

TABLE V. Raman frequencies of liquid  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ .<sup>a</sup>

$\text{CH}_3\text{OH}^b$		$\text{CH}_3\text{OD}^c$		$\text{CD}_3\text{OH}^d$		$\text{CD}_3\text{OD}^e$		Assignment
3390±50	br, w	2490±50	br, m	3350±100	br, w	2500±60		OH stretching $a'$
2989	m	2990	m-s	2245±5	p	2247		CH <sub>3</sub> asym. stretching $a'$ and $a''$ <sup>f</sup>
2943	p?	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 $a''$ )
				2074±1	p vs	2076	s	CH <sub>3</sub> sym. stretching $a'$
1448	dp m	{...}		2020±3	dp? vw			2×(asym. CH <sub>3</sub> bending $a'$ )
		{...}		1127±2	p m	1130	vw	CH <sub>3</sub> sym. bending $a'$
1468	dp m	1464	br, s}	1072±2	dp m	1069	vw	{CH <sub>3</sub> asym. bending $a''$ CH <sub>3</sub> asym. bending $a'$
1363	p? br, w	948		1360±10	br, w	...		OH bending $a'$
1160	vw	1226	w	894±5	dp m	824	vw	CH <sub>3</sub> rocking $a''$
1109	dp? w	1165	w					CH <sub>3</sub> rocking $a'$
1033	p s	1031	s	986±1	p vs	989	s	CO stretching $a'$

<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.

<sup>f</sup> 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  $\text{CH}_3\text{OH}-\text{CH}_3\text{OD}$ , 1.67 for  $\text{CD}_3\text{OH}-\text{CD}_3\text{OD}$ , and 1.53 for  $\text{CD}_3\text{OH}-\text{CH}_3\text{OD}$ . Also, the OH bending frequency in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  is 1346 and 1297  $\text{cm}^{-1}$ . 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  $\text{CD}_3\text{OH}$  there are two bands at 858 and 877  $\text{cm}^{-1}$  which are almost certainly the  $\text{CD}_3$  rocking bands. The bands are close together, and it seems likely that there is relatively little interaction with the OH bending motion,

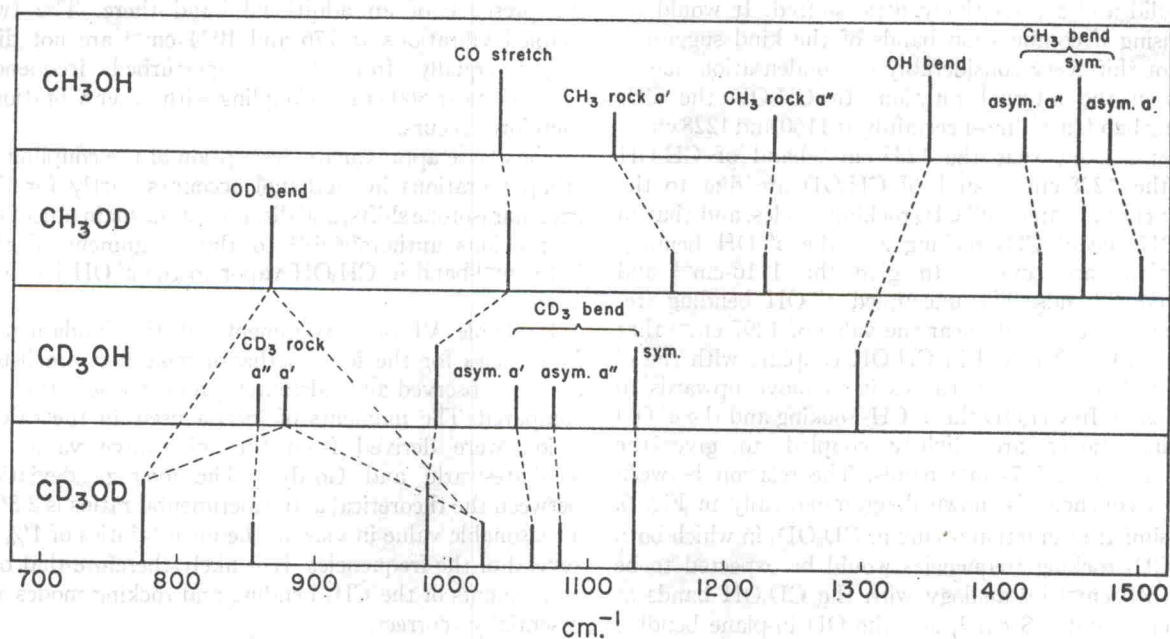


FIG. 6. Vapor-phase fundamental frequencies of the four isotopic methanols in the 700-to-1500- $\text{cm}^{-1}$  region. Strong coupling occurs between OH bending and  $a'$  CH<sub>3</sub> rocking in  $\text{CH}_3\text{OH}$ ; between OD bending and  $a'$  CD<sub>3</sub> rocking in  $\text{CD}_3\text{OD}$ ; and between CO stretching and CD<sub>3</sub> symmetrical bending in  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$ . There is also some coupling between OD bending and  $a'$  CH<sub>3</sub> rocking in  $\text{CH}_3\text{OD}$ .



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
<i>a''</i> CH <sub>3</sub> asym. stretching	2973	2965	2235	2228
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>I<sub>x</sub></i>	35.32	38.20	43.58	46.80
10 <sup>80</sup> <i>I<sub>y</sub>I<sub>z</sub></i>	224.1	274.8	503.8	577.5
10 <sup>40</sup> <i>I</i> internal rotation	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).