Absolute partial cross sections for the parent ionization of the CF_x ($x=1$–3) free radicals by electron impact

V. Tarnovsky and K. Becker
Physics Department, City College of the City University of New York, New York, New York 10031

(Received 21 December 1992; accepted 1 February 1993)

We report absolute partial electron-impact ionization cross sections from threshold to 200 eV for the formation of the parent CF_x^+ ions from the CF_x free radicals ($x=1$–3). Fast (3–3.5 kV) beams of CF_3, CF_2, and CF radicals were prepared by near-resonant charge transfer of CF_3^+, CF_2^+, and CF^+ with triethylamine (TEA), Xe, and NF_3. The CF and CF_3 neutral beams were found to contain primarily ground state neutral radicals with some evidence for the presence of a small amount of vibrational excitation (0.5 eV or less). Contributions to the CF_2^+ ion signal obtained at electron energies several electron volts below the 11.4 eV threshold for the ionization of ground state CF_2 radicals indicate the presence of CF_2 metastables (presumably in the $^3B_1$ state) in the CF_2 neutral beam. The level of CF_2 metastable contamination was found to depend critically on the exact experimental conditions. At 70 eV, the absolute parent ionization cross sections are 0.38 ± 0.07 Å^2 ($CF_3\rightarrow CF_3^+$), 1.03 ± 0.16 Å^2 ($CF_2\rightarrow CF_2^+$), and 1.25 ± 0.19 Å^2 ($CF\rightarrow CF^+$), respectively.

I. INTRODUCTION

The CF_4 molecule plays an important role as a widely used component in feedstock gas mixtures that are used in both the plasma assisted etching of microelectronic structures and in the deposition of thin films. While experimental and theoretical studies of electronic and atomic collisions involving the CF_4 molecule have received considerable attention in the past, there has been an even more increased level of activity devoted to the investigation of collision processes with CF_4 due to its importance in low-temperature processing plasmas in the last few years.[1–11] Almost all inelastic collisions with CF_4 lead to the breakup of the parent molecule and the formation of a variety of neutral and ionic excited as well as ground state fragments. In addition to atomic and ionic fluorine fragments F and F^+, the free radicals CF_3, CF_2, and CF and their ions are among the most abundant and reactive neutrals that result from the breakup of the CF_4 parent molecule. Subsequent atomic and electronic collision processes involving these free radicals play an important role in the plasma chemistry of CF_4-containing low-temperature etching and deposition plasmas.[12,13] Almost all experimental studies and most theoretical calculations have focused on the stable CF_4 parent molecule rather than on the free radicals CF_3, CF_2, and CF. The calculation of ionization cross sections for molecules and free radicals has relied primarily on semiempirical methods and largely untested additivity rules. It was only recently that improved semiempirical methods and attempts of incorporating detailed molecular structure information into model calculations of electron-impact ionization cross sections have been applied to a few selected complex molecules and free radicals with some success.[14,15]

In this paper, we present absolute partial ionization cross sections for the parent ionization of the free radicals CF_3, CF_2, and CF by electron impact obtained in our fast-beam apparatus. Measurements are reported for the processes $CF_3\rightarrow CF_3^+$, $CF_2\rightarrow CF_2^+$, and $CF\rightarrow CF^+$ from threshold to 200 eV. Detailed studies of the near-threshold regions of the cross sections were carried out in an effort to characterize the composition of the neutral beam and to minimize a possible beam contamination due to vibrationally excited ground state radicals and/or radicals in metastable and Rydberg states. Results are reported for parent ionization processes only where the data analysis is comparatively straightforward. Cross sections for the dissociative ionization of the three radicals will be reported in a separate publication in which we will analyze and quantify the capability of the present apparatus to collect fragments of dissociative ionization processes that are produced with a finite amount of excess kinetic energy. Up to now, experimental investigations of the electron-impact ionization and dissociative ionization of free radicals have been extremely scarce. The first studies along those lines were carried out in the present apparatus by Freund and collaborators[16] for CD_3 and CD_2. These authors also measured absolute partial cross sections for the electron-impact ionization and dissociative ionization of SiF_x ($x=1$–3) radicals[17–19] in addition to some earlier studies in CF_3.[20] Preliminary accounts of the results reported in this paper have already been presented at conferences[21,22] together with cross sections for the ionization of the NF_x ($x=1$–3) radicals which will be published in a separate paper.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The crossed-electron-beam–fast-neutral-beam apparatus used in the present experiments, the characteristics of its performance, a comprehensive analysis of potential sources of systematic uncertainties in the experimental procedure, and an estimate of the overall accuracy of the measured absolute cross sections have been described in detail in previous publications.[24–26] It suffices here to present a brief summary of the salient features of the apparatus and

 0021-9606/93/107868-07$06.00

of the experimental procedure and highlight only those aspects that are specific to the present experiments.

