

## **A (1+1')<sup>+</sup> multiphoton ionization study of CS<sub>2</sub> in the 68500–73000 cm<sup>-1</sup> energy region. The 3d and 5s Rydberg states**

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# A $(1+1')$ +1 multiphoton ionization study of CS<sub>2</sub> in the 68 500–73 000 cm<sup>-1</sup> energy region. The 3*d* and 5*s* Rydberg states

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The two color  $(1+1')$ +1 resonance enhanced multiphoton ionization spectrum of CS<sub>2</sub> has been recorded in the 68 500–73 000 cm<sup>-1</sup> excitation energy range. Strong bands were recorded in the 68 800–70 000 cm<sup>-1</sup> region and the upper states assigned to 3*d* and 5*s* gerade Rydberg states with quantum defects of 0.0 and 2.0, respectively. The two color spectra were recorded in both parallel and crossed polarization configurations to assist in state symmetry assignments. Some weaker features in the 70 500–71 500 cm<sup>-1</sup> region are most likely associated with vibronically induced transitions to a 5*p* Rydberg state. © 1996 American Institute of Physics. [S0021-9606(96)02325-2]

## I. INTRODUCTION

The two and three photon resonance enhanced multiphoton ionization (REMPI) spectra of CS<sub>2</sub> in the 62 000–65 000 cm<sup>-1</sup> energy range were first reported by Li *et al.*<sup>1,2</sup> They observed fairly strong one photon forbidden bands in both spectra and assigned the upper states to 3*d* Rydberg states. However, later higher resolution studies showed that these new states could be reassigned to the 4*p* Δ<sub>u</sub> Rydberg states.<sup>3,4</sup> The actual location of the 3*d* Rydberg states of CS<sub>2</sub> has been the subject of much debate but no unambiguous assignment has yet been made.

The Rydberg states of CS<sub>2</sub> have primarily been investigated by vacuum ultraviolet (vuv) photoabsorption<sup>5–10</sup> and by electron impact energy loss spectroscopy.<sup>11–13</sup> Suggested assignments to 3*d* Rydberg states have previously been made in the 62 000 to 70 000 cm<sup>-1</sup> range. However, a transition from the  $\tilde{X}^1\Sigma_g^+$  ground state to a Rydberg state of gerade symmetry (i.e., a (...2π<sub>g</sub><sup>3</sup>) *ns* or (...2π<sub>g</sub><sup>3</sup>) *nd* Rydberg state) is electronically forbidden in the electric dipole approximation and hence one photon vuv absorption from the ground state is not a good technique for the study of gerade Rydberg states. Electron impact energy loss spectroscopy has the advantage of being able to detect both spin forbidden and symmetry forbidden transitions but suffers from low resolution and ambiguities in the interpretation. Although there have recently been a number of high level *ab initio* studies on the low-lying (...2π<sub>g</sub><sup>3</sup> 3π<sub>u</sub><sup>1</sup>) valence states of CS<sub>2</sub><sup>14,15</sup> there has been scant theoretical work on Rydberg states other than the *ns* and *np* model potential calculations of Greening and King.<sup>8</sup> Hence, there is currently no reliable theoretical guide as to the assignment of gerade Rydberg states on the basis of energy position alone.

However, transitions from the ground state to gerade Rydberg states are two photon allowed and so should appear strongly in the two photon resonant spectrum. In previous  $(1+1')$ +1 REMPI work of CS<sub>2</sub> we found no evidence for 3*d*

or 5*s* gerade Rydberg states below 68 500 cm<sup>-1</sup>.<sup>3,16</sup> In the present study we extend this work to higher energy with the primary goal of locating the 3*d* and 5*s* Rydberg states. These Rydberg states are expected to have a geometry similar to that of the  $\tilde{X}^1\Sigma_g^+$  ground state since they are formed by the excitation of an electron from the nonbonding 2π<sub>g</sub> orbital to a nonbonding Rydberg orbital. Consequently, allowed transitions will be of linear–linear type and Franck–Condon considerations will lead to strong 0<sub>0</sub><sup>0</sup> origin bands and Δ*v*=0 sequence bands (depending on the vibrational population of the ground state) while Δ*v*≠0 bands will be very weak or absent. Hence, allowed Rydberg transitions should in theory be easy to identify.

## II. EXPERIMENT

A XeCl excimer laser was used to simultaneously pump two dye lasers. The first laser (beam 1) was frequency doubled to give ultraviolet radiation in the 217–230 nm range, while the second laser (beam 2) was tuned through the 370–440 nm range with the use of appropriate dyes. The two beams were made coaxial and counterpropagating and brought to the same focus inside a vacuum chamber by means of two quartz lenses with focal lengths of 35 and 15 cm for beams 1 and 2, respectively. The pulse energy of beam 1 was varied in the 10–100 μJ range while the pulse energy of beam 2 was varied in the 0.5–5 mJ range depending on the REMPI signal strength.

