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A resonance enhanced multiphoton ionization study of the CS$_2$ molecule: The 4p Rydberg states

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The resonance enhanced multiphoton ionization (REMPI) spectrum of jet-cooled CS$_2$ has been recorded in the one-photon wavelength range 460–500 nm, corresponding to the three photon excitation energy range 60 000–65 000 cm^{-1}. A previous assignment of one photon forbidden transitions in this region to 3d Rydberg states is shown to be incorrect and reassigned to the 4$p\pi$ $^{1,3}\Delta_u$ states. In fact all the observed states in this region can be assigned to 4p Rydberg states; the 4$p\sigma$ $^{1,3}\Pi_u$ states at 62 768 and 62 083 cm^{-1}, respectively, and the 4$p\pi$ $^{1,3}\Delta_u$ states at 64 214 and 63 698 cm^{-1}, respectively. Another band at 64 374 cm^{-1} may be due to a three photon excitation to the 4$p\pi$ $^1\Sigma_u^+$ Rydberg state. Our resolution is sufficient to resolve band shapes enabling symmetry assignments when coupled with their polarization behavior. The fact that the origin bands are not degraded and that $\Delta\nu=0$ sequence bands are strongly excited whereas $\Delta\nu\neq0$ transitions are either absent or very weak implies that the upper states have a linear geometry similar to that of the ground state. A comparison of singlet–triplet splittings suggests the 4$p\pi$ Δ_u states have stronger Hund's case (c) character than the 4$p\sigma$ Π_u state. While CS$_2^+$ was generally the predominant ion formed, resonance ionization through the $^1\Delta_u \leftarrow X$ $^1\Sigma_g^+$ origin band led to an unusual predominance of S$^+$ and CS$^+$ ions. This is explained by multiphoton fragmentation of CS$_2^+$ via an accidental one-photon resonance from the X $^2\Pi_{1/2}$ ($v=0$) ionic ground state. © *1995 American Institute of Physics.*

I. INTRODUCTION

The one photon vacuum ultraviolet absorption spectrum of CS$_2$ was first reported by Price and Simpson in 1938.[1] In the 60 000–65 000 cm^{-1} excitation energy region four groups of bands were observed and labeled the 1612, 1595, 1577, and 1553 Å bands, of which the 1595 Å band was most intense. Since then a number of one photon absorption[2,3] and electron energy loss[4–6] investigations have been carried out in this region, while, recently, McDiarmid and Doering[7] and Mualem and Gedanken[8] compared the room temperature and jet-cooled absorption spectra of CS$_2$ across the 1595 and 1612 Å bands. As summarized by McDiarmid and Doering,[7] the upper state of the 1595 Å band can be assigned to the 4$p\sigma$ $^1\Pi_u$ Rydberg state. In particular, the $^1\Pi_u \leftarrow X$ $^1\Sigma_g^+$ assignment is consistent with the low resolution magnetic circular dichroism (MCD) spectrum obtained by Gedanken,[9] which shows the upper electronic state to be degenerate, and the fact that the band appears strongly in one photon absorption. The weaker 1612 Å band has been variously assigned to the 1$_1^0$ hot band[1,8,9] or the spin-forbidden 4$p\sigma$ $^3\Pi_u \leftarrow X$ $^1\Sigma_g^+$ origin band.[3,4,6,7] Mualem and Gedanken[8] claim that there is a clear temperature dependence for this transition implying that it must be a hot band, but their result is in direct contradiction to that obtained by the earlier but similar study of McDiarmid and Doering[7] where no convincing evidence of a temperature dependence was observed. From Price and Simpson's experimental data,[1] there is a 36 cm^{-1} discrepancy between the measured position of the band maximum and that expected for the 1$_1^0$ hot

band (the ground state vibrational frequencies are well known[10,11]). It is therefore necessary, if this hot band assignment is true, to postulate that the discrepancy is due to differences in rotational structure between the origin band and the 1$_1^0$ hot band.[8] The MCD spectrum in the region of the 1612 Å band indicates that the upper state is degenerate,[9] which would therefore be consistent with both $^{1,3}\Pi_u$ upper state assignments. Electron energy loss studies may be expected to distinguish between these two assignments, since low electron impact energies and high scattering angles tend to favor spin-forbidden transitions over spin-allowed transitions. However, under such conditions, a broad band overlaps both the 1612 and 1595 Å bands, extending from 7.4 eV to ≈7.8 eV.[4,5] This has led to uncertainties in the interpretation, with Wilden and Comer[4] suggesting a spin-forbidden transition and Hubin-Franskin *et al.*[5] suggesting a spin-allowed transition. Of the other two bands observed by Price and Simpson, the 1577 Å band may be assigned to vibrational bands of the 4$p\sigma$ $^1\Pi_u \leftarrow X$ $^1\Sigma_g^+$ electronic transition,[1,7] while no definite assignment has been given to the 1553 Å band, although the MCD spectrum[9] indicates the upper state is nondegenerate, i.e., that it corresponds to a $^1\Sigma_u^+ \leftarrow$ $^1\Sigma_g^+$ type transition.

Recently, Li *et al.*[12] have recorded the room temperature (3+1) REMPI spectrum of CS$_2$ in a static cell and report one photon forbidden transitions at ≈64 200 cm^{-1} and ≈63 700 cm^{-1}, respectively. They assign these bands to electronically forbidden but vibronically allowed three photon resonances from the ground state to two 3d Δ_g Rydberg states. However, they were unable to resolve the individual band shapes due to the low resolution and the overlapping $\Delta\nu=0$ sequence bands. The band at ≈64 200 cm^{-1} (7.96 eV) has

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been observed in the electron energy loss studies of Wilden and Comer[4] (their band h) and Hubin-Franskin *et al.*[5] (their band C''') and both suggest this transition has the characteristics of a one-photon symmetry forbidden transition. Another feature in the electron energy loss spectrum at ≈ 7.86 eV ($\approx 63\,400$ cm^{-1}) has been suggested as a spin-forbidden transition by Wilden and Comer[4] (their band g) but an optically allowed transition by Hubin-Franskin *et al.*[5] (their C'' band). This feature in fact corresponds to Price and Simpson's optically allowed 1577 Å band. However in the electron energy loss spectrum overlapping features seem once again to be the cause of uncertainty, since in Wilden and Comers spectrum this feature appears to be overlapped with another feature which does seem to show the characteristics of a spin-forbidden transition.

