Dissociative electron attachment to the unstable carbon monosulfide molecule CS

K Graupner, T A Field and L Feketeova
Department of Physics and Astronomy, Queen’s University Belfast, Belfast BT7 1NN, UK
E-mail: t.field@qub.ac.uk

New Journal of Physics 8 (2006) 314
Received 28 September 2006
Published 11 December 2006
Online at http://www.njp.org/
doi:10.1088/1367-2630/8/12/314

Abstract. Dissociative electron attachment to the unstable CS molecule, carbon monosulfide, produced in a microwave discharge of carbon disulfide and helium has been observed in the electron energy range 0–10 eV. The S$^-$ ion is formed in two electron attachment bands with maxima at 5.43 ± 0.15 eV and 6.70 ± 0.15 eV and C$^-$ is formed in a band with a maximum of 6.40 ± 0.15 eV. Absolute cross sections for these processes are estimated to be 0.025, 0.003 and 0.002 Å$^2$ respectively. These interactions of CS with low energy electrons will play a role in technological plasmas containing carbon and sulfur and extraterrestrial environments where electrons are present with 5–7 eV energy. New results are also presented for the molecules S$_2$O, C$_3$S$_2$ and S$_2$F, which were also formed in the microwave discharge. For S$_2$O the previously reported S$^-$ band at 1.8 ± 0.3 eV is confirmed and a new O$^-$ attachment band at 5.4 eV is tentatively assigned to S$_2$O. Ionization thresholds of C$_3$S$_2$ (9.4 ± 0.3 eV) and S$_2$F (10.3 ± 0.4 eV) have been measured, apparently for the first time.

1 Author to whom any correspondence should be addressed.
1. Introduction

Unstable molecules and radicals are of major importance for the processes in the plasma gas phase as well as for its etching or deposition characteristics [1]. Carbon monosulfide is formed in plasmas of sulfur and carbon containing source gases. CS has been observed, for example, in a CH$_3$SCN discharge; it was reported that e$^-$ impact to CS in the CH$_3$SCN discharge could lead to the formation of C and S atoms in the plasma [2].

Plasmas with sulfur containing precursors can deposit n-type semiconducting CVD (Chemical Vapour Deposited) diamond films by incorporating S into the film structure [3]. CS and CS$_2$ produced in gas phase reactions have been observed in such a discharge and it was speculated that CS could be the species responsible for the incorporation of sulfur into the lattice [3]. Fluorescence spectroscopy of CS has been used to measure electric field strengths in a discharge [4].

CS may also play a role in atmospheric reactions, for example in the production of atmospheric carbonyl sulfide (OCS) [5], a possible source for the stratospheric sulfate aerosol layer which influences Earth’s climate [6]–[8]. The CS molecule is also of astrophysical importance as it is abundant in space; it has been found in molecular clouds [9], circumstellar envelopes [10], planetary nebulae [11], comets [12] and other galaxies [13]. Its production was observed in the collision of comet Shoemaker–Levy 9 with Jupiter [14]. The CS molecule is unstable and frequently described as a radical although it does not have any unpaired electrons in its ground electronic state.

In the present work dissociative electron attachment to CS is reported. Dissociative electron attachment to a diatomic or polyatomic molecule AB can be represented by

\[
AB + e^- \rightarrow (AB^-)^* \rightarrow A + B^-, \tag{1}
\]

where a free electron e$^-$ attaches to form (AB$^-$)*, a temporary negative ion, which can dissociate into the neutral fragment A and negatively charged fragment B$. A competing process is autodetachment, where the molecule looses the electron again and stays intact.

Electron impact ionization cross sections for formation of the parent ion has been measured experimentally for CS [15]. These experimental cross sections agree well at 20 eV and below.
with electron absorption cross sections calculated recently using the Schwinger variational method [16]. The experimental values are reasonably close to earlier electron impact ionization cross sections calculated with the Binary–Encounter–Bethe (BEB) model [17, 18]. To the authors’ knowledge there exists no previously reported experimental investigation of dissociative electron attachment to carbon monosulfide.

2. Method

The electron attachment spectrometer, the electron radical interaction chamber (ERIC), used here has been described previously [19] and is shown in figure 1. The gas sample, a mixture of CS$_2$ and He, enters the interaction region from above through a glass inlet system.

The interaction region is differentially pumped from below to minimize the pressure in the mass spectrometer and electron gun, which are pumped by a second pump. An Evenson microwave cavity in the inlet system connected to a 2.45 GHz microwave power supply is used to produce unstable molecules and radicals. Typically microwave powers of 40–80 W are used. The interaction region and the region where the unstable species are produced are separated by about 25 cm of glass tube.

Electrons emitted from the filament pass through a trochoidal electron monochromator [20] and are guided by a magnetic field of about 80 G. The deflection plate in the Faraday cup moves the electrons off-axis so that the electrons cannot reenter the interaction region.

Fragment anions formed in dissociative electron attachment in the interaction region are observed with a time-of-flight (TOF) mass spectrometer. A repeller plate pushes ions into the acceleration region where they are further accelerated. They then pass through a drift region and

![Figure 1. Schematic diagram of the ERIC.](http://www.njp.org/)
are detected with the multichannel plate detector labelled MCP in figure 1. At electron energies above \( \sim 9 \) eV positive ions are formed by electron impact, which can be detected by reversing the mass spectrometer potentials. The maximum operating pressure in the electron spectrometer and TOF mass spectrometer was less than \( 10^{-3} \) mbar.

The experiment is pulsed. A short, \( \sim 1 \) \( \mu \)s, pulse of electrons is sent through the interaction region. After the electrons have left the interaction region a pulse is sent to the ion repeller to push ions towards the ion detector. The repetition rate is 12 kHz. Conditions were chosen so that at most one ion is detected per ten cycles to minimize any paralysis of the detector due to the arrival of two ions of the same mass at the same time.

The electron energy resolution (FWHM) was determined using the attachment resonance of \( \text{SF}_6 \) at 0 eV to be approximately 250 meV. The electron energy scale was calibrated by comparing the observed positions of the attachment bands of \( \text{CS}_2 \) with the plasma turned off with literature values [21]–[23].

