The Infrared Spectrum of Methyl Chloride

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Certain new infrared absorption bands of CH_3Cl were mapped in the region from 0.7μ to 7.0μ. In each case the bands show the structure predicted by the theory of the symmetry properties of molecules having three equal atoms. It is also predicted that every third line in the $\perp$ bands shall be enhanced. This was observed in the present investigation as well as previously by Bennett and Meyer. Several new intervals between the lines in the $\perp$ bands were observed which may be of value with regard to a theoretical interpretation of this anomalous spacing. Two absorption regions, observed here, appear to give evidence of an interaction between the levels ν_1 and $2\nu_4$ thought to exist in some of the methyl compounds. These bands are $\nu_2+(\nu_1, 2\nu_4)$ at 5900 cm^{-1} and $\nu_3+(\nu_1, 2\nu_4)$ at 4200 cm^{-1}. A few lines of ν_3 in the P branch near the center were resolved. The Q branch proved to be much more pronounced than Bennett and Meyer's work shows.

I. INTRODUCTION

THE infrared vibration-rotation spectrum of the methyl halides was measured by Bennett and Meyer[1] who found that the $\perp$ bands showed an anomalous spacing of the lines. This effect, they suggested was due to an interaction between the vibration and the rotation of the molecule. A pair of $\parallel$ bands, separated by 85 cm^{-1}, was also found at 3.2μ which have recently been interpreted as $(\nu_1, 2\nu_4)$.[2] Normally the levels ν_1 and $2\nu_4$ would lie very close together. It is thought that in a number of methyl compounds they interact as in the case of the CO_2[3] molecule and that the observed separation is a result of this interaction. This resonance also serves to increase the intensity of the $\parallel$ component of $2\nu_4$ so that it is comparable with ν_1. Only in the case of ν_5 for CH_3F was resolution obtained by Bennett and Meyer so that the moments of inertia of the remaining molecules are unknown. The line of further investigation pointed out by the previous observations is as follows: (1) to acquire more experimental data on the anomalous spacing of the lines in the $\perp$ bands; (2) to obtain more experimental evidence of the supposed interaction between ν_1 and $2\nu_4$; (3) to determine, if possible, the moments of inertia $A=B$ from the resolution of one of the $\parallel$ bands; (4) to obtain experimental data on the complex structure of the harmonics and combination bands of $\perp$ vibrations predicted by the theory of molecules having three equivalent particles.[4]

Two infrared spectrometers, one of the Pfund[5] type designed by J. D. Hardy, and another designed by C. F. Meyer[6] were available for this investigation. Three gratings ruled with 7200 lines per inch, 4800 lines per inch and 2400 lines per inch were used for the 1.5μ–3.0μ, 4.0μ, and the 7.0μ regions, respectively. In addition, a concave grating of 15,000 lines per inch in a Paschen mounting was used in the photographic region. For the bolometric measurements a 25.4 cm cell closed with rocksalt windows, and a 1.5 meter cell having glass windows were used. In the photographic region the equivalent length of the absorption cell was 100 meters at atmospheric pressure.

II. EXPERIMENTAL RESULTS

The 1.6μ region

Two $\perp$ bands and one $\parallel$ band were found as shown in Fig. 1. The lowest frequency $\perp$ band occurs alone while the other $\perp$ one overlaps the $\parallel$ band. The predicted structure of the second harmonic of a $\perp$ vibration is a pair of close bands of $\parallel$ and $\perp$ character. This is just what is observed in curves b, c, Fig. 1, hence this pair has been designated as $2\nu_2$. The spacing of the lines in the $\perp$ component is 12.0 cm^{-1}. The zero branch of the $\parallel$ component is quite sharp and

[1] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).
[2] The bracket $(\nu_1, 2\nu_4)$ indicates that the wave functions representing the two perturbed levels are linear combinations of the wave functions of the levels ν_1 and $2\nu_4$.
[3] D. M. Dennison, Phys. Rev. **41**, 304 (1932).
[4] D. M. Dennison, Rev. Mod. Phys. **3**, 338 (1931).
[5] A. H. Pfund, J. Opt. Soc. Am. and Rev. Sci. Inst. **15**, 69 (1927).
[6] E. F. Barker and C. F. Meyer, Trans. Farad. Soc. **25**, 913 (1929).

