DISSOCIATIVE IONIZATION OF CARBON DISULPHIDE IN THE GAS PHASE. HEAT OF FORMATION OF THE CS RADICAL

M.-J. HUBIN-FRANSKIN[1], R. LOCHT and J. KATIHABWA

Institut de Chimie, Université de Liège, Sart Tilman par 4000, Liège 1, Belgium

Abstract

Measurements of the appearance potentials and the kinetic energies of S^+ and CS^+ ions formed by electron impact on carbon disulphide in the gas phase lead us to propose a value as low as 34 ± 6 kcal mole^{-1} for the heat of formation of the CS radical in its ground electronic state. It is also shown that the predissociations of the A $^2\Pi_u$ /or X $^2\Pi_g$ and the B $^2\Sigma_u$ molecular ion states by a repulsive $^4\Sigma^-$ state giving rise to S^+ ions, observed through metastable ions study, occur at 13.45 eV and 14.55 eV respectively.

1. Introduction

A recent study of dissociative electron attachment processes in carbonyl sulphide [1] leads us to discuss the value of the heat of formation of the CS radical. A review of the literature data showed that the published values covered a range between ≤ 52.5 kcal mole^{-1} [2], deduced from the analysis of the chemi-luminescence of CS_2 and COS reactions with metastable rare gas atoms, and 70 kcal mole^{-1} [3], measured by a mass spectrometric study of the equilibrium $CS_2 + S \rightleftharpoons CS + S_2$ in the gas phase. Determination of appearance potentials of S^+ and CS^+ formed by photon impact [4] leads to $\Delta H_f(CS) = 64.4$ kcal mole^{-1} whereas by electron impact [5,6] the value is 52.2 kcal mole^{-1}. These results have to be considered as a higher limit since the amount of kinetic and internal energy involved in the processes studied is unknown. The dissociative electron attachment process for COS in the gas phase producing O^- ions at 3.9 eV, recently studied [1], leads to a heat of formation as low as 32 kcal mole^{-1} for the CS radical.

The purpose of the present paper is to check this recent value of $\Delta H_f(CS)$ by appearance potential and kinetic energy measurements of the S^+ and CS^+ ions formed by impact of 10-16 eV electrons on carbon disulphide.

2. Experimental

The instrument as well as the experimental conditions used in the present work were described in detail elsewhere [7]. Briefly, the ions formed in a Niertype ion source are energy analyzed by a retarding lens before entering into a quadrupole mass spectrometer. The ion current can be continuously scanned either with respect to the retarding potential for a fixed electron energy or with respect to the electron energy for a fixed retarding potential. Both signals can be differentiated, stored in a multichannel analyzer and recorded on an *X-Y* recorder.

The carbon disulphide pressure is of the order of 5×10^{-7} torr in the ion source. The first ionization potential of CS_2 at 10.059 ± 0.008 eV [4] is used for the electron energy scale calibration[2]. The maximum of the thermal energy distribution of CS_2^+ is taken as the origin of the kinetic energy scale.

3. Results and discussion

3.1. Appearance potentials

The appearance potentials of the S^+ and CS^+ ions are listed in table 1 and compared to the literature data. The minimum threshold energies are found at 13.35 and 14.5 eV respectively; these values are considerably

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[1] "Chargé de Recherches" of the "Fonds National de la Recherche Scientifique".

[2] The appearance potentials are determined by the extrapolation method, as described in ref. [7].

lower than the previously published ones, whereas the second thresholds are in fairly good agreement with the literature. This discrepancy could be due to the low intensity of the ion currents near threshold and the use, in this work, of a more sensitive detection system combined with the first differentiation.

3.2. Heat of formation of the CS radical

The shape of the first derivative of the S^+ ionization efficiency curve close to threshold (fig. 1 a) shows that at 13.35 eV a dissociative ionization process, no ion pair formation is involved, since no peak is detected in the first derivative of the ion current. The first derivative of the retarding curve recorded near threshold (fig. lb) exhibits only one peak centered at thermal energy with a full width at half maximum of 140 meV.