3. Results and discussion

3.1. Dissociative electron attachment to \( \text{CS}_2 \)

Electron attachment to \( \text{CS}_2 \) has been described previously [21]–[23]. \( \text{S}^- \) formation was observed with electron energies of \( \sim 3.6, 6.2, 7.7 \) and 9.2 eV [22]. The first peak consists of two close resonances at 3.35 and 3.65 eV [21]. The ions \( \text{CS}^- \) and \( \text{S}_2^- \) are produced at 6.2 eV and \( \text{C}^- \) is formed at 6.5 and 7.7 eV. Dissociative electron attachment to electronically excited \( \text{CS}_2 \) in its \( \tilde{B}^1\text{B}_2 \) state gives \( \text{S}^- \) at 0.5 eV and \( \text{CS}^- \) at 1.2 eV [24].

Dissociative electron attachment spectra of \( \text{CS}_2 \) measured here are shown in figures 2–4. Figures 2(a) and (b) show two-dimensional plots of the anion intensity versus TOF and the electron energy. In plot (b) \( \text{C}^- \) and \( \text{CS}_2^- \) can be seen very weakly. The \( \text{CS}_2^- \) is most likely produced in the interaction region by secondary charge transfer reactions as reported in [22]. Figures 3 and 4 show integrated signals of the anions formed. The double peak at 3.6 eV could not be resolved clearly due to the current experimental electron energy resolution. There is perhaps some hint of the double peak structure in the data in figure 3 near 3.6 eV. The centroids of the three \( \text{S}^- \) peaks from \( \text{CS}_2 \) at 3.5, 6.2 and 7.7 eV were used in the energy calibration of the data. The differences between positions of the geometric centroids and the peak maxima were less than 0.15 eV.

3.2. Composition of the gas formed in the microwave plasma and positive mass spectra

The composition of the gas sample formed in the microwave discharge depended strongly on the inlet pressures of \( \text{CS}_2 \) and He as shown in figure 5. Figure 5 shows positive ion mass spectra recorded at \( \sim 20 \) eV electron energy of the gas in the inlet system with (a) a high inlet pressure of \( \text{CS}_2 \) and (b) a low pressure of \( \text{CS}_2 \). At high \( \text{CS}_2 \) inlet pressure, figure 5(a), the \( \text{CS}^+ \) signal is very strong whereas at low \( \text{CS}_2 \) pressure, figure 5(b), \( \text{S}_2^+ \) ions and background gas ions (\( \text{H}_2\text{O}^+, \text{N}_2^+, \text{O}_2^+ \)) are clearly visible. For comparison, a mass spectrum of \( \text{CS}_2 \) and He with the plasma off is shown in figure 6.

The presence of \( \text{CS} \) in the gas sample with the plasma on is confirmed by the appearance energy measurement shown in figure 7 for \( \text{CS}^+ \). Values of 13.6–16.2 eV have been reported for appearance energy for \( \text{CS}^+ \) from \( \text{CS}_2 \) whereas the evaluated literature value of the ionization energy of \( \text{CS} \) is 11.3 eV [25]. The observed appearance energy of \( \text{CS}^+ \) here with the plasma on,
Figure 2. Dissociative electron attachment spectra of CS₂. The horizontal axes are the TOF of the ions and vertical axes show the incident electron energy. (a) (Top panel) Dissociative electron attachment bands in CS₂. At 0 eV $^{35}$Cl⁻ and $^{37}$Cl⁻ are visible from DEA to residual CCl₄. (b) (Bottom panel) CS₂ attachment bands at 6.2, 7.7 and $\sim$9 eV. Also visible is O⁻ from DEA to residual water and CS⁻ formed in secondary processes.

11.3 $\pm$ 0.3 eV, is in good agreement with ionization energy of CS. The appearance energy of CS⁺ with the plasma off observed here, 16.0 $\pm$ 0.5 eV, is not out of line with previous measurements for the appearance energy of CS⁺ from CS₂.

CS is known to undergo spontaneous polymerization reactions leading to species of the type $C_nS_m$. Proposed reactions leading to the formation of $C_3S_2$ are [26]

\[ 2CS \rightarrow C_2S + S, \]  
\[ C_2S + CS \rightarrow C_3S_2. \]

$C_3S_2^+$ and also weakly $C_3S^+$ were observed in the positive ion mass spectrum with the plasma on. Most of the $C_3S^+$ detected, however, is likely to be due to dissociation of a larger ion rather
than ionization of C$_2$S as the observed appearance energy is relatively high at 15.5 ± 0.5 eV, see figure 8(a). The ionization threshold of C$_3$S$_2$ is determined to be 9.4 ± 0.3 eV from the data shown in figure 8(a). This is in good agreement with a predicted vertical ionization energy of 9.19 eV calculated here with a GAMESS [27]–[29] MP2 calculation using the 6-31G* basis set and Koopmans theorem [30]. The molecular geometry was optimized as part of the same calculation under linear D$_{\infty h}$ symmetry [31].

S$_2$O$^+$ and SO$^+$ were observed in the positive ion mass spectra with the plasma on particularly with low flows of CS$_2$. Appearance energy measurements are shown in figure 8(b). The SO$^+$ is a fragment ion because the ionization threshold of SO is 10.3 eV [25] but the observed appearance energy of SO$^+$ is 14.0 ± 0.5 eV. This appearance energy is in agreement with the reported appearance energies of the SO$^+$ fragment from S$_2$O of 13.7 and 14.5 eV [25]. The appearance
energy of $S_2O^+$, $10.6 \pm 0.3$ eV, is in agreement with the ionization energy of $S_2O$, $10.6$ eV [25]. Therefore, $S_2O$ was present in the gas stream.

When the microwave plasma was turned on with $CS_2$ in the gas stream a clearly visible black deposit was formed on the inside of the glass wall in the region of the microwave cavity. Etching the residual black deposit by introducing $He$ and $C_3F_6$, perfluoropropene, into the gas inlet system with the plasma on led to the production of the $S_2F$ radical. $S_2F^+$ was observed at mass 83 with an appearance energy of $10.3 \pm 0.4$ eV as shown in figure 9. It seems unlikely that this was a fragment ion due to its low appearance energy and also because no possible parent ion was observed in the mass spectrum with a lower appearance energy. A signal was also observed at mass 85 with the expected relative intensity of $^{34}S^{32}SF^+$ and $^{32}S^{34}SF^+$ ions.

Figure 5. Positive ion mass spectra with the plasma on and different inlet pressures of $He$ and $CS_2$; the inlet pressure of $CS_2$ is high in (a) and low in (b). The electron energy is $\sim20$ eV in both spectra.

