

Experimental observation of dissociative electron attachment to S_2O and S_2O_2 with a new spectrometer for unstable molecules

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Abstract

A new spectrometer, electron radical interaction chamber, has been developed to study dissociative electron attachment to unstable molecules such as free radicals. It includes a trochoidal electron monochromator and a time-of-flight mass spectrometer. Radicals are generated with a microwave discharge at 2.45 GHz. Preliminary data are presented for radicals formed when a mixture of helium and sulphur dioxide was passed through the microwave discharge. Several new resonances are observed with the discharge on. Resonances at 0 eV (S^-), 0.8, 1.2, 3.0 eV (SO^-) and 3.7 eV (SO^- and S_2O^-) are assigned to the radical S_2O_2 and a resonance at 1.6 eV (S^-) is assigned to S_2O . No new resonances have been assigned to SO , which was also generated in the microwave discharge.

1. Introduction

Dissociative electron attachment is a fundamental molecular fragmentation process and a major process in plasmas, electrical breakdown phenomena, combustion, the upper atmosphere and many other situations where there is a high density of free electrons. These are all environments where unstable free radicals have a crucial impact on the overall chemistry, but few studies of electron attachment to unstable molecules have been reported although many studies of stable molecules and clusters have been reported, see, e.g., [1, 2]. It appears that dissociative electron attachment has only been observed experimentally to stable free radicals, such as NO [3], or partially stable ones, such as $OCIO$ [4, 5]. Electron attachment to excited states, such as SO_2 in the \tilde{B}^1B_1 state [6, 7], and some exotic species, such as S_2 [8] and Na_2 [9], have also been performed.

In this work a new spectrometer has been developed to study dissociative electron attachment to unstable molecular species such as free radicals; first results are presented for S_2O and S_2O_2 . The motivation for this work is both interest in the physics of dissociative electron attachment to radicals and the desire to characterize these processes to provide data

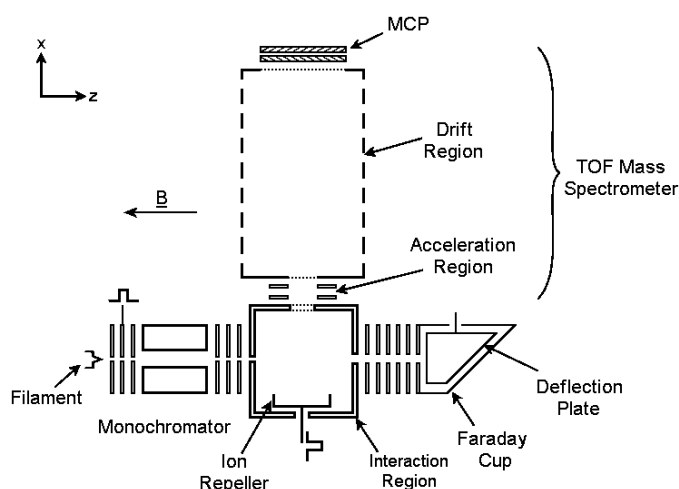


Figure 1. Schematic diagram of ERIC (electron radical interaction chamber).

for models of plasmas and other environments with high concentrations of radicals and free electrons. The need for characterization of dissociative electron attachment to radicals for plasma modelling has been highlighted by Graves *et al* [10]. They noted that ‘*The main roadblock to development of plasma models that will have industrially important uses is the lack of fundamental data on collisional, reactive processes occurring in the plasma and on walls bounding the plasma*’ and that ‘*There exist virtually no data on electron attachment to radicals, although such species are produced in large numbers in plasmas*’.

Theory has been used to calculate the scattering of low energy electrons by free radicals such as ClO, CF, CF₂ and CF₃ [11–14] for which there are no experimental data. In the case of the OClO radical there is agreement between experiment [4, 5] and theory [15] in the electron energy at which dissociative electron attachment occurs. The agreement between experiment and theory supports the use of this theoretical method for predicting the positions of dissociative electron attachment resonances.

