The $3\nu_3$ Bands of Carbon Disulfide and Carbon Dioxide

Norman M. Gailar and Earle K. Plyler

The $3\nu_3$ bands of carbon disulfide and carbon dioxide are described. This band of CS_2 is complex, containing two transitions from excited states and two transitions attributed to the isotopic molecule $CS^{32}S^{34}$ in addition to the primary transition 000→003 of CS_2[1]. A multiple-reflection cell of 6-meter path length, 20-cm optics, and negligible loss of aperture is described. Molecular constants are checked for CO_2 and found for CS_2. These latter constants are $B_0=0.1089$ cm$^{-1}\pm0.0004$, $\alpha_3=0.0007$ cm$^{-1}\pm0.00003$, $X_{33}=-5.2$ cm^{-1}, and $X_{23}=-3.3$ cm^{-1}.

The infrared absorption spectrum of carbon dioxide is well known. Carbon disulfide, however, although of similar structure, has received much less study. This is probably due to the difficulty of resolving the fine structure of its spectrum, caused by the large moment of inertia of this molecule. In order to resolve the fine structure, several requirements must be met. A spectrometer capable of resolving to 1 or 2 tenths of a wave number in the region of the spectrum must be used, and a path of sufficient length to permit measurable absorption must be devised.

Both conditions being obtainable in the Radiometry laboratory of the Bureau, the $3\nu_3$ band of CS_2 has been studied, along with the analogous band of CO_2. This latter band has been observed under low resolution by Barker and Wu[1] and under higher resolution by Goldberg, Mohler, Pierce, and McMath,[2] but they did not report the band origin.

The spectrometer used was a 15,000-line-per-inch grating spectrometer with a lead-sulfide detector. This instrument, previously described,[3] was capable of resolving to better than 0.1 cm^{-1} in the 2.2-μ (CS_2) region and to better than 0.2 cm^{-1} in the 1.4-μ (CO_2) region.

A multiple-reflection absorption cell was used to obtain a long path length. In designing the cell a major consideration was to avoid the loss of aperture when small mirrors were used. The cell was designed for use in the spectral region beyond the photographic. This prevents the use of a long exposure time to compensate for any loss of aperture. In order to keep slit widths at a minimum and resolution at a maximum, the path length was kept to 6 m. With this path length it was possible to design a cell with negligible loss of aperture and still use small-diameter optics. A cell of long, variable path-length and somewhat different optics has been described by White.[4]

Figure 1 is a schematic drawing of the cell with a central ray traced through the system. The lines representing this ray are numbered according to the number of the transversal of the cell they represent. The source, S, is placed off-axis and farther from the spherical mirror, M_1, than the radius, R, of this mirror. The radius of curvature of this mirror is 102 cm, and it has a diameter of 18 cm. Light from the source follows line 1 to M_1, line 2 to mirrors M_2 and M_3, line 3 back to M_1, etc. The plane mirrors, M_2, M_3, M_4, M_5, and M_6, are so arranged as to cause the final image of the source to be focussed on the entrance slit of the spectrometer. These plane mirrors were adjusted with the aid of a photocell, assuring maximum transmission of energy. Points X and X_2 are the points where the image of the source is focussed the first and second times. M_5 is placed considerably off-axis so that M_6 can reflect the light out of the cell without intercepting light going to M_1 or M_2. At no time is the off-axis condition as great as 8°. An aluminum tube 1 m long and 20 cm inside diameter forms the body of the cell.

An original record obtained on the recorder is shown in figure 2. The water absorption bands in this region distorted the CO_2 lines, and thus the various constants could not be calculated with the utmost accuracy. Table 1 shows the wavelength and vacuum wave number of the lines of this spectrum.

TABLE 1. *Wavelengths and wave numbers of the $3\nu_3$ band of CO_2*

J	R branch		P branch	
	Wavelength	Wave number	Wavelength	Wave number
	λ	cm^{-1}	λ	cm^{-1}
0	14336.3	6973.29	.....	.....
2	14333.4	6974.80	.....	.....
4	14330.6	6976.21	14344.6	6969.36
6	14327.9	6977.53	14348.4	6967.51
8	14326.0	6978.99	14351.9	6966.81
10	14322.6	6980.06	14355.7	6963.97
12	14320.4	6981.13	14359.5	6962.12
14	14318.2	6982.20	14363.9	6960.04
16	14316.2	6983.18	14368.1	6957.69
18	14314.6	6983.96	14372.6	6955.79
20	14312.9	6984.79	14377.2	6953.55
22	14311.5	6985.47	14382.0	6951.23
24	14310.1	6986.16	14387.0	6948.82
26	14308.9	6986.74	14392.3	6946.26
28	14307.9	6987.23	14397.5	6943.75
30	14307.0	6987.67	14403.0	6941.10
32	14306.4	6987.96	14408.4	6938.49
34	.....	.....	14414.1	6935.75
36	.....	.....	14420.0	6932.91

