

Dissociative attachment of electrons to CS₂

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Abstract. The formation of various negative ions from CS₂ by electron impact up to 50 eV is studied using a crossed beam geometry. A pulsed electron beam–pulsed ion extraction technique has been coupled with a specially designed time-of-flight mass spectrometer to make complete detection of all the ions irrespective of their kinetic energies and mass-to-charge ratios. The cross sections for the formation of different ions are put on an absolute scale using the relative flow technique. The formation of S₂[−] through dissociative attachment is confirmed and is explained as arising from the presence of a small number of CS₂ molecules with bending mode excitations in the neutral molecular beam. From the various thresholds the dissociation energy and electron affinity of CS are determined to be 6.5 and 0.8 eV respectively.

1. Introduction

Carbon disulphide has been the subject of both experimental and theoretical studies in recent years. The formation of CS₂^{*n*+} ions with *n* up to 3 and their dissociation into various fragment ions have been studied using photoionization, electron impact ionization and ion translational energy spectrometry (Mathur and Harris 1989). Apart from testing the many-body formalisms used for the quantum chemical descriptions and the chemical dynamics of quantum-state diagnosed ion–neutral interactions involving multiply charged molecular projectiles, these studies have also been of interest in understanding the cometary environment and planetary and stellar atmospheres (Vardya and Tarafdar 1987). The interest of astrophysicists in CS₂ has been kindled by the recent observation of various sulphur-containing molecules such as CS, S₂, H₂S and SO₂ in cometary atmospheres (Jackson *et al* 1982, Cosmovici *et al* 1982, Cosmovici and Ortolani 1984) and in oxygen-rich stellar atmospheres (Vardya and Tarafdar 1987). It has also been proposed that the detection of neutral and singly charged sulphur dimers in comets could be related to reactions involving CS₂ (A'Hearn and Feldman 1985). Against this background it is surprising that the data on the negative ion states of CS₂ are quite fragmentary. To our knowledge, no elastic electron scattering work has so far been reported. In addition no theoretical calculations of the negative ion states of CS₂ are available as of now.

Negative ion formation from CS₂ by means of dissociative attachment has been studied by Kraus (1961), Dillard and Franklin (1968), MacNeil and Thynne (1969) and Zeisel *et al* (1975). The first three groups have reported the appearance energies and the energies of the resonant peaks of different negative ions from CS₂. Even though there is good agreement on the appearance energies and peak positions of S[−], C[−] and CS[−] among all the three groups, there is substantial disagreement regarding

the formation of S_2^- . In addition, the relative cross sections for the formation of all these ions as a function of electron energy have received very little attention. The only measurement reported for absolute cross sections was made by Zeisel *et al* (1975), who measured the absolute cross sections for the formation of negative ions using a total ionization tube in the energy range 2.7 to 4.3 eV. This energy range only corresponds to the first resonant peak in the formation of S^- from CS_2 . Beyond these energies other negative ions also start appearing. No other measurements have been reported at higher energies for absolute cross sections, either partial or total. Considering these aspects, we have carried out extensive measurements using a crossed beam time-of-flight (TOF) apparatus on the various negative ions formed from CS_2 by electron impact up to an energy of 50 eV. The cross sections are put on an absolute scale by using the relative flow technique.

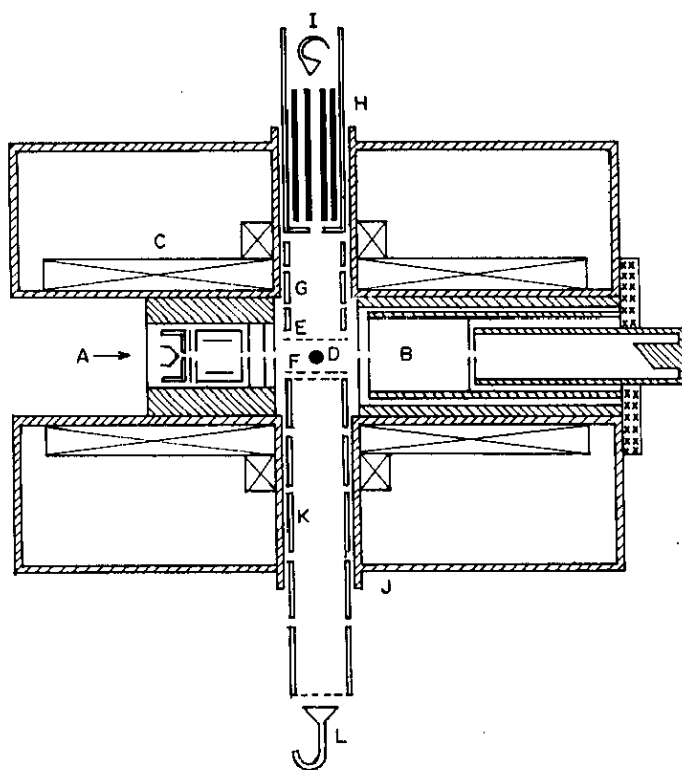


Figure 1. Schematic diagram of the experimental arrangement: A, electron gun; B, Faraday cup; C, magnetic coils; D, capillary array; E and F, extraction grids; G, electrostatic optics; H, quadrupole mass spectrometer; I and L, channel electron multipliers; J, UHV chamber for magnetic coils; K, TOF assembly.

2. Apparatus

A schematic diagram of the experimental arrangement is shown in figure 1. This is a modified version of the one reported earlier (Krishnakumar 1990). It consists of

a magnetically collimated, pulsed electron gun, a capillary array for production of the molecular beam, a relative flow arrangement, a pulsed ion extraction system, a Faraday cup, a quadrupole mass spectrometer, and a TOF mass spectrometer. The electron gun has the same design as the one used by Khakoo and Srivastava (1984) and later by Krishnakumar and Srivastava (1988) and is capable of providing pulsed beams with nanosecond risetimes. The magnetic field to collimate the electron beam was generated by a set of coils immersed in the vacuum chamber. Since the experiment requires the intersection of the electron beam and the molecular beam at a specified location with respect to the rest of the apparatus, great care was taken in the design and construction of the coils to provide a very well directed uniform magnetic field. Since the earlier work (Krishnakumar 1990) the coils have been modified with one set of inner coils and another set of outer coils. The outer coils could be used to correct for the non-uniformity of the magnetic field in the ionization region. The magnetic field used in the present measurements was about 80 G. Since most insulating materials of wires available for winding the solenoids had poor vacuum properties, the coils were enclosed in two identical annular UHV chambers of inner diameter 5 cm, outer diameter 20 cm and length 12 cm each.

