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**Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases**

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## Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases\*

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The infrared spectra of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  in the five phases gas, liquid, vitreous solid,  $\alpha$ -crystal, and (except perhaps for  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  for which the solid-solid transitions have not been studied)  $\beta$ -crystal have been recorded in the range 4000 to 300  $\text{cm}^{-1}$ . The Raman spectrum of liquid  $\text{CD}_3\text{OH}$  has been recorded. A complete assignment of the internal modes is given, which differs somewhat from previous assignments for the  $\text{CH}_3$  bending and rocking vibrations. No significant difference in spectrum occurred between the  $\alpha$ -crystal and  $\beta$ -crystal phases. Under the full symmetry of the  $\beta$ -phase determined by x-ray diffraction only one OH out-of-plane bending band should occur.

### 1. INTRODUCTION

IN connection with a study of the intermolecular forces in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ , a vibrational assignment was needed for the vapors and crystals at 0°K. The following previous investigations of the vibrational spectra of methanol and the deuterated methanols have been reported:  $\text{CH}_3\text{OH}$ : vapor infrared,<sup>1-7</sup> liquid infrared,<sup>8-12</sup> liquid Raman,<sup>13-26</sup> vapor Raman<sup>21</sup>;  $\text{CH}_3\text{OD}$ : vapor

Two bands are observed, and it is concluded that the carbon and oxygen atoms in one chain are not coplanar, as is required by the symmetry determined by x-ray diffraction [K. J. Tauer and W. N. Lipscomb, *Acta Cryst.* **5**, 606 (1952)], but that the chains are puckered and the x-ray symmetry arises because the puckered chains are irregularly distributed, a structure that had been previously suggested by Tauer and Lipscomb tentatively on the basis of high apparent thermal amplitudes. Bands occur in the crystal spectra near 500  $\text{cm}^{-1}$  and 340  $\text{cm}^{-1}$  at  $-180^\circ\text{C}$ . These are interpreted as lattice modes, probably the two infrared-active modes that involve translations of the molecules.

infrared,<sup>3,4,7,8,27</sup> liquid infrared,<sup>7</sup> liquid Raman,<sup>15,17,19</sup>  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$ : vapor infrared<sup>3,4</sup>;  $\text{CD}_3\text{OD}$ : liquid Raman.<sup>3,22</sup> No work on the solids has been reported, except for a very brief statement about the 3- $\mu$  region of solid  $\text{CH}_3\text{OH}$ .<sup>28,29</sup> There were a number of uncertainties in the assignment of the vapor frequencies. We have, therefore, recorded the infrared spectra of the four methanols  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ , in five phases, viz., gas, liquid, vitreous solid,  $\alpha$ -crystal, and, except perhaps for  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  for which solid-solid transitions have not been studied,  $\beta$ -crystal.

### 2. EXPERIMENTAL

#### 2.1 Materials

Reagent-grade methanol was dehydrated twice by treatment with magnesium turnings and distilled through a 19-in. Vigreux fractionating column, the middle third of the constant-boiling fraction being collected. The spectrum after purification differed in no way from that of the original alcohol, and vapor chromatographic analysis showed no impurities greater than 0.1%.

The deuterated methanols were purchased from the Merck Chemical Company, Montreal. Vapor-chromatographic analysis showed them to be free from impurities within 0.1% except for a trace of xylene, which was easily removed by a simple vacuum distillation. All four alcohols were anhydrous, as indicated by the absence in the vapor and solid spectra of the strong  $\text{H}_2\text{O}$  absorption band at 1640  $\text{cm}^{-1}$  or the corresponding  $\text{D}_2\text{O}$  absorption band at 1220  $\text{cm}^{-1}$ . However, a trace of atmospheric moisture was often introduced into the liquid samples, which were handled with a pipette. The  $\text{CD}_3$  groups in  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  were over 99% deu-

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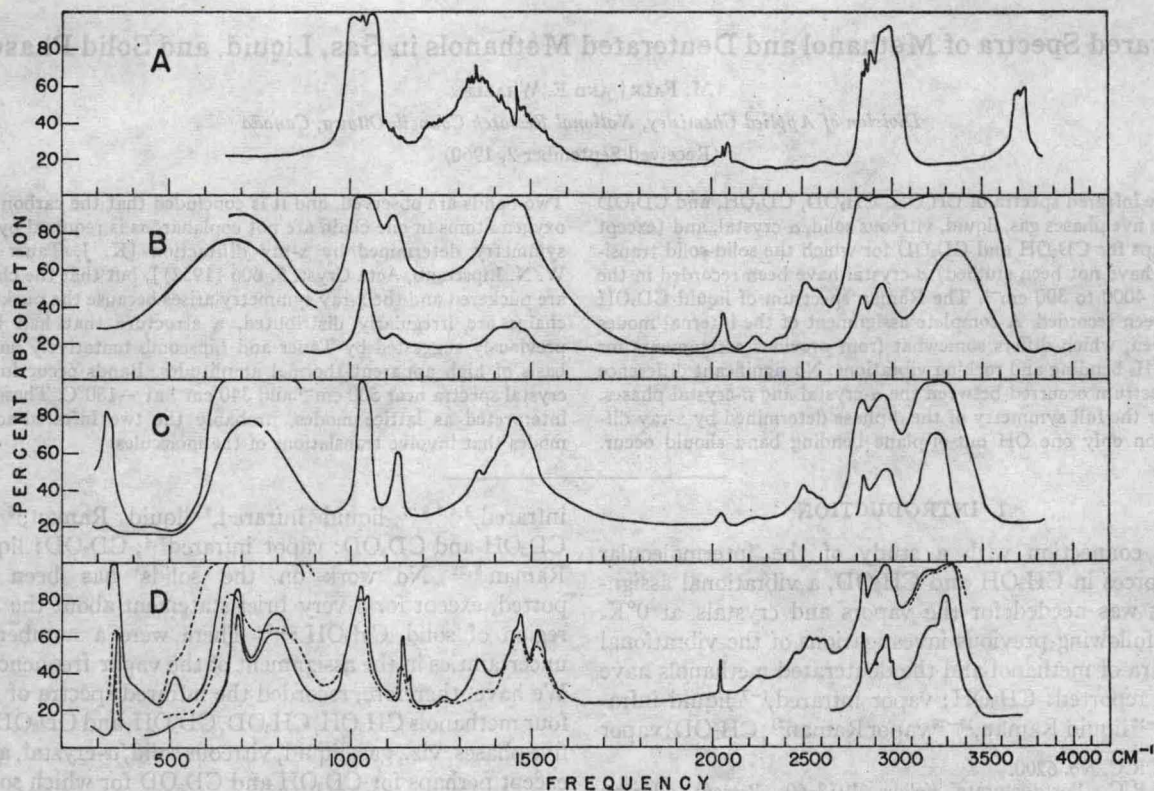


FIG. 1. Infrared absorption spectrum of  $\text{CH}_3\text{OH}$ . A—Vapor, 10-cm path-length, 80 mm Hg pressure, room temperature. B—Liquid, room temperature. Two sample thicknesses are shown, approximately 5 and 50  $\mu$ . C—Vitreous solid,  $-180^\circ\text{C}$ . D—Crystalline solid,  $-180^\circ\text{C}$  (full line) and  $-108^\circ\text{C}$  (broken line, shown only where the spectrum differs appreciably from that at  $-180^\circ\text{C}$ ). Several film thicknesses are shown.

terated, as shown by an almost complete lack of absorption in the CH stretching region. The OD groups in  $\text{CH}_3\text{OD}$  were about 95% deuterated.

## 2.2 Spectra

The vapor spectra were recorded using a standard 10-cm gas cell filled to about 80 mm Hg methanol pressure at room temperature. The liquid films were formed by squeezing a small drop between two flat silver-chloride or cesium-bromide disks. The solid samples were prepared by condensing small amounts of vapor onto a cesium-bromide disk mounted in a silver holder in a conventional low-temperature infrared cell. The disk was pressed tightly against the holder by a spring to ensure good thermal contact. The temperature was measured to about  $2^\circ\text{C}$  by a copper-constantan thermocouple embedded in the cesium-bromide disk; about  $-180^\circ\text{C}$  was normally registered with liquid nitrogen in the coolant reservoir, and the temperature registered when films of  $\text{CH}_3\text{OH}$  melted was  $-97 \pm 5^\circ\text{C}$ , compared with the true melting point of  $-98^\circ\text{C}$ .

The infrared spectra were recorded on a Perkin-Elmer model-21 double-beam spectrophotometer equipped with sodium-chloride and calcium-fluoride prisms, and on a Beckman IR-4 double-beam spectrophotometer equipped with cesium-bromide and, for some spectra, lithium-

fluoride prisms. The instruments were regularly calibrated using the spectrum of water vapor and of thin polyethylene films. The Raman spectrum of liquid  $\text{CD}_3\text{OH}$  was recorded on a Cary model-81 Raman Spectrophotometer and the polarization of the bands was determined by the Edsal and Wilson technique.

## 3. RESULTS

Composite tracings of the infrared spectra of all four methanols in the gas and liquid phases at room temperature, the vitreous solid (see below) at  $-180^\circ\text{C}$ , and the crystalline phases at  $-180^\circ\text{C}$  and  $-108^\circ\text{C}$ , are shown in Figs. 1-4. They were obtained by dividing the transmission of the cell containing the methanol sample by the transmission of the empty cell, except where the background was low and flat, when this procedure was not needed. The background noise was serious only below  $350\text{ cm}^{-1}$ ; it was smoothed out in replotting the spectra.