Figure 6. Positive ion mass spectra of $He + CS_2$ with the plasma off. The electron energy is $\sim20$ eV, which is, of course, below the ionization energy of helium.

New Journal of Physics 8 (2006) 314 (http://www.njp.org/)
Figure 7. Intensities of $\text{CS}^+$ and $\text{CS}_2^+$ observed with (a) the plasma off and (b) the plasma on as a function of electron energy. The presence of CS in the gas sample with the plasma on is confirmed by the appearance of $\text{CS}^+$ at the ionization energy of CS.

Figure 8. (a) Intensities of $\text{C}_2\text{S}^+$ and $\text{C}_3\text{S}_2^+$ as a function of electron energy with the plasma on at high $\text{CS}_2$ inlet pressure and (b) intensities of $\text{SO}^+$ and $\text{S}_2\text{O}^+$ with the plasma on with low $\text{CS}_2$ inlet pressure.

Therefore, it is concluded that the ionization threshold of $\text{S}_2\text{F}$ is $10.3 \pm 0.4 \text{ eV}$. It appears that this is a new measurement as no previous values have been found to compare it with. Theoretical ionization energy calculations for this molecule and other open shell molecules are significantly more complicated than for closed shell molecules, see e.g. [32], such as $\text{C}_3\text{S}_2$ and have not been pursued here.

Small signals of sulfur ions $\text{S}^+_n$ ($n = 3 \ldots 8$) were observed with the plasma on, visible in figure 5(b). In some measurements, mass 60 was observed weakly, see figure 5(b). This could be OCS formed in the plasma. Finally, the $\text{C}^+$ and most of the $\text{S}^+$ and $\text{S}_2^+$ ions observed are fragments of ionization as they appear far above the ionization thresholds of C, S and $\text{S}_2$. The possibility, however, that traces of S and $\text{S}_2$ were present in the gas stream cannot be excluded.
3.3. Electron attachment to CS

Spectra of the negative ions formed with the plasma on at different discharge and pressure conditions are shown in figures 10(a)–(c). Attachment bands, most visible in figure 10(a) appear at ∼5–7 eV which give S\(^-\) and C\(^-\). Another S\(^-\) band is observed at ∼1.8 eV in figures 10(b) and (c), but not (a). S\(^-\)_2 and S\(^-\)_3 ions are observed at ∼4 and ∼7 eV and S\(^-\)_4 at ∼4 eV only. Again these S\(^-\)_n peaks are visible in figures 10(b) and (c), but not (a). Finally S\(^-\) formation appears very weakly at ∼3.5 eV visible only in figure 10(b) and O\(^-\) is observed at ∼5.4 eV in figure 10(c). The CS\(_2\) inlet pressure was highest in the measurement shown in figure 10(a) and lowest in figure 10(c). The partial pressures of the different molecules in the gas sample varies with inlet pressure as seen in figure 5 where, for example, it can be seen that there is more CS present with higher CS\(_2\) inlet pressure.

The identification of the dissociative electron attachment peaks originating from the unstable CS molecule is not straightforward as the plasma contains several species that can give S\(^-\) and C\(^-\) through dissociative electron attachment. Some species can, however, be excluded or assigned as candidates for the different observed attachment bands by comparison with literature spectra where available. For example, the weak S\(^-\) signal at ∼3.5 eV can be assigned to DEA to CS\(_2\) as described in subsection 3.1. Furthermore, the positions of the S\(^-\)_2, S\(^-\)_3 and S\(^-\)_4 peaks are close to the positions of the peaks observed in dissociative electron attachment to sulfur vapour [33]. Dissociative electron attachment to sulfur vapour shows three attachment bands, at zero eV (S\(^-\)_n n = 1–8), at about 4 eV (S\(^-\)_n n = 2–5) and 7.5 eV (S\(^-\)_n n = 1–3), with S\(^-\)_2, S\(^-\)_3 and S\(^-\)_4 showing the highest intensities [33]. The intensity of S\(^-\) is in all cases lower than the intensity of S\(^-\)_2, S\(^-\)_3 and S\(^-\)_4. The similarity between the present data and these results for sulfur vapour has led to the conclusion that the formation of S\(^-\)_2, S\(^-\)_3 and S\(^-\)_4 is due to dissociative electron attachment to S\(_8\) and any smaller S\(_n\) species that may be present in the gas sample. The composition of the sulfur vapour cannot be obtained from measurements of appearance thresholds for two reasons. First, the signal of these ions is weak, which increases the uncertainty in appearance energy measurements. Secondly, the ionization energies of S\(_n\) molecules, ∼9.0 to 9.5 eV, are close...
Figure 10. Dissociative electron attachment spectra with the plasma on under different inlet pressure conditions. The CS$_2$ inlet pressure is highest in (a) and lowest in (c).
to appearance energies of $S^+_n$ fragment ions from larger $S_m$ molecules, ~10 to 13 eV, where, of course, $n < m$ [25]. Dissociative electron attachment to form $S^-_n$ ions was not observed at zero electron volt. It may be that the composition of the sulfur species produced in the plasma here is different to that of sulfur vapour in [33]. An alternative explanation is that the operation of the plasma reduced the sensitivity of the spectrometer to observe processes very close to zero electron energy. It is worth pointing out that the threshold for negative ion production from CS by dissociative electron attachment, ~5.3 eV see below, is well above zero energy.

Le Coat et al [33] also observed dissociative electron attachment to $S_2$ leading to the formation of $S^-$ at 2.4 and 4.55 eV. No $S^-$ attachment bands are seen at these energies in any of the spectra recorded and so it can be concluded from the negative spectra that at most a trace of $S_2$ was present in the gas sample.

An important observation from the data of Le Coat et al [33] is that sulfur vapour species, such as $S_8$ cannot be responsible for the $S^-$ attachment bands at ~1.8 and above 5 eV. Similarly, OCS, which was observed in some, but not all, of the measurements, can also be excluded as a candidate for the attachment bands at ~1.8 and above 5 eV as the positions of its known attachment bands [34] are different. It is unlikely that electronically excited CS$_2$ was present in the gas sample as it would have been observed by a drop in the ionization energy of CS$_2$ with the plasma on, which was not seen in the positive ion mass spectrum.