In this work we reinvestigate the 60 000–65 000 cm^{-1} energy region using REMPI time-of-flight spectroscopy of CS$_2$ expanded in a supersonic jet, in order to reduce the rotational temperature and hence to obtain improved resolution. We observe both the one photon forbidden transitions of Li *et al.*[12] and the Price and Simpson bands. With this improved resolution we are able to resolve the sequence bands from the origin bands and also observe the band shapes. Together with the polarization behavior of these bands the results imply a reassignment of the one photon forbidden bands to transitions from the ground state to the $4p\pi\ ^{1,3}\Delta_u$ Rydberg states. In summary, we are able to give a reasonably coherent analysis of all observed features and attempt to resolve conflicting observations reported in the literature.

II. EXPERIMENT

The basic time-of-flight apparatus has been described in Ref. 13. A XeCl excimer pumped dye laser (Lambda Physik EMG 201/FL2002) with an appropriate dye provided laser radiation in the fundamental wavelength range 460–500 nm with a bandwidth of ≈ 0.3 cm^{-1} and a pulse energy which was varied in the 2–7 mJ range. The laser radiation was focused into a vacuum chamber by a 15 cm focal length quartz lens. CS$_2$ mixed with helium buffer gas was expanded into the vacuum chamber via a pulsed valve (0.3 mm nozzle diameter/Laser Technics), perpendicular to the laser direction. The photoions generated in the REMPI process were accelerated and passed into a time-of-flight tube and detected and amplified with a pair of 1 in. diam multichannel plates. The signal after passing through a fast preamplifier (300 MHz) was fed into a two boxcar integrator unit (SRS 250) and interfaced to a PC for data storage. Calibration was achieved by synchronously recording an optogalvanic spectrum from a Fe–Ne hollow cathode lamp. A wavelength calibrated Soleil Babinet compensator was used to convert the linearly polarized laser output into circularly polarized light for polarization studies. Spectroscopic grade CS$_2$ was used after several repeated freeze thaw degassing cycles under vacuum.

III. RESULTS AND DISCUSSION

The CS$_2$ molecule is linear in its ground state with an electronic configuration of $...5\sigma_u^2 2\pi_u^4 2\pi_g^4, X\ ^1\Sigma_g^+$, where the
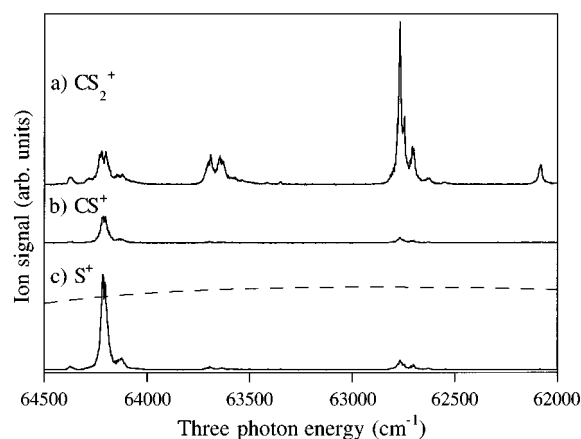

FIG. 1. The 3+1 REMPI spectrum of CS$_2$ in the three photon energy range 62 000–64 500 cm^{-1} recorded in the (a) CS$_2^+$ (b) CS$^+$ and (c) S$^+$ channels under the same experimental conditions. The dashed curve represents the relative laser pulse energy, with respect to the base line of (c). Spectra are not corrected for laser energy.

highest occupied molecular orbital, $2\pi_g$, is essentially of nonbonding character. One electron ionization from this orbital generates the $(...2\pi_g^3)X\ ^2\Pi_g$ cationic state, which is inverted with a spin–orbit splitting of 440 cm^{-1}.[10,14] As expected from the removal of a nonbonding electron, the cationic ground state has a geometry very similar to that of the neutral molecule.[10] In the 60 000–65 000 cm^{-1} excitation energy range of CS$_2$ both $4p$ and $3d$ Rydberg states may be present. Since Rydberg orbitals are generally nonbonding in character one may expect these Rydberg states to have a linear geometry and C–S bond length similar to CS$_2^+(X\ ^2\Pi_g)$, which forms the cationic core, and hence similar to CS$_2(X\ ^1\Sigma_g^+)$.

One electron excitation from the $2\pi_g$ orbital to the $4p_u$ Rydberg orbital, generates the following states: $(...2\pi_g^3)4p\sigma\ ^{1,3}\Pi_u$ and $(...2\pi_g^3)4p\pi\ ^{1,3}\Delta_u,\ ^{1,3}\Sigma_u^+$ and $^{1,3}\Sigma_u^-$. Similarly, one electron excitation from the $2\pi_g$ orbital to the $3d_g$ Rydberg orbital generates the following states: $(...2\pi_g^3)3d\sigma\ ^{1,3}\Pi_g$, $(...2\pi_g^3)3d\pi\ ^{1,3}\Delta_g,\ ^{1,3}\Sigma_g^+,\ ^{1,3}\Sigma_g^-$ and $(...2\pi_g^3)3d\delta\ ^{1,3}\Phi_g$, and $^{1,3}\Pi_g$. Note that the $4p$ and $3d$ Rydberg states have opposite u/g symmetry. Hence, with respect to this symmetry, one and three photon transitions from the $X\ ^1\Sigma_g^+$ ground state to the $4p$ Rydberg states are electronically allowed (i.e., $u \leftarrow g$) while corresponding transitions to the $3d$ Rydberg states are electronically forbidden (i.e., $g \leftarrow - g$). Three photon transitions to the $3d$ Rydberg states can occur through vibronic coupling but these transitions may be expected to be somewhat weaker. Of course, additional selection rules apply, corresponding to the other symmetry elements of the molecule, which will limit the number of $4p$ and $3d$ Rydberg states expected to be observed.

Figures 1(a)–1(c) show the 3+1 REMPI spectra of jet-cooled CS$_2$ in the three photon energy range 62 000–64 500 cm^{-1}, recorded in the CS$_2^+$, CS$^+$, and S$^+$ channels, respectively. In general, the spectra recorded in the CS$^+$ and S$^+$ channels were very similar but much weaker than that recorded in the CS$_2^+$ channel, indicating that these fragment
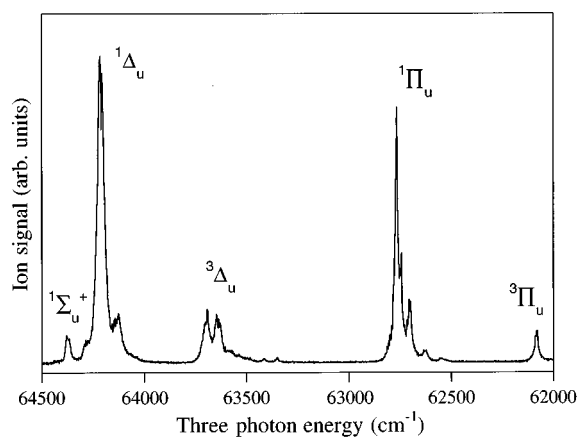
FIG. 2. The total ion 3+1 REMPI spectrum of CS_2, normalized with respect to the cube of the laser energy. The upper electronic states of each band are indicated (see later discussion).