Carbon disulfide mixed with helium buffer gas was expanded into the vacuum chamber through a pulsed valve perpendicular to the laser beams. The photoions generated in the REMPI process were detected in a home built time-of-flight mass spectrometer.<sup>17</sup> Previous studies show that in this jet source the CS<sub>2</sub> molecule is rotationally cooled to about 70 K while the vibrational temperature remains at essentially room temperature.<sup>3,4</sup>

For any given scan the wavelength of beam 1 was fixed while that of beam 2 was tuned giving a  $(1+1')$  energy range of 68 500–73 000 cm<sup>-1</sup>. The  $(1+1')$  resonant features were easily identified since their positions were unchanged on the

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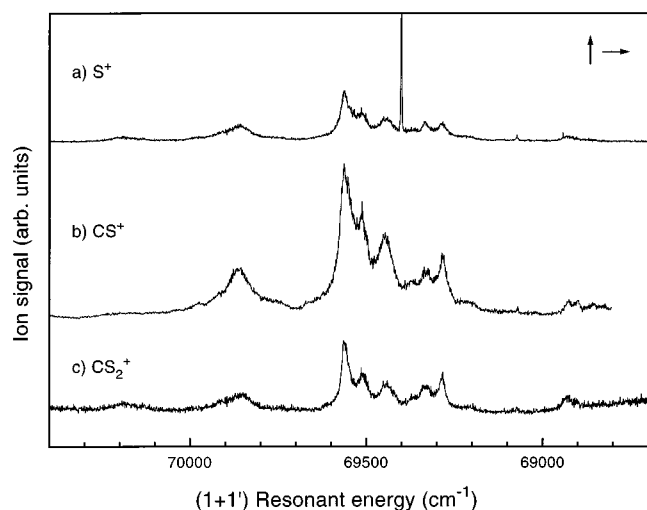


FIG. 1. The  $(1+1')$ +1 REMPI spectra of CS<sub>2</sub> recorded in the (a) S<sup>+</sup> (b) CS<sup>+</sup> and (c) CS<sub>2</sub><sup>+</sup> channels, with crossed polarized light. Spectra are normalized to the energy of beam 2.

$(1+1')$  transition energy scale as the fixed wavelength of beam 1 was varied. The fundamental outputs of both dye lasers were calibrated separately by recording optogalvanic spectra from a Fe–Ne hollow cathode lamp. Internal calibration of the spectra was also used, since some known S(<sup>1</sup>D<sub>2</sub>) atomic lines were identified during the study.<sup>18,19</sup> When recording the CS<sub>2</sub> spectra it was necessary to monitor the signals in three mass channels; CS<sub>2</sub><sup>+</sup>, CS<sup>+</sup>, and S<sup>+</sup> since all gave appreciable signals. Over the 68 500–72 000 cm<sup>−1</sup> region the CS<sup>+</sup> signal was generally more intense than the CS<sub>2</sub><sup>+</sup> and S<sup>+</sup> signals—see Fig. 1. However, all gave similar spectra indicating that the spectra were due to CS<sub>2</sub> resonances, although that recorded in the CS<sub>2</sub><sup>+</sup> channel was generally sharper and better resolved.

Under normal operating conditions beams 1 and 2 had crossed polarizations. Spectra were recorded in both parallel and crossed polarization configurations by using a Soleil Babinet compensator to rotate the polarization of beam 2 through 90°. As described in the next section, the transition probability of a  $(1+1')$  resonance depends on the relative orientation of the polarizations of the two beams. Here, it is convenient to define the polarization ratio  $\Omega$  as being the ratio of the signal intensity recorded with parallel polarized light compared to that recorded with crossed polarized light under otherwise identical conditions, i.e.,

$$\Omega = I_{\text{sig}}(\text{parallel})/I_{\text{sig}}(\text{crossed}). \quad (1)$$

To compare the spectral intensities under parallel and crossed polarization configurations it was necessary to record the spectra in all three channels, CS<sub>2</sub><sup>+</sup>, CS<sup>+</sup>, and S<sup>+</sup>. However, with our boxcar data acquisition system, only two channels could be recorded simultaneously.<sup>3,4</sup> Hence, in addition, the mass spectrum was recorded at the band maxima/centers of each  $(1+1')$  resonant feature and averaged over  $\approx 500$  laser shots by a fast digital oscilloscope (LeCroy 9414, 150 MHz), for both parallel and crossed polarization configurations. Here, the CS<sub>2</sub><sup>+</sup>, CS<sup>+</sup>, and S<sup>+</sup> ion signals could be

TABLE I. Possible transition operators in a  $(1+1')$  resonance from a  $^1\Sigma_g^+$  ground state for coaxially aligned beams.

Rotational branch	<i>O</i>	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
Upper state					
$^1\Sigma_g^+$	$T^2$	$T^2, T^1$	$T^2, T^1, T^0$	$T^2, T^1$	$T^2$
$^1\Pi_g$	$T^2$	$T^2, T^1$	$T^2, T^1$	$T^2, T^1$	$T^2$
$^1\Delta_g$	$T^2$	$T^2$	$T^2$	$T^2$	$T^2$

recorded simultaneously and the polarization ratio determined as a weighted average of the three ion signals, after subtraction of the background (nonresonant) ion signal due to beam 1 alone.

### III. THEORY

Here, we consider the expected dependence of the  $(1+1')$  transition probability on the relative polarization of the coaxial and counterpropagating beams. In particular, we consider the effect on the signal intensity of having the two beams with either parallel or crossed polarization. Details of the theory of two photon transition probabilities and their polarization dependence may be found in Ref. 20. Only the results of that part of the theory dealing with the current case will be considered. According to Ref. 20, the total two photon transition probability may be written as the sum of three parts

$$W_{J_i K_i \rightarrow J_f K_f}^{(2)} = \sum_{k=0}^2 C_k M_k R_k, \quad (2)$$

where  $J$  and  $K$  are the quantum numbers of the total angular momentum and its molecule fixed projection, and  $i$  and  $f$  label the initial and final states.  $C_k$  is a geometric factor determining the polarization behavior of the transition,  $M_k$  is a molecular factor determining the vibronic selection rules, and  $R_k$  is a rotational factor determining the rotational selection rules. The molecular factor  $M_k$ , contains matrix elements of the polarizability operator of rank  $k$  which in spherical tensor notation is written as  $T^k(A)$ .

