Infrared Absorption Bands of Methane

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The *fine structure of the infrared bands of methane* in the region 1–2μ has been observed, and four new bands located at 1.135, 1.187, 1.330 and 1.734μ. The 1.66μ band observed by Moorhead was re-observed with the result that some 14 new lines were added to it. The line spacing in all the bands in this region is of the order of 10.5 cm^{-1}, but varies from 9.44 to 10.8 cm^{-1}. All the bands have sharp zero branches with a tendency to shade off on the low-frequency side, except for the one at 1.33μ, which is quite symmetrical in all its branches. The positive branch of the 1.66μ band decidedly converges to the red (line spacing increases towards the high frequencies), which was also observed by Cooley in the 3.5μ band. The infrared data in the region observed favors the tetrahedral model assumed by Dennison for theoretical work. It is possible to use as a fundamental frequency $\nu_1=2913$ cm^{-1}, found in the Raman spectrum, in representing the harmonic and combination bands of methane instead of the usually assumed 4217 cm^{-1} ($=\nu_1+\nu_4$).

INTRODUCTION

THE infrared region from 1–2μ has been investigated with a spectrometer of sufficient resolving power to obtain the fine structure of six methane bands. All of these bands have been reported before, except for the ones at 1.135, 1.187, 1.33 and 1.738μ, but the fine structure has not been reported on any but the 1.66μ band.[1] The position of the bands as found by Ellis[2] agrees with our results within the experimental error of his wave-length determinations. The 1.37μ band was not investigated as it lies at the center of the 1.38μ water vapor band, which is very strong, and would require a vacuum spectrograph to eliminate it.

APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental work was done with an automatic recording spectroscope of the Littrow type, consisting of two 60° and one 30° prisms with faces 10 x 15 cm, and a collimating mirror with a 60 cm focus. The prisms were so arranged that the light traversed the path twice, giving a dispersion equivalent to five 60° prisms. A more complete description of the apparatus may be found in a previous paper.[3]

The methane gas used was obtained in small cylinders from the Fisher Scientific Co., Pittsburgh, and contained a small amount of ethane. However, comparison with the ethane spectrum showed there was not enough present to be detected. The methane was released into the case of the spectroscope (equivalent to a three meter path), but the gas pressure was not determined.

DISCUSSION

D. M. Dennison and S. B. Ingram[4] have reported a series of methane bands in the photographic, infrared region, 8900A, which they consider to be the third overtone $n=0\rightarrow4$ of the fundamental, $\nu_3=3014$ cm^{-1}, at 3.3μ. They give the equation $\nu=3085n-66n^2$, which for $n=3$ gives $\nu=8661$ cm^{-1}. The band at 1.16μ has its center at 8606 cm^{-1}, which agrees well with the above calculated value. According to Dennison's theory of degenerate energy states for the methane molecule there should be five groups of nearly coincident levels. The resulting pattern of lines would give a series of groups of lines which by the continuous recording method with an effective slit width of about 6A would be the apparent spacing of a single band. The grouping of the lines in the 8900A band gives a series of maxima about 10 cm^{-1} apart. This is the spacing of most of the bands of methane, and would help

[1] J. G. Moorhead, Phys. Rev. **39**, 83 (1932).
[2] J. W. Ellis, Proc. Nat. Acad. Amer. **42**, 202 (1927).
[3] H. J. Unger, Phys. Rev. **43**, 123 (1933).
[4] D. M. Dennison and S. B. Ingram, Phys. Rev. **36**, 1451 (1930).

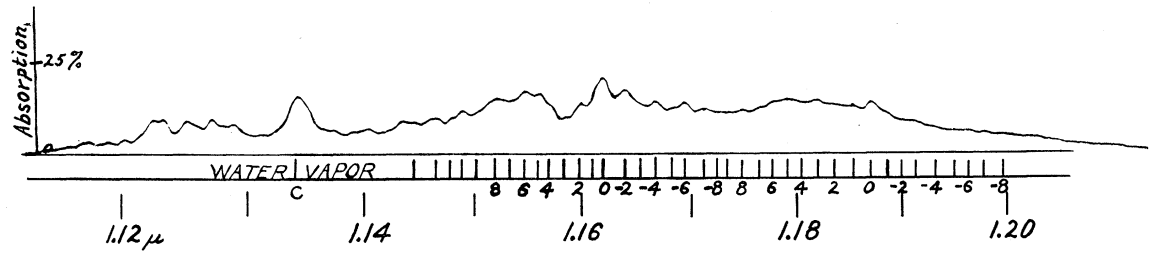

FIG. 1. The 1.134μ water vapor band with its center marked C overlaps the 1.13 and 1.162μ methane bands, but comparison allowed eight lines to be determined in each branch of the last band.

to explain the irregular intensity of the lines in some of the bands.

