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THE NEAR INFRARED ABSORPTION SPECTRA OF SOME HALOGEN DERIVATIVES OF METHANE

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Abstract

The infrared absorption spectra of CH_3Cl, CH_3Br, and CH_3I, in vapor form, were measured from 1.5μ to 3.0μ. The fine structure of bands in the 2.3μ region was resolved in the first order. The fine structure of bands in the 1.6μ region was resolved in the second order, but not in the first. Seven bands were found.

Introduction

Bennett and Meyer[1] investigated the infrared absorption spectra of the four halogen derivatives of methane, CH_3F, CH_3Cl, CH_3Br, and CH_3I, in the vapor form. They applied the theory of the spinning top type of molecule, as developed by Dennison and others.[2] Only a brief outline of the theory is given here. The halogen and the carbon atoms form the only axis of symmetry (see Figure 1). C represents the moment of inertia about Z, the

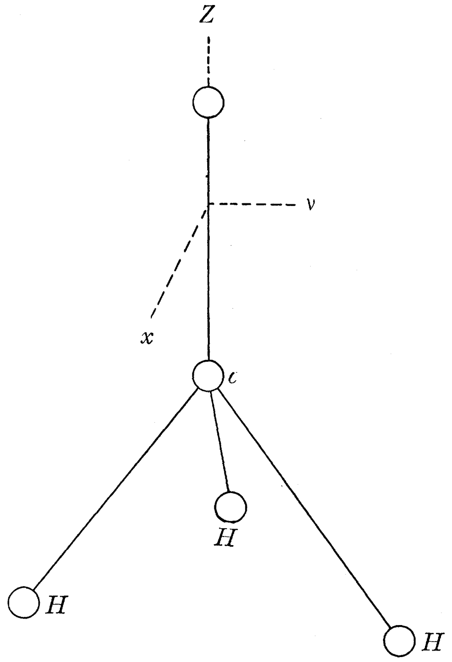

Fig. 1.

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[1] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).

[2] Dennison, Phys. Rev. **28**, 318 (1926). Other references are given in the article by Bennett and Meyer.

axis of symmetry. A and B represent the moments of inertia about the X- and Y-axes, respectively; then $A=B$. There are two possible normal modes of vibration. In the first type, the change of electric moment vibrates parallel to the axis of symmetry, giving rise to a "parallel" band. In the second type, the change of electric moment vibrates perpendicular to the axis of symmetry, giving rise to a "perpendicular" band.

In this investigation, the spectra of CH_3Cl, CH_3Br, and CH_3I, in vapor form, were studied in the region from 1.5μ to 3μ. Strong bands were found at the 1.6μ and 2.3μ regions. The fine structure of the 1.6μ region was resolved in the second order but not in the first. The fine structure of the bands of the 2.3μ region was resolved in the first order spectra. The bands in these two regions bear much resemblance to those reported by Bennett and Meyer, and the general method used by them in classifying their bands was used in this work.

EXPERIMENTAL PROCEDURE

The apparatus used and procedure followed have been described in a previous paper.[3] The pressures of the gases in the absorption cell are 70 cm Hg for CH_3Cl, 5 cm for CH_3Br and 20 cm for CH_3I. Chemically pure methyl iodide and methyl chloride were furnished by the Eastman Kodak Company. The methyl chloride was furnished by the Matheson Company of North Bergen, N.J. Comparison of the spectra obtained with the possible impurities named in the previous paper showed that the bands were due to the compounds themselves.

RESULTS

Bennet and Meyer[1] found seven series of bands between 3.3μ and 15μ. They classified them, according to their theory, as parallel and perpendicular bands, and lettered them from A to G. These seven series appeared to converge to the methane bands at 7.7μ, 3.3μ, and to the hypothetical methane band at 6.6μ of Dennison's theory,[4] in going from compound to compound of halogens of decreasing atomic weight. Variations were found in the frequency intervals of the Q branches in the perpendicular bands in going from series to series which indicated perturbations between the rotation and vibration. However, the doublet separation, the frequency difference between the maxima of the P and R branches remained quite constant for the same compounds, in going from series to series. No explanation was given for this phenomenon.

In this investigation seven bands were found in the region from 1.5μ to 2.5μ. These were lettered from H to N.

THE INDIVIDUAL SERIES

H Series. Parallel Type. The frequencies of the maxima of the P and R branches, and the doublet spacing, that is, the spacing of these maxima, are shown in Table VIII. These bands are not shown in the diagrams. The H band is a deep double band in all three compounds. The wave-lengths de-

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[3] Moorhead, Phys. Rev. **39**, 83 (1932).