The molecular beam was produced by a capillary array of 5 mm length with each capillary having a diameter of 0.05 mm. The array was embedded in the tip of a 2 mm diameter non-magnetic stainless steel tube. The tube was mounted in such a way that the molecular beam intersected the electron beam at right angles and in the centre of the extraction assembly. The relative flow arrangement was made up of a 1 Torr head MKS Baratron capacitance manometer, two Granville-Phillips needle valves and a set of control valves to switch the gas flow from the molecular beam mode to the static gas mode.

The ion extraction region consisted of two fine molybdenum wire meshes with transparency better than 90% mounted parallel to each other and symmetrically placed on either side of the interaction point at which the electron beam and the molecular beam crossed each other. On application of a voltage between the wire meshes, a uniform electric field was produced at right angles to both the electron beam and the molecular beam. The ions were extracted into the TOF mass spectrometer or a quadrupole mass spectrometer by suitable polarity of the electric field. In the present work all the measurements were carried out using the TOF spectrometer.

The TOF mass spectrometer was made of five cylindrical tubes of 2.5 cm inner diameter and mounted coaxially with a separation of 0.3 cm. These together formed a lens system which transported the ions without any loss to the channel electron multiplier used as the detector and operated in the pulse counting mode. The overall length of the flight tube was about 20 cm. The lens system was designed using the SIMION program (Dahl *et al* 1990) with special attention being paid to transporting, without loss, ions with up to 15 eV kinetic energy produced in the interaction region and with an initial velocity vector at 90° to the extraction field.

The entire apparatus was mounted in an oil-free UHV chamber made of stainless steel and pumped by a combination of sorption pumps, a getter pump and an ion pump. The effects of the magnetic field of the ion pump and the charged particles created within the pump were found to be negligible. The ultimate vacuum in the apparatus was about 3×10^{-9} Torr.

A schematic diagram of the pulsing arrangement is shown in figure 2. The electron pulse and the extraction pulse were timed in such a way that an extraction field of 300 V cm^{-1} could be applied in the interaction region without undue effect on the

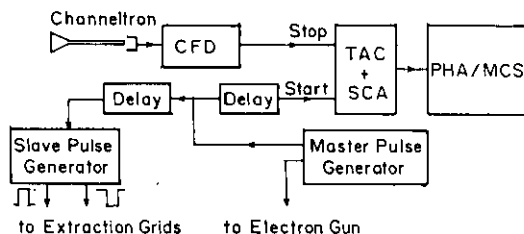


Figure 2. Schematic diagram of the pulsing and TOF arrangement.

electron beam. For obtaining the TOF spectra, the pulses from the channel electron multiplier and the synchronous pulse from the electron gun pulser were fed to the time-to-amplitude converter (TAC + single channel analyser (SCA)). The TAC output was fed to the pulse-height analyser (PHA) to obtain the TOF spectra. Particular mass peaks could be selected using a specific time interval in the TAC and choosing the SCA output. The excitation function for each ion was obtained by feeding the SCA output to the multichannel scaler (MCS) and scanning the electron energy with the help of a ramp generator which was controlled by the MCS itself.

The significant features of this apparatus designed specifically for measuring the dissociative ionization and attachment are as follows.

(i) The electron energy could be varied from 0.5 to 500 eV with a maximum variation of 10% in the electron beam current.

(ii) The pulsed electron beam and pulsed ion extraction technique along with the specially designed TOF spectrometer allows complete detection of all ions irrespective of their mass and kinetic energies. Non-uniform or incomplete collection of various fragment ions due to their varying kinetic energies has been one of the major difficulties in making accurate partial cross section measurements in both dissociative ionization and attachment.

(iii) Measurement of partial ionization cross section necessitates the use of a mass spectrometer to distinguish various ionic species. This makes absolute measurements of cross sections almost impossible. This has been circumvented by the use of a calibration procedure using a standard atom or molecule of known cross section. The relative flow technique (Krishnakumar and Srivastava 1988, 1990) has been established to be quite reliable for this purpose. The critical aspect of this calibration procedure is the comparison of the relative intensities of the species of interest with that of a standard species of known cross section. In this process it is necessary to determine the relative efficiency with which the ions are extracted from the ionization region, their transmission through the mass spectrometer and finally the efficiency with which they are detected. The overall efficiency as a function of the mass-to-charge ratio can be written as

$$K(m/e) = k_1 k_2 k_3 \quad (1)$$

where k_1 is the extraction efficiency from the ionization region, k_2 is the transmission efficiency of the mass analyser and k_3 is the efficiency of detection of the ion by the particle detector. In practice it is difficult to isolate k_1 , k_2 and k_3 and one measures only K . k_1 is independent of m/e . It is known that for most of the mass spectrometers k_2 is dependent on m/e . In addition it has been found that in the case of charged particle detectors like channel electron multipliers, which are

traditionally used for ion detection, the detection efficiency k_3 is dependent on the velocity with which the ions strike the detector surface. Thus for a given acceleration, ions of smaller m/e will have larger detection probability (Nagy *et al* 1980). In the case of measurements on the positive ions, $K(m/e)$ can be determined using cross sections for the formation of singly charged ions from their respective noble gas atoms in the mass range 4 to 132, by the relative flow technique (Krishnakumar and Srivastava 1988). But so far it has not been possible to apply it to the negative ions due to the non-availability of accurate cross sections in a wide m/e range. One could calibrate the set-up for positive ions and assume that it holds good for the negative ions as well. But it is not clear how good this assumption would be. This problem can be solved by the use of a TOF mass spectrometer in which it is relatively easy to ensure complete transmission of all the ions independent of m/e and even of their kinetic energies. The m/e dependence of K through k_3 can be taken care of by increasing the nose-cone voltages to such levels that there is saturation in the detection efficiency. In the present experiment the measurements were carried out with these provisions.