[1] E. F. Barker and T. Y. Wu, Phys. Rev. 45, 1 (1934).
[2] L. Goldberg, O. Mohler, A. Pierce, and R. McMath, Phys. Rev. 78, 74 (1950).
[3] Earle K. Plyler and Norman Gailar, J. Research NBS 47, 248 (1951) RP2268.
[4] John U. White, J. Opt. Soc. Am. 32, 285 (1942).

In analyzing the structure of the $3\nu_3$ band of CO_2, use was made of the well-known combination differences for linear molecules [4]

$$R(J-1)-P(J+1)=4B''(J+1/2), \qquad (1)$$

$$R(J)+P(J)=2\nu_0+2B'+2(B'-B'')J(J+1). \qquad (2)$$

Here B′ is the upper and B'' the lower-state rotational constant, ν_0 the band origin, J the rotational quantum number of the lower state of the transition, and P and R are the short and long wave-number branches, respectively. These relations yield $\nu_0=6972.4$ cm^{-1}, $\alpha_3=0.0032$ cm^{-1}, $B_0=0.3900$ cm^{-1}. These values are in good agreement with those reported by Benedict, Herman, and Silverman.[6] Using the value of 2349.3 cm^{-1} for ν_2 as reported by Herzberg (footnote 5), $X_{33}=-12.6$ cm^{-1}. The value of 22.5 cm^{-1} for X_{33} given by Benedict, Herman, and Silverman (footnote 6) is a *typographical* error and was intended to read 12.5 cm^{-1}.

The $3\nu_3$ band of CS_2 is presented in figure 3. Here five different band heads can be seen. The major

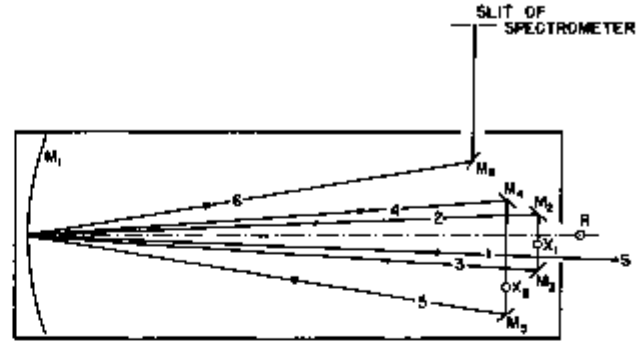

FIGURE 1. *Schematic drawing of multiple reflection absorption cell.*
The lettered components are described in the text.

[5] G. Herzberg, Infrared and Raman spectra of polyatomic molecules, chapters III, IV (D. Van Nostrand Co., New York, N. Y., 1945).
[6] W. S. Benedict, Robert C. Herman, and Shirleigh Silverman, J. Chem. Phys. 19, 1825 (1951).