A fast (3–3.5 kV) neutral beam of CF_3, CF_2, or CF radicals is prepared by near-resonant charge exchange of a primary mass selected ion beam with an appropriate charge transfer gas. The primary ion beam is extracted from a d.c. Colutron discharge through CF_4 (or a mixture of CF_4 and H_2). A single mass is subsequently selected by passing the primary ion beam through a Wien filter. After the charge exchange cell, the residual ions are removed from the beam by electrostatic deflection and most molecules in Rydberg states are ionized and removed from the beam in a region of high electric field. The remaining neutral beam then passes through a beam-defining aperture before it is crossed with a well-characterized electron beam of variable energy (5–200 eV). The neutral beam is monitored by a secondary emission detector (nichrome surface) and its absolute flux can be determined with a calibrated pyroelectric detector. The parent ions produced by electron-impact ionization of the radical beam in the interaction region retain their initial collimation and narrow energy spread because of the negligible momentum transfer from the electron to the ion. The product ions are focused in the entrance plane of an electrostatic hemispherical analyzer which separates ions of different energy (i.e., charge state) and, of course, the product ions from the neutrals. After the analyzer, the ions are detected by a channel electron multiplier (CEM) operated in the pulse counting mode.

As discussed in detail in previous publications,[24–26] careful operation of the apparatus allows a 100% collection efficiency and a near 100% detection efficiency of all atomic and molecular parent ions which are formed in the interaction region with essentially zero excess kinetic energy. Although the apparatus was designed to facilitate the measurement of all quantities that determine the ionization cross section in absolute terms so that no normalization to theory or any previous measurements would be required, it was found advantageous to modify the measurement of the neutral beam flux.[25,26] Rather than repeatedly exposing the pyroelectric detector to a comparatively intense ion beam for calibration purposes which can cause instabilities and drifts in the detector response, the pyroelectric sensitivity was calibrated by measuring its response to a (much weaker) neutral Kr beam whose flux was calculated using the well-established Kr ionization cross section as a benchmark.[25,27] In addition, measurements of the Kr and Xe ionization cross sections in the near-threshold regime were carried out frequently in order to (1) calibrate the electron energy scale relative to the well-known ionization energies of these two species; and (2) to compare the rise of the measured ionization cross sections in the energy regime just above threshold for the three radicals with that of the rare gases. This was done to check for a shift of the threshold compared to the ground-state ionization potential and/or for a broadening of the cross section shape in the threshold region which could be indicative of a possible contamination of the radical beam caused by metastable, electronically, and/or vibrationally excited species.

The stable, reproducible, and reliable operation of the d.c. Colutron discharge using CF_4 as a source for the CF_x ($x=1$–3) radicals was found to be problematic. While CF_4 is comparatively inert, some of the fragments produced in the discharge are highly reactive and give rise to complex chemical reactions that were found to be deleterious to the walls of the discharge vessel and the tungsten filament. The standard quartz vessel which was readily etched by the discharge reaction products was replaced by a carbon vessel. As discussed in connection with recent photoemission cross section measurements in CF_4,[4] the complex carbon–fluorine–tungsten chemistry that results from the "activitation" of CF_4 by a heated tungsten or thoriated tungsten filament can cause rapid changes in the voltage/current characteristics of the filament and, furthermore, reduces its lifetime considerably. This resulted in comparatively short-lived and often unstable primary ion beams and hence neutral beams which, in turn, rendered impossible the extended data acquisition times necessary to obtain reliable results with high statistical accuracy in a single run. The stability and lifetime of the primary CF_x ($x=1$–3) radical ion beams also depended on the actual discharge conditions (pressure, current, and cathode–anode voltage). The optimum operating conditions of the CF_x ion source had to be established empirically every time the system was turned on and were rarely reproducible from one time to the next. Under the best of operating conditions, we were able to run the Colutron source through CF_4 for a few days before it was necessary to replace the filament and to clean the discharge vessel. This has to be compared with stable operating conditions of the primary ion source of weeks and even months in the case of the rare gases. As a consequence, all data reported in this paper represent the combined results of several individual measurements taken over a period of several months.