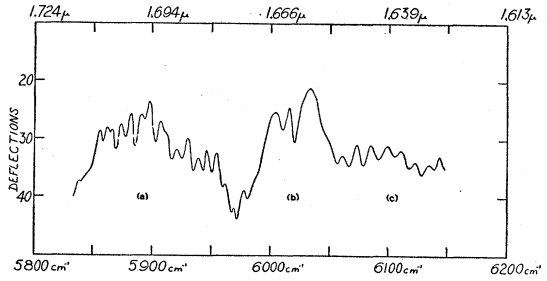

FIG. 1. Curve (*a*) shows the perpendicular structure of the band $\nu_2+(\nu_1, 2\nu_4)$. Curves (*b*) and (*c*) show the splitting up of the parallel, and perpendicular components of $2\nu_2$.

more intense than any found by Bennett and Meyer (with the exception of ν_5). The other $\perp$ band is thought to be $\nu_2+(\nu_1, 2\nu_4)$ involving the two resonance levels. This identification would indicate that the two $\parallel$ components of

TABLE I. (*Data on the* $\parallel$ *bands.*)

P branch	*Q* branch	*R* branch	$\nu_P-\nu_R$
4025.7 cm^{-1}	4047.1 cm^{-1}	4056.3 cm^{-1}	30.6 cm^{-1}
4078.0	4089.5	4106.3	24.3
4213.8	4230.6	4245.9	32.1
6003.4	6015.2	6034.0	30.6

TABLE II. (*Data on curves a and c, Fig. 1.*)

Observed ν	$\Delta\nu$	Observed ν	$\Delta\nu$
5855.1 cm^{-1}		5920.4 cm^{-1}	
	6.7		9.1
5861.8		5929.5	
	4.5		9.0
5866.3		5938.5	
	6.7		7.0
5873.0		5945.5	
	8.9		9.2
5881.9		5954.7	
	9.0		6.9
5890.9		5961.6	
	6.8		6.9
5897.7		5968.5	
	9.0		9.3
5906.7		5977.8	
	6.0		
5912.7			
	7.7		
6048.3		6110.7	
	11.9		12.2
6060.2		6122.9	
	12.0		11.0
6072.2		6133.9	
	12.0		8.6
6084.2		6142.5	
	14.4		
6098.6			
	12.1		

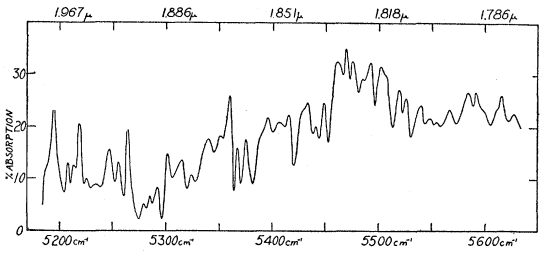

FIG. 2. Perpendicular structure to which no interpretation can at present be given.

$\nu_2+2\nu_4$ are much weaker than the two $\perp$ components since the region shows only $\perp$ structure. The data on this region are given in Tables I and II. For this region the 25.4 cm cell was used, and, since the background was free from atmospheric absorption, galvanometer deflections were plotted against cm^{-1}.

The 1.8μ region

The absorption in this region is shown in Fig. 2. The band is essentially of the $\perp$ variety, but it is so complex that no interpretation can at present be given to it. The absorption is considerably weaker here than at 1.6μ necessitating the use of the 1.5 meter cell. The curve is plotted in percent absorption because the background is complicated by the strong water vapor absorption. The complex appearance of this region is no doubt partly due to distortion by the water vapor lines.

The 2.4μ region

A. Fig. 3 shows the highest frequency absorption of the group of bands in the region of 2.4μ. Its structure is $\perp$ throughout. This absorption is believed to be composed of two overlapping $\perp$ bands, namely, $\nu_2+\nu_3$ having its center at 4383.8 cm^{-1} and $\nu_2+2\nu_5$ with its center at 4478.5 cm^{-1}. Theoretically both $\nu_2+\nu_3$, and $\nu_2+2\nu_5$ would be single $\perp$ bands, and this seems to agree with observation in that the edges of the region have sharply defined lines but the middle is distorted from overlapping. The average spacing of the lines in Table III is seen to be 8.5 cm^{-1}. The curves show clearly that every third line is enhanced as predicted by the theory of systems having three equivalent nuclei each with a spin angular momentum of $\frac{1}{2}(h/2\pi)$. As in the 1.6μ region the 25.4 cm cell was used and galva-

