Dissociative electron attachment to S₂F₁₀, S₂OF₁₀, and S₂O₂F₁₀

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(Received 29 December 1992; accepted 12 March 1993)

The absolute cross sections for dissociative electron attachment to the molecules S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ were measured in an electron transmission experiment. The corresponding negative-ion fragments were identified in a separate mass spectrometric measurement. For S_2F_{10} , the attachment of thermal electrons (energy less than 0.1 eV) appears to result primarily in the formation of F^- and SF_5^- with possibly a small fraction of SF_4^- and SF_6^- . The ions $F^$ and SF_5^- are also produced from two attachment resonances at electron energies of about 4.5 and 9.5 eV. Both S_2OF_{10} and $S_2O_2F_{10}$ have unusually large dissociative attachment cross sections (on the order of 10^{-12} cm²) at energies near 0.1 eV. Electron attachment to S_2OF_{10} yields primarily SOF_5^- , while $S_2O_2F_{10}$ yields both SF_5^- and SOF_5^- with possible minor fractions of $F^$ and SOF_3^- . Self-consistent-field calculations have been carried out on the neutral molecules and the corresponding anions to aid in the description of the observed dissociative attachment.

INTRODUCTION

The compounds disulfur decafluoride (S2F10), bis-(pentafluorosulfur) oxide (S2OF10), and bis(pentafluorosulfur) peroxide $(S_2O_2F_{10})$ are chemically related to SF_6 , formed from the reaction products of sulfur and fluorine in the presence of oxygen, and are known to be thermally stable in the gaseous state at room temperature (20 °C).¹⁻⁸ All three compounds can be formed by electrical discharges in SF₆ and SF₆/O₂ gas mixtures under a wide range of conditions.⁹⁻¹³ In the case of S_2F_{10} , which is known to be highly toxic,14 there is a need to develop methods for detecting trace levels of this species in the presence of SF₆. One of the proposed methods of analysis for S₂F₁₀ employs an electron capture detector coupled to a gas chromatograph.^{15,16} Since the transport times of S₂OF₁₀ and S₂O₂F₁₀ through a chromatographic column can be comparable to that of S_2F_{10} , it is possible that these compounds will interfere with the detection of S_2F_{10} . Information about negative-ion formation processes for these molecules is needed to assess the importance of such interference.

Little is known about the processes of negative-ion formation in S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ at electron impact energies less than 10 eV. The molecular structures are known¹⁷⁻²⁰ and processes forming positive ions have been investigated.^{3,21,22} In its ground electronic state, S_2F_{10} has D_{4d} symmetry (F_5S -SF₅) with a relatively weak S–S bond. The S–O–S and S–O–O–S bond structures in S_2OF_{10} and $S_2O_2F_{10}$ are nonlinear with the O–S and O–O bonds, respectively, being the weakest bonds in the molecules.

The present work was undertaken to determine the absolute cross sections for dissociative electron attachment

to S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$, and to identify the negative-ion fragments that are formed in the process. Dissociative attachment can be viewed as a resonant electron scattering process that results in formation of a temporary, antibonding negative-ion state that decays into a negative ion and one or more neutral fragments. The process allows formation of energetically stable negative ions as well as neutral fragments that may be in excited states. The approach used in the present work is essentially identical to that used in recent investigations^{23,24} of the compounds SO_2 , SOF_2 , SOF_4 , SO_2F_2 , and SF_4 .

MEASUREMENT METHODS

The absolute cross sections for dissociative electron capture were measured with an electron transmission spectrometer.^{24,25} The instrument consists of a thermionic electron source followed by a trochoidal monochromator, an accelerating lens, gas cell, and retarding lens that permits only unscattered electrons to be transmitted to a collector at which the transmitted current is measured. The instrument is immersed in a uniform magnetic field of about 7 mT (70 Gs). Cross sections for dissociative attachment processes are determined by measuring the product negative-ion current at the walls of the scattering cell. More details of the apparatus and experimental procedure are given elsewhere.²⁶

For the electron transmission studies, the electronenergy resolution was approximately 50 meV. The energy scale was determined by mixing nitrogen with the sample gas and observing the vibrational structure in the transmitted electron current due to electron scattering associated with the well-known ${}^{2}\Pi_{g}$ shape resonance of N₂ centered around 2.3 eV.²⁷ The uncertainty in the calibration of the energy scale is estimated to be less than 50 meV. Pressures in the collision cell were maintained between 0.02 and 0.05 Pa (0.15–0.38 mTorr) for all data presented here, and the

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temperature within the scattering region was maintained at room temperature.