The ratio of CF_3^+ to CF_2^+ to CF^+ extracted from the Colutron source was found to depend critically on the discharge operating parameters. Changes in these ratios of one order of magnitude could be obtained easily by changing the pressure, the gas composition (pure CF_4 vs CF_4/H_2), the cathode–anode voltage, the discharge current, and the filament heating current. Three different gases were tried for charge transfer neutralization—Xe [ionization potential (I.P.) = 12.13 V], NF_3 (I.P. = 13.0 V), and triethylamine (TEA) (I.P. = 8.1 V). The ionization potentials of the CF_x free radicals range from about 8.7 V for CF_3 to 9.1 V for CF to 11.4 V for CF_2 (Refs. 28–31). Even though the Xe ionization potential is energetically near resonant only for CF_2, we obtained consistently good neutralization yields with Xe for all three radicals.

III. RESULTS AND DISCUSSION

Absolute cross sections were measured for the formation of the parent ions CF_3^+, CF_2^+, and CF^+ by electron-impact ionization of CF_3, CF_2, and CF, respectively. Careful measurements of the threshold regions were carried out first in order to check the purity of the neutral radical beam and to determine and—if possible—minimize the amount of internal energy by using different charge trans-

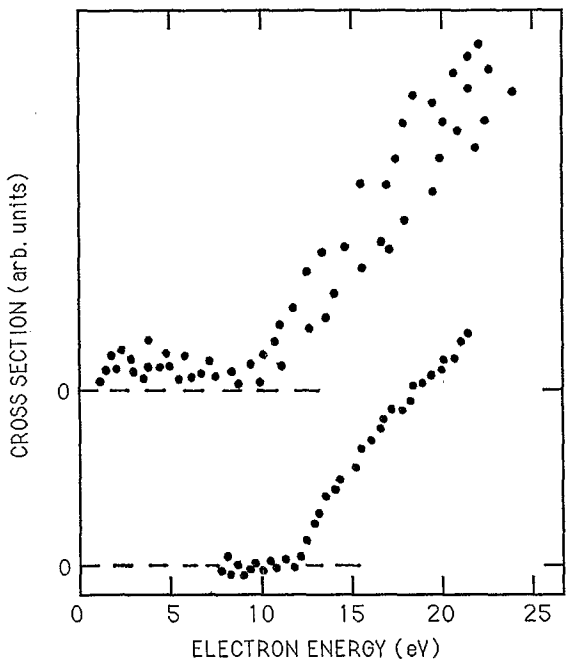

FIG. 1. Ionization thresholds for the formation of CF^+ (top data set) and Xe^+ (bottom data set). Both data sets represent data obtained in a single data run. The data sets have been corrected for the contact potential. The Xe^+ threshold data are used to calibrate the electron energy scale and to evaluate the energy spread in the electron beam (see the text for further details).

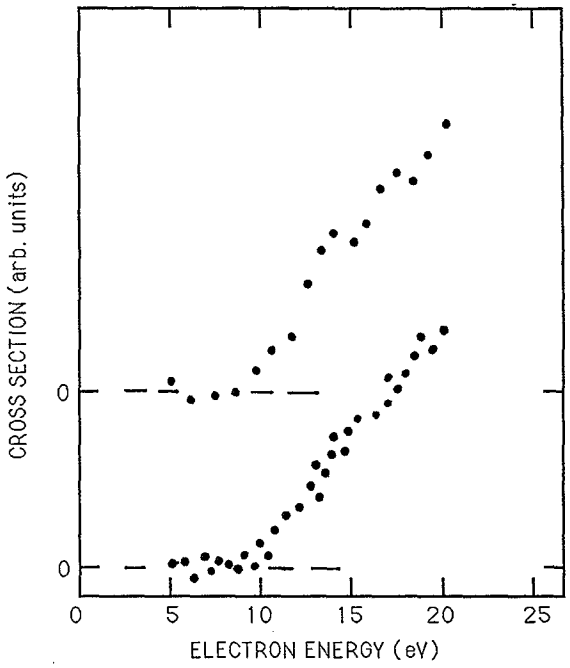

FIG. 2. Ionization threshold for the formation of CF_3^+ (top data set) and CF^+ (bottom data set). Both data sets have been obtained by combining several individual data runs. In addition, the CF_3^+ data have been smoothed (see the text for further details).

fer gases. Relative cross sections for parent ion formation were then measured from threshold to 200 eV. In each case, the operating conditions of the d.c. Colutron discharge were chosen to maximize the flux of the respective precursor ion under study CF_3^+, CF_2^+, or CF^+. Last, the absolute cross sections were determined at 70 eV by calibrating the neutral flux relative to the flux of Kr or Ar neutrals which, in turn, was obtained from the well-known benchmark single ionization cross sections for these species. This enabled us to put the relative cross sections over the entire energy range from threshold to 200 eV on an absolute scale. Double ionization of all three radicals was found to be too weak to be measured. Cross sections for the dissociative ionization of the radicals will be presented in a separate publications in which we will analyze in detail the added difficulties arising from the collection of fragment ions which are formed with excess translational kinetic energies of several electronvolts.[23]

