

Total dissociation cross section of CF_4 and other fluoroalkanes for electron impact

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Various techniques from the field of surface science have allowed the development of a method for measuring the total absolute cross section for electron-impact-induced dissociation of a number of molecules. The technique is particularly reliable for the fluoroalkanes such as CF_4 , CF_3H , C_2F_6 , and C_3F_8 . The total dissociation cross section for CF_4 has been measured for energies between threshold (~ 12.5 eV) and 600 eV. The magnitude of the cross section at its maximum is 5.5×10^{-16} cm². Less extensive data are presented for CF_3H , C_2F_6 , and C_3F_8 . Their cross sections at the maxima are 5.8×10^{-16} cm², 8.6×10^{-16} cm², and 1.18×10^{-15} cm², respectively. Arguments are presented which suggest that the total dissociation cross section for each of these gases is equal to the sum of the cross sections for excitation to all electronic and ionic states, i.e., the total cross section for electronic excitation. The results are discussed from the point of view of the Bethe theory. It is concluded that the Bethe asymptotic behavior is not yet attained in the energy range of these measurements.

I. INTRODUCTION

The interaction of electrons with molecules produces ionization, electronic excitation, and dissociation. If the final state of a molecule is easily detected, which is the case for positive and negative ions, fluorescent excited states, and in some cases metastable levels, then experimental cross sections are often available. In contrast, absolute total dissociation cross sections, which are of interest in many fields of physics and chemistry, are virtually unknown. This state of affairs is primarily a consequence of the experimental difficulties encountered when attempting to measure the number of neutral fragments created in electron-molecule collisions. The paucity of data is illustrated by the 1976 review article of Polak and Slovetsky,¹ who in Table II of their paper list six molecules for which some published information is available. They further suggest (on p. 258 of Ref. 1) that in only one case (i.e., the dissociation of nitrogen) have all the experimental problems been satisfactorily resolved. Therefore, the accuracy of the data for many other molecules is quite uncertain.

Various techniques from the field of surface science have allowed us to develop a method for

measuring the total cross section for electron-impact-induced dissociation to an accuracy of 20–25%. Results for nitrogen,^{2,3} methane,⁴ and ethane⁵ have been published. Extensive data for CF_4 and less extensive data for CF_3H , CF_2F_6 , and C_3F_8 are now reported here.

The experimental method consists of developing a situation satisfying two requirements. First, the gas of interest in a closed volume does not react with the vacuum-system surface and therefore remains in the gas phase indefinitely. Second, fragments produced from this gas by any method are removed from the gas phase with unit probability because they react chemically with a freshly evaporated metal film (often called a getter) or the surrounding walls to form a nonvolatile solid. Under this situation, the number of molecules leaving the gas phase is equal to the number of fragmentation events. In other words, the change in partial pressure within the closed volume is directly proportional to the number of gas-phase molecules dissociated. Therefore, the dissociation cross section σ is directly proportional to $(1/P)(dP/dt)$ where P is the pressure and t the time (see Sec. II for more detail). (Note that the cross-section measurements do not require a knowledge of the absolute pressure. This eliminates a large

potential source of error.)

The techniques used in the experiments reported in this paper might be unfamiliar to investigators studying collision phenomena even though the concept is quite old.⁶ Therefore, it is appropriate to make a few comments about the reliability of the results. Our original measurements dealt with nitrogen and involved less sophisticated techniques than were used in the present investigation; nevertheless, the results agree quite well with similar measurements made independently by Teloy⁷ and are internally consistent with results obtained by Niehaus,⁸ who used a different method. For a discussion of the relationship between our data for N_2 and those of Niehaus, see Ref. 9, p. 458 and Ref. 1, p. 270. Moreover, Zipf and McLaughlin⁹ examined numerous excitation channels contributing to the total cross section for the dissociation of N_2 by electron impact and determined excitation functions and cross sections. Their total cross sections, which were determined by summing the partial cross sections, are in good agreement with our measurements. Similar conclusions can be drawn for methane. Melton and Rudolph¹⁰ measured the total dissociation cross section for CH_4 at an electron energy of 100 eV using techniques different from ours, and their result is $\sim 3.5 \times 10^{-16} \text{ cm}^2$ which is to be compared to our result of $4.0 \times 10^{-16} \text{ cm}^2$. The discrepancy of 15% is well within experimental error. Manton and Tickner¹¹ investigated the dissociation of methane using yet another method. Analysis of their data by Polak and Slovetsky¹ indicates a cross section of $3.75 \times 10^{-16} \text{ cm}^2$ for 50-eV electrons. This is to be compared with our result of $3.8 \times 10^{-16} \text{ cm}^2$. These comparisons along with the experimental tests for possible artifacts described in Sec. II provide convincing evidence for the reliability of the methods used in this investigation. It should be emphasized, however, that the experimental checks described in Sec. II are essential since large systematic errors are quite probable with some gases.