We took extreme care in reducing the impurity levels in the CS₂ sample used for the present measurements. This was done by double distilling fresh spectroscopic grade CS₂ (from Spectrochem Ltd, India) at its boiling point and discarding the initial and last fractions of the distillate. To ensure the absence of any dissolved gases completely, the sample was repeatedly degassed by solidifying it using a low-temperature bath of alcohol slurry and pumping the uncondensed gases, which were mostly nitrogen and oxygen, by a sorption pump. The entire gas-handling line of the apparatus was made of copper and stainless steel.

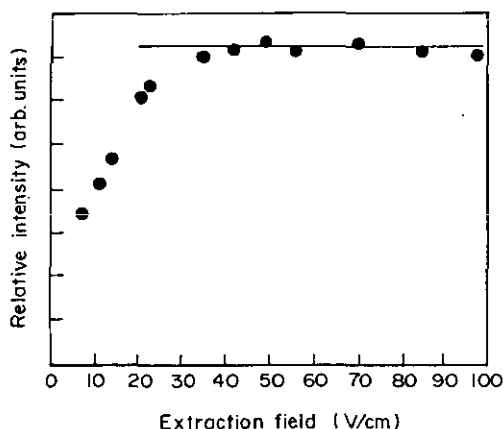


Figure 3. Extraction efficiency of O⁻ from O₂ as a function of the field strength for an incident electron energy of 200 eV.

2.1. Extraction efficiency

The performance of the system was tested by studying negative ion formation from O₂ and CO₂. The extraction efficiency as a function of the extraction field strength was measured for O⁻ from O₂ at 6.5 eV (at the resonant peak) and at several energies in the polar dissociation continuum. The curve obtained for an electron energy of

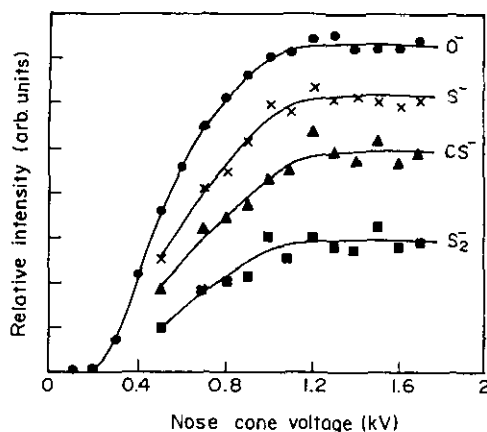


Figure 4. Detection efficiency as a function of the voltage on the nose cone of the channeltron for various negative ions. The voltage difference across the channeltron is kept constant.

200 eV is shown in figure 3. It can be seen that with a field strength of 40 V cm^{-1} the collection efficiency saturates. It was found that the ion optics voltages needed for complete collection varied as a function of the extraction voltage, albeit slowly. Also we found that at low extraction voltages the magnetic field used for the collimation of the electron beam affected the ion intensities slightly when its strength was large. This effect was reduced by switching off the current in the outer magnetic coils. The magnetic field strength was also adjusted by trial to have the best effect on the ion collection, but also to give a sufficiently good electron beam current profile. This field was about 80 G. Under these optimum conditions we measured the excitation efficiency curves for O^- from both O_2 and CO_2 . We found that these curves were in excellent agreement with the reported data (Rapp and Briglia 1965) up to 60 eV for the relative intensities and energy resolution. This showed that in the present set-up we have complete collection of all the ions irrespective of their kinetic energies and also that there is no variation in the volume overlap between the molecular beam and electron beam as the electron energy is varied.

2.2. Detection efficiency of the channeltron

We have used the well established cross section for the formation of O^- from O_2 (Krishnakumar and Srivastava 1990) to calibrate the cross section of various negative ions from CS_2 by the relative flow technique. In this respect it was necessary to determine the overall detection efficiency as a function of the mass-to-charge ratio. In the present experiment it was mainly dependent on the detection efficiency of the channeltron. In the absence of reliable cross sections for the formation of negative ions of different masses we could not determine the detection efficiency curve as a function of the mass-to-charge ratio for the channeltron. Hence the procedure we used was to operate the channeltron with sufficiently high nose-cone voltages at which the detection efficiency shows saturation. In order to obtain this voltage we measured the intensity variation of O^- from O_2 and S^- , CS^- , S_2^- from CS_2 as a function of the nose-cone voltage. From the results shown in figure 4 it can be seen that saturation is obtained by about 1200 V. We made all the present measurements with a nose-cone voltage of 1500 V.

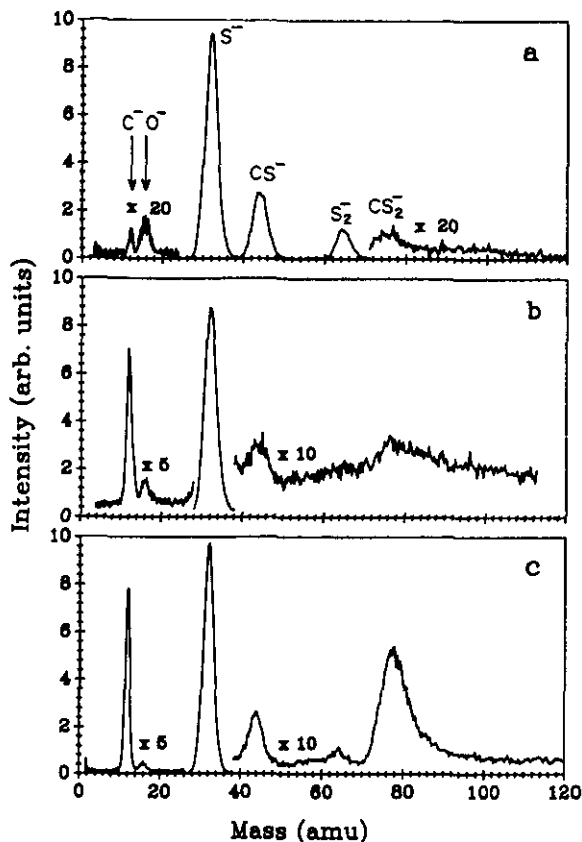


Figure 5. The mass spectra of negative ions from CS_2 : (a) electron energy 6 eV and background pressure 8×10^{-8} Torr; (b) electron energy 40 eV and background pressure 8×10^{-8} Torr; (c) electron energy 40 eV and background pressure 1.5×10^{-6} Torr.

