High Resolution Investigation of Some Infrared Bands of Carbon Disulfide

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Absorption bands of carbon disulfide have been measured with high resolution in the regions of 2180 and 2900 cm^{-1}. Bands have been observed due to several isotopic species. By combining the observed bands with those previously measured, a set of harmonicity constants for $^{12}C^{32}S_2$ has been obtained in cm^{-1} as follows: X_{11}, −1.070; X_{22}, 0.126; X_{33}, −6.54; X_{12}, 0.860; X_{13}, −7.86; X_{23}, −6.45; g_{22}, 0.656.

1. Introduction

The vibrational spectrum of carbon disulfide has already been extensively studied; the most recent work (in which earlier references are listed) is that of Stoicheff [1] [2] on the gaseous Raman spectrum, Schrotter [2] on the liquid Raman spectrum, and the infrared investigations by Allen, Plyler, and Blaine [3], Guenther, Wiggins, and Rank [4], and Guenther [5].

The spectra of CS_2 are of interest because (a) it is possible to observe the frequencies due to several isotopic species [$^{12}C^{32}S_2$, ~90%; $^{12}C^{32}S^{34}S$, ~8%; $^{13}C^{32}S_2$ ~1%]; (b) with sufficiently high resolution the l-type splitting in the $\pi-\pi$ bands can be obtained; in the symmetrical isotopic species alternate lines of the $\pi^+(\pi_c)$ and $\pi^-(\pi_d)$ subbands are missing; the consequent staggering of the rotational lines can be measured, though the actual separation of the doublets (such as would occur in the nonsymmetrical species) would need much greater resolving power; this gives an experimental value of the splitting constant q_H; (c) Fermi resonance occurs between levels such as 100 and 02^{0}0; from the experimental data some information about the positions of the unperturbed levels and the value of the interaction energy can be estimated.

The main purpose of the present work is to study a number of $\pi-\pi$ bands and their l-type splitting. The three combination bands of $^{12}C^{32}S_2$, $\nu_1+\nu_3$, $2\nu_1+\nu_3$, and $\nu_1+2\nu_2^2+\nu_3$, previously analyzed (see ref. [3]) were reinvestigated and their assignments checked, as there had been some criticism (see ref. [1]) of the derived rotational constants. The corresponding hot bands 11^{1}1−01^{1}0, 21^{1}1−01^{1}0, and 13^{1}1−01^{1}0 were identified and analyzed, and gave values of the splitting constant q_H and the rotational

constant α_l. One very weak band due to $^{13}C^{32}S_2$ was also successfully investigated.

Using the previously published work and the present analyses together with some unpublished results kindly provided by Dr. G. R. Wilkinson [6], it was possible to calculate a complete set of anharmonic constants which appear to be more reliable than those already available. There are now sufficient data to provide some checks on their values corrected for Fermi resonance.

2. Experimental Method

The infrared spectrum of CS_2 was measured in two regions by the use of a high resolution grating spectrometer [7]. Precise values of the positions of the individual lines were obtained by using the fringe system of a Fabry-Perot interferometer for calibration [8].

A sample of reagent grade carbon disulfide was obtained from the Allied Chemical and Dye Corporation. The only impurity observed in the infrared spectrum was a band of low intensity at 2062 cm^{-1} which, by its spacing and position, was identified as OCS. However, no lines were observed in the two regions studied which could not be attributed to CS_2.

The region from 2165 to 2200 cm^{-1} was measured with a 7500 lines/in. grating used single pass, and a cooled lead selenide cell was used as the detector. For the region from 2165 to 2200 cm^{-1}, as shown in figure 1, a 6 m cell was used with a pressure of the CS_2 gas of 3 mm (Hg).