The assignment of the remaining species to the observed dissociative electron attachment peaks has been made by comparison of the variation in intensities of negative electron attachment peaks with the plasma operated under different conditions compared to the variation in the densities of neutral species in the interaction region. The density of neutral species in the gas sample is estimated from the positive ionization curves recorded at each different pressure condition. A change in the intensity of a positive parent ion of each molecule should be accompanied by a similar change in the intensity of the dissociative electron attachment bands due to the same molecule in the negative ion spectrum. In fact, changes in the ratios of intensities between two molecules, say A and B, are considered. The change in the ratio of the intensities of two parent positive ions, $I_{A^+}$ to $I_{B^+}$, between two different pressure conditions $p_1$ and $p_2$ should be equal to the change in ratios of the intensities of the negative ions formed by the same molecules, $I_{a^-}$ to $I_{b^-}$, between $p_1$ and $p_2$ in the negative ion spectrum. This relationship can be represented by

$$\frac{I_{A^+}(p_1)/I_{B^+}(p_1)}{I_{A^+}(p_2)/I_{B^+}(p_2)} = \frac{I_{a^-}(p_1)/I_{b^-}(p_1)}{I_{a^-}(p_2)/I_{b^-}(p_2)}.$$  (4)

The relationship shown in equation (4) has been presented previously [19].

The unassigned electron attachment bands have been identified with equation (4). Calculations were made of $I_{A^+}/I_{B^+}$ to compare the intensity of each parent ion $A^+$ in the positive ion mass spectra with the parent ion of 'reference' molecules $B^+$. Reference molecules are molecules present in the gas sample, which have known electron attachment bands. Here, $S_8$ and CS$_2$ have been used as reference molecules. The electron attachment spectra of CS$_2$ are known and the bands of $S^-_n$ ($n = 2–4$) observed here are considered to originate from $S_8$ or from sulfur species whose number density is proportional to the number density of $S_8$ molecules. Calculations were also made of $I_a^-/I_b^-$ where the $a^-$ are the unidentified electron attachment bands and the $b^-$ are the electron attachment bands of the reference molecules. Spectra were recorded under four different sets of pressure conditions. The intensity of the reference molecules in the positive and
negative ion spectra, however, was sometimes rather low, which introduced some uncertainty into some of the ratios calculated. Care has been taken to ensure that fragment ions, such as CS$^+$ from CS$_2$, do not contribute to the intensity of parent ions, such as CS$^+$ from CS, by checking data with electron energies below fragmentation thresholds.

The observed attachment bands to be assigned were S$^-$ at 1.8 eV, S$^-$ at 5.43 eV, S$^-$ at $\sim$6.70 eV, O$^-$ at $\sim$5.4 eV and C$^-$ at $\sim$6.40 eV. The relative intensities of three peaks, S$^-$ at 5.43 eV, S$^-$ at $\sim$6.70 eV and C$^-$ at $\sim$6.40 eV, remained constant as the inlet conditions varied suggesting that they were due to dissociative electron attachment to the same molecule. By contrast, the intensity of S$^-$ at 1.8 eV varies strongly compared to the intensities of the peaks at 5.43, $\sim$6.70 and $\sim$6.40 eV as can be seen in figure 10. At high CS$_2$ inlet gas pressure the S$^-$ at 1.8 eV intensity is relatively low, whilst at low CS$_2$ pressure this peak is high. Application of equation (4) leads to the conclusion that the S$^-$ attachment band at 1.8 eV is most likely due to dissociative electron attachment to S$_2$O. The position of the maximum of this electron attachment band observed here, 1.8 ± 0.3 eV is in agreement with the previously reported value of 1.6 eV for formation of S$^-$ from S$_2$O [19] within the experimental uncertainties. No other dissociative electron attachment bands were observed for S$_2$O in that earlier measurement [19]. The small amount of O$^-$ detected at low pressures at $\sim$5.4 eV, which cannot be due to electron attachment to H$_2$O [35], is, however, tentatively assigned here to S$_2$O as well. In the earlier measurements S$_2$O was generated from SO$_2$ and strong dissociative electron attachment to residual SO$_2$ in the gas sample between 4 and 6 eV would have masked this new electron attachment band of S$_2$O at 5.4 eV, a possibility acknowledged in the earlier study.

Application of equation (4) to the remaining three peaks, S$^-$ at 5.43 eV, C$^-$ at $\sim$6.40 eV and S$^-$ at $\sim$6.70 eV, does not lead to an unambiguous assignment. Both CS and C$_3$S$_2$ could be responsible for these three bands. The lack of larger C$_n$S$_m^-$ fragments in the spectra favours assignment to CS over C$_3$S$_2$. Similarly, it would perhaps be unlikely that the C$^-$ ion would be so prominent in dissociative electron attachment to C$_3$S$_2$ because of the molecular rearrangement required for dissociation to give C$^-$. It is also more likely these three electron attachment bands are due to CS because their positions agree well with calculated thermodynamic threshold for formation of C$^-$ and S$^-$ from CS as discussed in subsection 3.1. Therefore, these three electron attachment bands are assigned to the unstable CS molecule. The integrated intensities of the bands assigned to CS are shown in figure 11; spectrum (a) has a linear vertical axis and (b) is logarithmic.
3.4. Dissociative electron attachment thresholds

The appearance energy $AE(B^-)$ of a fragment anion $B^-$ in dissociative electron attachment to a molecule $AB$ can be estimated using the equation

$$AE(B^-) = D(A-B) - EA(B) + E^*, \quad (5)$$

where $D(A-B)$ is the dissociation energy of the chemical bond that is broken, $EA(B)$ is the electron affinity of the fragment $B$ and $E^*$ is the excess energy above the thermodynamic limit. Below it is assumed that $E^*$ is zero.

In figure 11 the $S^-$ band at 5.43 eV appears to have an asymmetric peakshape, particularly compared to the $CS_2$ bands in figure 4. If it is assumed that there is a vertical onset for $S^-$ formation at its thermodynamic threshold on the low energy side of this band then the energy resolution of the electron beam may be calculated from the rise of the $S^-$ signal. The electron energy resolution calculated from this low energy rise of the $C^-$ band at $\sim 6.40 \text{ eV}$ is also $150 \text{ meV}$, which suggests that this band starts at the thermodynamic threshold for $C^-$ production. The experimental threshold determined from the position of half maximum on the $S^-$ signal rise is $5.26 \pm 0.15 \text{ eV}$.