FIG. 3. Expanded view of the energy normalized 3+1 total ion signal of CS_2, showing Price and Simpson's 1612 Å and 1577 Å bands and the weaker features of the 1595 Å band. $A = $ "$2_0^2/1_0^1$" and $B = $ "$1_0^1 2_1^1/2_1^3$" bands of the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transition. The 1_1^0 hot band of this electronic transition may be expected to have $\approx 2\%$ of the relative intensity of feature A, and would be expected at the position indicated by the arrow (see text for further details).

ions are being formed via some nonresonant process. However, there is an obvious anomaly at $\approx 64\,214\ cm^{-1}$ (corresponding to a fundamental wavelength of $\approx 467.2\ nm$), where the CS^+ and in particular the S^+ fragment ions appear strongly. Figure 2 gives the total ion signal in the same energy region, obtained by adding the signals in the CS_2^+, CS^+ and S^+ channels, since other ion signals (e.g., C^+ and S_2^+) were negligibly small at the laser power densities used. We estimate that the possible error in the relative intensity of the $64\,214\ cm^{-1}$ band compared to the other bands in this figure, as a result of obtaining the total ion signal in this way, is $\pm 20\%$. Before considering the one photon forbidden band systems at 64 214 and 63 698 cm^{-1} (labeled $^1\Delta_u$ and $^3\Delta_u$ in Fig. 2), which our results indicate have been previously misassigned, we shall set the stage for their analysis by first considering the 1577, 1595, and 1612 Å bands of Price and Simpson (see Figs. 2 and 3).
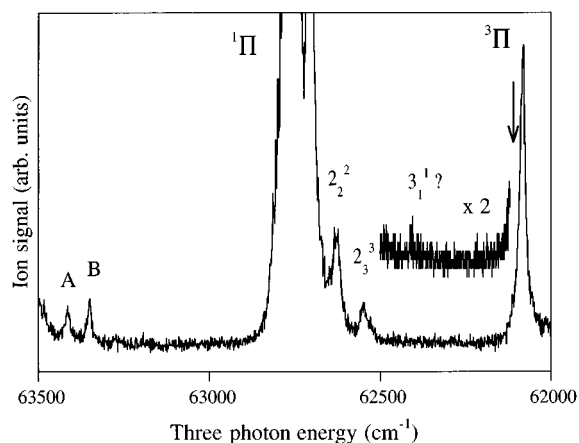
As shown in Fig. 2, the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ (3+1) REMPI spectrum is dominated by the 0_0^0 origin band and $\Delta\nu = 0$ sequence bands shifted to slightly lower energies (which together form the 1595 Å band). $\Delta\nu \neq 0$ bands are either very weak or absent. Moreover, the shape of the origin band appears highly symmetrical indicating that the rotational constant of the $4p\sigma\ ^1\Pi_u$ Rydberg state is very similar to that of the $X\ ^1\Sigma_g^+$ ground state. These two observations imply that the upper state geometry is linear with a bond length similar to that of the ground state. This is consistent with the upper state being a Rydberg state with an $X\ ^2\Pi_g$ CS_2^+ ionic core. Table I gives the measured band centers and suggested band assignments for the observed features in the (3+1) REMPI spectra. The assignments of the $\Delta\nu = 0$ se-

TABLE I. Band centers (in cm^{-1}) and assignments in the 3+1 REMPI spectra.[a]

Resonant State Band Assignment	$4p\sigma\ ^1\Pi_u$ ν_0	$\Delta\nu$	$4p\sigma\ ^3\Pi_u$ ν_0	$\Delta\nu$	$4p\pi\ ^1\Delta_u$ ν_0	$\Delta\nu$	$4p\pi\ ^3\Delta_u$ ν_0	$\Delta\nu$	$4p\pi\ ^1\Sigma_u^+$ ν_0	$\Delta\nu$
0_0^0	62 768(1) {62 774}		62 083(1) {62 080}		64 214(2)		63 698(2)		64 374(1) {64 416} {64 398}	
1_1^1	62 746.5(1.0) {62 754}	-21.5	$\approx 62\,060$	-23						
2_1^1	62 704(2) {62 702}	-64	62 013(4) {62 017}	-70	64 132(2)	-82	63 641(2)	-57	64 284(4) {64 324}	-90
2_2^2	62 627(3) {62 626}	-141	61 961(5) {61 960}	-122	64 053(3)	-161	63 578(4)? 63 534(4)?	-120 -164		
2_3^3	62 550(4)?	-218					63 488(4)?	-210		
3_1^1	62 405(3)?	-363								
$1_0^1 2_1^1/2_1^3$	63 352(2) {63 360}	$+584$								
$1_0^1/2_0^2$	63 413(2) {63 430}	$+645$								

[a]Values in braces correspond to Price and Simpson's (Ref. 1) one photon measurements. Values in parentheses correspond to the estimated error in determining the band center. Note that since the origin bands are generally symmetrical, their band centers should correspond approximately to the band origins. Bands marked by ? have uncertain assignments.