II. EXPERIMENTAL

A. Apparatus

The experiments were conducted in a closed volume that contained a quadrupole mass filter, a freshly evaporated titanium getter, the experimental tube (see Fig. 1), and an ionization gauge, which was operated at either 1- μA or 10- μA electron emission (see Ref. 4 for more details about the

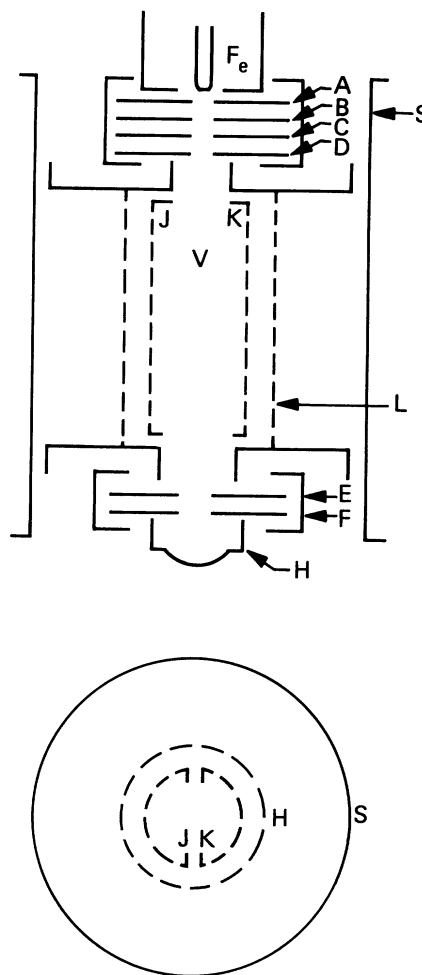


FIG. 1. Schematic of the experimental tube. Electrons were emitted from the tungsten filament F_e and collected at electrode H . The electrons were columnated by a solenoidal magnetic field of ~ 250 G parallel to the tube axis. Typical electrode potentials were as follows. Electrodes D - F were held at the same potential and defined the electron energy. The semicircular grid J was generally held at 2 V positive and grid K at 2 V negative with respect to D . This provided a small drawing-out field for ions without changing the energy of the electrons at the center of the tube. The circular grid L was held at the same potential as K . Electrodes A , B , and C were held at 6.3, 15, and 1 V positive with respect to the filament. Electrode H was held 75 V positive with respect to D - F for electron energies greater than 40 eV and was held at the same potential as F for electron energies less than 40 eV. (See text for explanation.) Currents to all electrodes were monitored. The tube was heated in a vacuum furnace at 1000°C for 1 h prior to use. The drawing is to scale and the distance between the filament surface and the point where the electrons are collected at H is 9.65 cm. The apertures in electrodes A - F are covered with a highly transparent mesh.

vacuum system). Electrons were emitted from the tube filament F_e (see Fig. 1) and collected at electrode H . A 75-V bias between F and H eliminated nearly all of the secondary electrons which would normally have been reflected. Therefore, accurate measurements of both the electron current and path length could be made. However, at low energies the acceleration of electrons between F and H could introduce significant error into the cross-section measurements and therefore F and H were held at the same potential. Dissociation cross sections were measured at 40 eV both with and without the 75-V bias and the ratio determined. The apparent cross sections obtained at electron energies less than 40 eV were then multiplied by this ratio in order to give the absolute cross sections shown in the figures and tables. This procedure is somewhat arbitrary but unfortunately there is no alternative. The error introduced by the presence of reflected secondary electrons is quite small (< 5%) and the use of the ratio technique further minimizes it. The use of the modern ultrahigh-vacuum techniques was standard procedure for the experiments reported in this paper.

B. Procedure

The number of fragmentation events is directly related to pressure change through the ideal-gas law, i.e.,

$$\frac{dN}{dt} = \left(\frac{V}{kT} \right) \frac{dP}{dt}, \quad (1)$$

where P is the pressure, k the Boltzmann constant, T the temperature, and N the number molecules in the closed volume V .

The fragmentation rate dN_1/dt due to reactions at the hot filament and due to electron bombardment in the ion gauge is given by

$$\frac{dN_1}{dt} = -C_1 N,$$

where C_1 is a constant to be determined experimentally. The fragmentation rate resulting from electron bombardment in the experimental tube is given by

$$\frac{dN_2}{dt} = -N_e D \sigma N / V,$$

where N_e is the number of electrons per second travelling a length D through the experimental tube (see Fig. 1) and σ is the fragmentation or dissocia-

tion cross section. The total fragmentation rate is

$$\begin{aligned} \frac{dN}{dt} &= \frac{dN_1}{dt} + \frac{dN_2}{dt} \\ &= -(C_1 + N_e D \sigma / V) N. \end{aligned}$$