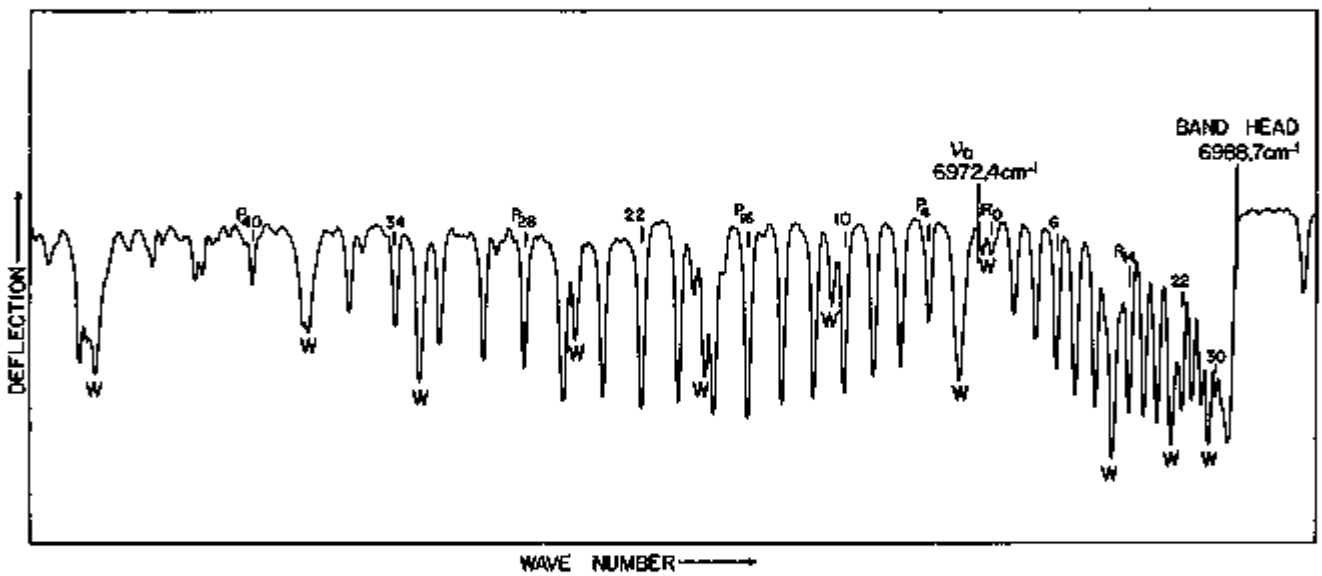

FIGURE 2. *The $3\nu_3$ absorption band of CO_2.*
Some lines are labeled with the J values of the transition. Wavelengths and vacuum wave numbers of all the lines are found in table 1. Lines labeled W are water absorption lines.

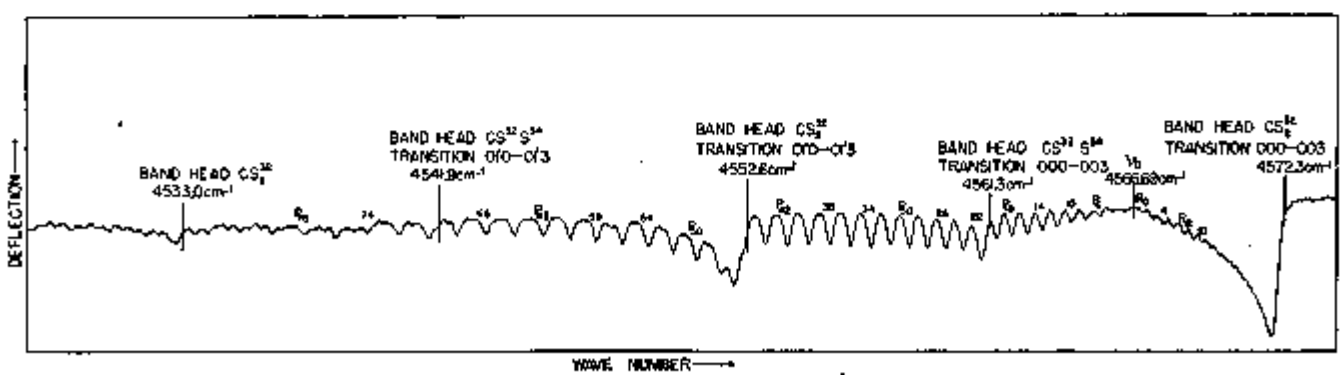

FIGURE 3. *The $3\nu_3$ absorption band of CS_2.*
Some lines are labeled with the J values of the transition. Wavelengths and vacuum wave numbers of all the lines are found in table 2.

band head and the rotational structure are of the 000→003 transition and occur at about 572.3 cm^{-1}. At 4561.3 cm^{-1} is the band head for the same transition for the isotopic molecule $CS^{32}S^{34}$. The band head of the transition $01^10 \rightarrow 01^13$ occurs at 4552.6 cm^{-1}, and the head for the same transition for the isotopic molecule occurs at 454 1.9 cm^{-1}. A very weak band head can be seen at 4533.0 cm^{-1}. This can be attributed to the pair of transitions $02^00 \rightarrow 02^03$ and $02^20 \rightarrow 02^23$. The band head of the transition 100→103 is expected to occur at approximately this position and may be superimposed at 4533.0 cm^{-1}.

The scarcity of lines in the R branch of the principal transition prevented the use of the combination differences (eq 1 and 2). Instead, the absorption lines were fitted to the equation

$$\nu = \nu_0 + (B' + B'')m + (B' - B'')m^2, \qquad (3)$$

(see footnote 5) in order to determine ν_0, B' and B''. These symbols have the same meanings as in eq 1 and 2. $m = J+1$ for the R branch, and $m = -J$ for the P branch. A least-square fit to this equation yielded $\nu_0 = 4566.69$ cm^{-1}, $B_0 = 0.1089$ cm^{-1}, and $\alpha_3 = (B'' - B')/3 = 0.007$ cm^{-1}. Table 2 contains the J and m values, the wavelengths, and vacuum wave numbers of the lines of this spectrum, and the wave numbers calculated from eq 3.