2. Method

The new spectrometer to investigate electron attachment to radicals, electron radical interaction chamber (ERIC), is shown schematically in figure 1. The gas sample enters the interaction region from above. The interaction region is differentially pumped from below to minimize the pressure in the mass spectrometer and electron gun. Gas enters the spectrometer through a glass inlet system. An Evenson microwave cavity in the inlet system connected to a 2.45 GHz microwave power supply can be used to generate radicals. Typical microwave powers used are 50 to 80 Watts. The interaction region and the microwave cavity are separated by approximately 25 cm of glass tube. The maximum operating pressure in the electron spectrometer and time-of-flight mass spectrometer was 1×10^{-5} mbar. It is estimated that the pressure in the differentially pumped interaction region is between one and two orders of magnitude higher.

Electrons from the filament are passed through a trochoidal electron monochromator, which is based on the original design of Stamatovic and Schulz [16] and the more recent scheme of Allan [17]. The electrons are guided by a magnetic field of 20 to 80 Gauss, which

enables the electron beam energy to be reduced to close to 0 eV in the interaction region. The electron beam is dumped in a Faraday cup. A bias potential applied to the deflection plate in the Faraday cup ensures that scattered electrons move off-axis and cannot be guided back into the interaction region by the magnetic field.

Fragment anions formed in dissociative electron attachment are observed with a time-of-flight mass spectrometer. The ion repeller pushes ions into the acceleration region where they are further accelerated before they pass through the drift region and strike the multichannel plate detector. The mass spectrometer dimensions and electric field strengths are optimized for second-order space focusing [18]. The distance from the centre of the electron beam to the edge of the interaction region is 1.0 cm. The lengths of the acceleration region and drift regions are 1.5 and 12.0 cm, respectively. With these dimensions second-order focusing should be obtained when the electric field strength in the acceleration region is double that in the interaction region. The design of the present spectrometer deviates slightly from these optimum dimensions as two grids rather than one are placed between the interaction and acceleration regions as shown in figure 1. Two grids are used to minimize the penetration of the electric field from the acceleration region into the interaction region.

Large electric fields are required in the interaction region to obtain the best mass resolution with the time-of-flight spectrometer. In contrast, it is necessary to have at most small electric fields to pass the low energy electron beam through the interaction region. The experiment is pulsed to satisfy these different requirements. The electron beam is blocked by a negative potential applied to a 'gate' electrode between the filament and the monochromator. A short $\sim 1 \mu\text{s}$ positive pulse is applied to open this gate, as indicated in figure 1, and a pulse of electrons is sent towards the interaction region. After the electrons have left the interaction region the ion repeller is pulsed with a $\sim 10 \mu\text{s}$ extraction pulse to extract the ions. The strength of the electric field generated by the extraction pulse is variable; here a field of $\sim 80 \text{ V cm}^{-1}$ was used. The experiment runs at a 10 kHz repetition rate.

The electron energy is set by floating the electron gun potentials relative to the interaction region. Energies of 0 to 50 eV and higher can be set. The upper limit is the isolation of the electron gun electrodes and power supplies. At higher electron energies, of course, positive ions are formed by electron impact ionization. The potentials of the mass spectrometer can be reversed to detect positive ions, which allows comparison between positive ion and negative ion mass spectra of each gas sample.

The experiment is controlled by an online computer, which sets the electron energy and records the mass spectra. A voltage generated by a digital to analogue converter card floats the electron gun power supplies to set the electron gun energy. The design of these power supplies is based on that of Allan [17]. Mass spectra are gathered with a time-to-digital converter (TDC) card (Roentdek TDC8/ISA). A start signal is sent to the TDC from the pulser that supplies the extraction pulse. Ion signals from the multichannel plates are amplified, discriminated and passed to the stop channel of the TDC. The TDC can record up to eight stops after each start. The detection system can be paralysed, however, by the arrival two ions at the same time when only one ion can be observed. The effect of this paralysis is minimized by restriction of the ion detection rate to a maximum of 1 ion per 10 extraction pulses; typically the rate is lower than this value.

