of free rotation. This would appear to correspond to a quantum number of the order of magnitude of 5 in the energy of the free hydroxyl rotator. This estimate of the barrier is accordingly between 400 and 600 cm^{-1}. A study of the far infra-red would be helpful in fixing this value.

It is beyond the scope of the present paper to discuss the transition between vibrational and rotational states. Since the potential function of the alcohol molecule is intermediate between the two extremes discussed here, it is clear that both the rotational and vibrational states are complicated by the presence of the three minimum potential barrier.

In conclusion the authors wish to express their gratitude to Professor D. M. Dennison for his interest in the work and for many helpful discussions during the development of the theory.

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The Infra-Red Absorption Spectra of CH_3OD and CH_2DOD

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The infra-red absorption spectra of CH_3OD and CH_2DOD between 2.5μ and 24μ have been examined with a KBr prism spectrometer, and with appropriate gratings. The observed bands represent all of the fundamental vibrations except the one of lowest frequency which is associated with torsional vibrations about the C—O bond. Since these molecules depart only slightly from axial symmetry, the bands, with the exception of three due to the hydroxyl radical, correspond in position and appearance to those of the methyl halides. The rotational structure for the 10μ band (ν_6) of CH_3OD has been resolved, and partial resolution is obtained in some other bands. The band ν_5 in CH_2DOD has two components arising probably from two forms of the molecule in which the hydroxyl D atom occupies different valleys of the threefold potential. The deformation vibration (ν_7) is single for CH_3OD but has four components in CH_2DOD, indicating a separation of levels which for the former molecule are degenerate. A comparison of the frequencies obtained with gaseous and liquid samples indicates large displacements of the bands arising from the hydroxyl valence and deformation vibrations, the former toward greater wave-lengths in the liquid, and the latter toward smaller wave-lengths.

THE Raman spectra of ordinary methyl alcohol in the liquid phase, and of two methyl alcohols containing deuterium, have recently been described by Halford, Anderson and Kissin.[1] While the particular modes of vibration to be associated with each observed frequency may be decided almost by inspection, it is only through measurements in the infra-red that the character of the motions is revealed. Moreover the true molecular frequencies must be observed for the gaseous state. A comparison of infra-red data for the gases with Raman data for the liquids yields information of interest particularly in connection with the problem of association.

The molecule of methyl alcohol departs slightly from axial symmetry, since the line connecting the atoms O and H is nearly perpendicular to that connecting C and O. The minimum moment of inertia corresponds to an axis which is very nearly parallel to the C—O line, and which, for convenience, may be referred to as the symmetry axis. The relatively large electric moment may be attributed principally to the hydroxyl group. Twelve fundamental vibrations are to be expected, some of which occur in pairs, corresponding to two dimensional oscillators with nearly equal frequencies in the plane determined by the atoms C, O and H, and normal to it. Six of these are associated primarily with the methyl radical, three with the C—O bond, and three with the hydroxyl group, the first nine being conveniently designated as in the methyl halides.[2]

[1] Halford, Anderson and Kissin, J. Chem. Phys. **5**, 927 (1937). See also Mizushima, Morino and Okamoto, Bull. Chem. Soc. Japan **11**, 698 (1936).

[2] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

The infra-red spectrum of CH_3OH has been reported in the preceding paper.[3] The observations here presented include certain bands of particular interest in the spectra of CH_3OD and of CH_2DOD. We are indebted to Professors Halford and Anderson for the preparation of these materials; the specimens are in fact the same ones upon which the Raman observations were made. Professor Randall kindly placed at our disposal a recording prism spectrograph for exploratory measurements, the absorption cell being a metal tube with windows of KBr and an optical path length of 80 cm. For measurements at high resolution a prism-grating spectrometer was used, with a 60° NaCl foreprism, and gratings ruled 4800 and 2400 lines per inch. With this instrument the absorption cells were 25 cm glass tubes without stopcocks, the windows being attached with Apiezon wax. A side arm held the liquid sample in sufficient quantity to saturate the chamber at room temperature; when intense absorption bands were under observation the vapor pressure was reduced by cooling this reservoir.