The observed frequencies and rough relative intensities are listed in Tables I-IV. They are usually the means of several measurements. The accuracy of the frequencies of sharp bands above  $2000\text{ cm}^{-1}$  is at least  $\pm 4\text{ cm}^{-1}$ , below  $2000\text{ cm}^{-1}$  at least  $\pm 2\text{ cm}^{-1}$ , and below  $500\text{ cm}^{-1}$  at least  $\pm 1\text{ cm}^{-1}$ . The centers of broad bands are measured much less accurately. The intensities of the bands below  $650$

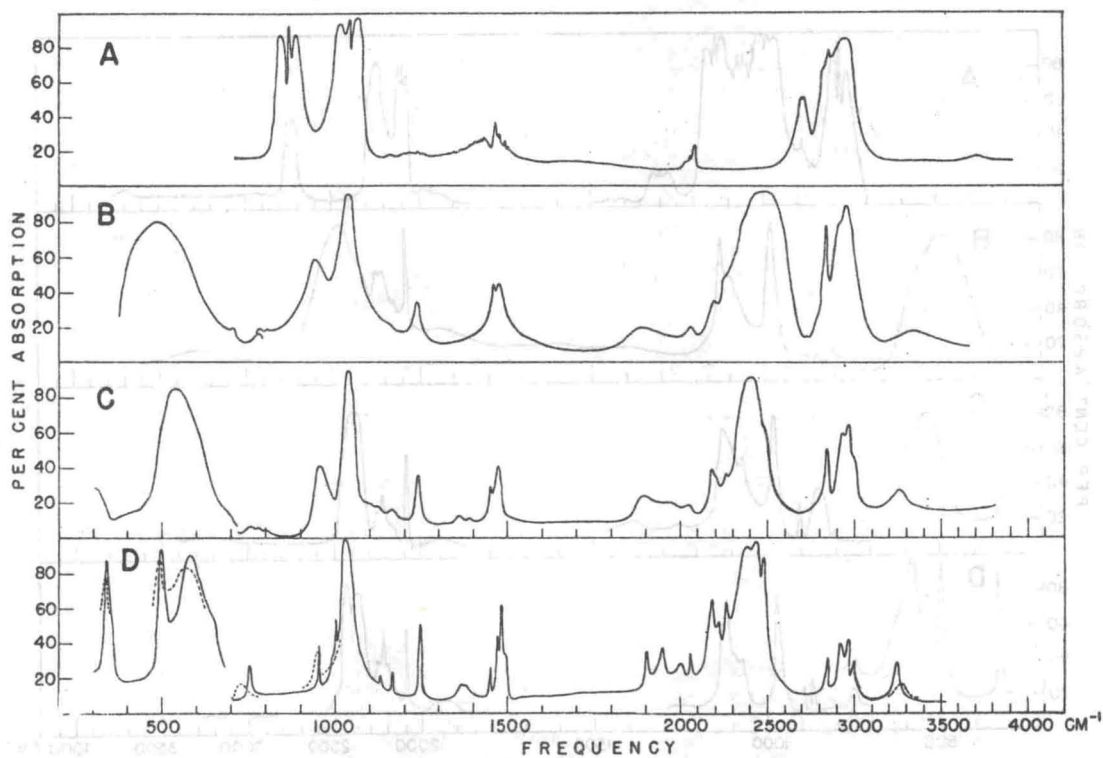


FIG. 2. Infrared absorption spectrum of  $\text{CH}_3\text{OD}$ . A—Vapor, 10-cm path-length, 80 mm Hg pressure, room temperature. B—Liquid, room temperature. C—Vitreous solid,  $-180^\circ\text{C}$ . D—Crystalline solid,  $-180^\circ\text{C}$  (full line) and  $-108^\circ\text{C}$  (broken line, shown only where the spectrum differs appreciably from that at  $-180^\circ\text{C}$ ).

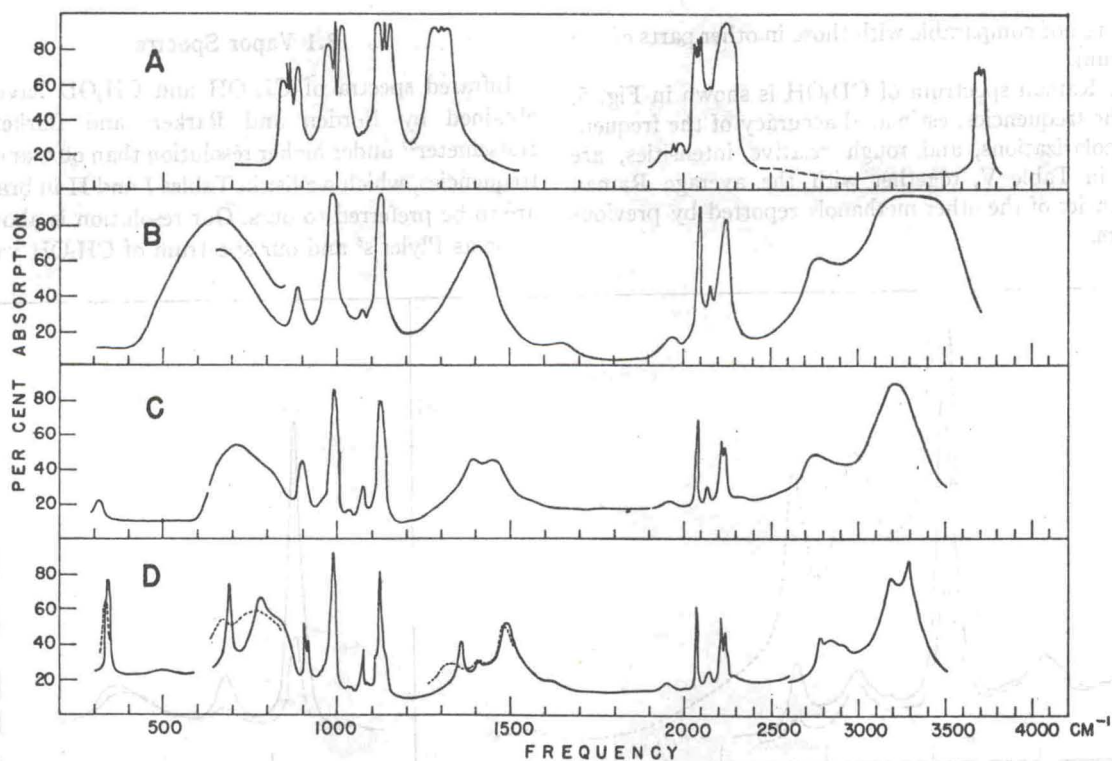


FIG. 3. Infrared absorption spectrum of  $\text{CD}_2\text{OH}$ . A—Vapor, 10-cm path-length, 80 mm Hg pressure, room temperature. B—Liquid, room temperature. C—Vitreous solid,  $-180^\circ\text{C}$ . D—Crystalline solid,  $-180^\circ\text{C}$  (full line) and  $-108^\circ\text{C}$  (broken line, shown only where the spectrum differs appreciably from that at  $-180^\circ\text{C}$ ).

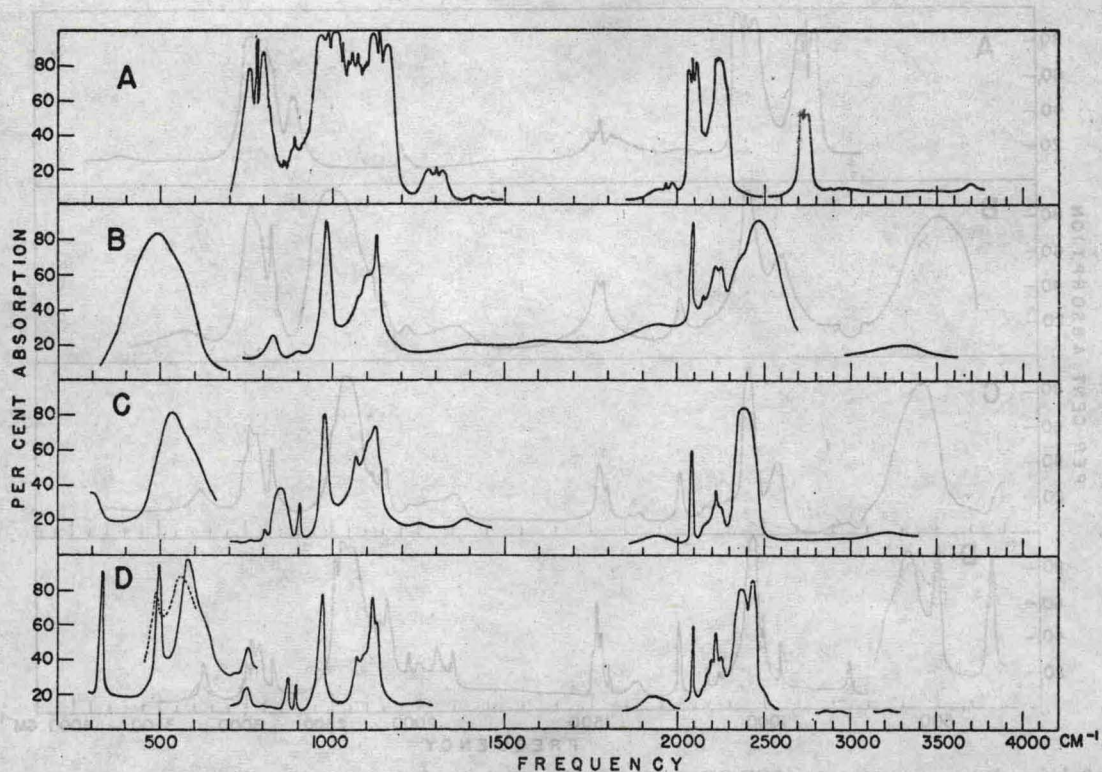


FIG. 4. Infrared absorption spectrum of  $\text{CD}_3\text{OD}$ . A—Vapor, 10-cm path-length, 80 mm Hg pressure, room temperature. B—Liquid, room temperature. C—Vitreous solid,  $-180^\circ\text{C}$ . D—Crystalline solid,  $-180^\circ\text{C}$  (full line) and  $-108^\circ\text{C}$  (broken line, shown only where the spectrum differs appreciably from that at  $-180^\circ\text{C}$ ).

