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The Raman Spectra of the Methyl Alcohols, CH_3OH, CH_3OD, and CH_2DOD *

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Measurements of the Raman spectra of CH_3OH, CH_3OD, and CH_2DOD, produced by the mercury lines at 2536 and 4358A units, are analyzed to yield a provisional assignment of the fundamental frequencies. The significance of the character of the OH and OD bands to the problem of internal rotation is discussed. A new approximation to a potential constant for the C—O bond is presented.

A PREVIOUS communication from this laboratory[1] presented data for the Raman spectra of CH_3OH and CH_3OD, excited by the mercury lines at 2536 and 4358A units. This paper presents additional lines and a few changes in position as the result of further examination of these spectra. The alcohol CH_2DOD has been prepared and subjected to a similar study.

CH_3OD was prepared by treating dry magnesium methylate with 99.8 percent D_2O and CH_2DOD was made by means of the reaction of diazomethane with D_2O in the presence of a small amount of D_2SO_4. Each of the alcohols was purified by fractional distillation.

A spiral mercury resonance lamp and a Hilger E3 spectrograph were used to obtain the shifts of the 2536 Hg line. For excitation by the 4358 Hg line the radiation from four quartz mercury arcs in an apparatus similar to that of Anand[2] was passed through successive filters of cobalt thiocyanate, praeseodymium nitrate, and sodium nitrite, and the scattered light was photographed in a Gaertner spectrograph (f: 3.5).

The data are summarized in Table I, which includes estimates of intensity indicated by numbers from one to ten, and provisional assignments to modes of motion of the molecule. The two columns for CH_3OH include all of the frequencies shown in a table compiled by Voge[3] from his own measurements and those of Kohlrausch and of Wood, except for a broad band found by Voge in the region about 1450 cm^{-1}. This band was omitted from the table because no well-defined center was distinguishable from the line at 1464, but the indications are that it is connected with one of the fundamental vibrations. The CH_3OD spectrum is in good agreement with the data of Mizushima, Morino and Okamoto,[4] which appeared shortly after the publication of our first communication. Microphotometer tracings of the spectra listed in Table I are reproduced in Figs. 1 to 6. The correspondence between the figures and the tabulation is indicated at the head of the columns

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[1] Bates, Anderson and Halford, J. Chem. Phys. **4**, 535 (1936).

[2] Anand, J. Sci. Inst. **8**, 258 (1931).

[3] Voge, J. Chem. Phys. **2**, 264 (1934).

[4] Mizushima, Morino and Okamoto, Bull. Chem. Soc. Japan **11**, 699 (1936).

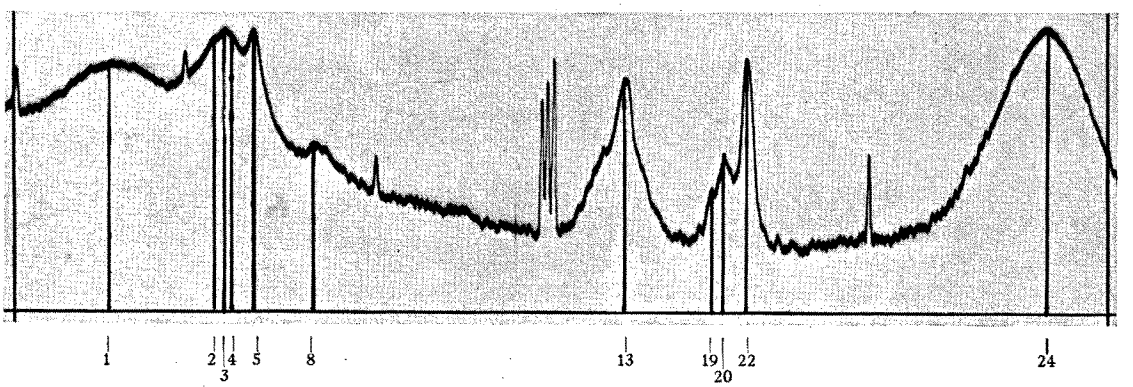

FIG. 1. CH_3OH.

