

A tentative multiphoton ionization of CS₂ molecule: Spectroscopy of $\tilde{A}^2\Pi_u$ state of CS₂⁺ ion

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Abstract. The spectroscopic study of excited molecular cation $CS_2^+(\tilde{A}^2\Pi_u)$ by a different method is presented. In this technique the decay of excited states is monitored by measuring the photons emitted. The peaks in the photon spectrum would correspond to the energy levels of the ion. The vibrational–vibrational, vibrational–electronic interactions have been observed. Symmetry forbidden excitation of one quantum of bending vibration is observed which gives unperturbed value for the bending vibration. The Renner–Teller splitting for the Δ_g and Σ_g^- components of the bending mode ($v'_2 = 1$) in the upper excited $\tilde{A}^2\Pi_u$ state has been observed. A tentative vibrational analysis of the $\tilde{A} \rightarrow \tilde{X}$ system has been made.

Keywords. Molecular spectroscopy; multiphoton ionization; Fermi resonance; Renner–Teller effect.

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1. Introduction

A knowledge of the structure and energy levels of molecular ions is important as it plays a key role in the fields of astrophysics, atmospheric photochemistry, ion-molecular reactions etc. The spectroscopy of molecular ions are studied by various techniques – the coarse and fine structure analysis by emission [1,2] and absorption [3,4] spectroscopy, and photoionisation mass spectroscopy [5] vibrational and vibronic interactions are studied using photoionisation (PIR) spectroscopy [6]. Photoelectron spectroscopy (PES) is useful in mapping the electronic structure of molecular ions [7–9]. The more recent zero kinetic energy photoelectron (ZEKE) method has high resolution [10]. In optical spectroscopy, the dispersed fluorescence or absorption is measured whereas in PIR, PES, ZEKE techniques, the photoelectron is analysed. In this present paper, a different method is described wherein the undispersed photons are collected and analysed. The molecular cations in the excited state are produced by the multiphoton ionization of the neutral molecule in the ground state by laser radiation. The excited ion relaxes by emitting a photon which is detected. The peaks in the photon spectrum would correspond to the energy levels of the

excited ion. Thus this technique would yield accurate values for the ionization potential, spin-orbit splitting constant and other molecular constants.

The spectroscopic studies on linear triatomic ions CO_2^+ , OCS^+ and CS_2^+ are wide and varied. These molecules have isoelectronic structure. The observation of Fermi resonances and Renner–Teller effect has also motivated these studies. CS_2 has been studied by conventional PES [11], PIR [12], emission spectroscopy [13], matrix isolation studies [14] and the recent ZEKE spectroscopy [15].

The near equivalence in the energies of symmetric stretch frequency ν_1 and the overtones of bending frequency ν_2 , coupled with the fact that they belong to the same symmetry species gives rise to the effect of Fermi resonances which has been observed for many pairs of levels of ν_1 and ν_2 vibrations. The excited electronic state has degenerate ${}^2\Pi$ symmetry. It is well known [16] that the potential function in a degenerate electronic state splits (Renner–Teller effect) into two when the molecule is bent. As a result of this Renner–Teller effect combined with the spin-orbit splitting, the bending mode energy levels would be split into several components. So far no high resolution studies on the bending mode of $\text{CS}_2^+(\tilde{A} \ {}^2\Pi_u)$ has been done and no data on the magnitude of Renner–Teller effect has been reported.

