

The Infra-Red Absorption Spectrum of CD_4

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The spectrum of CD_4 has been measured from 3.0μ to 10.5μ and three regions of absorption were observed. These bands with centers at 2992.8 cm^{-1} , 3103.7 cm^{-1} , 2259.0 cm^{-1} , and 995.86 cm^{-1} have been identified as $\nu_1 + \nu_4$, $\nu_3 + \nu_4$, ν_3 , and ν_4 by analogy with CH_4 . The line spacings obtained from these bands in CD_4 are $\Delta\nu_{\nu_1 + \nu_4} = 7.17\text{ cm}^{-1}$; $\Delta\nu_{\nu_3 + \nu_4} = 5.01\text{ cm}^{-1}$, $\Delta\nu_3 = 4.52\text{ cm}^{-1}$; $\Delta\nu_4 = 3.42\text{ cm}^{-1}$ as compared with 5.3 cm^{-1} , 13.5 cm^{-1} , 9.77 cm^{-1} and 5.41 cm^{-1} for the same bands in CH_4 . Values for the ζ 's of Johnston and Dennison have been obtained and are as follows: $\zeta_3 = 0.1465$ and $\zeta_4 = 0.3535$. Utilizing the line spacings given above and the expression $\Delta\nu_3 + \Delta\nu_4 = 3h/8\pi^2 A$ derived by Johnston and Dennison the value $1.044 \times 10^{-39}\text{ g cm}^2$ is obtained for the moment of inertia A .

I. INTRODUCTION

RECENT measurements on the infra-red absorption bands due to the spherically symmetrical hydrides of carbon,¹ silicon,² and germanium³ have seemed sufficiently interesting to justify an examination also of the spectra of these molecules where the hydrogen atoms have been replaced by the isotope of mass 2. The deuterium variety of these compounds is in general not easily obtained, but the carbon tetra-deuteride may be prepared simply by allowing aluminum carbide to react with a very pure sample of deuterium oxide. It was found to be necessary to bake out the aluminum carbide for several days, while running a vacuum pump, to drive off all occluded water vapor. This serves to eliminate all the ordinary methane molecules caused by interaction of the carbide with water vapor in the atmosphere.

We wish in this paper to report on measurements which we have made on the spectrum of CD_4 prepared in the manner described above using D_2O of 99.5 percent purity. The purity of the final sample of gas used in these measurements was good enough so that the absorption bands due to even the most likely hybrid methanes remained unobserved.

For our measurements we made use of the same prism-grating spectrometer used by previous investigators working in this laboratory on similar experiments. Two different gratings were required; one ruled with 800 lines per inch for the region near 10.0μ , and another ruled with 3600 lines per inch for the 3.3μ and the 4.4μ regions. The slit widths used in this experiment included spectral intervals of 0.6 cm^{-1} , 0.8 cm^{-1} , 0.6 cm^{-1} , in the regions 3.3μ , 4.4μ , and 10.0μ , respectively. Two absorption cells made of glass tubing fitted with windows of polished rocksalt were used; one two centimeters long and the other ten centimeters long. The former was used for measurements on the fundamental vibrations and the latter on the combination bands. Regions of intense absorption were found at 3.3μ , 4.4μ and 10.0μ and these have been studied in detail.

II. EXPERIMENTAL RESULTS

The 4.4μ region

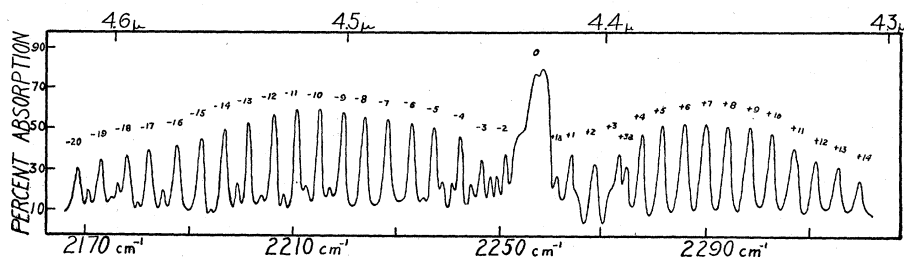
This region of absorption which corresponds to the 3.3μ band in the spectrum of CH_4 has been identified as ν_3 in Dennison's notation. The measurements for this band are plotted as percent absorption against a scale of frequencies in cm^{-1} and wave-lengths in μ and are shown in Fig. 1. The R branch of this band overlaps with the carbon dioxide fundamental making it impossible, because of atmospheric CO_2 , to measure as many lines on this side of the band as in the P branch. Deflections of the galvanometer were made on each setting with the cell in the beam

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¹ J. P. Cooley, *Astrophys. J.* **62**, 73 (1925); A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **48**, 864 (1935).

