TOTAL CROSS SECTIONS FOR ELECTRON SCATTERING AND ATTACHMENT FOR SF_6 AND ITS ELECTRICAL-DISCHARGE BY-PRODUCTS

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INTRODUCTION

Sulfur hexafluoride (SF_6), either pure or mixed with other gases, is commonly used as an insulator in high voltage-equipment. Consequently, many studies have been performed to investigate the decomposition of SF_6 in various electrical discharges including corona,[1] sparks,[2] and arcs.[3] These studies have shown that large quantities of toxic and corrosive by-products such as SO_2, SOF_2, SO_2F_2, SOF_4, SF_4, and S_2F_{10} are produced when SF_6 is dissociated in the discharge. Additionally, recent studies of SF_6 as an etching gas for semiconductor processing have indicated that stable sulfur oxyfluoride by-products can account for more than 10% of the neutral molecules in the plasma.[4]

A full understanding of the physical processes occurring in SF_6 discharges and of the electron attaching processes in decomposed SF_6 requires a detailed knowledge of the interaction of free electrons with SF_6 and its by-products. In this paper we present absolute cross sections for electron scattering and for negative-ion formation through electron attachment to SF_6 and to several by-products produced by electrical discharges in SF_6 (SO_2, SOF_2, and SO_2F_2). These results are compared with previous data where available, and calculations of electron attachment energies are presented to aid in the interpretation of the cross section data.

EXPERIMENT

An electron transmission spectrometer employing a trochoidal monochromator[5] forms the basis of these experiments. This instrument consists of a thermionic electron source followed by the trochoidal monochromator, an accelerating lens, a gas cell, and a retarding lens which permits only unscattered electrons to be transmitted to an electron collector. The instrument is immersed in a uniform magnetic field of about 70 gauss. The electron energy resolution was about 100 meV and the temperature was maintained at 328 K. Total electron scattering cross sections are obtained by measuring the attenuation of the transmitted current due to the introduction of a sample into the gas cell. Cross sections for electron attachment (lifetimes $> 10\ \mu s$) and dissociative attachment processes are determined from a measurement of the product negative ion flux to the walls of the gas cell.

The presence of the magnetic field introduces uncertainty in the length of the electron trajectories through the gas cell,[6] as well as uncertainty in the acceptance angle defined by the

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retarding lens which precedes the collector.[7] Additional uncertainty is associated with the measurement of the target gas pressure in the 0.2 to 1.0 mtorr (0.03 to 0.13 Pa) range at which the cross sections were determined. Overall, the cross sections reported are believed to be accurate to within 15% for electron energies above 1 eV. Below this energy, the uncertainty

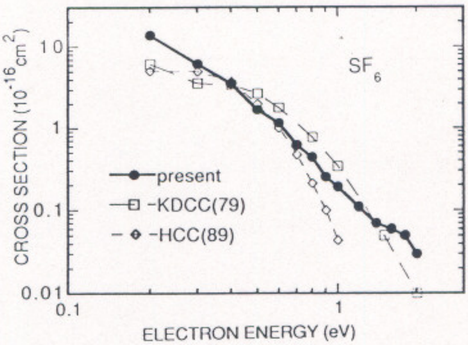

Fig. 1. Cross sections for electron attachment or dissociative attachment to SF_6 from 0.2 to 2 eV. Previous data from references 10 (HCC) and 13 (KDCC) are presented for comparison.

increases to as much as 50% at the lowest energies (≤ 0.2 eV). The limit of sensitivity in the dissociative attachment cross section measurements is about 2×10^{-18} cm^2. The precision of the measurements deteriorates as this limit is approached.

EXPERIMENTAL RESULTS AND DISCUSSION

SF_6

The total cross sections for electron scattering by SF_6 determined in the present experiment are not shown here but agree with previously reported values[8,9] to within the uncertainties discussed above.