In this contribution we present our studies on the excited CS_2^+ molecular cation. Many new Fermi resonances have been observed. We report the Renner–Teller splitting of the Δ_g and Σ_g components of the bending mode ($\nu_2' = 1$) in the ${}^2\Pi_{u3/2}$ and ${}^2\Pi_{u1/2}$ spin-orbit components of the excited $\tilde{A} \ {}^2\Pi_u$ state. The ground state of CS_2^+ cation is $\tilde{X} \ {}^2\Pi_g$. The excitation of the bending vibration (ν_2) from the ground $\nu_2'' = 0$ (of the ion) to the excited state ($\tilde{A} \ {}^2\Pi$) $\nu_2' = 1$ level is forbidden by symmetry selection rules for single photon excitation. Since the excited cation is produced directly from the neutral molecule, the selection rules regarding symmetry is no longer valid. Hence a number of excited levels which are symmetry forbidden for single photon excitation from the ground state molecular ion, has been observed. Observation of the symmetry forbidden excitation of $\nu_2 = 1$ yields accurate frequency for this normal vibration limited by the Renner–Teller interaction.

2. Experimental

The experimental setup is shown in figure 1. It consists of an excimer laser (Lambda Physik EMG 201 MSC) pumped dye laser (FL 3002). Rhodamine 6G was used to produce the fundamental in the region 575–590 nm. The UV second harmonic in the region 287.5–295 nm was generated by using a temperature stabilised (FL-37-1) angle-tuned BBO crystal. Typical power of 0.2–0.4 mJ was used. The laser radiation was focused into the centre of the reaction chamber by using a 10 cm focal length quartz lens. The chamber was evacuated by rotary pump/oil diffusion pump console down to a pressure of $< 10^{-4}$ torr. The CS_2 (Baker chemicals Co.) was purified by repeated freezing and thawing cycles. 50 m torr of CS_2 was flowed through the system. The photomultiplier tube (R. 943 OA2–Hamamatsu) was mounted perpendicular to the laser beam. The laser induced fluorescence was filtered using light baffles and focused on to the photocathode. The photo current was measured using a preamplifier and fed into a box-car averager (PAR 162) operating on single point averaging mode. The box-car was triggered simultaneously with the laser

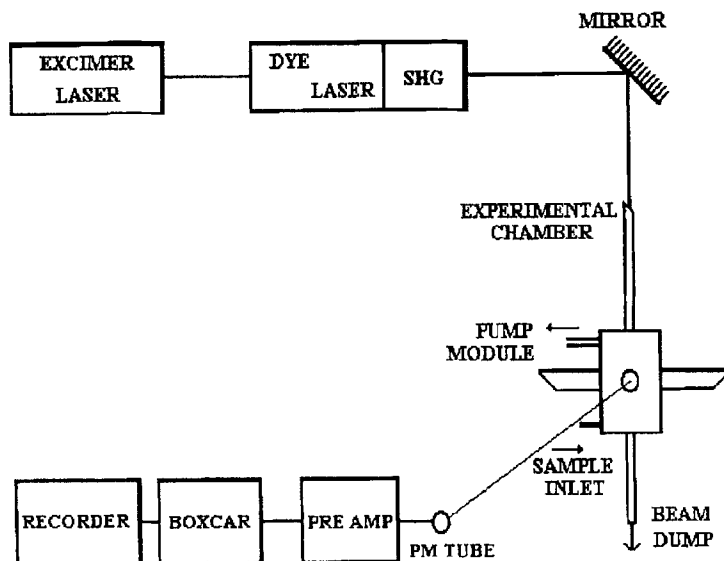


Figure 1. Layout of the experimental set-up.

and the gate (width: 100 ns) was scanned manually and fixed at the point of maximum response. The output from the box car averager was displayed on a strip chart recorder. The wavelength was read off the dye laser dial. The dial readings are calibrated with respect to sulfur atomic lines observed in the photodecomposition of CS₂ [18]. An accuracy of the order of $\pm 1 \text{ cm}^{-1}$ is achieved in the setting of the exciting radiation.

