Electron impact ionization of the SF_5 and SF_3 free radicals

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We measured absolute cross sections for the electron-impact ionization and dissociative ionization of the SF_5 and SF_3 free radicals from threshold to 200 eV using the fast-neutral-beam technique. The total single ionization cross sections at 70 eV were found to be 5.1×10^{-16} cm^2 (SF_5) and 3.2×10^{-16} cm^2 (SF_3). The cross sections reach their maximum at about 100 eV for both radicals, with values of 5.4×10^{-16} cm^2 (SF_5) and 3.5×10^{-16} cm^2 (SF_3). Dissociative ionization is important only for SF_5, where the SF_5^+ parent ionization cross section and the SF_4^+ fragment ionization cross sections have roughly the same value. By contrast, the ionization of SF_3 is dominated by the formation of SF_3^+ parent ions. A comparison of the measured total single ionization cross sections with calculated cross sections, using a modified additivity rule, shows excellent agreement for both radicals in terms of the absolute cross section values and the cross section shapes. Total single ionization cross sections were also calculated for SF_4, SF_2, and SF. [S0021-9606(98)00940-4]

I. INTRODUCTION

Sulfur hexafluoride, SF_6, is one of the most thoroughly studied polyatomic molecules in terms of its interaction with electrons, in particular in terms of positive and negative ion formation processes and breakdown characteristics. This is due to the early recognition of the excellent properties of SF_6 as an insulating dielectric gas, and its widespread use (i) in the electric power industry for electrical insulation in power generation, transmission, distribution and sub-station equipment, (ii) for pulsed power generation, (iii) in gas lasers, and (iv) more recently, also for plasma processing. It is interesting to note that more than 80% of the articles in the recent *Proceedings of the VIII International Symposium on Gaseous Dielectrics*[1] deal with experimental and theoretical studies involving ion formation processes and breakdown phenomena in SF_6 and SF_6-containing gas mixtures. Positive ion formation following electron impact on SF_6 under controlled single collision conditions has been studied experimentally by Rapp and Englander-Golden,[2] who measured the total SF_6 ionization cross section, and by Stanski and Adamzyk[3] and Märk and co-workers,[4] who determined the partial SF_6 ionization cross sections using two different mass spectrometric techniques. The total SF_6 ionization cross section has also been calculated by Kim and co-workers using the BEB approach,[5] and by Deutsch *et al.*[6] using a modified additivity rule. The two calculated cross sections agree very well with one another, and with the experimentally determined cross section. A summary of negative ion formation processes (i.e., electron attachment and dissociative attachment) following electron impact on SF_6 can be found in Refs. 7–9 which include the comprehensive review of Christophorou *et al.*[8] By contrast, there is virtually no information available regarding the interactions of electrons with the SF_x ($x=1-5$) free radicals which are readily produced from the parent SF_6 molecule by collisional dissociation and photodissociation. Sugai and co-workers reported relative neutral dissociation cross sections for SF_6 leading to the formation of SF, SF_2, and SF_3 radicals using an appearance energy mass spectrometric technique,[10] but were unable to put their relative cross sections on an absolute scale because of the lack of available radical ionization cross sections.

In this paper, we report absolute partial cross sections for the electron-impact ionization and dissociative ionization of the SF_5 and SF_3 free radicals, from threshold to 200 eV, using the fast-neutral-beam technique. SF_5 and SF_3 are the most abundant species in the mass spectral cracking pattern of SF_6, which does not have a stable parent ion,[11,12] and SF_5^+ and SF_3^+ are the ions with the largest partial SF_6 ionization cross section.[3,4] For both targets, the total single ionization cross section was determined from the measured partial ionization cross sections, and compared with the calculated total single ionization cross sections based on a modified additivity rule.[6] Excellent agreement between measured and calculated cross sections was found for both radicals, in terms of the absolute cross section values and the cross section shapes. Calculated total single ionization cross sections are also given for the SF_4, SF_2, and SF free radicals.

