Laser Excited Fluorescence of CS_2

PETER F. BERNATH, MICHAEL DULICK, AND ROBERT W. FIELD

Spectroscopy Laboratory and The Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

AND

J. L. HARDWICK

Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A OR6, Canada; and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Resonance fluorescence excited by ultraviolet lines of argon and krypton ion lasers has been observed from carbon disulfide. The strongest excitations are to single rotational levels within bands of Kleman's R system having $K = 0$ and 1. Fluorescence in each instance forms a long progression in the ground-state bending vibration, ν_2''. Vibrational levels as high as $(1,28°,0)$ have been identified.

INTRODUCTION

Resonance fluorescence spectroscopy has, with the advent of lasers operating over broad spectral regions, become an increasingly powerful tool for characterizing electronic transitions in polyatomic molecules and for obtaining extensive and detailed information about their ground and excited electronic states. In this paper, we describe the use of this technique to study highly excited vibrational levels of the ground electronic state of CS_2.

The argon and krypton ion lasers have several prominent lines in the near ultraviolet. Three of these, two argon lines and one krypton line, excite fluorescence strong enough to be dispersed by a grating monochromator. These lines, at 351.4, 351.1, and 350.7 nm, excite transitions within the electronic band systems designated as R and T (*1, 2*). The R system has been shown to be one spin component of the $\tilde{a}^3A_2 - \tilde{X}^1\Sigma^+_g$ electronic transition whose upper state transforms with spin electronic B_2 symmetry (*3–5*). The T system has been assigned by Jungen *et al.* (*2*) as belonging to a $^1A_2 - ^1\Sigma^+_g$ electronic transition whose upper state is perturbed through Renner–Teller coupling with the V state.

The low-lying vibrational levels of the ground electronic state of CS_2 have been extensively studied by high-resolution infrared and ultraviolet spectroscopy (*6, 19–20*). Considerable attention has been focused on accurate measurement and assignment of "hot" bands of CS_2, especially since the discovery of infrared laser transitions between vibrationally excited states (*10*). Smith and Overend (*11*) have used the observed vibrational energies to compute a potential function for CS_2 through quartic terms, and Blanquet and Courtoy (*9*) have more recently

reported a complete set of harmonic frequencies ω_i, anharmonicity constants x_{ij}, and Fermi resonance coupling parameters. Both papers demonstrate the existence of strong Fermi resonances which couple basis wavefunctions differing by one quantum of ν_1 and two quanta of ν_2.

Laser excited fluorescence in CS_2 has been reported previously by Silvers and McKeever (14), who excited the T state using a nitrogen laser, and by Vasudev and Brand (15), who used a pulsed dye laser to study the excitation spectrum in the region of the R system.

EXPERIMENTAL DETAILS

Fluorescence spectra excited at 350.7 nm were recorded at Ottawa, while those excited at 351.4 and 351.1 nm were recorded at MIT. The experiments at Ottawa used a commercial krypton ion laser (Coherent CR-3000K) operating multiline in the ultraviolet at a total nominal power of 2 W from the three ultraviolet lines. The laser lines were separated outside the laser cavity using a Pellin–Broca prism and an iris diaphragm and focused into the fluorescence cell. The laser light was then reflected back along the same path using a concave mirror. Fluorescence was dispersed with a 0.5 m double monochromator (Spex model 1302) equipped with 1800 line/mm holographic gratings used in the first order. Spectra were calibrated using emission lines from an iron hollow cathode lamp. Strong fluorescence lines of carbon disulfide could be recorded using a spectral slit width of slightly less than 1 cm^{-1}; for these lines, the estimated uncertainty of the measured wavenumber is 0.5 cm^{-1}. Many weaker lines, however, could be observed only by opening the slits to the point that the precision of measurement was degraded to about 5 cm^{-1}.

Fluorescence spectra obtained from the UV lines of the argon ion laser were recorded at MIT. A Coherent CR-18UV laser with about 3 W of total ultraviolet power was used. The lines were separated with an external Pellin–Broca prism. It was not possible to separate the 351.4- and 351.1-nm laser lines, so emission excited by both lines occurs in the fluorescence spectrum. It was pos-
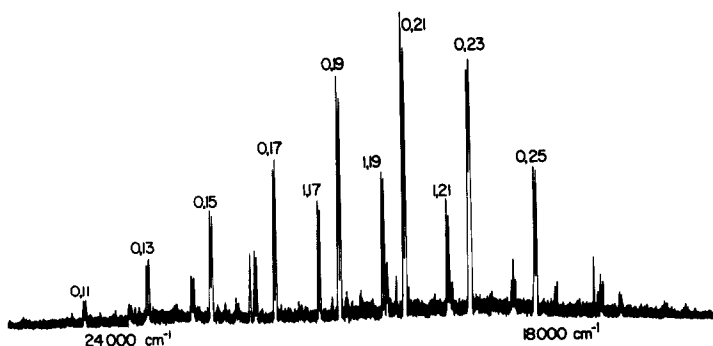