TABLE III. (*Data on the ⊥ bands of Figs. 3, 4, 6.*)

Observed ν	$\Delta\nu$	Observed ν	$\Delta\nu$
4323.9 cm^{-1}		4441.6 cm^{-1}	
	9.5		8.5
4333.4		4449.1	
	8.3		8.8
4341.7		4457.9	
	8.4		8.8
4350.1		4466.7	
	8.3		8.8
4358.4		4475.5	
	6.0		7.7
4364.4		4483.2	
	7.2		9.0
4371.6		4492.2	
	8.5		8.9
4380.1		4501.1	
	7.3		9.0
4387.4		4510.1	
	9.8		10.4
4397.2		4520.5	
	7.3		10.3
4404.5		4530.8	
	8.6		7.9
4413.1		4538.7	
	10.5		6.5
4423.6		4545.2	
	10.5		
4434.1			
	7.5		

Mean spacing of lines in low frequency side of band $=8.4$ cm^{-1}.
Mean spacing of lines in high frequency side of band $=8.6$ cm^{-1}.

4123.9 cm^{-1}		4182.3 cm^{-1}	
	12.8		4.9
4136.7		4187.2	
	11.3		5.0
4148.0		4192.2	
	9.7		6.6
4157.7		4198.8	
	3.3		6.7
4161.0		4205.5	
	4.3		8.3
4165.3		4213.8	
	3.8		
4169.1			
	13.2		
2389.7 cm^{-1}		2456.9 cm^{-1}	
	8.1		9.5
2397.8		2466.4	
	9.8		9.8
2407.6		2476.2	
	10.6		10.2
2418.2		2486.4	
	9.7		9.7
2427.9		2496.1	
	9.5		10.1
2437.4		2506.2	
	9.6		
2447.0			
	9.9		

Mean spacing of lines $=9.7$ cm^{-1}.

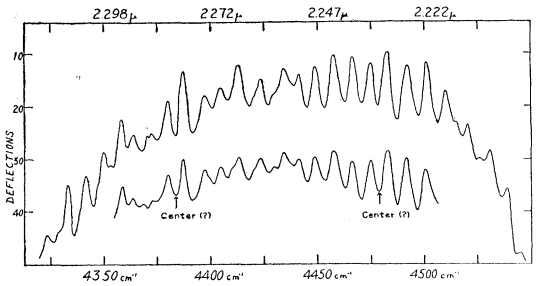

FIG. 3. Two overlapping perpendicular bands, $\nu_2+\nu_3$ and $\nu_2+2\nu_5$.

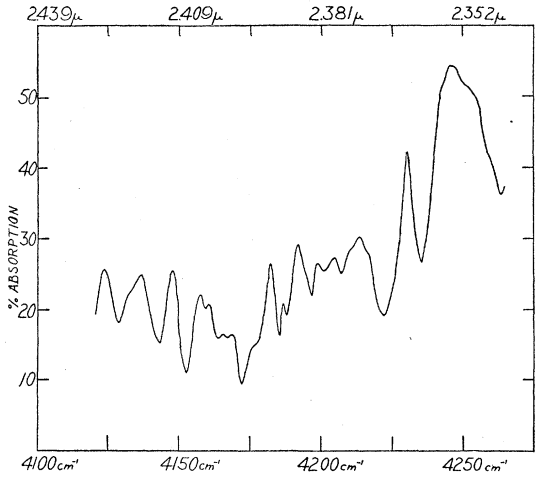

FIG. 4. Perpendicular and parallel structure showing the separation of the bands $\nu_3+(\nu_1, 2\nu_4)$.

nometer deflections were plotted against cm^{-1}. The slit widths included 1.6 cm^{-1} and readings were taken at intervals of 1.2 cm^{-1}.

B. At somewhat longer wave-lengths a pair of bands were observed of which one is ∥ and the other ⊥. These bands, shown in Fig. 4, have been designated as $\nu_3+(\nu_1, 2\nu_4)$ which is the second observed group thought to contain the resonance pair of levels. This identification is made because the separation of these bands is just the separation expected for a combination of some other level with the pair $(\nu_1, 2\nu_4)$. Theoretically $\nu_3+\nu_1$ is a ∥ band, and $\nu_3+2\nu_4$ is composed of a ∥ and a ⊥ component lying close together. This is in agreement with observation since one ∥ band is found, and the ⊥ structure shows such distortion as might be expected from overlapping. Again in this case the zero branch of the parallel band is very sharp and strong, in