TABLE II. Origins and vibrational frequencies.[a]

	$4p\sigma\ ^1\Pi_u$	$4p\sigma\ ^3\Pi_u$	$4p\pi\ ^1\Delta_u$	$4p\pi\ ^3\Delta_u$	$4p\pi\ ^1\Sigma_u^+$	$X\ ^1\Sigma_g^+$	$X\ ^2\Pi_{1/2}$	$X\ ^2\Pi_{3/2}$
T_{00}[b]	62 768	62 083	64 214	63 698	64 374	0.0	81 724	81 284
ν_1	636.5 (638)	≈635				658.0	624	616
ν_2	332 (325)	326 (334)	314	339	306	396.0	319 341	333
$2\nu_2$[c]	656 (654)	675 (682)	636	633? 677?		792.4 ($l=2$) 801.9 ($l=0$)	640	672
ν_3	1 172?					1 535.4	*1 201*	*1 203*

[a]All values are in units of cm^{-1}. Values in parentheses have been derived by McDiarmid and Doering (Ref. 7) from Price and Simpson's (Ref. 1) data. The ground state $X\ ^1\Sigma_g^+$ CS_2 values were obtained from Ref. 11 while those for the $X\ ^2\Pi$ cationic state were taken or derived from Refs. 14 and 15. Values in italics were obtained by dividing the frequency of the first overtone by two.
[b]T_{00} is assumed equal to the band center of the corresponding 0_0^0 band.
[c]The Rydberg state values were derived from the 2_2^2 bands using an average value (797 cm^{-1}) for the $2\nu_2$ level energy of the ground state. l is the vibrational angular momentum quantum number.

quence bands follow that given by McDiarmid and Doering.[7] The sharp 1_1^1 sequence band, which is partially overlapped by the origin band, appears to be very narrow and symmetric in shape, indicating again very similar geometries between the two vibronic states of this transition. We also observe a very weak but sharp, feature which we tentatively assign to the 3_1^1 sequence band. This gives an upper state ν_3' antisymmetric stretching frequency of 1172 cm^{-1} which is close to the $X\ ^2\Pi_g$ CS_2^+ ionic core value of ≈1200 cm^{-1}.[14,15] We note that Li et al.[12] assign a weak shoulder feature in their spectra to the 3_0^1 band giving ν_3'≈1300 cm^{-1} for the upper state. However, since the asymmetric stretch has σ_u symmetry, the overall vibronic transition would correspond to a $g \leftarrow g$ transition, which is forbidden in a three photon transition. It would also be forbidden in the C_{2v} point group, assuming weak vibronic coupling. In fact their shoulder feature is almost certainly just a sequence band of the 64 214 cm^{-1} one photon forbidden band. In Table II we give the electronic band origins and the upper state vibrational frequencies derived using the known ground state vibrational frequencies.[11] In all cases there is good agreement between the derived vibrational frequencies and those of the cationic core $X\ ^2\Pi_g$ state.[14,15] We note that the values given for the ν_2' and $2\nu_2'$ upper state levels correspond to average values over the vibronic components (which may be split as a result of Renner–Teller and Fermi resonance effects), since we were unable to resolve them, although the bands get broader across the sequence 2_0^0 to 2_3^3.

We also observe two weak bands associated with the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ electronic transition, at 63 413 cm^{-1} and 63 352 cm^{-1}, respectively which correspond to Price and Simpson's 1577 Å band (see Fig. 3). From the $\Delta\nu=0$ sequence band assignments we would expect the 1_0^1 and 2_0^2 bands at 63 405 and 63 424 cm^{-1}, respectively, giving an average of 63 414 cm^{-1}, and so the observed band at 63 413 cm^{-1} is possibly an unresolved overlap of the 1_0^1 and 2_0^2 bands. The band at 63 352 cm^{-1} seems consistent with an assignment either to $1_0^1 2_1^1$ or 2_1^3 or an overlap of both. Li et al.[12] have suggested that the 63 352 cm^{-1} band be assigned to the 1_0^1 band but this is not consistent with the position of the 1_1^1 band which they were unable to resolve.

These two bands (labeled A and B in Fig. 3) essentially vanish under the noise level when the light polarization is changed from linear to circular, indicating that the three photon transition moment is predominantly carried by the T_1^1 spherical tensor component.[16–18] This is consistent with the polarization dependence of the $4p\sigma\ ^1\Pi_u \leftarrow ^1\Sigma_g^+$ origin band, where the band center/maximum decreased to ≈35% of its original intensity when changing from linearly to circularly polarized light, while the band shape became broader and more intense at the wings, indicating that the transition moment is in fact carried by both T_1^1 and T_1^3 tensor components. When considering the polarization dependence of a multiphoton transition it is useful to introduce the polarization ratio, Ωp, defined as the ratio of the intensity of a particular transition recorded with circularly polarized light to that recorded with linearly polarized light.[16–18] Hence, at the center of the origin band we measure $\Omega p \approx 0.35$.

Considering now the band at 62 083 cm^{-1}, which corresponds to Price and Simpson's 1612 Å band, it appears essentially as a single narrow feature. It is separated from the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ origin band by 685 cm^{-1}. The 1_1^0 hot band of the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transition is expected at 658 cm^{-1} to lower energy—a difference of about 27 cm^{-1} from the band observed. As mentioned in Sec. I, the assignment of this feature to the 1_1^0 hot band requires that this band be severely degraded, whereas in fact, the observed band is highly symmetrical in nature, with a width (FWHM) of about 15 cm^{-1}. This implies that the upper state geometry is linear and very similar to that of the ground state. This rules out the possibility that this band is the 1_1^0 hot band and is therefore consistent with the $4p\sigma\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ assignment (see Fig. 3). However, Mualem and Gedanken,[8] claim that the relative band intensity is temperature dependent. Their conclusions are based on comparisons of the relative intensities of the 1595 and 1612 Å bands, recorded at room temperature in a static cell and in a supersonically expanded CS_2/buffer gas mixture (see their Fig. 2). Their absorption measurements employed a resolution of 0.4 Å (≈16 cm^{-1} at these wavelengths), which corresponds to the bandwidth of the monochromator used to disperse the light continuum. This instrumental bandwidth is very large and is comparable

TABLE III. Relative band intensities (percentage) of some bands recorded in the energy normalized total ion (3+1) REMPI spectrum.[a]

Band assignment	Band center/cm^{-1}	Measured	Calculated[b]
$4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$			
0_0^0	62 768	100	100
2_1^1	62 704	31(4)	30
2_2^2	62 627	8(2)	6.2
2_3^3	62 550	2(1)	1.2
3_1^1	62 405?	0.08(4)	0.06
$1_0^1 2_1^1/2_1^3$	63 352	1.0(4)	
$1_0^1/2_0^2$	63 413	0.9(4)	
1_1^0	(62 110)[c]		≈ 0.02
1612 Å band	62 083	13(2)	

[a]The energy did not vary by more than 5% across this region, and the signal was normalized to the cube of the laser energy. In the third column the values in parentheses are estimated errors.

[b]A room temperature ($kT = 207$ cm^{-1}) Boltzmann distribution was assumed for the ground state vibrational levels (see text for details). The ground state vibrational energy levels were taken from Ref. 11.

