

## The Infrared Spectrum of Heavy Water

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of observations are thrown together and treated statistically as a single set, the line through the observations, determined by the method of least squares, indicates a decrease in vapor pressure of 0.027 mm of Hg in 100 hours. We conclude that the vapor pressure of liquid normal deuterium over a period of 100 hours is constant to within the accuracy of our measurements. The *estimated probable error* calculated from our observations is  $\pm 0.27$  mm at 100 hours.

#### ROTATION IN THE CONDENSED STATES

Although it was surmised that there would be *free* rotation of deuterium molecules in the liquid and solid states just as in the case of hydrogen, we now have definite evidence from the ortho-para

vapor pressures that this is so. The latent heats of vaporization of solid and liquid deuterium are 355 and 305 calories per mole, respectively, and the rotational energy ( $J=1$ ) of  $p\text{-D}_2$  in the vapor phase at liquid hydrogen temperatures is 170 calories per mole.<sup>17</sup> If there were no rotation in the condensed states, the heats of vaporization of  $p\text{-D}_2$  would be about 170 calories per mole greater than the corresponding values for  $o\text{-D}_2$ . Actually there may be a small difference in the heats of vaporization of  $p\text{-D}_2$  and  $o\text{-D}_2$ , but it is less than for liquid hydrogen in which the difference is 3 calories per mole. We conclude, therefore, that there is free rotation in condensed states of deuterium just as in the case of hydrogen.

<sup>17</sup> Johnston and Long, J. Chem. Phys. 2, 389 (1934).

### The Infrared Spectrum of Heavy Water

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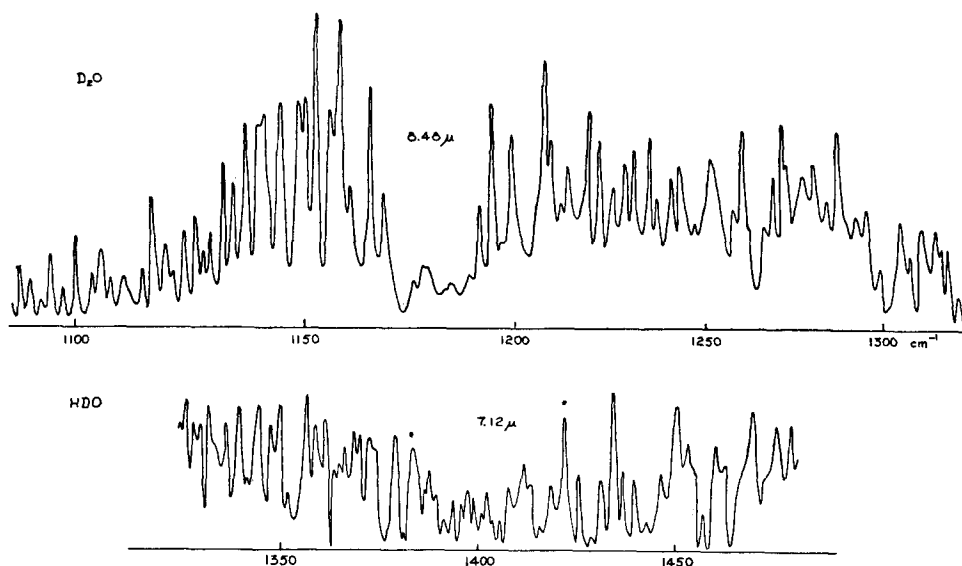
(Received August 15, 1935)

Samples of water vapor containing 90 and 40 percent of deuterium have been examined in the infrared, and the absorption bands  $\nu_2$  and  $\nu_3$  for  $\text{D}_2\text{O}$  and  $\nu_2$  and  $\nu_1$  for  $\text{HDO}$  have been located. The position of  $\nu_1$  for  $\text{D}_2\text{O}$  is known from Raman scattering. Of the nine fundamental frequencies for the three varieties of water, eight have now been observed. The ninth,  $\nu_3$  for  $\text{HDO}$ , should lie very close to the corresponding band for  $\text{H}_2\text{O}$  and is apparently completely masked. Computed values of these frequencies already

available agree very well with the measured ones. A fair degree of resolution is obtained in the bands  $\nu_3$ . The fine structure observed agrees approximately with that predicted by using the molecular dimensions obtained by Mecke, *viz.*, OH distance  $\sim 0.95 \times 10^{-8}$  cm and apex angle  $\sim 105^\circ$ . The magnitude of the interactions is so great, however, that precise determinations of these constants must await a more complete solution of the mechanical problem.