When the following reaction is considered

$$CS_2(X\ ^1\Sigma_g^+) + e^- \rightarrow CS(X\ ^1\Sigma^+) + S^+(^4S_u)_{KE=0} + 2e-, \tag{1}$$
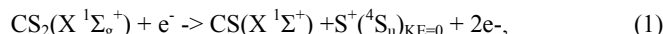
assuming no internal energy in the fragments, and using the appropriate thermochemical data (IP($S\ ^3P_g \rightarrow S^+\ ^4S_u$) = 238.89 kcal mole^{-1} [8], $\Delta H_f(S\ ^3P_g)$ = 65.7 kcal mole^{-1} [9], $\Delta H_f(CS_2)$ = 27.98 kcal mole^{-1} [9]), one calculates $\Delta H_{ff}(CS)$ = 31.3 kcal mole^{-1}.

This result is consistent with a recent value we found in a negative ion study [1] ($\leq$ 32 kcal mole^{-1}) and is considerably lower than that deduced by photo-ionization, photoemission spectroscopy and equilibrium kinetic studies.

As shown by the occurrence of a peak at 14.5 eV in the first derivative of the ionization efficiency curve of CS^+ (fig. 2a), the lowest threshold corresponds to an ion-pair, whereas at 14.7 eV a dissociative ionization process is involved. The CS^+ ions are formed essentially without kinetic energy in the electron energy range from threshold up to 25 eV (fig. 2b). Using IP(CS) = 11.33 eV [10], a low value for the appearance potential of CS^+ is shown to be consistent with a low value for the heat of formation of CS, in this case 40 kcal mole^{-1}, as is also found from the S^+ measurements. In conclusion, a mean value of $\Delta H_f(CS)$ = (34 $\pm$ 6) kcal mole^{-1} is proposed.

3.3. Dissociation limits

To interpret the fragmentation processes leading to S^+ and CS^+ ions, we need to know the corresponding dissociation limits; using the thermochemical data derived from photoelectron spectroscopy [10], from atomic spectra tables [8] and $\Delta H_f(CS)$ = (34 $\pm$ 6) kcal mole^{-1} proposed in this work, we calculate the dissociation limits of CS_2^+ (see table 2). In fig. 3, an energy level diagram is given for CS_2^+ as observed by photoelectron spectroscopy [11], for the Rydberg states of CS_2 known from UV absorption spectroscopy [12], for the dissociation limits calculated and the fragments observed in this work.

Table 1 : S^+ and CS^+ appearance potentials

Ion	Photoionization (eV) ref. [4]	Low energy electron impact (eV)					
		ref. [5]	ref. [6]	ref. [17]	ref. [13]	this work [a]	
S^+						13.35 KE $\approx$ 0	$S^+(^4S_u) + CS(X^1\Sigma^+)$
	14.81 $\pm$ 0.03	14.0 $\pm$ 0.5		14.85 $\pm$ 0.1	15 $\pm$1.0 KE $\approx$ 0.25	14.55 KE $\approx$ 0	$S^+(^4S_u) + CS(^1\Sigma^+) + E_{vibr.}$
CS^+						14.5 KE $\approx$ 0	$CS^+(X^2\Sigma^+) + S^-(^2P_u)$ / $CS^+(A^2\Pi) + S^-(^2P_u)$
		14.7 $\pm$ 0.5				14.7 KE$\approx$0	$CS^+(X^2\Sigma^+) + S(^3P_g)$
		15.7 $\pm$ 0.1	15.35 $\pm$ 0.1			15.65 KE$\approx$0	$CS^+(X^2\Sigma^+) + S(^1D_g)$ $CS^+(A^2\Pi) + S(^3P_g)$
	16.16			16.15 $\pm$ 0.1	16.3 $\pm$ 0.1		

[a] The values are reproducible within 0.05 eV.