FIG. 1. Fluorescence from CS_2 excited by the 350.7-nm line of the krypton ion laser. Some of the more prominent transitions are identified with the values of v_1'' and v_2'' on which the fluorescence terminates.

TABLE I

Vacuum Wavenumbers and Assignments of Terminal Vibrational States of CS$_2$
Fluorescence Excited at 28 502.8 cm^{-1}

v_1	v_2	P(61)	obs–calc	R(59)	obs–calc
0	9	25185 cm^{-1}	3 cm^{-1}	25212 cm^{-1}	3 cm^{-1}
0	11	24328.6	0.3	24355.1	0.0
1	11	23719.9	1.1	23746.4	0.9
0	13	23467.2	0.1	23494.8	0.9
1	13	22864.7	3.9	22892.3	1.8
0	15	22600.0	1.2	22627.8	1.3
1	15	22003.3	1.2	22030.0	-1.0
4	15	20214.9	1.0	20239.5	-1.2
0	17	21725.7	-0.7	21751.7	-1.7
1	17	21134.0	-0.6	21161.5	0.1
3	17	19953.1	0.1	19980.5	0.6
4	17	19364.0	0.7	19391.7	1.6
0	19	20847.5	-0.6	20875.4	0.3
1	19	20263.0	1.8	20290.3	1.4
3	19	19093.0	1.7	19119.8	1.5
0	21	19965.3	0.2	19992.7	0.5
1	21	19388.4	4.0	19416.1	4.7
2	21	18807.8	3.8	18834.7	3.6
3	21	18229	4	18255	4
0	23	19077.4	-0.3	19104.9	0.0
2	23	17934	?	17960	6
0	25	18188	2	18215	2
2	25	17047	1	17073	-1
unassigned		19974.1		20001.2	

Note. Excitation occurs in the *P* branch of the (1,7,0)–(0,1^1,0) band of the *R* system. Fluorescence terminating on states with $v_3 \neq 0$ has not been identified.

sible to confirm the exciting line for each progression by decreasing the current of the laser discharge. The 351.4-nm line is rather weak, so it reaches threshold at a higher current than the 351.1-nm line. Near the 351.4-nm threshold, the change in relative intensity of the fluorescence progressions identified the exciting line. Fluorescence progressions were dispersed by a 1 m Spex monochromator (model 1802) with a 1200 line/mm grating used in second order. Spectra were calibrated with argon and neon pen lamps. Accuracy of wavelength determination varied with wavelength and intensity of the fluorescence but is estimated to be about ±0.5 cm^{-1}. The temperature dependence of the fluorescence intensity was studied by heating the cell to ~200°C with heating tape and observing changes in intensity of selected fluorescence features.

ANALYSIS

Appearance of the Spectra

The fluorescence spectrum excited with the 350.7-nm krypton ion line is shown at low dispersion in Fig. 1. The main features of this spectrum are typical of the spectra excited by the other two lines as well.

The spectrum consists of a number of doublets with an internal separation of about 27 cm^{-1}. These begin at about 3000 cm^{-1} to the red of the exciting line and extend another 8000 cm^{-1} to lower wavenumber, reaching a maximum intensity at about 9000 cm^{-1} to the red of the excitation. A prominent vibrational interval of about 850 cm^{-1} may easily be identified as $2v_2''$, two quanta of the degenerate bending vibration. A somewhat less intense set of doublets, lying about 600 cm^{-1} to the red of the strongest lines, represents the main progression in $2v_2''$ with one quantum of the symmetric stretch (v_1'') added. Additional bands were observed which terminate on higher values of v_1''. The vacuum wavenumbers of the fluorescence lines are presented in Table I.

The observed intensity distribution in these fluorescence spectra is a conse-
quence of the change in geometry of CS_2 on electronic excitation; the ground
state is linear, while the excited electronic state has a bond angle estimated at
135° (1). The long progression in the bending vibration is thus expected solely
on the basis of the Franck–Condon principle.

