the electron energy distribution in a low-pressure discharge does not extend significantly beyond about 30 eV. For electron-molecule collisions at these relatively low energies, our results demonstrate that neutral dissociation is primarily responsible for the production of molecular radicals from methane and the hydrofluoromethanes; for higher fluoroalkanes, molecular radicals are produced by dissociative ionization as well as by neutral dissociation. For all the fluorocarbon gases, F atoms are produced by dissociative ionization above a threshold of about 20 eV. The threshold for molecular radical production, as well as F atom production by neutral dissociation, depends on the extent of fluorination of the parent gas and can be “tuned” from less than 10 eV to about 20 eV.

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