A transition carried by the  $T^k(A)$  polarizability operator, which gives rise to the  $k$  term of the right-hand side of Eq. (2), has the following selection rules:

$$k \geq |\Delta K| \quad \text{and} \quad k \geq |\Delta J|, \quad (3)$$

where  $\Delta K = K_f - K_i$  and  $\Delta J = J_f - J_i$ . Table I gives the allowed polarizability operators for each rotational branch of  $^1\Delta$ ,  $^1\Pi$ ,  $^1\Sigma \leftarrow ^1\Sigma$  type transitions. A transition carried solely by  $T^0(A)$ ,  $T^1(A)$ , or  $T^2(A)$  has an expected polarization ratio of  $\Omega = \infty$ , 0 or 4/3, respectively.<sup>20</sup> For a transition carried by more than one operator, the polarization dependence will lie somewhere between the upper and lower polarization ratio limits and will depend on the degree of importance each operator has to the overall transition. Table II gives the possible polarization ratios for each rotational branch of  $^1\Delta$ ,  $^1\Pi$ ,  $^1\Sigma \leftarrow ^1\Sigma$  type transitions.

TABLE II. Expected polarization ratio for a (1+1') resonance from a  $^1\Sigma_g^+$  state for coaxially aligned beams.

Rotational branch	O	P	Q	R	S
Upper state					
$^1\Sigma_g^+$	1.33	0–1.33	0–∞	0–1.33	1.33
$^1\Pi_g$	1.33	0–1.33	0–1.33	0–1.33	1.33
$^1\Delta_g$	1.33	1.33	1.33	1.33	1.33

#### IV. RESULTS AND DISCUSSION

In the energy region covered in this study some very strong two photon transitions were observed which suggests that gerade Rydberg states have been excited. In fact, the strong bands appeared only in the narrow energy range of 68 800 to 70 000 cm<sup>-1</sup>. No other transitions were observed which had a strength or character suggestive of a gerade Rydberg state although we scanned up to ≈73 000 cm<sup>-1</sup>. On this basis we assign the upper states of these transitions to gerade Rydberg states. Figure 1 shows the spectra recorded in the 68 700–70 400 cm<sup>-1</sup> energy region where the strong transitions were observed. These spectra were recorded under similar conditions and give the relative yield of the ions detected. The strong sulfur line at 69 401.3 cm<sup>-1</sup> corresponds to the S( $^1D_2$ )→S( $^1F_3$ ) two photon transition.<sup>18,19</sup> Figure 2 shows typical spectra recorded in the 68 500–70 500 cm<sup>-1</sup> region under crossed and parallel polarizations in the CS<sub>2</sub><sup>+</sup> channel. As can be seen in the figure many of the bands exhibit different polarization dependencies which suggests that there are many different electronic states embedded in this region. Table III gives the measured transition energies of the bands observed in this study. The bands have been labeled alphabetically for convenience.

Before we discuss the results in more detail it is first necessary to consider what gerade Rydberg states are expected in this energy region. A consideration of quantum defects and the fact that no gerade Rydberg states have been observed immediately above or below this energy region implies that the states are 3d and 5s Rydberg states converging to the ground state of the cation.<sup>3,17</sup> There are twelve 3d Rydberg states originating from a (...2π<sub>g</sub><sup>3</sup>)3d<sub>g</sub> electronic configuration and these are; (...2π<sub>g</sub><sup>3</sup>)3dσ<sup>1,3</sup>Π<sub>g</sub>, (...2π<sub>g</sub><sup>3</sup>)3dπ<sup>1,3</sup>Δ<sub>g</sub>, <sup>1,3</sup>Σ<sub>g</sub><sup>+</sup>, <sup>1,3</sup>Σ<sub>g</sub><sup>-</sup>, and (...2π<sub>g</sub><sup>3</sup>)3dδ<sup>1,3</sup>Φ<sub>g</sub>, and <sup>1,3</sup>Π<sub>g</sub>. Hence, four strong two photon transitions from the X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state may be expected with upper states; 3dσ<sup>1</sup>Π<sub>g</sub>, 3dπ<sup>1</sup>Δ<sub>g</sub>, <sup>1</sup>Σ<sub>g</sub><sup>+</sup>, and 3dδ<sup>1</sup>Π<sub>g</sub>. There are also two 5s Rydberg states, (...2π<sub>g</sub><sup>3</sup>)5s, <sup>1,3</sup>Π<sub>g</sub>, of which the <sup>1</sup>Π<sub>g</sub>←X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> transition should appear strongly in the two photon resonant spectrum. Hence, in this energy region we might expect to observe strong transitions to five Rydberg states; one <sup>1</sup>Σ<sub>g</sub><sup>+</sup> state, three <sup>1</sup>Π<sub>g</sub> states, and one <sup>1</sup>Δ<sub>g</sub> state.