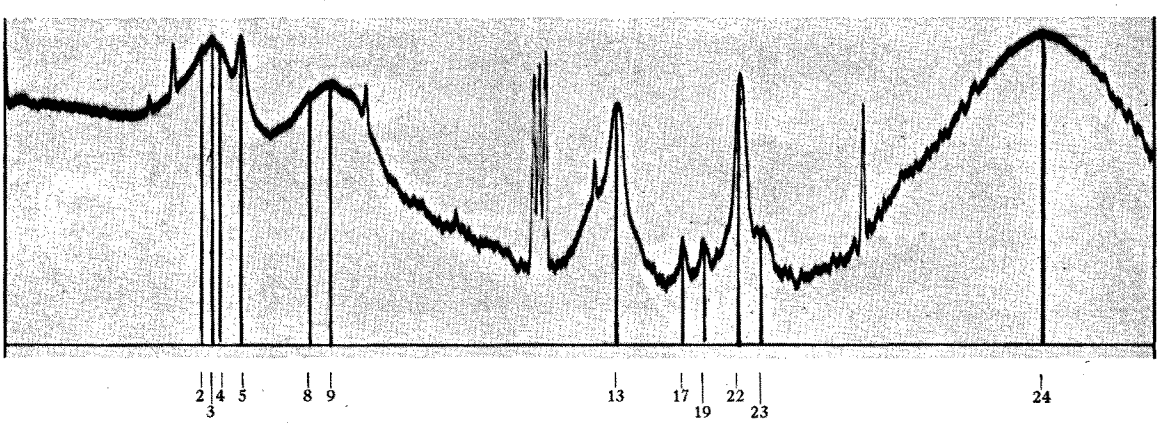

FIG. 2. CH_3OD.

TABLE I.

No.	CH_3OH 2536 (Fig. 1)	CH_3OH 4358 (Fig. 4)	CH_3OD 2536 (Fig. 2)	CH_3OD 4358 (Fig. 5)	CH_2DOD 2536 (Fig. 3)	CH_2DOD 4358 (Fig. 6)	ASSIGNMENT
(1)	3382±100	3415±100					OH stretch
(2)	2992(4)	2982(6)	2989(4)	2986(6)	2974(4)	2985(6)	ν_2
(3)	2936(8)	2948(10)	2946(7)	2947(10)	2945(10)	2952(10)	ν_1, $2\nu_4$
(4)	2913(4)	2914(6)	2915(4)	2918(6)			$\nu_3+\nu_4$?
(5)	2835(10)	2839(10)	2836(10)	2836(10)	2885(10)	2880(8)	ν_1, $2\nu_4$
(6)					2835(3)		?
(7)					2686(3)		$2\nu_{4-2}$?
(8)	2588(1)		2591(1)				$\nu_3+\nu_6$?
(9)			2494±50	2494±50	2501±50	2500 } band	OD stretch
(10)						2383 }	
(11)					2237(?1)		$2\nu_6$?
(12)					2171(8)	2181(5)	ν_{2-2}
(13)	1464(5)	1451(4)	1464(5)	1465(4)	1462(6)	1477(3)	ν_3, ν_4
(14)		1370(?)		1370(?)			
(15)					1350(6)	1336(3)	ν_{4-2}
(16)					1301(6)		
(17)			1226(1)				?
(18)		1171(3)		1179(4)			4047 excitation
(19)	1153(1)		1153(1)	1154(2)			ν_6
(20)	1104(2)	1119(3)					OH bend
(21)		1056(4)		1071(4)			4047 excitation
(22)	1029(6)	1029(6)	1031(6)	1034(5)	1032(8)	1043(5)	ν_5
(23)			942(2)		881(2)	907(1)	OD bend
(24)	(2536A)		(2536A)		(2536A)		
(25)		(4358A)		(4358A)		(4358A)	