In the regions from 2784 to 2845 and 2940 to 2980 cm^{-1} the measurement of the spectrum was obtained with a 10,000 lines/in. grating used double pass. The detector was a cooled lead sulfide cell and a resolution of about 0.03 cm^{-1} was obtained. A 6 m cell was used with a gas pressure of CS_2 of 25 mm (Hg). An example of the spectrum in this region is shown in figure 2.
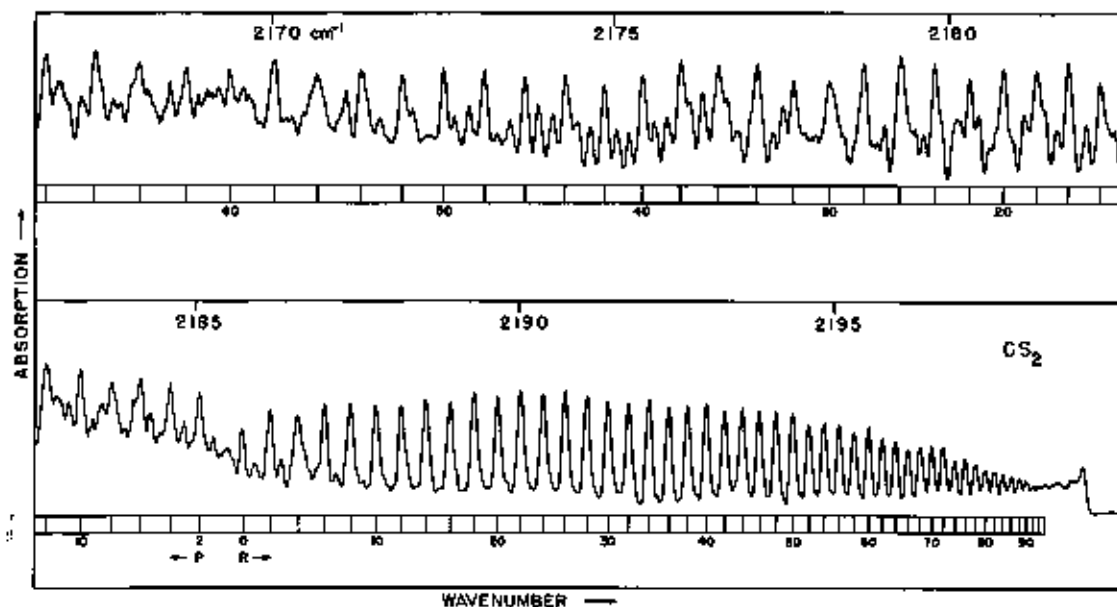

FIGURE 1. *The $\nu_1 + \nu_3$ band of CS_2 and the corresponding hot band.*

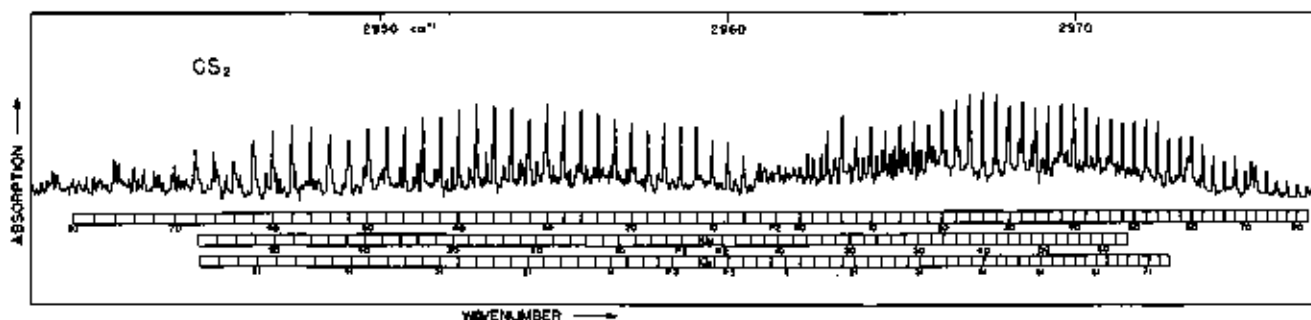The cell length was 6 m and the gas pressure was 3 mm (Hg).