The 1.13μ band could not be investigated because it lies in the region of the 1.134μ water vapor band, but several lines were determined by comparison with the water band, and the separation was found to be approximately 10 cm^{-1}, which agrees with the other bands of methane. The lines in this water vapor band were first investigated by McAlister and Unger,[5] but the results have never been published. This band contains about forty lines with a fairly sharp zero branch, and the wave-lengths are in excellent agreement with Abbot's[6] work on the atmospheric absorption of the solar radiation.

Fig. 1 shows the 1.13μ water vapor band and the superimposed methane band as well as the

TABLE I. 1.162μ *methane band.*

$\nu = 8606.41 + 8.728M - 0.0456M^2 + 0.0121M^3$

M	λ	ν	$\Delta\nu$
8	1.1522	8679.04	
			8.27
7	1.1533	8670.77	
			12.10
6	1.1549	8658.67	
			8.16
5	1.1560	8650.51	
			8.98
4	1.1572	8641.53	
			8.19
3	1.1583	8633.34	
			10.43
2	1.1597	8622.91	
			8.17
1	1.1608	8614.74	
			8.98
0	1.1620	8605.76	
			15.44
−2	1.1641	8590.32	
			10.32
−3	1.1655	8580.00	
			10.29
−4	1.1669	8569.71	
			10.36
−5	1.1683	8559.35	
			9.51
−6	1.1696	8549.84	
			11.59
−7	1.1712	8538.25	
			10.20
−8	1.1726	8528.05	
			Av. = 9.44

TABLE II. 1.187μ *methane band.*

$\nu = 8425.57 + 11.514M - 0.0274M^2 - 0.0104M^2$

M	λ	ν	$\Delta\nu$
9	1.1735	8521.51	
			10.91
8	1.1750	8510.60	
			10.09
7	1.1764	8500.51	
			9.39
6	1.1777	8491.12	
			9.36
5	1.1790	8481.76	
			10.06
4	1.1804	8471.70	
			10.75
3	1.1819	8460.95	
			12.15
2	1.1836	8448.80	
			12.83
1	1.1854	8435.97	
			13.50
0	1.1873	8422.47	
			9.92
−1	1.1887	8412.55	
			9.19
−2	1.1900	8403.36	
			10.58
−3	1.1915	8392.78	
			11.96
−4	1.1932	8380.82	
			11.92
−5	1.1949	8368.90	
			11.89
−6	1.1966	8357.01	
			9.77
−7	1.1980	8347.24	
			10.44
−8	1.1995	8336.80	
			Av. = 10.86

[5] E. D. McAlister and H. J. Unger, Phys. Rev. **37**, 1012 (1931).

[6] C. G. Abbot and H. B. Freeman, Smithsonian Misc. Col., Vol. 82, No. 1.

1.162μ and 1.187μ methane bands. Wave-lengths of the lines in the latter bands will be found in Tables I and II. Eight lines in each branch of the last two bands were selected and equations calculated to represent their spacings. It is customary to use a second degree equation of the form $\nu = A + BM - CM^2$, where M is an integral number taking positive and negative values, but a cubic equation gives better agreement. An equation for each band will be found in its wave-length table; they were calculated by the least square method as modified by Birge and Shea.[7]

A very interesting band was found at 1.330μ, which has not been reported before (Table III). It has a narrow symmetrical zero branch, the base of which is about 20 cm^{-1} in width. The positive branch consists of eleven distinct lines with the seventh one enhanced. This enhancement is similar to that of the lines in the positive branch of the 1.66μ band, Fig. 2. Little is known of the relative intensity of the negative branch as it runs into the 1.38μ water vapor band, but the position of six lines was determined by comparison with the known water vapor lines. Because of the symmetry of the zero branch and

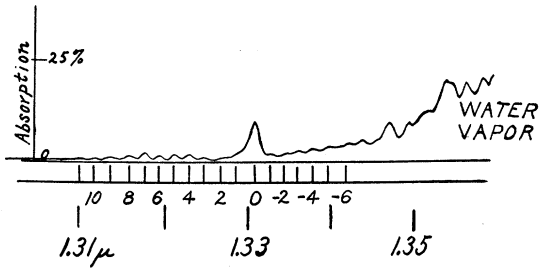

FIG. 2. The negative branch of this band overlaps the last few lines of the intense 1.37μ water vapor band. The zero and positive branches are very symmetrical.