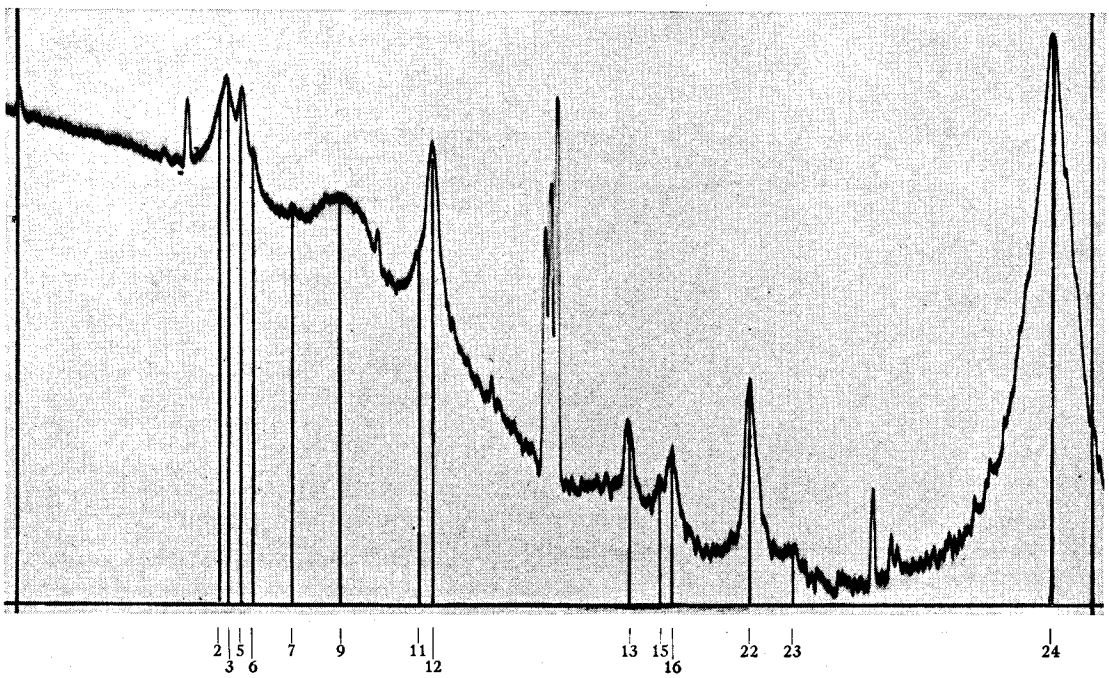

FIG. 3. CH_2DOD.

of the table. The numbers in the first column serve to identify the lines in the figures. Lines 2 and 4 do not show as well in the curves prepared for reproduction as in others which have been measured.

FUNDAMENTAL VIBRATIONS

Although in general the correlation of Raman shifts with fundamental vibrations is necessarily somewhat arbitrary and is therefore subject to uncertainty, it appears feasible from present knowledge of the magnitude of bond constants and of the vibrations of methyl compounds to make provisional assignments for methyl alcohol. For this purpose, reference to the work of Adel and Barker[5] on the methyl halides is of material assistance.

The notation adopted for the normal frequencies is taken from the scheme applied to the methyl halides by Dennison.[6] Its use in the methyl alcohol problem introduces the reasonable assumption that the dissymmetry occasioned by the position of the hydroxyl hydrogen atom will have negligible effect upon vibrations which belong primarily to the methyl and methoxy groups. In CH_3OH and CH_3OD, three motions (ν_1, ν_3 and ν_5) are described as parallel to the symmetry axis of the methoxy group and three (ν_2, ν_4 and ν_6) are perpendicular to the symmetry axis and doubly degenerate. CH_2DOD should show nine frequencies in these groups, three new ones occurring because of the splitting of the degenerate frequencies according to the orientation of their motion with respect to the plane of symmetry of the CH_2D group. These three deuterium frequencies are designated as ν_{2-2}, ν_{4-2}, and ν_{6-2}. Of the three additional degrees of freedom required to make up the total of twelve possessed by methyl alcohol as a hexatomic molecule, two should approximate, respectively, to bending and stretching of the OH or OD bond, while the third may be either free internal rotation or a torsional frequency, probably the latter.