As mentioned in Sec. I, and by comparison with the known spectra of the 4s and 4p Rydberg states, the spectrum should be characterized by strong 0<sub>0</sub><sup>0</sup> origin bands, with weaker 2<sub>1</sub><sup>1</sup> hot bands displaced by ≈60 cm<sup>-1</sup> to lower energy.<sup>3,9,17</sup> For a room temperature vibrational population the 2<sub>1</sub><sup>1</sup> bands will be expected to have approximately 30% of

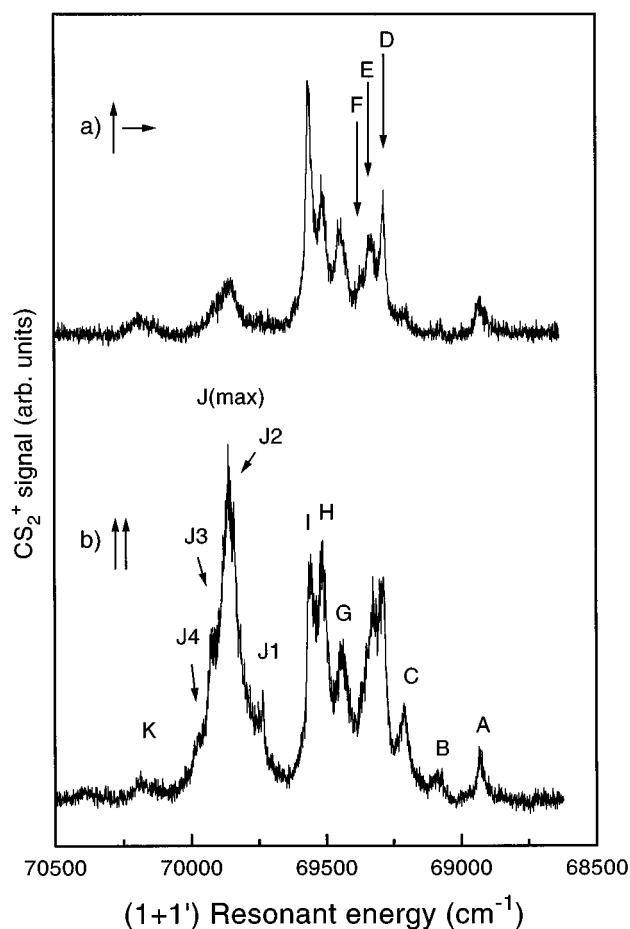


FIG. 2. The (1+1') + 1 REMPI spectra of CS<sub>2</sub> recorded with (a) crossed and (b) parallel polarized light. Spectra are normalized to the energy of beam 2. The fixed frequency of beam 1 was 43 571 cm<sup>-1</sup>.

the intensity of the 0<sub>0</sub><sup>0</sup> origin bands (see Table III of Ref. 3). In addition, since the coupling is not perfectly Hund's case (a) but has some degree of Hund's case (c) character, weaker triplet bands should appear to lower energy separated from the singlet bands by ≈450–600 cm<sup>-1</sup>, which is of the order of the spin–orbit splitting of the ground state cation.<sup>13,21</sup> Hence, *a priori*, we might expect to observe in the two photon spectrum five strong 0<sub>0</sub><sup>0</sup> origin bands with weaker 2<sub>1</sub><sup>1</sup> hot bands and 0<sub>0</sub><sup>0</sup> triplet bands displaced by ≈60 cm<sup>-1</sup> and ≈450–600 cm<sup>-1</sup> to lower transition energy, respectively.

For the (1+1') + 1 REMPI bands of CS<sub>2</sub> observed in this study we unfortunately do not have rotational resolution and the band shapes cannot be unambiguously modeled. Part of the problem is probably due to lifetime broadening as a result of predissociation. However, because the Rydberg upper state is expected to have a very similar geometry to the ground state the bands should not be degraded and so the band centre should correspond to the Q branch. In general the P and R branches should form weaker maxima to either side of the band centre while the S and O branches would be expected to form weak maxima in the wings of the band. From the known behavior of the rotational factors,  $R_k$ , in Eq.

TABLE III. Measured (1+1') REMPI band positions and polarization ratios.

Band <sup>a</sup>	Transition Energy (cm <sup>-1</sup> )	Ω	Suggested assignment	Ref. 12 <sup>b</sup> (cm <sup>-1</sup> )
A	68 930 69 073	1.30	<sup>3</sup> Π <sub>g</sub> / <sup>3</sup> Δ <sub>g</sub> (0 <sub>0</sub> <sup>0</sup> )	68 900
B	69 096	1.6		
C	69 212	2.4	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup> (2 <sub>1</sub> <sup>1</sup> )	
D	69 285	1.8?	<sup>1</sup> Π <sub>g</sub> / <sup>1</sup> Δ <sub>g</sub> (0 <sub>0</sub> <sup>0</sup> )	
E	69 330	2	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup> (0 <sub>0</sub> <sup>0</sup> )	69 300
F	69 369			
(sh)	69 426			
G	69 446	1.3	<sup>1</sup> Π <sub>g</sub> / <sup>1</sup> Δ <sub>g</sub>	
H	69 512	≈1.3	<sup>1</sup> Π <sub>g</sub> / <sup>1</sup> Δ <sub>g</sub> (0 <sub>0</sub> <sup>0</sup> )	69 520
I	69 563	0.9	<sup>1</sup> Π <sub>g</sub> (0 <sub>0</sub> <sup>0</sup> )	
J1 (bh)	69 735			
J2	69 841			
J (max)	69 861	4.8	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (0 <sub>0</sub> <sup>0</sup> )	69 912
J3	69 918			
(bh)	69 928			
J4	69 978			
	70 123			
K	70 193	≈1		
L	70 532	≈2	5p (2 <sub>1</sub> <sup>1</sup> )	
	71 007			
M	71 033			
N	71 294		5p (2 <sub>1</sub> <sup>0</sup> )	
O	71 556	≈1.3		