FIGURE 2. *The $\nu_1 + 2\nu_2^2 + \nu_3$ band of CS_2 with the overlapping hot band $\nu_1 + 3\nu_2^1 + \nu_3 - \nu_2^1$.*

The identification of the lines is shown below the spectrum. The cell length was 6 m and the gas pressure was 25 mm (Hg).

3. Determination of Molecular Constants

In the absence of resonance, the vibrational term values of a linear triatomic molecule (with respect to the lowest vibrational state) are given by the expression:

$$G_0[v_1,v_2,v_3] = \omega_1^0 v_1 + \omega_2^0 v_2 + \omega_3^0 v_3$$
$$+ X_{11}v_1^2 + X_{22}v_2^2 + X_{33}v_3^2 + X_{12}v_1 v_2$$
$$+ X_{23}v_2 v_3 + X_{13}v_1 v_2 + g_{22}l_2^2 \quad (1)$$

where l_2 is the quantum number of the vibrational angular momentum about the symmetry axis ($l_2 = v_2, v_2-2, \ldots 1$ or 0). The rotational energy is given by:

$$F(J) = [J(J+1)]B_v - [J(J+1)]D_v \quad (2)$$

with the condition that $J \geq l_2$. For nondegenerate vibrations the positions of the lines in the P and R branches are represented by the equation:

$$\nu = \nu_0 + (B_V' + B_V'')m + (B_V' - B_V'')m^2 - (D_V' - D_V'')m^2$$
$$- 2(D_V' + D_V'')m^3 - (D_V' - D_V'')m^4 \quad (3)$$

where $m = -J$ for the P branch, and $m = J+1$ for the R branch. From eq (3) the following combination relationships are obtained:

$$\Delta_2 F''[J] = R(J-1) - P(J+1)$$
$$= [4B_V'' - 6D_V''](J+\tfrac{1}{2}) - 8D_V''(J+\tfrac{1}{2})^3 \quad (4)$$

$$R(J) + P(J) = 2\nu_0 + [2B_V' - 4D_V'] + 2[(B_V' - B_V'')$$
$$- 6D_V']J(J+1) - 2(D_V' - D_V'')J^2(J+1)^2 \quad (5)$$

$$\Delta_2 F'(J) = R(J) - P(J) = [4B_V'$$
$$- 6D_V'](J+\tfrac{1}{2}) - 8D_V'(J+\tfrac{1}{2})^3. \quad (6)$$

Previous investigations of CS_2 suggest that it is

reasonable, as a first approximation, to put $D'_V \sim D''_V \equiv D_0$, eqs (3) to (6) then simplify to:

$$\nu = \nu_0 + (B'_V + B''_V)m + (B'_V - B''_V)m^2 - 4D_0m^2 \quad (7)$$

$$\Delta_2F''(J) = B''_V[4J+2] - 4D_0[2J+1][J^2+J+1] \quad (8)$$

$$R(J) + P(J) = 2\nu_0 + 2B'_V + 2[B'_V - B''_V]J(J+1)$$
$$- 4D_0[3J^2 + 3J + 1] \quad (9)$$

$$\Delta_2F'(J) = B'_V[4J+2] - 4D_0[2J+1][J^2+J+1]. \quad (10)$$

For the symmetrical isotopic species $^{12}C^{32}S_2$ and $^{12}C^{32}S_2$ only (4), (5), and (6) or (8), (9), and (10) can be used, since the levels corresponding to odd J-values are unpopulated.