Fig. 1. (a) *First derivative of the ionization efficiency curve of S^+ near threshold. The arrows give the position of the threshold energies listed in table 1. (b) First derivative of the retarding curve of the S^+ ions at 14.4 eV.*
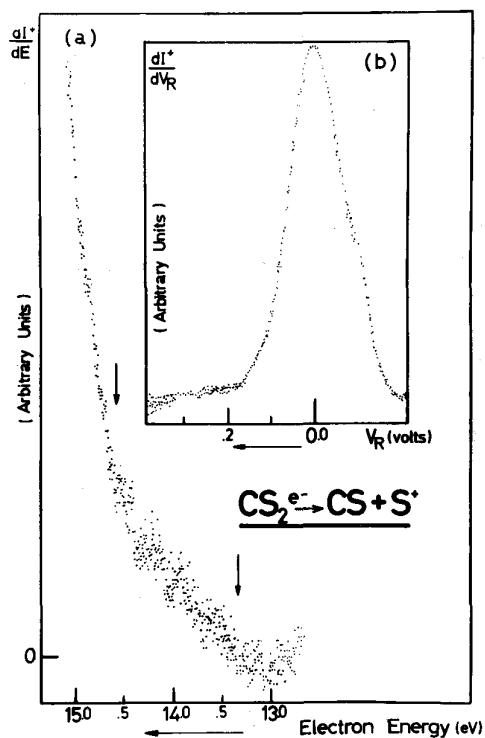

Fig. 2. (a) *First derivative of the ionization efficiency curve of CS^+ near threshold. The arrows give the position of the threshold energies listed in table 1. The peak around 15.5 eV is not a reproducible feature, (b) First derivative of the retarding curve of CS^+ at 15.9 eV.*
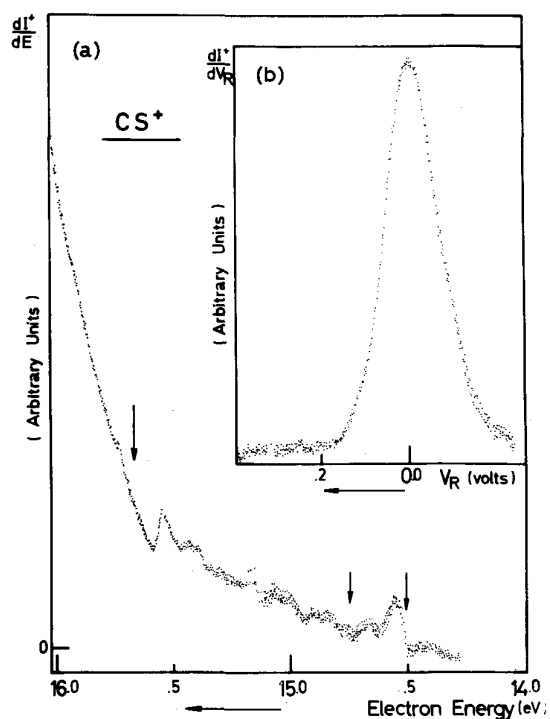
Table 2 *: Dissociation limits of CS_2^+*

Fragments	Limits (eV)	Molecular states
$S^+(^4S_u) + CS(X\,^1\Sigma^+)$	13.61 ± 0.3	$^4\Sigma^-$
$S^+(^2D_u) + CS(X\,^1\Sigma^+)$	15.45 ± 0.3	$^2\Sigma^-\,^2\Pi\,^2\Delta$
$CS^+(X^2\Sigma^+) + S(^3P_g)$	14.40 ± 0.3	$^4\Sigma^-\,^2\Sigma^-\,^4\Pi\,^2\Pi$
$CS^+(X^2\Sigma^+) + S(^1D_g)$	15.55 ± 0.3	$^2\Sigma^+\,^2\Pi\,^2\Delta$
$CS^+(A^2\Pi) + S(^3P_g)$	15.80 ± 0.3	$^{2,4}\Sigma^-\,^{2,4}\Sigma^+\,^{2,4}\Pi\,^{2,4}\Delta$
Ion pair dissociation limits of CS_2		
$S^-(^2P_U) + CS^+(X^2\Sigma^+)$	12.32	$^{1,3}\Sigma^+\,^{1,3}\Pi$
$S^-(^2P_U) + CS^+(A^2\Pi)$	13.78	$^{1,3}\Sigma^+\,^{1,3}\Pi\,^{1,3}\Sigma^-\,^{1,3}\Delta$

