"extra proton" is given by[2]

$$E_c=\frac{Ze^2}{b+R_0/3}\left[\frac{2}{5}+\int_{R_0}^{\infty}\frac{dr}{r}\exp\left(\frac{-(r-R_0)}{b}\right)\right]. \quad (4)$$

If we let

$$\rho=b/R_0,$$

$$I(\rho)=\int_{-R_0}^{\infty}\frac{dr}{r}\exp\left(\frac{-(r-R_0)}{b}\right),$$

and

$$f(\rho)=\frac{0.4+I(\rho)}{1+3\rho},$$

Eq. (4) becomes

$$E_c=3Z_0e^2f(\rho)/R_0.$$

If b is measured in units of 10^{-13} cm then

$$b=\frac{2.36}{\epsilon^{\frac{1}{3}}}\left(\frac{A_0+1}{A_0}\right)^{\frac{1}{3}},$$

where ϵ is expressed in m.m.u., and $f(\rho)$ is shown plotted in Fig. 10.

It is now assumed that the volume of the core is proportional to the number of core particles A_0 plus the fraction of the "extra neutron" within the sphere of radius R_0. Therefore,

$$R_0^3=r_0^3\left(A_0+\int_0^{R_0}U^2dv\right)$$

or

$$R_0=r_0[A_0+1/(1+3\rho)]^{\frac{1}{3}}.$$

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A Rotational Analysis of Some CS_2 Bands in the Near Ultraviolet System*

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Six bands in the λ3100 system of CS_2, photographed in absorption on a 30-foot grating spectrograph, have been analyzed and B values are given for their initial and final states. The band structure is of the simple PR branch type, all of the observed bands originating from ${}^1\Sigma^+_u-{}^1\Sigma^+_g$ transitions. The bands at λ3468, λ3501, and λ3535 originate in the normal state, giving a value $r_0=1.548$A for the normal carbon-sulphur separation. A partial vibrational analysis shows that for the bending vibration, $2\nu_2''=802$ cm^{-1}. Two progressions, $v_2''=0$ and $v_2''=2$, indicate that $\nu_2'=270$ cm^{-1}. Two bands, λ3501 and λ3601, have their common upper ${}^1\Sigma^+_u$ state perturbed by a ${}^1\Pi_u$ state. A perturbation analysis gives constants which are in good agreement with observation and in addition gives the B value for the perturbing ${}^1\Pi_u$ state. Evidence is presented which indicates that the excited electronic state of CS_2 is bent. It is shown that, even if the molecule is bent to 125°, the P and R series may still be represented by a simple quadratic formula exactly as for a linear molecule, for J values less than 25. The state nomenclature used (${}^1\Sigma^+_u$, ${}^1\Pi_u$, etc.) is that corresponding to the vibronic (electronic-vibrational) states of a linear molecule.

INTRODUCTION

THE analysis of the carbon disulphide spectrum has been of considerable interest to the band spectroscopist. Measurements on the Raman spectrum[1] of the liquid and on the infra-red spectrum of the gas[2-4] have determined the fundamental vibration frequencies in the normal state. Recent improvements in the resolving power of infra-red spectrometers have made possible a rotational analysis of the $\nu_1+\nu_3$ band. The analysis showed it to be of the parallel type with $B''=0.112$ and $B'=0.111$.[5]

An investigation of vibrational structures in the far ultraviolet absorption spectrum has been made by Price and Simpson.[6] They were unable to make a definite assignment of vibrational frequencies of the molecule in the excited states, but reported possible series.

The first reported attempt to analyze the well-known ultraviolet absorption system near

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* Assistance in the preparation of the materials was furnished by the personnel of Works Project Administration Official Project No. 665-54-3-87.

[1] S. C. Sirkar, Ind. J. Phys. **10**, 189 (1936).

[2] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **A132**, 236 (1931).

[3] D. M. Dennison and N. Wright, Phys. Rev. **38**, 2077L (1931).

[4] C. R. Bailey, Nature **140**, 851 (1937).

[5] J. A. Sanderson, Phys. Rev. **50**, 209 (1936).

[6] W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A165**, 272 (1936).

λ3200 was that of Wilson[7] who photographed the bands under various conditions of temperature and pressure with a low dispersion instrument. Jenkins[8] attempted a rotational analysis of some of these bands, but, with the 21-foot grating spectrograph used, he was unable to resolve them sufficiently for an analysis. He was, however, able to report that the band structures resembled those of a diatomic molecule. Watson and Parker[9] attempted a vibrational analysis of this system and reported a possible vibrational frequency of 270 cm^{-1} which has also been observed here (see below). Herzberg[10] has also attempted to analyze these bands.

Kusch and Loomis[11] have obtained magnetic rotation spectra of this same band system on a 21-foot grating spectrograph and reported possible vibrational series. In addition, they observed doublets separated by about 17 cm^{-1} in the magnetic rotation spectrum. In the present work[12] the same bands have been rephotographed with higher resolving power and six of them have been analyzed. The analysis shows that the Kusch-Loomis doublets agree with the P and R branches of the bands, the low frequency component being the P branch, the high frequency, the R branch.