The following procedure is used to determine σ experimentally. A pressure-versus-time curve is determined with the electron beam off ($N_e = 0$) and then with it on ($i_e \approx 50 \mu\text{A}$) and then again with it off. (The electron beam was turned on by applying a voltage to electrodes A and B . No other parameters were changed.) Typical data are shown in Fig. 2 for CF_4 and in Fig. 3 for CF_3H , CF_2F_6 , and C_3F_8 . An exponential least-squares fit to the first and third data segments yields C_1 while a similar fit to the second segment gives C_2 where

$$C_2 = C_1 + N_e D \sigma / V.$$

Then

$$\sigma = (V / N_e D) (C_2 - C_1).$$

The exponential fit to the experimental data is extremely good with the coefficient of determination (i.e., the parameter which determines how well the exponential curve fits the data, with a value of one indicating a perfect fit. For a precise definition see Ref. 12) usually being better than 0.99 and often better than 0.999. The least-squares analysis provides information much more precise than that which could be obtained from a graphical analysis

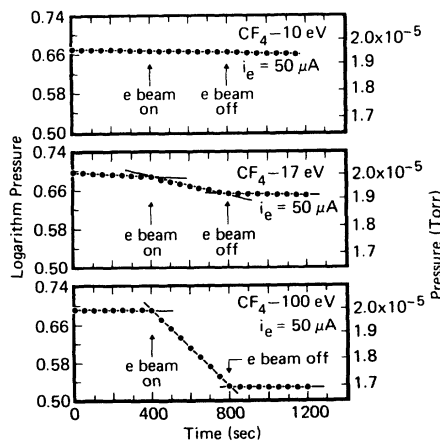


FIG. 2. Pressure versus time. Typical raw data for CF_4 . The electron beam was turned on and off by applying a voltage to electrodes A and B (see Fig. 1). All other system parameters including the filament temperatures remain unchanged during an experiment.

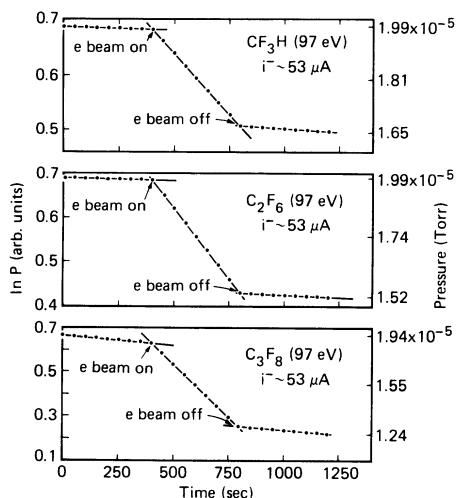


FIG. 3. Pressure versus time. Typical raw data for CF_3H , C_2F_6 , and C_3F_8 . The electron beam was turned on and off by applying a voltage to electrodes *A* and *B* (see Fig. 1). All other system parameters including the filament temperatures remain unchanged during an experiment.

such as that shown in Fig. 2. The random error in the determination of $C_2 - C_1$ is of the order of $\pm 6\%$. The volume V is known to $\pm 2\%$, the path length D to $\pm 9\%$, and the electron current to $\pm 3\%$. The total uncertainty in the measured dissociation cross section is $\pm 20\%$.

C. Influence of system parameters

The measured dissociation cross sections were found to be independent of electron current and pressure as is shown in Fig. 4. They were also independent of the ion-draw-out field and of the strength of the magnetic field which was used to focus the electrons. The magnetic field was varied by a factor of 2 and the resulting cross sections all fell within the $\pm 6\%$ random uncertainty (see Fig. 4). The electron energy was calibrated by using the ionization potential of argon, as shown in Fig. 5. The ionization potential for argon is known to be 15.76 eV and the energy scale was adjusted so that a linear extrapolation of the ion current to zero gave this value. The dc ion current was measured at electrode *S*.

Relative ionization cross sections for argon were measured in our tube and compared with the absolute values of Rapp and Englander-Golden.¹³ The shapes of the two curves were identical for energies up to 600 eV. Similar results for neon and

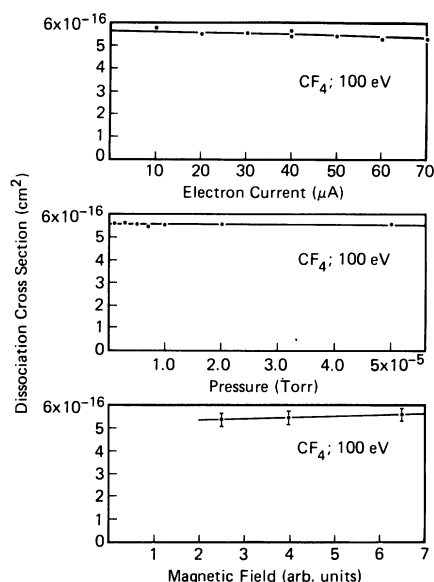


FIG. 4. Dissociation cross section versus electron current (top), versus pressure (middle), and versus magnetic field (bottom). This figure indicates that the measured cross sections are independent of various parameters. Most data presented in this paper were taken at $P = 2 \times 10^{-5}$ Torr and for a magnetic field of 5 in the units of this figure. The small dependence of the cross section upon magnetic field is not statistically meaningful since there is a $\pm 6\%$ uncertainty in the measured values for each point (see Sec. II).

methane were included in Ref. 4. Therefore, we assume that the shape of the cross-section curves presented in this paper are correct and that the absolute value is generally accurate to $\pm 20\%$.

