

## The InfraRed Absorption Spectra of CH<sub>3</sub>OD and CH<sub>2</sub>DOD

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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  $\text{cm}^{-1}$ . 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 $\text{CH}_3\text{OD}$ and $\text{CH}_2\text{DOD}$

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The infra-red absorption spectra of  $\text{CH}_3\text{OD}$  and  $\text{CH}_2\text{DOD}$  between  $2.5\mu$  and  $24\mu$  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  $10\mu$  band ( $\nu_5$ ) of  $\text{CH}_3\text{OD}$  has been resolved, and partial resolution is obtained in some other bands. The band  $\nu_5$  in

$\text{CH}_2\text{DOD}$  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 ( $\nu_7$ ) is single for  $\text{CH}_3\text{OD}$  but has four components in  $\text{CH}_2\text{DOD}$ , 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.<sup>1</sup> 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.<sup>2</sup>

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

<sup>2</sup> Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

The infra-red spectrum of  $\text{CH}_3\text{OH}$  has been reported in the preceding paper.<sup>3</sup> The observations here presented include certain bands of particular interest in the spectra of  $\text{CH}_3\text{OD}$  and of  $\text{CH}_2\text{DOD}$ . 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  $60^\circ$  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  $3.5\mu$  the two methyl frequencies  $\nu_1$  and  $\nu_2$  occur. These consist primarily of motions in which the hydrogen atoms approach and recede from one another. In  $\nu_1$  the change in electric moment is along the methyl axis, and the band is of the parallel type. It appears at  $2850\text{ cm}^{-1}$  in  $\text{CH}_3\text{OD}$ , and at  $2874\text{ cm}^{-1}$  in  $\text{CH}_2\text{DOD}$ . 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  $\nu_2$ , is perpendicular in character. In  $\text{CH}_3\text{OD}$  it involves two oscillations normal to one another and of almost identical frequencies. The band center, at approximately  $2965\text{ cm}^{-1}$ , 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  $\text{CH}_2\text{DOD}$  are of very different frequencies. One is only slightly displaced, giving rise to a band at about  $2944\text{ cm}^{-1}$ , but the second appears at about  $2180\text{ cm}^{-1}$ . These are shown on curves *b* and *c* of Fig. 1. In the latter curve there appears also a fairly intense zero branch at  $2158.4\text{ cm}^{-1}$  which may be the harmonic  $2\nu_5$ , although in  $\text{CH}_3\text{OD}$  the latter appears at  $2065.4\text{ cm}^{-1}$ , as indicated in curve *d*.

The second pair of methyl frequencies,  $\nu_3$  and  $\nu_4$ , lie in the region between  $6.8$  and  $8.0\mu$ , and are difficult to locate because of the strong atmospheric absorption due to water vapor. The frequencies  $\nu_3$  are  $1459\text{ cm}^{-1}$  for  $\text{CH}_3\text{OD}$  and  $1357\text{ cm}^{-1}$  for  $\text{CH}_2\text{DOD}$ , corresponding to vibrations in which the three hydrogen atoms move in phase approximately at right angles to the carbon bonds. In  $\nu_4$  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  $1480\text{ cm}^{-1}$  with a second group appearing in  $\text{CH}_2\text{DOD}$  near  $1330\text{ cm}^{-1}$ .

<sup>3</sup> Borden and Barker, J. Chem. Phys. 6, 553 (1938).

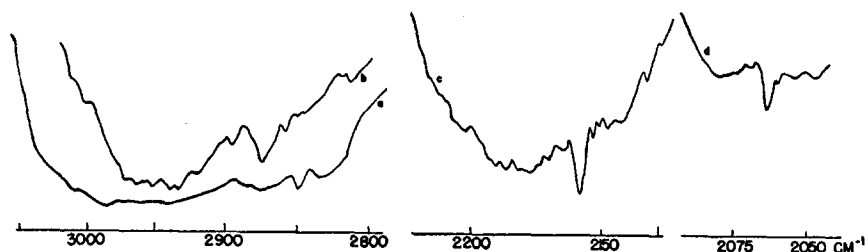


FIG. 1. Transmission at  $3.4\mu$  and  $4.8\mu$ . *a*,  $\nu_1$  and  $\nu_2$  for  $\text{CH}_3\text{OD}$ , 25 cm cell at  $-30^\circ\text{C}$ . *b*,  $\nu_1$  and  $\nu_2$  for  $\text{CH}_2\text{DOD}$ , at  $-30^\circ\text{C}$ . *c*,  $\nu_2'$  for  $\text{CH}_2\text{DOD}$ , at  $20^\circ\text{C}$ . *d*,  $2\nu_5$  for  $\text{CH}_3\text{OD}$ , at  $20^\circ\text{C}$ .