[7] R. T. Birge and J. D. Shea, University of California Publications in Mathematics, 2, 67–118 (1927).

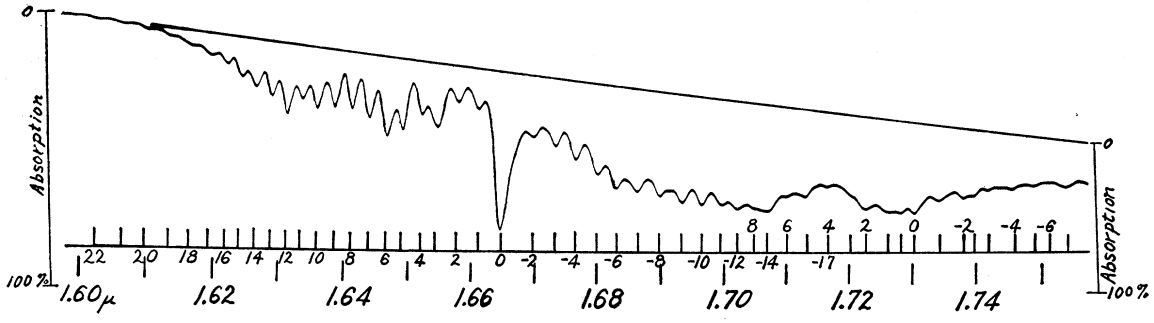

FIG. 3. The 1.66μ band, first investigated by Moorhead, shows an increase in line spacing towards the high-frequency end of the positive branch. The energy curve, which has been drawn in, slopes down rapidly in the direction of long wave-lengths because of strong absorption by the glass prisms.

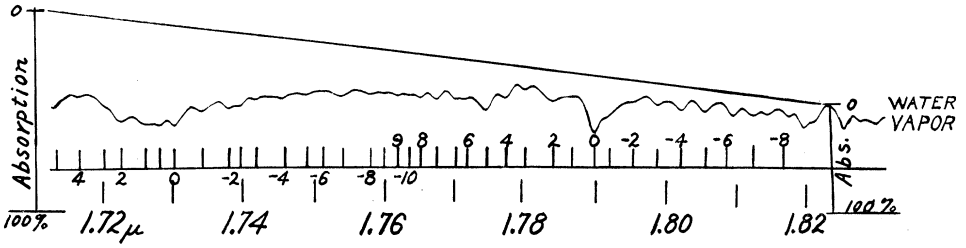

FIG. 4. This is a continuation of the curve in Fig. 3. The long wave-length end of the 1.79μ band runs into the 1.87μ water vapor band.

TABLE III. 1.33μ *methane band.*
$\nu = 7517.46 + 11.106M + 0.00859M^2 - 0.01515M^3$

M	λ	ν	$\Delta\nu$
11	1.3099	7634.2	
			9.3
10	1.3115	7624.9	
			11.0
9	1.3134	7613.8	
			11.6
8	1.3154	7602.2	
			12.1
7	1.3175	7590.1	
			10.2
6	1.3191	7580.9	
			9.8
5	1.3208	7571.1	
			10.3
4	1.3226	7560.8	
			9.7
3	1.3243	7551.1	
			10.8
2	1.3262	7540.3	
			10.8
1	1.3281	7529.5	
			13.6
0	1.3305	7515.9	
			11.3
−1	1.3325	7504.7	
			10.1
−2	1.3343	7494.6	
			9.0
−3	1.3359	7485.6	
			10.1
−4	1.3377	7475.5	
			10.6
−5	1.3396	7464.9	
			11.7
−6	1.3417	7453.2	
			Av. = 10.65

the uniform spacing of the positive and negative branch lines, this band indicates that it arises from a vibration that is only slightly, if at all, coupled with the rotation of the molecule.