The values of ν_1, ν_2 and ν_4, which are practically[7] invariant in methyl compounds, may be readily assigned. The line at 2987 cm^{-1} (CH_3OH and CH_3OD, 2980 for CH_2DOD) is ν_2, and the

[5] Adel and Barker, J. Chem. Phys. 2, 627 (1934).
[6] Dennison, Rev. Mod. Phys. 3, 280 (1931).
[7] Sutherland and Dennison, Proc. Roy. Soc. A864 (v148), 250 (1935).

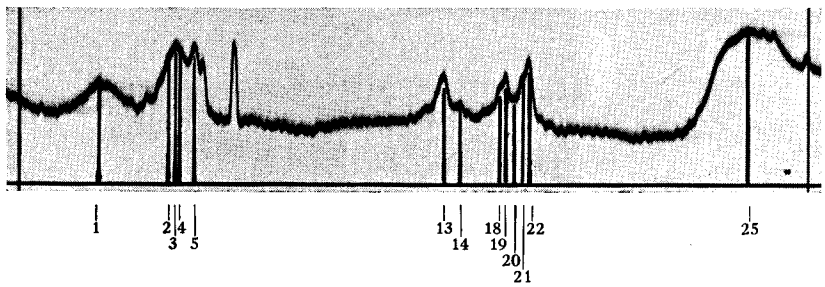

FIG. 4. CH_3OH.

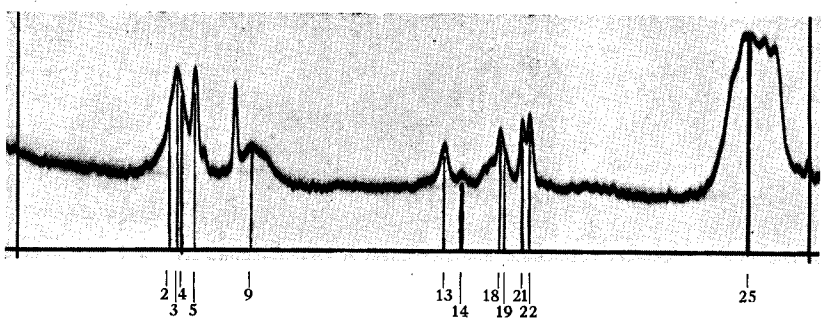

FIG. 5. CH_3OD.

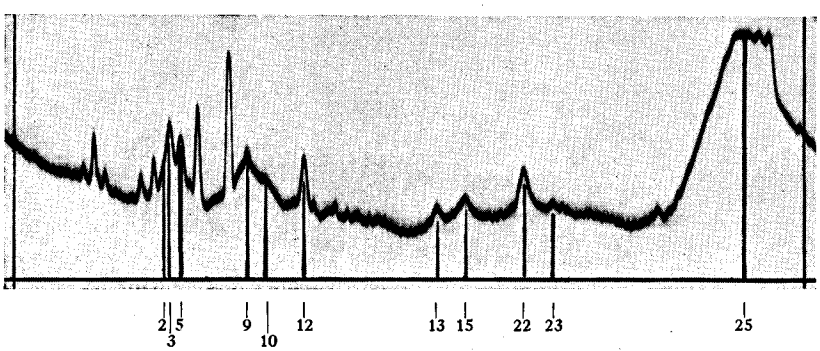

FIG. 6. CH_2DOD.