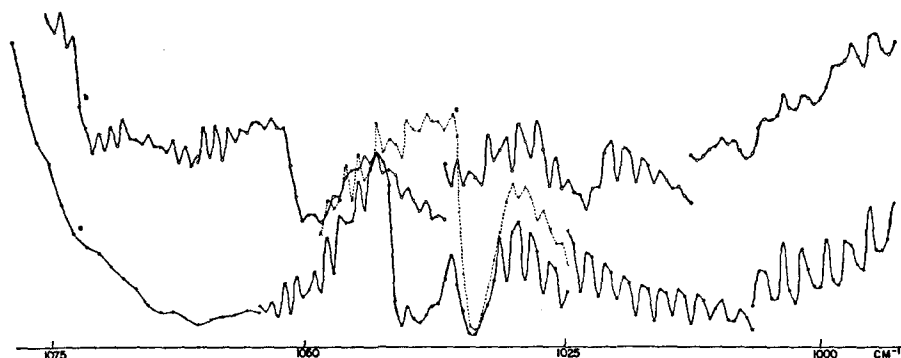


FIG. 2. Transmission at  $10\mu$ , showing  $\nu_5$ . *a*, CH<sub>3</sub>OD (with some CH<sub>3</sub>OH). *b*, CH<sub>2</sub>DOD. *c*, CH<sub>3</sub>OH. Discontinuities indicate changes in prism setting.

### THE C—O VIBRATIONS

In the methyl halides two frequencies are associated with the single carbon bond, one ( $\nu_5$ ) giving rise to a parallel band and the other ( $\nu_6$ ) to one of the perpendicular type. The absorption due to  $\nu_5$  is very intense in the methyl alcohols, and is indicated in Fig. 2. With CH<sub>3</sub>OD two zero branches were observed, one at  $1034\text{ cm}^{-1}$  and the other at  $1040\text{ cm}^{-1}$ . The fact that the former coincides exactly with the band of CH<sub>3</sub>OH 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  $2.7\mu$  showed that the OH band was present also. The second maximum at  $1040\text{ cm}^{-1}$  is  $\nu_5$  for CH<sub>3</sub>OD. 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<sub>2</sub>DOD there are also two maxima which appear to be rather broad zero branches at  $1023$  and  $1049\text{ cm}^{-1}$ . 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<sub>3</sub>OD, and the frequency correspondingly

higher. The fact that no maxima appear in this spectrum at  $1034$  and  $1040\text{ cm}^{-1}$  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<sub>3</sub>OD shows a distinct rotational structure, somewhat falsified, no doubt, by lines due to CH<sub>3</sub>OH. 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  $35.0 \times 10^{-40}\text{ g cm}^2$ , a little more than 1 percent greater than for CH<sub>3</sub>OH.

The perpendicular band  $\nu_6$  has not been observed for CH<sub>3</sub>OD. In CH<sub>2</sub>DOD two broad maxima consisting of groups of lines were located at about  $1330\text{ cm}^{-1}$  and  $1270\text{ cm}^{-1}$ . Whether the higher frequency group is a component of  $\nu_6$ , which should be double, or belongs to  $\nu_4$  is not clear.

### THE O—H AND O—D VIBRATIONS

The characteristic valence oscillation of the hydroxyl radical ( $\nu_7$ ) occurs at approximately  $2.7\mu$  for OH, and at  $4.0\mu$  for OD. The former is indicated in Fig. 3 as an absorption maximum around  $3680\text{ cm}^{-1}$  in the lower curve (C) taken with low dispersion, using CH<sub>3</sub>OH vapor. The determination of this band under high dispersion

TABLE I. Observed and computed frequencies for the band  $\nu_5$ .

$m$	$\nu$ OBS.	$\nu$ COMP.	$m$	$\nu$ OBS.	$\nu$ 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  $\text{CH}_3\text{OD}$  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  $\text{CH}_2\text{DOD}$ , its center having the frequency 2718.8. An almost



FIG. 3. Transmission at  $2.7\mu$ . *a*, Atmospheric water. *b*,  $\text{CH}_3\text{OD}$  (with some  $\text{CH}_3\text{OH}$ ). *c*,  $\text{CH}_3\text{OH}$ .

identical curve was obtained for  $\text{CH}_3\text{OD}$ , with the center at  $2720.4\text{ cm}^{-1}$ . 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  $5\text{ cm}^{-1}$ . 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  $\nu_5$ . The small number of rotation lines observed on each side is evidence that this parallel band is superposed upon a strong and

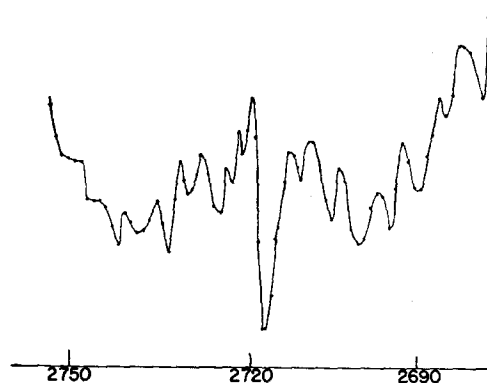


FIG. 4. Transmission at  $3.7\mu$  for  $\text{CH}_2\text{DOD}$ . Hydroxyl valence vibration  $\nu_7 = 2718.8\text{ cm}^{-1}$ .

rather narrow background, probably attributable to the perpendicular transitions.