Fluorescence was also observed from CS_2 excited by the three weak argon ion
laser lines at 335.8, 334.4 and 333.6 nm. These lines were not separated by the
external prism. They excited fluorescence similar to that obtained with N_2 laser
excitation (14), but the weak banded features were very complicated. The banded
features were superimposed on a wide, strong "continuum," with a peak intensity
at ~480 nm, which is presumably due to relaxed fluorescence. No analysis of
this emission was attempted.

Assignment

Although the three exciting lines are separated by only 0.7 nm, they excite at
least four distinct bands. The line at 351.1 nm excites a "cold" $\Sigma-\Sigma$ transition,
the line at 350.7 nm excites a band that is one quantum "hot" in v_2'', and the line
at 351.4 nm excites a band three quanta "hot" in v_2'' as well as a second weaker
transition.

350.7-nm Excitation

The line at 350.7 nm (28 502.8 cm^{-1}) excites a band designated by Kleman as
(1,7,0)–(0,1^1,0), which is violet degraded and forms a head at 28485.87 cm^{-1}.
Excitation occurs via a line which has not previously been rotationally assigned
but which, by virtue of the symmetry of the two states, must belong to a ^qP or
^qR branch. If the excitation were in the ^qR branch, the corresponding ^qP line,
falling 27 cm^{-1} to lower wavenumber, would occur to the red of the bandhead.
Thus, the excitation must be in the ^qP branch. The rotational quantum number
J' of the excited state may be determined from the separation of the lines of the
fluorescence doublets; assuming a value of $B'' \approx 0.11$ cm^{-1} for the typical level
on which fluorescence terminates leads to a value for J' of 60. Rotational assign-
ments have been given for this band through $J' = 43$ by Hallin (16). Extension
of this rotational analysis is not straightforward, however, due to numerous small
perturbations to this band. High-resolution absorption spectra show the lines of
interest to this analysis fall in a very crowded region where ground-state com-
bination differences cannot be relied upon to give a unique assignment. Two
measured absorption lines, one at 28 502.744 near the laser line and the correspond-
ing ^qR line at 28 529.170 cm^{-1}, reproduce the expected ground-state combination
difference to within 0.004 cm^{-1}, but it is possible that this separation could be
fortuitous. Owing to the relative lack of precision of the fluorescence spectrometer
and to the absence of any independent measurements of the rotational constants
for the vibrational levels on which fluorescence terminates, we place an error limit
on J' of ±2.

To a first approximation, the difference in vibrational term values of Π levels
may be calculated simply by taking the difference in wavenumber of the cor-

responding fluorescence features. Thus, $G''(0,13^1,0) - G''(0,11^1,0) \approx 861$ cm^{-1} and $G''(1,11^1,0) - G''(0,11^1,0) \approx 609$ cm^{-1}; these intervals are within experimental error of those reported by Silvers and McKeever of 863 and 604 cm^{-1} (14). This procedure should be viewed with some caution, since the vibration–rotation interaction constants are sizable and introduce measurable corrections even at our resolution.

351.1-nm Excitation

The argon ion laser line at 351.1 nm (28 472.8 cm^{-1}) excites fluorescence which extends with measurable intensity from 454 to 643 nm. The vacuum wavenumbers of the observed fluorescence lines are given in Table II. The most prominent vibrational intervals may again be assigned to differences of ν_1'' and $2\nu_2''$ in the terminal levels of fluorescence.

The observed vibrational intervals do not exactly match those of the fluorescence excited at 28 502.8 cm^{-1}, indicating that the initial vibrational levels of the transitions excited by these two laser lines are not the same. Indeed, the vibrational intervals observed in the 351.1-nm fluorescence cannot be fitted by assuming that the initial state is a Π vibrational level. Since the fluorescence intensity is slightly decreased upon increasing the temperature of the sample, the initial level is assigned to be the vibrationless level of the ground electronic state.

The principal rotational quantum number J' may be determined as before from the mean doublet separation. Its value is $J' = 35$, with a possible error of ± 2.

The upper vibronic state from which fluorescence occurs is most probably the level assigned by Kleman as (2,3,0) of the R state. The (2,3,0)–(0,0^0,0) band is reported to have a head at 28 473.1 cm^{-1} with a probable accuracy of about 0.2 cm^{-1} (1). The assumption that the excitation is the $P(36)$ line of this band is consistent both with the vibrational intervals calculated for Σ–Σ transitions and with the observation that the exciting line is very near the band head (which, for a violet degraded band, consists of numerous lines of the P branch).