The 1.66μ methane band investigated by Moorhead[1] was recorded as shown in Fig. 3; the zero branch is quite sharp and intense with a slight broadening on the low-frequency side, indicative of slight coupling between rotational and vibrational states. Wave-lengths are given in Table IV. The line spacing decreases towards the high frequencies for about 13 lines and then increases again. This increase in spacing is very decided, and is too large to be accounted for by experimental error. Because of the overlapping of this band with the 1.734μ band it was not possible to determine whether this divergence also occurs in the negative branch. Cooley[8] has found that the 3.5μ band of methane converges on the low-frequency side of the branches.

The spectral region from 1.60 to 1.81μ (Figs. 3 and 4) shows a continuous absorption with only the stronger lines resolved. There seem to be two other bands in this region besides the one at 1.66μ, and they have quite definite zero branches. Their positions are 1.734μ and 1.790μ, and the line spacings agree well with those of the other bands (Tables V and VI). Because of the intensity of the absorption under these bands it is very probable that there are other bands present.

Table VII gives the average line spacing of the entire group of methane bands and the corresponding moments of inertia of the molecule. The moment of inertia varies considerably for the different bands, and very probably represents a real difference in it for the various modes of vibration. It is interesting to note that the 3.5μ band lines have spacings of about 1.5 times the 10.5 cm^{-1} which is the spacing of the lines of all the other bands with the exception of the 7.67μ band where the spacing is about 0.5 times 10.5 cm^{-1}. It may be due to a combination band $\nu = \nu_2 + \nu_4$ of which ν_2 has not been investigated, and ν_4 exhibits the half spacing. The line spacing of overtones of ν_4 has not been determined. This still leaves the question unsettled as to whether the methane model is a tetrahedron or a pyramid with the four hydrogen atoms at the corners of the base.

Calculation of the moment of inertia of the methane molecule, I', from the most probable rotational frequency, ν_r, of the positive and negative branches, gives a rough check on that obtained from the line spacing. The I' calculated for the 7.67μ band agrees with the larger moment of inertia (see Table VII), which would favor the pyramid structure.

The data presented in this paper show that the overtone and combination bands of methane in the 1–2μ region can be explained as combinations of four fundamental frequencies required by the regular tetrahedron model for methane.

[8] J. P. Cooley, Astrophys. J. 62, 73 (1925).

TABLE IV. 1.665μ *methane band.*

The mean square average of $\Delta\nu$ for the + and − branches is 10.81 cm^{-1} and 10.72 cm^{-1}, respectively, while the average value is 10.62 in each.

$$\nu = 6009.70 + 11.131M - 0.0449M^2 - 0.00341M^3$$

Positive branch M	μ	ν	$\Delta\nu$	Negative branch M	μ	ν	$\Delta\nu$
0	1.6645	6007.8		0	1.6645	6007.8	
			12.3				18.0
1	1.6611	6020.1					
			12.4	2	1.6695	5989.8	13.2
2	1.6577	6032.5					
			11.3	3	1.6732	5976.6	11.4
3	1.6546	6043.8					
			9.1	4	1.6764	5965.2	12.1
4	1.6521	6052.9					
			10.4	5	1.6798	5953.1	11.0
5	1.6492	6063.5					
			8.9	6	1.6829	5942.1	11.6
6	1.6468	6072.4					
			11.1	7	1.6862	5930.5	11.7
7	1.6438	6083.5					
			9.6	8	1.6897	5918.2	12.2
8	1.6412	6093.1					
			9.3	9	1.6932	5906.0	10.8
9	1.6387	6102.4					
			9.3	10	1.6963	5895.2	10.8
10	1.6362	6111.7					
			10.1	11	1.6994	5884.4	9.6
11	1.6333	6121.8					
			8.7	12	1.7022	5874.8	9.7
12	1.6312	6130.5					
			9.0	13	1.7050	5865.1	9.6
13	1.6288	6139.5					
			8.7	14	1.7075	5856.5	9.2
14	1.6265	6148.2					
			9.4	15	1.7102	5847.3	9.6
15	1.6240	6157.6					
			8.4	16	1.7130	5837.7	10.5
16	1.6218	6166.0					
			8.7	17	1.7161	5827.2	m.s. av. = 10.72
17	1.6195	6174.7					
			11.5				
18	1.6165	6186.2					
			12.7				
19	1.6132	6198.9					
			13.8				
20	1.6096	6212.7					
			13.2				
21	1.6062	6225.9					
			15.5				
22	1.6022	6241.4					
			m.s. av. = 10.81				