² W. B. Steward and H. H. Nielsen, *J. Chem. Phys.* **2**, 712 (1934); *Phys. Rev.* **47**, 828 (1935).

³ W. B. Steward and H. H. Nielsen, *Phys. Rev.* **48**, 861 (1935).

FIG. 1. Curve showing the ν_3 absorption band of CD₄ at 4.4 μ .

and then out of the beam so percent absorption could be computed. It is believed that despite the CO₂ the line positions given are quite accurate. Readings were taken at spectral intervals of 0.9 cm⁻¹. Table I gives a list of the observed lines and their frequency positions.

The $\Delta\nu_3$ averaged over the whole band has been computed to be 4.52 cm⁻¹ as compared with 9.77 cm⁻¹ in CH₄. The center of the band, as determined from these measurements is at 2259.0 cm⁻¹. This value is in good agreement with the Raman spectrum value of 2258.0 cm⁻¹ given by MacWood and Urey.⁴

The 10.0 μ region

The fundamental vibration ν_4 of CH₄ gives rise to an absorption band near 7.7 μ . For CD₄ the vibration ν_4 absorbs in the region of 10.0 μ . The appearance of this absorption band as revealed by our measurements is shown in Fig. 2 where again percent absorption is plotted against a scale of frequencies in cm⁻¹ and wave-lengths in μ . The deflections of the galvanometer for cell in, and cell out of, the beam were read at intervals of 0.6 cm⁻¹. The center of this band is set at 995.86

cm⁻¹ which agrees with the value 987 cm⁻¹ predicted by Dennison and Johnston.⁵ As in the corresponding band in CH₄ the central line or Q branch is extremely broad and converges toward smaller frequencies. Appreciable convergence of the rotational lines in the band is observed. The extreme lines in the P branch have a spacing of about 5.4 cm⁻¹ while the extreme ones in the R branch have a spacing of about 2.5 cm⁻¹. From the average of the spacings over the whole band the $\Delta\nu_4$ is about 3.42 cm⁻¹ as compared with 5.41 cm⁻¹ in CH₄. An immediately obvious difference between this band and the ν_4 in CH₄ is that the lines on the high frequency side do not split up into multiplets. This may be due to the fact that the lines are appreciably closer together and thus more difficult to resolve. On the low frequency side the lines split into multiplets very early. Curve (b) Fig. 2 shows a strong peak observed in the first sample of gas made. This is clearly a Q branch of some hybrid molecule probably CHD₃ since on purification it shrinks and almost disappears as shown in (a) Fig. 2.

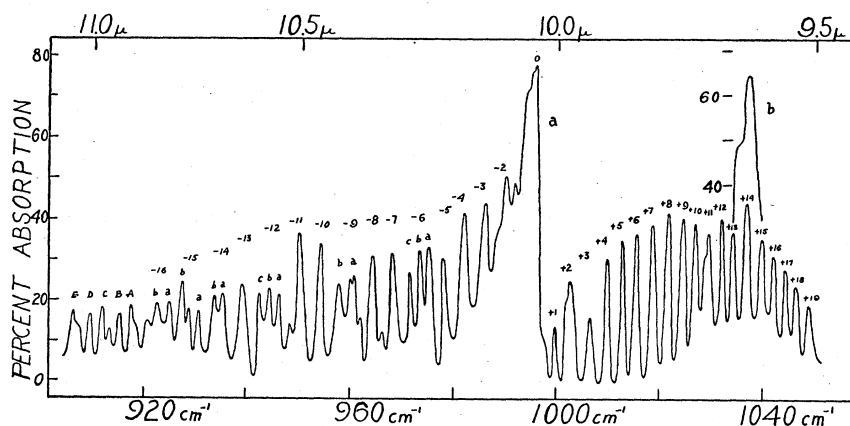
Table II lists the lines and their frequency positions numbered much in the same manner as

⁴ G. E. MacWood and H. C. Urey, J. Chem. Phys. **4**, 402 (1936).