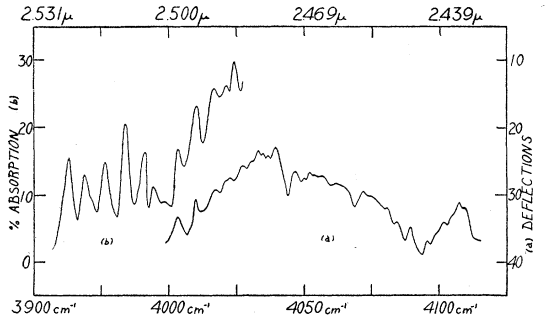

FIG. 5. One perpendicular and two parallel bands comprising $\nu_2+\nu_6$.

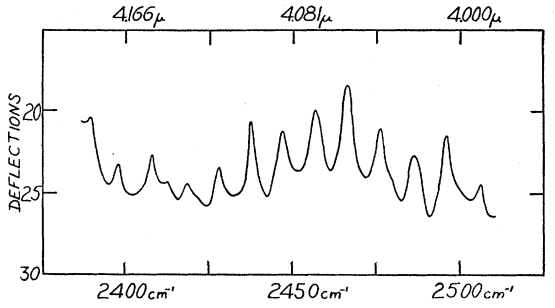

FIG. 6. The perpendicular structure of $\nu_6+2\nu_5$.

contrast to Bennett and Meyer's observations. The absorption was observed with the aid of the 1.5 meter cell and the curve was plotted in percentage absorption because of some strong atmospheric lines. The slits included 1.5 cm^{-1} and readings were taken at intervals of 1.6 cm^{-1}. Table III gives the frequencies of the lines in the $\perp$ band, while Table I contains the data on the $\parallel$ one.

C. The lowest frequency portion of the group at 2.4μ is shown in Fig. 5 and is composed of a $\perp$ and two $\parallel$ bands all overlapping to some extent. This group has been identified as $\nu_2+\nu_6$ since the character of the observed band agrees with that predicted for such a combination. The three bands are all of about the same intensity, but since the perpendicular part was plotted in percent absorption the ordinates are not directly comparable. Due to intense water vapor lines in the region, the authenticity of this band was for a time doubted. However, the gas was dried so carefully and such precautions were taken as to remove this doubt. Table IV shows the close agreement of some of the CH_3Cl lines with water vapor lines.[7] Another evidence indicating that the lines are due to CH_3Cl is the fact that every third line shows the characteristic enhancement. The zero branches of the parallel bands chosen to lie at 4047.1 cm^{-1} and at 4089.5 cm^{-1} are not very well defined. The region was measured with the 25.4 cm cell and the slit widths included 1.4 cm^{-1}, readings being taken at intervals of 1 cm^{-1}.

TABLE IV. (*Data on curve b of Fig. 5.*)

Observed ν (cm^{-1})	H_2O lines (cm^{-1})	$\Delta\nu$	Observed ν (cm^{-1})	H_2O lines (cm^{-1})	$\Delta\nu$
3963.0	3962.8	−0.2	3994.1	3995.7	1.6
3968.9	3970.3	0.14	4003.1		
3976.3	3976.6	0.3	4010.6	4009.3	−1.3
				4020.7	4.0
3983.7	3983.6	−0.1	4016.7		
				4012.2	−4.5
3991.1	3991.2	0.1	4024.2	4026.7	2.5

The 4.0μ region

Only the one $\perp$ band shown in Fig. 6, was found in this region. It is very clean throughout giving clearly an average spacing between lines of 9.7 cm^{-1}. The 1–1–2 intensity characteristic is shown more clearly in this band than in any other found. This band is believed to be $\nu_6+2\nu_5$ which according to theory must be a single $\perp$ band and should lie more free from overlapping than any other band in this region. The frequencies of the lines are given in Table III. Mapping of this band was accomplished with the 25.4 cm cell and the slits were set to include 2.5 cm^{-1}. Galvanometer readings taken at intervals of 1 cm^{-1} were plotted against cm^{-1}.

The 7.0μ region

Resolution of ν_3 would give the moments of inertia $A=B$ of the molecule. As Fig. 7 shows, this was not wholly successful despite the refinements in modern apparatus. Only a few lines in the negative branch near the center of the band were resolved giving a spacing of 1.3 cm^{-1}. These provide insufficient information for a reliable determination of the moments of inertia.