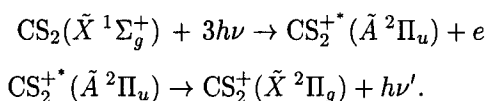
3. Results and discussion

The CS₂ molecule is linear in the ground state with an electron configuration $\dots (5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$ giving rise to $\tilde{X}^1\Sigma_g^+$ as the ground state. The highest occupied molecular orbital is $(2\pi_g)$. Removal of an electron from this orbital results in the formation of the CS₂⁺ cation in the ground $\tilde{X}^2\Pi_g$ state which lies at an energy of 10.08 eV. Removal of an electron from the inner closed $(2\pi_u)^4$ shell forms the cation in the excited $^2\Pi_u$ state. The molecular cation is produced by multiphoton ionisation resonance of the neutral molecule CS₂ in the ground $\tilde{X}^1\Sigma_g^+$ state. The energy of the single photon lies in the range of 4.2–4.3 eV. The $\tilde{A}^2\Pi_u$ state of CS₂⁺ lies at an energy of 12.7 eV above the ground state of the neutral molecule. Hence three photons are required to produce the ionized species.

The production of CS₂⁺ cation, in the case of single photon direct photoionization takes the molecule from its ground state to the ground state of the ion. The cross-section for photoionization is different from normal photoabsorption cross-section and it resembles a step function rather than a delta function in its dependence on radiation wavelength which reflects the Franck–Condon factors for transitions to the vibrational levels of the ion. In the case of polyatomic molecules, due to the super position of transitions from different

vibrational sublevels of the ground electronic state, the stepwise nature of dependence is smoothed out under normal conditions. The ionization cross-section reaches a peak in the region of vertical Franck–Condon transition. The same considerations are applicable in the case of multistep photoionization where the transition of the molecule into the state of the ion occurs from excited vibronic levels and must be included in the Franck–Condon factor between the two states [17]. The transition between well defined states of the ion and its parent molecule can be observed at the threshold of the ionization process when the photon energy is exactly equal to the energy difference between the two states involved [6].

By absorbing three UV photons, the CS₂ molecule is excited (via resonant/non-resonant intermediate states) to energy states from which it can undergo ionization when the excitation energy matches the threshold for ionization, thus producing CS₂⁺ cation in the excited electronic vibrational levels. The electron produced will have zero kinetic energy and the corresponding photon flux would be maximum (emission from the fluorescing cation). The process may be represented as:



The excited ion returns to the ground state/lower state by emitting a photon which is detected. The photon flux would be maximum when new vibronic levels are reached as the photoionization efficiency reaches a maximum when resonances of the ion occur.

The transition from the $\tilde{A} \rightarrow \tilde{X}$ state of the ion lies in the visible range. Thick glass plates were used as light filters over the window of the experimental chamber. Thus the peaks in the photon spectrum (fluorescence) would correspond to the energy levels of the ion. Molecular fragmentation is a major factor and photodissociation and photoionisation are competing processes at these wavelengths [18]. The photon spectrum of the $\tilde{A}^2\Pi_u$ state of CS₂⁺ ion is shown in figure 2. Since the excited cation is produced from the neutral molecule by multiphoton ionization, many vibronic levels are excited which otherwise would have been symmetry forbidden for excitation from the ground ionic state ($\tilde{X}^2\Pi_g$). One such level is the bending vibration ν_2 excited by one quantum of ν_2 (symmetry species Π_u). The standard notations for describing the band are used, though in this case $\nu_{2v}^{v'}$ indicate the bending vibration band of the ion and v' denotes the vibrational quantum number of the excited ion, v'' represents the vibrational quantum number in the ground state of the neutral molecule. All the bands discussed are ionic bands and hence no separate + sign added to indicate vibrational frequency ν_1, ν_2 etc of the ion. The observed spectrum of $\tilde{A}^2\Pi_u$ is only vibrationally resolved as the resolution capability of the present setup was not enough to separate the rotational levels in the ground state of CS₂ molecule (the rotational constant B_e'' is 0.109 cm⁻¹). The observed bands along with their tentative assignments are listed in table 1.