EXPERIMENTAL

A series of absorption photographs was made varying both the length of the column and the pressure of the vapor. Two Pyrex tubes of lengths 1 and 2½ meters, and diameter 4 cm, having quartz windows cemented on with De Khotinsky cement, were employed. Liquid carbon disulphide was introduced into a small bulb attached to one end of the tube. In order to make the low gas pressure in the tube accurately reproducible, it was controlled by immersing the bulb into baths of known constant temperature. Vapor pressures of 4 mm and 1.0 cm were obtained by immersing the bulb into melting chloroform (−63.5°C) and melting chlorbenzene (−45°C), respectively. Higher pressures were found to be sufficiently accurately reproducible by cooling the bulb to −78°C and then allowing it to warm up slowly; when a mercury manometer attached to the tube showed that the desired pressure was attained, the bulb was sealed off. Since carbon disulphide has a vapor pressure of 28 cm at room temperature, a large range of gas pressures could be obtained without the necessity of heating the absorption tube. The vapor in the tube was changed once every hour by evacuating the tube and repeating the above process. This was done in order to avoid possible contamination by the by-products of the photo-decomposition of CS_2.

A hydrogen lamp was utilized as a source of continuum for the region 2900A to 3350A. This lamp was constructed of Pyrex in the conventional manner, with two large electrodes and a 30-cm water-cooled capillary and two quartz windows. A palladium valve was permanently fixed in the lamp so that any loss of hydrogen could be replaced without admitting air into the lamp. The lamp was operated at 0.8 ampere at 2500 volts.

A tungsten filament lamp served as a source for the continuum in the region 3350A to 3700A. The lamp, which was specially designed for this purpose, used a heavy tungsten ribbon which could be considerably overloaded to give a high intensity in this spectral region. The filament was operated at 110 amperes and about 18 volts. At an estimated temperature of about 3600°K, the filament had a lifetime of 10–20 hours. Beutler and Metropolis[13] later improved the design and investigated some of the characteristics of this lamp.

The spectra analyzed were obtained in the second order of an aluminized, 30-foot radius grating having 30,000 lines per inch, and a useful surface of 5½ inches. The grating was ruled by Professor H. G. Gale in the Ryerson Laboratory. The resolving power attained on the plates is very near to 300,000.

Exposure times of 30 hours with the hydrogen lamp and 10–15 hours with the tungsten lamp were required. Such long exposure times were unavoidable in using a high dispersion grating and a very narrow slit (12 microns). This fact

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[7] E. D. Wilson, Astrophys. J. **69**, 34 (1929).

[8] F. A. Jenkins, Astrophys. J. **70**, 191 (1929).

[9] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).

[10] G. Herzberg, unpublished work.

[11] P. Kusch and F. W. Loomis, Phys. Rev. **55**, 850 (1939).

[12] Some of these results have been given in (a) Phys. Rev. **58**, 183L (1940); (b), Phys. Rev. **59**, 106A (1941).

[13] H. Beutler and N. Metropolis, J. Opt. Soc. Am. **30**, 115 (1940).

TABLE I. *Band at* λ*3468*, $\nu_0=28,816.35$.

J	Wave Numbers of Observed Lines $R(J)$	Wave Numbers of Observed Lines $P(J)$	$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
0	28,816.63			
2	17.10		1.59	
4	17.54	28,815.51	2.43	2.03
6	18.03	15.11	3.30	2.92
8	18.58	14.73	4.19	3.85
10	19.08	14.39	5.02	4.69
12	19.62	14.06	5.86	5.56
14	20.26	13.76	6.77	6.50
16	20.85	13.49	7.65	7.36
18	21.48	13.20	8.53	8.28
20	22.11	12.95	9.38	9.16
22	22.78	12.73	10.27	10.05
24	23.44	12.51	11.13	10.93
26	24.14	12.31	12.01	11.83
28	24.79	12.13		12.66
30	25.49			
32	26.22			
34	26.92			
36	27.65			
38	28.37			
40	29.10			

TABLE II. *Band at* λ*3501*, $\nu_0=28,548.83$.

J	Wave Numbers of Observed Lines $R(J)$	Wave Numbers of Observed Lines $P(J)$	$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
0	28,549.10*		0.73*	
2	49.52	28,548.37*	1.54	1.15*
4	50.00	47.98	2.42	2.02
6	50.52	47.58	3.29	2.94
8	51.06	47.23	4.15	3.83
10	51.61	46.91	5.04	4.70
12	52.19	46.57	5.90	5.62
14	52.79	46.29	6.76	6.50
16	53.04 53.42	.... 46.03	7.63	7.39
18	53.80 54.10	.... 45.79	8.50	8.31
20	54.54 54.85	.... 45.60	9.43*	9.25
22	55.27 55.62	45.42*		10.20*
24	55.99 56.41			
26	56.71			
28	57.45			
30	58.18			
32	58.94			
34	59.70			
36	60.49			
38	61.28			
40	62.09			
42	62.89			
44	63.69			
46	64.50			
48	65.32			
50	66.12			
52	66.96			
54	67.80			
56	68.63			
58	69.41			
60	70.26			
62	71.06			
64	71.87			
66	72.67			
68	73.48			
70	74.29			

* Indicates blended or weak lines.

provided the chief difficulty in obtaining satisfactory photographs, since the barometric pressure rarely remained constant during these long exposures. A change in pressure of only 0.3 inch is sufficient with this high resolving power to shift detectably the spectrum lines. The most favorable conditions for observation of the bands were as follows:

Region (in A)	Gas Pressure (in mm)	Column Length (in m)
3050–3150	4	1
3250–3350	10	1
3350–3450	60	1
3450–3550	120	1
3550–3700	240	2½

These conditions were determined by first photographing the spectrum under small dispersion.