Negative-ion formation from SF_6 by electron attachment and dissociative attachment has received considerable study. Christophorou and co-workers have performed several swarm studies[10] of electron attachment to SF_6, and Fenzloff *et al.*[11] have published a detailed study of the relative ion yields for dissociative attachment to SF_6. At very low energies (0–2 meV), Chutjian and co-workers[12] have measured absolute attachment cross sections using threshold photoelectron spectroscopy, while Kline and co-workers[13] have measured absolute cross sections for attachment and dissociative attachment from 0.01 eV to 15 eV in a beam experiment.

Absolute cross sections for electron attachment and dissociative attachment to SF_6 as measured by the present experiment are presented in Figure 1 for electron energies from 0.2 eV to 2.0 eV. At energies greater than 2 eV, the cross section was too small to measure in this experiment. Attachment and dissociative-attachment cross sections measured by Kline *et al.*[13] and calculated by Hunter *et al.*[10] from swarm data are shown for comparison. The cross sections in Figure 1 for Kline *et al.*[13] and for Hunter *et al.*[10] are the sum of their cross sections for SF_6^- and SF_5^- production. Note that our cross section values fall significantly below the values of Kline *et al.*[13] from about 0.4 eV to about 1.4 eV. This is in general agreement with analyses[10,14,15] of swarm data for which the experimentally determined electron-collision cross sections for SF_6 were adjusted downward in order to derive accurate transport, ionization, attachment, and dissociation coefficients of SF_6. At energies greater than 1.2 eV our results appear to agree well with Kline *et al.*.[13] It must be noted, however, that at these energies the magnitude of the cross section approaches the detection limits of the experiment (2×10^{-18} cm^2). At lower energies (~ 0.2 eV) we appear to be in agreement with the attachment cross section (1.2×10^{-15} cm^2) published by Chutjian and co-workers.[12]

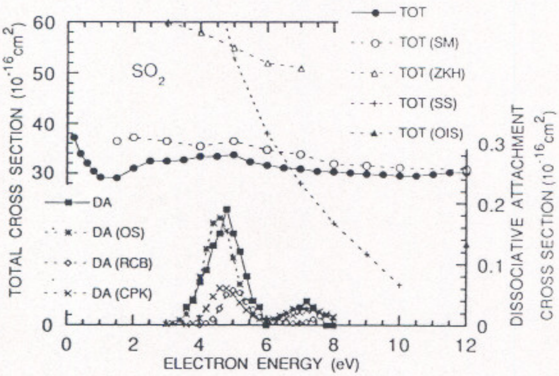

Fig. 2. Total electron-scattering cross sections and dissociative-attachment cross sections for SO_2. Previously published total cross sections from references 16 (ZKH), 17 (SS), 18 (SM), and 19 (OIS, total elastic-scattering cross section), and previously published dissociative-attachment data from references 21 (RCB), 22 (CPK), and 23 (OS) are shown for comparison.

SO_2

To date three conflicting experimental measurements of the total cross section for electron scattering by SO_2 have been published.[16-18] These three data sets are shown in Figure 2 along with the measurements from the present experiment. A single measurement[19] of the elastic scattering cross section at 12 eV is also shown. Our results are in closest agreement with the recent results of Szmytkowski and Maciag,[18] although discrepancies exceeding 20% are observed, especially at lower energies. Broad maxima observed near 2.5 eV and 5 eV in the cross sections measured here and in those of Szmytkowski and Maciag[18] correspond to the resonances observed by Sanche and Schulz[20] in derivative electron transmission spectra.

Previous measurements[21-24] of the cross sections for dissociative attachment to SO_2 differ in magnitude by as much as 70%. Figure 2 shows the measured dissociative-attachment cross sections from the present experiment and from Refs. 21–23. Qualitative agreement between these measurements is good with each experiment showing peaks near 4.7 eV and 7.2 eV. Mass spectrometric studies[24] have shown that the peak near 4.7 eV is composed primarily of O^- and SO^- while the peak near 7.2 eV is almost solely O^-. The peak near 4.7 eV corresponds to the broad maximum in the total cross section data near 5 eV. Although the dissociative-attachment data from our experiment are near the experimental detection limits, and therefore have fairly large error limits ($\pm\ 2 \times 10^{-18}$ cm^2), the present data are clearly in agreement with the values reported in Refs. 23 and 24, both of which show peak values near 18×10^{-18} cm^2.