TABLE II

Vacuum Wavenumbers and Assignments of Terminal Vibrational States
of CS$_2$ Fluorescence Excited at 28 472.8 cm^{-1}

v_1	v_2	P(36)	obs-calc	R(34)	obs-calc
1	14	22008.1 cm^{-1}	-1.4 cm^{-1}	22023.7 cm^{-1}	-1.6 cm^{-1}
0	16	21737.3	-3.0	21752.9	-3.5
1	16	21143.3	-2.2	21159.4	-1.9
0	18	20867.1	1.9	20885.2	4.2
1	18	20275.0	-1.0	20291.9	0.1
0	20	19982.4	-2.7	19998.0	-3.0
2	18	19683.8	-3.6	19700.5	-2.7
1	20	19400.0	-1.4	19416.2	-1.1
0	22	19099.8	-0.7	19115.1	-1.4
2	20	18817.9	-0.4	18834.2	0.0
1	22	18521.9	-0.3	18538.1	0.1
0	24	18208.9	-3.0	18228.8	0.9
2	22	17944.8	0.3	17961.2	0.7
1	24	17641.1	2.2	17656.7	1.8
0	26	17316.6	-2.8	17322.8	2.6
2	24	17061.6	-5.0	17077.3	-5.2
1	26	16751.7	0.0	16768.0	0.3
0	28	16422.3	-1.0	16438.0	-1.4
1	28	15863.1	2.2	15878.5	1.5
0	30	15525.3	1.5	15541.0	1.0
unassigned		17636.8		17653.0	

Note. Excitation occurs in the P branch of a band of the R system whose lower state is (0,0^0,0) and whose upper state is probably (2,3,0).

TABLE III

Vacuum Wavenumbers and Assignments of Terminal Vibrational States of the Strong Fluorescence
Progression Excited in CS_2 at 28 448.0 cm^{-1}

v_1	v_2	P(16)	R(14)
0	7	26777.2 cm^{-1}	26783.9 cm^{-1}
0	9	25928.9	25935.4
0	11	25075.1	25082.2
0	13	24215.1	24221.5
0	15	23346.3	23353.2
0	17	22474.7	22479.7
1	19	21015.3	21022.8

Note. Excitation occurs in the R branch of a band whose lower state is (0,3,0) and whose upper
state is near the $t + 1$ state.

351.4-nm Excitation

The argon ion laser line at 351.4 nm (28 448.0 cm^{-1}) excites two distinct transi-
tions in CS_2. The upper states of these transitions have different principal rotational
quantum numbers, and so the fluorescence from the two states may be distinguished
by the different spacing of the P and R lines.

The stronger of the two fluorescence progressions has a R–P separation of
about 6.7 cm^{-1}, indicating a value of $J' = 15 \pm 2$. Excitation takes place via the
R(14) line from the (0,3,0) level of the ground electronic state. The temperature
dependence of the fluorescence is consistent with this assignment. Our relatively
low resolution does not enable us to distinguish between the equally likely
$(0,3^1,0)$ and $(0,3^3,0)$ states, although the $(0,3^3,0)$ assignment is in marginally better
agreement with Kleman's data (*1*). The upper state has a term value of about
29 650 cm^{-1}, and may perhaps be assigned as either the Π or Φ component of the
state designated by Jungen *et al.* (*2*) as $t + 1$. The fluorescence frequencies for
this progression are given in Table III.

The weaker of the two fluorescence progressions has a R–P separation of about
15.5 cm^{-1}, leading to a value of 34 ± 2 for J'. The most likely assignment for the

TABLE IV

Vacuum Wavenumbers and Assignments of Terminal Vibrational States of the Weak Fluorescence
Progression Excited in CS_2 at 28 448.0 cm^{-1}

v_1	v_2	P(35)	R(33)
0	9	26761.9 cm^{-1}	26777.2 cm^{-1}
0	11	25910.1	25925.6
0	13	25051.1	25066.3

Note. Excitation occurs in the P branch of a band whose lower state is (0,5,0) and whose upper
state is near the $t + 5$ state.