The Methyl Vibrations

In the region of 3.5μ the two methyl frequencies ν_1 and ν_2 occur. These consist primarily of motions in which the hydrogen atoms approach and recede from one another. In ν_1 the change in electric moment is along the methyl axis, and the band is of the parallel type. It appears at 2850 cm^{-1} in CH_3OD, and at 2874 cm^{-1} in CH_2DOD. The displacement toward higher frequencies in the latter case in spite of increased mass is caused by a slight change in the direction of vibration. The second fundamental vibration ν_2, is perpendicular in character. In CH_3OD it involves two oscillations normal to one another and of almost identical frequencies. The band center, at approximately 2965 cm^{-1}, can be determined only to within three or four wave numbers, since almost no structure is apparent. Whether or not there is also absorption in this region due to the parallel component of $2\nu_4$, as indicated by Raman scattering, cannot be determined because of the breadth and intensity of the perpendicular band. The observations are represented by curve *a* of Fig. 1. The two corresponding motions in CH_2DOD are of very different frequencies. One is only slightly displaced, giving rise to a band at about 2944 cm^{-1}, but the second appears at about 2180 cm^{-1}. These are shown on curves *b* and *c* of Fig. 1. In the latter curve there appears also a fairly intense zero branch at 2158.4 cm^{-1} which may be the harmonic $2\nu_5$, although in CH_3OD the latter appears at 2065.4 cm^{-1}, as indicated in curve *d*.

The second pair of methyl frequencies, ν_3 and ν_4, lie in the region between 6.8 and 8.0μ, and are difficult to locate because of the strong atmospheric absorption due to water vapor. The frequencies ν_3 are 1459 cm^{-1} for CH_3OD and 1357 cm^{-1} for CH_2DOD, corresponding to vibrations in which the three hydrogen atoms move in phase approximately at right angles to the carbon bonds. In ν_4 the motions are similar except that the three hydrogens oscillate with phases differing by equal intervals, producing bands of the perpendicular type. In the spectrum these appear as groups of lines in the neighborhood of 1480 cm^{-1} with a second group appearing in CH_2DOD near 1330 cm^{-1}.

[3] Borden and Barker, J. Chem. Phys. 6, 553 (1938).

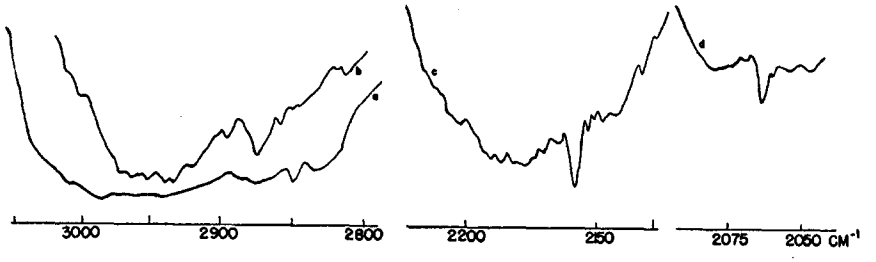

FIG. 1. Transmission at 3.4μ and 4.8μ. *a*, ν_1 and ν_2 for CH_3OD, 25 cm cell at −30°C. *b*, ν_1 and ν_2 for CH_2DOD, at −30°C. *c*, ν_2' for CH_2DOD, at 20°C. *d*, $2\nu_5$ for CH_3OD, at 20°C.

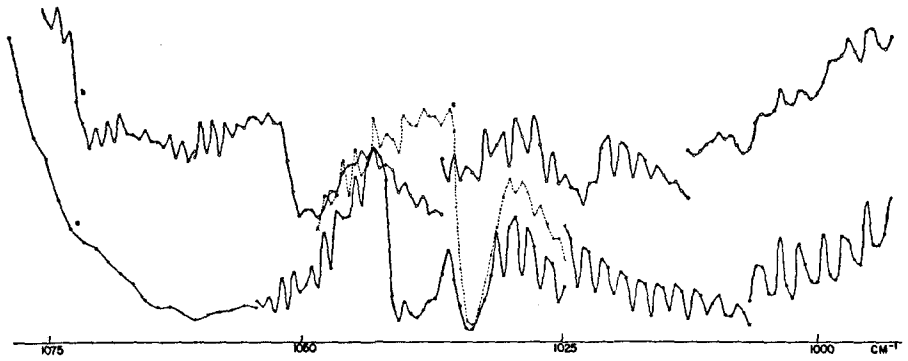

FIG. 2. Transmission at 10μ, showing ν_5. *a*, CH_3OD (with some CH_3OH). *b*, CH_2DOD. *c*, CH_3OH. Discontinuities indicate changes in prism setting.