II. EXPERIMENTAL DETAILS

A detailed description of the fast-beam apparatus and of the experimental procedure employed in the determination of absolute partial ionization cross sections has been given in previous publications from this laboratory.[13–17] The primary ion source is a commercially available Colutron source which can be operated in two different modes. In the standard mode of operation, a dc discharge between a heated filament and an anode through a suitably chosen feed gas, in this case SF_6, serves as the source of positively charged primary ions. In the case of SF_6, which has no stable parent ion, the discharge produces a mixture of SF_x^+ $(x=0-5)$ ions. These primary ions are accelerated to about 2–3 keV, mass selected in a Wien filter, and sent through a charge-transfer cell filled with a suitably chosen charge-transfer gas for resonant or near-resonant charge-transfer of a fraction of the primary ions. We were able to obtain sufficiently intense and sufficiently stable primary ion beams only for the two most intense fragment ions SF_5^+ and SF_3^+. The primary SF_4^+, SF_2^+, and SF^+ ion beams were too weak to allow us to produce neutral target beams of sufficient intensity and stability for reliable ionization cross section measurements. For both SF_5^+ and SF_3^+, whose ionization energies are in the range 10.5–12.0 eV,[18–20] Xe with an ionization energy of 12.14 eV[18] was found to be an appropriate charge neutralization target. The residual ions in the beam were removed from the neutral target gas beam by electrostatic deflection, and most species in Rydberg states are quenched in a region of high electric field.

As an alternative, we can operate the Colutron source as a source of negative primary ions as reported in our recent paper on the ionization of the fullerene C_{60}.[17] In this mode of operation, which is suitable for targets with large cross sections for attachment and dissociative attachment at very low (near-zero) energies, the heated filament serves as a source of zero-energy or near-zero-energy electrons and no (or only a small) voltage is applied between the filament and the anode. Negative ions are then produced by attachment and dissociative attachment. After acceleration to 2–3 kV, the extra electron is readily stripped from the negative ion by collisions in the charge-transfer cell filled with an appropriately chosen collision partner, or simply by collisions with background gas molecules in the vacuum chamber. In the case of SF_6, the most abundant negative ions formed under these circumstances are SF_6^-, SF_5^-, and, to a smaller extent, also F^-, as one would expect on the basis of the SF_6 attachment and dissociative attachment cross sections.[7–9] This mode of operation of the ion source also did not allow us to extract sufficiently intense primary ion beams to form neutral SF_4, SF_2, and SF beams of workable intensities for the purpose of our experiments.

The fast neutral target beam is subsequently crossed at right angles by a well-characterized electron beam (5–200 eV beam energy, 0.5 eV FWHM energy spread, 0.03–0.4 mA beam current). The product ions are focused in the entrance plane of an electrostatic hemispherical analyzer which separates ions of different charge-to-mass ratios (i.e., parent ions from fragment ions). The ions leaving the analyzer are detected by a channel electron multiplier (CEM). Absolute calibration of the relative cross sections can be achieved in two ways. The fast-beam apparatus affords the capability to measure all quantities that determine the absolute cross section directly. The target density, which is perhaps the most difficult quantity to determine, is obtained from the energy deposited by the fast target beam into a pyroelectric detector, which is first calibrated relative to a well-characterized ion beam.[13,15] As an alternative, the well-established Kr or Ar absolute ionization cross sections can be used to calibrate the pyroelectric crystal. The calibrated detector, in turn, is then used to determine the flux of the neutral target beam in absolute terms. The second procedure avoids the frequent and prolonged exposure of the sensitive pyroelectric crystal to fairly intense ion beams.[14,16]

We established that all fragment ions produced by dissociative ionization of SF_5 and SF_3 with an excess kinetic energy of less than 5 eV per fragment ion (less than 2.5 eV per fragment ion in the case of F^+), are collected and detected with 100% efficiency using a combination of *in situ* experimental studies and ion trajectory modeling calculations.[16,21,22] Furthermore, careful threshold studies revealed little evidence of the presence of excited target species (vibrationally excited species, metastables, and species in high-lying Rydberg states) in the incident-neutral SF_5 and SF_3 beams.

III. RESULTS AND DISCUSSION

For both targets, SF_5 and SF_3, the measurements were limited to the formation of singly charged ions, since cross sections for the formation of doubly charged ions were found to be below the detection sensitivity of our apparatus (peak cross sections below 0.05×10^{-16} cm^2). The absolute cross sections reported here were determined with uncertainties of $\pm15\%$ for the parent ionization cross sections, and $\pm18\%$ for the dissociative ionization cross sections. These error margins, which are similar to what we quoted previously for ionization cross sections measured for other free radicals in the same apparatus,[21] include statistical uncertainties and all known sources of systematic uncertainties.