Figure 2 shows the negative ions formed as a function of electron energy for a mixture of SF₆ and CCl₄. The electron energy resolution calculated from the width of the SF₆⁻ peak at 0 eV is $\sim 200 \text{ meV}$. The current resolution is sufficient for the present work, but lower than this has been reported for other trochoidal monochromators, which can operate at resolutions down to 30 to 100 meV (see, e.g., [16, 17]). The results for SF₆ and CCl₄ are consistent with previous measurements [19, 20].

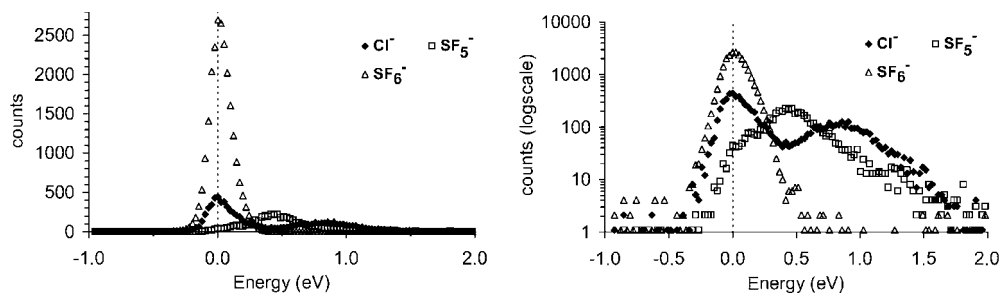


Figure 2. Spectrum of dissociative electron attachment to a mixture of SF₆ and CCl₄.

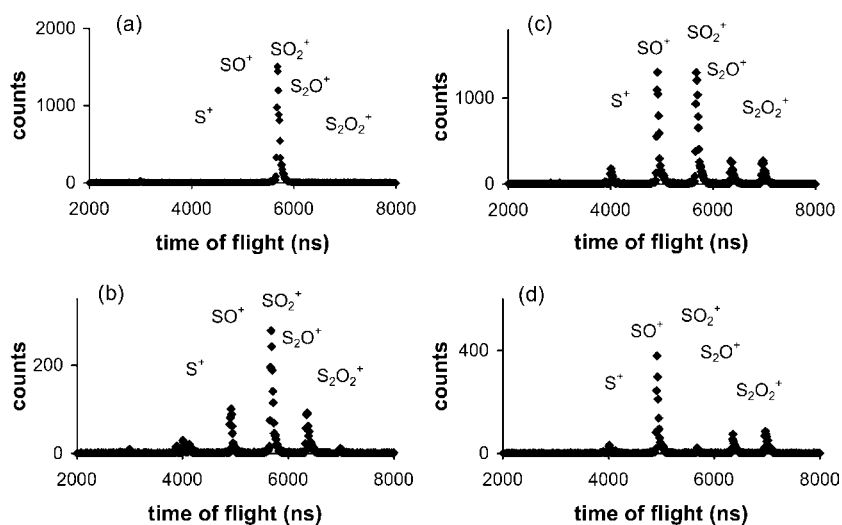


Figure 3. Positive ion mass spectra of gas samples with the microwave discharge off, (a), and on, (b), (c) and (d). The inlet pressures of SO₂ and helium were changed between spectra (b) and (c). The electron impact energy was 13 eV, (a), (b) and (c), and 11 eV (d).

3. Results

3.1. Generation of SO, S₂O and S₂O₂

Electron attachment to radicals generated in a microwave discharge of a mixture of helium and sulphur dioxide has been investigated. Positive ion mass spectra are shown in figure 3. The electron energies used were low; 13 eV for all spectra except (d) where 11 eV was used. Low electron energies were used to prevent dissociative ionization so that only parent ions are observed in the mass spectrum. Fragment ions would confuse the mass spectra; for example, ionization of SO₂ above 16 eV gives SO⁺ as well as SO₂⁺ [21]. Spectrum (a) was recorded with the microwave discharge off and spectra (b), (c) and (d) were taken with the discharge on. The relative ratios of the different radicals depended on the pressures of helium and sulphur dioxide in the inlet system; the variation in radical intensities between spectra (b) and (c) is due to different inlet pressures. Spectrum (d) was taken with 11 eV electron energy, but with the same inlet conditions as (c). The energy 11 eV was chosen because it is below the ionization energy of SO₂ (12.349 ± 0.001 eV), but above that of SO (10.294 ± 0.004 eV)