The largest uncertainties in the measurement are associated with the measurement of the target gas pressure and with our estimate of the length of electron trajectories through the target cell. The accuracy of the pressure measurement, accessed by intercomparison of the capacitance manometer with two absolute pressure gauges, is estimated to be $\pm 11\%$, introducing a corresponding uncertainty into the reported cross section. The presence of the magnetic field imparts a helical motion to the electrons and hence introduces an uncertainty in the path length through the target. This effect increases with decreasing electron energy. The reported cross sections were derived assuming a path length equal to the physical length of the cell, and are thus slightly overestimated since the helical motion increases the path length as discussed quantitatively in earlier publications.^{26,28} If one takes the most conservative approach, assuming that all of the thermal motion of electrons leaving the source is directed radially, the reported cross section would be too large by a factor of 1.1 for 1.0 eV electrons passing through the target, a factor of 1.2 at 0.5 eV, 1.4 at 0.2 eV, and 1.9 at 0.1 eV. It should be emphasized that these are maximum estimated errors. Scattering cross sections for nitrogen obtained with this instrument when compared to measurements made by different methods²⁶ suggest that the problem associated with the uncertainty in the path length is much less severe than implied by this worst case estimate.

Fragment-ion identifications were made from independent measurements using a linear time-of-flight (TOF) mass spectrometer as previously described.^{23,29,30} This system uses a pulsed electron beam from a thermionic emission source to produce negative ions, which are then accelerated into a field-free drift tube. The electron energy spread in this experiment is estimated to be 0.5 eV from observation of SF₆⁻ ions produced by resonant electron capture in pure SF₆ at threshold electron energies.

The relative intensities of the different ions were determined from TOF measurements made at different electronimpact energies. Negative ions which decay by dissociation or electron detachment in the flight tube are detected since the neutral fragments possess sufficient kinetic energy to trigger the detector. The contribution of short-lived ions to the detected signal is assessed with the use of a pair of electrostatic deflection plates at the downstream end of the flight tube. Only neutral fragments are detected when the deflection field is applied. Ions with lifetimes longer than the drift-tube flight time can reach the detector only when the deflection field is off. For the measurements discussed here, the TOF system was operated at gas pressures between 10^{-3} to 1.5×10^{-2} Pa.

The S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ samples had an estimated purity of greater than 99% at the time of preparation. Sample purities were confirmed prior to use with a gas chromatograph-mass spectrometer.⁹



FIG. 1. Electron-energy dependence of the absolute cross sections for dissociative electron attachment to S_2OF_{10} (long dashed line) and $S_2O_2F_{10}$ (short dashed line) in comparison with the previously measured (Ref. 24) electron attachment cross section for SF₆ (solid line) and calculated maximum *s*-wave capture limit $(\pi\lambda^2)$.

RESULTS

Absolute dissociative electron-attachment cross sections for S_2OF_{10} and $S_2O_2F_{10}$ are shown in Fig. 1, and for comparison, the electron-attachment cross section for SF_6 recently measured with the same instrument is included. Comparison of this electron-capture cross section for SF_6 has been shown in Ref. 24 to be in agreement with other measurements and demonstrates the suitability of the experimental technique for these types of measurements. In the energy range shown, the electron attachment process in SF_6 is known³¹ to yield primarily SF_5^- for electron energies above 0.2 eV and SF_6^- at lower energies. Cross sections for both S_2OF_{10} and $S_2O_2F_{10}$ are extraordinarily large, exceeding the maximum for the SF_6 cross section by about two orders of magnitude.

Figures 2 and 3 show, respectively, the negative-ion yields for S_2OF_{10} and $S_2O_2F_{10}$, observed with the TOF mass spectrometer. The species S_2OF_{10} yields primarily SOF_5^- . The yields of other ions are at least two orders of magnitude lower than that for SOF_5^- . In the case of $S_2O_2F_{10}$, the threshold attachment process results in the production of either SOF_5^- or SF_5^- with similar intensity. There is also evidence for formation of SOF_3^- and F^- from this resonance with much lower probability. However, there are other possible sources of SOF_3^- in the TOF instrument as will be discussed below.