$\text{cm}^{-1}$  are not comparable with those in other parts of the spectrum.

The Raman spectrum of  $\text{CD}_3\text{OH}$  is shown in Fig. 5, and the frequencies, estimated accuracy of the frequencies, polarizations, and rough relative intensities, are listed in Table V, together with the average Raman frequencies of the other methanols reported by previous authors.

### 3.1 Vapor Spectra

Infrared spectra of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  have been obtained by Borden and Barker<sup>2</sup> and Barker and Bosschieter<sup>27</sup> under higher resolution than ours and their frequencies, which we list in Tables I and II in brackets, are to be preferred to ours. Our resolution is about the same as Plyler's<sup>5</sup> and our spectrum of  $\text{CH}_3\text{OH}$  vapor is

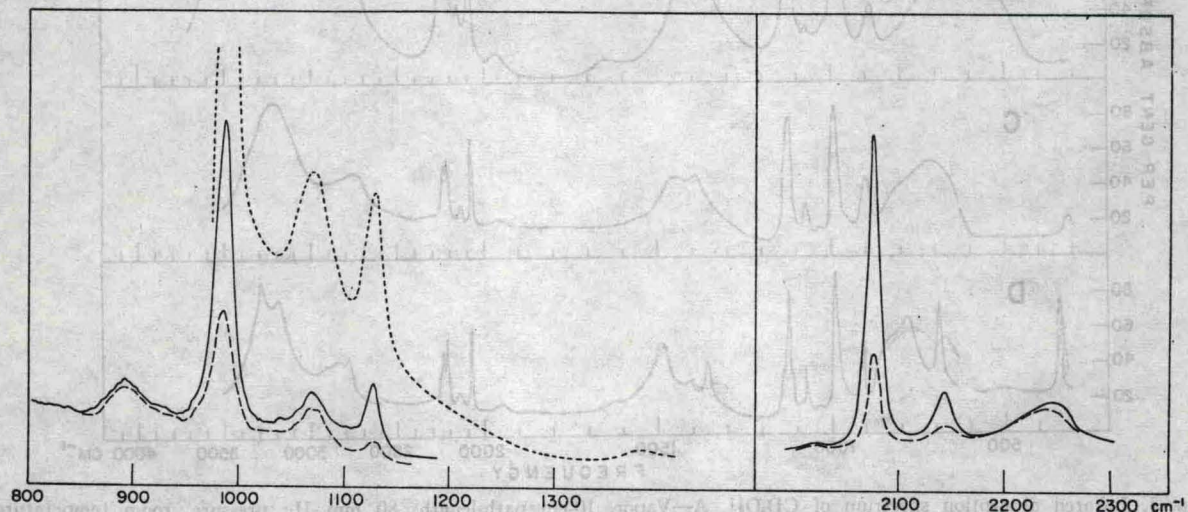


FIG. 5. Raman spectrum of liquid  $\text{CD}_3\text{OH}$ . Full line = exciting light polarized perpendicular to the scattered beam. Broken line = exciting light polarized parallel to the scattered beam. Short-dashed line: exciting light not polarized.

TABLE I. Infrared spectrum of CH<sub>3</sub>OH.<sup>a</sup>

Vapor <sup>b</sup>	Liquid	Crystal			Assignment <sup>c</sup>
		Vitreous -180°C	-180°C	-108°C	
R 3713 Q 3687 } s(3682) P 3673 }	3337 vs, br	3235 vs	3443 sh 3284 vs 3187 s	3297 vs 3193 s	(?) OH stretching <i>a'</i>
2973 vs(2977)	2934 vs	2982 sh, w 2951 vs	2982 m 2955 s 2912 sh, m	2980 m 2954 s	CH <sub>3</sub> asym. stretching <i>a'</i> and <i>a''</i> <sup>d</sup>
R 2869 Q 2845 } s(2844) P 2826 }	2822 s	2828 s	2829 s	2831 s	CH <sub>3</sub> sym. stretching <i>a'</i>
~2600 vw	2571 w 2502 w 2340 vw 2232 vw	2607 m 2537 m 2488 w 2230 w	2617 m 2562 m 2538 m 2457 w	2613 m - ~2540 m 2455 w	1346+1233(?) 1415+1116(?) 1346+1116(?) 2×1233(?) 1233+1116 2×1116
R 2078 Q 2056 } w(2053) P 2035 }	2053 w	~2040 w	~2040 w	~2040 w	2×1034
1477 m(1477) 1455 m(1455) 1415 w[1430?]	1480 sh 1455 m ~1420 <sup>f</sup>	1452 m 1415 sh	~1545 sh, vw 1458 sh ~1445 sh, m 1426 sh	- ~1459 sh - 1420	2×790 CH <sub>3</sub> asym. bending <i>a'</i> CH <sub>3</sub> sym. bending <i>a'</i> CH <sub>3</sub> asym. bending <i>a''</i>
1346 s(1340)	~1420 m, br	~1450 m 1350 w*	{1514 m 1470 m 1345 m	1506 m 1460 m {~1370 w, br ~1300 w, br}	OH in-plane bending <i>a'</i> 2×685
1233 w[1260] 1116 w[1209]	absent 1114 w	~1256 w 1124 w	1256 w {1162 vw 1142 w}	1257 w 1142 w	CH <sub>3</sub> rocking <i>a''</i> CH <sub>3</sub> rocking <i>a'</i>
R 1060 Q 1034 } vs(1034) P 1012 }	1029 vs	1032 vs	{1046 w 1029 vs}	1030 vs	CO stretching <i>a'</i>
	655 s	730 s ~320 m	~1011 vw {790 s 685 m 520 w 357 m	765 s {675 m ~520 sh, w 346 m	C <sup>18</sup> O stretching OH out-of-plane bending lattice mode (or overtone) lattice mode

<sup>a</sup> All frequencies are in cm<sup>-1</sup>, vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, br=broad.

<sup>b</sup> Data in parentheses are those of Borden and Barker (see the work cited in footnote 2) and those in square brackets are those of Noether (see the work cited in footnote 3).

<sup>c</sup> Species of vibrations apply to vapor only. "Sym." and "asym." refer to the internal symmetry of the methyl group.

<sup>d</sup> Fermi resonance in the solid occurs between one of the CH<sub>3</sub> asymmetric stretching modes and an overtone or combination of the CH<sub>3</sub> bending modes, giving the extreme frequencies in this group.

<sup>e</sup> Frequencies proposed for the components of overtone bands are those of the vapor, or those of the solid at -180°K if not observed in the vapor.

<sup>f</sup> Overrun by the OH in-plane bending band.

\* Probably due to partly crystallized material.

TABLE II. Infrared spectrum of CH<sub>3</sub>OD.<sup>a</sup>

Vapor <sup>b</sup>	Liquid	Crystal			Assignment <sup>c</sup>
		Vitreous -180°C	-180°C	-108°C	
	3340 w, br	3225 m	3233 m	3258 m	OH stretching (CH <sub>3</sub> OH)
	2990 sh, w	2985 sh, w	2993 w	2990 w	
2965 vs(2964)	2940 vs	2957 s	2962 s	2958 s	CH <sub>3</sub> asym. stretching <i>a'</i> and <i>a''</i> <sup>d</sup>
	2910 sh, s	2917 s	2917 s	2918 s	
R 2872					CH <sub>3</sub> sym. stretching <i>a'</i>
Q 2840 }s(2850)	2825 s	2835 s	2838 s	2938 s	
P 2825 }					
		2465 sh, m	2475 m	2475 sh, m	2×1228 <sup>e</sup>
R 2745					OD stretching
Q 2720 }m(2720)	2485 vs, br	2400 vs, br	{2431 vs	2440 vs	
P 2705 }			{2372 vs	2376 vs	
	2260 sh, vw	2256 w	2252 w	2252 w	1041+1228
	2190 w	2200 vw	2215 vw	2215 vw	1228+998(?)
		2175 w	2175 w	2177 w	1228+949
R 2082					2×1041
Q 2062 }w(2065)	2050 w	2051 w	2049 w	2050 w	
P 2043 }					
		~1967 vw, br	1997 w	1985 w	2×998
	1885 m, br	1885 w, br	1942 m	1935 m	1027+949
1500 (1480)	1472 m	1470 m	1897 w-m	1889 w-m	2×945; 2×949
1458 }m(1459)			{1486 w	1475 m	CH <sub>3</sub> asym. bending <i>a'</i>
1427 (1427)	1452 m	1444 w	{1476 m	~1465 sh, w	
1348 vvw			{1465 w	~1443 w	CH <sub>3</sub> sym. bending <i>a'</i>
			{1443 w		CH <sub>3</sub> asym. bending <i>a''</i>
		1376 vw	1375 w	1375 w	1040+344(?)
		1352 w	1362 w	1362 w	1027+344(?)
1228 w [1232]	1235 m	1233 m	1238 m	1236 m	CH <sub>3</sub> rocking <i>a''</i>
1160 vw [1207]	1155 sh, vw	1158 w	1163 w	1162 w	CH <sub>3</sub> rocking <i>a'</i>
		1123 vw	1130 vw	1128 vw	CH <sub>3</sub> rocking <i>a'</i> (CH <sub>3</sub> OH)
R 1061					CO stretching <i>a'</i>
Q 1041 }vs(1040)	1038 vs	1032 vs	{1040 sh, m	~1040 sh, w	
P 1015 }			{1027 vs	1027 vs	
					OD in-plane bending <i>a'</i>
R 885			{998 w	980 sh, vw	
Q 867 }s(863)	942 s	945 m, br	{985 sh, vw	943 m, br	
P 846 }			{949 m	725 m, br	
			{750 m	~640 sh, vw	OH out-of-plane bending (CH <sub>3</sub> OH)
			{640 sh, w		2×344(?)
	475 s	535 s	{577 s	565 s	OD out-of-plane bending
			{495 s	490 s	
		~290 br	344 s	333 s	lattice mode

<sup>a</sup> Abbreviations are given in Table I.