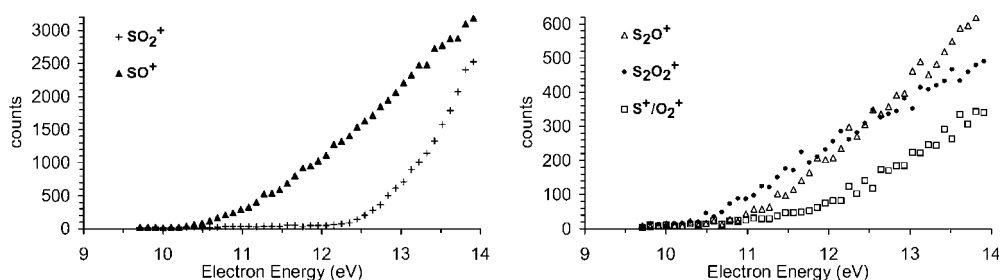


Figure 4. Variation of positive ion signal intensity as a function of electron energy. The results have been split between two plots with different vertical scales for clarity.

[22]. Spectrum (d) confirms that the SO⁺ peak is due to SO and not to fragmentation of electronically excited SO₂ molecules, which would also give rise to SO₂⁺.

Figure 4 shows the variation of positive ion intensities as a function of electron energy. The ionization energies of the species observed in the mass spectrum can be deduced from this measurement, which aids the identification of radicals in the mass spectrum. For example, S₂O and SO₃ both have nominal mass 80, but their ionization energies are 10.584 ± 0.005 eV and 12.80 ± 0.04 eV, respectively [22]. The data shown in figure 4 give an ionization energy of 10.6 ± 0.3 eV for the mass 80 ion in good agreement with the value for S₂O. Therefore, the mass 80 peak has been assigned to S₂O⁺. In the case of mass 32 the threshold observed here, 10.3 ± 0.3 eV, is in good agreement with the ionization energy of sulphur atoms, 10.360 eV [22]. There is also, however, a change in gradient at ~ 12.0 eV, which is close to the ionization energy of O₂, 12.070 eV [22]. Thus, the ion peak at mass 32 is assigned to S⁺ and O₂⁺.

The ion at mass 96 has been assigned to S₂O₂⁺. The ionization energy observed here, 10.35 ± 0.20 eV, is close to the value for S₂O₂ reported by Cheng and Hung [23] from a photoionization experiment, 9.93 ± 0.02 eV. The ionization potential of S₃, also mass 96, has been reported as 9.63 ± 0.03 eV [24] again by photoionization. Comparison of the photoionization yield curves with the present data support the assignment of the mass 96 peak as S₂O₂⁺. The photoion signal of S₂O₂⁺ is quite weak below 10.1 eV so it is not surprising that the ionization energy observed in this electron impact experiment, 10.35 ± 0.20 eV, is higher than the photoionization threshold.

The radicals identified in the gas stream here, SO, S₂O and S₂O₂, have been observed previously under similar conditions. Lovas *et al* [25] generated these three radicals in a 2.45 GHz microwave discharge of SO₂. Cheng and Hung [23] generated S₂O₂ and S₂O from SO, which they formed in the fast atom reactions $O + CS_2 \rightarrow SO + CS$ and $O + OCS \rightarrow SO + CO$. The so-called ‘self-reactions’ of SO, such as



where S₂O₂ is collisionally stabilized by any molecule or atom *M*, have been studied by Herron and Huie [26]. They have proposed that S₂O is formed by



3.2. Dissociative electron attachment to SO, S₂O and S₂O₂

Figure 5 shows dissociative electron attachment spectra gathered for a mixture of He and SO₂ with the discharge off, (a), and on, (b). Both linear and log plots are shown. The results with the discharge off are consistent with previous measurements of dissociative electron attachment to sulphur dioxide, see, e.g., [27–29, 7].