The absolute dissociative-attachment cross section data for S_2F_{10} , shown in Fig. 4, exhibits a peak near zero energy, similar to but smaller than the other compounds, as well as two smaller features at about 4.5 and 9.5 eV. The corresponding data from the TOF mass spectrometer experiment are shown in Fig. 5. The predominant negative ions formed in all three resonance processes are F^- and



FIG. 2. Electron-energy dependence of the anion yield from $S_2 OF_{\rm 10}$ using the TOF mass spectrometer.



FIG. 3. Electron-energy dependence of the anion yield from $S_2O_2F_{10}$ using the TOF mass spectrometer:



FIG. 4. Electron-energy dependence of the absolute cross section for dissociative electron attachment to $S_2F_{10}\,.$



FIG. 5. Electron-energy dependence of the anion yield from ${\rm S_2F_{10}}$ using the TOF mass spectrometer.

 SF_5^- . There is also evidence for the production, with low probability, of SF_6^- and SF_4^- in the threshold attachment process.

It should be noted that the raw data for the absolute cross section is complicated by a background current, which becomes significant at electron energies above 6 eV. This current is due to electrons that experience multiple scattering within the collision region, thus permitting them to cross magnetic field lines and reach the wall of the gas cell and contribute to the measured current. The TOF data are free of this effect and were used to estimate a correction for the data shown in Fig. 4.

When S_2F_{10} was introduced into the TOF mass spectrometer, a peak appeared at mass 105 u corresponding to SOF_3^- (see Fig. 6). It is known that S_2F_{10} can readily react on hot surfaces with adsorbed H_2O to form oxyfluorides.^{4,9} Thus the SOF_3^- most likely is formed by reactions of S_2F_{10} on the surfaces near the filament. Moreover, there is evidence¹¹ that SF_5 radicals from dissociation of S_2F_{10} react



FIG. 6. Typical negative-ion mass spectrum from S_2F_{10} with the electron beam energy set to approximately 0.5 eV.

J. Chem. Phys., Vol. 98, No. 12, 15 June 1993

9468

with OH to form SOF_4 at low pressures. Dissociation of gas phase water near the hot filament in the TOF apparatus may produce OH; thus SOF_4 may be formed in the region near the filament. Previous work^{23,24} has shown that dissociative attachment to SOF_4 leads predominantly to SOF_3^- with relatively large probability near zero energy. The SOF_4 could also form SOF_5^- (which was also observed in the S_2F_{10} TOF mass spectrum) through fast F⁻ transfer reactions.³²

The presence of SOF_4 in the mass spectrometer would not affect our assignment of ions to S_2F_{10} as indicated in Fig. 5, however, it could have an effect on the results for $S_2O_2F_{10}$ shown in Fig. 3. Experiments in our laboratories and elsewhere³ have shown that $S_2O_2F_{10}$ is thermally unstable and can decompose into reactive species like SF_5 that form SOF_4 . For this reason, the assignment of the ion SOF_3^- to $S_2O_2F_{10}$ must be considered tentative.

DISCUSSION

No parent negative ions $(S_2F_{10}^-, S_2OF_{10}^-, \text{ or } S_2O_2F_{10}^-)$ were detected in the TOF experiment. This implies that, even at thermal energies (<0.1 eV), electron attachment to S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ results in dissociation. Although the calculations discussed in the next section indicate that $S_2F_{10}^-$ and $S_2O_2F_{10}^-$ are stable, the formation of these ions requires collisional stabilization that is improbable at the low pressures in the TOF apparatus.