<sup>b</sup> Data in parentheses are from Barker and Bosschieter (see the work cited in footnote 27), and those in square brackets are from Noether (see the work cited in footnote 3).

<sup>c</sup> See Table I.

<sup>d</sup>

essentially identical with his. Our frequencies of CD<sub>3</sub>OH and CD<sub>3</sub>OD vapor are more accurate than Noether's because his resolution was lower and he has impurities in his deuterated methanols.

The present assignments for the four methanols are the same as Noether's,<sup>3</sup> Herzberg's,<sup>30</sup> and Plyler's<sup>5</sup> except for the bending and rocking vibrations of the CH<sub>3</sub> and CD<sub>3</sub> groups, which we shall now discuss in detail.

#### CH<sub>3</sub> Bending Modes

Three CH<sub>3</sub> bending modes are expected, viz., an *a'* internally symmetrical mode which has an approximately

<sup>30</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 334.

parallel band envelope, and two internally asymmetrical modes of species *a'* and *a''* which have approximately perpendicular band envelopes. It seems likely that the sharp peak at 1455 cm<sup>-1</sup> in CH<sub>3</sub>OH is the *Q* branch of an approximately parallel band and so is probably due to the *a'* symmetrical bending mode.<sup>2</sup> The bands with centers at 1415 and 1477 cm<sup>-1</sup>, both of which appear to be approximately perpendicular, may be the *a'* and *a''* CH<sub>3</sub> internally asymmetrical bending modes. The *a'* mode is somewhat arbitrarily assigned to the higher frequency. In CH<sub>3</sub>OD the bands are a good deal clearer owing to the absence of the OH bending mode. The sharp peak at 1458 cm<sup>-1</sup> is clearly the *Q* branch of the approximately parallel band due to the CH<sub>3</sub> internally symmetrical bending mode, and the central gaps of the

TABLE III. Infrared spectrum of CD<sub>3</sub>OH.<sup>a</sup>

Vapor <sup>b</sup>	Liquid	Vitreous -180°C	Crystal		Assignment <sup>c</sup>	
			-180°C	-108°C		
R 3708 Q 3690 P 3675	s(3680)	3310 vs, br	3195 vs, br	{3285 vs 3175 s}	3297 vs 3197 s	OH stretching <i>a'</i>
	2752 m, br	2760 m, br	{2920 w 2830 w 2772 m}	2920 w 2830 w ~2770 m	2×1488 <sup>e</sup> 1488+1405 2×1405	
2235 vs(2232)	2232 vs	{2235 m 2213 s	2250 sh, w 2236 m 2214 s	2236 m ~2214 s	CD <sub>3</sub> asym. stretching <i>a'</i> and <i>a''</i> <sup>d</sup>	
2147 vw	2145 w	2135 w	2138 w	~2138 w	2×1075	
R 2098 Q 2077 P 2059	s(2094)	2078 s	2075 s	2075 s	~2074 s	CD <sub>3</sub> sym. stretching <i>a'</i>
		~2020 vw	~2020 vw	~2020 vw	2×1047	
R 1983 Q 1966 P 1947	w(1975)	1962 w	1957 w	{1969 sh, vw 1949 w}	1947 w}	2×988
R 1310 Q 1297 P 1274	vs(1289)	1391 br	1445 s	{1488 vs 1405 w}	1479 vs 1404 w}	OH in-plane bending <i>a'</i> <sup>t</sup>
			1389 s	1354 s	1320 br, m	2×685 <sup>f</sup>
R 1145 Q 1134 P 1112	vs(1123)	1122 vs	1122 vs	{1131 sh, w 1121 vs}	1118 vs}	CD <sub>3</sub> sym. bending <i>a'</i>
1075 w(1080?)	{1090 sh, vw 1069 w}	~1106 sh	1106 vw	1083 sh, w	~1086 sh, w}	C <sup>13</sup> D <sub>3</sub> sym. bending
		1066 m	1069 m	1069 m	1069 m}	CD <sub>3</sub> asym. bending <i>a''</i>
1047 (1055?)	1020 sh, vw	1026 w	{1031 w 1023 w}	1029 w 1023 w}		CD <sub>3</sub> asym. bending <i>a'</i>
R 1007 Q 988 P 966	vs(990)	982 vs	983 vs	{987 sh, w 980 vs}	~987 sh, w 981 vs}	CO stretching <i>a'</i>
877 m(879)		950 sh, vw	{953 vw 947 vw}	953 vw 947 vw}		CD <sub>3</sub> rocking <i>a''</i>
858 m(856)	882	895	{912 w 902 m 823 sh, m}	909 vw 900 vw}		CD <sub>3</sub> rocking <i>a'</i>
	665 s, br	708 br	{776 s, br 685 s}	741 s, br 670 s}		510+339(?) OH out-of-plane bending
		~314 w	~510 w, br 339 s	~490 w, br 332 m		lattice mode (or overtone) lattice mode

<sup>a</sup> Abbreviations are given in Table I.<sup>b</sup> Data in parentheses are those of Noether (see the work cited in footnote 3).<sup>c</sup> See Table I.<sup>d</sup> See Table I.<sup>e</sup> Rather weak Fermi resonance seems to occur between 2×685 and one of the OH in-plane bending modes.

bands due to the internally asymmetrical modes are probably at 1500 and 1427 cm<sup>-1</sup>. In the Raman spectra of the liquids the three bands are incompletely resolved. In crystalline CH<sub>3</sub>OH the corresponding bands are overrun by the OH bending mode, but in crystalline CH<sub>3</sub>OD the three bands due to the three CH<sub>3</sub> bending modes are clearly seen.

There are strong, approximately parallel bands in the vapor spectra of CD<sub>3</sub>OH and CD<sub>3</sub>OD with *Q* branches at 1134 and 1135 cm<sup>-1</sup>, respectively, which are clearly due to the *a'* CD<sub>3</sub> internally symmetrical bending mode. In confirmation of this the corresponding Raman band in CD<sub>3</sub>OH at 1127 cm<sup>-1</sup> is polarized. There are two weak bands at somewhat lower frequencies, those in CD<sub>3</sub>OD having their central gaps at 1080 cm<sup>-1</sup> and 1035 cm<sup>-1</sup>

and those in CD<sub>3</sub>OH being somewhat weaker and less well resolved at 1075 cm<sup>-1</sup> and 1047 cm<sup>-1</sup>. These are probably the two CD<sub>3</sub> internally asymmetrical bending bands. The assignment of the higher frequency to the *a''* mode is again rather arbitrary, but gives somewhat better agreement with the product rule. The two bands are not resolved in the Raman spectrum, only one maximum, which is depolarized, occurring at 1070 cm<sup>-1</sup>. There are two bands in the infrared spectra of solid CH<sub>3</sub>OH and CD<sub>3</sub>OD, though possible contributions from one of the CD<sub>3</sub> rocking modes (see below) render interpretation uncertain.

The three CH<sub>3</sub> bending bands are not in the same order of frequency as the three CD<sub>3</sub> bending bands. Thus, in CH<sub>3</sub>OH and CH<sub>3</sub>OD the frequency of the CH<sub>3</sub>



TABLE IV. Infrared spectrum of CD<sub>3</sub>OD.<sup>a</sup>

Vapor <sup>b</sup>	Liquid	Vitreous -180°C	Crystal		Assignment <sup>c</sup>
			-180°C	-108°C	
3684 w (~3680) 2976 } 2953 }vw 2933 } 2871 vw	3310 w, br	3195 w, br	3193 w 2975 }vw 2925 }	3216	OH stretching (CD <sub>3</sub> OH) CH stretching (CD <sub>2</sub> HOD and CDH <sub>2</sub> OD)
R 2746 Q 2724 }s(2725) P 2708 }	2474 vs, br  (2365 sh)	2384 s, br	{2432 s 2361 s}	2432 s 2361 s}	OD stretching a'
2242 } 2228 }vs(2227) 2215 }	2250 m 2225 m 2215 sh, vw	2240 w 2213 m 2190 sh, w	2240 m 2212 s 2189 m-w {2150 sh, vw 2130 sh, vw}	2248 m } 2223 s }	(?) CD <sub>3</sub> asym. stretching a' and a'' <sup>d</sup>
R 2100 Q 2080 }vs(2081) P 2063 }	2082 s	2075 s	2075 s	~2075 s	CD <sub>3</sub> sym. stretching a'
R 1977 Q 1959 }w(1966) P 1943 }	~1940 br	1925 w	1980 sh, w {1935 w 1920 w}	~1920 w	1116+862(?) 2×983
R 1310 Q 1297 }m(1290?) P 1273 }	~1380 vw, br	1382 w 1256 vw	{1420 w 1395 w}	{1422 w 1395 w}	OH bending (CD <sub>3</sub> OH) <sup>f</sup> CD <sub>2</sub> H rocking (?)
R 1155 Q 1135 }vs(1121) P 1117 }	1124 vs	1117 vs	1116 vs	1116 vs	CD <sub>3</sub> sym. bending a'
1080±10 w(1075?) ~1060 w(1045?) ~1024±10 w(?)	1097 s 1068 sh, m ~1080(?)	~1100 sh, w 1062 m ~1125(?)	~1080 sh, vw 1064 w 1131 w	~1085 sh, vw 1064 w	CD <sub>3</sub> asym. bending a'' CD <sub>3</sub> asym. bending a' CD <sub>3</sub> rocking and OD in-plane bending a'
R 1001 Q 983 }vs(987) P 962 }	979 vs	975 vs	968 vs	969 vs	CO stretching a'
892 w(?) 856 w(?)	898 w	896 m	895 m	892 m	(?) CD <sub>3</sub> rocking a''
R 797 Q 776 }s(775) P 753 }	818 m	831 m, br	862 m	857 w	CD <sub>3</sub> rocking and OD in-plane bending a'
		800 w ~730 vw	745 w ~630	~755 sh, vw ~630	(?) OH out-of-plane bending (CD <sub>3</sub> OH) 2×336(?)
	483 s, br	533 s ~300(?)	{578 s 495 s 336 vs}	{556 s 487 s 325.5 s}	OD out-of-plane bending lattice mode