The location of the band origins can be calculated to a good first approximation by assuming that the differences, $\nu_{\text{band head}} - \nu_0$, remain constant. This is shown by considering eq 3. A band head is expected when $d\nu/dm = 0$ or when $m = -(B' + B'')/2(B' - B'')$. Substituting this value of m into eq 3, $\nu_{\text{band head}} - \nu_0 = -(B' + B')^2/4(B' - B'')$ for the difference between the band head and the band origin. Comparing this difference for two transitions $(\nu_{\text{band head}} - \nu_0)_{000\rightarrow 003} - (\nu_{\text{band head}} - \nu_0)_{01^10 \rightarrow 01^13} = -(B_{003} + B_{000})^2/4\,(B_{003} - B_{000}) + (B_{01^13} + B_{01^10})^2/4\,(B_{01^13} - B_{01^10})$. Expressing these $4B'$s in terms of the equation $B(\nu) = B_e = \sum_i \alpha_i(\nu_i + (d_i)/2)$ see footnote 5) and noting that $B_e \gg \alpha_i$, to a good approximation, we find $(\nu_{\text{band head}} - \nu_0)_{000\rightarrow 003} - (\nu_{\text{band head}} - \nu_0)_{01^10 \rightarrow 01^13} < B_e$.

Since B_e is approximately 0.1 cm^{-1}, it is seen that the difference between band head and band origin is equal for the transitions 000→003 and $01^10 \rightarrow 01^13$ to within experimental error.

Using this relation, ν_0 for $01^10 \rightarrow 01^13$ is found to be 4546.7 cm^{-1}. Taking the value of ν_0 for 000→001 of 1532.5 cm^{-1} as measured at the Bureau on a prism spectometer, it is found that $X_{23} = -5.2$ cm^{-1} and $X_{23} = -3.3$ cm^{-1}.

TABLE 2. *Wavelengths band wave numbers of the $3\nu_3$ band of CS_2*

J	m	Wavelength	Wave number observed	Wave number calculated
		Å	cm^{-1}	cm^{-1}
R19	19	21875.73	4570.02	4570.04
18	17	21876.91	4569.78	4569.76
14	16	21878.37	4569.48	4569.46
15	15	21879.78	4569.18	4569.15
10	11	21881.47	4568.83	4568.82
R8	9	21883.11	4568.46	4568.47
6	7	21884.31	4568.15	4568.10
4	5	21885.99	4567.74	4567.72
2	3	21888.47	4567.36	4567.32
P2	−4	21896.98	4566.79	4566.80
6	−6	21898.16	4566.35	4566.32
8	−8	21900.60	4564.84	4564.83
10	−10	21902.18	4564.32	4564.33
12	−12	21905.39	4563.80	4563.81
P14	−14	21908.19	4563.26	4563.27
16	−16	21910.39	4562.70	4562.71
18	−18	21912.71	4562.10	4562.14
20	−20	21916.46	4561.54	4561.55
22	−22	.....	.....	4560.96
P24	−24	21922.46	4560.28	4560.33
26	−26	21925.40	4559.80	4559.69
28	−28	21928.65	4559.00	4559.02
30	−30	21931.89	4558.32	4558.36
32	−32	21936.16	4557.64	4557.68
P34	−34	21938.52	4556.95	4556.97
36	−36	21941.98	4556.23	4556.25
38	−38	21945.58	4555.48	4555.52
40	−40	21949.21	4554.73	4554.76
42	−42	21952.94	4553.99	4553.99
P44	−44	21956.63	4553.19	4553.21
46	−46	.....	.....	4552.43
48	−48	21964.16	4551.63	4551.59
50	−50	21968.24	4550.78	4550.75
52	−52	21972.30	4549.94	4549.90
P54	−54	21976.44	4549.07	4549.03
56	−56	21980.76	4548.20	4548.14
58	−58	21985.11	4547.30	4547.24
60	−60	21989.50	4546.38	4546.32
62	−62	21994.11	4545.43	4545.38
P64	−64	21998.66	4544.49	4544.44
66	−66	22003.44	4543.50	4543.47
68	−68	22008.69	4542.43	4542.49
70	−70	22012.96	4541.54	4541.49
72	−72	22018.38	4540.53	4540.47
P74	−74	22023.48	4539.46	4539.44
76	−76	22028.26	4538.38	4538.39
78	−78	22033.47	4537.36	4537.32
80	−80	22038.88	4536.20	4536.24
82	−82	22044.06	4536.07	4536.14
P84	−84	22049.99	4533.91	4534.02

WASHINGTON, JANUARY 21, 1952.