<sup>a</sup>Symbols used, sh=shoulder, bh=band head.<sup>b</sup>From the electron impact study of Hubin-Franskin *et al.*<sup>12</sup>

(2), the  $^1\Delta_g \leftarrow ^1\Sigma_g^+$  transition should exhibit a strong  $Q$  branch. Whether or not the  $^1\Sigma_g^+$ ,  $^1\Pi_g \leftarrow ^1\Sigma_g^+$  transitions exhibit a strong  $Q$  branch depends on the particular rank  $k$  contribution to the overall transition.<sup>20</sup> In any case, as is shown in Table II, monitoring the polarization ratio at the band center should provide useful information in determining the symmetry of the upper state. The measured polarization ratios of the bands observed in this study are given in the third column of Table III.

As is shown in Fig. 2, band  $J$  shows the largest intensity change when going from crossed to parallel polarization, with a measured polarization ratio of 4.8. From Table II, only the  $Q$  branch of a  $^1\Sigma_g^+ \leftarrow ^1\Sigma_g^+$  type transition is expected to have a polarization ratio greater than 1.33. Consequently, band  $J$  is assigned to the  $3d$   $^1\Sigma_g^+$  Rydberg state. The surprising feature about this band is that it is quite broad and seems to have overlapping structure and yet the polarization study suggests that it is predominantly of  $Q$  branch structure, i.e., we would have expected this band to be narrower. Since we only expect one Rydberg state of  $^1\Sigma_g^+$  symmetry the other (1+1') REMPI bands must be assignable to  $^1\Pi_g$ ,  $^1\Delta_g$ , and triplet Rydberg states.

Apart from band A, the other bands to lower energy are at least partially overlapped so that the measured polarization ratios are not particularly accurate. Band I is the only feature showing a definite decrease in intensity when changing from crossed to parallel polarization with a polarization ratio of 0.9. From Table II this suggests that it cannot be a  $^1\Delta_g$  state and so band I is assigned to a  $^1\Pi_g$  Rydberg state, either  $3d$  or

$5s$ . Band  $E$ , which overlaps band  $D$  is broad with a polarization ratio of  $\approx 2$ . Its polarization ratio does not appear to be consistent with a  $^1\Pi_g$  or  $^1\Delta_g$  assignment. It is likely that it corresponds to the  $^3\Sigma_g^-$  state, which would give a  $^1\Sigma_g^+ - ^3\Sigma_g^-$  separation of around  $530$  cm<sup>-1</sup>. Band  $C$  is most likely related to band  $E$  and is probably the corresponding  $2_1^1$  band. The fourth column of Table III gives our suggested assignments on the basis of the measured polarization ratios and the relative band intensities. We note that some of our suggested origin bands may be overlapped by  $2_1^1$  hot bands, which would effect the measured polarization dependence.

Although, there is uncertainty in the particular assignments of many of the bands, the assignment of bands I and J to  $^1\Pi_g$  and  $^1\Sigma_g^+$  Rydberg states seem most certain, while of the remaining bands at least two and possibly three appear to be singlet origin bands, suggestive that most and possibly all the two photon allowed singlet gerade Rydberg states are of sufficient intensity and lifetime to be observed.

In the electron impact spectra<sup>12,13</sup> there appear to be electric dipole forbidden bands corresponding to our bands A, “D/E,” “H/I,” and J. This can be seen by comparing the (1+1') REMPI band positions given in the second column of Table III with the electron impact band positions reported by Hubin-Franskin *et al.*<sup>12</sup> given in the fifth column. Of the previously suggested assignments of  $3d$  and  $5s$  Rydberg gerade states only those given by Hubin-Franskin *et al.*<sup>12</sup> (excluding their  $R_4$  “nd” series) are more or less in reasonable agreement with the results obtained in this study. That is the  $3d$  and  $5s$  Rydberg states of CS<sub>2</sub> appear to be confined to a relatively narrow energy region between  $68\,800$ – $70\,000$  cm<sup>-1</sup> and that the  $5s$  states overlap the  $3d$  states. Hence, it seems that the  $3d$  and  $5s$  Rydberg states of CS<sub>2</sub> form a “supercomplex”.<sup>22</sup>

Greening and King<sup>8</sup> using a model potential calculate the position for the  $5s$  Rydberg state at  $8.84$  eV, i.e.,  $71\,300$  cm<sup>-1</sup>. On the basis of our work we would place the singlet  $5s$  Rydberg state in the  $69\,300$ – $69\,600$  cm<sup>-1</sup> region. This yields a quantum defect ( $\delta$ ) in the range,  $1.99$ – $2.03$ , i.e.,  $\delta=2.0$ . This quantum defect is close to the value of  $\delta=1.9$  obtained for the  $4s$  Rydberg state of CS<sub>2</sub>.<sup>17</sup> Similarly, from this work we place the singlet  $3d$  Rydberg states in the  $69\,300$ – $70\,000$  cm<sup>-1</sup> energy region which yields a quantum defect in the range  $-0.03$  to  $0.06$ , i.e.,  $\delta\approx 0.0$ . This is similar to the quantum defect of the  $3d$   $\Delta_g$  Rydberg state of S<sub>2</sub> which has a value of  $\delta=-0.03$ .<sup>23</sup>