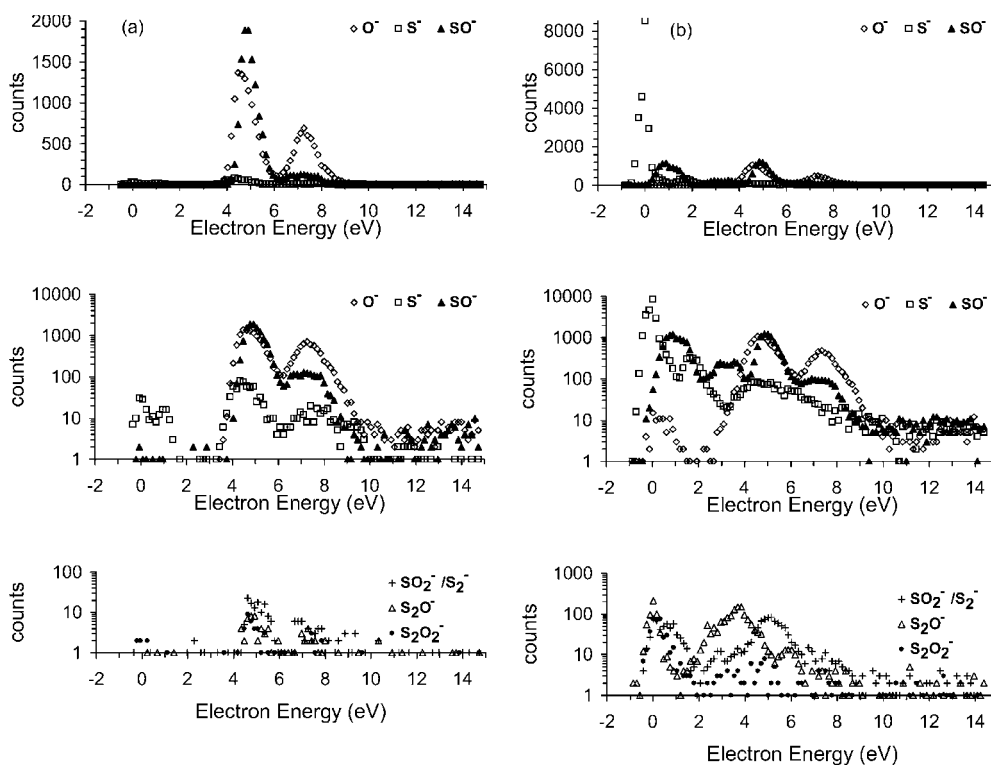


Figure 5. Dissociative electron attachment spectra observed with the microwave discharge off, (a), and on, (b). The same data are presented both with linear vertical axes, top panel, and logarithmic vertical scales, lower panels. The results for the negative ions are split between two logarithmic plots in (a) and (b) for clarity.

Several new resonances are observed with the discharge on in figure 5(b). The new resonance at 0 eV, seen in the S^- ion spectrum, and those observed between 0 and 3.5 eV, in the SO^- ion spectrum, are particularly clear. An obvious method of analysing the present data would be to subtract spectrum (a) from spectrum (b) to remove the contribution of SO_2 and allow the radical resonances to be observed more clearly. In practice, however, subtraction of spectrum (a) has not correctly removed the contribution of SO_2 from spectrum (b). The most likely explanation for this difficulty is that the microwave discharge heats the SO_2 , which effects the shape and relative intensity of its resonances.

All three radicals, SO , S_2O and S_2O_2 , were present in the gas stream at the same time, of course. Therefore, the determination of which new resonances were due to each radical was non-trivial. Three different inlet pressure conditions were used to enable the assignment of the new resonances. Positive ion mass spectra and dissociative electron attachment spectra were gathered under all three different inlet pressure conditions. Significant variation in radical intensity was achieved as can be seen by comparison of mass spectra (b) and (c) in figure 3, which were recorded with different inlet conditions.

The determination of which radical was responsible for each of the new resonances observed required several steps. The first step was the identification of a reference molecule present in the mass spectrum with known dissociative electron attachment resonances. Here the reference molecule was SO_2 . The second step was to determine the ratios of the radical ion signals to the reference SO_2^+ ion signal in all the positive ion mass spectra. Thirdly, the

Table 1. Summary of new resonances observed with estimated absolute cross sections (see text). Confidence in the table refers to the confidence of the assignment of the ion observed to the radical precursor.

