

TABLE I. Infrared spectrum of CH₃OH.^a

Vapor ^b	Liquid	Crystal			Assignment ^c
		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 a'
2973 vs(2977)	2934 vs	2982 sh, w 2951 vs	2982 m 2955 s 2912 sh, m	2980 m 2954 s	CH ₃ asym. stretching a' and a'' ^d
R 2869 } Q 2845 }s(2844) P 2826 }	2822 s	2828 s	2829 s	2831 s	CH ₃ sym. stretching a'
~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 ^f	1452 m 1415 sh	~1545 sh, vw 1458 sh ~1445 sh, m 1426 sh	~1459 sh 1420	2×790 CH ₃ asym. bending a' CH ₃ sym. bending a' CH ₃ asym. bending a''
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 a' 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 ₃ rocking a'' CH ₃ rocking a'
R 1060 } Q 1034 }vs(1034) P 1012 }	1029 vs	1032 vs	{1046 w } {1029 vs }	1030 vs	CO stretching a'
	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 ¹⁸ O stretching OH out-of-plane bending lattice mode (or overtone) lattice mode

^a All frequencies are in cm⁻¹. vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, br=broad.

^b 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).

^c Species of vibrations apply to vapor only. "Sym." and "asym." refer to the internal symmetry of the methyl group.

^d Fermi resonance in the solid occurs between one of the CH₃ asymmetric stretching modes and an overtone or combination of the CH₃ bending modes, giving the extreme frequencies in this group.

^e 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.

^f Overrun by the OH in-plane bending band.

* Probably due to partly crystallized material.

TABLE II. Infrared spectrum of CH₃OD.^a

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

^a Abbreviations are given in Table I.^b Data in parentheses are from Barker and Bosschier (see the work cited in footnote 27), and those in square brackets are from Noether (see the work cited in footnote 3).^c See Table I.

essentially identical with his. Our frequencies of CD₃OH and CD₃OD 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,³ Herzberg's,³⁰ and Plyler's⁵ except for the bending and rocking vibrations of the CH₃ and CD₃ groups, which we shall now discuss in detail.

CH₃ Bending Modes

Three CH₃ bending modes are expected, viz., an *a'* internally symmetrical mode which has an approximately

³⁰ 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⁻¹ in CH₃OH is the *Q* branch of an approximately parallel band and so is probably due to the *a'* symmetrical bending mode.² The bands with centers at 1415 and 1477 cm⁻¹, both of which appear to be approximately perpendicular, may be the *a'* and *a''* CH₃ internally asymmetrical bending modes. The *a'* mode is somewhat arbitrarily assigned to the higher frequency. In CH₃OD the bands are a good deal clearer owing to the absence of the OH bending mode. The sharp peak at 1458 cm⁻¹ is clearly the *Q* branch of the approximately parallel band due to the CH₃ internally symmetrical bending mode, and the central gaps of the