A second degree of freedom ( $\nu_8$ ) 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<sub>3</sub>OD the three potential valleys are identical, and the lowest vibration state should be single while the second is double but degenerate. In CH<sub>2</sub>DOD, 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 22 $\mu$ , taken with the 80 cm cell, indicated no absorption by CH<sub>3</sub>OD. In CH<sub>2</sub>DOD two very weak bands appeared near 16 $\mu$ ; 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<sub>3</sub>OD gives a single band at 863 cm<sup>-1</sup>. In CH<sub>2</sub>DOD 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<sup>-1</sup>. 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  $\nu_5$  due to the C—O bond, are not appreciably shifted, but the hydroxyl frequencies show a large displacement. The O—H valence vibration  $\nu_7$ , found at 3650 cm<sup>-1</sup> in CH<sub>3</sub>OH vapor is reduced in frequency to about 3300 cm<sup>-1</sup> in the liquid, as has been shown by Errera and others. The corresponding bands for CH<sub>3</sub>OD and CH<sub>2</sub>DOD are shifted from 2720 cm<sup>-1</sup> to about 2500 cm<sup>-1</sup>. The deformation bands  $\nu_9$  in the deuterium alcohols move to higher frequencies in the liquid phase, from 863 cm<sup>-1</sup> to about 940 cm<sup>-1</sup> for CH<sub>3</sub>OD.<sup>4</sup> This effect could not be verified<sup>4</sup> for CH<sub>3</sub>OH, since  $\nu_9$  has not been observed in the vapor. Its position is indicated by Raman measurements as 1104 cm<sup>-1</sup> in the liquid, and in the vapor it is probably obscured by the

<sup>4</sup> G. Bosschieter, J. Chem. Phys. 5, 992 (1937).

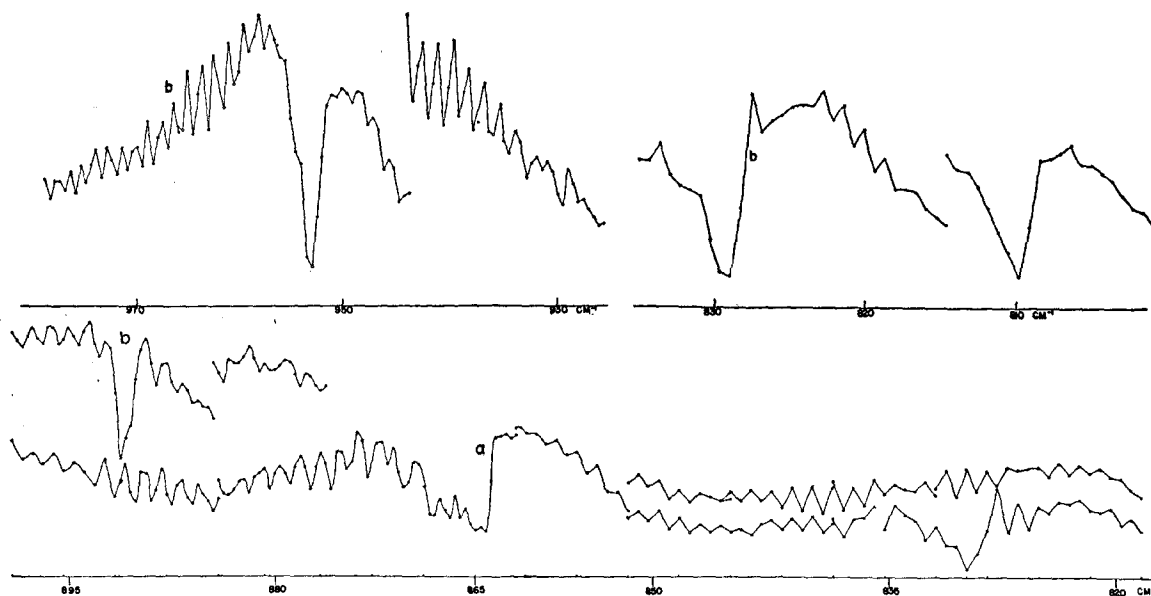


FIG. 5. Transmission at 12 $\mu$  showing  $\nu_9$ . a, CH<sub>3</sub>OD. b, CH<sub>2</sub>DOD.

intense  $10\mu$  band. A considerable intermolecular influence upon  $\nu_6$  might also be expected in the liquid. A bond between hydroxyl groups in adjacent molecules<sup>5</sup> 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 considera-

tions of symmetry. The only line in the Raman spectrum which can be assigned to  $\nu_6$  has a frequency of approximately  $1160\text{ cm}^{-1}$  for both  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ , as compared with about  $1340\text{ cm}^{-1}$  for the gases.

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

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<sup>5</sup> W. H. Zachariasen, J. Chem. Phys. **3**, 158 (1935).