SOF_2

The total electron-scattering cross sections for thionyl fluoride (SOF_2) from the present experiment are shown in Figure 3. A prominent resonance is observable at 0.6 eV with a weaker resonance appearing as a shoulder near 2.0 eV.

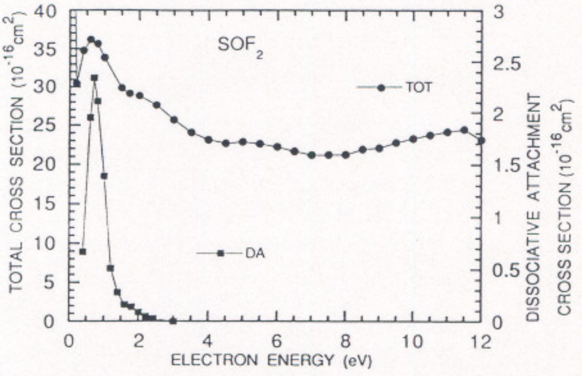

Fig. 3. Total electron-scattering cross sections and dissociative-attachment cross sections for SOF_2.

The dissociative-attachment cross section data from the present experiment are also shown in Figure 3. Note that the peak near 0.7 eV and the shoulder near 2 eV correspond to the resonances observed in the total cross section for electron scattering. Mass spectrometric studies of negative-ion formation[24] show an F^- peak near 0.6 eV and a shoulder near 2 eV, in agreement with the present data. Sauers *et al.*[24] also observed the formation of SOF_2^- at threshold electron energies but at peak intensities approximately 200 times smaller than for F^-. This small current would be undetectable in the present experiment.

SO_2F_2

Figure 4 shows the total cross sections for electron scattering by SO_2F_2. It is interesting to note that no prominent resonance peaks are observed. Additionally, the total electron-scattering cross section for SO_2F_2 is the lowest of any of the compounds investigated here.

The cross section for dissociative attachment to SO_2F_2 is also shown in Figure 4. The magnitude of the dissociative-attachment cross sections for SO_2F_2 is much smaller than for SOF_2, probably because there are no corresponding resonances in the total electron-scattering cross section. The peak in the dissociative-attachment cross section near 3.4 eV is in agreement with previous mass spectrometric studies by Wang and Franklin[25] and by Sauers and co-workers.[24] These studies indicate that this peak is produced by the formation of SO_2F^-, F_2^-, and F^-, and that the increase in the cross section at low energies is evidently due to the formation of the parent ion, $SO_2F_2^-$, by electron attachment. The cross section for dissociative attachment has been calculated from recent swarm studies[26] of SO_2F_2 at room temperature to be 1.06×10^{-16} cm^2 for 0.22 eV electrons. However, this value is more than an order of magnitude larger than the dissociative-attachment value measured by this experiment.

THEORY

In previous work we have found a high degree of correlation between the energies of shape resonances observed in electron transmission spectroscopy and those observed near inner-shell ionization edges in electron energy-loss or x-ray absorption spectroscopy.[6,27] The former involve temporary capture of low-energy electrons into low-lying, unfilled molecular orbits; the latter involve transitions of inner-shell electrons to analogous orbitals. For the inner-shell electron excitation process, the resonant state is stabilized by the positive core that is created. These energies differ by a stabilization energy, SE, given by the sum of the attachment energy, AE, which characterizes a resonance feature in the electron transmission spectrum (or total electron-