DATA

The most intense bands are located at 3100A with the system extending symmetrically on each side for about 600A. The system consists of an unusually large number of bands. Consequently, few bands are to be found free from overlapping.

High dispersion photographs of the spectrum show that the bands are simple in appearance, resembling those of a diatomic molecule. Practically all of the bands are of the *PR* branch type. A few, whose structure is too overlapped to permit an analysis to be made, may possibly be of the *PQR* branch type.

Six of the bands were found to be sufficiently free from overlapping to permit a rotational analysis to be made. In spite of the high resolving power attained, the bands were not completely resolved in the neighborhood of the head. The wave numbers of those lines of each band which were capable of measurement are listed in Tables I–VI. Lines which are weak or which consist of unresolved blends are designated by an asterisk (*). Those lines which are not so designated are estimated to be accurate to plus or minus 0.01 cm^{-1}. It will be noted that some *R* lines in the bands at λ3601 and λ3501 consist of

TABLE III. *Band at λ3535, $\nu_0=28{,}273.74$.*

	WAVE NUMBERS OF OBSERVED LINES			
J	$R(J)$	$P(J)$	$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
0	28,274.03*		0.66*	
2	74.43*	28,273.37*	1.48*	1.06*
4	74.95*	72.95	2.36*	2.00*
6	75.42*	72.59	3.22*	2.83*
8	76.00	72.20	4.15	3.80*
10	76.58*	71.85*	5.03	4.73
12	77.21	71.55	5.94	5.66
14	77.79	71.27	6.73	6.52
16	78.47	71.06	7.65	7.41
18	79.10	70.82	8.53	8.28
20	79.79	70.57	9.39	9.22
22	80.53	70.40		10.13
24	81.23			
26	81.99			
28	82.77			
30	83.55			
32	84.37			
34	85.20			
36	86.05			
38	86.92			
40	87.79			
42	88.70			
44	89.62			
46	90.58			
48	91.53			
50	92.50			
52	93.48			
54	94.46			
56	95.48			
58	96.51			
60	97.55			
62	98.58			
64	99.67			
66	28,300.74			
68	01.87			

* Indicates blended or weak lines.

TABLE IV. *Band at λ3601. $\nu_0=27{,}746.94$.*

	WAVE NUMBERS OF OBSERVED LINES			
J	$R(J)$	$P(J)$	$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
0				
2	27,747.65*		1.57*	
4	48.12	27,746.08	2.42	2.04*
6	48.63	45.70	3.31	2.93
8	49.14	45.32	4.16	3.82
10	49.68	44.98	5.04	4.70
12	50.25	44.64	5.91	5.61
14	50.84	44.34	6.78	6.50
16	51.44	44.06	7.65	7.38
18	51.81 52.11	.... 43.79	8.55*	8.32
20	52.50 52.79	.... 43.56	9.55*	9.23*
22	53.18 53.55	.... 43.24*		10.31*
24	53.88			
26	54.57			
28	55.26			
30	55.98			
32	56.67			
34	57.38			
36	58.12			
38	58.86			
40	59.60			
42	60.33			
44	61.08			
46	61.80			
48	62.57			
50	63.30			
52	64.04			

* Indicates blended or weak lines.

pairs with the same J value. These lines are the result of a perturbation which will be discussed below.

ROTATIONAL ANALYSIS

The carbon disulphide molecule is expected to obey Bose-Einstein statistics because the sulphur atom (mass 32) has an even number of protons and neutrons. This means that the total wave function should be symmetric in the nuclei. Since the spins of the sulphur atoms are zero, only symmetric rotational functions are to be expected. Consequently, alternate lines should be missing in Σ to Σ and Σ to Π transitions.

The notation (Σ, Π, and so on) here and below is that corresponding to the vibronic,[14] i.e., electronic-vibrational states of a linear molecule. It is in general the vibronic rather than merely the electronic states involved which determine the structure of any band in a polyatomic molecule's spectrum.

Figure 1 shows a microphotometer trace of the band at λ3501. As is seen from the figure, the first P line is separated from the first R line by $1\frac{1}{2}$ spacings, thus indicating missing alternate lines.[15] A consideration of the relative intensities (see Fig. 1) of the first few lines of the P and R branches shows that even J values are present in the lower state. Similar considerations show that five of the six measured bands have even J values in their lower states, which are designated ${}^1\Sigma^+{}_g$, and upper states which must then according to the selection rules for linear molecules and in view of the PR band structure, be ${}^1\Sigma^+{}_u$. The other band at λ3468 *apparently* has a Q branch and an analysis was first reported assuming this to be correct.[12a] However, the B values calculated from this band were then found to differ markedly from the other five bands. Also few, if any, other bands in this system have Q

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[14] R. S. Mulliken, J. Phys. Chem. **41**, 168 (1937).