The close proximity of the energy levels, ν_1 (symmetric stretching vibration) and the overtone $2\nu_2$ (bending vibration) and the fact that these vibrations have the same symmetry species, (the levels $(\nu_1, \nu_2, 0)$ and $(\nu_1 - 1, \nu_2 + 2, 0)$ will have the same symmetry species) lead these states to perturb each other and consequently they are shifted from each other [16]. This vibrational–vibrational interaction, a Fermi resonance, is observed in the \tilde{A} state of CS₂⁺. We have observed the $\nu_2' = 1$ band of CS₂⁺ which gives an unperturbed value of bending vibration ν_2 . It is seen that $\nu_1 > 2\nu_2$. The Fermi resonance has been observed for

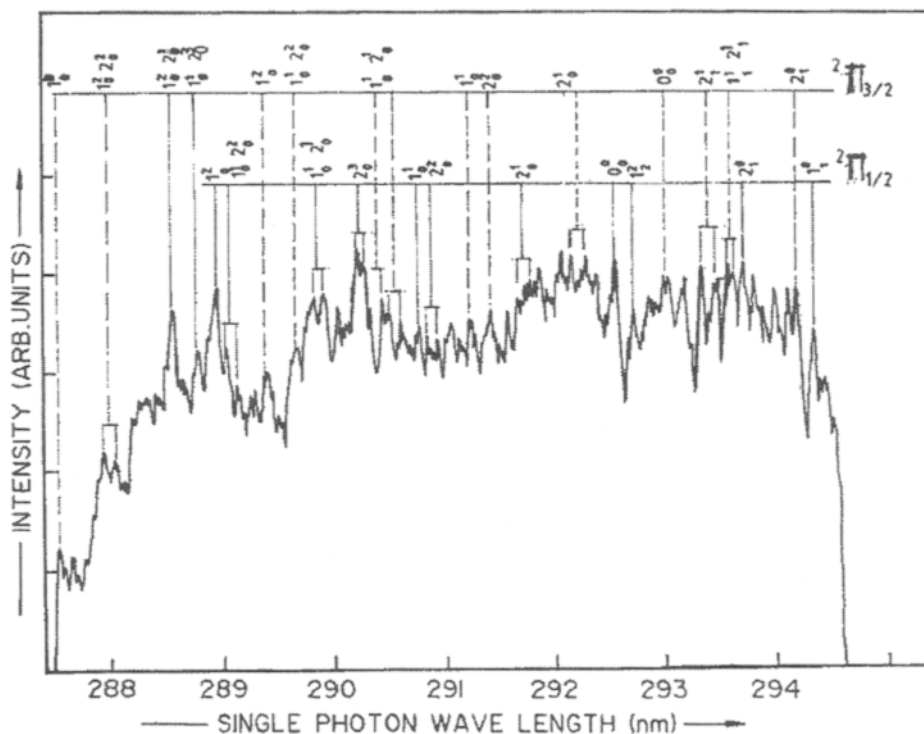


Figure 2. Photon spectrum of the $\tilde{A}^2\Pi_u$ state of CS₂⁺ ion.

the pairs of levels (1, 0, 0)–(0,2,0); (1,1,0)–(0,3,0); (2,0,0)–(1,2,0); (2,1,0)–(1,3,0) and (3,0,0)–(2,2,0) for both the $\Pi_{3/2}$ and $\Pi_{1/2}$ components and the observed frequencies are given in table 1.