<sup>a</sup> Abbreviations given in Table I.<sup>b</sup> Data in parentheses are those of Noether (see the work cited in footnote 3).<sup>c</sup> See Table I.<sup>d</sup> Doubling in the crystal is probably due to Fermi resonance with 2×705 cm<sup>-1</sup>.

internally symmetrical bending mode appears to be between those of the two asymmetrical bending modes, whereas in CD<sub>3</sub>OH and CD<sub>3</sub>OD it appears to be a good deal higher. This is probably caused by interaction of the CH<sub>3</sub> internally symmetrical bending motion with the CO stretching motion. The CO stretching frequency drops from 1034 cm<sup>-1</sup> in CH<sub>3</sub>OH and 1041 cm<sup>-1</sup> in CH<sub>3</sub>OD to 988 cm<sup>-1</sup> in CD<sub>3</sub>OH and 983 cm<sup>-1</sup> in CD<sub>3</sub>OD, and at the same time the deuteration shift of the CH<sub>3</sub> internally symmetrical bending frequency is only 1.28 instead of the expected 1.36. The isotope shifts are

shown diagrammatically in Fig. 6. The apparent inversion of the order of frequency for the two CH<sub>3</sub> and CD<sub>3</sub> internally asymmetrical bending modes is quite uncertain

#### CH<sub>3</sub> Rocking Modes

There are two CH<sub>3</sub> rocking modes, of species a' and a''. In the absence of interaction of the motions with the motions of other atoms the frequencies are expected to be close together. However, we note that the shift of the OH bending frequency on deuteration is high, being

TABLE V. Raman frequencies of liquid CH<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD.<sup>a</sup>

CH <sub>3</sub> OH <sup>b</sup>		CH <sub>3</sub> OD <sup>c</sup>		CD <sub>3</sub> OH <sup>d</sup>		CD <sub>3</sub> OD <sup>e</sup>		Assignment
3390±50	br, w	2490±50	br, m	3350±100	br, w	2500±60		
2989	m	2990	m-s	2245±5	p}m	2247	}	CH <sub>3</sub> asym. stretching <i>a'</i> and <i>a''</i> †
2943	p? s	2945	vs	2230±5	dp}			
2910	m	2909	m	2213±8	p vw	2216		
2835	p vs	2835	vs	2141±1	p m	2147	m	2× (asym. CH <sub>3</sub> bending <i>a''</i> )
				2074±1	p vs	2076	s	CH <sub>3</sub> sym. stretching <i>a'</i>
1448	dp m	{...}		2020±3	dp? vw			2× (asym. CH <sub>3</sub> bending <i>a'</i> )
1468	dp m	{...}		1127±2	p m	1130	vw	CH <sub>3</sub> sym. bending <i>a'</i>
1363	p? br, w	948		1072±2	dp m	1069	vw	{CH <sub>3</sub> asym. bending <i>a''</i> CH <sub>3</sub> asym. bending <i>a'</i>
1160	vw	1226	w	894±5	dp m	824	vw	OH bending <i>a'</i>
1109	dp? w	1165	w					CH <sub>3</sub> rocking <i>a''</i>
1033	p s	1031	s	986±1	p vs	989	s	CH <sub>3</sub> rocking <i>a'</i>
								CO stretching <i>a'</i>

<sup>a</sup> p=polarized, dp=depolarized, other abbreviations are as in Table I.

<sup>b</sup> Average values from the works cited in footnotes 13, 14, 15, 16, 17, 19, 20, 22, 23, 24, 25. Polarization data are from the works cited in footnotes 13, 14, 25.

<sup>c</sup> Average values from the works cited in footnotes 15, 17, 18, 19. There are no polarization data.

<sup>d</sup> This work.

<sup>e</sup> Average values from the work cited in footnotes 3 and 22. There are no polarization data.

† Fermi resonance occurs between the *a'* asymmetric stretching mode and an overtone or combination of the CH<sub>3</sub> symmetric bending mode giving the extreme frequencies in this group.

1.55 for CH<sub>3</sub>OH-CH<sub>3</sub>OD, 1.67 for CD<sub>3</sub>OH-CD<sub>3</sub>OD, and 1.53 for CD<sub>3</sub>OH-CH<sub>3</sub>OD. Also, the OH bending frequency in CH<sub>3</sub>OH and CD<sub>3</sub>OH is 1346 and 1297 cm<sup>-1</sup>. There is evidently considerable coupling in at least three of the methanols between the OH bending motion and the motions of other atoms. The *a'* CH<sub>3</sub> rocking motion is a likely candidate for coupling with the OH bending

motion and so we may expect that in some of the methanols the *a'* and *a''* rocking frequencies will be quite widely separated.

In CD<sub>3</sub>OH there are two bands at 858 and 877 cm<sup>-1</sup> which are almost certainly the CD<sub>3</sub> rocking bands. The bands are close together, and it seems likely that there is relatively little interaction with the OH bending motion,

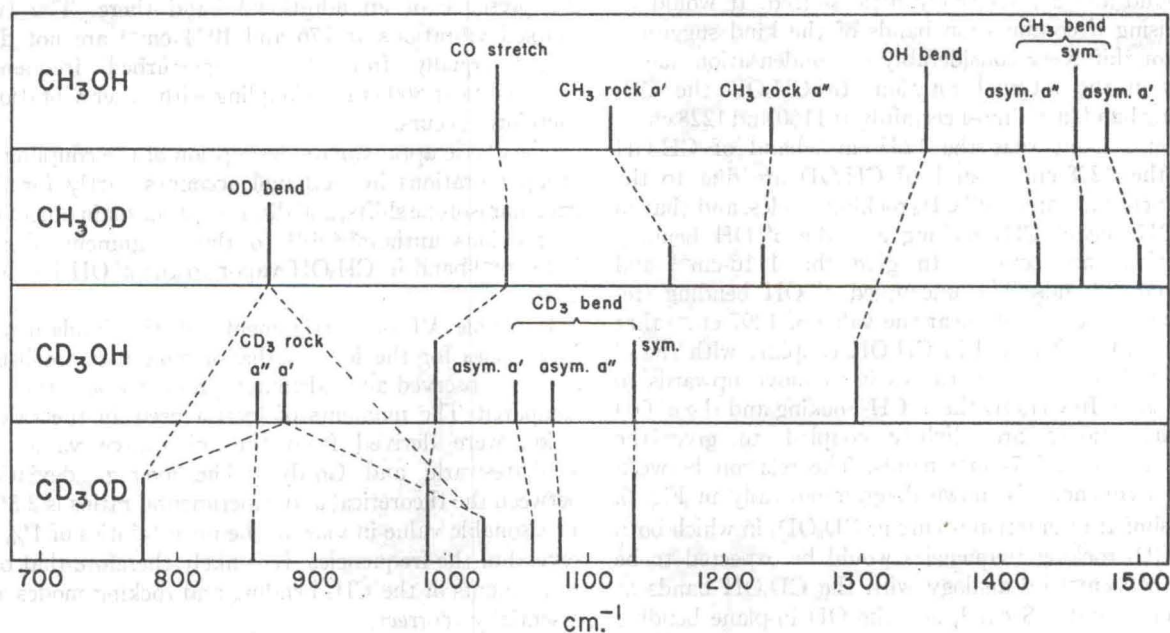


FIG. 6. Vapor-phase fundamental frequencies of the four isotopic methanols in the 700-to-1500-cm<sup>-1</sup> region. Strong coupling occurs between OH bending and *a'* CH<sub>3</sub> rocking in CH<sub>3</sub>OH; between OD bending and *a'* CD<sub>3</sub> rocking in CD<sub>3</sub>OD; and between CO stretching and CD<sub>3</sub> symmetrical bending in CD<sub>3</sub>OH and CD<sub>3</sub>OD. There is also some coupling between OD bending and *a'* CH<sub>3</sub> rocking in CH<sub>3</sub>OD.

TABLE VI. Fundamental frequencies of isotopic methanols in vapor-phase and product-rule ratios.

	CH <sub>3</sub> OH	CH <sub>3</sub> OD	CD <sub>3</sub> OH	CD <sub>3</sub> OD
(OH stretching	3687	2720	3690	2724
CH <sub>3</sub> asym. stretching	2973	2965	2235	2228
CH <sub>3</sub> sym. stretching	2845	2840	2077	2080
<i>a'</i> CH <sub>3</sub> sym. bending	1455	1458	1134	1135
CH <sub>3</sub> asym. bending	1477	1500	1047	1060
OH bending	1346	867	1297	776
CO stretching	1034	1041	988	983
CH <sub>3</sub> rocking	1116	1160	877	1024
(CH <sub>3</sub> asym. stretching	2973	2965	2235	2228
<i>a''</i> CH <sub>3</sub> asym. bending	1415	1427	1075	1080
CH <sub>3</sub> rocking	1233	1228	858	856
Molecular weight	32.04	33.05	35.06	36.07
10 <sup>40</sup> I <sub>z</sub>	35.32	38.20	43.58	46.80
10 <sup>80</sup> I <sub>y</sub> I <sub>z</sub>	224.1	274.8	503.8	577.5
10 <sup>40</sup> I <sub>internal rotation</sub>	1.009	1.621	1.116	1.912
<i>a'</i> ratio observed		0.504	0.210	0.114
<i>a'</i> ratio calculated		0.536	0.216	0.115
<i>a''</i> ratio observed		1.002	0.415	0.397
<i>a''</i> ratio calculated		1.009	0.414	0.416

