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Mass spectrometric study of the photoionization of CS. The dissociation energy of the CS molecule

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Abstract

A mass spectrometric study of the photoionization of CS provides 11.319 ± 0.006 eV for the ionization potential, in agreement with literature values. Three Rydberg series converging to the C² Σ^+ state of the molecular ion are identified. Their limit is 18.003 ± 0.006 eV. The threshold for dissociative ionization of CS towards S⁺ is located at 70.05 ± 0.1 nm and yields $D^0(CS, 0 \text{ K}) = 709.4 \pm 2.5 \text{ kJ/mol}$. This result is briefly compared with prior data. $D^0(CS, 0 \text{ K}) = 709.6 \pm 1.2 \text{ kJ/mol}$ are selected as the best estimates for these quantities.

1. Introduction

Mass spectrometric identification of the ions formed by the photoionization of a molecule gives access to the determination of its ionization potential and the location of excited states in the molecular ion. Thresholds for dissociative ionization can often also be measured and used to determine dissociation or bond energies in the neutral molecule [1].

Photoionization and mass analysis were applied to study the CS molecule. The ionization potential of this molecule and the state energies of three excited states of its molecular ion have already been measured by He(I) photoelectron spectroscopy (PES) [2-4]. Mass spectrometry and the use of the hydrogen pseudo continuum to examine photoionization (PI) of the molecule also resulted in determination of its ionization potential [5,6] and in the observation of pronounced autoionization in the wavelength interval 110-100 nm [6]. Studies of chemical equilibria, dissociative processes in CS₂ and COS, and optical spectra have served to obtain dissociation energies for CS. The average of thermochemical measurements is $D^0(CS, 0 \text{ K}) = 707.5 \pm 25 \text{ kJ/mol}$ (= 169.1 ± 6 kcal/mol) and is preferred in the JANAF tables [7]. The data recommended in the gas phase ion and neutral thermochemistry tables [8] are deduced from appearance potentials in CS₂. The spectroscopic result based on a short extrapolation of the vibrational levels in the A' state is $D^0(CS, 0 \text{ K}) = 709.6 \pm 1.2 \text{ kJ/mol}$ [9]. It was selected in the compendium of constants for diatomic molecules [10] and in the tabulation of thermodynamic properties of individual substances [11].

The present investigation was directed towards a mass spectrometric study of the ions formed by the photoionization of CS in the wavelength interval 80–65 nm. This made possible an independent determination of the dissociation energy of CS. The threshold for ionization was also measured.

The experimental apparatus comprises a 1 m near normal incidence vacuum ultraviolet monochromator, a capillary discharge lamp, a VUV light detector and a quadrupole mass spectrometer. The hydrogen many line spectrum was used to study the region near the threshold for ionization, the entrance and the exit slit each being 50 µm wide; the helium Hopfield continuum and 100 µm slit-widths were employed in the 80-65 nm region. The bandwidth was thus about 0.05 and 0.1 nm, respectively. In both regions the wavelength scale was calibrated with known lines, such as the Lyman lines in the one and the He(I) resonance line in the other interval. Spectra were recorded with 0.01 nm increments in wavelength. Ion accumulation times were up to 100 s long. CS was produced by passing undiluted CS_2 at a pressure of about 0.5 mbar through a 25 mm outer diameter air cooled pyrex discharge tube terminated towards the ion source by a 2 mm inner diameter and 0.1 m long capillary. The CS₂ was a commercial pro analysis product. It was contained in a reservoir placed in a melting ice bath to keep the inlet pressure constant. The discharge was generated with an EMS 216L cavity and a 2450 MHz EMS Microtron 200 power supply. A stable discharge could be maintained for at least 48 h. The CS yield was maximum at minimum power setting (≈ 20 W). The cavity was located 0.4 m from the ionization region. Both the transit time and the pressure in the discharge tube hence in all probability ensured that the CS reaching the ionization region was thermalized.