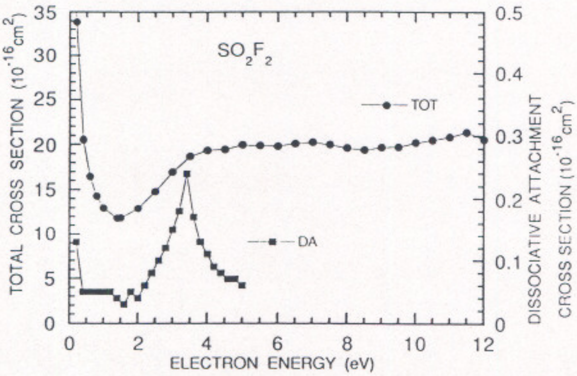

Fig. 4. Total electron-scattering cross sections and dissociative-attachment cross sections for SO_2F_2. The apparent increase in the dissociative attachment cross section at low energies is due to the formation of long-lived parent ions (see Ref. 24).

Table 1. Calculated term values (TV), attachment energies (AE), and stabilization energies (SE) for SO_2 and SF_4 in electron volts.

	SO_2 b_2	SF_4 b_2
TV	10.07	7.99
AE	−0.65	1.02
SE	9.42	9.01

scattering cross section) and the term value, TV, which is the difference between the inner-shell ionization edge and the inner-shell excitation energy to the state analogous to the resonant state observed in low-energy electron scattering: SE = AE + TV. The stabilization energy has been found to be relatively constant in a series of similar molecules, thus if SE can be estimated and TV is available for a particular unfilled orbital, it is possible to make reasonable assignments of features observed in low-energy electron scattering and dissociative-attachment cross section measurements.

To aid in the interpretation of our measurements we have, as in previous work, carried out an extensive series of *ab initio* Hartree-Fock calculations on both neutral and core-ionized sulfur fluorides and oxyfluorides within the approximation of the equivalent ion core virtual orbital model.[6,28] In particular, in order to establish the relation (for the series of molecules under investigation here) between term values from inner-shell excitation spectroscopy and attachment energies from electron transmission measurements, we have calculated TV and AE at the ΔSCF level[29] for the lowest virtual b_2 orbitals of SO_2 and SF_4. The calculated term values agree with experiment to within 1 eV or better. For SO_2, such a procedure is well defined for the calculation of the AE, since the $^2B_2$ negative ion state is stable (that is the AE is negative). The calculated attachment energy agrees within 0.5 eV with the measured[30] electron affinity of SO_2. For SF_4 the anion state is unbound at the neutral geometry and thus the calculated vertical attachment energy is unstable to the addition of diffuse functions and would indeed go to zero if a sufficient number of such functions were employed. However, using the same type basis as for the TV calculation, an attachment energy of 1.02 eV is calculated. As shown in Table 1, the values of SE implied by these calculations is 9.4 eV for SO_2 and 9.0 eV for SF_4. An average value for SE of 9.2 eV has been used in Table 2 to predict, from measured

Table 2. Projected values of AE's (in eV's) based on experimentally determined TV + 9.2 eV. Values derived from calculated TV's are in parenthesis.

SF_6		SO_2		SOF_2		SO_2F_2		SF_4	
		b_1	5.9	a′	(6.3)	a_1	6.4	b_1	3.2
$t1_u$	4.9	a_1	3.5	a′	(3.6)	a_1	4.0	a_1	3.2
$a1_g$	1.9	b_2	−1.0	a″	1.5	b_2	3.0	b_2	0.2

term values,[8,31–33] the energies and assignments of resonances observed in low energy electron scattering for other sulfur fluorides and oxyfluorides.

This approach suggests: (1) dissociative attachment to SF_6 proceeds through a threshold electron capture process, (2) dissociative attachment to SO_2 is associated with electron capture into the b_1 and higher unfilled molecular orbitals, (3) dissociative attachment to SOF_2 proceeds through the two lowest anion states, and (4) dissociative attachment to SO_2F_2 is primarily associated with electron capture in the lowest unoccupied molecular orbital.

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