D. Background and experimental requirements

Fragmentation often yields stable gases as well as radicals. The fate of these particles depends strongly upon their chemical properties. The radicals, which are very reactive chemically, are probably adsorbed on the walls which surround the region where they are created. They disappear from the gas phase independent of whether a getter is present. In contrast, the partial pressure of some stable gases (for example, hydrogen) increases in the absence of a titanium getter but remains negligibly small when the getter is present. Consequently, it is certain that these gases are adsorbed at the getter surface.

It should be emphasized that because of the small total pressure used in these experiments (see Fig. 4), gas-phase ion-molecule or radical-molecule

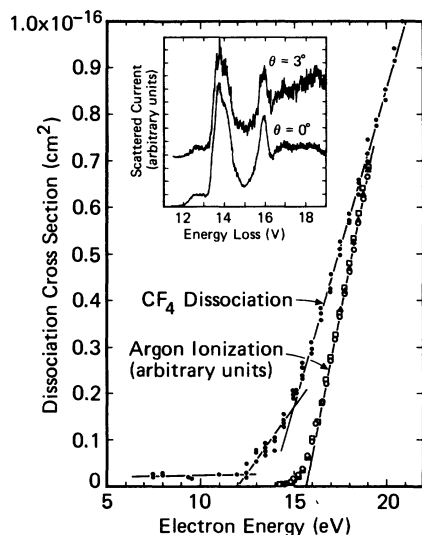


FIG. 5. Dissociation cross section versus electron energy, and relative argon ionization cross section versus electron energy. Ionization cross sections for argon (not absolute) measured in our experimental tube were used to calibrate the energy scale. The ionization potential for argon is 15.76 eV and the energy scale adjusted so that a linear extrapolation of the ion current to zero yielded this value. This insert is electron-impact energy-loss spectra from Ref. 14, taken at scattering angles $\theta=0^\circ$ and $\theta=3^\circ$. The almost constant signal corresponding to $\sim 2 \times 10^{-18} \text{ cm}^2$ below 12.5 eV is believed to be an artifact.

reactions do not occur. At these low pressures, reactions with the wall occur long before gas-phase reactions have a chance to happen.

There are three experimental problems which must be solved in order to obtain reliable results. First, some gases are dissociated so rapidly by reactions at hot filaments that it is difficult to observe dissociation by the electron beam. This is a major problem for H_2 , O_2 , and many hydrocarbons but is only a minor problem for the fluoroalkanes used in these experiments. These fluoroalkane gases react very slowly with tungsten even at temperatures as high as 2500 K. They did, however, react much faster with the low work function filaments used in our previous experiments on methane and ethane. Therefore, in the present experiments, all the filaments were changed to tungsten. The second major experimental problem involves the desorption of impurity gases from the walls into the closed volume. This problem was readily solved by using a freshly evaporated titanium getter which rapidly pumped impurity gases but which did not react with the fluoroalkanes. The

third experimental problem is related to the reversible adsorption of the gas of interest on the vacuum system walls and other surfaces. When reversible adsorption occurs then a change in pressure is not related to the number of dissociative events since the number of undissociated molecules adsorbed on the wall does not remain constant. This is expected to make it difficult, for example, to work with H_2O and CO . However, reversible adsorption is not a problem for the fluoroalkanes nor for methane, ethane, or N_2 .

In order to demonstrate that the change in partial pressure is directly proportional to the number of fragmentation events, four criteria must be experimentally established. First, it must be shown that the molecules of interest do not leave the gas phase as a consequence of an interaction between electrons and molecules adsorbed at the surface where the beam is collected. The validity of this first criterion was verified by showing that the number of molecules which leave the gas phase as a result of electron impact was negligibly small when the electrons travel most of their path length at low energy ($< 8 \text{ eV}$) and are accelerated to 100 eV just before being collected at the surface. An opposite result would have been expected if dissociation of adsorbed molecules were producing a pressure change. Secondly, it must be established that undissociated ions or undissociated, excited neutral species do not leave the gas phase because of a reaction at the surrounding surfaces. Fortunately, it appears that all electronic-excitation pathways ultimately lead to dissociation for the fluoroalkanes used in this work. (For a discussion of this subject see Sec. III.) Therefore, this second criterion is irrelevant for these gases. Thirdly, it must be shown that none of the fragmentation products remain in the gas phase. This criterion was particularly simple to establish for the fluoroalkanes using mass spectrometry. For example, mass analysis of CF_4 in our system using an EAI quadrupole mass filter and 21-eV electrons produces only one mass peak, i.e., CF_3^+ at 69 amu. The intensity of all other mass peaks was less than 1% of the 69-amu peak. After the pressure had been reduced by a factor of 2 as consequence of fragmentation by the electron beam, the 69-amu CF_3^+ peak was still the only observable peak. There were no stable gases or radicals that had remained in the gas phase. Only CF_4 was present but at a reduced pressure. Fourthly, it must be established that fragments are not recombining at surfaces to reform the parent molecule, e.g., CF_4 . Recombination, if it were occurring,