Fig. 3. *Energy level diagram for CS_2^+ as observed by photoelectron spectroscopy [11], for the Rydberg states of CS_2 known from UV absorption spectroscopy [12], for the calculated dissociation limits and for the fragments observed in this work.*
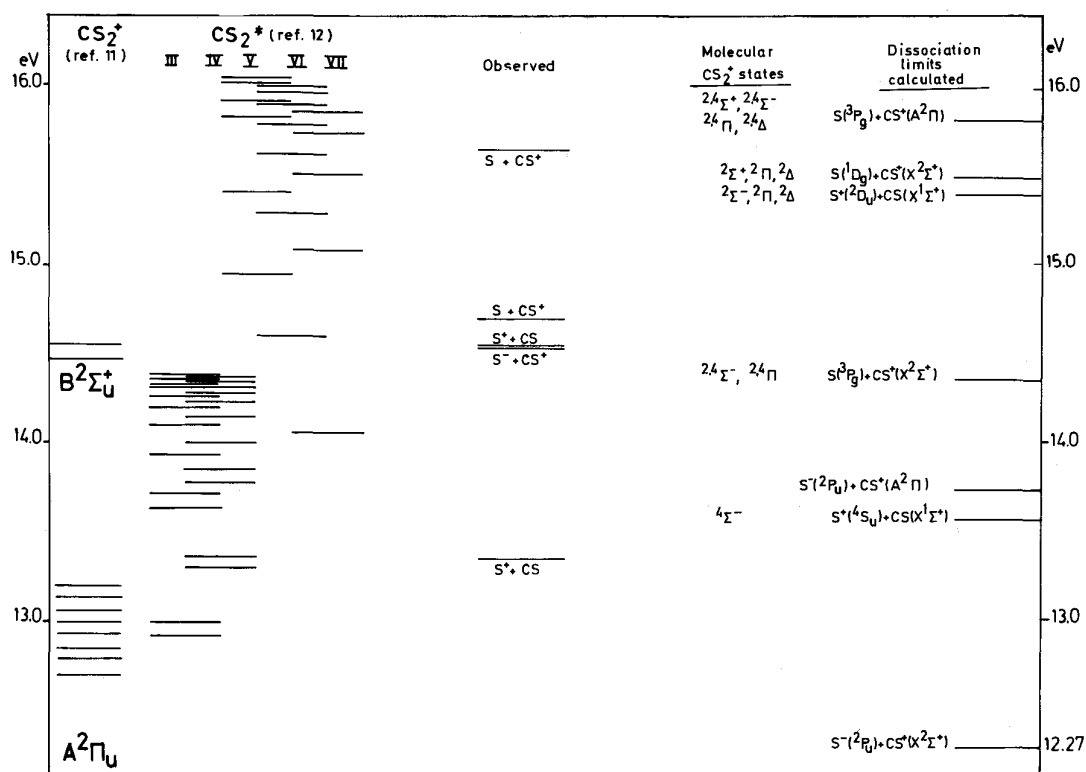
3.4. S^+ formation

The ionization efficiency curve of S^+ recorded in the energy range of 2 eV above the lowest threshold (fig. la) shows two distinct dissociative ionization processes: the first at 13.35 eV and the second at 14.55 eV.

The kinetic energy distribution has been measured at different electron energies between threshold and 25 eV; only one structureless peak is observed with a maximum at 0.0 eV and a full width at half maximum (fwhm) of 140 meV. This fwhm is larger than the 80 meV observed for the distribution of molecular ions. This broadening can only be ascribed to the width of the dissociative ionization process or to unresolved vibrational and/or rotational structure.

As seen before, the first threshold observed at 13.35 eV is ascribed to process (1) discussed above. According to the correlation rules, the intermediate molecular state must be $CS_2^+(^4\Sigma^-)$.

A second ionization process occurs at 14.55 eV, which also leads to S^+ ions with only thermal energy. As is seen in fig. 3, these ions appear at about 1 eV under the second dissociation limit of CS_2. Reaction (1) and the same $^4\Sigma^-$ molecular ion state have to be invoked in this case, the excess energy being stored as internal motion of the CS radical.