[c]Expected position.

to the bandwidths of the individual vibrational bands, and so care should be taken in order not to saturate the more intense bands. Mualem and Gedanken's[8] room temperature spectrum (the top trace of their Fig. 2) does appear to show signs of saturation and so their temperature dependence may in fact be accounted for by saturation effects. The relative intensities of the $^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$, 0_0^0 origin band and the 2_1^1 and 2_2^2 sequence bands may be estimated as follows. If it is assumed that the $X\ ^1\Sigma_g^+$ and $4p\sigma\ ^1\Pi_u$ potentials are approximately the same, at least in the vicinity of the energy minima, which appears to be the case here, then the Franck–Condon factors for the origin band and the $\Delta v = 0$ sequence bands will be identical (and ≈ 1), where it has been implicitly assumed that the electronic transition moment remains constant.[19] Hence, in a first approximation the relative band intensities will be determined by the ground state vibrational population only, which is proportional to the product of the Boltzmann factor and the ground state vibrational degeneracy, $(v_2'' + 1)$.[19] This gives an expected room temperature absorption ratio for the 0_0^0, 2_1^1, and 2_2^2 bands of 1:0.30:0.06 (see Table III). Mualem and Gedanken's room temperature ratio for these bands is $\approx$1:0.85:0.35 (as estimated from their Fig. 2). McDiarmid and Doering[7] employed a similar apparatus with a transmission resolution of ≈ 8 cm^{-1} but did not observe a temperature effect for the 1612 Å band. They did observe however, a $0_0^0:2_1^1$ intensity ratio for the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transition of about 1:0.50 for both their room temperature and jet cooled CS$_2$ spectra indicating a vibrational temperature of about 400 K. To explain this they suggested strong nonadiabatic coupling via the bending motion. However, it seems possible that some saturation has occurred. In our jet spectra we measure a ratio of approximately 1:0.31:0.08, for the intensity ratio of the 0_0^0, 2_1^1, and 2_2^2 bands, see Table III, indicating a room temperature Boltzmann distribution for the ground state vibrational levels, which may be explained by inefficient vibrational relaxation in our jet. The same effect has been noted by Fischer et al.[14] in the nonresonant two photon zero kinetic energy (ZEKE) photoelectron spectrum

of CS$_2$ and by Liu et al.[20] in a study of rotational relaxation of CS$_2$ in an argon free jet. In expansions of CO/He gas mixtures the lowest rotational temperature achieved with our system was about 70 K, which is quite high considering that rotational cooling is expected to be much more efficient than vibrational cooling.

The "$1_0^1/2_0^2$" band at 63 413 cm^{-1} (band A in Fig. 3) has a relative intensity of approximately 1% compared to the origin band in our spectra. Hence, the Franck–Condon factor for the 1_0^1 transition may be estimated as ≈ 0.005 (assuming that for the origin band it is ≈ 1). If the Franck–Condon factor for the 1_1^0 transition is similar to this, then considering that the room temperature Boltzmann population of the $v_1'' = 1$ level is about 4% of that of the ground vibrational level, we may expect the 1_1^0 hot band to have a relative intensity of approximately 0.02% compared to the origin band whereas in fact the relative intensity of the 1612 Å band is $\approx$13%. Looking again at Mualem and Gedanken room temperature spectrum,[8] the relative intensity of this band appears to be $\approx$40%, which again suggests that their room temperature spectrum is saturated. Hence, the actual 1_1^0 band is too weak to be observed and would be hidden by the "tail" of the much more intense, by two to three orders of magnitude, $^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ band (see Fig. 3).

The polarization behavior of the $4p\sigma\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ band was similar to that observed for the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ origin band. We also observe a weak shoulder to lower energy which we assign to the 1_1^1 sequence band and two other weak bands which seem consistent with a 2_1^1 and 2_2^2 sequence band assignment. Price and Simpson observe some of these bands and they have been similarly assigned by McDiarmid and Doering.[7]

It was found that relatively more ion fragments compared to CS$_2^+$ were generated via the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ three photon resonance than via the $4p\sigma\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ three photon resonance. In addition, for the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ band system, the relative degree of final ion fragmentation increased with the increase of vibrational excitation in the upper state. However, the band shapes recorded in the CS$^+$ and S$^+$ fragment channels were similar to that recorded in the CS$_2^+$ channel, indicating that the fragmentation was caused by nonresonant multiphoton processes in CS$_2^+$ after being initially formed in the REMPI process. In fact the CS$(X\ ^1\Sigma)$+S$^+$(^{4}S) dissociation limit of CS$_2^+$ is two photon accessible, while the CS$^+$($X\ ^2\Pi$)+S(^{3}P) dissociation limit is three photon accessible, across the fundamental wavelength region of this study.[21]

The $4p\sigma\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ transition is of course spin-forbidden in the Hund's case (a) approximation. It will gain intensity via the isoconfigurational spin–orbit interaction which will mix the $4p\sigma\ ^1\Pi_1$ and $^3\Pi_1$ case (a) states.[22] Hence the $^3\Pi_1$ spin–orbit state will gain some singlet character through this interaction. This is the reason why only one of the multiplet components of the $^3\Pi$ state is observed, since the $^3\Pi_0$ and $^3\Pi_2$ substates do not interact with the $^1\Pi_1$ state. This interaction is important in considering the change from Hund's case (a) to Hund's case (c) coupling behavior.[22]

To summarize, the $4p\sigma\ ^{1,3}\Pi_u \leftarrow X\ ^1\Sigma_g^+$ (3+1) REMPI spectra have been observed. The symmetrical nature of the
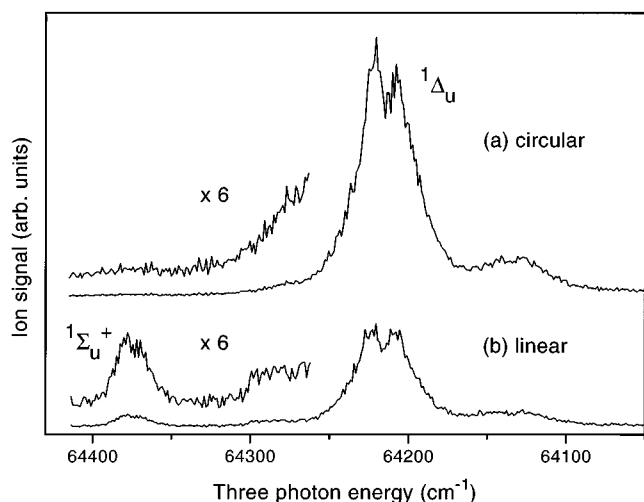
FIG. 4. Total ion 3+1 REMPI spectra recorded with (a) circularly and (b) linearly polarized light.
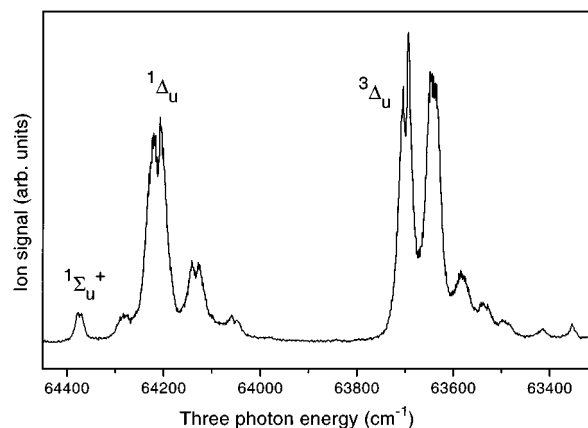