TABLE V

Vibrational Constants Determined by Least-Squares Fitting of Fluorescence
Lines and Previously Reported Band Origins

Constant	Previous Value (9)	This Work
ω_1	672.709 ± 0.057	672.713 ± 0.023
ω_2	398.261 ± 0.020	398.135 ± 0.008
ω_3	1558.710 ± 0.016	1558.680 ± 0.015
x_{11}	-1.021 ± 0.017	-1.031 ± 0.007
x_{12}	-2.897 ± 0.214	-3.152 ± 0.017
x_{13}	-7.664 ± 0.014	-7.650 ± 0.009
x_{22}	1.094 ± 0.058	1.210 ± 0.005
x_{23}	-6.446 ± 0.005	-6.446 ± 0.004
x_{33}	-6.540 ± 0.003	-6.536 ± 0.003
g_{22}	-0.884 ± 0.053	-0.841[a]
y_{222}	-	-0.0058 ± 0.0002
k_{122}	42.31 ± 0.62	41.470 ± 0.047
λ_1	0.49 ± 0.03	0.491 ± 0.010
λ_2	0.42 ± 0.04	0.459 ± 0.007
λ_3	0.014 ± 0.002	-0.050 ± 0.013
δ	$(7.24 \pm 0.09) \times 10^{-5}$	7.24×10^{-5} [b]

[a] Constrained to this value by other constants.

[b] Fixed at the previously determined value.

Note. All values are in cm⁻¹. Errors given are one standard deviation.

initial level of the laser excited transition, based entirely on vibrational intervals in fluorescence, is (0,5,0). Excitation occurs via the $P(35)$ line if this assignment is correct. The term value of the upper state would then be about 30 480 cm⁻¹, close to the $t + 5$ level of Jungen *et al.* (2). The value of l in the initial level cannot be identified; thus, the upper state could be the Π, Φ, or H component of this severely perturbed level of the T state.

VIBRATIONAL CONSTANTS

The fluorescence lines observed in this work can be used in connection with previously published high-resolution infrared data to establish harmonic and anharmonic vibrational constants for CS_2. In order to fit the observed frequencies,

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TABLE VI

Vibrational Term Values for the Ground Electronic State of CS_2

v_1	v_2^{ℓ}	v_3	ν_{obs}	ν_{calc}	ref.
0	1^1	0	396.099	396.084	10,13
0	2^0	0	801.865	801.849	10
1	0^0	0	658.000	658.025	10
0	2^2	0	792.85	792.837	11
0	3^1	0	1206.982	1206.992	20
1	1^1	0	1046.564	1046.564	7
0	4^0	0	1619.777	1619.789	20
1	2^0	0	1447.083	1447.055	7,10
2	0^0	0	1313.696	1313.675	10
0	4^2	0	1611.84	1611.849	20,11
0	5^1	0	2031.634	2031.652	20
0	6^0	0	2450.053	2450.060	20
0	6^2	0	2442.90	2442.862	20,11
0	0^0	1	1535.354	1535.341	11
0	1^1	1	1924.987	1924.980	11
0	2^0	1	2324.538	2324.532	8
1	0^0	1	2185.479	2185.483	8
0	3^1	1	2723.365	2723.370	7
1	1^1	1	2567.439	2567.436	8
0	4^0	1	3129.983	3129.975	9
1	2^0	1	2961.759	2961.750	7
2	0^0	1	2833.193	2833.195	21
0	4^2	1	3121.88	3121.872	7,11
1	2^2	1	2950.99	2950.993	10,11
1	3^1	1	3355.187	3355.196	7
2	1^1	1	3207.437	3207.474	21
1	4^0	1	3757.466	3757.481	7
2	2^0	1	3597.047	3597.033	9
3	0^0	1	3478.386	3478.381	9
1	4^2	1	3748.48	3748.485	7,11
0	0^0	3	4566.809	4566.818	9
0	1^1	3	4943.563	4943.565	19
1	0^0	3	5201.151	5201.134	9
0	5^3	0			
-0	3^3	0	826.400	826.381	20
1	3^3	1			
-0	3^3	0	2145.6697	2145.657	10

Note. Calculated values are obtained from the constants of Table V. Observed values are taken from the literature; whenever possible, "hot" band origins have been converted into term values with respect to the $(0,0^0,0)$ level by adding the term value of the lower level of the "hot" band. The $l = 3$ bands are presented as band origins, since no reliable value for the $(0,3^3,0)$ term value exists.

the constant y_{222} must be introduced in addition to the constants determined by previous studies.

The wave number ν_F of any fluorescence line is approximated by

$$\nu_F = \nu_L + G''(v_1,v_2^l,v_3) + B''[J''(J'' + 1) + l^2] - G(v_1,v_2^l,v_3) + B[J(J + 1) + l^2]. \quad (1)$$

Here ν_L is the wavenumber of the exciting line, G'' and G are the vibrational term values of the initial level from which excitation occurs and the terminal level of fluorescence, B'' and B are the principal rotational constants of those levels, J'' and J are the principal rotational quantum numbers, and l is the vibrational angular momentum quantum number.

