Absolute cross sections for the electron impact ionization of the NF_2 and NF free radicals

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We report measurements of the absolute cross sections for the electron-impact ionization of the NF_2 and NF free radicals from threshold to 200 eV. At 70 eV, the absolute parent NF_2 and NF ionization cross section are 1.25 ± 0.23 Å^2 and 1.05 ± 0.19 Å^2, respectively. We found little evidence of the presence of vibrationally excited radicals in the incident target beam for both NF_2 and NF. We also studied the dissociative ionization of NF_2 and NF. The absolute cross section for the formation of the NF^+ fragment ions from NF_2 was found to be 0.75 ± 0.15 Å^2 at 70 eV. The NF^+ fragment ions are formed with little excess kinetic energy. The only significant pathway leading to the observed NF^+ fragment ions is the single positive ion formation. Our data show no indication of the presence of double positive ion formation channels or positive–negative ion pair formation processes. Cross sections for the formation of the atomic fragment ions F^+ and N^+ from both NF_2 as well as NF were found to be small with maximum values of less than 0.1 Å^2 at 70 eV in all cases.

I. INTRODUCTION

The NF_3 molecule is a widely used constituent of low-temperature processing plasmas used in the plasma-assisted etching of Si, SiO_2, Mo, and $MoSi_2$ and of other refractory metal silicides.[1–5] The reactive species in a NF_3-containing plasma are primarily parent ions, fragment ions, and reactive neutral radicals such as NF_2 and NF which are produced by electron collisions with the parent NF_3 molecule. Experimental and theoretical studies of collision processes involving the NF_3 molecule are scarce. Parent and fragment emissions from the vacuum ultraviolet to the near infrared produced by single electron impact on NF_3 have been measured extensively in our laboratory.[6–10] Earlier mass spectroscopic investigations of the electron impact ionization of NF_3 have been carried out[11] and recently, the electron-impact ionization of NF_3 has been studied by two groups.[12,13] Data on collisions with the NF_2 and NF free radicals do not exist to our knowledge. Experimentally determined absolute cross sections for the ionization and dissociative ionization of several other fluorine-containing free radicals, viz. SiF_x and CF_x ($x=1$–3), have also been reported recently.[14–18] In addition, calculations of total single ionization cross sections of these species using improved semiempirical and semiclassical methods have been carried out by Deutsch, Märk, and collaborators.[19–22]

In this paper, we present absolute partial ionization cross sections for the parent and dissociative ionization of NF_2 and NF by electron impact from threshold to 200 eV using the fast-neutral-beam technique. Careful studies of the near-threshold region of the parent ionization cross sections were carried out which served as a check for the purity of the incident fast beam, i.e., as a check for the presence or absence of Rydberg radicals, radicals in metastable states and vibrationally excited radicals in the incident fast neutral beam. Near-threshold studies of the dissociative ionization cross sections determine the appearance energies of the various fragment ions which when compared to spectroscopically and thermochemically determined minimum energies for the formation of a particular fragment ion provide insight into the mechanism through which this fragment ion is formed and give an indication of the excess kinetic energy released in the dissociation process.

II. EXPERIMENTAL DETAILS

A description of the experimental apparatus and of the experimental procedure can be found in previous publications.[13,18,23,24] Briefly, a dc Colutron discharge through NF_3 operated at a positive bias of typically 3–3.5 kV in conjunction with a Wien filter for mass selection serves as the source for fast primary NF_2^+ and NF^+ ion beams. Neutrals are formed by passing the ion beam through a low-pressure charge exchange cell filled with Xe. The Xe ionization energy of 12.14 eV is close to the ionization energies of NF_2 and NF which are respectively 11.63 and 12.26 eV,[25] so that the condition for near-resonant charge transfer is satisfied in both cases. The residual ions are removed from the beam by electrostatic deflection and most Rydberg molecules are quenched by passing the beam through a region of high electric field (typically 5 kV/cm). The neutral beam is subsequently crossed by a well-characterized electron beam of variable energy (5–200 eV). The product ions are focused in the entrance plane of an electrostatic hemispherical analyzer which separates ions of different energy (i.e., charge state). The ions after leaving the analyzer are detected by a channel electron multiplier (CEM) operated in the pulse counting mode. Although the apparatus is in principle capable of determining absolute ionization cross sections without normalization to theory or previous experiments, we followed the previously described procedure of using the well-established Kr or Ar absolute ionization cross sections to calibrate the pyroelectric crystal (see, e.g., Tarnovsky and Becker[26]).