THE C—O VIBRATIONS

In the methyl halides two frequencies are associated with the single carbon bond, one (ν_5) giving rise to a parallel band and the other (ν_6) to one of the pependicular type. The absorption due to ν_5 is very intense in the methyl alcohols, and is indicated in Fig. 2. With CH_3OD two zero branches were observed, one at 1034 cm^{-1} and the other at 1040 cm^{-1}. The fact that the former coincides exactly with the band of CH_3OH as indicated by the broken line, suggests that this sample had been contaminated with ordinary hydroxyl hydrogen, the tendency to exchange in this position being well known. Observations at 2.7μ showed that the OH band was present also. The second maximum at 1040 cm^{-1} is ν_5 for CH_3OD. It is somewhat broader than the one at 1034, indicating that the replacement of the hydroxyl hydrogen by deuterium produces a molecule somewhat farther removed from axial symmetry. The increase in frequency again indicates a larger restoring force due to the change in direction of vibration.

In the absorption curve for CH_2DOD there are also two maxima which appear to be rather broad zero branches at 1023 and 1049 cm^{-1}. These are probably to be explained by the fact that this compound exists in two forms depending upon the azimuthal position of the hydroxyl D with respect to the methyl D. In approximately two-thirds of the molecules the hydroxyl D will lie between an H and a D of the methyl group, the obliquity of the vibration with respect to the C—O line with being even greater than in CH_3OD, and the frequency correspondingly higher. The fact that no maxima appear in this spectrum at 1034 and 1040 cm^{-1} indicates that no exchange of hydrogens occurs in the methyl group, and also demonstrates the effectiveness of the procedure employed for the preparation of the material.

The band obtained with CH_3OD shows a distinct rotational structure, somewhat falsified, no doubt, by lines due to CH_3OH. As shown in Table I, the frequencies agree reasonably well with those computed from the equation

$$\nu = 1040.6 \pm 1.58m - 0.008\ m^2,$$

where m is the ordinal number of any line counting from the center. This indicates a mean moment of inertia for axes normal to the symmetry line, of approximately 35.0×10^{-40} g cm^2, a little more than 1 percent greater than for CH_3OH.

The perpendicular band ν_6 has not been observed for CH_3OD. In CH_2DOD two broad maxima consisting of groups of lines were located at about 1330 cm^{-1} and 1270 cm^{-1}. Whether the higher frequency group is a component of ν_6, which should be double, or belongs to ν_4 is not clear.

THE O—H AND O—D VIBRATIONS

The characteristic valence oscillation of the hydroxyl radical (ν_7) occurs at approximately 2.7μ for OH, and at 4.0μ for OD. The former is indicated in Fig. 3 as an absorption maximum around 3680 cm^{-1} in the lower curve (*C*) taken with low dispersion, using CH_3OH vapor. The determination of this band under high dispersion

TABLE I. *Observed and computed frequencies for the band* ν_5.

m	ν OBS.	ν COMP.	m	ν OBS.	ν COMP.
+9	1053.7	1054.2	−13	1018.4	1018.6
+8	1052.5	1052.8	−14	1016.7	1016.8
+7	1051.3	1051.3	−15	1015.0	1015.1
+6	1050.0	1049.8	−16	1013.4	1013.3
+5	1048.2	1048.4	−17	1011.7	1011.4
+4	1047.0	1046.8	−18	1009.8	1009.5
+3	1045.8	1045.3	−19	1007.8	1007.3
+2	1044.0	1043.8	−20	1005.9	1005.8
			−21	1004.0	1003.9
−6	1030.5	1030.8	−22	1002.0	1002.0
−7	1028.7	1029.1	−23	1000.1	1000.1
−8	1027.7	1027.4	−24	998.0	997.8
−9	1025.3	1025.8	−25	996.4	995.8
−10	1023.5	1024.2	−26	994.2	994.1
−11	1021.8	1022.2	−27	992.1	992.1
−12	1020.1	1020.4	−28	990.5	990.0

is a matter of some difficulty because of the intense absorption due to atmospheric water vapor, which is indicated in curve *A*. Measurements taken under the same conditions with CH_3OD in the cell are recorded in curve *B*. The very considerable absorption is evidence of the presence of hydroxyl H.