FIG. 5. The 3+1 REMPI spectrum in the 63 300–64 450 cm^{-1} three photon energy range recorded in the CS_2^+ channel. The spectrum is not corrected for laser energy.

origin bands (i.e., lack of rotational degrading) and the relative intensity of $\Delta\nu=0$ sequence bands compared to $\Delta\nu\neq0$ bands indicate that the upper Rydberg states have a linear geometry similar to that of the ground state. The observation of the $^3\Pi_u \leftarrow X\,^1\Sigma_g^+$ band can be explained by spin–orbit mixing between the $^1\Pi_1$ and $^3\Pi_1$ states similar to that observed for the $4s\sigma\,^{1,3}\Pi_g$ Rydberg states.[13]

Now we shall consider the bands at 64 214 and 63 698 cm^{-1} which do not appear in the one photon spectrum. The fact that these bands appear strongly in the three photon spectrum, see Fig. 2, and not in the one photon spectrum indicates that the upper states are either Δ or Φ states. A polarization dependence study of these bands shows that both gain intensity and retain their band shapes going from linearly polarized to circularly polarized light, with polarization ratios of $\Omega p\approx2.5$ and 2.2, respectively, which is consistent with the above conclusion.[16–18] Two other bands at higher energy at 64 374 cm^{-1} and 64 285 cm^{-1}, respectively, essentially vanish under the noise level, when changing from linearly to circularly polarized light which suggests these two bands may be associated with a different upper electronic state (see Fig. 4). These two features will be discussed later.

As shown in Fig. 2, the relative intensities and energy separation of the two bands at 64 214 and 63 698 cm^{-1} are rather similar to those observed for the $4p\sigma\,^{1,3}\Pi_u \leftarrow X\,^1\Sigma_g^+$ bands at lower energy. It therefore seems likely that these two bands correspond to transitions from the $X\,^1\Sigma_g^+$ ground state to the singlet and triplet components of another Rydberg state. The 64 214 cm^{-1} band appears stronger in intensity than the electronically allowed $4p\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ transition, which also appears to be the case reported by Li et al.[12] (their Figs. 1 and 3), who give the room temperature 3+1 REMPI spectra in this same region, albeit with a lower resolution. It therefore seems a little surprising that they should assign this band to a three photon forbidden electronic transition $3d\,\Delta_g \leftarrow X\,^1\Sigma_g^+$, which only becomes allowed through vibronic coupling. The 64 214 cm^{-1} band consists of a main

band and weaker bands to the lower energy side in exact analogy to the $4p\sigma\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ bands (see Figs. 2 and 5 and Table I). It therefore seems highly probable that the 64 214 cm^{-1} band corresponds to a 0_0^0 origin band while the weaker bands correspond to the $\Delta\nu=0$ sequence bands, 2_1^1 and 2_2^2. The 1_1^1 sequence band cannot be identified and would be expected to be overlapped by the 0_0^0 origin band and/or the 2_1^1 sequence band. The shape of the origin band, although symmetric with perhaps some slight red degrading, is different to that observed for the $^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ band (see Figs. 2 and 4). For a three photon transition from a $^1\Sigma_g^+$ lower state, transitions to a Π_u or Φ_u upper state will exhibit a strong Q branch. This is the reason why the $^{1,3}\Pi_u \leftarrow X\,^1\Sigma_g^+$ bands appear sharp with a clear maximum at their band centers. However the 64 214 cm^{-1} band (and the 63 698 cm^{-1} band, see Fig. 5) is broader and exhibits a clear dip at its center suggesting a very weak Q branch. This observation can be used to distinguish a Δ upper state from a Φ upper state, since a $\Delta_u \leftarrow X\,^1\Sigma_g^+$ transition will have a very weak, exponentially decreasing Q branch. This indicates that the upper states are Δ_u states and not Φ_u or Π_u vibronic states as suggested by Li et al.[12] These band shape arguments were confirmed by band simulations using standard multiphoton line strength factors and for simplicity assuming Hund's case (a) coupling.[17,23] The known rotational constants of the $X\,^2\Pi_g$ state of CS_2^+ may be used as an approximation of the upper Rydberg states[10,15] while the rotational constants for the ground state are well known.[10,11] Of course, linear CS_2 is centrosymmetric with zero nuclear spin which means only the rotational levels symmetric to the interchange of the sulfur nuclei exist.

The approximately symmetrical nature of the origin band at 64 214 cm^{-1}, the presence of $\Delta\nu=0$ sequence bands and the absence of $\Delta\nu\neq0$ bands indicate that the upper state is linear with a C–S bond length similar to that of the ground state. It seems clear now that the correct assignment of this band is a transition from the $X\,^1\Sigma_g^+$ ground state to the $4p\pi\,^1\Delta_u$ Rydberg state. The band at 63 698 cm^{-1}, which can also be assigned to a Δ_u state since it is broad and also exhibits a central dip in its band shape (see Figs. 2 and 5)
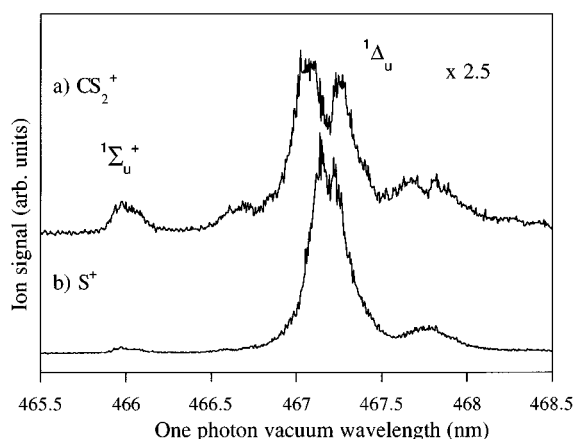
FIG. 6. The 3+1 REMPI spectrum in the 465.5–468.5 nm fundamental wavelength range (a) CS_2^+ signal (b) S^+ signal.