Fragment ions resulting from the dissociative ionization of a molecule are often formed with a certain amount of excess kinetic energy which can interfere with the complete extraction of the ions from the interaction region and/or can cause ion losses during the transport of the ions from the

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interaction region to the detector.[18,27,28] The "open" design of the fast-beam apparatus[18] enables the 100% detection of fragment ions formed with excess kinetic energies of up to several electronvolts with essentially 100% efficiency in most cases. Extensive ion trajectory modeling calculations using the SIMION software package[29] were carried out in connection with absolute cross section measurements for the dissociative ionization of the CF_x (x=1–3) free radicals using the same fast-beam apparatus.[18] It was demonstrated that no significant ion losses occur in these cases as long as the excess kinetic energies are less than about 5 eV per molecular fragment ion and less than 4 eV per fragment for the atomic fragment ions. Since the ratio of fragment mass to parent mass is the crucial factor determining the ion trajectory after the break-up of the parent molecule in the interaction and since NF_x and CF_x (x=1,2) have very similar masses, the results of the CF_x ion trajectory modeling calculations applied essentially unchanged to the case of NF_2 and NF.

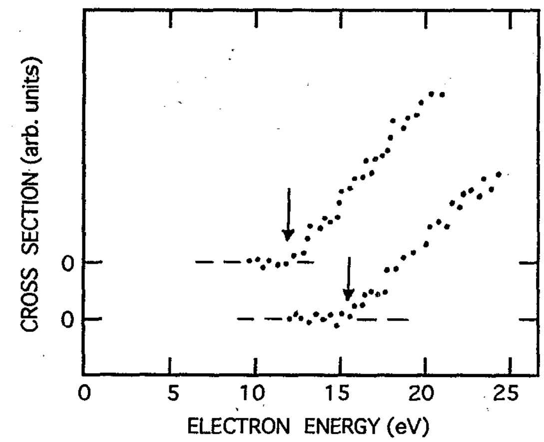

FIG. 1. Ionization threshold for the formation of NF_2^+ parent ions (top data set) and NF^+ fragment ions (bottom data set) from NF_2. The threshold for each data set has been marked by an arrow.

III. RESULTS AND DISCUSSION

Absolute NF_2 and NF parent ionization cross sections were measured from threshold to 200 eV with special emphasis on the near-threshold region. As demonstrated previously in the case of CF_x and NF_3 parent ionization cross sections detailed studies of the cross sections in the near-threshold region can serve as an *in situ* check of the purity of the fast neutral beam, i.e., as a check for the presence or absence of Rydberg molecules, molecules in metastable states and vibrationally excited molecules in the incident beam formed in the charge-transfer process.[18] In the case of the dissociative ionization, the near-threshold measurements determine the appearance energy of the various fragments which when compared to spectroscopically and thermochemically determined minimum energies for the formation of a particular fragment ion provide insight into the mechanism through which this fragment ion is formed and give an indication of the excess kinetic energy released in the dissociation process.[30–32]

A. The electron-impact ionization of NF_2

Figure 1 shows the measured threshold data for the formation of the NF_2^+ parent ions (top data set) and of the NF^+ fragment ions (bottom data set) from NF_2. Both data sets display the cross section in arbitrary units as a function of electron energy. Both threshold data sets are the result of several individual data runs which were combined after each data set was corrected for the contact potential (which was determined relative to the Xe^+ appearance energy) and for possible contributions from Rydberg molecules to the ion signal. Both data sets display prominent thresholds with little enhanced curvature which indicates that there are few, if any, vibrationally excited NF_2 radicals in the incident fast neutral beam. The NF_2^+ parent ion data (top data set) show an appearance energy of 11.8±0.4 eV which is very close to the 11.63±0.05 eV ionzation energy of the NF_2 radical.[25] The NF_2^+ cross section rises smoothly from threshold with increasing impact energy. The NF^+ fragment ion data (bottom data set) display an onset at 15.7±0.4 eV which is very close to the 15.12±0.15 eV minimum energy required for the break-up of NF_2 into NF^+ and F.[25,30–32] We attribute the observed onset to this process and note that the NF^+ fragment ions are formed with little excess kinetic energy. None of the threshold data sets for NF^+ from NF_2 displayed evidence of any structure in the energy range around 33 eV, which is the onset of the double positive ion pair formation $NF_2 \rightarrow NF^+ + F^+$. Positive ion pair formation was found to be a significant channel in the dissociative ionization of the CF_2 radical[18] and in the formation of NF^+ fragment ions from the NF_3 molecule.[13] Furthermore, no evidence was found in the NF^+ threshold data of an ion signal extending below the threshold for the single positive ion formation $NF_2 \rightarrow NF^+ + F$ which indicates that the positive–negative ion pair formation process $NF_2 \rightarrow NF^+ + F^-$ which was observed previously in the dissociative ionization of the SiF_x radicals[14–16] plays no role in the case of the dissociative ionization of the NF_2 radical.