would be a function of a number of adsorbed species (e.g., fluorine atoms) on the surface. The rate of recombination would tend to increase as the number of adsorbed fluorocarbon radicals was increased. This would be evident since the apparent dissociation cross section would necessarily decrease with the number of runs. Several hundred experiments were conducted and they were highly reproducible. The very first run for CF_4 yielded an identical cross section to that obtained near the end of the experiments. Therefore, we conclude that recombination was *not* a problem in these experiments. Since the four essential criteria have been met, the measurements reported in this paper must yield total dissociation cross sections.

III. RESULTS AND DISCUSSION

A. Dissociation of CF_4

The measured cross sections are presented in Figs. 5 and 6 and in Table I. An apparent threshold for dissociation occurs at ~ 12.5 eV, and a

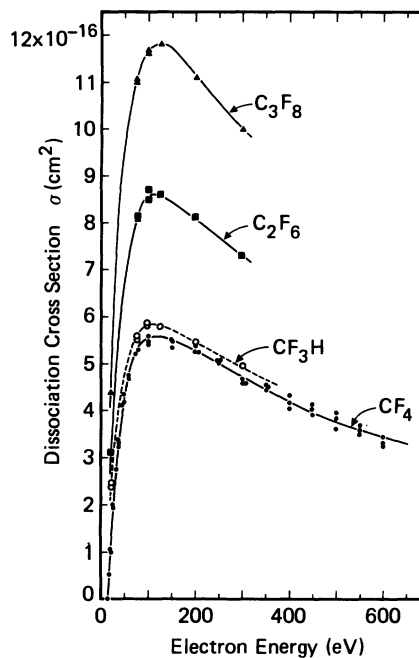


FIG. 6. Dissociation cross section versus electron energy.

TABLE I. Dissociation cross section in units of 10^{-16} cm^2 . The data on CH_4 are taken from Ref. 4, and the data on C_2D_6 from Ref. 5. All other data are based on the present work.

Energy (eV)	CF_4	CF_3H	CH_4	C_2F_6	C_2D_6	C_3F_8
22	1.17	2.4	2.7	3.1	3.5	4.39
30	2.50					
40	3.50					
50	4.30		3.8		7.0	
60						
72	5.20	5.5	4.0	8.1	7.6	11.0
80					7.65	
90					7.6	
100	5.55	5.8	4.0	8.5	7.5	11.6
125		5.7	3.8	8.6	7.3	11.8
150	5.51		3.6		7.1	
175			3.5		6.9	
200	5.32	5.4	3.3	8.1	6.7	11.1
250	5.02		3.0		6.4	
300	4.72	4.9	2.8	7.3	6.0	10.0
350	4.45		2.6		5.6	
400	4.20		2.5		5.3	
450	3.98		2.4		4.9	
500	3.78		2.3		4.6	
550	3.60				4.3	
600	3.45		2.1		4.1	

discontinuity in slope is observed at ~ 15 eV. The cross section increases linearly with energy from 15 to 22 eV. The cross section reaches a maximum of $\sim 5.5 \times 10^{-16}$ cm² at ~ 100 eV.

The data are quite consistent with information from spectroscopic experiments. Harshbarger and Lassette¹⁴ investigated CF₄ using a high-resolution electron-scattering spectrometer, and measured the number of forward-scattered electrons which had lost a given amount of energy in exciting a CF₄ molecule. Some of their data are shown in Fig. 5 (insert). There are features at 12.5, 13.7 and 14.0 eV (a shoulder), and at 15.8 eV. Similar structure is seen in the optical absorption spectra of Cook and Ching.¹⁵ The threshold for electronic excitation seen at 12.5 eV is quite consistent with the threshold observed in our experiments at about the same energy. The strong transition, which has a maximum at 15.8 eV, could easily account for the change in slope which our cross section measurements exhibit at around 15 eV.

The type of excitations which lead to these features has been discussed in detail by Robin.¹⁶ He suggests that the 12.5-eV feature results from excitation of an electron from a $1t_1$ orbital to a $3s$ Rydberg orbital, whereas the strong features around 14 eV result from the $1t_1 \rightarrow 3p$ and $4t_2 \rightarrow 3s$ transitions. The feature at 15.8 eV is assigned to a $4t_2 \rightarrow 3p$ transition. It appears that all of these transitions leave an electron in a Rydberg orbital.