ALL available evidence indicates that the three atoms of the water molecule form an isosceles triangle. Hence there should be three active fundamental vibrations, and the bands should be of two types, involving changes in electric moment parallel to or perpendicular to the bisector of the apex angle. If this angle were smaller than  $86.5^\circ$  two of the fundamental bands should have zero branches and the other should not since the moment of inertia ( $B$ ) about an axis bisecting the apex angle would then be less than the one ( $A$ ) about a perpendicular axis lying in the plane. A larger angle ( $A < B$ ) would require

one band with and two without zero branches. Only two fundamental bands have been identified however, and one is of each type. The fact that the one of lower frequency at  $6.26\mu$  ( $\nu_2$ ) has no zero branch strongly suggests the obtuse form. The fundamental  $\nu_1$  has not been observed in the infrared. It must be weak, and is apparently masked by  $\nu_3$ , the intense band at  $2.67\mu$ . In this region it would be exceedingly difficult to locate if no zero branch occurs. Its small intensity suggests that the associated motion must be nearly symmetrical (hence the designation  $\nu_1$ ) and consequently that it should yield the strong-

FIG. 1. The absorption bands  $\nu_2$  for  $D_2O$  and  $HDO$ .

est Raman line. This, according to Bender,<sup>1</sup> lies at  $3654\text{ cm}^{-1}$ , corresponding to  $2.74\mu$ .

The vibration bands have structures which are clearly characteristic of an asymmetrical rotator, but of one in which interactions play a large part. Precise molecular constants can be obtained from any resolved band only after these interactions have been properly evaluated, but adequate formulae for accomplishing this have not yet been developed. Mecke<sup>2</sup> and his associates have obtained a very satisfactory correlation for the many observed bands by assigning "apparent" moments of inertia which vary from band to band in a consistent manner and which, by extrapolation, yield values characterizing the vibrationless state. This approximation indicates an apex angle of about  $105^\circ$  and an OH distance of about  $0.95 \times 10^{-8}\text{ cm}$ .

The mechanical problem of determining the normal vibrations for  $H_2O$  has recently been discussed from two different points of view. Van Vleck and Cross,<sup>3</sup> employing the idea of directed valence, and introducing known atomic wave

functions, have computed the fundamental frequencies for  $H_2O$  and  $HDO$ . Bonner,<sup>4</sup> on the other hand, has evaluated the constants of the potential function for  $H_2O$  starting with the observed frequencies and assuming the dimensions indicated by Mecke. This makes possible a prediction of the fundamental frequencies for  $D_2O$ . A test of these hypotheses and of Mecke's conclusions, is provided by the observations presented below.

We have examined the absorption spectrum of heavy water vapor with the prism grating spectrometer, using a cell 24 cm long with windows of rocksalt, which has a heating coil wound on its outer surface. The water, with a deuterium content of about 90 percent, was placed in a glass reservoir projecting outward from the bottom of the cell far enough so that its temperature is not raised appreciably by the heater. The temperature of the cell and windows was maintained at about  $10^\circ$  above that of the room, and the salt windows have remained for months unclouded. With a high concentration of  $D_2O$  the bands  $\nu_2$  and  $\nu_3$  for that molecule are

<sup>1</sup> Bender, Phys. Rev. **47**, 252 (1935).

<sup>2</sup> Mecke, Zeits. f. Physik **81**, 313 (1933).

<sup>3</sup> Van Vleck and Cross, J. Chem. Phys. **1**, 357 (1933).

<sup>4</sup> Bonner, Phys. Rev. **46**, 458 (1934).

TABLE I. Wave numbers of prominent lines in the  $\nu_2$  bands of  $D_2O$  and  $HDO$ .