Figure 2 shows the absolute cross sections for the formation of the NF_2^+ parent ions (●) and of the NF^+ fragment ions (■). The parent cross section was obtained by normalizing the measured relative cross section function to the Kr benchmark cross section at 70 eV. The relative measured

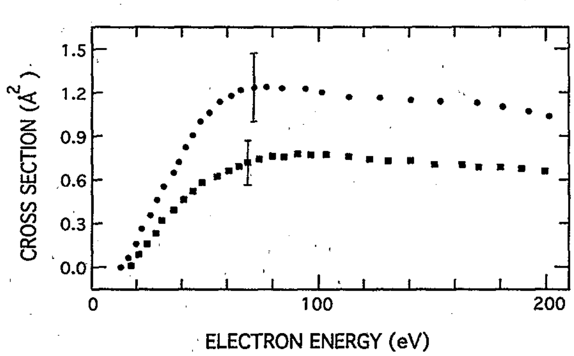

FIG. 2. Absolute cross sections for the formation of NF_2^+ parent ions (●) and NF^+ fragment ions (■) from NF_2 as a functon of electron impact energy. The absolute uncertainties are indicated by the error bars at 70 eV.

TABLE I. Absolute cross sections for the ionization of NF_2 by electron impact. The cross sections are given in units of $Å^2$ $(=1\times10^{-16}$ $cm^2)$.

	Ionization cross section (in $Å^2$)	
Electron energy (eV)	NF_2^+	NF^+
12	0.01	...
13	0.02	...
14	0.03	...
15	0.05	...
16	0.07	0.01
17	0.09	0.04
18	0.12	0.07
19	0.15	0.10
20	0.18	0.13
22	0.23	0.17
24	0.29	0.21
26	0.34	0.24
28	0.40	0.27
30	0.45	0.30
32	0.51	0.34
34	0.57	0.37
36	0.64	0.41
38	0.70	0.45
40	0.76	0.49
45	0.91	0.54
50	1.05	0.61
60	1.21	0.68
70	1.25	0.75
80	1.24	0.78
90	1.23	0.79
100	1.21	0.78
120	1.18	0.76
140	1.16	0.73
160	1.13	0.72
180	1.10	0.70
200	1.05	0.68

dissociative ionization cross section was normalized with respect to the parent NF_2 ionization cross section. The absolute NF_2^+ and NF^+ cross section values are also listed in Table I. At 70 eV, we determined absolute cross sections of 1.25 ±0.23 $Å^2$ (NF_2^+) and 0.75 ± 0.15 $Å^2$ (NF^+). The NF_2^+ cross section peaks around 70–80 eV and falls off slowly toward higher impact energies to a value slightly above 1 $Å^2$ at 200 eV. The NF^+ cross section, on the other hand, rises more slowly to a broad maximum of about 0.8 $Å^2$ in the energy range 80–100 eV followed by a gradual decline with increasing impact energy to about 0.7 $Å^2$ at 200 eV. We assign an overall uncertainty of $\pm18\%$ to the absolute parent ionization cross section which is the same uncertainty that we determined previously for the $CF_x(x=1-3)$ and NF_3 parent ionization cross sections.[13,17] As before in the case of the dissociative ionization of the CF_x radicals,[18] we assign a slightly larger uncertainty of $\pm20\%$ to the NF^+ cross section from NF_2. Based on the small excess kinetic energy of the NF^+ fragment ions as inferred from the measured appearance energy (see discussion above) we do not expect any significant losses of NF^+ ions. No appreciable ion signals corresponding to the formation of the atomic fragment ions N^+ and F^+ were found and we put a conservative upper limit on the combined N^+ and F^+ cross section of 0.1 $Å^2$ at 70 eV.