The observed excited state of CS₂⁺ has $^2\Pi_u$ symmetry and its interaction with the vibrational motion will have the potential distorted along its bending co-ordinate. As a result of this effect (Renner–Teller effect) each of the levels involving the bending vibration will be split into several components as shown in figure 3. The Renner–Teller (R–T) splitting has been observed for the excited $^2\Pi_u$ state. From figure 3 it is seen that the Renner–Teller species for the $v_2 = 1$ level are Δ_g , Σ_g^- and Σ_g^+ . Two components are observed which are tentatively assigned as Δ_g (274 cm⁻¹) and Σ_g^- (299 cm⁻¹) for the $^2\Pi_{3/2}$ spin-orbit component. This was based on the assignment made for the vibronic species of the ground $\tilde{X}^2\Pi_g$ state of CS₂⁺ ion by ZEKE method [15]. Renner–Teller splitting is also seen for levels at 103168 cm⁻¹ (0,3⁴,0), 103194 cm⁻¹ (0,3²,0) and 103222 cm⁻¹ (1,1²,0), 103265 cm⁻¹ (1,1⁰,0) for the $^2\Pi_{u3/2}$ component. Similar components have also been observed for $^2\Pi_{u1/2}$ spin orbit component and the components have been given tentative assignments. This is the first observation of the Renner–Teller splitting in the excited state. But the combination of Renner–Teller effect and spin-orbit splitting make each level in the bending mode to split into several components. This coupled with the Fermi resonance further complicate the spectra. Hence determination of accurate values for R–T splitting for higher levels of bending mode was not successful.

Table 1. Assignment of the peaks observed in the photon spectrum of multiphoton excited CS₂ molecule.

Single photon λ Å	Energy ^a		Assignment		ΔE	Assignment	
	$E = 3\nu$ (cm ⁻¹)	ΔE	² Π _{3/2}	$\tilde{X}^{-1}\Sigma_g^+$		² Π _{1/2}	$\tilde{X}^1\Sigma_g^+$
287.57	104.293	1989					
.718	240	1936	300	000			
.997	138	1834	220	000			
288.096	102	1798					
.635	103.907	1603	210	000			
.854	828	1524	130	000			
298.032	766				1281	200	000
.133	729				1243	120	000
.212	700						
.410	620						
.491	600	1296	200	000			
.70	507	1203	120	000			
.90	454				969	110	000
290.00	418				933	110	000
.116	376				891		
.294	313				828	030	000
.372	285				800	030	000
.431	265	961	110	000			
.547	222	918	110	000			
.627	194	890	030	000			
.700	168	864	030	000			
.866	110				625	100	000
.996	063				580	020	000
291.364	102.952	648	100	000			
.524	876	572	020	000			
.693	821				336		
291.783	102.786				301 Σ _g	010	000
.863	758				273 Δ _{3/2}	010	000
292.302	603	299 Σ _g	010	000			
.374	578	274 Δ _{5/2}	010	000			
292.640	485	181	A		000	000	000
.729	454	150			-31	100	100
.800	429				56	200	200
.959	373				112	010	010
293.078	331				154	110	110
.158	304	000	000	000			
.217	260	-44					
.457	200	104	010	010			
.517	179	125					
.676	123	181	020	020			
.700	115	189					
.780	087	217			398	000	010
294.300	101.907	397	000	010			

^a Vacuum wave numbers taken from Table of Wave numbers Vol. I, C D Coleman, W R Bozman, W F Meggers. *Natl. Bur. Stand.* (1960)

Since the experiment was performed with CS₂ gas at room temperature, many hot bands have been observed in both the stretching and bending mode as can be seen from figure 2 and table 1. The peaks at 102087 cm⁻¹ and 101907 cm⁻¹ have been identified as the 2₁⁰ hot