A. Measured partial ionization cross sections for SF_5 and SF_3

Figure 1 shows the absolute cross sections for the formation of SF_5^+ parent ions and SF_4^+ fragment ions from the SF_5 free radical from threshold to 200 eV. Both curves represent the result of a single data run. The peak cross sections for the formation of all other singly charged fragment ions were found to be less than 0.05×10^{-16} cm^2. The two cross section curves are very similar in magnitude and shape, except for a slight shift in the appearance energy of the SF_4^+ cross section to higher energies. We find cross sections at 70 eV (which is the typical electron energy for which data in mass spectral data bases are given) of $2.47\pm0.38\times10^{-16}$ cm^2 (SF_5^+) and $2.60\pm0.45\times10^{-16}$ cm^2 (SF_4^+). The cross section values are also listed in Table I for easier ref-

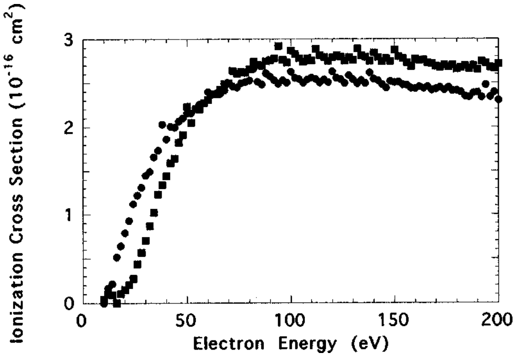

FIG. 1. Absolute cross sections for the formation of SF_5^+ parent ions (circles, ●) and SF_4^+ (squares, ■) fragment ions from SF_5 as a function of electron energy.

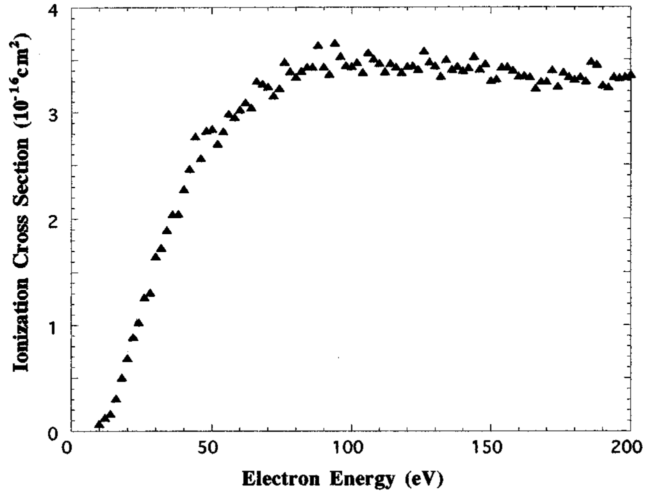

FIG. 2. Absolute cross sections for the formation of the SF_3^+ parent ions (triangles, ▲) from SF_3 as a function of electron energy.

erence. Note that the cross section values in Table I represent the average of several individual data runs. Both cross section curves reach their peak at somewhat higher energies around 100 eV, with maximum cross section values of 2.58 $\times 10^{-16}$ cm^2 (SF_5^+) and 2.82$\times 10^{-16}$ cm^2 (SF_4^+).

Figure 2 shows the absolute cross section for the formation of SF_3^+ parent ions from SF_3 from threshold to 200 eV. In contrast to the above case of SF_5, where we found essentially equal cross sections for the formation of the SF_5^+ parent ion and the SF_4^+ fragment ion, the electron impact ionization of SF_3 is totally dominated by the formation of parent ions. All other partial ionization cross sections for this radical were found to have peak values at or below 0.05 $\times 10^{-16}$ cm^2. We find a value for the SF_3^+ cross section of $3.2\pm 0.5\times 10^{-16}$ cm^2 at 70 eV, and a maximum cross section of 3.47$\times 10^{-16}$ cm^2 at about 100 eV. The cross section values are also listed in Table II for easier reference.