The thresholds for formation of $S^-$ and $C^-$ from $CS_2$ and $CS$ have been calculated with equation (5). The bond energy of the $C-$S bond can be calculated from the heats of formation of $CS$ ($280.33 \text{ kJ mol}^{-1}$), $S$ ($276.98 \text{ kJ mol}^{-1}$) and $C$ ($716.67 \text{ kJ mol}^{-1}$) [25] leading to $D(C-S) = 7.39 \text{ eV}$. A literature value is $D(C-S) = 7.379 \pm 0.025 \text{ eV}$ [36]. The electron affinities of $S$ and $C$ are $2.077$ and $1.262 \text{ eV}$ respectively [25]. The thermodynamic threshold for the reaction $CS + e^- \rightarrow C + S^-$ lies then at $5.302 \pm 0.025 \text{ eV}$, which is in excellent agreement with the experimentally determined threshold of $5.26 \pm 0.15 \text{ eV}$. The calculated threshold for the production of the carbon anion $C^-$ is $6.117 \pm 0.025 \text{ eV}$, which agrees with the experimental value, $6.21 \pm 0.15 \text{ eV}$, within the experimental uncertainty.

In the case of $CS_2$ the energy of the $S-$CCCS bond can be calculated using the heats of formation of $S$ ($276.98 \text{ kJ mol}^{-1}$) [25]), CCCS ($567 \text{ kJ mol}^{-1}$) [37]) and SCCCS ($412.5 \text{ kJ mol}^{-1}$) [38]) which lead to $D(S-CCCS) = 4.47 \text{ eV}$. As the electron affinity of sulfur is $EA(S) = 2.077 \text{ eV}$ the calculated threshold for formation of $S^-$ from $CS_2$ is $AE(S^-) = 2.39 \text{ eV}$, much lower than the experimentally observed threshold at $5.26 \pm 0.15 \text{ eV}$, which is confirmation that $CS_2$ is not responsible for these electron attachment bands between 5 and 7 eV. The determination of the threshold for $C^-$ formation from $CS_2$ is more complex. For the dissociation of SCCCS into $C^-$ and SCCS the $S-$CCCS and the SC-CCS bonds have to be broken and the $S-$CCS bond is formed. The appearance energy of $C^-$ thus is calculated using

$$AE(C^-) = D(S-CCCS) + D(SC-CCS) - D(S-CCS) - EA(C). \quad (6)$$

The bond energy of the $S-$CCS bond is calculated using the heats of formation of SCCS ($376.66 \text{ kJ mol}^{-1}$) [38]), $S$ and CCS ($586 \text{ kJ mol}^{-1}$) [37]) to be $D(S-CCS) = 5.04 \text{ eV}$. The bond energy of the SC-CCS bond is calculated using the heats of formation of SCCCS, $CS$ and

*New Journal of Physics 8 (2006) 314 (http://www.njp.org/)*
CCS to be 4.70 eV. The predicted thermodynamic threshold for C\(^-\) formation from C\(_3\)S\(_2\) is calculated as AE(C\(^-\)) = 2.87 eV, which again is significantly lower than the observed value of 6.21 \(\pm\) 0.15 eV.

There are two low lying excited electronic state of the carbon atom; \(^1\)D and \(^1\)S, which lie 1.264 and 2.684 eV above the ground state respectively [39]. The calculated threshold for formation of C (\(^1\)D) + S\(^-\) from CS is 6.566 \(\pm\) 0.025 eV, which is in agreement with the half maximum position of the low energy rise of the smaller second S\(^-\) electron band at 6.49 \(\pm\) 0.15 eV. It is not possible to determine from the experimental data if the second S\(^-\) band rises at the threshold for C (\(^1\)D) + S\(^-\) production because the high energy tail of the first S\(^-\) band interferes with the low energy rise of this second S\(^-\) band. It is not certain from the experimental data whether or not the rise of the second band is so steep that it is effectively vertical. The similarity, however, in the calculated threshold for formation of C (\(^1\)D) + S\(^-\) from CS and the experimental half maximum position strongly suggest that this second S\(^-\) band corresponds to formation of C (\(^1\)D) + S\(^-\). No experimental evidence has been found for formation of C (\(^1\)S) + S\(^-\) from CS, which is energetically allowed above 7.986 \(\pm\) 0.025 eV.

There are also excited \(^1\)D and \(^1\)S electronic states of the sulfur atom 1.145 and 2.750 eV above the ground state [40], but no experimental evidence was observed to indicate that C\(^-\) is formed in conjunction with these low lying excited states of S. The threshold for formation of C\(^-\) + S (\(^1\)D) is 7.262 eV, which is higher than that of any process observed here. Furthermore, the formation of sulfur atoms in singlet states is, of course, spin forbidden as the temporary CS\(^-\) state will be a doublet and the ground state of C\(^-\) is quartet; \(^4\)S.

The anion C\(^-\) has an excited \(^2\)D state with an electron affinity of 0.033 eV [41]. The threshold for formation of C\(^-\) (\(^2\)D) + S is 7.346 eV, but again this is not observed. No electronically excited states of S\(^-\) are known [41].

It is concluded from these comparisons between experimental and theoretical threshold that the three bands shown in figure 11 are due to dissociative electron attachment to CS rather than C\(_3\)S\(_2\).

Dissociation of S\(_2\)O to give O\(^-\) or S\(^-\) is thermodynamically allowed at the observed positions at 1.8 and 5.4 eV respectively. The dissociation energy of the SS–O bond is determined from the heats of formation of S\(_2\)O (\(-56.48\) kJ mol\(^{-1}\)), O (249.17 kJ mol\(^{-1}\)) and S\(_2\) (128.6 kJ mol\(^{-1}\)) [25] to be 4.50 eV. As the electron affinity of O is 1.461 eV [25] the dissociation threshold for the formation of O\(^-\) from S\(_2\)O lies at 3.04 eV. The dissociation energy of the S–SO bond is calculated from the heats of formation of S\(_2\)O, S and SO (5.01 kJ mol\(^{-1}\)) [25] to be 3.51 eV leading to a dissociation threshold of 1.43 eV for S\(^-\) formation.