The hot bands analyzed in the present work are all of the $\pi - \pi$ type with $l_2 = 1$ in both the upper and lower states. The rotational levels are split, the l-type doubling, and the resultant absorption corresponds to two subbands which are conventionally labeled $\pi^+(\pi_c)$ and $\pi^-(\pi_d)$, each of which has its own set of molecular constants. Assuming that the centrifugal distortion constants, D_0, are the same in both states the lines of either subband are given by the formula:

$$\nu = \nu_0 - (B'_V - B''_V) + (B'_V + B''_V]m$$
$$+ (B'_V - B''_V)m^2 - 4D_0m^3 \quad (11)$$

from which the following approximate combination relationships [corresponding to (8), (9), and (10)] are derived:

$$\Delta_2F''(J) \equiv R(J-1) - P(J+1)$$
$$= B''_V[4J+2] - 4D_0J(J+1)(2J+1) \quad (12)$$

$$R(J) + P(J) = 2\nu_0 + 2B''_V$$
$$+ 2[B'_V - B''_V]J(J+1) - 12D_0J(J+1) \quad (13)$$

$$\Delta_2F'(J) \equiv R(J) - P(J)$$
$$= B'_V[4J+2] - 4D_0J(J+1)(2J+1). \quad (14)$$

In the P and R branches the transitions occur between $\pi^+(\pi_c)$ or $\pi^-(\pi_d)$ levels in both upper and lower states giving the two subbands. The weak Q branch arises from $\pi^+(\pi_c)$ (upper) $-\pi^-(\pi_d)$ (lower) transitions or vice versa. Rotational lines corresponding to $J < 1$ (i.e., $Q(0)$, $R(0)$, and $P(1)$ in the present instance) are absent. For the symmetrical isotopic species (only bands due to $^{12}C^{32}S_2$ were analyzed) alternate lines of each subband are missing (J odd for $\pi^-(\pi_d)$, J even for $\pi^+(\pi_c)$) giving a characteristic staggering of the lines of the complete band. Were the Q-branch resolvable a similar staggering of the lines would be observed. The resolution available is inadequate to separate the doublets which should be observed for such unsymmetrical species as $^{12}C^{32}S^{34}S$.

After analysis of the data by standard methods the value of B_e (and hence r_e) can be obtained using the relationship:

$$B_V = B_e - \sum \alpha_i[V_i + d_i/2] \quad (15)$$

where d_i is the degeneracy.

Each of the rotational constants α_i can be considered to be made up from three contributions:

$$\alpha_i = \alpha_i^{(harm.)} + \alpha_i^{(anharmon.)} + \alpha_i^{(coriolis)}.$$

The relevant formulae for the linear XY_2 molecule are conveniently tabulated by Herzberg [9, p. 376].

The l-type splitting in a degenerate π vibrational state ($l_2 = 1$) is given by Nielsen [10]:

$$\Delta\nu = q_N(v_2+1)J(J+1)$$

so that

$$\Delta\nu = 2q_N J(J+1) \text{ when } v_2 = 1. \quad (16)$$

Herzberg [11] originally suggested that for such a state:

$$\Delta\nu = q_H J(J+1) \quad (17)$$

$$q_H = 2[\alpha_i^{(harm.)} + \alpha_i^{(coriolis)}] \quad (18)$$

q_H being one half of q_N (see ref. [9], p. 377-8).[3]

The general formulas for the l-type splittings of the degenerate vibrational states of any linear molecule are summarised by Nielsen. The shifts of the perturbed levels from the unperturbed values of a linear XY_2 molecule in a π state ($l_2 = 1$) with $v_2 = 1$ are:

$$\text{shift } \left.\begin{array}{c}\pi_c^+ \\ \pi_d^-\end{array}\right\} = \pm 2q^0 J(J+1) \quad (19)$$

where

$$q^0 = -B_e^2/2\omega_2[1 + 4\omega_2^2/(\omega_3^2 - \omega_2^2)]$$

(Nielsen, Amat, and Goldsmith [12]); this implies that $\Delta\nu = -4q^0J(J+1) = q_NJ(J+1)$ and the Herzberg q_H is:

$$q_H = +2B_e^2/\omega_2 + 8B_e^2\omega_2/(\omega_3^2 - \omega_2^2) \quad (20)$$

in agreement with his original suggestion.