Above  $70\,000$  cm<sup>-1</sup>, only much weaker bands were observed. Figure 3 shows the spectrum recorded over the  $69\,500$ – $72\,000$  cm<sup>-1</sup> region, while Fig. 4 shows spectra recorded in the  $70\,400$ – $72\,800$  cm<sup>-1</sup> region under greater sensitivity. The bands labeled from L to O seem too weak to be attributable to singlet Rydberg states of gerade symmetry. Now, in one photon absorption<sup>6–8</sup> and electron impact<sup>11–13</sup> there is a very strong transition at  $70\,925$  cm<sup>-1</sup>, which is the strongest feature of the  $1420$  Å group of Tanaka *et al.*<sup>6</sup> The assignment of this one photon band is uncertain although it is thought to be a  $0_0^0$  origin band of a singlet  $np$  Rydberg state.<sup>7,8,12,13</sup> Greening and King<sup>8</sup> suggest an assignment to the  $5p$   $^1\Sigma_u^+$  Rydberg state, which implies a quantum defect

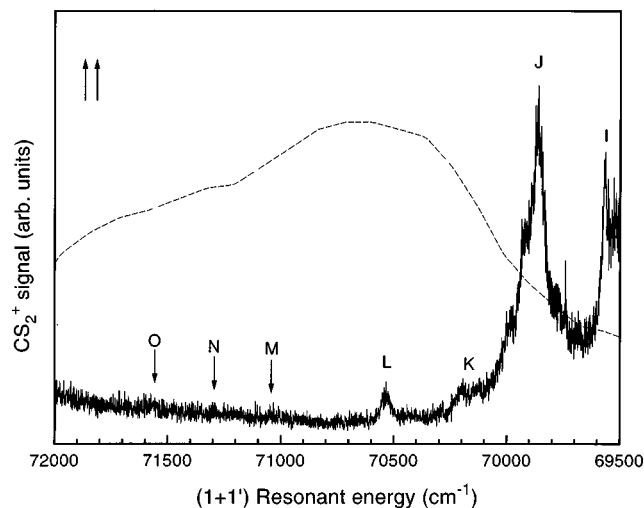


FIG. 3. The  $(1+1')$  REMPI spectrum of CS<sub>2</sub> recorded with parallel polarized light over the 69 500–72 000 cm<sup>-1</sup> transition energy region. The dashed curve gives the laser energy variation of beam 2. The spectrum has been normalized to the energy of beam 2. The fixed frequency of beam 1 was 44 793 cm<sup>-1</sup>.

of 1.81, although their calculated position is 9.00 eV (72 600 cm<sup>-1</sup>). The value of the quantum defect should be compared to the quantum defects of the  $4p\ ^1\Pi$  and  $^1\Delta$  Rydberg states which are 1.59 and 1.49, respectively.<sup>3</sup> Hence, if this assignment is correct the  $5p$  Rydberg state is depressed in energy. Now band *L*, at 70 532 cm<sup>-1</sup>, is  $\approx 393$  cm<sup>-1</sup> lower in energy than the strong one photon 70 925 cm<sup>-1</sup> band. This difference is equal, to within the accuracy of determining the band origins, to the ground state bending frequency,<sup>24</sup>  $\nu_2 = 396$  cm<sup>-1</sup>. Consequently, one very likely assignment of band *L*, is to the  $2_1^0$  hot band of the one photon allowed 70 925 cm<sup>-1</sup>  $5p$  Rydberg state.

The weak  $(1+1')$  REMPI feature at 71 294 cm<sup>-1</sup> (see Table III and Fig. 4) which is labeled as band *N*, may then be assigned to the corresponding  $2_1^1$  band. This would imply an upper state  $\nu_2$  bending frequency of  $\approx 370$  cm<sup>-1</sup> which is similar to the cationic ground state value of  $\approx 330$  cm<sup>-1</sup>.<sup>21</sup> Although, the  $5p$  Rydberg states are electronically forbidden in the two photon excitation spectrum, the  $2_1^0$  and  $2_1^1$  bands may gain intensity through vibronic couplings. A similar situation is found for the  $4p\ \Delta_u$  Rydberg states and more weakly for the  $4p\ ^1\Pi_u$  state.<sup>4</sup> The polarization ratio of band *L* is suggestive of a  $\Delta\Lambda=0$  type transition which would be consistent with a  $2_1^0$ ,  $\Pi_u \leftarrow \Pi_u$  two photon transition implying a  $5p\ ^1\Pi_u$  upper state assignment. However, band *L* is quite weak compared to the nonresonant background signal and it is possible that there is a large error in the measured polarization ratio.