It is surprising that both S_2OF_{10} and $S_2O_2F_{10}$ have such large attachment cross sections, among the largest observed for any molecule. As can be seen in Fig. 1, the cross sections for electron capture to $S_2O_2F_{10}$ and S_2OF_{10} exceed the theoretical s-wave limit by significantly more than the estimated measurement uncertainties. The s-wave capture limit imposed by the Wigner threshold condition³³ for scattering from a central potential as considered by others³⁴ in the interpretation of data on electron attachment. However, contributions from other partial waves can be significant for electron interactions above thermal energies.³⁴ Moreover, there is reason to question the applicability of partial-wave analysis and therefore the s-wave limit to electron scattering from the large, nonspherically symmetric molecules considered here for which the interaction potentials are multicentered. Additionally, the consistency of the results presented here for S2O2F10 and S_2OF_{10} with the s-wave limit near zero energy is impossible to assess since the present data do not extend below 0.1 eV. The behavior of electron capture cross sections for very low energy electrons (less than 100 meV) would be better investigated using experimental techniques similar to those of Chutjian and co-workers³⁴ or Klar and co-workers.³⁵

The fact that SOF_5^- is the predominant negative ion formed from dissociative electron attachment to S_2OF_{10} is consistent with the assumption of a relatively weak sulfuroxygen bond in the intermediate parent negative-ion state. The formation of either SF_5^- or SOF_5^- from $S_2O_2F_{10}$ with nearly equal probability implies a rupture of one of the O-O or S-O bonds.

Similar to S_2OF_{10} and $S_2O_2F_{10}$, S_2F_{10} exhibits a large (greater than 10^{-16} cm²) cross section for dissociation

near zero energy. In addition, two attachment resonances occur at higher energies (4.5 and 9.5 eV). Both result in the formation of F⁻ and SF₅⁻. For the 4.5 eV process, both fragment ions appear with nearly equal probability, whereas F- appears to predominate at the 9.5 eV resonance. The formation of SF_5^- is expected if the dissociation occurs along the weak sulfur-sulfur bond. It is speculated that F⁻ formation at the high-energy resonances results predominantly from an indirect process involving decay of the SF₅⁻ anion formed in its lowest antibonding state. The recent calculations of Ziegler and Gutsev³⁶ indicate that the dissociation channel of lowest energy for the SF₅ anion leads to F^- formation. The dissociation energy for SF_5^- is estimated to be 2.9 eV. Based on estimates of the heats of formation and on the uncertainties of these estimates for $S_2F_{10} \mbox{ and } S_2F_9, ^{11} \mbox{ direct formation of } F^- \mbox{ can occur at } 0.5$ ± 0.46 eV electron energy, indicating that a direct dissociative attachment process for F⁻ formation at thermal energy is possible. Similarly, using 2.7 ± 0.2 eV for the electron affinity³⁷ of SF₅, SF₅⁻ formation by direct dissociative attachment to S_2F_{10} is possible at thermal electron energies from an estimated heat of reaction of -0.75 ± 0.48 eV. Thus the F⁻ and SF₅⁻ ions observed at zero electron energy can be attributed to direct dissociative electron attachment to S_2F_{10} .

The suggestion of thermal decomposition of S_2F_{10} in the TOF apparatus raises the possibility that some of the observed SF_6 may not come from electron attachment to S_2F_{10} since thermal decomposition of this substance is known to produce SF_6 .^{4–6,9} On the other hand, it is also known that SF_6^- produced by low-energy electron attachment to SF_6^- has a lifetime for autodetachment of a few microseconds to milliseconds depending on the state in which it is formed.³⁸ Tests using the deflection plates in the mass spectrometer flight tube gave no evidence for the presence of short lived SF_6^- , implying that the observed signal originated from a dissociative-attachment process. Thus, the possibility that SF_6^- is indeed formed directly from electron attachment to S_2F_{10} cannot be ruled out. The process may be the consequence of a structural rearrangement.¹⁸

CALCULATIONS

To help in understanding the electron attachment behavior of S₂F₁₀, S₂OF₁₀, and S₂O₂F₁₀, we have carried out ab initio self-consistent-field (SCF) calculations on the neutral molecules and their anions, much like those performed earlier39 on simpler molecules such as SF4. For comparison, we have also included SF₆ in our calculations, as it provides a test of the accuracy of the calculational method. Unpolarized split-valence bases at geometries optimized using polarized split-valence bases were employed for SF₆, S₂F₁₀ (D_{4d}), and S₂OF₁₀ (C_{2v}). The S₂O₂F₁₀ is too large and asymmetric to use polarized split-valence bases for geometry optimization. Its geometry was optimized only at the semiempirical PM3 level.⁴⁰ Calculated geometries of SF₆ and S₂F₁₀ have been reported previously.³⁹ All calculations were performed with the program GAMESS.⁴¹ The bond lengths (R) for S_2OF_{10} at the

TABLE I. Vertical electron attachment energies for SF₆, S₂F₁₀, S₂OF₁₀, and S₂O₂F₁₀ obtained from virtual orbital eigenvalues (ϵ_i) and anion-neutral total energy differences ($\Delta E_{\rm SCF}$) using 3-21G bases at 3-21G^a SCF optimized geometries.

