

TABLE III. Infrared spectrum of CD₃OH.^a

Vapor ^b	Liquid	Vitreous -180°C	Crystal		Assignment ^c	
			-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 ^e 1488+1405 2×1405	
2235 vs(2232)	2232 vs	{2235 m 2213 s	2236 m 2214 s	2236 m ~2214 s	CD ₃ asym. stretching <i>a'</i> and <i>a''</i> ^d	
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 ₃ 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> ^t
			1389 s	1354 s	1320 br, m	2×685 ^f
R 1145 Q 1134 P 1112	vs(1123)	1122 vs	1122 vs	{1131 sh, w 1121 vs}	1118 vs}	CD ₃ sym. bending <i>a'</i>
1075 w(1080?)	{1090 sh, vw 1069 w}	~1106 sh	1106 vw	1083 sh, w	1104 sh, vw ~1086 sh, w}	C ¹³ D ₃ sym. bending CD ₃ asym. bending <i>a''</i>
1047 (1055?)	1020 sh, vw	1026 w	1069 m	{1031 w 1023 w}	1029 w 1023 w}	CD ₃ 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 ₃ rocking <i>a''</i>
858 m(856)	882	895		{912 w 902 m 823 sh, m}	909 vw 900 vw}	CD ₃ rocking <i>a'</i> 510+339(?)
	665 s, br	708 br		{776 s, br 685 s}	741 s, br 670 s}	OH out-of-plane bending
		~314 w	~510 w, br	339 s	~490 w, br 332 m	lattice mode (or overtone) lattice mode

^a Abbreviations are given in Table I.^b Data in parentheses are those of Noether (see the work cited in footnote 3).^c See Table I.^d 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⁻¹. In the Raman spectra of the liquids the three bands are incompletely resolved. In crystalline CH₃OH the corresponding bands are overrun by the OH bending mode, but in crystalline CH₃OD the three bands due to the three CH₃ bending modes are clearly seen.

There are strong, approximately parallel bands in the vapor spectra of CD₃OH and CD₃OD with *Q* branches at 1134 and 1135 cm⁻¹, respectively, which are clearly due to the *a'* CD₃ internally symmetrical bending mode. In confirmation of this the corresponding Raman band in CD₃OH at 1127 cm⁻¹ is polarized. There are two weak bands at somewhat lower frequencies, those in CD₃OD having their central gaps at 1080 cm⁻¹ and 1035 cm⁻¹

and those in CD₃OH being somewhat weaker and less well resolved at 1075 cm⁻¹ and 1047 cm⁻¹. These are probably the two CD₃ 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⁻¹. There are two bands in the infrared spectra of solid CH₃OH and CD₃OD, though possible contributions from one of the CD₃ rocking modes (see below) render interpretation uncertain.

The three CH₃ bending bands are not in the same order of frequency as the three CD₃ bending bands. Thus, in CH₃OH and CH₃OD the frequency of the CH₃

TABLE IV. Infrared spectrum of CD₃OD.^a

Vapor ^b	Liquid	Crystal			Assignment ^c
		Vitreous -180°C	-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 ₃ OH) CH stretching (CD ₂ HOD and CDH ₂ 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 ₃ asym. stretching a' and a'' ^d
2140 vw	2145 w				2×1060 or 2×1080 ^e
R 2100 Q 2080 }vs(2081) P 2063	2082 s	2075 s	2075 s	~2075 s	CD ₃ 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	{1420 w 1395 w	{1422 w 1395 w}	OH bending (CD ₃ OH) ^f
R 1155 Q 1135 }vs(1121) P 1117	1124 vs	1117 vs	1256 vw 1248 vw	~1255 vw	CD ₂ H rocking (?) CD ₃ 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 ₃ asym. bending a'' CD ₂ asym. bending a' CD ₃ 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 ₃ rocking a''
R 797 Q 776 }s(775) P 753	818 m	831 m, br	862 m	857 w	CD ₃ rocking and OD in-plane bending a'
		800 w ~730 vw	745 w ~630 {578 s 495 s	~755 sh, vw ~630 {556 s 487 s}	(?) OH out-of-plane bending (CD ₃ OH) 2×336(?) OD out-of-plane bending lattice mode
	483 s, br	533 s ~300(?)	336 vs	325.5 s	

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

internally symmetrical bending mode appears to be between those of the two asymmetrical bending modes, whereas in CD₃OH and CD₃OD it appears to be a good deal higher. This is probably caused by interaction of the CH₃ internally symmetrical bending motion with the CO stretching motion. The CO stretching frequency drops from 1034 cm⁻¹ in CH₃OH and 1041 cm⁻¹ in CH₃OD to 988 cm⁻¹ in CD₃OH and 983 cm⁻¹ in CD₃OD, and at the same time the deuteration shift of the CH₃ 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 CH₃ and CD₃ internally asymmetrical bending modes is quite uncertain

CH₃ Rocking Modes

There are two CH₃ 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