Another feature in the 70 000–72 000 cm<sup>-1</sup>  $(1+1')$  REMPI region is band *O* at 71 556 cm<sup>-1</sup>, see Fig. 4. This band is fairly sharp and has a measured polarization ratio of  $\approx 1.3$  which is indeterminate for an unambiguous assignment, although it probably implies that  $\Delta\Lambda=1$  or 2. It is very close to the calculated position of the  $5s\ ^1\Pi_g$  Rydberg state of Greening and King<sup>8</sup> at 71 300 cm<sup>-1</sup>. However, this as-

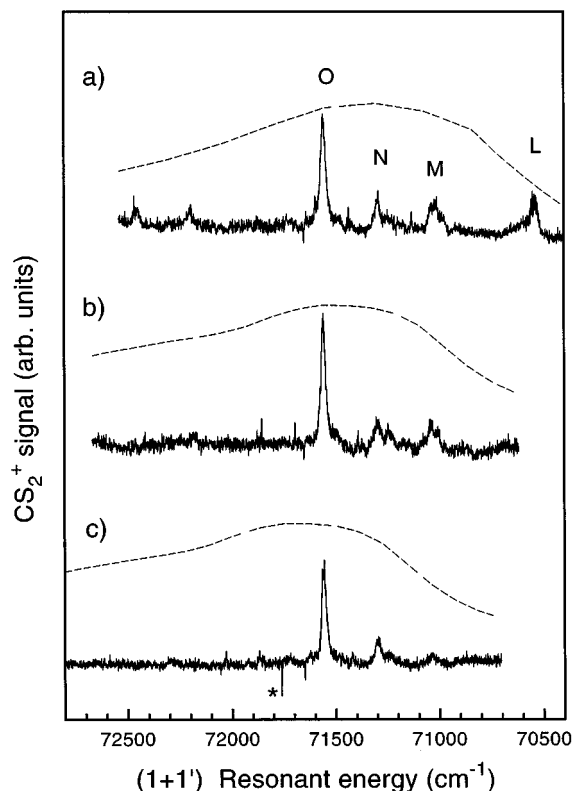


FIG. 4. The  $(1+1')$  REMPI spectra of CS<sub>2</sub> recorded with parallel polarized light over the 70 400–72 800 cm<sup>-1</sup> range and in the CS<sub>2</sub><sup>+</sup> mass channel. The fixed frequency of beam 1 was (a) 45 822, (b) 45 647, and (c) 45 388 cm<sup>-1</sup>. The dashed curves give the laser energy variations of beam 2. The spectra are uncorrected for laser energy variations. The downward spike marked by an asterisk in (c) was produced by blocking temporarily beam 2 and indicates the background ion signal due to beam 1 alone.

signment seems most unlikely as band *O* is weak, much weaker than the bands observed in the 68 800–70 000 cm<sup>-1</sup> range. If it were an ungerade singlet  $5p$  Rydberg state it would have to correspond to either a  $2_0^1$  or  $2_1^0$  vibronically induced band. Since, there is no corresponding  $0_0^0$   $5p$  Rydberg band appearing in the one photon absorption spectrum,<sup>6</sup> band *O* would have to correspond to the  $5p\ ^1\Delta_u$  state. By analogy to that observed for the vibronically induced bands of the  $4p\ \Delta_u$  states,<sup>4</sup> both the  $2_0^1$  and  $2_1^0$  bands would be expected with an energy separation ( $\nu_2' + \nu_2''$ ) in the 700–770 cm<sup>-1</sup> range. Unfortunately there does not appear to be any corresponding band to either side of band *O*. Hence, from the current experimental results we are unable to give a reliable assignment to band *O*.

No other sharp or obvious  $(1+1')$  resonant features were recorded in the CS<sub>2</sub><sup>+</sup> or CS<sup>+</sup> mass channel up to  $\approx 73$  000 cm<sup>-1</sup>, the upper limit of this study.

## V. CONCLUSION

The  $(1+1')$  resonance enhanced multiphoton spectrum of CS<sub>2</sub> has been recorded in the 68 500–73 000 cm<sup>-1</sup> excitation energy range. Only in the 68 800–70 000 cm<sup>-1</sup> region are strong bands observed and so their most natural assignment is to the  $3d$  and  $5s$  gerade Rydberg states. This

implies quantum defects of 0.0 and 2.0 for the  $3d$  and  $5s$  Rydberg states, respectively, values which are reasonable when compared to the quantum defects of atomic sulfur and other sulfur containing molecules. The relative intensities of these bands were found to depend strongly on the relative polarizations of the two laser beams used. From their polarization behavior some assignments to particular states were possible although many of the bands still have uncertain assignments. In the  $70\,000\text{--}72\,000\text{ cm}^{-1}$  region we appear to have observed the  $2_1^0$  and  $2_0^1$  vibronically induced bands of the strong one photon transition at  $70\,925\text{ cm}^{-1}$  which is believed to be a  $0_0^0$  band of a  $5p$  Rydberg state.

#### Note added in proof

Morgan *et al.*<sup>27</sup> have very recently published an article on the (2+1) and (3+1) REMPI spectra of CS<sub>2</sub>. In their (2+1) spectra they show two bands centered at  $69\,414$  and  $69\,847\text{ cm}^{-1}$  which clearly correspond to an unresolved overlap of our bands  $I$  to  $C$  and our band  $J$ , respectively. The upper states are presumed to be  $[3/2]5s(^3\Pi_g)$  and  $[1/2]5s(^1\Pi_g)$  states, respectively [their Table IV and Fig. 3(b)]. However these assignments are inconsistent with the polarization dependence observed in this study and so the actual assignments must include the  $3d$  Rydberg states. We note their final comment regarding the so-called  $d$  Rydberg origin of Li *et al.*<sup>2</sup> at  $63\,323\text{ cm}^{-1}$  is not applicable because these features had in Ref. 4 been conclusively reassigned to two photon photon vibronically induced transitions to the  $4p$  Rydberg states. The fact that Morgan *et al.*<sup>47</sup> did not observe these features in the (2+1) REMPI spectrum can be simply explained by the fact that these electronically forbidden (2+1) transitions will be swamped by the electronically allowed (1+2) transitions which occur over the same fundamental wavelength range.