A. Threshold measurements

The measured threshold data are shown in Figs. 1–3. Figure 1 shows a set of raw data obtained for the formation of CF^+ and a threshold data set obtained in Xe which was always run for reasons of comparison. A small contribution to the Xe^+ data from the ionization of Xe Rydberg atoms in the neutral beam has been removed according to the procedure described by Freund and collaborators.[24,25] The electron energy scale has been corrected for contact potentials by using the spectroscopic ionization energy of 12.14 eV for Xe as a calibration standard. The Xe^+ thresh-

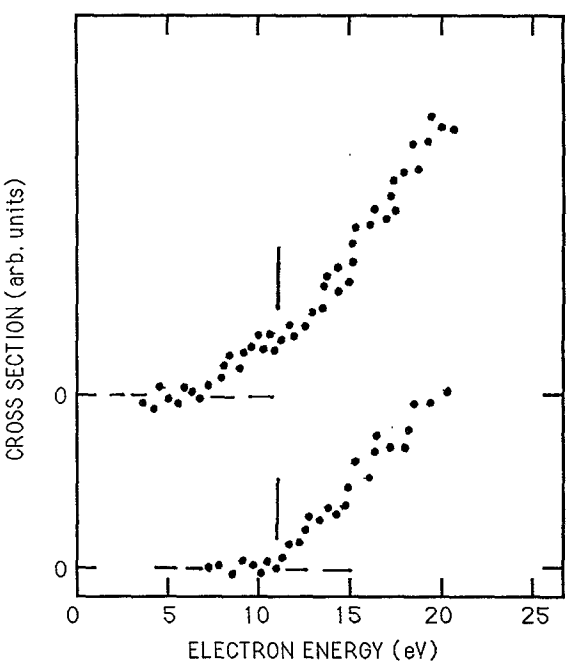

FIG. 3. Ionization threshold for the formation of CF_2^+. Both data sets have been obtained by combining several individual data runs. The top data set was obtained at a low pressure in the charge exchange cell and contains a fraction of CF_2 radicals in the $^3B_1$ metastable state. The bottom data set was obtained at a high pressure in the charge exchange cell and contains only ground state CF_2 radicals. The thresholds corresponding to the ionization of ground state CF_2 radicals has been marked by vertical bars (see the text for further details).

old data also served to monitor the energy spread in the electron beam. The CF^+ data shown in Fig. 1 represent the result of a single data accumulation period lasting for several hours. The only correction applied to the CF^+ threshold data set is a correction for the contact potential. Three observations can be made: (i) the major onset of the measured CF ionization cross section occurs between 9 and 10 eV, which coincides well with the spectroscopic ionization threshold of 9.1 eV for a ground state CF radical; (ii) there is substantial scatter in the CF data obtained in a single data run which makes it difficult (1) to determine the onset to better than about ± 1 eV and (2) to determine if and to what extent vibrationally excited ground state CF radicals might be present in the neutral beam; and (iii) there is evidence for a nonzero ionization signal below the main onset which peaks ~ 3 eV. The first observation indicates that the direct ionization of ground state CF radicals constitutes the main contribution to the observed CF^+ ion signal. The second observation mandates that meaningful CF threshold data can only be obtained by combining the results of several independent data runs. The third observation indicates the presence of species other than ground state CF radicals in the neutral beam. We attribute the nonzero CF^+ ion signal below the main onset to CF radicals in Rydberg states which survive long enough to reach the interaction region. This interpretation is based primarily on the shape and energy dependence of the observed below-threshold signal. This below-threshold signal was present in all CF^+ threshold runs. We applied a procedure similar to what was done in the case of the rare gases[24,25] to remove this signal from the CF data sets. Below-threshold signals peaking at very low electron energies were also found in CF_2^+ and CF_3^+ threshold data sets, albeit less prominent, and were removed from the data sets in a similar fashion.