whose frequency, 1297 cm<sup>-1</sup>, is relatively far away. In CH<sub>3</sub>OH there are two broad bands with very complicated structure with centres near 1116 and 1233 cm<sup>-1</sup> and it seems likely that these are the methyl rocking bands. These bands were observed, but not assigned, by Plyler<sup>5</sup> who suggested tentatively that the complicated structure in these regions may be due to combinations of the internal rotation with the CO stretching and CH<sub>3</sub> rocking modes. This does not appear to be entirely correct because the two vapor bands are clearly also present in the solid and are relatively little shifted. It would be surprising if combination bands of the kind suggested did not shift very considerably on condensation due to shifts in the internal rotation. In CH<sub>3</sub>OD the CH<sub>3</sub> rocking bands are almost certainly at 1160 and 1228 cm<sup>-1</sup>. It seems likely that the 1233-cm<sup>-1</sup> band of CH<sub>3</sub>OH and the 1228-cm<sup>-1</sup> band of CH<sub>3</sub>OD are due to the relatively uncoupled *a''* CH<sub>3</sub> rocking modes, and that in CH<sub>3</sub>OH the *a'* CH<sub>3</sub> rocking and the *a'* OH bending vibrations are coupled to give the 1116-cm<sup>-1</sup> and 1346-cm<sup>-1</sup> bands. The uncoupled *a'* OH bending frequency is presumably near the value of 1297 cm<sup>-1</sup> that it has in CD<sub>3</sub>OH, and in CH<sub>3</sub>OH coupling with the *a'* CH<sub>3</sub> rocking vibration causes it to move upwards to 1346 cm<sup>-1</sup>. In CH<sub>3</sub>OD the *a'* CH<sub>3</sub> rocking and the *a'* OD bending modes are slightly coupled to give the 1160-cm<sup>-1</sup> and 867-cm<sup>-1</sup> bands. The relation between these frequencies is shown diagrammatically in Fig. 6.

A similar interaction occurs in CD<sub>3</sub>OD, in which both the CD<sub>3</sub> rocking frequencies would be expected to be near 860 cm<sup>-1</sup> by analogy with the CD<sub>3</sub>OH bands at 877 cm<sup>-1</sup> and 858 cm<sup>-1</sup>, and the OD in-plane bending frequency would be expected to be near 867 cm<sup>-1</sup>, the frequency in CH<sub>3</sub>OD. In fact, a strong band occurs at 776 cm<sup>-1</sup> and this must be due to coupled *a'* OD bending and *a'* CD<sub>3</sub> rocking modes. The *a''* CD<sub>3</sub> rocking mode

is at 856 cm<sup>-1</sup>, relatively unshifted from CD<sub>3</sub>OH. The other band due to the coupled *a'* OD bending and *a'* CD<sub>3</sub> rocking vibrations is presumably increased in frequency to near 1024 cm<sup>-1</sup>, a value which fits well with the product rule (see below). This whole region, both in the vapor and in condensed phases, contains considerable structure due to the CD<sub>3</sub> bending modes, and the exact position of the CD<sub>3</sub> rocking band is uncertain. However, the increased absorption of CD<sub>3</sub>OD as compared to CD<sub>3</sub>OH in the region 1000 to 1100 cm<sup>-1</sup> confirms the presence of an additional band there. The two coupled vibrations at 776 and 1024 cm<sup>-1</sup> are not displaced equally from their unperturbed frequency expected near 860 cm<sup>-1</sup>. Coupling with other vibrations therefore occurs.

The above approximate description of the coupling of group vibrations in methanol accounts partly for the irregular isotope shifts, and disposes of the main objection of previous authors<sup>2,8,11,12</sup> to the assignment of the 1346-cm<sup>-1</sup> band in CH<sub>3</sub>OH vapor to the *a'* OH bending mode.

In Table VI our assignments of the fundamental frequencies for the four methanol molecules are listed and the observed and calculated product-rule ratios are compared. The moments of inertia used in the calculation were derived from the microwave values of Venkateswarlu and Gordy.<sup>31</sup> The average deviation between the theoretical and experimental ratios is 2.5%, a reasonable value in view of the uncertainties of 1% in several of the frequencies. It is likely therefore that our assignments of the CH<sub>3</sub> bending and rocking modes are essentially correct.

Several combination bands were observed, and tentative assignments are advanced in Tables I-IV.

<sup>31</sup> P. Venkateswarlu and W. Gordy, J. Chem. Phys. **23**, 1200 (1955).

TABLE VII. Vapor and crystal frequencies in  $\text{cm}^{-1}$  of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ .

	vapor	$\text{CH}_3\text{OH}$ crystal	shift	vapor	$\text{CH}_3\text{OD}$ crystal	shift
<i>a'</i> fundamentals:						
OH stretching	3687	{3261 <sup>a</sup> 3173 <sup>a</sup> }	-470 <sup>b</sup>	2720	{2420 <sup>a</sup> 2366 <sup>a</sup> }	-327 <sup>b</sup>
$\text{CH}_3$ asym. stretching	2973	2955	-18	2965	2962	-3
$\text{CH}_3$ sym. stretching	2845	2829	-16	2840	2838	-2
$\text{CH}_3$ asym. bending	1477	1468	-9	1500	1476	-24
$\text{CH}_3$ sym. bending	1455	1445	-10	1458	1465	+7
OH bending	1346	{1514 <sup>a</sup> 1492 <sup>a</sup> }	+146 <sup>b</sup>	867	{998 <sup>a</sup> 949 <sup>a</sup> }	+107 <sup>b</sup>
CO stretching	1034	1029	-5	1041	1027	-14
$\text{CH}_3$ rocking	1116	1142	+26	1160	1163	+3
<i>a''</i> fundamentals:						
$\text{CH}_3$ stretching	2973	2955	-18	2965	2962	-3
$\text{CH}_3$ bending	1415	1426	+11	1427	1443	+16
$\text{CH}_3$ rocking	1233	1256	+23	1228	1240	+12
crystal fundamentals:						
OH bending		{824 <sup>a</sup> 698 <sup>a</sup> }			{593 <sup>a</sup> 502 <sup>a</sup> }	
translation frequency (?)		520 <sup>a</sup>			359 <sup>a</sup>	
translation frequency		372 <sup>a</sup>				

<sup>a</sup> Frequencies extrapolated to 0°K.

<sup>b</sup> Shifts calculated using averages of the two components in the crystal.

### 3.2 Liquid Spectra

The frequencies of the liquid bands are listed in Tables I-IV. Assignments were made mainly by comparison with vapor spectra.

The infrared spectra of all four liquids are as expected, and there is little difference between the infrared and Raman liquid frequencies. The infrared bands are mostly fairly broad, and those due to OH stretching and bending motions are, as is common with hydrogen-bonded substances, very broad. The usual shifts from the vapor frequencies occur, i.e.,  $\text{CH}_3$  stretching and bending and CO stretching modes are little affected, and the OH stretching frequency decreases and the OH bending frequency increases. A very broad band, which is not present in the vapor, occurs in the range 450 to 850  $\text{cm}^{-1}$  in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  and in the range 350 to 630  $\text{cm}^{-1}$  in  $\text{CH}_3\text{OD}$  and  $\text{CD}_3\text{OD}$ , which is clearly due to the out-of-plane bending mode of the hydrogen-bonded OH, and was already so assigned in liquid  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  by Stuart and Sutherland.<sup>5,32</sup>

### 3.3 Solid Spectra

Solid films condensed at liquid-nitrogen temperature were visibly transparent and their spectra consisted of broad bands resembling those of liquids. Only relatively small shifts from the liquid frequencies occurred, the largest shifts being observed for the OH and OD out-of-plane bending modes. One new band of moderate intensity appeared near 300  $\text{cm}^{-1}$ . The solids were presumably glasses.

<sup>32</sup> A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.* **20**, 1977 (1952).

Upon warming, the films became snowy-white at about  $-140^\circ\text{C}$ , their spectra became sharper, all fundamental bands that involve mainly motions of the O-hydrogen atom split into two components of comparable intensity, some weak bands in the region 2100 to 2600  $\text{cm}^{-1}$  sharpened and resolved into several components, a few other bands appeared to split into two closely separated components of unequal intensity, and the band near 300  $\text{cm}^{-1}$  sharpened. The transformation was irreversible, and evidently the films had crystallized.

Further sharpening of the spectrum and some additional splitting into two components of unequal intensity occurred when the crystalline films were cooled to  $-180^\circ\text{C}$ . Some bands were sensitive to temperature, those involving OH motion generally broadening and shifting towards the vapor frequencies as the temperature increased. These changes were completely reversible.

In both  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  there is a first-order solid-solid phase transition, at  $-113.5^\circ\text{C}$  in  $\text{CH}_3\text{OH}$  and at  $-109.9^\circ\text{C}$  in  $\text{CH}_3\text{OD}$ <sup>33,34</sup> and this presumably also occurs in  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$ , perhaps at somewhat higher temperatures. An attempt was made to observe a change of spectrum when the phase changed. Films of all four methanols were held near  $-120^\circ\text{C}$  and  $-108^\circ\text{C}$  for two hours. By comparison with observations on bulk specimens<sup>35,36</sup> this should be long enough for the phase change to be complete. There was no essential

<sup>33</sup> D. W. Davidson, *Can. J. Chem.* **34**, 1243 (1956).

<sup>34</sup> D. W. Davidson, *Can. J. Chem.* **35**, 458 (1957).

<sup>35</sup> L. A. K. Staveley and A. K. Gupta, *Trans. Faraday Soc.* **45**, 50 (1949).

<sup>36</sup> L. A. K. Staveley and M. A. P. Hogg, *J. Chem. Soc.* 1013 (1954).

difference between the spectra, the small changes in frequency and breadth of bands being consistent with the temperature variation of the bands in the low-temperature phase.