3.5. Dissociative electron attachment cross sections

It is possible to estimate absolute cross sections for electron attachment to CS if the relative number density of CS and CS\(_2\), \(n_{CS}/n_{CS_2}\), can be estimated. The cross section for dissociative electron attachment to CS, \(\sigma_{CS}\), can be calculated from this relative density, the ratio of intensities of the dissociative electron attachment bands, \(I_{CS}/I_{CS_2}\), and the known cross section for electron attachment to the reference molecule CS\(_2\), \(\sigma_{CS_2}\), with

\[
\sigma_{CS} = \frac{n_{CS_2}}{n_{CS}} \frac{I_{CS}}{I_{CS_2}} \sigma_{CS_2}.
\]
Table 1. Summary of results. The columns are D(A–B) bond dissociation energy, EA(B) electron affinity of the fragment B, AE(B−) calculated threshold for the formation of the fragment B−, Observed AE(B−) experimentally observed threshold for B−, Observed Max electron energy at dissociative electron attachment band maximum and Cross sections. See text for references.

| Fragments: | D(A–B) (eV) | EA(B) (eV) | AE(B−) (eV) | Observed AE (eV) | Observed Max (eV) | Cross section σ(Å²) |
|------------|-------------|------------|-------------|-----------------|------------------|---------------------|
| CS S−      | C (3P)      | 7.379      | 2.077       | 5.302           | 5.26 ± 0.15      | 5.43 ± 0.15         | 0.025               |
| S−         | C (1D)      | 7.379      | 2.077       | 6.566           | 6.49 ± 0.15      | ~6.70 ± 0.15        | 0.0029              |
| C−         | S           | 7.379      | 1.262       | 6.117           | 6.21 ± 0.15      | ~6.40 ± 0.15        | 0.0024              |
| S₂O S−     | SO          | 3.51       | 2.077       | 1.43            | –                | 1.8 ± 0.3           | ~0.09               |
| O−         | S₂          | 4.50       | 1.461       | 3.04            | –                | ~5.4                | < 0.02 ?            |

At 3.35 eV the cross section σ\(_{CS₂}\) has a value of 3.7 × 10\(^{-3}\) Å\(^2\) [21]. The relative intensities I\(_{CS}\) and I\(_{CS₂}\) of the dissociative electron attachment bands were determined from the electron attachment spectra. The relative number densities n\(_{CS}\) and n\(_{CS₂}\) have been determined using electron impact ionization cross sections for CS [15, 16] and CS₂ [17, 18] and the intensities of the positive ions CS\(^+\) and CS₂\(^+\) in mass spectra recorded at 13, 15 and 20 eV under the same conditions as the electron attachment spectra. Estimates of absolute cross sections have been made in this way for all sets of data where the reference molecule was CS₂ present. The maximum variation between measurements was a factor of two for the S− bands and three for C−. The uncertainty in the average cross section values presented here is expected to be an order of magnitude at most. The cross sections determined here are presented in table 1. The CS cross sections are presented with two significant figures because the uncertainties in their relative intensities are significantly smaller than the absolute uncertainties.

There are two main sources of uncertainty for these measurements; first, the variation in the composition of the gas sample due to changing conditions in the microwave source. Positive mass spectra cannot be recorded at exactly the same time as the negative ion spectra, but the changeover between recording positive and negative ion spectra is kept as short as possible to minimize this source of uncertainty. Furthermore, measuring times were also short to minimize any effects due to changes in the discharge over time. The second main source of uncertainty is the low intensity of the reference signal of S− from CS₂ in the electron attachment spectrum as the number density of CS₂ is low and the electron attachment cross section of CS₂ is rather small, 3.7 × 10\(^{-3}\) Å\(^2\) [21].

The cross section for the S− peak at 1.8 eV from S₂O estimated here, 0.09 Å\(^2\), is within an order of magnitude of the value reported previously, 0.3 Å\(^2\), [19] from different experiments with the same apparatus where SO₂ and He were passed through the microwave discharge to generate SO, S₂O, SO₂ and S₂O₂. There were additional uncertainties in the determination of this S₂O cross section. It was necessary to use CS as the reference molecule in one dataset where there was not sufficient signal from CS₂. It is expected that the previously reported value of 0.3 Å\(^2\) is more reliable than the present one. The quality of the data for the weaker O− signal from S₂O at 5.4 eV only allowed the estimation of an upper limit to its cross section.
3.6. Dissociation dynamics

It is interesting to compare the dissociative electron attachment to CS observed here with previous measurements for CO [42]–[44], which is, of course, valence-isoelectronic with CS. The dissociative electron attachment spectra of CO and CS are remarkably similar. O\(^-\) is observed with a sharp onset at the thermodynamic threshold for O\(^-\) formation from CO at 9.63 eV, in the same way that S\(^-\) is observed from CS at its thermodynamic threshold. A second smaller O\(^-\) signal from CO appears at 10.88 eV, the threshold for formation of O\(^-\) + excited C (\(^1\)D), with another sharp onset, which is analogous to the second smaller S\(^-\) peak observed here from formation of S\(^-\) + C (\(^1\)D). In the case of CO the second O\(^-\) peak is largely obscured by the high energy tail of the first O\(^-\) band except in experiments where the kinetic energy of the fragment O\(^-\) ion is selected [42]. It is interesting to note that the two S\(^-\) peaks observed here from CS are observed without kinetic energy selection of the fragment ion.

As well as the similarity between O\(^-\) from CO and S\(^-\) from CS there is also some similarity between the formation of C\(^-\) from CS and CO. A C\(^-\) peak is observed for both CO and CS in between the two peaks of O\(^-\) and S\(^-\). Above 10.2 eV C\(^-\) is produced from CO with a cross section 3300 times smaller than for the O\(^-\) peak above 9.63 eV [44]. C\(^-\) production from CS shows a maximum at \(\sim\)6.40 eV with a cross section about ten times smaller than the intensity of the first S\(^-\) peak, see figure 11. In contrast to CS where the C\(^-\) has an onset at the thermodynamic threshold, however, the formation of C\(^-\) from CO is delayed by about 0.37 eV [45].