Figure 2 shows threshold data for the formation of, respectively, CF_3^+ (top data set) and CF^+ (bottom data set) that were obtained by combining several individual data runs for each radical. Each individual data run was corrected for the contact potential and for any Rydberg contributions to the ionization signal before the individual data runs were combined. The CF_3^+ threshold data had to be smoothed in addition. The comparatively poor statistical quality of the CF_3^+ threshold data is the result (1) of the comparatively small absolute CF_3 ionization cross section (see also Sec. III B) and (2) of a neutral CF_3 beam which was more unstable than either the CF or the CF_2 beams. We determined a threshold of 8.5 ± 0.8 eV which is in good agreement with the ionization threshold of the ground state CF_3 radical.[28–31] The CF_3^+ threshold data were not sensitive enough to establish unambiguously the presence and the level of vibrational excitation of the CF_3 radicals in our neutral beam and to investigate the effect systematically, i.e., for different charge exchange gases and/or as a function of the pressure in the charge exchange cell. A possible broadening or enhanced curvature in the threshold region of the individual CF_3^+ data runs was obscured by the large scatter in the data. The CF_3^+ data set displayed in Fig. 2 (top curve) was obtained by combining several individual data sets and after data smoothing still does not allow a meaningful analysis of the effect of vibrational excitation of the CF_3 radicals in the fast beam. The CF^+ threshold data shown in the lower part of Fig. 2 are of higher statistical accuracy due to better counting statistics and a more stable neutral beam. The onset at 9.4 ± 0.4 eV is close to the spectroscopic threshold of 9.1 eV for the ionization of a ground state CF radical.[28–31] There is some evidence of a slight curvature indicative of the presence of vibrationally excited CF radicals in the neutral beam. The level of vibrational excitation is at most 0.5 eV as can be seen from a comparison of the CF^+ onset with the Xe^+ onset displayed in Fig. 1.

Figure 3 shows two sets of CF_2^+ threshold data. Each data set has been obtained by combining the results of several individual runs carried out under similar experimental conditions. The top diagram was obtained at very low pressures in the charge exchange cell. It displays a first onset ~ 7.5 eV followed by a distinct break in the cross section curve at ~ 12 eV at which the cross section starts to rise more rapidly with increasing impact energy. The lower data set was obtained at significantly higher charge exchange pressures (higher by up to one order of magnitude). The lower data set displays a single onset at 11.5 ± 0.4 eV which is very close to the second onset at 12 eV observed in the top data set (the two onsets have been marked by vertical bars in Fig. 2) and, very importantly, it is also very close to the spectroscopic ionization threshold for the ground state CF_2 radical at 11.4 eV. We interpret these results as follows: The lower data set appears to have been obtained under experimental conditions where the neutral CF_2 beam contains only radicals in the ground state. While a slight curvature in the threshold region exceeding the curvature observed for the Xe threshold in Fig. 1 by about 0.3 eV might again indicate the presence of some vibrational excitation, all CF_2 radicals in the beam are in the electronic ground state. By contrast, the upper data set appears to have been obtained with a neutral beam that contains a small fraction of CF_2 radicals in the excited metastable $^3B_1$ state [corresponding to the $\cdots(6a_1)(2b_1)$ electron configuration]. A similar situation was observed by Shul *et al.*[19] in their study of the electron-impact ionization of the SiF_2 free radical. These authors also found evidence of the presence of a SiF_2 metastable state in their SiF_2 neutral beam. Based on the similarity between the CF_2 and the SiF_2 radicals as discussed by Herzberg,[32,33] the metastable $^3B_1$ state in CF_2 can be expected to lie roughly 4 eV above the ground state which would correspond to an ionization energy for that state close to the 7.5 eV onset observed in our data. The absence of the metastable CF_2 radicals in the neutral beam obtained at the higher pressures in the charge exchange cell might be explained in terms of collisional quenching of the metastables at the higher pressures.

B. Cross section measurements

Relative cross sections for the ionization of each parent radical were measured for electron energies from threshold to 200 eV. Several data runs for each radical were added to

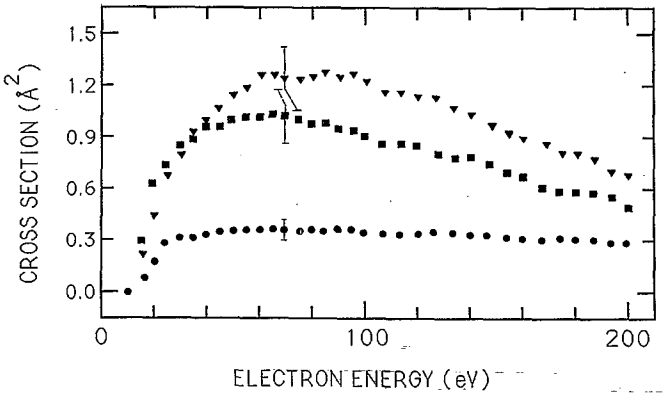

FIG. 4. Absolute electron-impact ionization cross sections for the formation of the CF_x (x=1–3) parent ions as a function of electron energy. The various plot symbols denote CF_3^+ (●), CF_2^+ (■), and CF^+ (▼). Also indicated is the total uncertainty of each absolute cross section at an impact energy of 70 eV.