[15] R. S. Mulliken, Rev. Mod. Phys. **3**, 150 (1931), Fig. 33.

TABLE V. *Band at λ3637, $\nu_0=27{,}471.96$.*

J	WAVE NUMBERS OF OBSERVED LINES		$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
	$R(J)$	$P(J)$		
0				
2		27,471.51		
4	27,473.14	71.12	2.39*	2.02
6	73.64	70.75	3.26	2.89
8	74.19	70.38	4.16	3.81
10	74.75	70.03	5.05	4.72
12	75.32	69.70	5.91	5.62
14	75.92	69.41	6.80	6.51
16	76.54	69.12	7.67	7.42
18	77.19	68.87	8.57	8.32
20	77.85	68.62	9.43	9.23
22	78.53	68.42	10.31	10.11
24	79.21	68.22		10.99
26	79.92			
28	80.66			
30	81.42			
32	82.20			
34	82.97			
36	83.75			
38	84.58			
40	85.43			
42	86.22			
44	87.08			
46	87.94			
48	88.83			
50	89.74			
52	90.64			
54	91.53			
56	92.46			
58	93.40			
60	94.38			

* Indicates blended or weak lines.

TABLE VI. *Band at λ3673, $\nu_0=27{,}190.08$*

J	WAVE NUMBERS OF OBSERVED LINES		$\Delta_2F''(J+1)$ $=R(J)-P(J+2)$	$\Delta_2F'(J)$ $=R(J)-P(J)$
	$R(J)$	$P(J)$		
0				
2	27,190.67*		1.50*	
4	91.17*	27,189.17*	2.41	2.00*
6	91.67*	88.76*	3.30	2.91*
8	92.23	88.37	4.18	3.86*
10	92.71	88.05	5.02	4.66
12	93.26	87.69	5.91	5.57
14	93.83	87.35	6.82	6.48
16	94.41	87.01	7.67	7.40
18	95.01	86.74	8.55	8.27
20	95.62	86.46	9.42	9.16
22	96.25	86.20	10.30	10.05
24	96.89	85.95	11.18	10.94
26	97.56	85.71	12.05	11.85
28	98.23	85.51	12.91	12.72
30	98.92	85.32	13.81	13.60
32	99.62	85.11		14.51
34	27,200.34			
36	01.07			
38	01.81			
40	02.60			
42	03.38			
44	04.19			
46	04.98			
48	05.80			
50	06.60			
52	07.42			
54	08.31			
56	09.13			
58	10.02			
60	10.92			

* Indicates blended or weak lines.

branches (see above). Hence this band has been re-analyzed, assuming that it also is of the type ${}^1\Sigma^+{}_u-{}^1\Sigma^+{}_g$ and that the apparent Q branch is simply the overlapping head of another band. The new analysis gives (see below) Δ_2F'' values which are the same as those of λ3501 and λ3535, and hence is probably correct.

The CS_2 molecule is well known to be linear in its normal state. The rotational term values should then be given by the formula

$$E/hc=\text{const.}+BJ(J+1)+DJ^2(J+1)^2, \quad (1)$$

where $B=h/8\pi^2Ic$ and D is the centrifugal expansion term.

Mulliken[16] has suggested that CS_2 is triangular in the excited electronic state of the bands discussed here. The molecule then becomes an asymmetrical top. If, however, the apex angle 2α is not too small, the rotational term formula can be expanded in an expression very similar to that of a symmetrical top with a symmetry axis parallel to the line joining the two sulphur atoms and with angular momentum $Kh/2\pi$ around this axis. For $K=0$ the terms are given by

$$E/hc=\text{const.}+BJ(J+1)\\ -(D+S)J^2(J+1)^2+\cdots, \quad (2)$$

where $B=h/16\pi^2c(1/I_C+1/I_B)$, and where I_C and I_B are the largest and the middle moment of inertia. The coefficient D (centrifugal expansion parameter) is extremely complicated for the asymmetrical top and cannot be evaluated here. The coefficient S may be considered as a parameter giving the deviations of the energy of a rigid asymmetrical top from that given by the usual symmetrical top formula. By using Eq. (10) of Wang's[17] expression for the energy of an asymmetrical top, and by making the approximation that the large moment of inertia is equal to the middle moment of inertia, S can be shown to be

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[16] R. S. Mulliken, J. Chem. Phys. **3**, 720 (1935).

[17] S. C. Wang, Phys. Rev. **34**, 243 (1929).

(for $K=0$):

$$S=\frac{h\mu^3 \cot^6\alpha}{2048 I_C m^3 \pi^2 c}, \tag{2a}$$

where α is the half-apex angle; $\mu=2mM/2m+M$, where m = atomic weight of sulphur and M the atomic weight of carbon; I_C is the large moment of inertia.