Dissociative electron attachment to CS can be assigned as follows

\[
\text{CS}(^1\Sigma^+) + e^- (5.43 \text{ eV}) \rightarrow S^- (^3\Pi) + C(^3\Pi),
\]

(8)

\[
\text{CS}(^1\Sigma^+) + e^- (6.70 \text{ eV}) \rightarrow S^- (^3\Pi) + C(^1\Pi),
\]

(9)

\[
\text{CS}(^1\Sigma^+) + e^- (6.40 \text{ eV}) \rightarrow C^- (^4S) + S(^3\Pi).
\]

(10)

It is not straightforward to determine the nature of the electron attachment resonance or resonances that lead to dissociation of CS. Each of the three dissociative electron attachment bands observed here appears to be cut off at low energy by the threshold for formation of the ion. Therefore, the positions of the maxima of the electron attachment resonances responsible for dissociation, are not known as they are likely to be below the thermodynamic thresholds. GAMESS RHF STO-3G calculations of CS, CS\(_2\), OCS and CO performed here indicate that the lowest unoccupied orbital of each of these molecules is \(\pi^*\). CO, CS\(_2\) and OCS all show \(^2\Pi\) shape resonances at between 1 and 2 eV in electron scattering measurements [23, 46,47], and in the case of OCS in the dissociative electron attachment spectrum [34], which can be assigned to electron attachment into these \(\pi^*\) orbitals. Therefore, it is expected that the lowest lying electron attachment resonance of CS is \(^2\Pi\) with attachment of the free electron into the lowest \(\pi^*\) orbital.

It is sometimes possible to find a linear relationship between the calculated unoccupied molecular orbital energies and the experimentally observed positions of electron attachment resonances for a family of related molecules [48, 49]. Such linear relationships can be used to predict the positions of electron attachment resonances from calculated unoccupied molecular orbital energies [50]. Here, for example, the lowest \(^2\Pi\) resonance of CS could be predicted from the energy of the lowest \(\pi^*\) orbital of CS using a linear relationship between the lowest \(^2\Pi\)
resonances and the lowest \( \pi^* \) unoccupied orbitals of CS\(_2\), OCS and CO. There is not, however, a simple linear relationship between the energies of the lowest \( ^2\Pi \) resonances and \( \pi^* \) orbital energies calculated with GAMESS of CO, CS\(_2\) and OCS. A sensible linear relationship may not even be found with only CS\(_2\) and OCS. Thus, it has not been possible here to predict the energy of the first \( ^2\Pi \) resonance of CS. Calculations of the integral elastic scattering cross sections for electron collisions with CS indicate the presence of broad \( ^2\Pi \) and \(^2\Delta\) resonances around 7 eV [16]. These resonances could possibly play a role in the electron attachment observed here, but it is expected to be very unlikely that the first \( ^2\Pi \) resonance of CS would be as high as 7 eV. The lowest \( ^2\Pi \) is more likely to be in the range of 0–3 eV given that those of CS\(_2\), OCS and CO are between 1 and 2 eV. It may be that some of the dissociative electron attachment observed here above 5 eV is due to the high energy tail of the first resonance, but without further theoretical input it is not possible to comment further.

The anion CS\(^-\) is isoelectronic to the radical NS. NS has a \(^2\Pi\) ground state with an electronic configuration of \(7\sigma^22\pi^43\pi^1\) outside a core of \(1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^56\sigma^21\pi^1\) [51]. The NS ground state corresponds to the lowest expected \( ^2\Pi \) shape resonance of CS where the extra electron is placed in the lowest \( \pi^* \) orbital of the ground state CS molecule, which has the outer electronic configuration \(7\sigma^22\pi^4\). All the electronically excited states of NS from a \(^4\Pi\) to \(1^2\Sigma^+\) at 7.0 eV above the ground state have the electronic configuration \(7\sigma^22\pi^33\pi^2\) or \(7\sigma^12\pi^43\pi^2\), except for the Rydberg states [51]. Therefore, it is expected that all the equivalent higher resonance states of CS\(^-\) are ‘core excited’ where an electron from the \(7\sigma^22\pi^4\) ‘core’ and the extra attaching electron are placed in the \( \pi^* \) orbital. There are, of course, no Rydberg states of negative ions. Dipole bound anion states are the nearest equivalents to Rydberg states, but the dipole moment of ground state CS, 1.96 Debye [52], is too low to support them [53].

In the case of CO, angular and energetically resolved measurements of the O\(^-\) fragments led to the conclusion that electron attachment responsible for the two peaks above 9.63 and 10.88 eV proceeds under formation of \(^2\Pi\) excited states of CO\(^-\) [42, 45]. The electronic states of the NO molecule, which is isoelectronic to CO\(^-\), are very similar to those of NS. Again the ground state of NO corresponds to the \(^2\Pi\) shape resonance of CO\(^-\) at low energy. It has been suggested that excited \(^2\Pi\) states of NO may correspond to the negative ion resonances that lead to dissociative electron attachment; again these excited states would correspond to ‘core excited’ negative ion states [42, 45].

4. Conclusions

Dissociative electron attachment to the CS unstable molecule produced in a microwave discharge has been investigated. Three dissociative electron attachment bands of CS have been observed; formation of S\(^-\) at 5.43 eV, C\(^-\) at \(~6.40\) eV and S\(^-\) at \(~6.70\) eV. The fragments are all produced in their ground states except at 6.70 eV the carbon atom is excited and the products are S\(^-\)+C (\(^1D\)). All three of these bands appear at their thermodynamic thresholds. Absolute cross sections for these bands have been estimated and are shown in table 1.

Dissociative electron attachment to CS is remarkably similar to dissociative electron attachment to CO, carbon monoxide, which is valence-isoelectronic. The identity of the electron attachment resonances which enable dissociative electron attachment is not clear. Consideration of the NS radical, which is isoelectronic to the CS\(^-\) anion, suggests that the resonances observed are ‘core excited’ where the free electron excites one of the valence electrons as it attaches to the
molecule. Theoretical calculations of potential energy curves for CS$^-$ resonances, including core excited resonances, are very desirable to aid in the understanding of the molecular dynamics. Furthermore, parallel calculations of CO and CS might reveal why C$^-$ is observed so weakly from CO, but much more strongly from CS.

The previously observed formation of S$^-$ in dissociative electron attachment to S$_2$O at 1.8 eV is confirmed here and formation of O$^-$ at 5.4 eV is tentatively assigned to S$_2$O. The ionization energies of the S$_2$F radical, 10.3 ± 0.4 eV, and C$_3$S$_2$, 9.4 ± 0.3, have been measured, apparently for the first time.

Acknowledgments

The authors thank John Dyke for his encouragement and advice concerning the generation of CS. KG thanks the European Social Fund (ESF) for providing a PhD studentship. The authors also gratefully acknowledge financial support from the EPSRC (GR/N04362/2) and Royal Society (RSRG 21245).