[4] Dennison, Astrophys. Jour. **62**, 84 (1925).

crease rapidly with decreasing atomic weight of the halogen atom and the bands appear to converge to one of the methane bands in the 2.31μ region. Accurate readings were difficult because of a region of atmospheric water vapor bands.

I and J Series. Perpendicular Type. The wave-lengths of the lines of these bands are given in Tables I, III, and V. The curves are shown in Fig. 2. These bands are clearly separated in the iodide, but converge more and more closely toward each other in passing to halides of smaller atomic weight. In this convergence, the wave-lengths of the *I* band decrease, while those of the *J* band increase. These bands converge to one or two of the methane bands in the 2.2 μ region. Part of the fine structure is very uniform and distinct in the iodide and bromide, but in the chloride it is confused because of the overlapping of the two bands. In parts of the iodide and bromide bands, every third line is deeper than the other two. This characteristic was noted by Bennett and Meyer in some of the bands investigated by them. No simple explanation of this appears possible. In all the compounds the *J* band appears to be stronger than the *I* band.

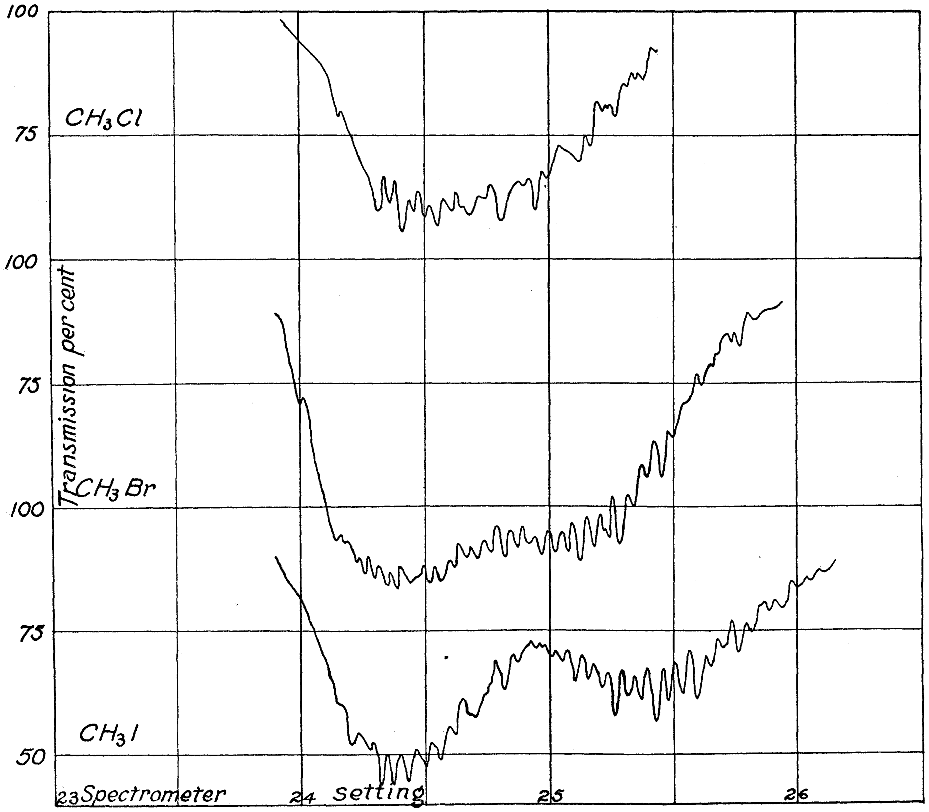

Fig. 2. Left *J*-Band. Right *I*-Band.

K and L Series. Parallel Type. M Series. Perpendicular Type. The wave-lengths of the lines are given in Tables II, IV, and VI. The maxima of the envelopes and doublet spacing of the parallel bands are shown in Table VIII. The frequency differences of the Q branches of the M band are shown in Table IX. Fig. 3. shows the second order spectra of these bands. These three series form a deep band region. The intensities, wave-lengths, and general appearance of the bands are similar for all three compounds, and they also bear much resemblance to the E, F, and G group of bands described by Bennett and Meyer. The K and L series are parallel bands superposed on the wise absorption region which is supposed to be a single series, Series M. In the case of the iodide, the K band appears to have P and R branches but no Q branch. In the bromide and chloride, the K bands appear to have P, Q, and R branches, although they are so masked by the fine structure of the M series that the maxima of the envelopes cannot be determined. In each of the compounds, the L series stands out prominently from the background of the M