The assignment of the bands was made mainly by comparison with the vapor spectra, and is given in Tables I-IV. However, the coupling that occurs in the vapor is modified in the solid, and the identification of some of the bands is uncertain. Bands due to dilute  $\text{CH}_3\text{OH}$  in  $\text{CH}_3\text{OD}$  and to dilute  $\text{CD}_3\text{OH}$  in  $\text{CD}_3\text{OD}$  occur. These are listed in Tables II and IV and discussed in Sec. 4.4. In  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  there is a band near  $500\text{ cm}^{-1}$ , and in all four there is a band near  $320\text{ cm}^{-1}$ . They are discussed in Sec. 4.3. For a later paper we shall need the frequencies of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  at  $0^\circ\text{K}$ . Those that shift with temperature have been extrapolated linearly to  $0^\circ\text{K}$  using the data of Tables I-IV and some data at intermediate temperatures which we have not reported. The results are in Table VII.

The sum of the frequency shifts from vapor to crystal for  $\text{CH}_3\text{OH}$  is 1.49 times that for  $\text{CH}_3\text{OD}$ , and that for  $\text{CD}_3\text{OH}$  is 1.44 times that for  $\text{CD}_3\text{OD}$ . The factor expected if the force constants for the four methanols are the same in the vapor and are the same in the solid is 1.41, in rough agreement with the experiment.

The two  $\text{CH}_3$  internally asymmetrical stretching modes of species  $a'$  and  $a''$  are not resolved in the vapor. In the crystalline solid the bands are much narrower and several peaks occur. The two modes appear to be separated in all four methanols by about 20 to  $30\text{ cm}^{-1}$ . This is readily accounted for by the occurrence of Fermi resonance between one of the internally asymmetrical  $\text{CH}_3$  stretching modes and the first overtone of one of the  $\text{CH}_3$  bending modes, resulting in a shift of both the overtone and the stretching mode.

Bands occur in the spectrum of  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  at  $1370$  and  $1354\text{ cm}^{-1}$  at  $-180^\circ\text{C}$ . The intensity of these bands decreases very markedly as the temperature is increased and small shifts of frequency downwards occur. The downward shifts are consistent with the bands' being first overtones of the OH out-of-plane bending mode at  $685\text{ cm}^{-1}$  in both  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$ , and the intensity is possibly due to Fermi resonance with the OH in-plane bending mode that is symmetrical relative to the chain. The resonance decreases as the frequency of the out-of-plane bending mode shifts downward with rising temperature.

#### 4. DISCUSSION OF SPECTRA OF CRYSTALLINE SOLIDS

##### 4.1 $\beta$ -Phase

The high temperature ( $\beta$ ) phase of methanol belongs to the centro-symmetrical space group  $D_{2h}^{17}-Cmcm$ .<sup>37</sup> The molecules are arranged in hydrogen-bonded zig-zag chains and two chains, each containing two molecules,

<sup>37</sup> K. J. Tauer and W. N. Lipscomb, *Acta Cryst.* **5**, 606 (1952).

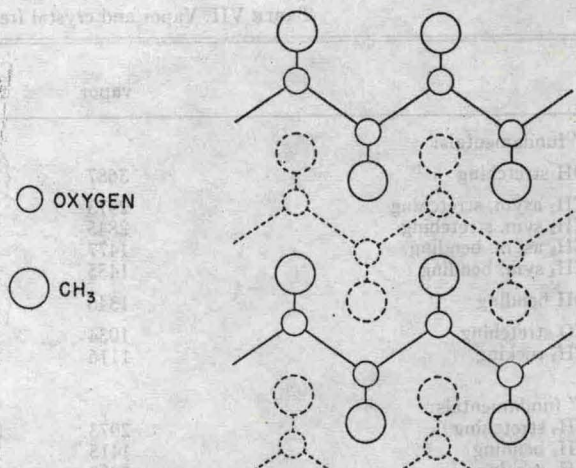


FIG. 7. Diagrammatic sketch of the crystal of methanol. Atoms represented by solid lines are in the plane of the paper, and those represented by broken lines are below the plane of the paper.

pass through the unit cell. The structure is shown diagrammatically in Fig. 7. The full symmetry of the x-ray diffraction pattern implies that the methyl group (treated as one atom) and the oxygen and hydrogen atoms of one chain lie in one plane, and that the hydrogen atoms are midway between the oxygens. The rather large thermal amplitude of approximately  $0.32\text{ \AA}$  rms perpendicular to the chain<sup>37</sup> and the high dielectric constant of the  $\beta$ -phase<sup>34,38,39</sup> were interpreted<sup>37</sup> to indicate that the apparent x-ray symmetry might be the mean of two forms in which the methyl groups are off the plane of the oxygen atoms in the same chain.

The only infrared-active fundamental modes of a crystal are those which are totally symmetrical with respect to translation, i.e., those in which all unit cells vibrate in phase.<sup>40,41</sup> If the crystal is anharmonic then combinations of forbidden fundamentals with lattice modes may be active, and their intensity will probably be quite strongly temperature-dependent. In none of the bands that we observed does the intensity increase markedly as the temperature increases from  $-180^\circ\text{C}$  to  $-108^\circ\text{C}$ , and so we will assume that only allowed fundamentals are seen.

There are four molecules in the unit cell, and consequently each internal mode of the isolated methanol molecule gives four modes in the crystal that may be active, and so some splitting of the frequencies of the isolated molecule is expected.

Experimentally, each of the three bands that are due to the motions of the O-hydrogen atoms have two components of comparable intensity, usually about 50 to  $100\text{ cm}^{-1}$  apart. The other bands are either not split

<sup>38</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **56**, 1084 (1934).

<sup>39</sup> C. P. Smyth and S. A. McNeight, *J. Am. Chem. Soc.* **58**, 1597 (1936).

<sup>40</sup> S. Bhagavantam and T. Venkatarayudu, *Group Theory and its Applications to Physical Problems* (Andhra University, Waltair, India, 1951).

<sup>41</sup> D. F. Hornig, *J. Chem. Phys.* **16**, 1063 (1948).

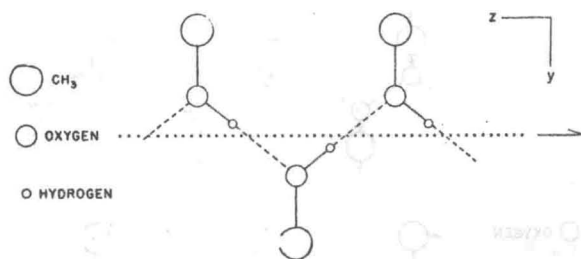


FIG. 8. Symmetry of one chain in the methanol crystal.

or are split by only 10 to 20  $\text{cm}^{-1}$ , and the higher-frequency component is usually far less intense than the lower. It seems very likely that the splitting of the O-hydrogen bands is due to coupling of the motions of molecules in the same unit cell. The splitting of the other bands is referred to below.

We consider first the spectrum of the whole unit cell.

#### Space-Group Analysis

For analyzing the crystal spectrum, the analysis based on the factor group of the space group<sup>40,42</sup> is appropriate. The factor group of the space group  $D_{2h}^{17}$  is isomorphous with the point group  $D_{2h}$ . We call the  $a$ ,  $b$ , and  $c$  axes of the unit cell the  $x$ ,  $y$ , and  $z$  directions, so that the  $x$  axis is perpendicular to the plane of the chains, the  $z$  axis is parallel to the chain axis, and the  $y$  axis is the remaining axis. Under the symmetry  $D_{2h}$  both the OH stretching and OH in-plane bending modes split into four components in the crystal, two, of species  $b_{1u}$  and  $b_{2u}$ , being infrared-active, and two, of species  $b_{1g}$  and  $b_{2g}$ , being Raman-active. The OH out-of-plane bending vibration gives four components in the crystal, one of which, of species  $b_{3u}$ , is infrared-active, two, of species  $a_g$  and  $b_{1g}$ , are Raman-active, and one,  $a_u$ , is forbidden in both Raman and infrared spectra. We find experimentally that the OH stretching and in-plane bending modes give two infrared-active modes, as expected, but the OH out-of-plane bending mode also gives two components, which disagrees with the above predictions. The possibility that the splitting occurs because of Fermi resonance with an overtone is very unlikely because similar bands occur in all four methanols. It follows, therefore, that the symmetry of the unit cell is lower than the apparent x-ray symmetry.

There are two possible causes of the high apparent x-ray symmetry. Either the hydrogen atoms are not observed, or the chains are of lower symmetry, but they are irregularly oriented in such a way as to give this apparent x-ray symmetry. It seems likely, therefore, that either the O-hydrogen atoms are not at the midpoint of the line joining the oxygen atoms, or the methyl groups are not coplanar with the oxygen atoms, or both these dissymmetries occur. Whichever occur, each chain has two possible orientations, and it is likely

that these orientations are irregularly distributed, so giving the apparent x-ray symmetry. If this occurs, then there are no rigorous selection rules. However, as only a limited number of bands occurs, approximate selection rules must hold, and these are almost certainly those appropriate for an isolated chain. The isolated-chain approximation has frequently been used for discussing the spectrum of polymer molecules,<sup>43-46</sup> in which, however, the covalent bonding along the chains is much stronger than the hydrogen-bonding in the methanol chains. Accordingly, we now discuss the spectrum expected for an isolated chain.

#### Line-Group Analysis

A possible structure of the isolated chain that is consistent with the observed x-ray symmetry and with the arguments of the foregoing paragraphs is a chain in which the carbon, oxygen, and hydrogen atoms are coplanar and the hydrogen atom is not midway between the two oxygen atoms. The spectrum of the chain is best considered in terms of the one-dimensional space group (or line group)<sup>44</sup> that describes the symmetry of the chain. The symmetry elements of the chain (Fig. 8) are an infinite number of translations along the  $z$  axis, one  $C_2$  screw axis along the  $z$  axis, one reflection plane  $yz$ , and one glide plane  $xz$ . The only modes that are potentially active in infrared or Raman spectra are those that are in phase in all unit segments of the chain,<sup>43,44</sup> and consequently the factor group of the line group is appropriate for analyzing the spectrum. It is isomorphous with the point group  $C_{2v}$ . Under this symmetry both the OH stretching and OH in-plane bending modes give two components, of species  $a_1$  and  $b_2$ , both of which are infrared-active, as observed. The two components of the OH out-of-plane bending mode are of species  $a_2$  and  $b_1$ , of which only the  $b_1$  mode is infrared-active. Since two infrared modes are observed, then the planar chain with the hydrogen not midway between the two oxygen atoms is not consistent with the infrared spectrum. It follows that further relaxation of the symmetry is necessary, and hence that either the carbon or the hydrogen or both are out of the plane of the oxygen atoms.