At $\lambda = 58.43$ nm the relative intensities $I(CS_2^+)/I(CS^+)/I(S^+)$ were 100/20/10 in the absence of discharge. The CS^+ and S^+ ions were then formed by dissociative ionization of CS₂ with thresholds at 78.7 and 83.75 nm respectively [12–14]. With the discharge running under optimum conditions the relative intensities were reproducibly 80/100/20, implying that both CS and CS₂ contributed to the ion intensities measured for CS⁺ and S⁺ at $\lambda = 58.43$ nm. To obtain results pertaining to CS only, spectra were consequently recorded with and without running the discharge.

For the calculations the conversion factors were 1 $eV = 806554.10 m^{-1} = 96485.309 J/mol$ (= 23060.542 cal/mol) [15]. Literature data were recalculated accordingly where necessary. To ensure consistency in numerical values expressed in different units, one more digit is given than warranted by the accuracy of the measurements and of the additional data needed for their evaluation.

3. Results and discussion

3.1. Molecular ion CS⁺

Fig. 1 shows the photoionization efficiency (PIE) curve for CS^+/CS in the wavelength interval 110– 109 nm. In this region there is no interference from dissociative ionization of CS₂ since the threshold for formation of CS^+/CS_2 is located at 78.7 nm [13]. The onset for ionization of CS corresponds to a step with an inflection point at 109.54 ± 0.05 nm. All evidence gained here and in the literature supports

109.2 110.2 λ/nm Fig. 1. Photoionization spectrum of the CS molecule near threshold.



Electronic state	Photoelectron spectroscopy			Photoion spectroscopy		
	Ref. [2] ^a	Ref. [3] ^b	Ref. [4] ^b	Ref. [5] *	Ref. [6] ^c	this work
$\overline{X^2\Sigma^+}$	11.33	11.33	11.34	11.33	11.318	11.319 ± 0.006
A ² II	12.79	12.76	12.78			
$B^{2}\Sigma^{+}$	15.84		15.83			
$C^{2}\Sigma^{+}$	18.00		18.03			18.003 ± 0.006

Table 1 Adiabatic state energies in CS⁺ (eV)

^a Reported uncertainty: 0.01 eV. ^b Reported uncertainty: 0.02 eV. ^c Reported uncertainty: 0.007 eV.

that this threshold corresponds to the true adiabatic ionization potential. The present value, 11.319 ± 0.006 eV, is in agreement with the literature data, obtained in both PES and PI studies (Table 1). The steplike rise at 109.54 nm is followed by autoionization as was observed in Ref. [6].

Fig. 2 gives the PIE curve for formation of the CS^+ ion in the wavelength interval 80–65 nm. Curve (A), recorded with the discharge running, represents the sum of the CS^+/CS_2 and CS^+/CS intensities. The contribution of dissociative ionization of CS_2 to the total CS^+ intensity is given by curve (B). The latter is the scaled PIE curve measured under the

same conditions as curve (A), at an identical CS_2 inlet flow rate, but without discharge. Curve (B) is in agreement with those obtained in previous mass spectrometric studies of the photoionization of CS_2 [12–14]. Curve (C), offset for clarity, is the difference of curves (A) and (B) and represents the PIE curve for CS^+/CS .

Three Rydberg series, labeled I to III in Fig. 2, converge towards the $C^{2}\Sigma^{+}$ state of the CS⁺ ion. The wavelengths of the maxima in the Rydberg states are listed in Table 2 together with convergence limits and effective quantum numbers *n* obtained by iteration. The corresponding state energy of $C^{2}\Sigma^{+}$,



Fig. 2. Photoionization efficiency towards CS⁺ for the molecules CS (curve (C)) and CS₂ (curve (B)) in the wavelength interval $\lambda = 65-80$ nm with indication of three Rydberg series in CS.