must be the corresponding transition to the $4p\pi\ ^3\Delta_u$ Rydberg state. This is in exact analogy to that found for OCS by Weinkauf and Boesl.[24] In their study they observe the corresponding $4p\sigma\ ^{1,3}\Pi \leftarrow X\ ^1\Sigma^+$ and $4p\pi\ ^{1,3}\Delta \leftarrow X\ ^1\Sigma^+$ transitions in both the 2+1 and 3+1 REMPI spectra (OCS of course does not have u/g symmetry). Let us now consider the quantum defects. If the Rydberg orbitals are dominated by sulfur character, as appears to be the case for many small sulfur containing molecules,[24–30] then we may expect quantum defects analogous to that found for atomic sulfur, which are for the ns, np, and nd Rydberg series approximately 2.0, 1.6, and 0.3, respectively.[31] Using the known ionization potential of CS_2 (Ref. 14) and the electronic term values (T_{00}) given in Table II, one can derive a quantum defect in the range $\delta=1.62–1.58$ for the $4p\sigma\ ^{1,3}\Pi_u$ Rydberg states and $\delta=1.52–1.48$ for the $4p\pi\ ^{1,3}\Delta_u$ states. By comparison, for OCS, the $4p$ Rydberg states (i.e., the D, E, F, G, and P bands corresponding to transitions to the $4p\pi\ ^3\Delta$, $4p\sigma\ ^3\Pi$, $4p\pi\ ^1\Delta$, $4p\sigma\ ^1\Pi$, and $4p\pi\ ^1\Sigma^+$, Rydberg states, respectively[24]) have quantum defects in the range $\delta=1.61–1.49$ while the $4p$ Rydberg states of S_2 have quantum defects in the range $\delta=1.63–1.43$.[28–30] Incidentally, the $3d\ \Delta_g$ Rydberg state of S_2 has an unusually low quantum defect of $\delta=-0.03$.[30]

The ion fragment pattern via the $4p\pi\ ^1\Delta_u \leftarrow X\ ^1\Sigma_g^+$ three photon resonance differs from that via the $4p\sigma\ ^1\Pi_u \leftarrow X\ ^1\Sigma_g^+$ three photon resonance, since there is a very large fragmentation "resonance" through the 0_0^0 origin band. The overall band shape is similar but narrower in the CS^+ and S^+ channels compared to the band shape obtained in the CS_2^+ channel (see Figs. 1 and 6). This suggests that the fragmentation is occurring after CS_2^+ has been formed. The fundamental photon energy at the band center of this three photon resonance is 21 405 cm^{-1}. This is, to within the estimated error, in perfect resonance with a known transition in CS_2^+. Balfour,[15] from a partial rotational analysis of the $A-X$ emission system of CS_2^+, gives the band origin of the intense $2_0^2\ A\ ^2\Pi_{1/2} \leftarrow X\ ^2\Pi_{1/2}$ band as 21 406 cm^{-1}. There are a few inferences that can now be made. The minimum number of photons required to generate S^+ and CS^+ from the CS_2^+

ground state is two and three respectively,[21] which explains why S^+ is more intense than CS^+. Hence, the $A-X$ accidental resonance provides a one photon resonance enhancement for an overall two to three photon fragmentation of CS_2^+. The fact that the band appears narrower in the CS^+ and S^+ channels compared to the CS_2^+ channel, suggests that this accidental resonance is only effective for low J transitions. The three photon resonant $^1\Delta_u$ Rydberg state must have a cationic core corresponding predominantly to the ground vibrational level of the $X\ ^2\Pi_{1/2}$ state. This is consistent with the present assignment. In the case (c) limit, the np "$^1\Delta_u$" Rydberg states will converge to the $X\ ^2\Pi_{1/2}$ spin–orbit level of CS_2^+ while the np "$^3\Delta_u$" states will converge to the corresponding lower energy $X\ ^2\Pi_{3/2}$ level.[22] In the intermediate case (a–c) coupling regime, which should be the case here, the cationic core will correspond to an unequal mixture of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components and for the $^1\Delta_u$ state the $^2\Pi_{1/2}$ component will be predominant. We note that the singlet–triplet splitting of 516 cm^{-1} for the $4p\pi\ ^{1,3}\Delta_u$ states (see Table I) is anomalously small when compared to the splittings of 685 and 659 cm^{-1} observed, respectively, for the $4p\sigma\ ^{1,3}\Pi_u$ and $4s\sigma\ ^{1,3}\Pi_g$ (Ref. 13) Rydberg states. This indicates that the $^{1,3}\Delta_u$ states have greater case (c) character since in the limit of case (c) behavior the splitting would approach the splitting in the cationic core which is 440 cm^{-1}.[14]

We now consider the 63 698 cm^{-1} band which corresponds to the $4p\pi\ ^3\Delta_u \leftarrow X\ ^1\Sigma_g^+$ transition. As mentioned above, the polarization behavior, the band shape, the fact that both the $4p\sigma\ ^3\Pi_u$ and $4s\sigma\ ^3\Pi_g$ (Ref. 13) bands are observed to the low energy side of the corresponding singlet states and comparisons with OCS,[24] all point to this assignment. The sequence bands to the low energy side of the origin band have spacings somewhat consistent (although different) with that observed for the other Rydberg transitions and are tentatively assigned accordingly (see Fig. 5 and Tables I and II). Again, the most intense vibrational features are the $\Delta\nu=0$ sequence bands and we have not identified any of the possible $\Delta\nu\neq0$ bands. However, this triplet band system shows several anomalies. In particular, if the 2_1^1 sequence band assignment is correct for the second band component, there appears to be an anomalous intensity enhancement (see Figs. 2 and 5). It is possible that the vibrational levels of the $^3\Delta_u$ Rydberg state are perturbed by the vibrational levels of the $^1\Pi_u$ Rydberg state, which lies about 930 cm^{-1} to lower energy. This could result in extra singlet character in some of the vibrational levels of the $^3\Delta_u$ state, giving rise to the anomalous intensity distribution. In fact the term value (with respect to the CS_2 ground vibronic state) for the $^3\Delta_u$ (0,1,0) level occurs at 64 037 cm^{-1} while the $^1\Pi_u$ (2,0,0) level is expected at $\approx$64 040 cm^{-1}. However, the vibronic symmetries for these two particular levels do not seem appropriate for a strong interaction (Φ_g/Π_g and Π_u, respectively, and A_2+B_2 and A_1+B_1, respectively, in C_{2v} symmetry). The origin band, i.e., the first band component, appears to be somewhat blue-degraded. In addition, although the signals in the S^+ and CS^+ channels are very much weaker than that in the CS_2^+ channel, they exhibit a different band structure at low laser energy densities. These ion fragment effects are currently being investigated.