Referring to Eqs. (1) and (2), it is seen that the forms of the expression for E/hc are essentially the same (for $K=0$) whether the molecule is linear or bent in the upper state. It seems reasonable to assume[18] that the selection rules $\Delta J=\pm 1$, for $\Delta K=0$, also hold. Hence the usual procedure for the evaluation of rotational constants for linear or diatomic molecules may be followed. Further, in this case it is convenient to adopt the conventional symbols for the vibronic states of a linear molecule for the upper state designations, even though the molecule may be bent in these states.

The following combination relations were used to evaluate the molecular constants:

$$F'(J+1)-F'(J-1)\equiv\Delta_2F'(J) = R(J)-P(J). \tag{3a}$$

$$F''(J+2)-F''(J)\equiv\Delta_2F''(J-1) = R(J)-P(J+2). \tag{3b}$$

The values of $\Delta_2F'(J)$ and $\Delta_2F''(J+1)$ obtained from six measured bands are listed in the tables. They are related to the coefficients B, D, and S in the following manner:

$$\Delta_2F''(J+1)=4B''(J-\tfrac{1}{2})-8D''(J-\tfrac{1}{2})^3. \tag{4a}$$

$$\Delta_2F'(J)=4B'(J+\tfrac{1}{2})-8(D'+S)(J+\tfrac{1}{2})^3. \tag{4b}$$

D for the linear molecule has been shown by Shaffer[19] to be of the same form as for a diatomic molecule, namely:

$$D=4B^3/\nu_1^2 \tag{5}$$

where B is the coefficient in (1) and ν_1 is the totally symmetrical normal frequency of the molecule. From (5) with $B''=0.109$ cm^{-1} (see below) and $\nu_1=655$ cm^{-1}, D'' is found to be 1.21×10^{-8} cm^{-1}. D' is not known, but even if it were ten times D'', which seems a safe upper limit, terms in D in Eqs. (4a) and (4b) would be negligible up to $J=30$. Substitution of numerical magnitudes in Eq. (2a) shows that, even if the apex angle is as small as 125°, the term in S in Eq. (4a) may be neglected, compared with errors of measurement, for J less than 25.

The B values were obtained, by use of Eqs. (4), from the Δ_2F values. Because of blending near the head of the P branch, the Δ_2F values extend only up to J values of 20 or 30, although R lines can be extended up to $J=70$ in some cases. Each B value listed in Table VII represents the weighted mean of all the separately calculated B values for the state. The probable error was calculated from the usual statistical formula for a small number of samples.

The moment of inertia, I'', and the carbon-sulphur distance, r'', given in Table VII were calculated in the usual manner for the lower states, in which the molecule is linear. It seems quite certain (see below) that the bands at λ3535, λ3501, and λ3468 come from the vibrationless state. The corresponding value $r_0''=1.548$A (see Table VII) may be compared with $r_0''=1.54\pm0.03$A given by electron diffraction experiments.[20]

I', calculated in the same manner as I'', is an effective moment of inertia as is shown in the following formula (see Eq. (2)):

$$(1/I')=1/2(1/I_C+1/I_B).$$

The moments of inertia and r' could be calculated from I' if the apex angle were known. For example, if the apex angle is 180°, r' for λ3501 is 1.522A, while if 2α is 125°, r' is 1.735A. The fact that I' is slightly smaller than I'' may be taken as evidence that the molecule is bent in the

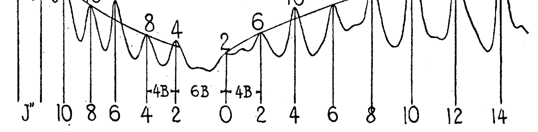

FIG. 1. A microphotometer trace of the origin of the band at λ3501. The numbers above each peak are proportional to the intensities calculated from the formula $I \propto (J'+J''+1)$.

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[18] R. S. Mulliken, Phys. Rev. **60**, 506 (1941) (this issue, following paper).

[19] W. H. Shaffer, unpublished work.

[20] P. P. Debye, Physik. Zeits. **40**, 404 (1939).

TABLE VII. *Summary of results of rotational analyses.*

BANDS	B (cm^{-1})	I (g cm$^2\times10^{40}$)	r in A	STATE
		Lower States		
λλ3468, 3501, 3535	0.1092 ± 0.0001	253.2	1.548	$^1\Sigma_g{}^+$
λλ3601, 3637, 3673	0.1096 ± 0.0001	252.3	1.545	$^1\Sigma_g{}^+$
		Upper States		
λ3673	0.1116 ± 0.0001	247.7		$^1\Sigma_u{}^+$
λλ3637, 3535	0.1124 ± 0.0002	245.9		$^1\Sigma_u{}^+$
λλ3601, 3501 (corrected for perturbation)	0.1121 ± 0.0001	246.6		$^1\Sigma_u{}^+$
perturbing state of λλ3501, 3601	0.1138 ± 0.0002	242.9		$^1\Pi_u$
λ3468	0.1117 ± 0.0002	247.4		$^1\Sigma_u{}^+$

TABLE VIII. *Verification of some combination relations.*

J	$R_{3501}(J)$ $-R_{3601}(J)$	$R_{3535}(J)$ $-R_{3637}(J)$	DIFFERENCE	$R_{3501}(J)$ $-R_{3535}(J)$	$R_{3601}(J)$ $-R_{3637}(J)$	DIFFERENCE
4	801.88	801.81	0.07	275.05	274.98	0.07
12	801.94	801.89	0.05	274.98	274.93	0.05
16	801.98	801.93	0.05	274.95	274.90	0.05
30	802.20	802.13	0.07	274.63	274.56	0.07
38	802.42	802.34	0.08	274.36	274.28	0.08
50	802.82	802.76	0.06	273.62	273.56	0.06

upper state. For a linear molecule one would expect $r'>r''$, since the excited electron in all probability goes to an anti-bonding state[16] and this requires $I'>I''$. However, if the molecule is bent, the observed $I'<I''$ is possible even if $r'>r''$.