Radical	Ion	E _{peak} (eV)	σ (Å ²)	Confidence
S ₂ O ₂	S ⁻	0.0	30	Medium
S ₂ O ₂	SO ⁻	0.8	2.7	High
S ₂ O ₂	SO ⁻	1.2	1.9	High
S ₂ O ₂	SO ⁻	3.0	0.48	High
S ₂ O ₂	SO ⁻	3.7	0.53	High
S ₂ O ₂	S ₂ O ⁻	3.7	0.31	High
S ₂ O	S ⁻	1.6	0.30	High

ratios of the new resonance intensities to the intensities of each of the different resonances due to the reference molecule SO₂ were determined. The fourth step was to determine the changes in all these ratios from one set of inlet conditions to another. These changes were calculated by division of the ratio under the second inlet conditions by the ratio under the first set of inlet conditions. In principle, the changes for each new resonance should be identical to the changes for the positive ion signal of the radical which caused it. Thus, the final step was to compare the changes in new resonance ratios with the changes in the radical ion signals to identify the molecule responsible for each new resonance. Here three different inlet conditions were used; if they are labeled A, B and C then the changes from A → B, A → C and B → C were determined and used to assign the resonances.

In practice the assignment of resonances to individual radicals was straightforward and unambiguous except in the case of the S⁻ band at 0 eV, which has been assigned with medium confidence. Cross sections for dissociative electron attachment at 0 eV rise very strongly as the electron energy approaches 0 eV; it is suspected that the difficulty encountered in the assignment of the resonances at 0 eV is due to small variations in the minimum electron beam energy in the centre of the interaction region, which have caused larger variations in the 0 eV resonance intensities. The assignment of the resonances observed is presented in table 1.

Somewhat surprisingly no resonance of the SO radical has been observed. SO resonances may have relatively small cross sections and be hidden by stronger overlapping resonances of, for example, SO₂. Furthermore, there may be other weaker resonances of S₂O and S₂O₂, which are similarly hidden.

Some weak peaks in the dissociative electron attachment spectra appear to be due to secondary charge transfer processes. It was not possible to make measurements at different inlet pressures and check to see if the peak strengths are linear with pressure or not as would normally be done to establish the primary or secondary nature of ion signals. The problem here was that pressure variation in the microwave discharge effects the relative concentrations of all molecules in the interaction region. Secondary peaks, however, will be evident because they have a similar appearance to primary peaks. In the present experiment technique the neutral number densities are constant, but the number densities of primary ions vary with electron energy. In a reaction between a primary ion and a neutral to give a secondary ion one expects any secondary ion signal to vary with electron energy in the same way as the primary ion signal with a constant relative intensity of secondary to primary ion except, of course, if the primary ion is not formed in the same state at all electron energies. For example, the SO₂⁻/S₂⁻ ion signal in figure 5 (b) shows peaks at about 1 eV and 5 eV and appears similar to the SO⁻ ion signal, though at much reduced intensity. Charge transfer processes between

singly charged atomic ions and neutral atoms have high cross sections when the difference in the ionization energies of the two species is small [30]. This principle also applies for molecules, but Franck–Condon factors must also be taken into account [31]. Here for negative ion charge transfer it is the difference in electron affinities that is critical. It is interesting to note that the electron affinity of SO, 1.125 ± 0.005 eV [32], is very close to the electron affinity of SO₂, 1.107 ± 0.008 eV [33]. Therefore, SO₂[−] is probably formed by charge transfer from SO[−] to SO₂. Similarly, the electron affinity of S, 2.077 eV [34], is close to the electron affinity of S₂O, 1.877 ± 0.008 [33]. The S₂O[−] peak at 0 eV is probably due to charge transfer from S[−] to S₂O; the shapes of the S₂O[−] and S[−] peaks are very similar at 0 eV. The S₂O[−] peak at 3.7 eV is not due to charge transfer because the relative intensity of S₂O[−] to S[−] at 3.7 eV is significantly higher than at 0 eV. Moreover, the shapes of the S₂O[−] to S[−] ion signals around 3.7 eV are different.