TABLE I. *Methyl chloride 2.3μ band region.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}
24.31	2.2212	4502.0	25.12	2.2936	4360.0
.36	2.2253	4493.8	.17	2.2983	4351.0
.41	2.2297	4484.9	.215	2.3022	4343.6
24.455	2.2337	4476.9	.235	2.3040	4340.3
.505	2.2382	4467.8	.27	2.3070	4334.6
.555	2.2427	4458.9	.325	2.3120	4325.3
.61	2.2478	4448.8	.35	2.3142	4321.1
.66	2.2522	4440.1	.385	2.3175	4315.0
.68	2.2541	4436.4	.445	2.3230	4304.8
.745	2.2600	4424.8	.555	2.3330	4286.3
.81	2.2658	4413.5	25.585	2.3356	4281.6
.90	2.2740	4397.5	.67	2.3432	4267.6
.945	2.2782	4389.4	26.685	2.4340	4108.5
.995	2.2827	4380.8	.905	2.4537	4075.6
			27.035	2.4653	4056.2
			27.16	2.4768	4037.5

TABLE II. *Methyl chloride 1.6μ band region, second order.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Frequency Difference cm^{-1}	Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}
35.89	1.6248	6154.6	10.2	37.12	1.6785	5958
.95	1.6275	6144.4	11.	.23	1.6834	5940
36.01	1.6304	6133.4	9.6	.30	1.6865	5930
.07	1.6329	6123.8	13.2	.34	1.6882	5924
.15	1.6365	6110.6	9.8	.44	1.6926	5908
.21	1.6391	6100.8	15.4	.54	1.6969	5893
.305	1.6432	6085.4	10.4	.62	1.7004	5881
.37	1.6461	6075.0	12.8	.68	1.7030	5872
.45	1.6495	6062.2		.78	1.7074	5857
.62	1.6565	6037.		.90	1.7127	5839
.84	1.6661	6002.		38.06	1.7197	5815
.97	1.6721	5980.		.18	1.7249	5797
				.26	1.7285	5785

TABLE III. *Methyl bromide 2.3μ band region.*

Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}
24.00	2.1930	4560.0		25.12	2.2937	4359.8	10.3
.145	2.2060	4533.1		.18	2.2991	4349.5	10.1
.16	2.2072	4530.6		.24	2.3045	4339.4	
.22	2.2127	4519.3	6.3	24.285	2.3083	4332.2	7.2
.255	2.2158	4513.0	7.5	.34	2.3134	4322.6	9.6
.295	2.2195	4505.5	8.1	.39	2.3180	4314.1	8.5
.34	2.2235	4497.4	8.1	.45	2.3233	4304.2	9.9
.385	2.2275	4489.3	10.6	.50	2.3280	4295.5	
24.445	2.2328	4478.7		.615	2.3383	4276.6	
.515	2.2392	4465.9		.72	2.3478	4259.3	
.56	2.2432	4457.9		.825	2.3570	4242.7	
.61	2.2477	4449.0		.97	2.3702	4219.0	
.66	2.2522	4440.1		26.10	2.3818	4198.6	
.705	2.2563	4432.0		.23	2.3935	4178.0	
.765	2.2618	4421.3		.33	2.4025	4162.3	
.82	2.2666	4411.9	9.2	.42	2.4105	4148.5	
.87	2.2713	4402.7	7.7	.49	2.4167	4138.0	
.915	2.2753	4395.0	8.4	27.30	2.4894	4017.0	
.965	2.2797	4386.6	9.8	27.46	2.5046	3992.8	
25.02	2.2848	4376.8	9.2	27.85	2.5384	3939.5	
.075	2.2896	4367.6	7.8	28.20	2.5697	3891.5	

TABLE IV. *Methyl bromide 1.6μ band, second order.*

Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}
35.985	1.6291	6138.2		37.10	1.6777	5960.4	9.2
36.05	1.6320	6127.4		.16	1.6803	5951.2	9.4
.10	1.6343	6118.8		.22	1.6830	5941.8	10.
.185	1.6380	6105.0		.285	1.6858	5931.8	
.255	1.6410	6093.8		.47	1.6939	5903.	
.45	1.6496	6062.0		.56	1.6978	5890.	
.595	1.6559	6039.0		.65	1.7018	5876.	
36.965	1.6720	5980.8	11.4	.76	1.7065	5860.	
37.04	1.6752	5969.4	9.0	37.84	1.7102	5847.	