Series I		Series II		Series III		
λ (nm)	n	λ (nm)	n	λ (nm)	n	
76.65	2.728	74.28	3.220	74.955	3.051	
72.83	3.728	71.85	4.268	72.21	4.041	
71.28	4.726	70.80	5.263	70.98	5.040	
70.505	5.706	70.22	6.267			
70.03	6.751	69.895	7.174			
69.755	7.712	69.67	8.106			
69.56	8.720	69.49	9.193			
$\lambda_{\rm lim} = 68.87 \pm 0.01 \text{ nm}$		$\lambda_{\rm lim} = 68.86 \pm 0.02 \text{ nm}$		$\lambda_{\rm lim} = 68.88 \pm 0.01 \text{ nm}$		

Table 2 Rydberg states and series limits

18.003 \pm 0.006 eV, agrees with the values measured by PES (Table 1). The onset of the C² Σ^+ ionization continuum is accompanied by a decrease in the PIE curve for formation of the CS⁺ ion and to an increase in the ion yield for the S⁺ ion. It follows that the C² Σ^+ state of CS⁺ is predissociated into C(³P) + S⁺(⁴S^o), the only fragments that can be formed at 18 eV.

3.2. Fragment ion S⁺

Fig. 3 displays the PIE curve for formation of the S^+ fragment ion in the wavelength interval 71-65

nm. As in the case of CS^+ , curves (A) and (B), which are again scaled, were recorded with the discharge on and off respectively and (C) is the difference of the two. No offset is used in this figure. The onset for dissociative ionization of CS towards S^+ was located at 70.05 \pm 0.1 nm (17.699 \pm 0.025 eV; 1707.73 \pm 2.4 kJ/mol) by calculating the intercept between lines representing intensities below 69.9 nm and above 70.2 nm. Starting at about 69.2 nm the S^+ intensity rises abruptly until the wavelength reaches 68.87 nm (18.003 eV), where the limit of the three Rydberg series present in the PIE curve of CS^+ is located. On lowering the wavelength, the S^+



Fig. 3. Photoionization efficiency towards S⁺ for the molecules CS (curve (C)) and CS₂ (curve (B)) in the wavelength interval 65-71 nm.

intensity increases in a second step and levels off at 68.38 nm (18.132 eV). The location of the two steps and their relative heights, about 5/1, agree with the state energies and the intensity ratio of the v = 0 and v = 1 levels in the PES spectra [2,4]. The latter provide 105000 ± 4000 [2] and 105500 ± 3000 m⁻¹ [4] for the vibration frequency compared to 104000 ± 4000 m⁻¹ obtained here.

3.3. $D^{0}(CS, 0 K), D^{0}(CS^{+}, 0 K), \Delta_{f}H^{0}(CS, 0 K)$ and $\Delta_{f}H^{0}(CS^{+}, 0 K)$

Considering that CS was thermalized, at least upon reaching the ionization region, the threshold energy for formation of S⁺, 70.05 \pm 0.1 nm, was converted to the value expected at 0 K, 1709.02 \pm 2.5 kJ/mol, by adding 1.29 kJ/mol (10824 m⁻¹). The latter is the energy calculated for the level with the highest population at 300 K with the rotational constant $B(CS) = 82 \text{ m}^{-1}$ [10] and $J_{\text{H}} = 11$. Subtraction of the ionization potential of atomic sulfur, IP(S) = 8355930 m⁻¹ [16], yields $D^0(CS, 0 \text{ K}) = 709.43 \pm$ 2.5 kJ/mol (7.353 \pm 0.025 eV) for the dissociation energy of CS, virtually identical with the value deduced from the emission spectrum of CS in the vacuum and near ultraviolet, $D^0(CS, 0 \text{ K}) = 709.63 \pm$ \pm 1.2 kJ/mol or 7.355 \pm 0.012 eV [9].