A Rydberg state is characterized as a system where a single excited electron spends most of the time at so large a distance from the ion core that the core can be represented almost as a point charge (see Ref. 16, p. 10). It is this size, i.e., a radius much larger than core orbitals, which qualitatively distinguishes a Rydberg orbital in a molecule. Since the Rydberg electron is nonbonding, the ion core will tend to dissociate as if the Rydberg electron were absent. Therefore, it is reasonable to assume that much of the information available from dissociative ionization can be used to understand *qualitatively* dissociative processes resulting from Rydberg excitations. Dissociative ionization produces about 75% CF₃⁺, 11% CF₂⁺, and 7% C⁺. The number of CF₄⁺ ions is negligibly small.¹⁷ By analogy, the predominant fragment produced by excitation of a Rydberg state is expected to be CF₃ and F, i.e.,



The cross section should be less than 1×10^{-18} cm² for electron energies less than 12 eV. The rea-

son that most of the experimental points lie above the energy axis in this region is believed to be due to noise and to a small systematic error of unknown origin. Harlan and Franklin¹⁸ investigated dissociative attachment (i.e., $\text{CF}_4 + e \rightarrow \text{CF}_3^- + \text{F}$ or $\text{CF}_3 + \text{F}^-$) and found that the cross sections at the maxima were 6×10^{-19} cm² for CF₃⁻ and $4-6 \times 10^{-19}$ cm² for F⁻. The cross sections suggest a resonance with half-widths of 2-3 eV and maxima at around 7 eV. There is no evidence for these dissociative attachment processes in our experiments. It should be emphasized, however, that the two experiments are consistent with each other since we would have been unable to detect a dissociative attachment cross section whose magnitude was less than $\sim 2 \times 10^{-18}$ cm².

Mass-spectrometry experiments always show the absence of a CF₄⁺ ion under normal circumstances. Therefore all ionization processes eventually lead to dissociation. There are some ionic states which are known to be stable against dissociation,¹⁹ but fragment ions are probably formed when they deexcite to the ground ionic state, which is unstable. The fraction of the total number of dissociative events which are due to ionization can be crudely estimated. Beran and Kevan²⁰ have measured total ionization cross sections for a number of gases for 70-eV electrons. Their results appear to be systematically too large, compared, for example, with the results of Rapp and Englander-Golden.¹³ However, Ref. 20 reports the same ionization cross section for CH₄ and for CF₄. If one assumes that the cross section for CH₄, as reported by Rapp and Englander-Golden, is correct and if one assumes on the basis of Beran and Kevan's data²⁰ that it is equal to that of CF₄, then the ionization cross section for CF₄ at 70 eV would be $\sim 3.6 \times 10^{-16}$ cm². The total cross section for dissociation is 5.1×10^{-16} cm² at this energy and therefore ionization events appear to account for $\sim 70\%$ of the dissociative events. Dissociation into neutral fragments, of course, dominates near threshold.

B. Dissociation of the fluoroalkanes

The electron-impact energy-loss spectra of CF₄ show no indication of vibrational structure. The optical absorption spectra are continuous¹⁵ and there is, to our knowledge, no evidence for molecular band spectra²¹ of CF₄. Moreover, ionization leads to dissociation as indicated by the lack of a

parent peak in the mass spectra.¹⁷ These results suggest that dissociation occurs so rapidly that vibrational levels are broadened because of their short lifetime. Since there is no state which exhibits vibrational structure, it appears that *all* types of electronic excitation lead to dissociation. A similar conclusion has been drawn previously.²² A possible exception might be excitation to forbidden states which may not have been detected in the electron-loss or optical experiments. Hence, we conclude that the total cross sections for dissociation measured in the present experiments are also the sum of the partial cross sections for excitation to all electronic and ionic levels, i.e., *the total cross section for electronic excitation*. The arguments made for CF₄ are also valid for CF₃H, C₂F₆, and C₃F₈. None of these gases exhibit vibrational structure in their electron-impact energy-loss spectra nor a significant parent ion in the mass spectra (see p. 179 and p. 188 of Ref. 16).

On the basis of arguments similar to those above (i.e., the lack of vibrational structure in the spectra), the total cross section for dissociation of methane would be equal to the sum of the dissociation cross section plus the cross section²³ for production of CH₄⁺:

$$\sigma(\text{CH}_4^+) = 1.45 \times 10^{-16} \text{ cm}^2.$$

This leads to a surprising observation. At an energy near their maxima (e.g., at 100 eV) the total cross section for electronic excitation of CF₄, CF₃H, and CH₄ are almost identical, i.e.,

$$\sigma_{\text{tot}} \sim (5.5 \text{ to } 6.0) \times 10^{-16} \text{ cm}^2$$

(see Table I). Moreover, the total cross sections for C₂D₆ and C₂F₆ are quite similar. Furthermore, because some ionic and neutral states in ethane are nondissociative, the total cross section for electronic excitation at their maxima may be almost identical for these two gases. Moreover, a few measurements on CF₃H₃ at 100 eV indicate a cross section for dissociation of $\sim 9 \times 10^{-16} \text{ cm}^2$. The reliability of the latter data is somewhat uncertain but the magnitude of the cross section is similar to that of C₂F₆. We know of no theoretical explanation for the observation that all the fluoromethanes have similar cross sections near their maxima nor why the fluoroethanes seem to exhibit a similar tendency.