We also determined ionization energies for SF_5 and SF_3, and the appearance energies for SF_4^+ fragment ions from SF_5. Our values, which are summarized in Table III, are in good agreement with the experimental values reported in Ref. 10 and with published ionization energies and appearance energies based on thermochemical data.[12,17–20,23]

TABLE I. Absolute cross sections for the formation of $SF_5{}^+$ and $SF_4{}^+$ ions from SF_5 by electron impact. The cross sections are given in units of 10^{-16} cm^2.

Electron energy (eV)	Ionization cross section (in 10^{-16} cm^2)	
	$SF_5{}^+/SF_5$	$SF_4{}^+/SF_5$
12.0	0.10	⋯
14.0	0.24	⋯
16.0	0.40	0.11
18.0	0.54	0.20
20.0	0.69	0.28
22.0	0.84	0.43
24.0	1.09	0.57
26.0	1.20	0.70
28.0	1.32	0.87
30.0	1.45	1.02
35.0	1.69	1.39
40.0	1.95	1.65
45.0	2.05	1.95
50.0	2.15	2.17
60.0	2.35	2.39
70.0	2.47	2.60
80.0	2.54	2.71
90.0	2.56	2.80
100.0	2.58	2.82
120.0	2.56	2.78
140.0	2.52	2.75
160.0	2.42	2.70
180.0	2.39	2.67
200.0	2.34	2.63

TABLE II. Absolute cross sections for the formation of $SF_3{}^+$ from SF_3 by electron impact. The cross sections are given in units of 10^{-16} cm^2.

Electron energy (eV)	Ionization cross section (in 10^{-16} cm^2)
	$SiF_3{}^+/SF_3$
12.0	0.08
14.0	0.22
16.0	0.34
18.0	0.49
20.0	0.62
22.0	0.76
24.0	1.00
26.0	1.20
28.0	1.34
30.0	1.50
35.0	1.95
40.0	2.28
45.0	2.62
50.0	2.82
60.0	3.03
70.0	3.20
80.0	3.35
90.0	3.45
100.0	3.47
120.0	3.43
140.0	3.40
160.0	3.36
180.0	3.32
200.0	3.29

TABLE III. Ionization energies for SF_5 and SF_3 and the appearance energy for $SF_4{}^+$ ions from SF_5 as determined in this work in comparison with other measured and calculated data.

	Ionization/appearance energy (eV)		
Ion/parent	This work	Ref. 10 (experiment)	Refs. 12, 17–20, 23 (data tables)
$SF_5{}^+/SF_5$	11.2 ± 1.0	11.7	11.41
$SF_4{}^+/SF_5$	14.5 ± 1.0	15.5	14.83
$SF_3{}^+/SF_3$	11.0 ± 1.0	10.6	10.33

B. Total single ionization cross sections and comparison with calculations

As discussed in the recent paper by Deutsch *et al.*,[6] there is excellent agreement among the various measured total single ionization cross sections for SF_6, and between the experimental data and the two calculated cross sections using the modified additivity rule[6] and the BEB method.[5] We also used the modified additivity rule[6] to calculate the total single ionization cross sections for all SF_x ($x=1-5$) radicals. Figure 3 shows the total single ionization cross sections for SF_5 and SF_3 derived from the partial cross sections reported in this paper, in comparison with the calculated cross sections. The experimental data for SF_5 are the sum of the measured partial SF_5^+ and SF_4^+ cross sections. The agreement between the measured and calculated total single ionization cross sections is excellent over the entire range of impact energies from threshold to 200 eV. We note that no allowance was made in the experimental data for contributions to the cross section from the unobserved fragment ions (SF_3^+, SF_2^+, SF^+, S^+, and F^+). Thus, the experimental data represent a lower limit of the total single ionization cross section. Based on the very weak signals that we observed for ions other than SF_5^+ and SF_4^+, we put an upper limit on the contributions from all other singly charged ions of 0.25×10^{-16} cm^2 at 70 eV. The experimental data for SF_3 in Fig. 3 are identical to the partial SF_3^+ cross sections, and no allowance was made for contributions to the cross section from the unobserved fragment ions (SF_2^+, SF^+, S^+, and F^+). The experimental cross section thus represents a lower limit of the total single ionization cross section. As in the case of SF_3, the agreement between the measured and calculated SF_3 cross sections is excellent over the entire range of impact energies from threshold to 200 eV. Based on the very weak signals that we observed for ions other than SF_3^+ from SF_3, we put an upper limit on the possible contributions from all other singly charged ions of 0.2×10^{-16} cm^2 at 70 eV.