⁵ D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

TABLE I. Frequencies of the lines in ν_3 .

LINE NO.	ν	LINE NO.	ν	LINE NO.	ν	LINE NO.	ν
+14	2319.2 cm ⁻¹	+3a	2274.7 cm ⁻¹	-3	2246.9 cm ⁻¹	-13a	2199.3 cm ⁻¹
+13	2314.7	+3	2273.5	-4	2242.3	-14	2196.5
+12	2310.5	+2	2268.7	-5	2237.6	-15	2192.1
+11	2306.2	+1	2264.2	-6	2232.9	-16	2187.5
+10	2301.9	+1a	2261.5	-7	2228.4	-16a	2185.0
+9	2298.6	0	2259.0	-8	2223.9	-17	2182.6
+8	2294.5	-1	—	-9	2219.5	-18	2178.0
+7	2290.4	-2	2251.2	-10	2215.0	-19	2173.1
+6	2286.0	-2a	2249.5	-11	2210.6	-20	2168.5
+5	2282.0	-2b	2248.2	-12	2206.2		
+4	2277.9			-13	2201.2		

FIG. 2. Curve showing the ν_4 absorption band of CD_4 at 10.0μ .

in the work reported by us on ordinary methane.

The 3.3μ region

The absorption in this spectral region is the result of two overlapping bands identified by analogy from CH_4 as $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ with centers at 2992.8 cm^{-1} and 3103.7 cm^{-1} , respectively. The investigation of this region was made difficult by some atmospheric water vapor absorption since this work was done in the summer. Again percent absorption was plotted by taking readings with the cell in the beam and out of the beam. Deflections were taken at intervals on the circle corresponding to 0.9 cm^{-1} . The curve in Fig. 3 shows both bands fairly well resolved and plotted in percent absorption against a scale of frequency in cm^{-1} and wavelength in μ . Although the R branch of $\nu_1 + \nu_4$ overlaps with the P branch of $\nu_3 + \nu_4$ it is possible to obtain a fair value of the $\Delta\nu$ for each band. The $\Delta\nu_{\nu_1 + \nu_4}$ is 7.17 cm^{-1} as compared with $\Delta\nu = 5.3$

cm^{-1} for CH_4 . The $\Delta\nu_{\nu_3 + \nu_4}$ is 5.01 cm^{-1} as compared with 13.5 cm^{-1} for CH_4 . The most important lines in these two bands are tabulated with their frequency positions in Table III.

III. DISCUSSION OF RESULTS

The theory of the methane molecule taking into account first-order interactions between rotation and vibration has been discussed by Johnston and Dennison.⁶ In this discussion they have pointed out that the spacing between rotational lines in a band is in general not related to the actual moment of inertia in any very simple manner. The following equation,

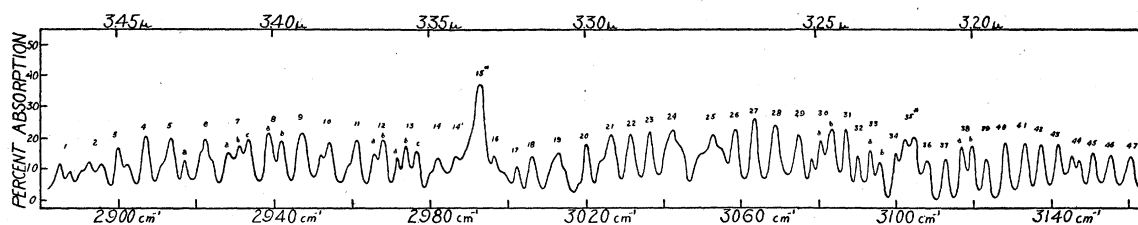
$$\Delta\nu_3 + \Delta\nu_4 = (2 - \zeta_3 - \zeta_4)h/4\pi^2 A = 3h/8\pi^2 A$$

derived by them relates the actual moment of

⁶ M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

TABLE II. Frequencies of the lines in ν_4 .