TABLE V. *Methyl iodide 2.3μ band.*

Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}
24.20	2.2108	4523.2		25.21	2.3017	4344.6	8.5
.27	2.2172	4510.2	8.9	.26	2.3062	4336.1	9.
.32	2.2216	4501.3	9.3	.31	2.3110	4327.1	9.7
.37	2.2262	4492.0	10.7	.365	2.3162	4317.4	9.9
.43	2.2315	4481.3	12.6	.43	2.3215	4307.5	8.5
.50	2.2378	4468.7	10.	.48	2.3261	4299.0	9.9
.555	2.2428	4458.7		.54	2.3315	4289.1	8.3
.63	2.2497	4444.5		25.59	2.3360	4280.8	10.1
.66	2.2522	4440.1		.65	2.3415	4270.7	8.7
.70	2.2558	4433.0		.705	2.3463	4262.0	9.1
.81	2.2658	4413.5		.76	2.3513	4252.9	8.8
.87	2.2712	4402.9		.815	2.3562	4244.1	
.94	2.2775	4390.8		.89	2.3632	4231.5	
25.005	2.2832	4379.8	7.8	.94	2.3675	4223.9	
.05	2.2873	4372.0	9.	26.01	2.3740	4212.3	
.10	2.2920	4363.0	8.9	.055	2.3778	4205.6	
.155	2.2967	4354.1	9.5	27.78	2.5322	3949.0	
				27.95	2.5475	3925.4	

series, exhibiting P and R branches and the very definite absence of a Q branch. The M series is a wide region of absorption. The band centers could not be determined, due to the presence of the K and L bands. Where sections

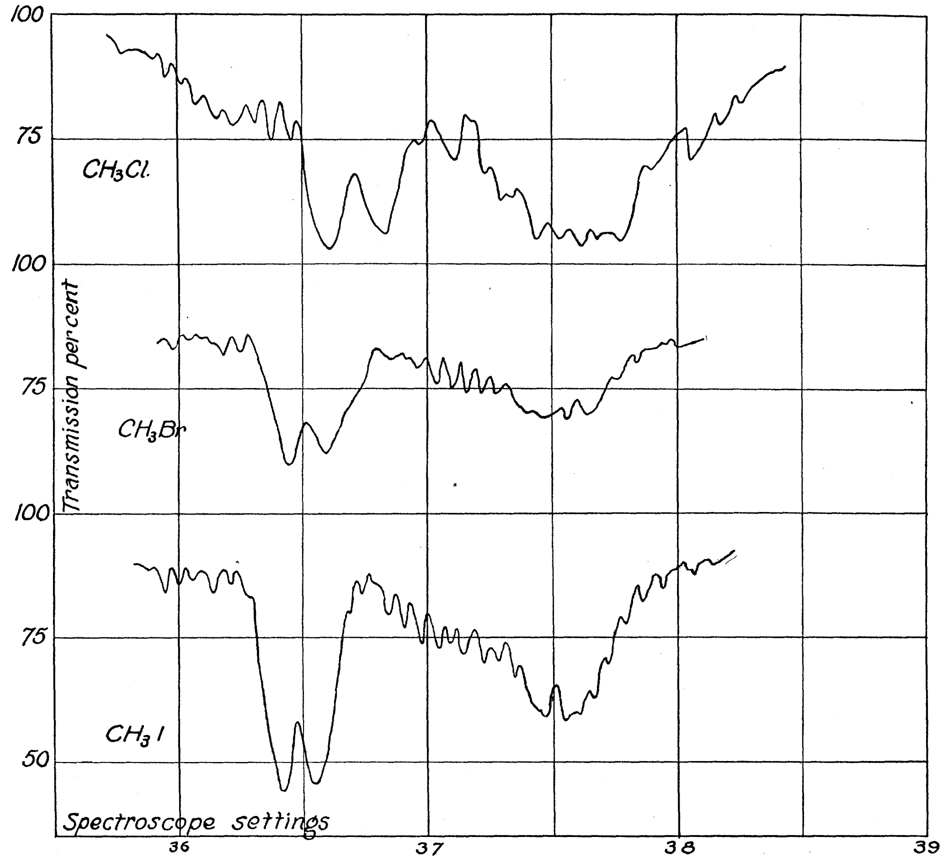

Fig. 3. Left L-Band. Right K-Band. M-Band as background.