The absolute cross sections, σ_{new} , shown in table 1 are estimates. They have been calculated from the number densities of the radical relative to the SO₂ reference molecule, $n_{\text{radical}}/n_{\text{SO}_2}$, and the relative intensities of new DEA resonances compared to reference SO₂ resonances, $I_{\text{new}}/I_{\text{SO}_2}$, with known absolute cross sections, σ_{SO_2} , by

$$\sigma_{\text{new}} = \frac{n_{\text{SO}_2}}{n_{\text{radical}}} \frac{I_{\text{new}}}{I_{\text{SO}_2}} \sigma_{\text{SO}_2}. \quad (3)$$

The relative intensities of the dissociative electron attachment resonances were measured from the present spectra. Previously reported absolute cross sections for SO₂ resonances, however, vary by more than a factor of two [27–29, 7]. Here, average values from previously reported cross sections have been taken. The relative number densities of radicals to SO₂ have been estimated from the intensities of their positive ions in mass spectra with two assumptions. First, it is assumed that the electron impact ionization cross sections of all molecules rise with similar shapes from zero at threshold to maximum values at similar electron energies. Secondly, it is assumed that the maximum cross section value for all molecules can be estimated additively with a value of 1.4 \AA^2 for each oxygen atom [35] and 3.0 \AA^2 for each sulphur atom [36]. This method gives coarse estimates of relative number densities.

The overall calculation leads to rough estimates of absolute cross sections, which are expected to be within a factor of 3 of the true values. The cross sections are mostly quoted to two significant figures in table 1, however, because of the higher accuracy expected for the relative intensities between DEA resonances of the same radical. It should be stressed that these estimates have been calculated as no absolute cross sections are known for these new resonances and they should give an indication, to plasma modelers for example, of how important each resonance is.

4. Discussion

One striking feature of the new SO[−] bands observed between 0 and 4 eV is that they appear very similar to the bands of SO[−] from SO₂ as observed in figure 5, shifted down in energy by about 3.5 eV. The first triplet state of SO₂ ($\tilde{a} \text{ } ^3\text{B}_1$) lies 3.195 eV above the singlet ground state. Thus, one might be tempted to assign the new SO[−] bands to resonances of SO₂ in the first triplet state. The new SO[−] bands observed here, however, are not due to SO₂ in this triplet state because the other ionic products seen in these SO₂ resonances, principally O[−], are not observed. The reason for the similarity of the new SO[−] bands observed between 0 and 4 eV to the bands of SO[−] from SO₂ is not clear; it may be coincidence or there may be some reason due to a similarity in the electronic structures of SO₂ and S₂O₂, the precursor of SO[−]

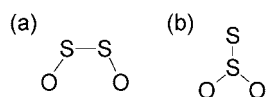


Figure 6. Schematic diagram of S₂O₂ geometries; (a) cis-planar and (b) trigonal.

between 0 and 4 eV. Calculations may shed light on the reason for the similar shapes of the SO⁻ bands.

It has been calculated that the neutral ground states of S₂O₂ in the two geometries shown schematically in figure 6 have very similar energy, see, e.g., [37]. Lovas *et al* [25] observed the cis-planar form (a). The trigonal geometry, (b), has not been observed experimentally. It would be of interest to calculate the positions of electron attachment resonances for both isomers. Comparison between theoretical and the present experimental results could identify the isomer present here. It is most likely that the cis-planar molecule was formed as Lovas *et al* also generated S₂O₂ with a microwave discharge.

5. Conclusions

The new spectrometer ERIC has the capability of recording spectra of dissociative electron attachment to unstable molecules such as free radicals. It is possible to make rough estimates of absolute cross sections for DEA resonances of radicals. In the present study of sulphur/oxygen radicals the assignments of the new resonances rely on varying the inlet conditions and comparing the variation of resonance intensity with the variation of radical intensity in the positive ion spectrum, because a mixture of radicals was present in the interaction region for each measurement.

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