It is interesting to compare the measured cross sections for the ionization and dissociative ionization of NF_2 with the previously measured CF_2 and SiF_2 cross sections.[14–18] There are noteworthy similarities as well as significant differences. The SiF_2, NF_2, and CF_2 parent ionization cross sections are all similar in magnitude. Two channels were found to contribute to the formation of the CF^+ fragment ions, viz. the single positive ion formation as well as the double positive ion formation.[18] By contrast, the single positive ion formation is the only channel that was identified in the formation of the NF^+ and SiF^+ fragment ions. While the overall absolute CF^+ cross section at 70 eV was larger than the CF_2 parent ionization cross section by about 15%, the contribution to the CF^+ cross section that is attributable to the single positive ion formation is smaller than the CF_2^+ cross section by about 20%. This is similar to what we found in the case of the NF^+ and NF_2^+ cross sections from NF_2 where the parent ionization cross section was also larger (by about 40%) than the fragment ion cross section. The cross section for the formation of SiF^+ fragment ions from SiF_2, on the other hand, was almost twice as large as the SiF_2^+ cross section at 70 eV.[15] Both fragment ions NF^+ from NF_2 and CF^+ from CF_2 are formed with little excess kinetic energy as was the SiF^+ ion from SiF_2.[15] However, the threshold regions for the SiF_2^+ and the SiF^+ cross sections were found to exhibit significant structure which indicated that several different processes contributed to the observed ion signal in each case. This is not the case for NF_2^+, NF^+, CF_2^+, and CF^+. Furthermore, while the atomic Si^+ fragment ions from SiF_2 were observed with significant intensity (cross section of 0.5 $Å^2$ at 70 eV), neither the corresponding N^+ fragment ions from NF_2 nor the C^+ fragment ions from CF_2 were observed with appreciable intensity (cross sections below 0.1 $Å^2$ at 70 eV). Atomic fluorine ions, F^+, on the other hand, were not observed from SiF_2 or NF_2, but they were produced in the dissociative ionization of CF_2 via two channels, the single positive ion formation $CF_2\rightarrow CF+F^+$ and the positive ion pair formation $CF_2\rightarrow CF^++F^+$.

B. The electron-impact ionization of NF

Figure 3 shows the threshold data for the formation of NF^+ parent ions. The data set displays the cross section in arbitrary units as a function of electron energy. The threshold data are the result of several individual data runs which were combined after each data set was corrected for the contact potential (which was determined relative to the Xe^+ appearance energy) and for possible contributions from Rydberg molecules to the ion signal. The data sets displays a prominent onset at 12.1 ± 0.4 eV with slightly enhanced curvature which is indicative of the presence of a some vibrationally excited NF radicals in the incident fast neutral beam. A comparison of the region of curvature in the NF^+ data with the curvature of the Xe^+ threshold data suggests a level of vibrational excitation of at most 0.3 eV. Previous experience provided no evidence that such a comparatively small level of vibrational excitation will affect the measured absolute ionization cross sections.[13,18,19] The measured onset of 12.1 eV is in good agreement with the well-known 12.26 ± 0.05 eV ionization energy of the NF radical.[25]

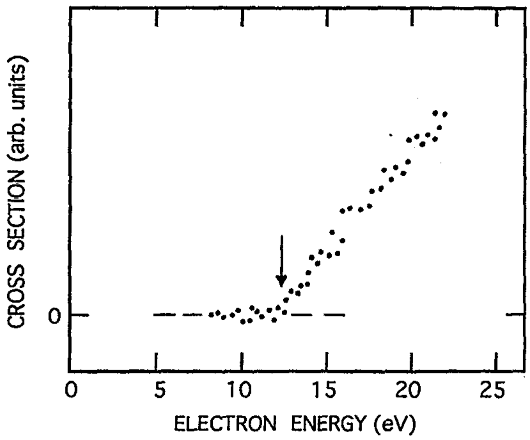

FIG. 3. Ionization threshold for the formation of NF^+ parent ions from NF. The threshold has been marked by an arrow.