Molecule	Label and nature of virtual orbital	(eV)	$\Delta E_{\rm SCF}$ (eV)
SF ₆	a_{1g} , S-F σ^*	3.2	2.2
	t_{1u} , S–F σ^*	8.4	
S_2F_{10}	a_2 , S–S σ^* , S–F σ^*	0.2	-0.8
	e_1 , S–S π^* , S–F σ^*	6.5	
	a_2 , S–S σ^* , S–F σ^*	7.3	
	$e_3, S-S\pi^*, S-F\sigma^*$	8.8	
S_2OF_{10}	a_1 , S–O–S σ^*	1.9	0.9
$S_2O_2F_{10}$	$_2O_2F_{10}$ a, O–O σ^* , S–S σ^*		-1.0

^aGeometry optimized at the semiempirical PM3 level; anion calculation at the restricted open shell Hartree–Fock level.

3-21G SCF level were calculated to be R(S-O) = 0.1618 nm and R(S-F) = 0.1537-0.1542 nm, and the angle formed by the S-O-S bonds was calculated to be 155°, in reasonable agreement with the experimental values¹⁹ of 0.1586 and 0.1558-0.1572 nm and 142.5°, respectively. For S₂O₂F₁₀, the PM3 optimized geometry has R(O-O) = 0.1479 nm, R(S-O) = 0.178 nm, R(S-F) = 0.1551-0.1561 nm, and the S-O-O angle equal to 136° compared to experimental values²⁰ of 0.143, 0.166, and about 0.156 nm, and 111°, respectively.

Calculated electron attachment energies of SF_6 , S_2F_{10} , S_2OF_{10} , and $S_2O_2F_{10}$ are compared with the energies of experimentally observed resonances. For the present discussion, the attachment energy (AE) is defined as the internal energy change when an electron is captured by a neutral gaseous molecule. The AE is therefore positive if the resulting anion is less stable than the neutral molecule. Calculated vertical attachment energies assume no change in the geometry of the molecule during the electron capture process, while adiabatic attachment energies allow for changes in the anion geometry, leading to a new minimum energy geometry.

Vertical electron attachment energies for the four molecules as derived from the virtual orbital eigenvalues ϵ_i (i.e., within Koopmans' approximation) and as differences in total SCF energies of the anion and the neutral (ΔE_{SCF}) are given in Table I. ΔE_{SCF} and ϵ_i give only approximate values for the attachment energy. For those cases in which $\Delta E_{\rm SCF}$ is negative at the geometry of the neutral, corresponding to a bound state anion, the $\Delta E_{\rm SCF}$ method is valid, but ignores correlation differences between the neutral and the anion. We have also employed a small basis with none of the diffuse functions needed to accurately describe the anion electron density. For cases in which $\Delta E_{\rm SCF}$ is positive, the anion is unbound, technically a scattering resonance, so our bound state approach is not formally correct. Our results will be unstable toward the addition of diffuse and/or continuum basis functions. This difficulty can be removed in simpler cases using stabilization methods.42 Even without stabilization, calculations using split valence bases often give results in reasonable agreement with experiment using the ΔE_{SCF} approach as

TABLE II. A comparison of calculated vertical and adiabatic electron 'attachment energies for SF₆, S₂F₁₀, and S₂OF₁₀. The experimental values are shown in parentheses for SF₆. Adiabatic AE's are obtained as the total energy of the relaxed geometry anion minus the energy of the geometry optimized neutral.