As can be seen in Tables I–VI, most of the P branches are unresolved beyond $J=24$, so it is not possible to form combination differences involving lines of higher J value. If the P branch were resolved to $J=40$ or 50, it would be possible to form combination differences which would depend appreciably on the J^3 terms. According to Eq. (4b) the coefficient of $(J+\frac{1}{2})^3$ can be expressed as a function of the apex angle by using the results of Shaffer and Nielsen.[21] Hence, if combination differences for high enough J values were available, the apex angle might be determined. An attempt is being made to obtain some information from the R branch alone for which lines with much higher J values can be observed.

VIBRATIONAL ANALYSIS

Tables I–VI show that many of the bands have, within experimental error, identical Δ_2F values and, therefore, have states in common. The following agreements are found: (a) The Δ_2F' values are the same for λ3501 and λ3601. This is confirmed by an identical perturbation in these two bands (see below). (b) The Δ_2F' values are the same for λ3535 and λ3637. (c) The Δ_2F'' values are the same for λ3601, λ3637, and λ3673. (d) The Δ_2F'' values are the same for λ3501, λ3468, and λ3535. The following combination relations must *also* hold if some of the foregoing Δ_2F agreements are correct:

$$R_{3501}(J)-R_{3535}(J)=R_{3601}(J)-R_{3637}(J)$$
$$=F_B'(J+1)-F_A'(J+1),$$

where A and B refer to two of the upper state vibrational levels. Also,

$$R_{3501}(J)-R_{3601}(J)=R_{3535}(J)-R_{3637}(J)$$
$$=F_B''(J)-F_A''(J).$$

It will be noted in Table VIII, which was made from a few lines chosen at random, that the agreement predicted by the above combination relations is fulfilled except for one thing, namely, in each set the $R_{3501}(J)-R_{\text{other}}(J)$ are all higher by nearly a constant amount, $0.05-0.08$ cm^{-1}, than the $R_{\text{other}}(J)-R_{3637}(J)$. This can be reasonably explained by errors in the absolute

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[21] W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

values of the wave-lengths which are unavoidable because of an insufficient number of wave-length standards in this spectral region.

The bands at λ3501 and λ3601, which have been shown above to have a common upper state, have their origins separated by 801.89 cm^{-1}. A consideration of the normal state fundamental vibrations, $\nu_1 = 655$ cm^{-1}, $\nu_2 = 397$ cm^{-1}, $\nu_3 = 1523$ cm^{-1}, shows that the only reasonable explanation of the above separation is that 801.89 $cm^{-1} = 2\nu_2''$. The fact that $2\nu_2$ obtained here is somewhat more than twice the value of ν_2 obtained from Raman spectra data may be explained by an expected vibrational perturbation of $2\nu_2$ by ν_1, analogous to the well-known perturbation in CO_2.[22] Also ν_2 for liquid CS_2, which was used in obtaining the Raman spectra, may be different from the vapor. It is interesting to note that the B value for the level $2\nu_2$ is greater than for the ground level (cf. Table VII). The same relation has been found in CO_2. It is just what would be expected for a bending vibration of a linear molecule.

The bands at λ3468, λ3501, and λ3535, which have a common lower state, as is shown above, form a progression whose difference is about 270 cm^{-1}. Similarly, the bands at λ3637, λ3673, and λ3601 form another progression whose difference is also about 270 cm^{-1} (see Table IX). This frequency has been noted by Wilson,[7] Watson and Parker,[9] and recently by Kusch and Loomis.[11] The latter using both absorption and magnetic rotation data reported four progressions, one of which was found to fit partially with the present scheme. The agreement is not exact since Kusch and Loomis' measurements were made on the band heads while the present work lists the band origins. Band head measurements are not given in the tables here because higher resolution shows that some of the bands do not converge to a head. A comparison of the present results with those of Kusch and Loomis is given in Table IX. It will be noted that the inclusion of 27,467.1 and 27,741 in the Kusch and Loomis progression disagrees with the present work.

Kusch and Loomis[11] have suggested that the 270 cm^{-1} vibration is probably ν_1'. However, intensity measurements made by varying the vapor pressure in the tube show that the bands in the $\nu_2'' = 0$ progression are about 5 times as strong as those in the $\nu_2'' = 2$ progression, whereas the Boltzmann factor would predict that the $\nu_2'' = 0$ progression should be about 50 instead of 5 times stronger. Obviously, the bands of the $\nu_2'' = 2$ progression must have a higher transition probability. It is likely, therefore, that it is the ν_2' vibration of a bent molecule which is excited. Hence it is concluded that ν_2' is about 270 cm^{-1}.