C. The Bethe theory

On the basis of the first Born approximation, the cross section for excitation of a state n by elec-

trons at high incident energy T is given by²⁴

$$\sigma_n = \frac{4\pi a_0^2 R}{T/R} \frac{f_n}{E_n} \ln \left[\frac{4c_n T}{R} \right], \quad (3)$$

where a_0 is the Bohr radius of atomic hydrogen ($a_0 = \hbar^2/me^2 = 5.29 \times 10^{-9} \text{ cm}$), and R is the Rydberg energy ($R = me^4/2\hbar^2 = 13.606 \text{ eV}$). Further, E_n is the energy required for excitation of the n th level and f_n is the optical (dipole) oscillator strength

$$f_n = \frac{E_n}{R} M_n^2, \quad (4)$$

where M_n^2 is the dipole matrix element squared measured in a_0^2 . Thus, one may write

$$\sigma_{\text{tot}} = \sum_n \sigma_n = \frac{4\pi a_0^2}{T/R} \sum_n \frac{R}{E_n} f_n \ln \left[\frac{4c_n T}{R} \right], \quad (5)$$

where the summation should be interpreted as an integration when the final state belongs to a continuum. Thus, Eq. (5) can be written

$$\sigma_{\text{tot}} = \frac{4\pi a_0^2}{T/R} M_{\text{tot}}^2 \ln \left[\frac{4c_{\text{tot}} T}{R} \right], \quad (6)$$

where M_{tot}^2 can be defined as

$$\begin{aligned} M_{\text{tot}}^2 &= \int_{\text{threshold}}^{\infty} \frac{dM^2}{dE} dE \\ &= \int_{\text{threshold}}^{\infty} \frac{R}{E} \frac{df}{dE} dE. \end{aligned} \quad (7)$$

An analogous formula has often been used to describe ionization.²⁴⁻²⁶

As first suggested by Fano, the analytical form of the Bethe cross section [Eq. (6)] suggests a plot of $T\sigma_{\text{tot}}/(4\pi a_0^2 R)$ versus $\ln(T/R)$. Then, M_{tot}^2 is the slope of the resulting curve. Remembering that the total dissociation cross section for CF₄ is equal to σ_{tot} , we show a Fano plot for this case in Fig. 7. From the slope we find that M_{tot}^2 is 19.2 for electrons whose energy lies between 200 and 600 eV.

An expected value of M_{tot}^2 can also be calculated from published optical data for the absorption cross section (σ_{opt} in cm^2) as a function of energy. The oscillator-strength density can be written

$$\frac{df}{dE} = \frac{mc}{\pi e^2 \hbar} \sigma_{\text{opt}} = 9.11 \times 10^{15} \sigma_{\text{opt}}, \quad (8)$$

where E is in eV. Then

$$\begin{aligned} M_{\text{tot}}^2 &= \int_{\text{threshold}}^{\infty} \frac{mcR}{\pi e^2 \hbar} \frac{\sigma_{\text{opt}}}{E} dE \\ &= 1.24 \times 10^{17} \int_{\text{threshold}}^{\infty} \frac{\sigma_{\text{opt}}}{E} dE. \end{aligned} \quad (9)$$

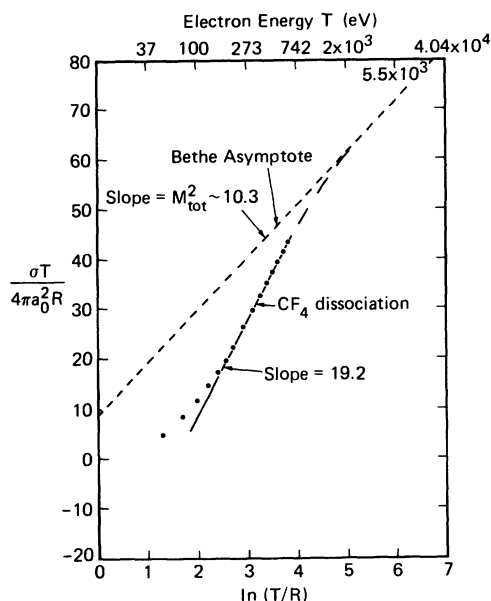


FIG. 7. Fano plot for the total dissociation cross section (solid curve with experimental points). T is the electron energy, R the Rydberg energy, σ the cross section, and a_0 the Bohr radius. The dashed curve labeled "Bethe asymptote" is schematic and is intended to summarize our conclusions about the relationship between theory and experiment. The slope, M_{tot}^2 , was chosen to agree with optical data (see text) and the intercept was chosen so that two curves could be joined in a manner which was similar to that of other analogous plots (see Refs. 30–32).