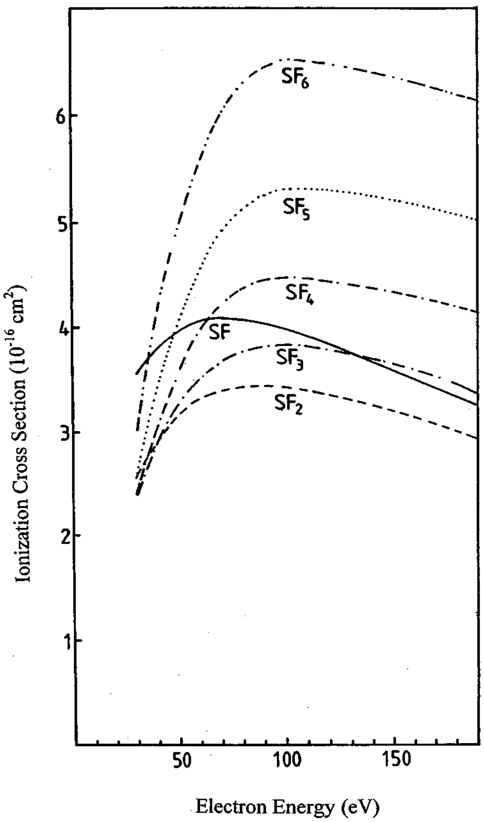

FIG. 4. Calculated total single ionization for SF_x ($x=1-6$) as a function of electron energy.

Figure 4 summarizes the calculated total single ionization cross sections for all five SF_x ($x=1-5$) radicals and the stable SF_6 molecule. We note the partial ''inversion'' of the calculated cross sections. Inversion here refers to the fact that, for energies above about 50 eV (i.e., away from the near-threshold region of the cross sections), the ordering of the total single ionization cross sections $\sigma^+(SF_x)$ for SF, SF_2, and SF_3 is inverted, i.e., $\sigma^+(SF)>\sigma^+(SF_2)$ and $\sigma^+(SF)>\sigma^+(SF_3)$. We note in particular that $\sigma^+(SF_x)$ lies below the atomic ionization cross section $\sigma^+(S)$ for $x=1-3$, based on the measured atomic sulfur ionization cross section reported by Freund and co-workers.[14]

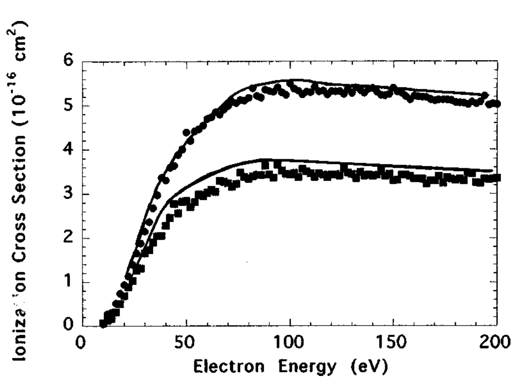

FIG. 3. Experimentally determined (squares, ■, for SF_3 and circles, ●, for SF_5) and calculated (solid lines) total single ionization cross sections as a function of electron energy for SF_5 and SF_3. (See text for further details.)

IV. SUMMARY

The fast-beam technique has been used in a series of measurements of the electron-impact ionization and dissociative ionization of the SF_5 and SF_3 free radicals for impact energies up to 200 eV. The most noteworthy findings are: (i) the ionization of SF_5 leads to SF_5^+ and SF_4^+ cross sections of essentially equal magnitude and shape as a function of impact-energy, (ii) the ionization of SF_3 is entirely dominated by the formation of SF_3^+ parent ions, (iii) a comparison of the experimentally determined total single ionization cross sections, with calculated cross sections based on the modified additivity rule, showed very good agreement for both radicals, (iv) calculated total single ionization cross sections for all SF_x ($x=1-6$) compounds show a partial inversion of the cross sections for SF_3, SF_2, and SF, and (v) the measured total single SF_3 cross section is smaller than the ionization cross section of atomic sulfur, thus confirming one aspect of the predicted cross section inversion.

ACKNOWLEDGMENTS

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