improve the statistical accuracy of the cross section shapes. The raw data were corrected for variations in both the electron beam current and the neutral beam flux. In addition, small corrections (less than 5%) were made to the measured shapes below 50 and above 150 eV as discussed by Wetzel *et al.*[24] [cf. Eq. (15) in their paper]. The absolute parent ionization cross sections for the three CF_x (x =1–3) radicals are shown in Fig. 4 and the cross section values are also given in Table I. Several independent absolute measurements were made for each species over a period of several days at a fixed electron energy of 70 eV. These measurements yielded average values of 1.25 ± 0.05 Å^2 ($\pm4.0\%$ uncertainty), 1.03 ± 0.07 Å^2 ($\pm6.8\%$ uncertainty), and 0.38 ± 0.04 Å^2 ($\pm10.5\%$ uncertainty) for, respectively, CF, CF_2, and CF_3. The uncertainties refer to the one-standard deviation statistical uncertainty in the absolute calibration. The larger uncertainty in the case of the CF_3 radical is due to (1) neutral beam fluctuations and instabilities which were less prominent for the CF and CF_2 beams and (2) the smaller CF_3 ionization cross section. When combined (in quadrature) with other statistical and systematic uncertainties which are typically in the range $\pm12\%$–14% (cf. Refs. 24–26 for a detailed discussion), overall uncertainties in the cross sections of $\pm15\%$ (CF), $\pm16\%$ (CF_2), and $\pm18\%$ (CF_3) were obtained yielding absolute cross section values at 70 eV of 1.25 ± 0.19, 1.03 ± 0.16, and 0.38 ± 0.07 Å^2 for, respectively, CF, CF_2, and CF_3. These error margins have been indicated in the cross section data displayed in Fig. 4. We note that all measurements for the CF_2 radical were carried out under experimental conditions where the neutral beam was essentially free from any measurable metastable contamination (cf. discussion in Sec. III A).

The only other measurements of the CF_x parent ionization cross sections are two previous preliminary reports of this work[21,22] and the preliminary results of Wetzel *et al.*[20] which were limited to the CF_3 radical. The absolute cross sections reported earlier were systematically smaller than the current values by about 20%. The main reason for these discrepancies were (1) contaminants in the neutral radical beams and (2) a small offset in the reading of the lock-in amplifier which was used to measure the response of the pyroelectric crystal to the various neutral beams. Both effects tended to overestimate the neutral beam flux without contributing to the ion count rate. The problems associated with impurities in radical beams and the care that has to be exercised in the preparation and in the characterization of radical beams have also been discussed by Freund and collaborators[17–19] in connection with their studies of the electron-impact ionization of the SiF_x radicals. The effect of vibrational excitation of the radicals in the neutral beam is difficult to quantify. Threshold measurements, which are in principle suitable to investigate the presence and the level of vibrational excitation of the neutral beam species, were not sufficiently sensitive in the case of the CF_x radical beams to determine the precise level of vibrational excitation. For CF and CF_2, where the quality of the threshold data was best, we found some broadening and a slightly enhanced curvature of the cross section in the threshold region indicative of the presence of a small amount (0.5 eV or less) of vibrational excitation. While it

TABLE I. Cross sections for parent ionization of CF_3, CF_2, and CF by electron impact.

	Parent ionization cross section (Å^2)		
Electron energy (eV)	CF_3^+	CF_2^+	CF^+
10	0.015	0.05	···
11	0.029	0.09	···
12	0.041	0.15	0.03
13	0.060	0.18	0.07
14	0.099	0.26	0.13
15	0.111	0.35	0.18
16	0.145	0.39	0.23
17	0.157	0.42	0.28
18	0.167	0.47	0.33
19	0.194	0.55	0.40
20	0.204	0.64	0.45
22	0.270	0.69	0.55
24	0.303	0.73	0.63
26	0.315	0.78	0.70
28	0.320	0.82	0.76
30	0.325	0.87	0.81
32	0.329	0.89	0.86
34	0.335	0.91	0.91
36	0.338	0.93	0.95
38	0.346	0.96	0.99
40	0.350	0.98	1.01
45	0.358	0.99	1.08
50	0.360	1.01	1.15
55	0.372	1.03	1.18
60	0.374	1.03	1.23
65	0.380	1.05	1.25
70	0.376	1.03	1.25
80	0.368	0.99	1.26
90	0.365	0.96	1.25
100	0.350	0.91	1.23
120	0.342	0.86	1.14
140	0.333	0.78	1.04
160	0.318	0.67	0.90
180	0.306	0.58	0.79
200	0.292	0.49	0.67

is difficult to quantify the effect of vibrational excitation on our measured data, there is no experimental evidence that indicates that it is large. One might, in fact, argue as pointed out by Hayes *et al.*[18] that vibrational excitation may not be very important when the measured cross section data are used in modeling calculations of processing plasmas where the formation mechanisms for the various radicals might produce complex vibrational distributions similar to those obtained here.