2.3. Excitation functions

To begin with, the TOF mass spectra were taken at different electron energies to ensure proper mass resolution under the optimum conditions used for complete collection of ions. One such mass spectrum obtained at 6 eV is shown in figure 5(a). In this one can see S^- , CS^- and S_2^- with very good resolution. Small quantities of C^- and O^- are also seen in the spectrum. It was found that the O^- was being formed from the background gases. The excitation function for each atom was taken by selecting the individual peak using the SCA provision in the TAC and by scanning the electron energy in the range of 0 to 50 eV at 0.1 eV intervals. In order to obtain details of the resonant peaks the measurements were also carried out in the range of 0 to 10 eV at smaller intervals. The energy scan was controlled by the multichannel analyser in the MCS mode with a dwell time of 0.1 s/channel. During the entire scan the pressure of the gas behind the capillary and inside the chamber was kept constant. The electron current was found to vary by only a few per cent from 1 eV onwards. The data were corrected for this variation. The time averaged current was about 1 nA.

2.4. Calibration for the absolute cross sections

The absolute cross sections were obtained using the relative flow technique using O^- from O_2 as the standard. The expression for the unknown cross section, in this case that of S^- from CS_2 , is given by

$$\sigma\left(\frac{S^-}{CS_2}\right) = \sigma\left(\frac{O^-}{O_2}\right) \frac{N(S^-)}{N(O^-)} \frac{F(O_2)}{F(CS_2)} \frac{I_e(O_2)}{I_e(CS_2)} \frac{K(O^-)}{K(S^-)} \sqrt{\frac{M(O_2)}{M(CS_2)}} \quad (2)$$

where N is the number of ions collected for a specific time, M is the molecular weight of the parent molecules, F is the flow rate, I_e is the electron current, K is the detection efficiency and σ is the cross section. In the present measurements as discussed in the previous sections $K(O^-)/K(S^-)$ is made unity. The details of the relative flow calibration procedure are similar to those discussed earlier (Krishnakumar 1990). The cross section for O^- from O_2 has been taken from Rapp and Briglia (1965), is $1.45 \times 10^{-18} \text{ cm}^2$ at the resonant peak of 6.5 eV. Using this, the S^- cross section from CS_2 at 3.6 eV corresponding to the first resonant peak was determined. Then the entire excitation function was normalized to obtain absolute cross sections for the whole energy range. A similar procedure was used for obtaining the absolute cross sections for CS^- , S_2^- and C^- .

2.5. Errors and their estimation

The possible sources of errors in this type of experiment have already been dealt with in detail (Krishnakumar and Srivastava 1990). In the present experiment it has been found that the variation in the electron beam current and pressure were minimal. The major contribution to the uncertainty in the excitation function has been from the statistical fluctuation due to the low count rate. We estimate this to be 5% in the case of S^- , 10% in the case of CS^- , S_2^- and C^- over the range 1 to 50 eV. The uncertainty in the absolute cross section has major contributions from flow rate measurements (2%), statistical errors from counting (about 3%), and the uncertainty in the standard cross section used for calibration. The uncertainty in the cross section of O^- from O_2 is estimated to be 10% from a comparison of various data (Krishnakumar and Srivastava 1990). The possible systematic error due to the mass dependence in the detection efficiency has been minimized by keeping the nose cone of the channeltron at a sufficiently high voltage where the detection efficiency is saturated (see figure 4). We estimate the combined uncertainty due to this as well as the uncertainty in the collection and transmission of the ions to be 5%. Thus the overall uncertainty in the present measurements is about 15%.

3. Results and discussions

3.1. CS_2^-

The negative ion mass spectra obtained at 6 and 40 eV are shown in figure 5. At 6 eV, figure 5(a), three peaks corresponding to S^- ($m/e = 32$), CS^- ($m/e = 44$) and S_2^- ($m/e = 64$) are very dominant compared with the peaks corresponding to C^- ($m/e = 12$) and O^- ($m/e = 16$) (from the background H_2O and O_2). We also observe a small amount of CS_2^- ($m/e = 76$). This spectrum was taken with

the very low pressure of 0.03 Torr behind the capillary and a background pressure of 8×10^{-8} Torr, in order to eliminate any pressure effects. At 40 eV and at the same pressure, figure 5(b), the dominant peaks were C^- and S^- with CS^- being very low in intensity. CS_2^- is also seen in small quantity. S_2^- is practically absent. Since there has been much discussion about the ion-molecule reactions in the earlier reported negative ion data of CS_2 , we obtained the mass spectra at various pressures at electron energies of 6 and 40 eV. One such spectrum at 40 eV with a pressure of 0.26 Torr behind the capillary and 1.5×10^{-6} Torr background pressure is shown in figure 5(c). In this spectrum we see a noticeable enhancement of CS_2^- . S_2^- has become barely visible. A detailed examination showed that at 40 eV, C^- and S^- showed a linear pressure dependence, whereas CS^- and CS_2^- showed a non-linear pressure dependence with CS^- decreasing and CS_2^- increasing. The dependences of the intensity of CS^- and CS_2^- on the pressure were determined to have a power 0.87 and 1.3 respectively. This indicates the possibility of an ion-molecule reaction occurring when CS^- is consumed to produce CS_2^- , basically due to a charge transfer from CS^- to CS_2 . This type of reaction has, in fact, been discussed by Kraus *et al* (1961), and Dillard and Franklin (1968) at 6 eV electron energy using pressures in the range of 10^{-2} Torr in static gas geometry. It is surprising to note that this charge transfer reaction is quite significant even at the very low pressures at which we were operating. At a background pressure of 1×10^{-6} Torr we estimate the beam pressure in the interaction region to be about 10^{-4} Torr only, that too within a very small volume. Measurements carried out at 6 eV up to a pressure of 0.3 Torr behind the capillary and a background pressure of 1×10^{-6} Torr also showed a different behaviour compared with that at 40 eV. At 6 eV, the intensities of S^- and CS^- were linear with pressure, thereby overruling the possibility of their involvement in any ion-molecule reactions. But the variation in the intensity of S_2^- was smaller than that expected of a linear behaviour showing the depletion of S_2^- intensity at higher pressures. We could not examine the behaviour of C^- and CS_2^- with pressure at this energy due to their very low intensities.