References

[1] Graves D B, Kushner M J, Gallagher J W, Garscadden A, Oehrlein G S and Phelps A 1996 Database Needs for Modeling and Simulation of Plasma Processing (Washington, DC: National Research Council, National Academy Press)
[2] Li P, Tan Y L and Fan W Y 2004 Chem. Phys. 302 171
[3] Petherbridge J R, May P W, Fuge G M, Rosser K N and Ashfold M N 2002 Diamond Relat. Mater. 11 301
[4] Maurmann S, Gavrilenko V, Kunze H-J and Oks E 1996 J. Phys. D: Appl. Phys. 29 1525
[5] Sze N D and Ko M K W 1981 Geophys. Res. Lett. 8 765
[6] Crutzen P J 1976 Geophys. Res. Lett. 3 73
[7] Turco R P, Whitten R C, Toon O B, Pollack J B and Hamill P 1980 Nature 283 283
[8] Deutscher N M, Jones N B, Griffith D W T, Wood S W and Muncray F J 2006 Atmos. Chem. Phys. Discuss. 6 1619
[9] Williams J P and Blitz L 1998 Astrophys. J. 494 657
[10] Woods P M, Schóier F L, Nyman L-Å and Olofsson H 2003 Astron. Astrophys. 402 617
[11] Woods P M and Nyman L-Å 2005 H$_2$CO and CS in planetary nebulae Astrochemistry throughout the Universe: Recent Success and Current Challenges, International Astronomical Union Symp. 231, 29 August–2 September 2005, Asilomar, CA ed D C Lis, G A Blake and E Herbst (Cambridge: Cambridge University Press)
[12] Biver N et al 1997 Earth Moon Planets 78 5
[13] Martín S, Martín-Pintado J, Mauersberger R, Henkel C and García-Burillo S 2005 Astrophys. J. 620 210
[14] Kaiser R L, Ochsenfeld C, Head-Gordon M and Lee YT 1998 Science 279 1181
[15] Freund R S, Wetzl R C and Shul R J 1990 Phys. Rev. A 41 5861
[16] Sobrinho A M C and Lee MT 2005 Int. J. Quantum Chem. 103 703
[17] Kim Y-K, Hwang W, Weinberger N M, Ali M A and Rudd M E 1997 J. Chem. Phys. 106 1026
[18] Online at http://physics.nist.gov/PhysRefData/Ionization/ (2006)
[19] Field T A, Slattery A E, Adams D J and Morrison D D 2005 J. Phys. B: At. Mol. Opt. Phys. 38 255
[20] Stamatovic A and Schulz G J 1970 Rev. Sci. Instrum. 41 423
[21] Ziesel J P, Schulz G J and Milhau J 1975 J. Chem. Phys. 62 1936
[22] Krishnakumar E and Nagesha K 1992 J. Phys. B: At. Mol. Opt. Phys. 25 1645
[23] Dressler R, Allan M and Tronc M 1987 J. Phys. B: At. Mol. Phys. 20 393
[24] Rangwala S A, Kumar S V K and Krishnakumar E 2001 Phys. Rev. A 64 (Preprint hep-ph/0209117)
[25] Linstrom P J and Mallard W G (ed) 2005 NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Gaithersburg, MD: National Institute of Standards and Technology) 20899 Online at http://webbook.nist.gov
[26] Moltzen E K, Klabunde K J and Senning A 1988 Chem. Rev. 88 391
[27] Schmidt M W et al 1993 J. Comput. Chem. 14 1347
[28] Gordon M S and Schmidt M W 2005 Advances in electronic structure theory: GAMESS a Decade Later (Amsterdam: Elsevier)
[29] Online at http://www.msg.ameslab.gov/GAMESS/GAMESS.html
[30] Koopmans T 1934 Physica 1 104
[31] Xie Y and Schaefer H F III 1999 J. Mol. Struct. (Theochem.) 460 117
[32] Gritsenko O V and Baerends E J 2004 J. Chem. Phys. 120 8364
[33] Le Coat Y, Bouby L, Guillotin J P and Ziesel J P 1996 J. Phys. B: At. Mol. Opt. Phys. 29 545
[34] Iga I and Srivastava S K 1995 J. Mol. Struct. (Theochem.) 335 31
[35] Melton C E 1972 J. Chem. Phys. 57 4218
[36] Coppens P, Reynard J C and Drowart J 1979 J. Chem. Soc. Faraday Trans. 2 75 292
[37] Le Teuff Y H, Millar T J and Markwick A J 2000 Astron. Astrophys. Suppl. Ser. 146 157
[38] McBride B J, Zehe M J and Gordon S 2002 NASA Glenn coefficients for calculating thermodynamic properties of individual species NASA Report
[39] Moore C E 1993 Tables of spectra of hydrogen, carbon, nitrogen, and oxygen atoms and ions CRC Handbook of Chemistry and Physics 76th edn, ed J W Gallagher (Boca Raton, FL: CRC Press) p 336
[40] Martin W C, Zalubas R and Musgrove A 1990 J. Phys. Chem. Ref. Data 19 821
[41] Andersen T, Haugen H K and Hotop H 1999 J. Phys. Chem. Ref. Data 28 1511
[42] Hall R I, Caez I, Schermann C and Trone M 1977 Phys. Rev. A 15 599
[43] Denifl G, Muigg D, Stamatovic A and Mark T D 1998 Chem. Phys. Lett. 288 105
[44] Stamatovic A and Schulz G J 1970 J. Chem. Phys. 53 2663
[45] Christophorou L G, McCorkle D L and Christodoulides A A 1984 Electron attachment processes Electron–Molecule Interactions and Their Applications Vol 1, ed L G Christophorou (New York: Academic)
[46] Szymkowsk C and Zubek M 1978 Chem. Phys. Lett. 57 105
[47] Buckman S J and Lohmann B 1986 Phys. Rev. A 34 1561
[48] Staley S W and Smnad J T 1994 J. Phys. Chem. 98 116
[49] Aflatooni K, Gallup G A and Burrow P D 2000 J. Phys. Chem. A 104 7359
[50] Graupner K, Merrigan T L, Field T A, Youngs T G A and Marr P C 2006 New J. Phys. 8 117
[51] Lie G C, Peyerimhoff S D and Buenker R J 1985 J. Chem. Phys. 82 2672
[52] Winnewisser G and Cook R L 1968 J. Mol. Spectrosc. 28 266
[53] Kalcher J 2001 Croatia Chemica Acta 74 903