[7] Plyler and Sleator, Phys. Rev. **37**, 1493 (1931).

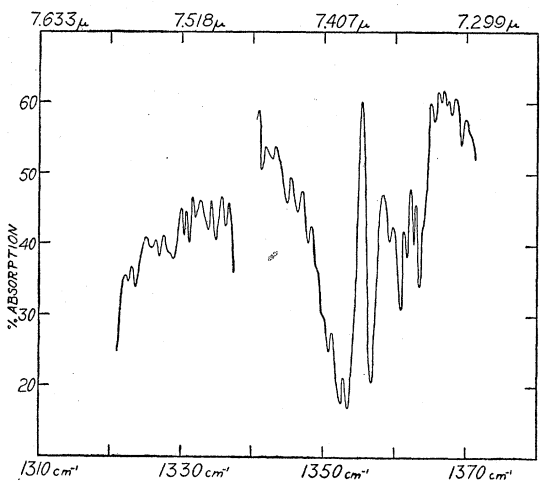

FIG. 7. This curve shows the result of the new attempt to resolve ν_3.

It is believed that the failure is due partly to the isotope effect in this vibration, partly to strong water vapor absorption and partly to inadequate resolving power. The zero branch, however, has a very different appearance from that found by Bennett and Meyer, being very sharp and as high as the positive and negative branches of the band. Its position agrees very exactly with that determined in the earlier work. The slits include 0.67 cm^{-1} and galvanometer readings were taken every 0.35 cm^{-1}. The final curve was plotted in percent absorption.

TABLE V. (*Data on photographic bands.*)

Observed ν	$\Delta\nu$	Observed ν	$\Delta\nu$
9992.6 cm^{-1}		10061.4 cm^{-1}	
	5.8		16.8
9998.4		10078.2*	
	3.3		6.9
10001.7		10085.1*	
	7.4		6.8
10009.1		10091.9*	
	9.2		8.7
10018.3		10100.6*	
	7.0		6.3
10025.3		10106.9*	
	7.8		4.0
10032.1		10110.9	
	7.7		2.4
10039.8		10113.3	
	4.0		7.4
10043.8		10120.7	
	8.5		3.9
10052.3		10124.6	
	5.1		
10057.4			
	4.0		

Mean spacing of lines = 6.7 cm^{-1}.
* Lines most accurately measured.

13772.7 cm^{-1}		13816.9 cm^{-1}	
	5.9		10.7
13778.6		13827.6	
	28.0		9.7
13806.6		13837.3	
	10.3		

The photographic region

Two bands were found photographically at 0.72μ and at 1.0μ, both apparently of the $\perp$ type. Prints of these do not reproduce well and are omitted here, but the frequencies of the lines are given in Table V. The lines marked with an asterisk were most accurately measured and given a spacing of 6.7 cm^{-1}. No interpretation of the 0.72μ band can satisfactorily be given at this time, but the one at 1.0μ is believed to be $\nu_4+3\nu_1$, a single $\perp$ band.

TABLE VI.

Observed ν	Identification	Character of observed bands	Predicted character
2967.0 cm⁻¹	(ν_1, $2\nu_4$)	∥, ∥	∥, ⊥, ∥
2879.6 cm⁻¹			
3047.2	ν_2	⊥	⊥
1355.3	ν_3	∥	∥
1459.6	ν_4	⊥	⊥
732.3	ν_5	∥	∥
1019.9	ν_6	⊥	⊥
2461.8	$\nu_6+2\nu_5$	⊥	⊥
3981.0			
4047.9	$\nu_2+\nu_6$	⊥, ∥, ∥	⊥, ∥, ∥
4089.6			
4175.8			
4230.6	$\nu_3+(\nu_1, 2\nu_4)$	⊥, ∥	⊥, ∥, ⊥
4383.8	$\nu_2+\nu_3$	⊥	⊥
4453.5	$\nu_2+2\nu_6$	⊥	⊥
5400.0	?	⊥	—
5900.0	$\nu_2+(\nu_1, 2\nu_4)$	⊥	∥, ⊥, ⊥, ∥, ∥
6050.0	$2\nu_2$	∥, ⊥	∥, ⊥
10000.0	$\nu_4+3\nu_1$	⊥	⊥
13800.0	?	⊥	—

In conclusion we submit Table VI giving the centers of the observed bands, and the present interpretation of them. The character of these bands as observed is compared with that predicted by the theory of such molecules which have three equivalent particles.