Momigny et al. [13], in an electron impact study of the metastable transitions in CS_2, observed at 15 ± 1 eV two kinds of S^+ ions: one produced by a slow rate decaying metastable molecular state, with a kinetic energy release lower than 0.25 eV, the second, in the same energy range, due to a fast rate component. The authors interpreted the first as the result of the predissociation of the $B^2\Sigma_u^+$ by the $^4\Sigma^-$ state, the second as due to the predissociation of the $X^2\Pi_g$ or $A\ ^2\Pi_u$ by the same $^4\Sigma^-$ state. The present results are consistent with these observations and thus confirm that two processes for the formation of S^+ occur around 15 ± 1 eV, at 14.55 and 13.45 eV, respectively. As Brehm et al. [14] observed in photoion and photoelectron coincidence measurement: that the X, A and B states of CS_2^+ are stable parent ions, the predissociated levels of these states could then be populated by some preionized Rydberg states, lying in this energy range (fig. 3), autoionizing through non-radiative transitions.

3.5. CS^+ formation

The kinetic energy measurements show that the CS^+ ions appear essentially without kinetic energy from the lowest threshold at 14.5 eV to at least 25 eV; this behaviour, which is comparable to that of the S^+ ions, is shown for 15.9 eV in fig. 2b and is the same for the whole energy range analyzed. The lowest threshold corresponds to an ion pair formation, as is seen in fig. 2a by the occurrence of a peak at 14.5 eV in the first derivative of the ionization efficiency curve; this peak is a very reproducible structure, appearing in the averaged (1500 runs) recordings, whereas the little peak at 15.5 eV is a spurious, not reproducible feature. This result is consistent with earlier negative ion measurements performed on an Atlas CH4 mass spectrometer [15]; sulphur negative ions were shown to be formed by an ion pair process with a threshold estimated at 14.2 eV. Using EA(S) = 2.077 eV [16], the ionization potentials of CS [10] and $\Delta H_f(CS) = 34 \pm 6$ kcal mole^{-1}, the dissociation limits of the neutral molecule leading to the ion pair are calculated at 12.32 eV for $S^-(^2P_u) + CS^+(X\ ^2\Sigma^+)$ and at 13.78 eV for $S^-(^2P_u) + CS^+(A\ ^2\Pi)$ (fig. 3). The CS^+ ions observed are formed by one of these reactions, and include some internal energy; the CS_2 parent electronic state may be one of the two Rydberg states lying in this energy range: the $n = 3$ member of the series V at 14.47 eV or $n = 3$ of the series VII at 14.61 eV [12].

The first dissociative ionization process giving rise to CS^+ ions has a threshold measured at 14.7 eV, which is, within the experimental error on the heat of formation of CS, consistent with the first dissociation limit $S(^3P_g) + CS^+(X\ ^2\Sigma^+)$ calculated at 14.40 ± 0.3 eV. The molecular state could have the following symmetries: $^4\Sigma^-$, $^2\Sigma^-$, $^2\Pi$ or $^4\Pi$. Like the S^+ ions formed at 14.5 eV through the $^4\Sigma^-$ state, the CS^+ might be the result of another decay channel of the $^4\Sigma^-$ state. If predissociation of the $B^2\Sigma^+$ state by the $^4\Sigma^-$ one is also involved in this case, then a slow rate of formation of CS^+ should be observed as a metastable transition.

At 15.65 eV, a second dissociative ionization process leads to an increase of the CS^+ current. In this energy range, two dissociation limits could contribute to the CS^+ ions, one at 15.55 ± 0.3 eV leading to $S(^1D_g) + CS^+(X\ ^2\Sigma^+)$, the other at 15.86 ± 0.3 eV leading to $S(^3P_g) + CS^+(A\ ^2\Pi)$. Since no stable molecular ionic state is populated by Franck— Condon transitions in this energy range, we must assume that the dissociating levels result from a population through autoionizing Rydberg states.

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