Equation (9) has been numerically integrated using the absorption cross sections for CF_4 of Cook and Ching¹⁵ and of Lee *et al.*²⁷ in an energy range from threshold to 68 eV. For energies between 68 and 270 eV, we have assumed that $df/dE = 13.3E^{-1}$. This functional dependence would, for example, roughly fit the known data of Lee *et al.*²⁷ for energies between 30 and 70 eV. From the optical data we obtain an estimate $M_{\text{tot}}^2 = 10.3$. This is roughly one-half the value obtained from the electron-impact data.

This discrepancy can arise in three ways: (1) the optical data could be in error, (2) the electron-impact data could contain a systematic error, or (3) the electron-impact data could have been taken in an energy range where the Bethe theory does not apply. The third alternative is the correct answer in our opinion.

If all dissociation cross sections were multiplied by 0.6 then M_{tot}^2 derived from the electron-impact data would roughly agree with M_{tot}^2 derived from the optical data. However, we believe that our

data are much too accurate to allow this procedure (see Secs. II B and II C). Moreover, it is also our opinion that the optical data are correct. This opinion can be partially substantiated by checking sum rules. The integral $\int (df/dE)dE$ should give the number of electrons in the molecule. Using the previously mentioned data and assumptions leads to a value of 35 for this integral. Neglecting K -shell electrons, one would have expected a value of ~ 32 . In addition, the polarizability is given by

$$\alpha_0 = \frac{e^2 \hbar^2}{m} \int E^{-2} \frac{df}{dE} dE .$$

Integration of this equation yields a value of $2.6 \times 10^{-24} \text{ cm}^3$, while the literature value²⁸ is $\sim 2.9 \times 10^{-24} \text{ cm}^3$.

Since neither the optical data nor the electron-impact data are believed to contain significant error, it is suggested that the Bethe theory does not accurately describe the dissociation cross section at these low electron energies. It is suspected that the cross section reaches the Bethe asymptote in a manner which is illustrated schematically in Fig. 7. The curve labeled Bethe asymptote in this figure has a slope which is determined by the optical absorption data and a constant ($\text{In}c_{\text{tot}} = -0.56$) which is adopted but is not unrealistic when compared with the general trend in the ionization data of Rieke and Prepejchal.²⁹ However, their c_i value for CF_4 seems to differ significantly from that of many other gases. On the other hand, the value for c_{tot} chosen by us in Fig. 7 falls close to the values of c_i obtained for a variety of different gases in their work.

It is not surprising that the dissociation cross section does not reach the Bethe asymptote at the low electron energies used in this work. Total ionization cross sections frequently do not reach the Bethe limit in this energy range.^{30–32} As an example, consider the electron-impact ionization of methane. A Fano plot of the total ionization cross section using the data of Rapp and Englander-Golden¹³ for electron energies between 200 and 900 eV yields a value of ~ 7 for M_i^2 . Berkowitz, Inokuti, and Person²³ have calculated M_i^2 from photoabsorption data and arrived at a value of 3.77. The latter value is also supported by the newer experimental data of Backx and Van der Wiel.³⁴ This discrepancy can be interpreted as an indication that the Bethe asymptotic behavior is not yet reached for the ionization of methane in this energy range.

Cross-section data often show a straight-line

behavior on the Fano plot at incident energies below the true asymptotic region. Other examples are seen in the electron-impact ionization cross sections of He⁺ and Li⁺, for both of which experimental data³⁵ are reliable and the Bethe asymptotes²⁹ are theoretically well established. Moreover, straight-line behavior below the Bethe asymptotic region has been noted by Tawara, Harrison, and de Heer,³⁶ who specifically discussed the *K*-shell ionization cross section of CH₄, N₂, O₂, Ne, and Ar; however, it is unclear whether the findings of Ref. 35 on the *K*-shell ionization might have bearings on our present findings related mainly to the outermost shells. With the observation on methane (in the preceding paragraph) and with the present result on CF₄, we must regard the straight-line behavior below the asymptotic region as something general and probably significant, but have been unable even to propose a tentative theoretical explanation.

IV. SUMMARY AND CONCLUSIONS

(1) The absolute total cross section for the dissociation of CF₄ by electron impact has a maximum value of 5.5×10^{-16} cm² at ~ 100 eV with monotonically decreasing values at both higher and lower energies. An extrapolation of the cross-section data yields an apparent threshold for dissociation of ~ 12.5 eV. There are, however, dissociative attachment processes which occur at lower energy but were undetected in our experiments because of lack of sensitivity.

(2) Arguments have been presented which suggest that the total dissociation cross sections for the fluoroalkane gases presented in this paper are equal to the sum of the cross sections for excitation to all ionic and electronic states, i.e., the total cross section for electronic excitation.

(3) It is suggested that the dissociation cross section of CF₄ in the energy range covered by these experiments does not yet reach the Bethe asymptotic behavior.

(4) At their maxima, the total cross section for electronic excitation of CF₄, CF₃H, and CH₄ are almost equal. This is also the case for C₂F₆ and C₂H₆. A reason for this observation remains obscure.

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