4. Experimental Results

Three main regions of absorption of CS_2 have been investigated; the results are collected in table 1 which also includes some previously published data on $^{12}C^{32}S_2$. In the spectral range 2135 to 2199 cm^{-1} the band $\nu_1 + \nu_3$ and the corresponding hot band $11^11 - 01^10$ of $^{12}C^{32}S_2$ have been identified. Together these account for nearly all the lines observed. Those remaining are weak and may belong to the $\nu_1 + \nu_3$ band of $^{13}C^{32}S_2$, which should also fall in this region. The absorption between 2222 to 2266 cm^{-1} is due to the $2\nu_2^2 + \nu_3$ band of $^{13}C^{32}S_2$, which was analyzed without difficulty as there is little interference from other bands. The region 2784 to 2845 cm^{-1} is rather complex; it includes the $2\nu_1 + \nu_3$ band and the hot band $21^11 - 01^10$ of $^{12}C^{32}S_2$, and the $3\nu_1 + \nu_3 - \nu_1$ band of $^{12}C^{32}S_2$, all of which

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[3] The splitting constant q_B is given by $(B_V^c - B_V^d)$ [i.e., by $(B_V^c - B_V^d)$]; this notation is also used by Guenther et al., and Tidwell, Plyler, and Benedict [13] working with N_2O.

I. $^{12}C^{32}S_2$

Band	ν_0 cm⁻¹	B'' cm⁻¹	$B'-B''$ ΔB cm⁻¹	B' cm⁻¹	D'' cm⁻¹	$D'-D''$ ΔD cm⁻¹	D' cm⁻¹	$B'd^+-B'c^+$ q_B	
$\nu_1+\nu_3$	2185.492	0.10912	-8.6×10^{-4}	0.10825₂	1.38×10^{-7}	~0	1.38×10^{-7}	....	(a)
11^11-01^10 $\pi+c$ (odd)	2171.42	.10940	$-8.6_9\times10^{-4}$	.10854₁	~2×10^{-7}	~0	~2×10^{-7}	q''~1×10^{-4}	(a)
11^11-01^10 $\pi-d$ (even)	2171.42	.10950	$-8.4_9\times10^{-4}$	.10865₁	~2×10^{-7}	~0	~2×10^{-7}	q'~$1.1_5\times10^{-4}$	(a)
$2\nu_1+\nu_3$	2833.191	.109071	-1.003×10^{-3} $\pm2\times10^{-5}$	.108068	0.8×10^{-7}	$+0.118\times10^{-8}$	0.92×10^{-8}	....	(a)
21^11-01^10 $\pi+c$ (odd)	2811.350	.10940	-8.8×10^{-4}	.10851₅	~3×10^{-8}	~0	~3×10^{-8}	q''~1×10^{-4}	(a)
21^11-01^10 $\pi-d$ (even)	2811.350	.10960	$-8.7_6\times10^{-4}$	.10862₃	~3×10^{-8}	~0	~3×10^{-8}	q'~1.1×10^{-4}	(a)
$\nu_1+2\nu_2^0+\nu_3$	2961.791 ±0.0016	.109040 $\pm1\times10^{-5}$	-4.562×10^{-4}	.108584	0.88×10^{-8} $\pm.134\times10^{-8}$	$<5\times10^{-11}$	0.88×10^{-8} $\pm.134\times10^{-8}$	....	(a)
13^11-01^10 $\pi+c$ (odd)	2959.117	0.10940	-5.2×10^{-4}	.10888	~4×10^{-8}	~0	~4×10^{-8}	q''~1×10^{-4}	(a)
13^11-01^10 $\pi-d$ (even)	2959.117	.10950	-4.4×10^{-4}	.10906	~3×10^{-8}	~0	~3×10^{-8}	q'~1.8×10^{-4}	(a)
$2\nu_3$	4566.810	.109099 $\pm2.3\times10^{-5}$	2.133×10^{-5}	.109096 $\pm2\times10^{-5}$	1.05×10^{-8} $\pm0.36\times10^{-8}$	$+0.03\times10^{-8}$	1.08×10^{-8} $\pm0.33\times10^{-8}$	....	(b)
01^13-01^10 $\pi+c$ (odd)	4547.454	0.109321	2.126×10^{-5}	0.107195	1.1×10^{-8}	~0	1.1×10^{-8}	$q''=6.7\times10^{-7}$	(b)
01^13-01^10 $\pi-d$ (even)	4547.454	.109389	2.129×10^{-5}	.107259	1.1×10^{-8}	~0	1.1×10^{-8}	$q''=6.4\times10^{-7}$	(b)
Pure Rotation (Raman)	....	.10910 $\pm6\times10^{-5}$	....	....	1.0×10^{-7}	....	....	....	(c)