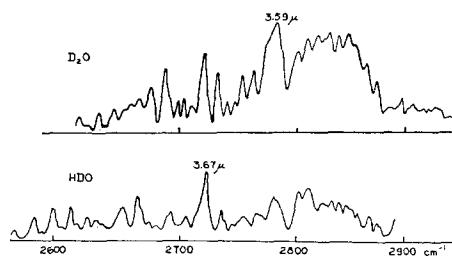
$D_2O$			$HDO$		
POSITIVE BRANCH	TRANSITION	NEGATIVE BRANCH	POSITIVE BRANCH	TRANSITION	NEGATIVE BRANCH
1190.7	$1_{-1} \rightarrow 1_{+1}$	1168.0	1412.0	$2_{-2} \rightarrow 2_0$	1387.5
1193.5	$2_{-2} \rightarrow 2_0$	1165.0	1422.0*	$1_{-1} \rightarrow 1_{+1}$	1383.7*
1199.0	$0_0 \rightarrow 1_0$	1160.0	1425.8	$1_{+1} \rightarrow 2_{-1}$	1379.0
1206.4	$2_0 \rightarrow 2_{+2}$	1156.8	1431.5	$1_0 \rightarrow 2_0$	1373.8
1207.4	$1_0 \rightarrow 2_0$	1155.2	1434.8	$0_0 \rightarrow 1_0$	1372.8
1211.4	$2_{+2} \rightarrow 3_0$	1153.0	1437.0		1369.0
1218.5		1149.3	1440.0		1366.0
1221.3		1148.0	1447.5		1361.0
1225.5		1144.5	1451.0		1359.0
1228.0		1140.0	1453.5		1356.0
1230.5		1139.0	1460.5		1350.0
1234.5		1135.5	1463.0		1347.6
1251.5		1131.5	1470.0		1344.5
1259.5		1116.3	1476.0		1339.6
1270.0		1100.0	1480.0		1332.0
1284.5		1095.5			

readily identified, both being shifted from the corresponding bands of  $H_2O$ . No indication of  $\nu_1$  could be obtained although its position as determined by Raman scattering is not unfavorable for observation. Rank, Larsen and Bordner<sup>5</sup> place it at  $2666\text{ cm}^{-1}$ , corresponding to  $3.75\mu$ .

The absorption curve for  $D_2O$  vapor in the neighborhood of  $8.5\mu$  ( $\nu_2$ ) appears in Fig. 1. There is a very transparent region extending some  $10\text{ cm}^{-1}$  each way from the band center at  $1179.1\text{ cm}^{-1}$ , with strong narrow lines occurring on either side in a somewhat symmetrical fashion. The two lines nearest the center are separated by  $22.7\text{ cm}^{-1}$  and have low intensities, while the next pair are strong. In  $H_2O$  the central gap is  $40.3\text{ cm}^{-1}$  wide, the first lines being strong, and the second ones weak. This reversal in relative intensities indicates the change in statistics when deuterons replace protons. In Table I the wave numbers are given for the more prominent absorption maxima.

The second strong absorption band of  $D_2O$  ( $\nu_3$ ) occurs at  $2784\text{ cm}^{-1}$  ( $3.59\mu$ ), and is represented in the upper curve of Fig. 2. The resolution obtained is far from complete, but the pattern has a striking resemblance to that of the corresponding  $H_2O$  band when the latter is about equally resolved. The zero branch is rather broad, and the positive branch is strong and closely packed indicating considerable convergence. The negative side appears weaker, being more spread out,

<sup>5</sup> Rank, Larsen and Bordner, J. Chem. Phys. 2, 464 (1934).

FIG. 2. The absorption bands  $\nu_3$  for  $D_2O$  and  $\nu_1$  for  $HDO$ .

and although it shows several intense peaks they are probably not single lines.

When only one of the hydrogen atoms in a water molecule is replaced by deuterium the vibrations lose all symmetry, and the principal axes are inclined to the bisector of the apex angle. The vibration  $\nu_1$ , which is principally a motion of the H and D atoms toward and away from one another, involves a change in electric moment having a considerable component along the axis  $A$ . In contrast to the case of  $H_2O$  this gives rise to a band with a well-developed zero branch. It lies very near to the pair of bands  $\nu_1$  and  $\nu_3$  of  $D_2O$ , and is shown in the lower curve of Fig. 2. No corrections have been made here for  $D_2O$  absorption, since it should be relatively weak with the vapor used. The rather intense maximum appearing in both curves at  $2720\text{ cm}^{-1}$  indicates the band center.

The fundamental vibration  $\nu_2$  is one in which the motion of the H and D atoms is almost normal to the line connecting them. The resulting change in electric moment has a very small component along the axis  $A$ , and the zero branch is scarcely at all developed. This band lies at  $1403\text{ cm}^{-1}$  ( $7.12\mu$ ), and is shown in the lower curve of Fig. 1. Since both  $H_2O$  and  $D_2O$  absorb strongly in this region the minor details of the curve cannot be considered as significant; the strong lines are unmistakable, however. The graph does not present the absorption as observed, but is corrected to eliminate the effect of  $H_2O$ . No attempt has been made to eliminate  $D_2O$  absorption, since the corrections are approximate at best. The positions of some of the important lines are given in Table I.

We have been unable to find any trace of the fundamental  $\nu_3$  for  $HDO$ , although in  $H_2O$  and

TABLE II.

