[CONTRIBUTION FROM THE RADIOMETRY SECTION, ATOMIC AND RADIATION PHYSICS DIVISION, NATIONAL BUREAU OF STANDARDS]

The Infrared Spectrum and Rotational Constants of Carbon Disulfide

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Three vibrational–rotational bands of carbon disulfide have been observed under high resolution. An analysis of the rotational structure leads to the values $B_0 = 0.10927 \pm 0.00003$ cm.$^{-1}$ and $D_0 = (4.34 \pm 0.55) \times 10^{-8}$ cm.$^{-1}$ for the rotational constants. From B_0 one finds $r_0 = 1.553$ Å.

Introduction

One of the problems most profitably attacked by high resolution infrared is the determination of the rotational constants of molecules which cannot be studied by microwave techniques. Those molecules which have no permanent dipole moment form such a class. Carbon dioxide has been studied successfully by high resolution infrared techniques,[1] and the present report concerns the analogous molecule carbon disulfide. Previous high resolution work on CS_2 was limited to the $3\nu_3$ band[2] near 4567 cm.$^{-1}$. The analysis of this band was not very satisfying since the main band was badly overlapped by hot bands. The measurements on three bands not previously resolved and not badly obscured by overlapping absorption are reported here.

Experimental

The spectra were recorded on the grating instruments of the Radiometry Section which have been described previously.[2,3] The wave lengths of the rotational lines were measured by comparison with the fringe-system of a Fabry–Perot interferometer.[3]

The results obtained in one region of the spectrum are shown in Fig. 1. The measured wave numbers of the lines of the three bands used to determine the rotational constants are given in Table I. In each region of absorption "hot bands" are present but due to the small spacing of the lines in the main band, no analysis was possible. One isotopic band was observed somewhat lower than the 2185 cm.$^{-1}$ band, but it also was too badly overlapped for analysis although the pattern indicates that it belongs to the molecule S^{32}–C^{12}–S^{34}.

Rotational Analysis.—The strongest absorption in each region is due to $CS_2{}^{32}$. Since S^{32} has a spin of zero every other line is missing, hence only P and R branch lines originating in states of even J are observed.

For each of the lines in a given band, an equation of the type

$$\nu = \nu_0 + 2(B' + B'')m + 2(B' - B'')m^2 + 4Dm^3 \qquad (1)$$

was formed. The resulting sets of equations were solved by the method of least squares for the best estimates of B, B_0, D and ν_0. The values of B_0 obtained for the three bands from this analysis varied somewhat. As a result the values of B_0 and D_0 were obtained from the set of equations

$$\Delta F_2 = R(J - 1) - P(J + 1) = 4B_0(J + {}^1/_2) + 8D_0(J + {}^1/_2)^3 \qquad (2)$$

The ΔF_2 values were obtained by averaging the ΔF_2 values of the three bands. Care was taken to eliminate any ΔF_2 value which depended on an absorption peak which was a blend of a main band transition and a "hot band" transition. The set of equations 2 were then solved by the method of least squares for B_0 and D_0. The best estimates obtained by this procedure are given in Table II.

TABLE I

OBSERVED FREQUENCIES AND ROTATIONAL ASSIGNMENTS OF CS_2 (CM.$^{-1}$)