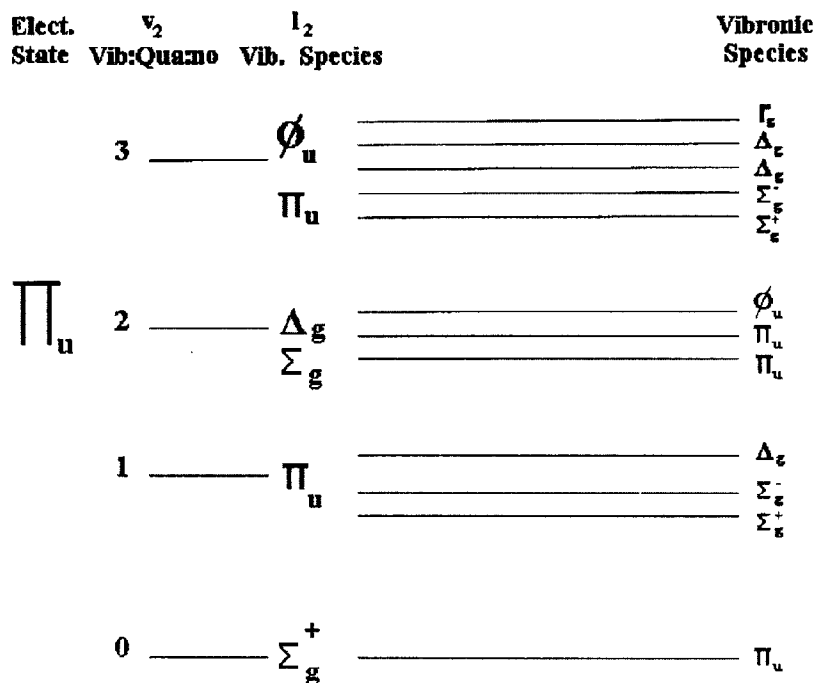


Figure 3. Renner-Teller splitting of the ${}^2\Pi_u$ electronic state of CS₂⁺ for zero spin-orbit interaction.

band for the ${}^2\Pi_{u1/2}$ and ${}^2\Pi_{u3/2}$ states respectively as the energy difference compares very well with the ground state bending vibration frequency ν_2 of the neutral CS₂ molecule. The $\tilde{X}^1\Sigma_g^+$ ground state of CS₂ molecule has three vibrational modes: the symmetry stretch is 658 cm⁻¹, the degenerate bend is 397 cm⁻¹ and the asymmetric stretch is 1533 cm⁻¹ [16]. Hot sequence bands involving the bending vibration ν_2'' has been observed. They are shifted to the red side of the 0-0 band as the vibrational frequencies in the excited ion is smaller compared to ground state. Thus 2_1^1 and 2_2^2 as well as 1_1^1 and 1_2^1 bands have been observed.

The parent, neutral CS₂ as well as the molecular cation CS₂⁺ have linear geometry. The bond length changes from 1.554 Å (\tilde{X} CS₂) to 1.564 Å ($\tilde{X}^2\Pi_g$ of CS₂⁺) to 1.615 Å ($\tilde{A}^2\Pi_u$ of CS₂) [13]. By Frank-Condon principle and the selection rules for linear-linear type transitions, the ν_1' progressions involving the symmetric stretch vibrations is strongly allowed whereas progressions in $2\nu_2'$ bending vibrations are expected to be weak. Under favourable conditions, transitions involving an even quanta of ν_2 can borrow intensity from the strongly allowed transitions. Also when an intermediate state takes part in the ionization process, the overall Frank-Condon factor have to be taken into account. This is in agreement with the observation where the bands involving $\nu_1' = 2$ is more intense than $\nu_1' = 1$ or $\nu_1' = 0$ symmetric stretching ν_1 bands. The bands involving 1_0^3 occur in the region where the dye laser intensity has fallen sharply and the spectrum shown in figure 2

is not normalised. From 1_0^1 band the value for the symmetric stretch ν_1 is obtained. The separation of 0_0^0 bands of the ${}^2\Pi_{u3/2}$ and ${}^2\Pi_{u1/2}$ state gives directly the spin orbit splitting constant A of the \tilde{A} state. The spectrum also gives information about the ionization potential, from the observed 0_0^0 (3/2) and 0_0^0 (1/2) bands. The adiabatic ionization potential 12.684 eV (${}^2\Pi_{3/2}$) and 12.707 eV (${}^2\Pi_{1/2}$) compares well with the value observed from other methods. The values of the molecular constant and its comparison with the values obtained by other techniques are listed in table 2. The accuracy of the bending vibration observed is limited by the Renner–Teller interaction. So also the accuracy of the symmetric stretch vibration is limited by the Fermi interactions.