II. $^{13}C^{32}S_2$

Band	ν_0 cm⁻¹	B'' cm⁻¹	$B'-B''$ ΔB cm⁻¹	B' cm⁻¹	D'' cm⁻¹	$D'-D''$ ΔD cm⁻¹	D' cm⁻¹	$B'd^+-B'c^+$ q_B	
$2\nu_2^0+\nu_3$	2250.15₁	0.10908	-3.48×10^{-4}	.10873	1.08×10^{-7}	~0	1.08×10^{-7}	....	(a)

a Present work.
b A. H. Guenther, T. A. Wiggins, and D. H. Rank, J. Chem. Phys. 28, 682-7 (1958).
c B. P. Stoicheff, Can. J. Phys. 36, 218-230 (1958).

overlap. These account for nearly all the prominent lines, though some weak lines are also observed which were not assigned. The absorption in the region 2931 to 2999 cm⁻¹ corresponds to the $\nu_1+2\nu_2^0+\nu_3$ band and the hot band 13^11-01^10 of $^{12}C^{32}S_2$, with the band $2\nu_1+2\nu_2+\nu_3-\nu_1$ of $^{13}C^{32}S_2$ at the lower end of the range. Most of the observed lines have been assigned except rather weak ones at lower frequencies.

The data presented in table 1 show that there is reasonable agreement between the values of the ground state constant B_{000} of $^{12}C^{32}S_2$ as determined from four infrared bands and the pure rotational Raman spectrum. In particular the values derived from the revised analyses of $\nu_1+\nu_3$, $2\nu_1+\nu_3$, and $\nu_1+2\nu_2^0+\nu_3$ now fall in line with those of other investigators, though perhaps 0.10904 cm⁻¹ for the latter band is rather small. It appears that 0.10910 cm⁻¹ is a reliable value for B_{000}; this makes the C–S distance $r_0=1.5545$ A as proposed previously [Guenther et al.]. The calculated value of D_{000} $[4B_0^3/\omega_3^2]$ is 1.20×10^{-8} cm⁻¹ [Guenther et al., Stoicheff]; the experimental determinations are scattered about this figure. From these, a value of $D_{000}=1.02\pm0.3\times10^{-8}$ cm⁻¹ would seem probable.

The situation is less satisfactory for the 01^10 levels, which have also been observed in four different bands. The present results (three bands) are con-

sistent among themselves [though the B'' values from the 21^11-01^10, and 13^11-01^10 bands were used effectively to analyze the 11^11-01^10 band, for which the experimental data were less precise], but they are larger than those derived from the 01^13-01^10 band by Guenther et al., and these constants are probably not so accurate. Further, the results obtained for D_{000} in the present analyses are somewhat larger than would be expected.