J	$\nu_1 + \nu_3 =$ 2185.521		$2\nu_1 + \nu_3 =$ 2833.139		$\nu_1 + 2\nu_2^0 + \nu_3 =$ 2961.734	
	R	P	R	P	R	P
0	2185.72[a]	.....	2833.35[a]	.....	.....	.....
2	2186.14	2185.04	2833.78	2832.68	2962.37	.....
4	2186.55	2184.61	2834.20	2832.24	2962.78	2960.86
6	2186.96	2184.16	2834.63	2831.78	2963.23	2960.43[a]
8	2187.40	2183.71	2835.01	2831.30	2963.64	2959.97
10	2187.80	2183.25	2835.41	2830.85	2964.05	2959.51
12	2188.17[a]	2182.75	2835.80	2830.39	2964.47	2959.07
14	2188.56	2182.31	2836.18	2829.90	2964.95	2958.60
16	2188.96	2181.79	2836.53	2829.41	2965.34	2958.13
18	2189.32	2181.30	2836.89	2828.89	2965.77	2957.67
20	2189.68	2180.86	2837.22	2828.38	2966.13	2957.17
22	2190.02	2180.30		2827.85	2966.52	2856.72
24	2190.36	2179.78	2837.97	2827.34	2966.90	2956.25
26	2190.73	2179.27	2838.31	2826.81	2967.28	2955.75
28	2191.07	2178.70	2838.62	2826.27	2967.66	2955.28
30	2191.38	2178.20	2838.90	2825.71	2968.03	2954.79
32	2191.72	2177.70	2839.22	2825.14	2968.39	2954.28
34	2192.04	2177.10	2839.50	2824.58	2968.78	2953.78
36	2192.36	2176.54	2839.81	2823.98	2969.13	2953.27
38	2192.64	2176.00	2840.05	2823.41	2969.54	2952.78
40	2192.96	2175.40	2840.35	2822.80	2969.90	2952.27
42	2193.24	2174.84		2822.24	2970.25	2951.75
44	2193.50	2174.26	2840.87	2821.67	2970.59	2951.24
46	2193.80	2173.66		2821.00	2970.94	2950.73
48	2194.07	2173.06	2841.28	2820.39	2971.29	2950.21
50	2194.32	2172.46		2819.77	2971.64	2949.70
52	2194.55	2171.86		2819.10	2971.97	2949.17
54	2194.81	2171.24		2818.47	2972.30	2948.64
56	2195.06	2170.60		2817.84	2972.63	2948.10
58	2195.29	2169.98		2817.15	2972.99	2947.57
60	2195.52	2169.34		2816.45	2973.24	2947.05
62	2195.74	2168.68		2815.74		2946.50
64	2195.96	2168.03		2815.04		2945.97
66	2196.16	2167.38		2814. 9		2945.42
68	2196.34	2166.72		2813.70		2944.87
70		2165.37		2812.92		2944.28
72		2164.64		2812.32		2943.79
74						2943.18
76						2942.65
78						2942.06
80						2941.47
82						2940.90
84						2940.34
86						2939.68

[a] Indicates blended lines not used in final calculations.

TABLE II

RESULTS OF BAND ANALYSES

v_1	v_2	v_3	ν_0 (cm.$^{-1}$)	$B' - B_0$ (cm.$^{-1}$)
1	0	1	2185.521 ± 0.002	0.000891 ± 0.000008
2	0	1	2833.139 ± .006	.001016 ± .000005
1	2	1	2961.734 ± .004	.000460 ± .000002

$B_0 = 0.10927 \pm 0.00003$ cm.$^{-1}$

$D_0 = (4.34 \pm 0.55) \times 10^{-8}$ cm.$^{-1}$

Discussion

The B_0 values of CO_2 and CS_2 have now been determined from high resolution infrared. Since these molecules are linear and symmetric, these

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(2) N. M. Gailar and Earle K. Plyler, *ibid.*, **48**, 392 (1952).

(3) E. K. Plyler, L. R. Blaine and W. S. Connor, *J. Opt. Soc. Am.*, **45**, 102 (1955).