Taking account of rotational ¹ [17] but provisionally omitting the presence of other thermally acquired excitation in CS₂ and in CS₂⁺, calculation of D^0 (CS, 0 K) ² [18,19] with threshold energies E_c (0 K) for various dissociation processes observed in these molecules, yields: CS₂ \rightarrow CS(¹Π) + S(³P₂), λ_c = 133.7 ± 0.2 nm [20], $E_c = 895.95 \pm 1.3$ kJ/mol, $D^0 = 713.31 \pm 1.8$ kJ/mol; CS₂ \rightarrow CS⁺ + S + e, λ_c = 78.70 ± 0.1 nm [13], $E_c = 1521.24 \pm 1.9$ kJ/mol, $D^0 = 716.02 \pm 2.3$ kJ/mol; CS₂ \rightarrow CS + S⁺ + e, λ_c = 83.7 ± 0.17 nm [12], $E_c = 1430.44 \pm 3.0$ kJ/mol, $D^0 = 714.29 \pm 3.2$ kJ/mol; 83.75 ± 0.1 nm [13], E_c

 $= 1429.59 \pm 1.8 \text{ kJ/mol}, D^0 = 715.14 \pm 2.2$ kJ/mol; $\lambda_c = 83.85 \pm 0.02$ nm [14], $E_c = 1427.88$ ± 0.7 kJ/mol, $D^0 = 716.85 \pm 1.4$ kJ/mol; CS₂⁺ + $Xe \rightarrow S^+ + CS + Xe$, $E_c = 458.55 \pm 3.9 \text{ kJ/mol}$ [21], $D^0 = 714.72 \pm 4.1$ kJ/mol. All $D^0(CS, 0 \text{ K})$ values so obtained are systematically higher than the spectroscopic result (709.63 \pm 1.2 kJ/mol [9]) and that derived here (709.43 \pm 2.5 kJ/mol). As already noted [11] this suggests that the thresholds reported for the dissociative processes mentioned actually pertain to transitions from vibrationally excited molecules in CS₂ in the $v_2 = 1$ if not in the $v_1 = 1$ or in the $v_2 = 2$ modes ($v_1 = 65798 \text{ m}^{-1}$, $v_2 = 39670$ m^{-1} [17]) and likewise in CS₂⁺ ($v_1 = 62400 m^{-1}$, $v_2 = 20480 \text{ m}^{-1}$ [17]). In the latter, population of the ${}^{2}\Pi_{1/2}$ substate with a term value of 0.0545 eV [18] may in addition have to be considered.

The best estimates for $D^{\circ}(CS, 0 \text{ K})$ and for $D^{0}(CS^{+}, 0 \text{ K})$ are hence respectively 5932000 \pm 10000 m⁻¹ = 709.63 \pm 1.2 kJ/mol = 7.355 \pm 0.012 eV [9] and 617.10 \pm 1.3 kJ/mol = 6.396 \pm 0.013 eV (the stationary electron convention being adopted). The corresponding enthalpies of formation are: $\Delta_{f}H^{0}(CS, 0 \text{ K}) = 276.49 \pm 1.3 \text{ kJ/mol}$ and $\Delta_{f}H^{0}(CS^{+}, 0 \text{ K}) = 1368.61 \pm 1.4 \text{ kJ/mol}$.

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 $^{{}^{1}\}overline{B(CS_{2})} = 10.910 \text{ m}^{-1}$ [17], $J_{H} = 30 \text{ at } 300 \text{ K}; B(CS_{2}^{+}) = 10.914 \text{ m}^{-1}$ [17], $J_{H} = 30 \text{ at } 300 \text{ K}.$

² Additional data used in the calculations are: $T_0[CS(A^{1}\Pi)] =$ 3879760 m⁻¹ [10], IP(CS) = 11.319±0.006 eV [6, this work], IP(CS₂) = 10.0685±0.0020 eV [18], $\Delta_f H^0(CS_2, g, 0 K) =$ 115.91±1.0 kJ/mol [11], $\Delta_f H^0(C, g, 0 K) =$ 711.19±0.45 kJ/mol [19], $\Delta_f H^0(S, g, 0 K) =$ 274.93±0.15 kJ/mol [19].

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