two strong high frequency lines (2835 and 2945 for CH_3OH and CH_3OD, 2883 and 2948 for CH_2DOD) arise from the interaction of ν_1 and $2\nu_4$ from which $\nu_1=2890$ and $\nu_4=1445$ may be taken as not far from correct for the symmetrical methoxy group. A correction for anharmonicity would bring ν_4 into coincidence with the weak band with center at 1452 reported by Voge, or with the relatively strong line at 1464. The weaker line at the lower frequency is the better assignment, because the perpendicular motions of this type of molecule tend to appear only weakly in the Raman effect. Consistency requires that $\nu_3=1464$, a conclusion that receives support from the occurrence of a line at 2915 cm^{-1} which must be either $\nu_3+\nu_4$ or $2\nu_3$, since $2\nu_4$ has already been accounted for. It follows that $\nu_3>\nu_4$ since $\nu_3+\nu_4$ (or $2\nu_3$) $>2\nu_4$.

The assignment $\nu_5=1031$ agrees with the generally accepted view that this is the C—O bond frequency. By comparison with the methyl halides, ν_6 should lie in the region between 1100 and 1300 cm^{-1}. The best selection appears to be the line at 1153 cm^{-1} which is observed as a shift of both the 2536 and the 4358 Hg lines for CH_3OH and CH_3OD. The deuterium line at

2176 cm^{-1} (columns 5 and 6) is undoubtedly ν_{2-2}; that at about 1340 cm^{-1} is probably ν_{4-2}. Neither ν_6 nor ν_{6-2} appears in the CH_2DOD spectrum.

The broad band with center at 3400 cm^{-1}, which has been reported by a number of previous workers for CH_3OH,[8] has been ascribed to the OH stretching motion. The corresponding OD band in the CH_3OD spectrum is narrower and more intense, and has its center at 2500 cm^{-1}, close to the position predicted from the assumption that the frequency ratio is determined by the masses of the protium and deuterium atoms. The similar band for CH_2DOD shows two intensity maxima, at 2500 and 2380 cm^{-1}, with the higher frequency maximum about twice as intense as the lower. This suggests that rotation of the OD group about the C—O bond is restricted, and that the two frequencies result from three more or less stable orientations of this group with respect to the plane of symmetry of the CH_2D radical. Two of these would be dynamically equivalent mirror images, accounting for the greater intensity of the one maximum. Unfortunately it is not possible to say with confidence that this is the correct explanation, because the effect of association in the liquid state cannot be eliminated, and the possibility of a splitting due to interaction of the OD frequency with a combination involving the new deuterium frequencies must be considered. It is interesting, however, that the production of sharp intensity maxima suggests the presence of vibrational states in the torsional motion. Further discussion of the character of the torsional motion is best deferred until data on the molecules containing the CHD_2 and CD_3 groups become available. The preparation of CHD_2OD and CD_3OD is now being studied in this laboratory.

In the original communication the CH_3OH line at about 1110 cm^{-1} was ascribed to the OH bending motion, primarily because it was not found in the CH_3OD spectrum. This line (20) appears distinctly only in the ultraviolet CH_3OH spectrum. Its acceptance as a line in the visible spectrum is based upon this fact together with the difference between the densitometer curves for CH_3OH and CH_3OD (Figs. 4 and 5). The same assignment has been made independently by Mizushima, Morino, and Okamoto. It should be recognized, however, that this conclusion may not be the correct one, since a line arising from association might be expected to behave in the same manner. What appears to be the corresponding OD line is found at 942 cm^{-1} on one of the CH_3OD plates and at 881 and 907 cm^{-1} on the CH_2DOD plates.