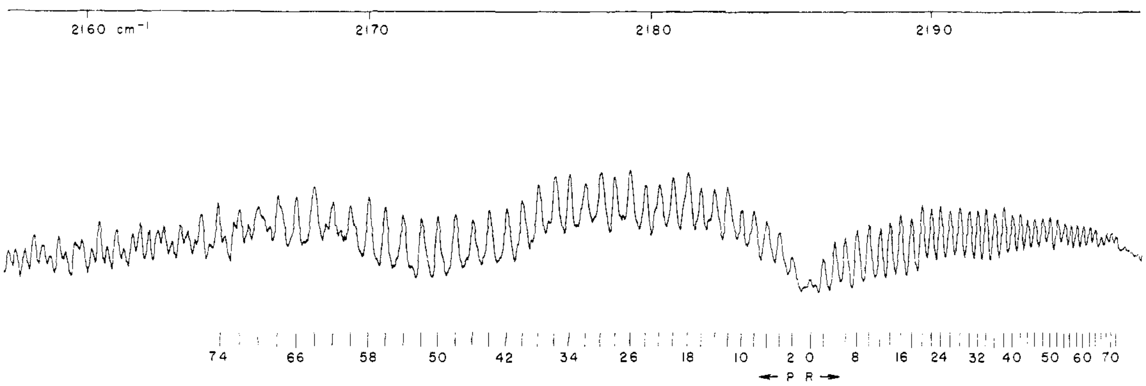

Fig. 1.—The $\nu_1 + \nu_3$ band of CS_2 with center at 2185.52 cm.$^{-1}$. The P branch is overlapped by another band. The cell length was 1 meter and the pressure was 3 cm.

data are sufficient to determine the bond distances in these two molecules. The B_0 value of O^{16}-$C^{12}S^{32}$ has also been determined from infrared measurements but does not provide sufficient information to determine the two bond distances in the molecule. Fortunately, microwave values are available for several isotopic species of OCS. Unfortunately, zero-point energies vary enough among the isotopic species to give several values of the bond distances depending on which pair of B_0 values are used to evaluate these parameters. Since the carbon atom will be fairly close to the center of mass the isotopic pair O^{16}–C^{12}–S^{32} and O^{16}–C^{13}–S^{32} seem to be the most appropriate pair to use in evaluating r_{CO} and r_{CS}. This is borne out by the fact that the B_0 values are very nearly equal. Thus using this pair of B_0 values and the B_0 values of CO_2 and CS_2 determined from the infrared work, the bond distances for the three molecules have been calculated. These values are compared in Table III. It is readily seen that within experimental error the C–O distance in CO_2 and OCS are the same. The same is true of the C–S distance in CS_2 and OCS.

TABLE III

COMPARISON OF BOND LENGTHS IN CO_2, OCS AND CS_2

Molecule	r_{CO}	r_{CS}
CO_2	1.162	
OCS	1.163	1.559
CS_2		1.553

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Electronic Correlation in Molecules. III. The Paraffin Hydrocarbons[1]

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It is shown that the isomerization energy of paraffin hydrocarbons arises principally from an electronic correlation effect. The dispersion force formulation, which corresponds to the dipole–dipole approximation, is used for interactions between all pairs of non-adjacent atoms in the molecule and an expression for the total electronic correlation energy between non-adjacent atoms is given. The theoretical isomerization energies for the butanes and pentanes agree quite satisfactorily with observed values. By use of empirical values for C–C and C–H bond energies a general expression for ΔH_f° at 0°K. for the paraffin hydrocarbons is also presented.

In a brief note[2] one of us has pointed out that the anomalous trend in dissociation energy for the halogen series is at least partially explained by the correlation energy of the unshared pairs of electrons or in other words the London or dispersion energy. The trend in polarizability of the halogens shows an abrupt drop from chlorine to fluorine and this leads to a great reduction in correlation energy. In this paper, we report calculations which show that the isomerization energies for the paraffin hydrocarbons arise principally from the same electron correlation effect.

We note that several completely empirical treatments for the correlation of the isomerization energies have been made and are quite satisfactory.[3]

We realize that electrostatic interactions of the time average charge distribution also may be significant. However, the information necessary for a quantitative calculation is not available, and the paraffins are known to be relatively non-polar.

In these calculations, we assume that the C–C

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(1) This research was assisted by the American Petroleum Institute through Research Project 50.

(2) K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

(3) J. R. Platt, *J. Phys. Chem.*, **56**, 328 (1952); K. Ito, THIS JOURNAL, **75**, 2430 (1953).