The region in which the O−D valence vibration occurs is a much more favorable one, since no atmospheric absorption interferes. Fig. 4 shows the band observed with CH_2DOD, its center having the frequency 2718.8. An almost identical curve was obtained for CH_3OD, with the center at 2720.4 cm^{-1}. The change in electric moment associated with this motion has components parallel to and perpendicular to the symmetry axis, both of course having the same frequency. The perpendicular one is probably greater in magnitude, and the band associated with it should exhibit a strong central maximum consisting of a family of zero branches spaced at intervals of approximately 5 cm^{-1}. These zero branches correspond to $\Delta K = \pm 1$, where K measures the angular momentum about the symmetry axis. There is some indication of such structure, but superposed upon it are a set of lines with spacing appropriate to the parallel band, as in ν_5. The small number of rotation lines observed on each side is evidence that this parallel band is superposed upon a strong and rather narrow background, probably attributable to the perpendicular transitions.

FIG. 3. Transmission at 2.7μ. *a*, Atmospheric water. *b*, CH_3OD (with some CH_3OH). *c*, CH_3OH.

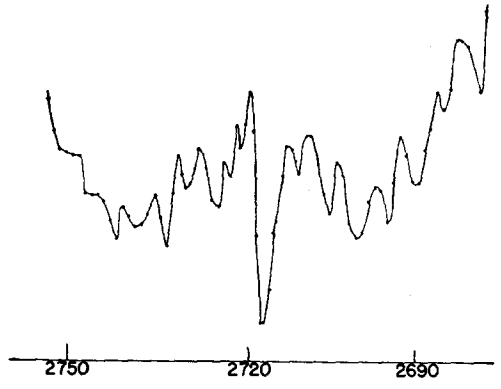

FIG. 4. Transmission at 3.7μ for CH_2DOD. Hydroxyl valence vibration $\nu_7 = 2718.8$ cm^{-1}.

A second degree of freedom (ν_8) for the hydroxyl D atom involves motions of low frequency normal to the D−O−C plane. In the absence of restraints this would become free rotation on the single carbon band. While the evidence here presented is not conclusive, it appears probable that free rotation occurs in only a relatively small number of molecules which have been excited to upper states of this motion, and that the normal state is an oscillation in one of the potential minima provided by the methyl radical. There is at least the negative argument that free rotation should introduce low states of considerable population, and in consequence,

combination bands which could hardly escape detection. For CH_3OD the three potential valleys are identical, and the lowest vibration state should be single while the second is double but degenerate. In CH_2DOD, however, one of the valleys differs from the other two, and this degeneracy would be removed, so that two low frequency bands should appear. Prism curves including the region from 13 to 22μ, taken with the 80 cm cell, indicated no absorption by CH_3OD. In CH_2DOD two very weak bands appeared near 16μ; these, however, could not be observed with the grating instrument in which it was necessary to use the shorter cell.

The so-called hydroxyl deformation vibration is normal to the O—D line, but in the D—O—C plane. This introduces a change in electric moment with its major component parallel to the symmetry axis. The resulting bands have strong zero branches, somewhat broadened, and degraded toward higher frequencies. They are shown in Fig. 5. The CH_3OD gives a single band at 863 cm^{-1}. In CH_2DOD four frequencies are observed, the two different types of molecules previously mentioned each being responsible for a pair of bands. The frequencies are 952.9, 892.3, 829.5, and 810.1 cm^{-1}. It might be expected that the splitting of the excited state would be greater in the more prevalent than in the less prevalent molecular type, the latter having a plane of symmetry, but it is not yet clear how these four bands are to be assigned.