MacNeil and Thynne (1969) have studied the pressure dependence of the S^- , CS^- and S_2^- ion currents at 6.3 eV. They found that the CS^- dependence on the source pressure was linear, and those of the S^- and S_2^- were proportional to about 1.3 power of pressure. They interpreted these as being due to possible contributions resulting from the thermal decomposition of CS_2 on the filament. Our measurements conclusively prove that the origin of the ions S^- , CS^- and S_2^- at 6 eV is the dissociative attachment process and no secondary collision is involved in their formation. Since the C^- formation occurs at different energies compared with the other ions the contribution of the secondary reaction to its formation has already been eliminated.

It is not clear why the CS^- ions formed at two different electron energies behave differently as a function of pressure. One possible explanation is that at 6 eV, the CS^- is formed in its ground state, and at 40 eV it is formed in an excited state which has an extremely high cross section for charge exchange with CS_2 . The depletion of S_2^- formed at 6 eV can also be attributed to very large cross sections for charge exchange reactions.

The formation of CS_2^- at 6 eV as well as at higher energies could be attributed to the previously mentioned secondary processes. We have noticed the relatively long tail of the CS_2^- peak in the TOF mass spectrum towards the higher mass side showing the possible presence of an ion of mass higher than CS_2^- . As mentioned in section 2, we took extreme care in reducing the impurity levels in the CS_2 sample used for this

experiment. The sample was also tested for the presence of any heavier molecules by taking positive ion spectra at different incident electron energies. We did not see any peaks with a mass higher than that of CS_2^+ . The tail of the CS_2^- peak towards the higher mass side could be considered as additional evidence for a charge exchange reaction between CS^- and CS_2 resulting in the formation of CS_2^- in the following way. It is expected that a good percentage of the CS^- ions formed due to the polar dissociation will have fairly large kinetic energies. Assuming that the ions have an isotropic distribution, almost half of the ions will initially be travelling in a direction opposite to that of the extraction field. These ions will eventually turn around under the influence of the extraction field and a small fraction of these will pass through the molecular beam once again forming CS_2^- ions due to collisions. The ions thus formed will have a time delay corresponding to the flight time of the CS^- ions before undergoing collision. Calculations show that the higher the initial kinetic energy of the CS^- ions, the longer the tail will be. Using the SIMION program we estimate from the length of the tail that the CS^- could have an energy of about 4 eV. By the same token one may also expect a corresponding, but smaller tail at the lower mass side, caused by the faster CS^- ions flying initially towards the mass spectrometer. That we did not see this could be due to the fact that the ions initially travelling against the field direction traverse the molecular beam twice and also that they have to go through an almost zero velocity phase during their flight thereby increasing the collision probability compared with those initially travelling along the field direction.

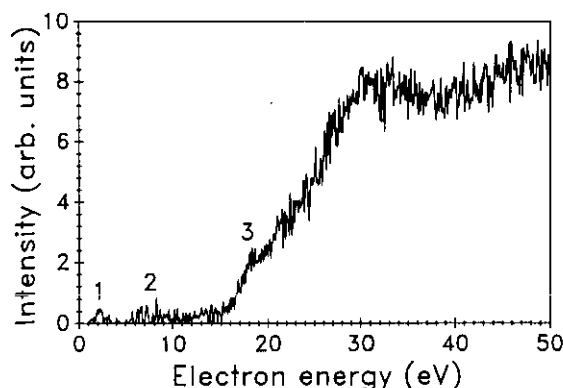


Figure 6. Variation of the CS_2^- intensity as a function of the incident electron energy. The data were obtained at a background pressure 1.5×10^{-6} Torr.

The variation in the intensity of CS_2^- as a function of the electron energy is given in figure 6. This was taken at a background pressure of 1.5×10^{-6} Torr. The relative intensity of CS_2^- with respect to S^- at 40 eV at this pressure is 0.12. The ratio of CS^- to S^- at this energy, taking into account the pressure dependence, i.e. by extrapolating to zero pressure, is 0.055. The variation in CS^- also shows only 0.87-power dependence on pressure which does not seem to be compatible with the 1.3-power dependence on pressure of CS_2^- . This shows that the entire quantity of CS_2^- we have observed could not have been formed by the collisions of CS^- with CS_2 . As discussed earlier other dominant ions S^- and C^- did not show any non-linear

behaviour with pressure in the range we studied, thus ruling out their involvement in the formation of CS₂⁻. The discrepancy in the CS₂⁻ intensity could possibly be explained as being due to additional contributions from a small amount of the (CS₂)₂ (carbon disulphide dimer) which may be present in the molecular beam. This may also explain the structures 1, 2 and 3 seen in the CS₂⁻ data shown in figure 6. In order to investigate the presence of (CS₂)₂ we collected the positive ion spectra at several electron energies. We could not get conclusive evidence of its presence from these spectra. But the possibility that (CS₂)₂⁺ is not stable and, hence, cannot be detected cannot be overruled.