The present values of the splitting constants q_B'' and q_B' are all about 1×10^{-4} cm⁻¹ for levels in which $l_2=v_2=1$. This is of the right order of magnitude, the calculated value being $q_B=7.74\times10^{-5}$ cm⁻¹ (using $\nu_3=1535.35$ cm⁻¹) and those previously published being 6.4 and 6.7×10^{-5} cm⁻¹ (Guenther et al.). The theoretical treatment suggests that all π states $(l_3=1)$ with $\nu_2=1$ should have the same q_B and this appears to be the case. The only other level observed (13^11) has a larger value for this constant. It is about twice as large as the q_B for a $\nu_2=1$ and $l_2=1$ state as would be expected from eq (16).

The values of α_i for $^{12}C^{32}S_2$ are obtained using eq (15); those already available are $\alpha_1=1.55\times10^{-4}$ cm⁻¹ [Stoicheff], and $\alpha_3=7.11\times10^{-4}$ cm⁻¹ [Guenther et al.]. The experimental figure for $\alpha_1+\alpha_3$, 8.65×10^{-4} cm, derived from ΔB of $\nu_1+\nu_3$, is in excellent agreement with that calculated from the published values,

8.66×10^{-4} cm^{-1}. For $2\nu_1 + \nu_3$, the observed figure for $2\alpha_1 + \alpha_3$ is 1.035×10^{-4} cm^{-1}, compared with the calculated value of 1.021×10^{-4} cm^{-1}; the agreement in this case is adequate. For the $\nu_1 + 2\nu_2^0 + \nu_3$ band ΔB is 4.562×10^{-4} cm^{-1}, so that using the published values of α_1 and α_3, α_2^0 comes out at -2.05×10^{-4} cm^{-1}; this is in good agreement with the result derived by Wilkinson from unpublished observations. It would seem therefore that the present figure of 4.562×10^{-4} for $\alpha_1 + 2\alpha_2^0 + \alpha_3$ can be confidently used to calculate B_e, which with $B_0 = 0.10910$ cm^{-1}, is 0.10932_8 cm^{-1}. The corresponding value for r_e is 1.5529 A.

The results of the calculations for the α_i derived from observations on the hot bands are shown in table 2, which includes those previously published. The present measurements for these bands are less precise and the agreement is probably as good as can be expected.

Table 1 also includes the results of the analyses of one very weak band of the isotopic species $^{13}C^{32}S_2$. The value of the ground state constant B_{000} is 0.1090 cm^{-1}, which hardly differs from that of $^{12}C^{32}S_2$, as would be expected; the corresponding value of r_0 is 1.554_0 A. Isotopic substitution has not altered the equilibrium C–S internuclear distance [compare the results of Guenther (see ref [5]), on the species $^{12}C^{32}S^{34}S$].

The anharmonicity constants derived from eq (1) were calculated for $^{12}C^{32}S_2$ using the ten frequencies shown by (b) in table 3. The five Raman frequencies are the same as those used by Stoicheff (see ref [1]), and so the corresponding anharmonicity constants are identical. The five infrared frequencies were chosen to give the best all round agreement between the observed and calculated figures for the fourteen remaining bands. It is unfortunate that there is no recent determination available for ν_2^1, which must be used to calculate g_{22}. The values computed for the constants are (in cm^{-1}):

$$\omega_1^0 = 659.23; \quad X_{11} = -1.25; \quad X_{12} = -7.74;$$

$$\omega_2^0 = 396.55; \quad X_{22} = +2.25; \quad X_{23} = -6.44;$$

$$\omega_3^0 = 1541.82; \quad X_{33} = -6.52; \quad X_{13} = -7.79; \quad g_{22} = -2.00,$$

where only the values of X_{23} and X_{33} are not affected by Fermi resonance.

Table 3 shows that the differences between the observed and calculated frequencies are not too serious except for the $\nu_1 + 2\nu_2^0 + \nu_3$ and $13^11 - 01^10$ bands. The other discrepancies are explicable either because Q branch measurements were used for most of the Raman lines, or more probably because of Fermi resonance between many of the levels.