Figure 4 shows the absolute NF ionization cross section. The relative cross section was measured from threshold to 200 eV and put on an absolute scale by normalization relative to the Kr benchmark cross section. The cross section values are also listed in Table II. At 70 eV, we determined an absolute cross sections of 1.05±0.19 Å^2. The NF^+ cross section rises gradually and peaks in the range 90–110 eV with a maximum value of 1.10 Å^2. The decline toward higher impact energies is gradual. We assign an overall uncertainty of ±18% to the absolute NF ionization cross section which is the same uncertainty that we assigned to the NF_2 and NF_3 parent ionization cross sections.[13] As before in the case of the NF_2 radical, no appreciable ion signals corresponding to the formation of the atomic fragment ions N^+ and F^+ were found and we put a conservative upper limit on the combined N^+ and F^+ cross section of 0.1 Å^2 at 70 eV.

A comparison of the NF ionization cross section with the CF and SiF ionization cross sections[16–18] reveals that both the NF and the CF ionization cross sections are similar in magnitude and in shape and both are much smaller than the SiF ionization cross section. For both the NF and the CF radicals, the dissociative ionization, i.e., the formation of atomic fragment ions N^+ or C^+, respectively, and F^+ plays only a very minor role with peak cross sections of less than 0.1 Å^2 at 70 eV. In the case of the SiF radical, on the other hand, the cross section for the production of Si^+ fragment ions exceeds 2 Å^2 at 70 eV, whereas the formation of F^+ fragment is also only a minor channel with a peak cross section of about 0.25 Å^2.

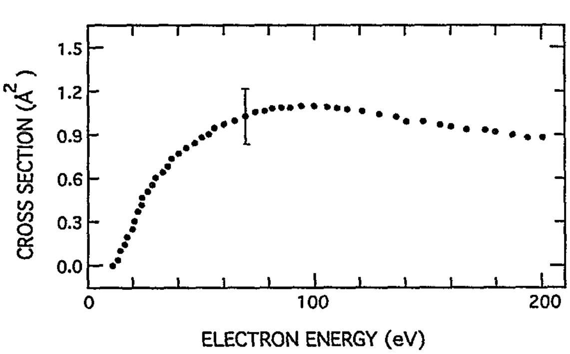

FIG. 4. Absolute cross sections for the formation of the NF^+ (●) parent ions from NF as a function of electron energy. The absolute uncertainty is indicated by the error bar at 70 eV.

TABLE II. Absolute cross sections for the ionization of NF by electron impact. The cross sections are given in units of Å^2 ($=1\times10^{-16}$ cm^2).

Electron energy (eV)	Ionization cross section (in Å^2) NF^+
13	0.02
14	0.06
15	0.11
16	0.16
17	0.19
18	0.24
19	0.27
20	0.32
22	0.36
24	0.43
26	0.50
28	0.56
30	0.61
32	0.63
34	0.66
36	0.71
38	0.75
40	0.78
45	0.84
50	0.90
60	1.00
70	1.05
80	1.08
90	1.09
100	1.10
120	1.07
140	1.00
160	0.97
180	0.94
200	0.89

IV. CONCLUSIONS

We studied the electron-impact ionization of the NF_2 and NF free radicals by means of the fast-beam technique. Absolute ionization cross sections were measured from threshold to 200 eV for the formation of the NF_2^+ parent ions and NF^+ fragment ions from NF_2. At an impact energy of 70 eV, we determined cross sections of 1.25±0.23 Å^2 (NF_2^+) and 0.75 ±0.15 Å^2 (NF^+). The NF^+ fragment ions are formed with very little excess kinetic energy and the only mechanism contributing to the NF^+ ion signal is the single ion formation $NF_2 \rightarrow NF^+ + F$. The ionization of the NF radical results in a NF^+ parent ionization cross section of 1.05±0.0.19 Å^2 at 70 eV. For both free radicals NF_2 and NF, the formation of the atomic fragment ion N^+ and F^+ is not a significant process. In each case, the combined N^+ and F^+ cross sections are less than 0.1 Å^2 at 70 eV.

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