Morgan *et al.* elegantly demonstrate by application of REMPI-photoelectron spectroscopy that the apparent splitting of the  $4p\ ^3\Delta_u$  origin level is caused by mixing with the (0,2<sup>2</sup>,0) vibrational level of the  $4p\ ^3\Sigma_u$  Rydberg state. Consequently, in our previous study of the (1+1')+1 spectrum of CS<sub>2</sub> in the  $4p$  Rydberg region, Ref. 4, the so-called  $^3\Delta_u(A)$  origin may be associated with the  $4p\ ^3\Sigma_u(0,2^2,0)$  level while the  $^3\Delta_u(B)$  origin may be associated with the  $4p\ ^3\Delta_u(0,0,0)$  state, although in reality they are mixed states. Reference 4 shows that the vibronic mixing between the  $^3\Delta_u$

and  $^3\Sigma_u$  states does not stop there but continues on up into the higher vibrational levels. For example Fig. 7(c) of Ref. 4 effectively shows that the  $^3\Sigma_u(0,3^1,0)$  and  $^3\Delta_u(0,1^1,0)$  levels are also mixed.

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- <sup>1</sup>L. Li, X. T. Wang, X. N. Li, and X. B. Xie, Chem. Phys. **164**, 305 (1992).
- <sup>2</sup>L. Li, X. T. Wang, X. N. Li, and X. B. Xie, Chem. Phys. Lett. **202**, 115 (1993).
- <sup>3</sup>J. Baker, M. Konstantaki, and S. Couris, J. Chem. Phys. **103**, 2436 (1995).
- <sup>4</sup>J. Baker and S. Couris, J. Chem. Phys. **103**, 4847 (1995).
- <sup>5</sup>W. C. Price and D. M. Simpson, Proc. R. Soc. London Ser. A **165**, 272 (1938).
- <sup>6</sup>Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, J. Chem. Phys. **32**, 1205 (1960).
- <sup>7</sup>J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, Chem. Rev. **71**, 73 (1971).
- <sup>8</sup>F. R. Greening and G. W. King, J. Mol. Spectrosc. **59**, 312 (1976).
- <sup>9</sup>R. McDiarmid and J. P. Doering, J. Chem. Phys. **91**, 2010 (1989).
- <sup>10</sup>R. Muallem and A. Gedanken, Chem. Phys. Lett. **188**, 383 (1992).
- <sup>11</sup>D. G. Wilden and J. Comer, Chem. Phys. **53**, 77 (1980).
- <sup>12</sup>M.-J. Hubin-Franskin, J. Delwiche, A. Poulin, B. Leclerc, P. Roy, and D. Roy, J. Chem. Phys. **78**, 1200 (1983).
- <sup>13</sup>J. P. Doering and R. McDiarmid, J. Phys. Chem. **87**, 1822 (1983).
- <sup>14</sup>A. Q. Zhang and P. H. Vaccaro, J. Phys. Chem. **99**, 1799 (1995).
- <sup>15</sup>D. C. Tseng and R. D. Poshusta, J. Chem. Phys. **100**, 7481 (1994).
- <sup>16</sup>J. Baker and S. Couris, J. Chem. Phys. **104**, 6130 (1996).
- <sup>17</sup>S. Couris, E. Patsilnakou, M. Lotz, E. R. Grant, C. Fotakis, C. Cossart-Magos, and M. Horani, J. Chem. Phys. **100**, 3514 (1994).
- <sup>18</sup>V. Kaufman and W. C. Martin, J. Phys. Chem. Ref. Data **22**, 282 (1993).
- <sup>19</sup>T. V. Venkitachalam and A. S. Rao, Appl. Phys. B **52**, 102 (1991).
- <sup>20</sup>S. H. Lin, Y. Fujimura, H. J. Neusser, and E. W. Schlag, *Multiphoton Spectroscopy of Molecules* (Academic, Orlando, 1984), Chap. 4.
- <sup>21</sup>I. Fischer, A. Lochschmidt, A. Strobel, G. Niedner-Schatteburg, K. Muller-Dethlefs, and V. E. Bondybey, Chem. Phys. Lett. **202**, 542 (1993).
- <sup>22</sup>H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).
- <sup>23</sup>M. Barnes, J. Baker, J. M. Dyke, and R. Richter, Chem. Phys. **166**, 229 (1992).
- <sup>24</sup>G. Blanquet, E. Baeten, I. Cauuet, J. Walrand, and C. P. Courtoy, J. Mol. Spectrosc. **112**, 55 (1985).
- <sup>25</sup>G. Black, R. L. Sharpless, and T. G. Slinger, J. Chem. Phys. **66**, 2113 (1977).
- <sup>26</sup>E. K. Moltzen, K. J. Kalabunda, and A. Senning, Chem. Rev. **88**, 391 (1988).
- <sup>27</sup>R. A. Morgan *et al.*, J. Chem. Phys. **104**, 6117 (1996).