Finally we consider the relatively weak band at 64 374 cm^{-1}, which lies on the high energy side of the $^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ band (see Figs. 2, 4, and 5). The intensity of this band is reduced when changing from linearly to circularly polarized light with $\Omega p \leqslant 0.15$, indicating that the upper state is either a Σ_u^+ or Π_u state, assuming a Σ_g^+ lower state. However, the band shape is suggestive of a Σ_u^+ rather than a Π_u upper state as it does not have a sharp central maximum. Rather there are indications of a weak dip at the band center which is indicative of a missing Q branch. This band is accompanied by another yet weaker band ≈ 90 cm^{-1} to lower energy at 64 284 cm^{-1}, which has a similar polarization behavior to it, but which is partially overlapped by the $^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ band. This is rather analogous to the other band systems in this region suggesting an assignment of the 64 374 cm^{-1} band to the 0_0^0 band of a $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ electronic transition, accompanied by its 2_1^1 sequence band at 64 284 cm^{-1}. In fact the upper state most likely corresponds to the $4p\pi\,^1\Sigma_u^+$ Rydberg state. Again the band shape appears symmetric, indicative of a linear upper Rydberg state. The corresponding $4p\pi\,^3\Sigma_u^-$ Rydberg state will be expected to be lower in energy than the $4p\pi\,^1\Sigma_u^+$ and $4p\pi\,^1\Delta_u$ states,[32] and may be overlapped with the $^3\Delta_u$ state. Now the $4p\pi\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ origin band occurs at the one photon energy 21 458 cm^{-1}, which is about 50 cm^{-1} above the 2_0^2 band of the $A\,^2\Pi_{1/2} \leftarrow X\,^2\Pi_{1/2}$ transition in CS$_2^+$ and about 16 cm^{-1} below the 1_0^1 band.[15] Hence, there is no corresponding accidental resonance in the cation as there is for the $^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ resonance enhanced ion signal and consequently the S$^+$ and CS$^+$ signals are relatively weak.

We note that these bands should be seen, in the absence of the Δ_u states, in the one photon absorption spectrum. Indeed Price and Simpson[1] do observe such an absorption feature—their 1553 Å band—see the last column of Table I. However there seems to be a discrepancy of about 35 cm^{-1} between Price and Simpson's measured band position and ours. They observe two features of equal intensity at 64 398 and 64 416 cm^{-1}, respectively. It is possible that these two features correspond to the maxima of the P and R branches of the $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition. Assuming that the upper state has a geometry identical to that of the ground state cation and a room temperature Boltzmann population in the ground state, the one photon P and R branch maxima are expected to be separated by 13–14 cm^{-1}, which compares reasonably well to the 18 cm^{-1} separation given by Price and Simpson, considering that they suggest relative errors of the order of 2–3 cm^{-1}. The 1553 Å band can also be observed in Greening and King's[3] absorption spectrum (their Fig. 4). Gedanken suggests that the upper state is nondegenerate from an analysis of the MCD spectrum[9] which is consistent with the $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ band assignment.

The assignment of the upper state to the $4p\pi\,^1\Sigma_u^+$ state is also consistent with that observed for OCS, where the $4p\pi\,^1\Sigma^+$, $^1\Delta$, and $^3\Delta$ states have been identified.[24] In addition the expected energy ordering for a simple $\pi^3\,4p\pi$ configuration is, in decreasing energy, $^1\Sigma^+$, $^1\Delta$, $^1\Sigma^-$, $^3\Sigma^-$, $^3\Delta$, and $^3\Sigma^+$, which is consistent with the present assignment of the $^1\Sigma_u^+$, $^1\Delta_u$, and $^3\Delta_u$ states.[32] The same energy ordering is also found for OCS.[24] It is not clear however, why the $4p\pi\,^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition is so much weaker than the $4p\sigma\,^1\Pi_u$, $4p\pi\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ transitions. It may be that the $^1\Sigma_u^+$ state is relatively more dissociative. However, because of this the assignment is somewhat tentative.

IV. CONCLUSION

We have reinvestigated the 60 000–65 000 cm^{-1} energy region of jet cooled CS$_2$ by 3+1 time-of-flight REMPI spectroscopy. From the relative band intensities, band shapes, polarization behavior, and various comparisons with related molecules we reassign two one photon forbidden transitions at 64 214 cm^{-1} and 63 698 cm^{-1} to the vibrational origin bands of the $4p\pi\,^{1,3}\Delta_u \leftarrow X\,^1\Sigma_g^+$ transitions. We also observe another feature which we somewhat tentatively assign to the $4p\pi\,^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition, which corresponds to Price and Simpson's 1553 Å band in the one photon absorption spectrum. In addition we can firmly rule out Price and Simpson's 1612 Å band as the 1_1^0 hot band of the $^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition which confirms its assignment to the $4p\pi\,^3\Pi_u \leftarrow X\,^1\Sigma_g^+$ transition. It is suggested that previous claims of a temperature dependence to this band may be explained by saturation effects. Hence, this energy region of CS$_2$ can be described simply as transitions to the $4p\sigma,\pi$ Rydberg states, which have linear geometries and C–S bond lengths similar to the ground states of CS$_2$ and CS$_2^+$. The observation of the $^3\Delta_u$ and $^3\Pi_u$ states can be explained by spin–orbit interaction with the corresponding singlet states giving rise to some case (c) behavior. However we do note that the $^3\Delta_u \leftarrow {}^1\Sigma_g^+$ transition presents several anomalies which may partly be associated with interactions between the $^3\Delta_u$ state and the vibrational levels of the lower $^1\Pi_u$ state. We are currently analyzing the $(1+1')+1$ two color REMPI spectrum in this same energy region, and preliminary results confirm our assignments of the $^{1,3}\Delta_u$ Rydberg states.

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