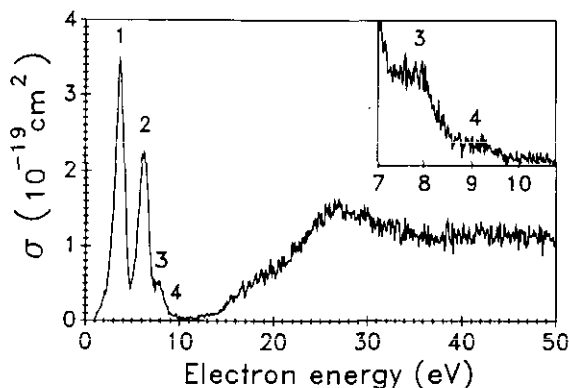


Figure 7. The cross section for the formation of S⁻ from CS₂. The inset is an enlarged view of the 7-11 eV range. The measurements were carried out at a background pressure 3×10^{-7} Torr.

3.2. S⁻

The cross sections for the formation of S⁻ ions are given in figure 7. The absolute cross section we obtained for the formation of S⁻ at the first resonant peak is $0.35 \pm 0.5 \times 10^{-18}$ cm². This is in good agreement with the data obtained by Zeisel *et al* (1975) with higher energy resolution. They observed that this resonant peak is split into two with a separation of 300 meV. According to them the maximum of the cross section occurs at 3.35 eV with a magnitude of 0.37×10^{-18} cm². The centre of the peak occurs at 3.5 eV where they obtained a cross section of 0.295×10^{-18} cm². We did not see this type of splitting. It may be due to the relatively poor resolution of 0.5 eV in the present experiment. As a result our value has to be compared with the average value of the cross sections at those two energies obtained by Zeisel *et al* (1975), which is 0.33×10^{-18} cm². This is in excellent agreement with our result. This agreement between the two sets of measurements using different techniques establishes the validity of the assumption we have made regarding the detection efficiency of the channeltron. The assumption has been that at sufficiently high nose-cone voltages the detection efficiency becomes independent of the m/e ratio of the ions. This adds further credibility to the accuracy of the cross sections we have measured for the ions, namely C⁻, CS⁻ and S₂⁻. The cross sections for the various ions at the peaks as well as at 40 eV are given in table 1.

The resonant peaks in the S⁻ cross sections are numbered 1 to 4 in figure 7. The peaks 1, 2 and 3 have been observed by Kraus (1961), Dillard and Franklin (1968) and MacNeil and Thynne (1969). We found that these peaks were centred at

Table 1. Cross sections for the formation of various ions.

Ion	Electron energy (eV)	Cross section (10^{-20} cm^2)
S^-	3.6	35 ± 5
	6.2	23 ± 3.5
	7.7	4.9 ± 0.7
	9.2	1.1 ± 0.2
	40.0	11.5 ± 1.7
CS^-	6.2	6.7 ± 1.0
	40.0	0.65 ± 0.1
S_2^-	6.2	2.5 ± 0.4
C^-	6.5	0.22 ± 0.03
	7.7	0.19 ± 0.03
	12.8	0.09 ± 0.014
	40.0	1.5 ± 0.23

3.6, 6.2 and 7.7 eV respectively, which agrees well with earlier measurements. The relative intensities of the three peaks were found to be in the ratio of 1:0.009:0.002 by MacNeil and Thynne and 1:0.42:0.23 by Kraus. We find that the intensities of the three peaks are in the ratio of 1:0.65:0.14. We attribute the differences as being due to possible discriminations as a function of the kinetic energy of the ions in the earlier experiments. The fourth peak at about 9.2 eV is very low in intensity and has not been reported earlier. We estimate the cross section at this peak to be $1.1 \times 10^{-20} \text{ cm}^2$.

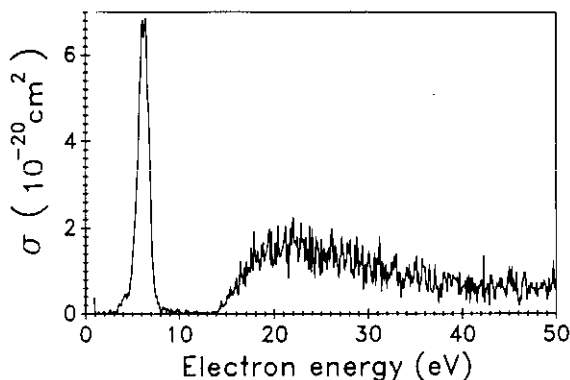


Figure 8. The cross section for the formation of CS^- from CS_2 . The measurements were carried out at a background pressure 5×10^{-7} Torr.

3.3. CS^- , S_2^- and C^-

The CS^- , S_2^- and C^- data are given in figures 8, 9 and 10 respectively. The resonant peaks in CS^- and S_2^- are centred at 6.2 eV which is the same energy as that of peak 2 in S^- . The observation of CS^- at this energy is consistent with all earlier reports. As for S_2^- , only MacNeil and Thynne (1969) have reported observing it.

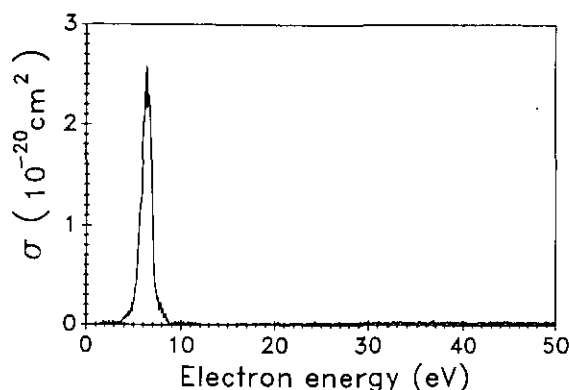


Figure 9. The cross section for the formation of S₂⁻ from CS₂. The measurements were carried out at a background pressure 5×10^{-7} Torr.

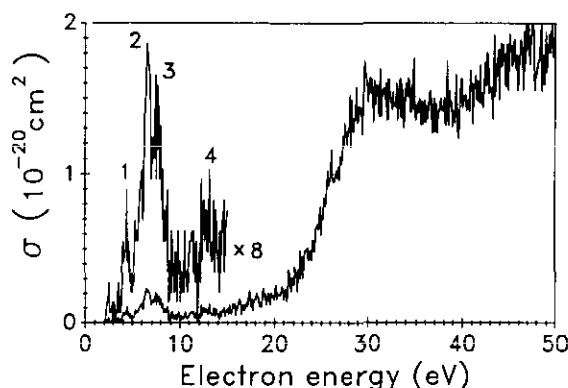


Figure 10. The cross section for the formation of C⁻ from CS₂. The measurements were carried out at a background pressure 5×10^{-7} Torr.