	<i>A</i>	<i>B</i>	<i>C</i>	<i>A/B</i>	$\Delta\nu$ comp.	$\Delta\nu$ obs.
H <sub>2</sub> O	1.03	2.07	3.10	0.49	35.6	40.3
HDO	1.18	3.74	4.92	0.32	35.4	38.3
D <sub>2</sub> O	1.86	4.14	6.00	0.45	20.8	22.8

D<sub>2</sub>O it yields strong bands with prominent zero branches. Its predicted position lies very close to that of the band center for H<sub>2</sub>O at 2.67 $\mu$ . A detailed examination of the whole region occupied by this band with samples of water vapor containing 25 and 40 percent of deuterium shows no observable differences from the corresponding H<sub>2</sub>O pattern.

If we adopt tentatively the molecular dimensions indicated by Mecke for the vibrationless state of H<sub>2</sub>O, and compute moments of inertia without making allowances for the effects of interaction, the values shown in Table II are obtained (the unit is 10<sup>-40</sup> g cm<sup>2</sup>). A simple test of this configuration is to compute the wave number interval between the first lines on either side of the band center. For H<sub>2</sub>O these are a pair of strong lines and for D<sub>2</sub>O they are weak, but in either case they are easily recognized. The predicted value of this interval,  $\Delta\nu = (1/A - 1/C)h4\pi^2c$ , is compared in the table with that observed for each molecule, the agreement being fairly satisfactory. It is clear that by changing the molecular dimensions slightly a better check could be obtained, but this procedure would hardly be justified since the differences are in large part due to interactions as yet not evaluated. If the "apparent" moments of inertia appropriate to this band are computed by Mecke's formulae, and  $\Delta\nu$  determined, the situation is not appreciably improved. The result is 44.2 cm<sup>-1</sup> for H<sub>2</sub>O.

In the case of HDO the observed displacement of the innermost lines from the band center is very much less than the predicted value, and there is no alternating intensity to assure a correct assignment. As indicated in the curve, the first strong maxima on either side form a group of three or more closely spaced lines, and these are followed by several strong single lines. The interval between the first pair of such single lines (indicated by an asterisk in Fig. 1 and in Table I)

TABLE III. Fundamental frequencies of the three water molecules.

Raman spectra in *italics*. Computed values in parentheses.

	$\nu_1$	$\nu_2$	$\nu_3$
H <sub>2</sub> O	3654 <sup>1</sup> , <sup>5</sup>	1596	3756
HDO	2720	1403	
	2718 <sup>5</sup>	(1400) <sup>3</sup>	(3750) <sup>3</sup>
D <sub>2</sub> O	2666 <sup>5</sup>	1179	2784
	(2656) <sup>4</sup>	(1180) <sup>4</sup>	(2789) <sup>4</sup>

is the  $\Delta\nu$  shown above. The origin of the group of lines lying within this interval may be explained by reference to a figure given by Dennison.<sup>6</sup> The ordinates are values of  $\rho = A/B$ . Both H<sub>2</sub>O and D<sub>2</sub>O fall in the middle section, but for HDO this ratio is only about 0.32, at which value a group of lines originating in states with  $J > 1$  lies inside those for which the transition is  $1_{-1} \rightarrow 1_{+1}$ . An example is  $2_{-2} \rightarrow 2_0$ . The adjacent figure (19) in the same paper indicates how a central zero branch would develop if there were any appreciable component of the change in electric moment along the axis of *A*. A few of the rotation pairs in these bands may be identified, and transitions assigned with some confidence. These are listed in Table I. In the present status of the problem it does not seem wise to attempt to extend these assignments much further, since the various lines are affected quite differently by interactions.

A summary of the observed and computed values for the various fundamental frequencies is presented in Table III. For the two symmetrical molecules  $\nu_1$  has been observed only by Raman scattering, and  $\nu_2$  and  $\nu_3$  only in the infrared. It should be added that several of the infrared bands have also been observed with a prism spectrograph by Bartholomé and Clusius.<sup>7</sup> Their precision is not as great as that obtained when the bands are resolved, but the agreement is reasonably good.

We are indebted to Professors Anderson, Bates and Halford of the Chemistry Department for samples of heavy water, and to the Faculty Research Fund for the purchase of other samples.

<sup>6</sup> Dennison, Rev. Mod. Phys. **3**, 280 (1931), Fig. 20, p. 327.

<sup>7</sup> Bartholomé and Clusius, Zeits. f. Elektrochemie **40**, 529 (1934).