TABLE V. 1.734μ *methane band.*
$\nu = 5767.62 + 12.471M + 0.0280M^2 - 0.0256M^3$

M	λ	ν	$\Delta\nu$
8	1.7075	5856.5	
			9.2
7	1.7102	5847.3	
			9.6
6	1.7130	5837.7	
			10.5
5	1.7161	5827.2	
			12.2
4	1.7197	5815.0	
			9.5
3	1.7225	5805.5	
			11.8
2	1.7260	5793.7	
			13.4
1	1.7300	5780.3	
			11.6
0	1.7335	5768.7	
			14.0
−1	1.7377	5754.7	
			12.9
−2	1.7416	5741.8	
			12.1
−3	1.7453	5729.7	
			10.5
−4	1.7485	5719.2	
			8.8
−5	1.7512	5710.4	
			8.5
−6	1.7538	5701.9	
			13.3
−7	1.7579	5688.6	
			5.8
−8	1.7597	5682.8	
			11.3
−9	1.7632	5671.5	
			10.5
−10	*	5661.0	
			10.6
−11	1.7698	5650.4	
			Av. = 10.85

* Calculated.

TABLE VI. 1.790μ *methane band.*
$\nu = 5588.88 + 9.607M - 0.0546M^2 + 0.00853M^3$

M	λ	ν	$\Delta\nu$
9	1.7615	5677.0	
			11.0
8	1.7649	5666.0	
			8.3
7	1.7675	5657.7	
			12.1
6	1.7713	5645.6	
			9.6
5	1.7743	5636.0	
			8.5
4	1.7770	5627.5	
			9.5
3	1.7800	5618.0	
			10.1
2	1.7832	5607.9	
			9.7
1	1.7863	5598.2	
			11.0
0	1.7898	5587.2	
			7.8
−1	1.7923	5579.4	
			9.3
−2	1.7953	5570.1	
			10.5
−3	1.7987	5559.6	
			10.8
−4	1.8022	5548.8	
			10.8
−5	1.8057	5538.0	
			10.1
−6	1.8090	5527.9	
			11.3
−7	1.8127	5516.6	
			13.0
−8	1.8170	5503.6	
			Av. = 10.2

TABLE VII. *Average line spacing of the entire group of methane bands.*

Band μ	Line separation $\Delta\nu$ cm^{-1}	Moment of inertia I (c.g.s.)	I' (c.g.s.)
1.162	9.44	5.86×10^{-40}	5.8×10^{-40}
1.187	10.86	5.10	4.6
1.330	10.65	5.20	4.5
1.665	10.62, 10.4*	5.21, 5.31*	4.2
1.738	10.85	5.10	
1.790	10.2	5.42	6.0
2.2	10.7	5.17*	
3.31	9.77	5.66†	4.3†
3.5	15.3	3.61	
7.67	5.41	(5.1 or 10.2)†	11.0†
$I = h/4\pi^2c^2(\Delta\nu)$		$I' = 3RT/8\pi^2N\nu_r^2$	

* Moorhead.
† Cooley.

TABLE VIII. *Fundamental frequencies of methane and the possible classification of the bands in the* 1–2μ *region.*

$\nu_1 = 2913$ cm^{-1} (Raman spectrum) $\nu_3 = 3014$ cm^{-1}
$\nu_2 = 1520$ $\nu_4 = 1304$
$n\nu_1 = 2913n - 15n^2$ represents the overtones of ν_1.

Band μ	ν (obs.) cm^{-1}	Classification*
1.135	8800	$\nu_1+2\nu_3 = 8819$ cm^{-1}
1.1620	8606	$3\nu_3 = 8661$
1.1873	8423	$2\nu_1+2\nu_4 = 8434$
1.3305	7516	$\nu_2+2\nu_3 = 7548$
1.6645	6008	$2\nu_3 = 6028$
1.7335	5769	$\nu_1+\nu_2+\nu_4 = 5737$
1.7898	5587	$\nu_1+2\nu_4 = 5521$

* $\nu = 3085n - 66n^2$ used for ν_3.