They obtained resonant peaks in the S₂⁻ cross sections at 4.1 and 6.3 eV. The 4.1 eV peak was attributed by them to the ion-molecule reaction



The present measurements do not show this peak.

In analogy to the case of CO₂, Zeisel *et al* (1975) have suggested the formation of S⁻ at 3.6 eV as due to the formation of CS₂⁻ in the ground state $4\pi_g^4 5\pi_u^1$ configuration which is a ²Π_u state. It may be noted that this assignment was made assuming a linear geometry for the CS₂⁻ state. So far there is no conclusive evidence, either theoretical or experimental, in support of this.

The resonance at 6.2 eV dissociates through different channels giving S⁻, CS⁻ and S₂⁻. Considering the almost identical nature of the peaks in all the three ionic channels, we may conclude that the initial state of the CS₂⁻ is the same in all cases. It is likely that the relative intensities of the three negative ion fragments would have a strong dependence on the vibrational excitation of the initial neutral state. This might manifest itself as a strong temperature dependence on the relative intensities of S⁻, CS⁻ and S₂⁻ ions at this energy.

Due to the electric current in the solenoid which produces the magnetic field used for collimating the electron beam the entire apparatus attained a temperature higher than the room temperature. At equilibrium this temperature was found to be about 100°C (measured using a thermocouple). All the measurements reported here were carried out at this temperature. We have found some signature of a temperature dependence in the relative intensities of the ions. We are in the process of making detailed measurements as a function of temperature.

Using thermochemical values $D_0(\text{CS-S}) = 4.66$ eV (Zeisel *et al* 1975), $D_0(\text{C-S}) = 7.2$ eV (Gaydon 1953), $D_0(\text{S-S}) = 4.4$ eV (Knop *et al* 1988) and electron affinity, $EA(\text{S}_2) = 1.66$ eV (Celotta *et al* 1974) we find that the threshold for the formation of S_2^- is 5.8 eV. Our measurements show the threshold to be 5.1 eV which is in good agreement with 5.2 eV reported by MacNeil and Thynne (1969). The difference in the calculated and measured values for S_2^- threshold may be due to inaccurate thermochemical values. It is most likely that the error is in $D_0(\text{C-S})$. Using the threshold for S_2^- from the present measurement, we get an upper limit for $D_0(\text{C-S})$ of 6.5 eV.

The formation of S_2^- and S_2 (corresponding to the formation of C^- discussed later) from the compound state of CS_2^- necessitates the simultaneous breaking of two C-S bonds and formation of a new S-S bond. From the low values of the threshold energy determined for S_2^- formation, it is likely that S_2^- is formed in the ground state with very little vibrational excitation. Knop *et al* (1988) give an equilibrium internuclear distance for S_2^- to be 2.0 Å. Assuming that the two CS bond lengths in neutral CS_2 , which are 1.6 Å each, are unaltered on electron capture, in order to bring the two S atoms together within a distance of 2 Å, the S-C-S bond angle has to be 78°. This would mean that either the CS_2^- is formed with very large bending mode vibrational energy or the CS_2^- state has a strongly bent configuration. This necessitates that being a linear molecule, the initial neutral state of CS_2 to which the electron capture occurs should have certain amount of bending mode excitation. At 100°C, which we estimate to be the temperature of the interaction region, we could have 1% of the molecules with $v = 3$ for the bending mode vibration. Electron attachment to these molecules with excited bending modes could lead to the formation of non-linear CS_2^- molecules. If the autodetachment time is comparable with the bending mode vibration, there could be a substantial amount of S_2^- formation.

A similar case is the O_2^- formation from CO_2 discussed by Spence and Schulz (1974). In fact the previous discussion on S_2^- formation is based on their arguments for the formation of O_2^- . In this respect it may be worth mentioning the difference between the CO_2 and CS_2 cases. In the case of CO_2 , at the particular energies where O_2^- was formed, other negative ion fragments, which were expected to be formed from the large fraction of molecules without bending mode excitation, were not found. This was explained in terms of the larger survival probability against autodetachment of the compound negative ion state formed from molecules with bending mode excitation compared with the rest. In the case of CS_2 , we see S^- and CS^- , both also with larger intensities than S_2^- at the same energy. This is the expected behaviour, since just as S_2^- is formed by dissociative attachment from those molecules with bending mode vibrations, there should be a corresponding probability for the same process to occur for S^- or CS^- from the larger fraction of molecules without bending mode excitation at the same electron energy. Thus in the case of CS_2 we need not invoke intricate *survival factors* to explain the preferential selection of the bent configurations as in the case of CO_2 .

Compared with S⁻, CS⁻ and S₂⁻ ions the cross sections for resonance attachment forming C⁻, given in figure 10, seem to be very low. However, we do see some structure corresponding to four peaks, numbered 1, 2, 3 and 4 at 4.4, 6.5, 7.7 and 12.8 eV, respectively. Resonant peaks in C⁻ have been reported by MacNeil and Thynne (1969) at 6.8 and 8.2 eV, respectively, and by Kraus (1961) at 6.9 and 8.3 eV, respectively. Dillard and Franklin (1968) also observed the C⁻ peaks at the same energies as those given by Kraus. We are not able to explain the difference in the position of peak 3 which is lower by about 0.5 eV compared with these measurements. In addition, based on thermochemical data, we would assume that peak 1 did not originate from CS₂. Using the various dissociation energies mentioned earlier while discussing the S₂⁻ data and the electron affinity of C (1.27 eV as given by Massey (1976)), thresholds for the formation of C⁻ through the processes



and



are ≥ 6.2 eV and ≥ 10.6 eV, respectively. Thus the C⁻ peak we observe at 4.4 eV cannot be explained by any of the previous processes. In order to see if this peak originated from any molecules in the background gases, we collected the data up to an energy of 50 eV after shutting off the CS₂ beam. We did not see any contribution from the background gases. Thus the origin of this peak remains unexplained.