We now inquire whether the spectrum is consistent with the methyl group's being out of the plane of the oxygen atoms and the hydrogen atom's being midway between the oxygen atoms. The assumed structure of the chain is that of the low-temperature form (see below) in which the methyl groups on one side of the chain are above the plane of the oxygen atoms and those in the other side are below the plane. There are two possible chains consistent with this structure according

<sup>43</sup> C. Y. Liang, S. Krimm, and G. B. B. M. Sutherland, *J. Chem. Phys.* **25**, 543 (1956).

<sup>44</sup> M. C. Tobin, *J. Chem. Phys.* **23**, 891 (1955).

<sup>45</sup> R. E. Moynihan, *J. Am. Chem. Soc.* **81**, 1045 (1958).

<sup>46</sup> A. Novak and E. Whalley, *Trans. Faraday Soc.* **55**, 1484 (1959).

<sup>42</sup> H. Winston and R. S. Halford, *J. Chem. Phys.* **17**, 607 (1949).

as the methyl groups on a particular side of the chain are above or below the plane of the chain. They are assumed to be irregularly distributed so as to give the x-ray symmetry. We assume, as we assumed above, that, although rigorous selection rules do not hold, the observed spectrum is closely related to the spectrum of an isolated chain. The corresponding point group is  $C_{2h}$ . The hydrogen atom is at the center of symmetry, and so all motions of the hydrogen atom destroy the center of symmetry. Their species are therefore either  $a_u$  or  $b_u$  and they are allowed in the infrared spectrum.

The infrared spectrum thus strongly confirms Tauer and Lipscomb's somewhat tentative suggestion that the chains in methanol are puckered. It does not prove that the O-hydrogen atom is not midway between the oxygen atoms, though this seems likely by analogy with other compounds.

We now discuss briefly the splitting of the vibrations that do not involve mainly O-hydrogen atoms. If the symmetry of the chain is  $C_{2h}$ , then in the isolated-chain approximation only one active vibration occurs for each of these vibrations in the vapor. If the symmetry  $C_{2h}$  is destroyed by moving the O-hydrogen atom, it is likely that the intensity of bands that were forbidden and that now become active will be rather low. This agrees with experiment. Another explanation of the experimental results is that the low-intensity component is due to a combination of the main vibration with a low-frequency lattice vibration. It is not possible at present to decide between these two explanations and so the chain symmetry  $C_{2h}$  cannot be rigorously eliminated.

#### 4.2 $\alpha$ -Phase

According to Tauer and Lipscomb the low-temperature ( $\alpha$ ) phase has probably the space symmetry  $C_{2h}^2 - P2_1/m$ .<sup>37</sup> The molecules are arranged in hydrogen-bonded zig-zag chains, the methyl groups on one side being above the plane of the oxygen atoms and the methyl groups on the other side being below. Weak superlattice reflections suggested that the unit cell may be twice that proposed and that perhaps the methyl groups are alternately staggered relative to their neighbors in the chain. Such small changes in symmetry should make no detectable difference in the infrared spectrum and are neglected in this discussion.

No significant change in spectrum is observed in passing from the  $\beta$  to the  $\alpha$  phase. The heat of transition is only 170 cal mole<sup>-1</sup><sup>36</sup> so only very small shifts of frequency are expected. The number of fundamental bands does not alter, and hence the selection rules are not significantly altered, as expected for the structure of the  $\alpha$ -phase proposed by Tauer and Lipscomb. If we neglect a possible superlattice, there are only two molecules in the unit cell. If the hydrogen atoms are midway between the oxygen atoms then the point group isomorphic with the factor group is  $C_{2h}$ , and as discussed above each of the three O-hydrogen motions should give two

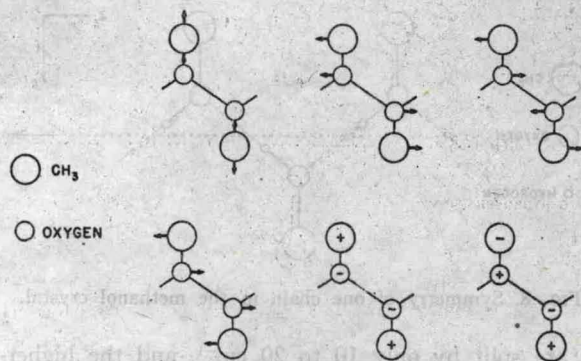


FIG. 9. Expected infrared-active fundamentals of a methanol chain that involve motion of the whole molecules.

infrared-active components. Any reduction in symmetry will not affect the number of infrared-active bands due to the motions of the O-hydrogen atom.

#### 4.3 Lattice Modes

A weak, moderately broad band occurs in the spectrum of CH<sub>3</sub>OH at  $-180^\circ\text{C}$  at  $520\text{ cm}^{-1}$  and in CD<sub>3</sub>OH at  $\sim 510\text{ cm}^{-1}$ . The OD out-of-plane bending bands obscure any band of similar frequency that may occur in CH<sub>3</sub>OD and CD<sub>3</sub>OD. A moderate, sharp band occurs in the spectra of all the methanols at the following frequencies at  $-180^\circ\text{C}$ : CH<sub>3</sub>OH,  $357\text{ cm}^{-1}$ ; CH<sub>3</sub>OD,  $344\text{ cm}^{-1}$ ; CD<sub>3</sub>OH,  $339\text{ cm}^{-1}$ ; CD<sub>3</sub>OD,  $331.5\text{ cm}^{-1}$ . The frequency of all these bands decreases on warming, and the bands are not observed in the liquids. In the spectra of the vitreous films the band near  $500\text{ cm}^{-1}$  is not observed, and the bands near  $340\text{ cm}^{-1}$  are considerably broader and at a lower frequency than in the crystalline films. The isotope shifts for both bands are small, and so they cannot be connected with the CH<sub>3</sub> internal rotation. Neither is it possible to explain them as difference bands involving the internal fundamentals. They must, therefore, be due to external modes of the molecules. The  $500\text{-cm}^{-1}$  band is quite weak and it might be an overtone.

Since there are two molecules in the unit cell in the  $\alpha$  phase, neglecting the possible superlattice, there are six nonzero fundamentals in which the whole molecules move that are potentially active in the infrared. These are roughly represented in Fig. 9. Modes 1 and 2 are closely related to translational modes of the isolated molecules. The four other modes that are derived from the translations of isolated molecules are three translations of the chain and one rotation about the chain axis, which are of zero frequency in the isolated chain. If the symmetry of the chain is  $C_{2h}$ , and the O-hydrogen atoms are midway between the oxygen atoms then vibrations 1, 2, 3, and 6 of Fig. 9 preserve the center of symmetry and should be infrared-inactive. Vibrations 4 and 5, which destroy the center of symmetry should be infrared-active. The first overtones of all these vibrations are fully symmetrical and should be infrared-in-

active. If the O-hydrogen atoms are not midway between the oxygen atoms then the symmetry is  $C_2$  and all the vibrations represented in Fig. 9 and their first overtones are infrared-active.

The isotope shifts for both observed bands are roughly those expected for a translational mode, and it would be difficult to reconcile them with vibrations 4 and 5 of Fig. 9. It seems likely that they are due to the translational modes 1 and 2. If this is so, then whether they are due to overtones or fundamentals the symmetry of the chain cannot be  $C_{2h}$ , and the O-hydrogen atom must be off the midpoint of the O-O line. This is not unexpected, the O-O distance being much longer than usually required for symmetrical hydrogen bonds.

#### 4.4 Bands Due to Dilute Isotopic Molecules

Bands that we ascribe to  $CH_3OH$  and  $CD_3OH$  occur in crystalline  $CH_3OD$  and  $CD_3OD$ , respectively; they are included in Tables I-IV. The OH stretching, in-plane bending, and out-of-plane bending are observed for  $CD_3OH$  in  $CD_3OD$ . The OH stretching and out-of-plane bending bands are observed for  $CH_3OH$  in  $CH_3OD$ , the OH in-plane bending being hidden by  $CH_3OD$  absorption. Unlike the corresponding bands in the pure crystals, the bands of the isotopically diluted species show no splitting. This is to be expected, since no coupling can occur with vibrations of neighboring molecules, which now have too different frequencies.

The uncoupled frequency should fall between the two observed frequencies of the coupled molecules for the following reason. During a vibration the lone-pair electrons that take part in hydrogen-bonding will move in

phase with the nuclei. The two observed bands correspond to motion of adjacent molecules in phase and out of phase. In one of these vibrations the lone-pair electrons will move in step with the hydrogen atom of the adjacent molecule and in the other vibration they will move  $\pi$  radians out of step. Consequently, the coupling will cause one frequency to be higher than in a molecule whose neighbors do not move and will cause the other frequency to be lower. The frequencies of dilute  $CH_3OH$  in  $CH_3OD$  and of dilute  $CD_3OH$  in  $CD_3OD$  are probably close to the values they would have if the neighboring molecules did not vibrate. It follows therefore, that the frequency, of a dilute molecule should fall between the two observed frequencies of the coupled molecules. This is indeed observed.

In all the other vibrations of a crystal that correspond to a given vibration of the isolated molecule, adjacent unit cells vibrate out of phase. It follows that the lone-pair electrons of one molecule will be out of step by between 0 and  $\pi$  radians with the O-hydrogen atom of the neighboring molecule. It seems likely that these frequencies will be between those corresponding to a phase difference of 0 and  $\pi$  radians and so that the two observed frequencies are the extremes of the set of crystal frequencies corresponding to a given mode of the isolated molecule.

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