A direct comparison of our experimental data with theoretical cross section calculations is all but impossible. There are no reliable theoretical models to calculate absolute partial or total electron-impact ionization cross sections for complex molecules and radicals. On the other hand, improved semiempirical methods, new additivity rules, and attempts aimed at incorporating some detailed molecular structure information into model calculations have been underway for some time and have to date been applied to a few selected molecules and radicals.[14,15] However, all these models facilitate only the calculation of the total cross section for single ionization, i.e., the cross section summed over all channels and thus combining the parent ionization with all possible dissociative ionization channels. This prevents a direct comparison of our measured parent ionization cross sections with the results of these calculations. The only situation where there is some justification for a meaningful comparison is in the case of the CF radical. There are only two unobserved dissociative ionization channels for CF, viz., the formation of C^+ and F^+ ions, respectively. Previous work in SiF_x by Freund and collaborators[17–19] and in CF_4 by Bruce and Bonham[34] and by Märk[35] suggests that the cross section for F^+ formation is most likely very small. A modified additivity rule[14,36] predicts a total single ionization cross section for the CF radical of 1.5 Å^2 at 70 eV, while a second model[14,36] which combines a Mulliken population analysis with an improved Gryzinski-type formula, the so-called DM formalism,[37] predicts a value of 2.4 Å^2 at the same energy. This should be compared with our measured value of 1.25 $\pm$0.19 Å^2 (at 70 eV) for the formation of only the CF^+ parent ion. Experimental efforts to measure the cross sections for the dissociative ionization channels of all CF_x radicals are currently underway in our laboratory. The results of these measurements will facilitate a more meaningful test of the calculations. Adding the cross sections for the formation of the C^+ and F^+ fragment ions to the cross section for formation of the CF^+ parent ion will most likely result in a better agreement between experiment and the calculations.

IV. CONCLUSIONS

We report absolute electron-impact cross sections for the parent ionization processes $CF_3 \rightarrow CF_3^+$, $CF_2 \rightarrow CF_2$, and $CF \rightarrow CF^+$ as a function of impact energy from threshold to 200 eV. Absolute values at 70 eV were measured to be 1.25$\pm$0.19 Å^2 (CF), 1.03$\pm$0.16 Å^2 (CF_2), and 0.38 $\pm$0.07 Å^2 (CF_3). The CF_x neutral beams were produced by near-resonant charge transfer between ground state radical ions and Xe. All absolute cross section measurements were carried out under experimental conditions where the fast neutral beams consisted predominantly of radicals in the electronic ground state. Some level of vibrational excitation of the parent radicals was observed (typically 0.5 eV or less), but we do not have any experimental evidence that would suggest that the effect of vibrational excitation on the cross sections is significant.

ACKNOWLEDGMENTS

We are very grateful to Dr. R. S. Freund and R. C. Wetzel for many helpful discussions and for their invaluable advice and assistance during the course of this work. Thanks must go to Professor R. A. Bonham for his interest in this work and for many helpful discussions. We would also like to thank Professor H. Deutsch, Dr. M. Schmidt, and Dr. R. Basner for many stimulating discussions. We acknowledge the expert technical assistance provided by J. Altmann and his staff in the machine shop and by Feng Du in the electronics shop. The material presented in this publication is based on work supported in part by the National Science Foundation through Grants No. CTS-8902405 and No. CTS-9017211 and by the City University of New York through PSC-CUNY Grant No. 663353. Additional support through a NATO Collaborative Research Grant (No. CRG-920089) is also gratefully acknowledged.