From the energy thresholds derived earlier, it is clear that peaks 2 and 3 correspond to the process given by equation (4). The mechanism for the formation C⁻ through this process is similar to the one discussed for the formation of S₂⁻. The possibility that peaks 2 and 3 may be due to Renner-Teller splitting of the bent CS₂⁻ state cannot be ruled out. This effect has been observed by Spence and Schulz (1974) in the O₂⁻ data from CO₂. The peak 4 at 12.8 eV has not been reported earlier. Based on energy considerations this peak could be due to the process given by equation (5).

3.4. Polar dissociation continua

A comparison of the polar dissociation continua given in figures 7 to 10 is worthy of note. S⁻ has the maximum cross section followed by C⁻ and then CS⁻. There seems to be practically little intensity for S₂⁻. S⁻ has a fairly broad hump in the 15 to 20 eV region, followed by a broad peak at 27 eV. Between 32 and 50 eV the cross section seems to remain constant. The continuum of CS⁻ has a relatively sharp onset at 14 eV and seems to have a smooth behaviour with the maximum at about 22 eV. C⁻ has the most complex continuum. There seems to be a relatively broad structure between 15 and 20 eV and breaks at 21 and 24 eV signifying specific thresholds. There is a broad peak centred around 31 eV and beyond 37 eV the cross section seems to increase. It has been found that S₂⁺ is formed from CS₂ by electron impact (Mazumdar *et al* 1989). In this respect it is interesting to note that very little S₂⁻ is seen from the polar dissociation process. The formation of C⁻ through polar dissociation could have either S₂⁺ or (S + S⁺) as the other fragments. Using available thermochemical data we calculated the threshold for the C⁻ + S₂⁺ channel to be 16.14 eV and that for C⁻ + S⁺ + S to be 20.52 eV. We are not able to see

the threshold for the first process clearly. But the break we observe at 21 ± 0.5 eV seem to agree well with the calculated threshold for the latter process. We have also determined the threshold for the formation of S^- through polar dissociation to be 14 ± 0.5 eV. This agrees well with the value one could obtain by combining the electron affinity of sulphur (2.08 eV) (Lineberger and Woodward 1970) and the appearance energy of CS^+ from CS_2 (16.16 eV) (Rosenstock *et al* 1977). There have been only two reported measurements on the electron affinity of CS. Photo-detachment data (Burnett *et al* 1982) give this value as 0.2 eV and the other one gives ≤ 1.2 eV (MacNeil and Thynne 1969). Using the photoionization data for the threshold for simultaneous formation of S^+ and CS from CS_2 (Rosenstock *et al* 1977) and the threshold of 14 eV we have determined that for the formation of S^+ and CS^- from CS_2 through polar dissociation we calculate the electron affinity of CS to be 0.8 ± 0.5 eV.

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References

- A'Hearn M F A and Feldman P D 1985 *Ices in the Solar System* ed J Klinger, D Benesat, A Dollfus and R Smoluchowski (Dordrecht: Reidel) p 463
- Burnett S M, Feigerle C S, Stevens A E and Lineberger W C 1982 *J. Phys. Chem.* **86** 4486–8
- Celotta R J, Bernett R A and Hall J L 1974 *J. Chem. Phys.* **60** 1740–5
- Cosmovici C B, Barbieri C, Bonoli C, Bortoletto F and Hamzaoglu E 1982 *Astron. Astrophys.* **114** 373–87
- Cosmovici C B and Ortolani S 1984 *Nature* **310** 122–4
- Dahl D A, Delmore J F and Applehans A D 1990 *Rev. Sci. Instrum.* **61** 607–9
- Dillard J G and Franklin J L 1968 *J. Chem. Phys.* **48** 2369–52
- Gaydon A J 1953 *Dissociation Energies and Spectra of Diatomic Molecules* (London: Chapman and Hall)
- Herzberg G 1950 *Spectra of Diatomic Molecules* (New York: Van Nostrand)
- Jackson W M, Halpern J B, Feldman P D and Rahe J 1982 *Astron. Astrophys.* **107** 385–9
- Khakoo M A and Srivastava S K 1984 *J. Phys. E: Sci. Instrum.* **17** 1008–13
- Knop O, Boyd R J and Choi S C 1988 *J. Am. Chem. Soc.* **110** 7299–301
- Kraus K 1961 *Z. Naturf. a* **16** 1378–85
- Kraus K, Müller-Duysing W and Neuert H 1961 *Z. Naturf. a* **16** 1385–7
- Krishnakumar E 1990 *Int. J. Mass Spectrom. Ion Processes* **97** 283–94
- Krishnakumar E and Srivastava S K 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 1055–82
- 1990 *Phys. Rev. A* **41** 2445–52
- Lineberger W C and Woodward B W 1970 *Phys. Rev. Lett.* **25** 424–7
- MacNeil K A J and Thynne J C J 1969 *J. Phys. Chem.* **73** 2960–4
- Mathur D and Harris F M 1989 *Mass Spectrom. Rev.* **8** 269–91
- Massey H 1976 *Negative Ions* (Cambridge: Cambridge University Press) p 58
- Mazumdar S, Kumar S V K, Marathe V R and Mathur D 1989 *Rapid Commun. Mass Spectrom.* **3** 24–6
- Nagy P, Skutlartz A and Schmidt V 1980 *J. Phys. B: At. Mol. Phys.* **13** 1249–67
- Rapp D and Briglia D D 1965 *J. Chem. Phys.* **43** 1480–9
- Rosenstock H M, Draxl K, Steiner B W and Herron J T 1977 *J. Phys. Chem. Data* **6** Supplement 1
- Spence D and Schultz G A 1974 *J. Chem. Phys.* **60** 216–20
- Vardya M S and Tarafdar S P 1987 *Astrochemistry* (Dordrecht: Reidel) p 604
- Zeisel J P, Schulz G J and Milhaud J 1975 *J. Chem. Phys.* **62** 1936–40