The resolution of our method was better than the methods reported in table 2 with which our results are compared. The data obtained from photo electron spectroscopy technique are on the lower side when compared to other methods as it has the poorest resolution. Our results compare very well with the photoionization resonance (PIR) method. The vibrational frequency $\nu_1 = 648 \text{ cm}^{-1}$ for the $\Pi_{3/2}$ component, is in reasonable agreement with the 622 cm^{-1} reported and the ν_1 value for the $\Pi_{1/2}$ component is in excellent agreement (625 cm^{-1} by both methods). In our case the bending vibration is split into two R–T components and for comparison we have to take the mean value as the PIR method could not resolve the R–T components. Hence the ν_2 frequency 286 cm^{-1} and 287 cm^{-1} (for the $\Pi_{3/2}$ and $\Pi_{1/2}$) inferred here agree well with 279 cm^{-1} and 286 cm^{-1} respectively obtained by the PIR method. Similarly there is reasonable agreement of the adiabatic potential energy for the two components by both methods as also close similarity in the spin-orbit splitting constant (A). On the basis of the close agreement between the vibrational frequency and other molecular constants, it is reasonable to assume that the excited CS_2 ionic species belong to the $\tilde{A} {}^2\Pi_u$ state.

Table 2. Molecular constants of $\tilde{A} \text{CS}_2^+$ ion in comparison with other methods.

Technique	State	vib: ν_1 cm^{-1}	frequency ν_2 cm^{-1}	IP eV	SO splitting A cm^{-1}
PES ^a	${}^2\Pi_{3/2}$	585	—	12.698	172
	${}^2\Pi_{1/2}$	—	—	12.720	—
PIR ^b	${}^2\Pi_{3/2}$	622	279	12.696	189
	${}^2\Pi_{1/2}$	625	286	—	—
Optical ^c	${}^2\Pi_{3/2}$	612	275	12.697	176
	${}^2\Pi_{1/2}$	602	—	12.719	—
This method	${}^2\Pi_{3/2}$	648	$299 \Sigma_g$	12.684	181
			$274 \Delta_{5/2}$		
			$273 \Delta_{3/2}$		
	${}^2\Pi_{1/2}$	625	$301 \Sigma_g$	12.707	

^a [11]; ^b [12]; ^c [13]

4. Conclusion

The cation CS₂⁺ is produced in the excited $\tilde{A}^2\Pi_u$ state when the photon energy is exactly equal to the threshold energy for ionization. The excited molecular cations are studied using a different technique in which the photons emitted by the decaying ions are detected. In this technique we are looking at the radiative relaxation of excited levels rather than a specific transition to ground or lower level. Hence the requirement is only for a photomultiplier having a wide range of sensitivity. (185–900 nm response). The peaks in the photon spectrum would correspond to the energy levels in the excited state.

The symmetry forbidden excitation in the bending mode (2_0^1) is observed which gives unperturbed value limited by the Renner–Teller interaction for this normal mode. The $\nu_2 = 1$ vibration of the $\tilde{A}^2\Pi_{u1/2}$ splits into two Renner–Teller components at 301 cm⁻¹ (Σ_g^-) and 273 cm⁻¹ ($\Delta_{g3/2}$). Similarly R–T components for the $2\Pi_{u3/2}$ components are also observed and accurate value of splitting obtained for the first time.

The observed spectrum does not correspond to the single and two photon excited spectra of CS₂ molecule nor the known energies of the photofragments CS and S atom, both neutral and ionic species in their ground and excited states. The observed spectrum matches well with the reported vibrational energy levels and vibrational frequencies for the $\tilde{A}^2\Pi_u$ state of CS₂⁺ ion determined by other methods. The analysis of the observed spectrum was also based on this knowledge and this technique yields values for the ionization potential, the spin-orbit splitting constant, the fundamental vibrations ν_1 and ν_2 , for the upper excited state comparable to any other technique.

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