In addition to the assigned fundamentals and the high frequency combinations used in support of the assignments, a number of other lines are found in the spectra. Some of them may be accounted for as combinations, as shown in the last column of the table. The line at 2835 in the ultraviolet CH_2DOD spectrum is too high for the combination $\nu_3+\nu_{4-2}$, and may be a triple combination. There seems to be no good explanation for the lines at 1226 cm^{-1} (column 4), 1370 cm^{-1} (columns 3 and 5) and 1301 cm^{-1} (column 6), but their presence does not invalidate the selection of fundamentals if it is assumed that frequencies peculiar to the liquid state may appear. Furthermore, extra frequencies might appear in the CH_2DOD spectrum if two stable orientations of the OD group occur. The lines in the CH_3OH and CH_3OD spectra at about 1060 and 1175 cm^{-1} have been ascribed to excitation of the hydrogen frequencies by the 4047 Hg line, although they are somewhat more intense than would be predicted. Their absence from the CH_2DOD spectrum is explained by the fact that the exciting light was filtered through different filters resulting in a considerable decrease in intensity of the 4047 excitation.

Potential Constant of the C—O Bond

The frequency ν_5 has been used as the basis for a calculation of the Hooke's law constant of the C—O bond,[9] assuming that the methyl and hydroxyl groups act as point masses, and leads to the value $c=4.96(\times 10^5)$ dynes/cm. This assumption receives support from the calculations of Sutherland and Dennison, who have shown that when it is applied to the methyl halides it leads to a constant for the C—X bond

[8] Venkateswaran and Karl, Zeits. f. physik. Chemie **B1**, 466 (1928); Dadieu and Kohlrausch, Monatshefte **55**, 379 (1930); Medard, Comptes rendus **198**, 1407 (1934).

[9] Bonner, J. Chem. Phys. **5**, 293 (1937).

in substantial agreement with the result of a detailed analysis.

A minor refinement is suggested by the fact that ν_5 is the same, within the limits of error, for CH_3OH and CH_3OD, showing that the frequency does not depend upon the total mass of the hydroxyl group. A calculation using the mass of the oxygen atom instead of the OH group gives the result $c=4.74$.

A further approximation may now be made which takes into account the relative motion of the constituent atoms of the methyl group. Three constants may be calculated from ν_1, ν_3, and ν_5, if it is assumed for the purpose that these frequencies are analogous to the parallel frequencies of the methyl halide molecule. Sutherland and Dennison have expressed the frequencies in terms of the masses and four potential constants, making necessary the use of data from other methyl compounds in order to obtain a solution. It seems preferable here to employ a three-term potential function, producing a result which, although it may be less general, can more properly be said to yield the next approximation to the value of the C–O constant. Introducing the constants, k_1 for C–H stretching, k_2 for the sum of the expansions of the H–C–H and H–C–O angles, and c for C–O stretching, into the three relations gives the equations:

$$\lambda_1\lambda_3\lambda_5=\frac{M_1+M_2+3m}{m^2M_1M_2}k_1k_2c,$$

$$\lambda_1\lambda_3+\lambda_3\lambda_5+\lambda_5\lambda_1=\frac{c}{9}\left\{\frac{M_1+M_2+3m}{M_1M_2m}(k_1+8k_2)+\frac{M_1+M_2}{M_1M_2m}(8k_1+k_2)\right\}+\frac{M_2+3m}{M_2m^2}k_1k_2,$$

$$\lambda_1+\lambda_3+\lambda_5=\frac{M_2+3m}{9mM_2}(k_1+8k_2)+\frac{8k_1+k_2}{9m}+\frac{M_1+M_2}{M_1M_2}c.$$

λ has been substituted for $4\pi^2\nu^2$, M_1 is the mass of the oxygen atom, and M_2 and m are the masses of the carbon and hydrogen atoms. Simultaneous solution for the three constants yields two sets of values,

$$k_1=4.792,\quad k_2=0.684,\quad c=7.39$$

and

$$k_1=4.795,\quad k_2=0.875,\quad c=5.77,$$

of which the second set is the more reasonable physically. This new value for the C–O bond is not necessarily any nearer to the most representative one than is the constant 4.74 determined from ν_5 alone. The difference between the two, however, serves to show the magnitude of the uncertainty involved in the approximate calculations. It may be concluded, in any event, that considerable relative motion of the atoms of the methyl group is involved in the vibration ν_5.