[1] I. Iga, M. V. V. S. Rao, S. K. Srivastava, and J. C. Nogueira, Z. Phys. D **24**, 111 (1992).
[2] C. Ma, M. R. Bruce, and R. A. Bonham, Phys. Rev. A **44**, 2912 (1991).
[3] S. Wang, J. L. Forand, and J. W. McConkey, Can. J. Phys. **67**, 699 (1989).
[4] U. Müller, T. Bubel, G. Schulz, A. Sevilla, J. Dike, and K. Becker, Z. Phys. D **24**, 131 (1992).
[5] M. R. Bruce, C. Ma, and R. A. Bonham, Chem. Phys. Lett. **190**, 285 (1992).
[6] M. B. Roque, R. B. Siegel, K. E. Martus, V. Tarnovsky, and K. Becker, J. Chem. Phys. **94**, 341 (1991).
[7] J. Sasaki, I. Kuen, and F. Howorka, J. Chem. Phys. **88**, 1938 (1987).
[8] H. U. Poll, C. Winkler, V. Grill, D. Margreiter, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. **112**, 1 (1992).
[9] U. Müller, W. Haas, and R. Brenn, Chem. Phys. Lett. **201**, 382 (1993).
[10] I. R. Lambert, S. M. Mason, R. P. Tuckett, and A. Hopkirk, J. Chem. Phys. **89**, 2683 (1988); J. F. M. Aarts, S. M. Mason, and R. P. Tuckett, Mol. Phys. **60**, 761 (1987).
[11] Extensive lists of references to earlier work regarding experimental and theoretical studies of electronic and atomic collision processes with the CF_4 molecule can be found in the above listed Ref. 1–10.
[12] C. J. Mogab, A. C. Adams, and D. L. Flamm, J. Appl. Phys. **49**, 3796 (1978).
[13] C. I. M. Beenakker, J. H. J. van Dommelen, and R. P. J. van der Poll, J. Appl. Phys. **52**, 480 (1981).
[14] D. Margreiter, H. Deutsch, M. Schmidt, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. **100**, 157 (1990).
[15] H. Deutsch, C. Cornelissen, L. Cespiva, V. Bonacic-Koutecky, D. Margreiter, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. (in press).
[16] F. A. Biaocchi, R. C. Wetzel, and R. S. Freund, Phys. Rev. Lett. **53**, 771 (1984).
[17] T. R. Hayes, R. C. Wetzel, F. A. Biaocchi, and R. S. Freund, J. Chem. Phys. **88**, 823 (1988).
[18] T. R. Hayes, R. J. Shul, F. A. Biaocchi, R. C. Wetzel, and R. S. Freund, J. Chem. Phys. **89**, 4035 (1989).
[19] R. J. Shul, T. R. Hayes, R. C. Wetzel, F. A. Biaocchi, and R. S. Freund, J. Chem. Phys. **89**, 4042 (1989).
[20] R. C. Wetzel, F. A. Biaocchi, and R. S. Freund, contributed paper, 37th Gaseous Electronics Conference, Boulder, CO, 1983.
[21] V. Tarnovsky and K. Becker, Bull. Am. Phys. Soc. **37**, 1130 (1992).
[22] V. Tarnovsky, K. Becker, H. Deutsch, and T. D. Märk, Bull. Am. Phys. Soc. **37**, 2009 (1992).

[23] V. Tarnovsky and K. Becker, Int. J. Mass Spectrom. Ion Proc. (submitted for publication).
[24] R. C. Wetzel, F. A. Biaocchi, T. R. Hayes, and R. S. Freund, Phys. Rev. A **35**, 559 (1987).
[25] R. S. Freund, R. C. Wetzel, R. J. Shul, and T. R. Hayes, Phys. Rev. A **41**, 3575 (1990).
[26] V. Tarnovsky and K. Becker, Z. Phys. D **22**, 603 (1992).
[27] D. Rapp and P. Englander-Golden, J. Chem. Phys. **43**, 1464 (1965).
[28] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Chunney, and R. L. Nuttall, J. Phys. Chem. Ref. Data **11**(2), 1 (1982).
[29] *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions* (Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., U.S. Government Printing Office, Washington, D.C., 1969), No. 36.
[30] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levine, and W. G. Mallard, J. Phys. Chem. Ref. Data, **17**(1), 1 (1988).
[31] M. W. Chase, Jr., K. A. Davis, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data, **14**(1), 1 (1985).
[32] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand–Reinhold, New York, 1966), Vol. 1.
[33] G. Herzberg, *The Spectra and Structure of Simple Free Radicals* (Cornell University, Ithaca, NY, 1970).
[34] M. R. Bruce and R. A. Bonham, Int. J. Mass Spectrom. Ion Proc. **123**, 97 (1993).
[35] H. U. Poll, C. Winkler, V. Grill, D. Margreiter, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. **112**, 1 (1992).
[36] H. Deutsch (private communication, 1992).
[37] H. Deutsch and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. **79**, R1 (1987).