In order to ascertain if the lowest of the observed vibrational states is the normal state, a search was made for bands approximately 800 cm^{-1} to the violet of the bands at λ3501, λ3535, and λ3468. One fairly intense band was found 790 cm^{-1} from λ3501, but it does not show the characteristic perturbation which it should have if its upper state were in common with λ3501 (see below). No other possibilities were found. Hence it is fairly certain that the lowest observed state is the normal state.

BAND PERTURBATIONS

The bands at λ3501 and λ3601 show a perturbation which is the same in both bands. The maximum perturbation occurs at the eleventh line of both the P and R branches. In view of the J numbering established in Fig. 1 and given in Table II, this shows that it is the upper state

TABLE IX. *A comparison of a progression given by Kusch and Loomis with those of the present work.*

KUSCH AND LOOMIS*	$v_2'' = 0$ PROGRESSION† ‡		$v_2'' = 2$ PROGRESSION
27,467.1 (4)			
273.9			
27,741			
246.1			
27,987.1 (4)	27,987.1 KL (6)	*797*	27,190.08 (2)
282.8	*286.6*		*281.88*
28,269.9 (7)	28,273.74 (7)	*801.78*	27,471.96 (2)
273.6	*275.09*		*274.98*
28,543.5 (10)	28,548.83 (10)	*801.89*	27,746.94 (3)
272.3	*267.52*		
28,815.8 (8)	28,816.35 (10)		
265.1	*264.6*		
29,080.9 (10)	29,080.9 KL (10)		
255.7	*255.7*		
29,336.6 (8)	29,336.6 KL (8)		
268.7	*268.7*		
29,605.3 (8)	29,605.3 KL (7)		

* Data taken from Kusch and Loomis.

† Frequencies designated KL taken from column one; note that these refer to heads.

‡ Absorption intensities, determined from a microphotometer trace, are given in parentheses.

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[22] G. Placzek, *Handbuch der Radiologie*, Vol. 6, Part 2, p. 328.

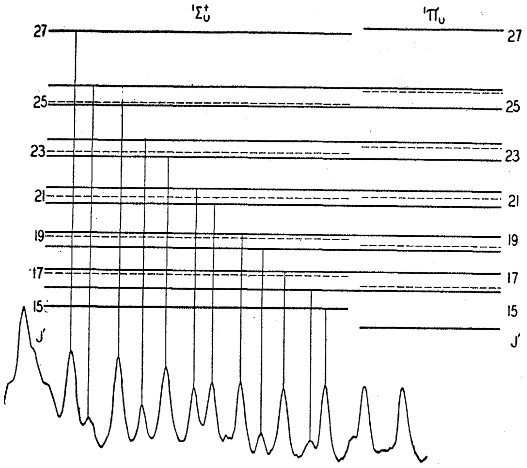

FIG. 2. The analysis of the perturbation in λ3501. The broken lines represent the unperturbed levels. The perturbed $^1\Sigma^+{}_u$ and $^1\Pi_u$ levels are connected to indicate a mixing of the wave functions of the two states. The curve given below is a reproduction of a microphotometer trace of the band at λ3501. It will be noted that the stronger component of each pair of lines comes from the level which is closest to the unperturbed $^1\Sigma^+{}_u$ level.

which is common to both. Also the Δ_2F' values for the two bands are found to be the same (see above). This perturbation must be caused by a neighboring state whose rotational levels have approximately the same energy as the observed state, and in addition satisfy the Kronig rules for perturbations. These state that only levels of identical rigorous symmetry type (+ or −, *s* or *a*) and equal J can perturb one another. For a linear or triangular CS_2 molecule which is not too much bent, $\Delta K=0, \pm 1$ may be expected.[23]

If we let T_1 and T_2 be the actual term values for any J value of the perturbed and perturbing states, and $T_1{}^0$ and $T_2{}^0$ be the values they would have if they had not perturbed each other, we may write:

$$T_1{}^0=A_1+B_1J(J+1)-\cdots,$$
$$T_2{}^0=A_2+B_2J(J+1)-\cdots.$$

Following Dieke's discussion for diatomic molecules[24] let us define δ, a, and b as follows:

$$\delta\equiv T_2{}^0-T_1{}^0=(A_2-A_1)+(B_2-B_1)J(J+1)\equiv a+bJ(J+1). \quad (6)$$

The perturbed levels T_2 and T_1 are given by:

$$T_2,\, T_1=\tfrac{1}{2}(T_2{}^0-T_1{}^0)\pm[S_{12}{}^2+\delta^2/4]^{\frac{1}{2}}. \quad (7)$$