Molecule	Orbital	$\Delta E_{\rm SCF}$ (eV)	Adiabatic AE (eV)
SF ₆	a_{1e}	2.2 (2.6)	-1.4(-1.0)
S_2F_{10}	a2	-0.8	-5.2
S_2OF_{10}	<i>a</i> ₁	0.9	-2.6

we have demonstrated for some smaller sulfur oxyfluorides.³⁹

The calculated $\Delta E_{\rm SCF}$ falls approximately 1 eV below ϵ_i for the ground-state anion of each compound. It is expected that this "shift" is qualitatively applicable to the higher-energy states and the calculations of ϵ_i may thus be used to estimate the energies of higher-energy scattering resonances.³⁹ For SF₆, the calculated AE for the a_{1g} orbital (or scattering resonance) at the $\Delta E_{\rm SCF}$ level is 2.2 eV, in reasonable agreement with the experimental resonance position of 2.5 eV.⁴³ The eigenvalue of the $t_{1\mu}$ orbital less 1 eV is 7.4 eV, compared to an experimental value of 7.0 eV.43 Differences between calculations and experimental values are expected to increase for molecules of lower symmetry. Estimating AEs of S_2F_{10} as ϵ_i minus 1 eV would suggest resonances at about 5.5, 6.3, and 7.8 eV. These energies are near the values of the two higher-energy features in Figs. 4 and 5. It is difficult to assign particular orbitals to these features since the calculations provide no estimates of the intensity of a resonance. The a_2 state of $S_2F_{10}^-$ and the a state of $S_2O_2F_{10}^-$ are calculated to be stable at the ΔE_{SCF} level at the neutral geometries, however, since no evidence of parent ion formation for S₂F₁₀ and S₂O₂F₁₀ was observed in the data, it can be assumed that the lifetimes of these metastable ions are less than 1 μ s.

Adiabatic AE values will be more negative than vertical AEs. For SF_6 , we calculate an adiabatic AE of -1.4 eV (i.e., an electron affinity of +1.4 eV), while the experimental value is about -1.0 eV.⁴⁴ For S_2F_{10} and S_2OF_{10} , the calculated adiabatic AEs are -5.2 and -2.6 eV, respectively. These values are given in Table II.

The bonding character of the virtual molecular orbitals to which electrons are added in these molecules can provide some understanding of the anions produced by dissociative attachment. In general, if a virtual orbital is antibonding between two atoms, we would expect the bond between them to have a higher probability of breaking. The ${}^{2}A_{1e}$ state of SF₆, formed by populating the a_{1e} lowest unoccupied molecular orbital (LUMO), shows an elongated S-F bond as in previous studies,45 and is consistent with formation of F^- and SF_5^- . For S_2F_{10} , the a_2 LUMO is S–S σ^* and S–F σ^* in character, consistent with rupture of the S-S or S-F bond to give SF5 or F- fragments. At the 3-21G SCF level in D_{4d} symmetry, the S-S bond distance increases by 0.042 nm and the S-F bond distances increases by 0.002-0.005 nm when an electron is added to S_2F_{10} . Similarly, for S_2OF_{10} at the 3-21G level, electron addition gives an increase in S–O distance of 0.013 nm and an increase in S–F distances of 0.09–0.013 nm.

CONCLUSIONS

The dissociative attachment cross sections measured for S_2OF_{10} and $S_2O_2F_{10}$ are among the largest reported for any gas-phase molecule. These exceptionally large cross sections make S_2OF_{10} and $S_2O_2F_{10}$ of particular interest in investigations of low energy electron attachment processes of gaseous dielectrics. Because of the magnitude of these cross sections, it can be concluded that the presence of S_2OF_{10} and $S_2O_2F_{10}$ may cause significant interference in the detection of S_2F_{10} by gas chromatographic techniques utilizing electron capture detectors.

The apparent production of stable SF_6^- by dissociative electron attachment to S_2F_{10} is of significance. Experimental investigations of SF_6^- have long been hampered by the difficulties of producing the ions with known internal energy. The long lifetimes of the SF_6^- ions observed here indicate that this dissociative attachment process may represent a possible source of SF_6^- in a well-defined state. Unambiguous determination of the source of SF_6^- from S_2F_{10} would require modifications to the TOF mass spectrometer to remove the hot electron source from the collision region. Assembly of this type of electron source/ collision cell for a different mass spectrometer system is currently under way.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation, Grant No. CHE-91-20504 (University of Maryland) and in part by the U.S. Department of Energy and the Electric Power Research Institute (National Institute of Standards and Technology and the Oak Ridge National Laboratory). The authors are grateful to D. Des Marteau for preparing the gas samples used in this work, and to L. G. Christophorou for use of the time-of-flight apparatus.

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