Fermi resonance occurs between many of the vibrational levels of CS_2 and has already been discussed in detail by Stoicheff (1958). He used the frequencies denoted by c in table 3 to evaluate ω_1^0, ω_2^0, x_{11}, x_{22}, x_{12}, g_{22}, together with δ (the separation of the unperturbed levels 100 and 02^{0}0), and W, the matrix element, of the cubic term α_{122} in the potential energy, which gives rise to the perturba-

tion between the 100, and 02^00 levels. The sign of W was found from the experimental value of the rotational constant α_2. Using the same data and methods it seems that slight modifications are needed for some of the constants (table 4).

TABLE 4. *Frequencies for infinitesimal amplitudes and vibrational constants of $^{12}C\ ^{32}S_2$ [in cm^{-1}]*

$\omega_1 = 672.88\ (671.36)$;	$\omega_1^o = 669.72\ (668.69)$;
$\omega_3 = 398.61\ (398.62)$;	$\omega_2^o = 395.97\ (395.97)$;
$\omega_3 = 1556.61\ (1651.92)$;	$\omega_3^o = 1541.89\ (1537.64)$
$x_{11} = -1.070\ (-1.05_0)$;	$x_{12} = 0.960\ (0.88_0)$;
$x_{33} = 0.126\ (0.12_0)$;	$x_{13} = -7.86\ (-4.9_0)$;
$x_{33} = -6.54\ (-3.13_0)$;	$x_{23} = -6.45\ (-6.6_7)$;
$g_{22} = 0.666\ (0.67_1)$;	$W = -36.05\ (-36.06)$;
	$\delta = 124.80\ (124.80)$.

Figures in parentheses are those calculated by Stoicheff.

The frequencies $3\nu_3$, $3\nu_3 + \nu_2^1 - \nu_2^1$ and ν_2 are used to obtain ω_3^o, x_{33} and x_{22};[4] all these are uncomplicated by Fermi resonance. Since new and improved infrared data are now available, the present values are more reliable than those listed by Stoicheff. To calculate x_{13} Stoicheff was forced to assume that the diad $(\nu_1 + \nu_3)$, $(2\nu_2^o + \nu_3)$ could be described by the same values of δ and W as ν_1 and $2\nu_2^o$. The frequency of $(2\nu_2^o + \nu_3)$ is now available, and it appears that this assumption is not correct. The value of x_{13} can be calculated directly from the sum of the two frequencies $(\nu_1 + \nu_3) + (2\nu_2^o + \nu_3) = 4510.032$ cm^{-1} and is seen to differ significantly from that proposed earlier. Table 4 also includes revised values for the frequencies at infinitesimal amplitudes.

The twelve constants in table 4 are derived from nine Raman and six infrared frequencies; of the remaining nine frequencies, only one $02^23 - 02^20$ (obs. (est.) 4528.09 cm^{-1}, calc., 4528.12 cm^{-1}) is not affected by Fermi resonance. The other eight frequencies are all members of incomplete Fermi polyads, so that it is unfortunately not possible to get any checks on the constants corrected for Fermi interaction.

The Fermi resonance between the levels ν_1 and $2\nu_2^o$ (and corresponding levels) in CS$_2$ is quite weak ($\delta = 124.80$ cm^{-1}) and is not as important as in the analogous molecule CO$_2$ (compare Courtoy [14]). Even so, the shift of the observed levels (± 9.67 cm^{-1} for $2\nu_2^o$ and ν_1) is quite large, and the calculated values of the anharmonic constants, taking the interaction into account, differ, in most cases, markedly from the uncorrected values. New observations on other frequencies and more accurate data on ν_2^1 would be most desirable to provide checks on the values of the constants listed in table 4.

5. References

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[4] In table 3 $\nu_1 + \nu_2$ was used instead of ν_1 to get these constants as at that time no figure was available for the latter frequency; the two sets of values are nearly identical.