For a perturbation of class A, ($\Delta\Lambda=\pm 1$ for the diatomic case)

$$S_{12}{}^2=\alpha^2J(J+1), \quad (7a)$$

while for class B perturbations S_{12} is independent of the J value. The + sign goes with T_2 or T_1 according as δ is positive or negative. The sign of δ reverses as one goes through the maximum of the perturbation. Extra lines in the band involve the T_2 levels, while the regular or main lines involve the T_1 levels. As can be seen from Eq. (7), the interval from any main line to the corresponding extra line is

$$|T_2-T_1|\equiv\Delta\nu=(4S_{12}{}^2+\delta^2)^{\frac{1}{2}}. \quad (8)$$

Intensities of the main lines and extra lines may be calculated in the usual manner. Letting I_1 be the intensity of the main line arising from the transition to the T_1 level and I_2 be the intensity of the extra line arising from the transition to the T_2 level, it is found that

$$I_1/I_2=(\Delta\nu+\delta)/(\Delta\nu-\delta). \quad (9)$$

The microphotometer trace in Fig. 2 of the perturbed part of the R branch of λ3501 shows that the lines at $J'=21$, which are separated by 0.30 ± 0.005 cm^{-1}, have practically equal intensity. Hence, from Eq. (9), δ must be nearly zero for these lines. However, the lines at $J'=19$, whose intensities are in the ratio 2 : 1, are also separated by 0.30 ± 0.01 cm^{-1}. From this intensity ratio Eq. (9) shows that, in this case, δ must be about 0.1 cm^{-1}. Hence it is seen from Eq. (8) that S_{12} is not constant, which means that these perturbations most likely are of the class A type, i.e., the $^1\Sigma^+{}_u$ state is perturbed by a $^1\Pi_u$ state. It must be pointed out, however, that the above reasoning depends rather critically on the measured value of $\Delta\nu$. For example if the lines at $J'=19$ are separated by 0.32 cm^{-1} instead of 0.30 cm^{-1}, the class B equations are satisfied. However, it is found that these equations then give poor agreement for the perturbations at other J' values, so it seems safe to conclude that the perturbation is of class A.

From a careful study of the five measured $\Delta\nu$'s (for $J'=17$, 19, 21, 23, 25), α^2 and $\delta(J)$ of (7) have been determined. From Eq. (8), α^2 was found to be 4.87×10^{-5} cm^{-1}. The numerical

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[23] R. S. Mulliken, Phys. Rev., **59**, 873 (1941).

[24] G. H. Dieke, Phys. Rev. **47**, 870 (1935).

form for Eq. (6) was found to be

$$\delta = -0.712 + 0.00157J(J+1). \qquad (10)$$

Equations (7a) and (8) with the above constants yield good agreement with observation for the five $\Delta\nu$'s. Also, the intensities calculated from (9) agree quite well with those measured from the microphotometer trace. The B value for the perturbing $^1\Pi_u$ state as given by Eq. (6), and the constants in (10), is 0.1138 cm^{-1}.

It is also possible to compute, with the aid of the above constants, the deviations ϵ between the actual and the unperturbed positions of the main lines from the relation

$$T_1 - T_1{}^0 \equiv \epsilon = \pm\tfrac{1}{2}(|\Delta\nu| - |\delta|), \qquad (11)$$

with the sign of ϵ always opposite to that of δ. (The same formula but with opposite choice of sign also holds for $T_2 - T_2{}^0$ for the "extra" lines.) The theoretical ϵ's, computed according to Eq. (11), in which δ from Eq. (10) and Eqs. (7a), (8) with $\alpha^2 = 4.87\times10^{-5}$ are used, are shown by the continuous curves in Fig. 3. The "observed" points in Fig. 3 represent the deviations of the observed lines from the quadratic,

$$\nu = 28{,}548.83 + 0.2211M + 0.00278M^2, \qquad (12)$$

where $M = J''+1$ for the R branch and $M = -J''$ for the P branch. This equation was obtained by fitting a few of the low numbered P and R lines, and also the midpoint of the two strongly perturbed R lines at $J' = 21$, to a quadratic of this form. It will be noted that the agreement of observed and calculated ϵ's is good for J' values up to the maximum of the perturbation. The increasing deviations beyond this point are apparently due to the fact that the quadratic Eq. (12) is a poor approximation for high J values, where J^3 and J^4 terms evidently become important. Similar large deviations from a quadratic form are also found in some of the other bands where no perturbation is present.

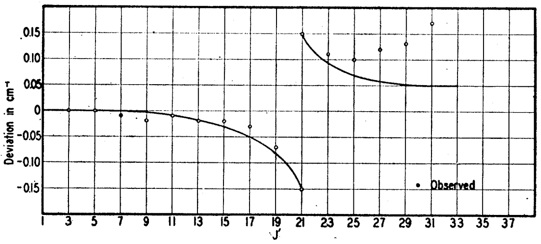

FIG. 3. The perturbation in λ3501. The deviations (calculated minus observed) of the observed lines from the positions predicted by Eq. (12) are shown, for the R branch, by the circles. The continuous curves give the *theoretical* deviations ϵ computed from Eq. (11), with δ from Eq. (10) and by using Eqs. (7a), (8) with $\alpha^2 = 4.87\times10^{-5}$. It will be noted that, according to the theoretical curves, a constant deviation of 0.05 cm^{-1} should remain after the perturbation. Actually, larger deviations are observed.

In conclusion, I wish to express my gratitude to Professor R. S. Mulliken, who suggested this problem and whose many suggestions and criticisms have proved invaluable. I also wish to thank Dr. H. G. Beutler for his generous assistance with the experimental problems.