The value of B for any vibrational level of the ground electronic state may be estimated for the purpose of this paper as

$$B_{v_1v_2v_3} = B_{0,0,0} - \sum_i \alpha_i v_i, \quad (2)$$

where $B_{0,0,0} = 0.1091165$ cm⁻¹ (*10*), $\alpha_1 = 21.0 \times 10^{-5}$ cm⁻¹ $\alpha_2 = -21.3 \times 10^{-5}$ cm⁻¹, and $\alpha_3 = 71.4 \times 10^{-5}$ cm⁻¹ (*9*). If the vibrational angular momentum l is equal to 1, l-type doubling must be taken into account, and the doubling constant q must be a function of the vibrational quantum number v_2. We have done this by setting

$$B_{eff} = B_{v_1v_2v_3} \pm \frac{1}{2}q_{v_2},$$

$$q_{v_2} = 7.5 \times 10^{-5}(v_2 + 1)\ \text{cm}^{-1}, \quad (3)$$

where the positive sign refers to the *oo* levels (even J) and the negative sign refers to the *oe* levels (odd J).

The vibrational term values for CS₂ may be written, neglecting Fermi resonance, as

$$G(v_1,v_2^l,v_3) = \sum_i \omega_i\left(v_i + \frac{1}{2}d_i\right)$$

$$+ \sum_{i<j} x_{ij}\left(v_i + \frac{1}{2}d_i\right)\left(v_j + \frac{1}{2}d_j\right) + y_{222}(v_2 + 1)^3 + g_{22}l^2. \quad (4)$$

Here d_i is the degeneracy of the ith level. These terms form the diagonal elements of the transformed vibrational Hamiltonian matrix. Fermi resonance adds off-diagonal terms which depend on the vibrational and rotational quantum numbers (*9*):

$$\langle v_1v_2^lv_3|H|v_1 - 1, v_2 + 2^l, v_3\rangle = \frac{1}{2}\{v_1[(v_2 + 2)^2 - l^2]\}^{1/2}$$

$$\times \left[-\frac{k_{122}}{2} + \lambda_1 v_1 + \lambda_2(v_2 + 2) + \lambda_3\left(v_3 + \frac{1}{2}\right) + \delta\{J(J + 1) - l^2\}\right]. \quad (5)$$

Not all the parameters of Eqs. (4) and (5) are independent. Amat and Pimbert (*17*) have pointed out that g_{22} is determined by the relationship:

$$g_{22} = \frac{1}{3}\left\{\frac{k_{122}^2}{2}\left[-\frac{1}{\omega_1} + \frac{1}{2(2\omega_2 + \omega_1)}\right] - x_{22}\right\} - B. \quad (6)$$

Accordingly, g_{22} was constrained in the present work to the value determined by Eq. (6). The value of the parameter δ was fixed at that determined by Blanquet and Courtoy (9), and the remaining constants of Eqs. (4) and (5) were found using an iterative, weighted, least-squares technique. Previously reported band origins were reduced to vibrational term values wherever possible (Table VI) and these were used in the fit together with the fluorescence line positions of Tables I and II. The constants giving the best fit to the data are reproduced in Table V, and the differences between the calculated and observed data are given in Tables I, II, and VI. Although not all the fluorescence line positions are fitted to within the estimated experimental uncertainty, the inclusion of any additional parameters in the Hamiltonian is unwarranted at this time due to the unknown effect of local perturbations.

CONCLUSION

The ultraviolet lines of the argon and krypton ion lasers excite only rather weak and poorly characterized transitions in CS_2. Despite this handicap it is possible, because of the spectral purity and high intensity of the excitation combined with favorable Franck–Condon factors, to obtain extensive and reasonably precise information about high vibrational levels of the ground electronic state. Additional experiments with tunable lasers should be very fruitful, providing information about excited electronic states as well as even more extensive ground-state data.

Although the line positions and intensity distribution of the fluorescence spectra exhibit remarkable regularity, an inspection of the Fermi resonance matrix elements demonstrates that this regularity is deceptive. The matrix elements coupling members of a polyad are, in many instances, greater than the separation between them (e.g., $\langle 0\ 21^1\ 0|H|1\ 19^1\ 0\rangle = -204\ cm^{-1}$). Thus, even though the spectra appear simple, the harmonic oscillator basis functions are a poor description of the actual molecular wavefunctions.

ACKNOWLEDGMENTS

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