LINE NO.	ν	LINE NO.	ν	LINE NO.	ν	LINE NO.	ν
+19	1049.08 cm^{-1}	+6	1015.83 cm^{-1}	-6	975.31 cm^{-1}	-14	935.20 cm^{-1}
+18	1046.57	+5	1012.59	-6	973.42	-14	933.45
+17	1044.38	+4	1009.96	-6	971.79	-15	930.97
+16	1042.19	+3	1006.76	-7	968.83	-15	927.77
+15	1040.02	+2	1003.29	-8	964.56	-16	925.08
+14	1036.93	+1	1000.14	-9	960.33	-16	922.88
+13	1034.78	0	995.86	-9	958.23	-16	917.81
+12	1032.03	-1	—	-10	954.31	-16	915.65
+11	1029.60	-2	990.22	-11	950.16	-16	912.08
+10	1026.86	-3	986.59	-12	946.31	-16	909.71
+9	1024.47	-4	982.44	-12	944.53	-16	907.12
+8	1021.77	-5	978.04	-12	942.75	-16	907.12
+7	1018.79			-13	939.21	-16	907.12

FIG. 3. Curve showing the combination bands $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ at 3.3μ .TABLE III. Frequencies of lines in $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$. The lines with asterisks are the Q branches.

LINE NO.	ν	LINE NO.	ν	LINE NO.	ν	LINE NO.	ν
1	2885.3 cm ⁻¹	11	2961.1 cm ⁻¹	21	3027.0 cm ⁻¹	35*	3103.7 cm ⁻¹
2	2894.2	12	2965.7	22	3031.9	36	3107.5
3	2900.3	12	2968.1	23	3036.8	37	3112.7
4	2907.5	13	2971.6	24	3042.9	38	3118.5
5	2913.7	13	2973.9	25	3050.2	38	3118.5
5a	2917.1	13	2976.9	26	3058.9	39	3123.6
6	2922.7	14	2982.7	27	3063.9	40	3128.2
7	2928.9	14'	2986.9	28	3069.5	41	3133.4
7	2931.2	15*	2992.8	29	3075.2	42	3138.0
7	2933.5	16	2996.4	30	3081.9	43	3141.9
8	2939.2	17	3002.3	30	3081.9	44	3146.5
8	2942.1	18	3006.5	31	3087.1	45	3150.8
9	2947.8	19	3013.1	32	3090.3	46	3155.7
10	2954.1	20	3020.4	33	3094.7	47	3161.0
				34	3099.9		

inertia A to the measurable line spacings in ν_3 and ν_4 , and also to the ζ_3 and ζ_4 which represent the magnitudes of an internal angular momentum due to the vibration of the molecule arising from the fact that ν_3 and ν_4 are triply degenerate. Choosing $\Delta\nu_3 = 4.52$ cm⁻¹ and $\Delta\nu_4 = 3.42$ cm⁻¹, we obtain a value of 1.044×10^{-39} g cm² for A , which is about twice the value 5.47×10^{-40} g cm² for ordinary methane. It is also possible to calculate the ζ 's. Since $\Delta\nu_3 = (1 - \zeta_3)h/4\pi^2 A$ and $\zeta_3 + \zeta_4 = \frac{1}{2}$ we obtain the values $\zeta_3 = 0.1465$ and $\zeta_4 = 0.3535$. The theory further predicts that $\Delta\nu_4$ should be equal to $\Delta\nu_{\nu_1 + \nu_4}$, and that $\Delta\nu_{\nu_3 + \nu_4} = 5h/16\pi^2 A$. Experimentally it is found that $\Delta\nu_4 = 3.42$ cm⁻¹ whereas the band $\nu_1 + \nu_4$ shows a $\Delta\nu = 7.17$ cm⁻¹

which is not at all good agreement. An alternate explanation is that this band may be due to CHD₃ which should have a band in this region with a spacing of about 7 cm⁻¹.

Using the relation given by Johnston and Dennison for $\Delta\nu_{\nu_3 + \nu_4}$ we obtain a value of 6.52 cm⁻¹ as compared with the average value over the whole band of 5.01 cm⁻¹. This is not good agreement but is about as close agreement as was obtained in the case of ordinary methane.

The splitting up of rotation into multiple structure is not accounted for by their theory, but must no doubt be ascribed to interactions of higher order than the first between rotation and vibration.