TABLE VI. *Methyl iodide 1.6μ band, second order.*

Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}
35.95	1.6275	6144.2	9.8	37.095	1.6775	5961.2	7.6
36.005	1.6301	6134.4	9.2	.145	1.6796	5953.6	12.6
.06	1.6326	6125.2	14.6	.225	1.6832	5941.0	9.2
.15	1.6365	6110.6	9.8	.285	1.6858	5931.8	9.8
.21	1.6391	6100.8	12.2	.35	1.6886	5922.0	
.285	1.6424	6088.6		.46	1.6934	5905.	
.42	1.6482	6067.0		.55	1.6973	5892.	
.55	1.6539	6046.4		.61	1.7000	5882.	
.74	1.6621	6016.2		.66	1.7021	5875.	
.84	1.6665	6000.6	10.8	.72	1.7048	5865.	
.91	1.6695	5989.8	10.	.79	1.7079	5855.	
.975	1.6724	5979.8	11.	.86	1.7110	5845.	
37.045	1.6753	5968.8	7.6	.94	1.7145	5833.	

of sufficient regularity could be picked out, the frequency differences of the Q branches were computed.

TABLE VII. *Band centers 1.6μ region, first order.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Series
	Methyl Chloride		
15.80	1.4500	6896.	N
18.09	1.6582	6031.	L
18.19	1.6673	5998.	
18.55	1.7000	5882.	K
	Methyl Bromide		
15.85	1.4543	6876.	N
18.00	1.6500	6061.	L
18.08	1.6572	6034.	
18.52	1.6970	5893.	K
	Methyl Iodide		
16.03	1.4706	6806.	N
17.97	1.6472	6071.	L
18.05	1.6545	6044.	
18.55	1.7000	5882.	K

TABLE VIII. *Maxima of the envelopes of the branches, parallel bands. Observed frequencies.*

Series	P Branch	R Branch	Doublet Spacing
	Series H		
CH_3Cl	4037. cm^{-1}	4065. cm^{-1}	28 cm^{-1}
CH_3Br	3993.	4017.	24
CH_3I	3925.	3949.	24
	Series K (second order) Approximate centers		
CH_3Cl		5880. cm^{-1}	
CH_3Br		5890.	
CH_3I		5900.	
	Series L (second order)		
CH_3Cl	6002. cm^{-1}	6037. cm^{-1}	35 cm^{-1}
CH_3Br	6036.	6062.	26
CH_3I	6046.	6067.	21
	First order		
CH_3Cl	5998.	6031.	33
CH_3Br	6034.	6061.	25
CH_3I	6044.	6071. (App)	27 (App)

Doublet Spacing (Bennett and Meyer)

Series	CH_3F	CH_3Cl	CH_3Br	CH_3I
A	43 cm^{-1}	35 cm^{-1}	cm^{-1}	cm^{-1}
C	—	28	25	23
E	44	23	23	21
F	—	28	23	21

N Series. This band was found to be very weak in all the compounds studied. Repeated observations were taken and the band was proved to be genuine, but nothing could be learned about its type. This band probably converges to the 1.37μ band of methane. No curves are shown of this band.

COMPARISON BETWEEN THE SERIES

Table VIII gives the doublet separation of the parallel bands measured by the author, and also the doublet separations of the bands measured by Bennett and Meyer. This doublet separation remains nearly constant with the same compound for different series. Part of the variation is due to the errors of observation. The doublet spacing in general increased with the decrease in atomic weight of the halogen in the compound. The doublet spacings of the bands studied in this investigation agree well with the results given by Bennett and Meyer.

Table IX shows the frequency difference for the bands in the different perpendicular series. In most cases, only short sections were available so that the accuracy possible is not high. With this limitation in mind, it is seen that the frequency difference of the three bands measured does not vary much from band to band, or from compound to compound in the same band. According to the simple theory, the frequency difference depends upon the moment of inertia, *C*, and this should be the same for all compounds in the same series, unless there is a finite displacement of the hydrogen atoms in the molecule. It is seen in Table IX that this variation of the frequency differences is greater in the series investigated by Bennett and Meyer than in the series investigated by the author.

TABLE IX. *Average frequency intervals between lines perpendicular type (methyl halides).*

	Moorhead			Bennett and Meyer		
	Series *I* cm^{-1}	Series *J* cm^{-1}	Series *M* cm^{-1}	Series *B* cm^{-1}	Series *D* cm^{-1}	Series *G* cm^{-1}
CH_3F	—	—	—	5.65	11.5	7.5
CH_3Cl	—	—	11.55	6.95	12.	8.2
CH_3Br	9.0	8.1	9.8	7.42	11.9	9.0
CH_3I	9.5	10.3	10.3	7.70	11.8	9.0

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