The Effect of Association

Condensation from the vapor to the liquid state modifies some of these frequencies very considerably. This effect is apparent from a comparison of Raman and infra-red data, and has also been verified by observations upon the absorption of liquids. The methyl bands, and ν_5 due to the C—O bond, are not appreciably shifted, but the hydroxyl frequencies show a large displacement. The O—H valence vibration ν_7, found at 3650 cm^{-1} in CH_3OH vapor is reduced in frequency to about 3300 cm^{-1} in the liquid, as has been shown by Errera and others. The corresponding bands for CH_3OD and CH_2DOD are shifted from 2720 cm^{-1} to about 2500 cm^{-1}. The deformation bands ν_9 in the deuterium alcohols move to higher frequencies in the liquid phase, from 863 cm^{-1} to about 940 cm^{-1} for CH_3OD.[4] This effect could not be verified for CH_3OH, since ν_9 has not been observed in the vapor. Its position is indicated by Raman measurements as 1104 cm^{-1} in the liquid, and in the vapor it is probably obscured by the

[4] G. Bosschieter, J. Chem. Phys. 5, 992 (1937).

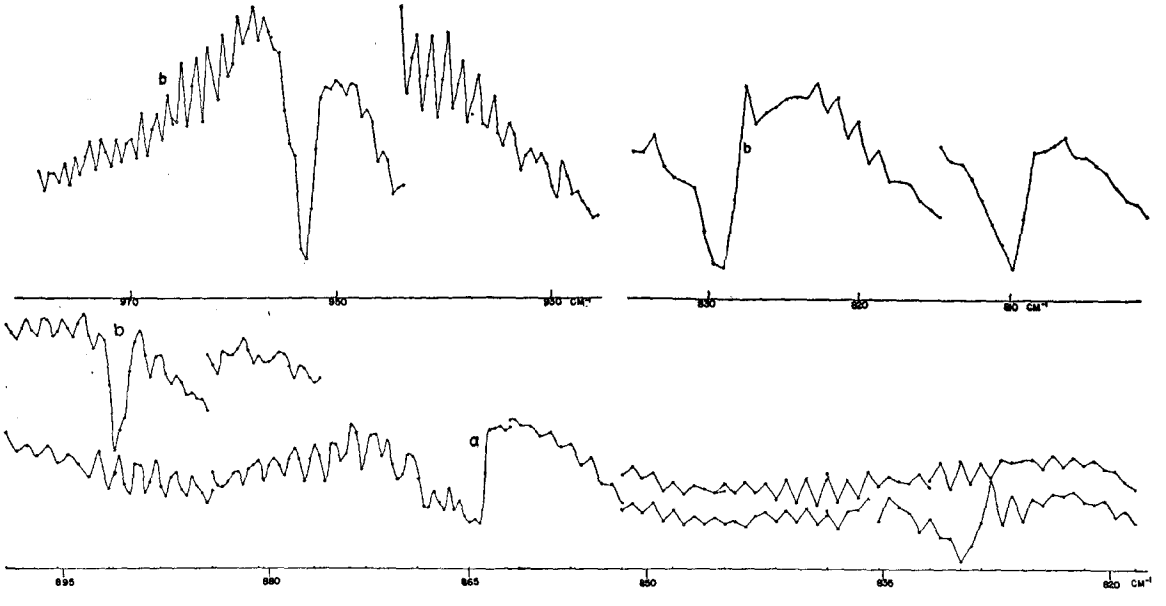

FIG. 5. Transmission at 12μ showing ν_9. *a*, CH_3OD. *b*, CH_2DOD.

intense 10μ band. A considerable intermolecular influence upon ν_6 might also be expected in the liquid. A bond between hydroxyl groups in adjacent molecules[5] would result in a further separation of the two components of this motion, though one of the components might be excluded from Raman transitions by considerations of symmetry. The only line in the Raman spectrum which can be assigned to ν_6 has a frequency of approximately 1160 cm^{-1} for both CH_3OH and CH_3OD, as compared with about 1340 cm^{-1} for the gases.

This investigation owes partial support to the Faculty Research Fund of the University of Michigan, which assistance is gratefully acknowledged.

[5] W. H. Zachariasen, J. Chem. Phys. **3**, 158 (1935).