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Joseph W. Ellis and Barthold W. Sorge

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of the curves are not as large and, while the differences of the curves in that region are not certain, yet they merit some confidence. It is probably not without significance that in deuterium oxide there are noticed slightly sharper peaks, particularly in the case of the smaller one. This one has been found³ to disappear with rising temperature in the case of water, being unobservable at 40°C, and to be more marked as the freezing point is approached. In fact, with water the two peaks are distinctly sharpened in going from 21°C to 2°C, with the one at the diffraction angle of 13°C being displaced to the left and the one at 19° displaced to the right. The sharper peaks with D₂O are precisely what would be anticipated from these earlier experiments for the

D₂O is nearer to its freezing point, as well as its temperature of maximum density. To use the new term of Bernal and Fowler,⁵ the "structural temperature" of the deuterium oxide is less than that of water. It would be valuable to extend the careful comparisons of x-ray diffraction curves of deuterium oxide and water over a wide range of temperature, in order that the correctness of the tentative interpretation just made may be ascertained.

I wish to make appropriate acknowledgments to Professor G. N. Lewis for the deuterium oxide, to Professor J. N. Pearce for the conductivity water and to Dr. W. D. Phelps, research assistant, who is responsible for the observational data upon which this report is based.

The Infrared Absorption Spectrum of Water Containing Deuterium

JOSEPH W. ELLIS AND BARTHOLD W. SORGE, *University of California at Los Angeles*

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Absorption percentages for the region 1–10 μ are presented for one sample of water, 60 percent of whose hydrogen is deuterium, and for a second sample containing 99.5 percent deuterium oxide. Maxima are picked out as the three fundamental frequencies for the molecules DOD and HOD. These are compared with values predicted by an

isotopic shift calculation based on data chosen from the spectrum of ordinary water. All other higher frequency maxima are interpreted as overtones or combination bands, but only after a fourth fundamental frequency is chosen in the examples of HOH and DOD.

THIS paper reports the experimental determination of the infrared absorption spectrum in the region 1–10 μ of two samples of water containing different percentages of deuterium. On the basis of data selected from infrared and Raman spectra of ordinary water a calculation has been made to locate approximately the three fundamental frequencies of each of the molecules DOD and HOD. Certain absorption bands found in the newly determined spectra are identified with those calculated frequencies and the higher frequency bands are interpreted in terms of overtones and combinations of these fundamentals. Complete identification of all of the bands is possible, however, only after a fourth fundamental, associated with polymers, is selected.

SAMPLES OF WATER USED

The first sample studied was one kindly given us by Dr. Kaplan who had previously obtained it

for another purpose through the courtesy of Professor G. N. Lewis of the University of California at Berkeley. It was rated as containing 60 percent of its hydrogen as deuterium. The second specimen was purchased from the California Isotope Company, Berkeley, California, and was guaranteed by this firm to contain originally 99.5 percent of deuterium oxide. This company's density determination yielded 1.117 g/cm³, this somewhat larger value than usual arising from an excess of O¹⁸.

THE EXPERIMENTAL EQUIPMENT

For the region 2.5–10 μ a Hilger wave-length spectrometer, type D35, with a single 60° rock-salt prism was used. Temperature variation in the index of refraction of the prism was held to a minimum by making the observations in a sub-basement. Because of the large losses of light in the absorption cells, rather large slit widths had

to be used. The greatest slit width was 0.25 mm, corresponding to an average $\Delta\lambda$ range of 0.17μ . A Hilger linear thermopile, non-evacuated, and a Leeds and Northrup high sensitivity galvanometer were used in conjunction with this instrument.

For the region 1– 2.5μ a recording quartz spectrograph,¹ yielding a far greater resolving power than the Hilger instrument, was employed. The slit subtended an average $\Delta\lambda$ range of 0.002μ . A vacuum thermocouple and a Leeds and Northrup high sensitivity galvanometer are parts of this recording device.

For part of the longer wave measurements a cell was made up using 0.1 mm mica windows, separated by platinum strips 0.01 mm thick. This cell was set before the slit of the spectrograph so that the light rays coming from the spherical condenser mirror made a 30° angle of incidence with the windows. The usual procedure was followed of placing alternately before the slit the filled cell and two similar pieces of mica also held at a 30° angle. The purpose of using the mica sections at an angle was to prevent the formation of interference maxima and minima in the spectrum.² Although precaution was taken to guard against interference effects, no attempt was made to align the windows with respect to the plane of the optic axes. This lack of precaution is held responsible for the appearance in two of the spectra of a spurious apparent absorption band at 5.6μ , the location of a well-known absorption band of mica. Tests made after the spectra were recorded revealed that the magnitude of the absorption by mica at 5.6μ was dependent upon the orientation of the plane of the optic axes. The assumption is made that here, as in most crystals, the absorption coefficient is greatly dependent upon the plane of polarization of the light beam. A large amount of plane polarization gets introduced into the beam in the spectroscope used because of reflection at the prism, cell and mirror surfaces, thus affording the necessary lack of symmetry in the light beam required by the above explanation of the 5.6μ maximum.

The practical limit of observation through a mica cell is about 7μ . Therefore, to increase the

range of observation to 10μ a cell with rocksalt windows was used for the more concentrated deuterium sample. It was practically impossible to determine the cell thickness here but from an examination of the intensity of absorption it is estimated to have been about twice as great as the mica cells containing the less concentrated sample and the ordinary water used for comparison purposes, i.e., about 0.02 mm.

In the shorter wave region glass cells ranging in thickness from 0.25 to 6 mm were used.

As sources of radiation a Nernst filament and a tungsten lamp were used for the longer and shorter wave-lengths, respectively.

THE ABSORPTION SPECTRA

Fig. 1C records the percentage curves for ordinary distilled water. The percentage absorption values have been computed directly from galvanometer readings in the longer wave region and from the photographically recorded deflections in the shorter wave region. The maxima of well-known bands occur at 6.20, 4.70, 3.03, 1.93 and 1.445μ . Considerable asymmetry exists in the 6.20μ band, suggesting that it is probably not a simple band. The somewhat low value for the 1.93μ peak is yielded through the use of very narrow slits, the width being indicated by a ruled line above 1.8μ . Had much wider slits been used, doubtless the band would have appeared more symmetrical and the maximum would probably have occurred near 1.96μ , as usually found. That the difference between 1.93 and 1.96μ represents an experimental error is impossible, for the errors in calibration do not exceed 0.005μ . The 5.6μ maximum is the spurious one referred to above. Absorption at 1.78μ , once erroneously interpreted as a doublet,³ appears as a single band with this instrument of high resolving power.

Fig. 1B represents the observed spectrum for the water containing 60 percent of deuterium. The following maxima occur: 6.75, 6.2, 3.95, 3.03, 2.44, 2.015, 1.915, 1.650, 1.570, 1.425 and 1.360μ . Again the 5.6μ mica band appears. For the short wave spectrum the light beam was sent directly through the small capillary stem of the glass capsule container, yielding an effective thickness of about 0.5 mm. The existence of the weaker bands was verified also by using a thicker

¹ Ellis, R. S. I. 4, 123 (1933).

² Meyer and Bronk, *Astrophys. J.* 59, 252 (1924); Ellis, J. O. S. A. 23, 88 (1933).

³ Ellis, *Phys. Rev.* 38, 693 (1931).

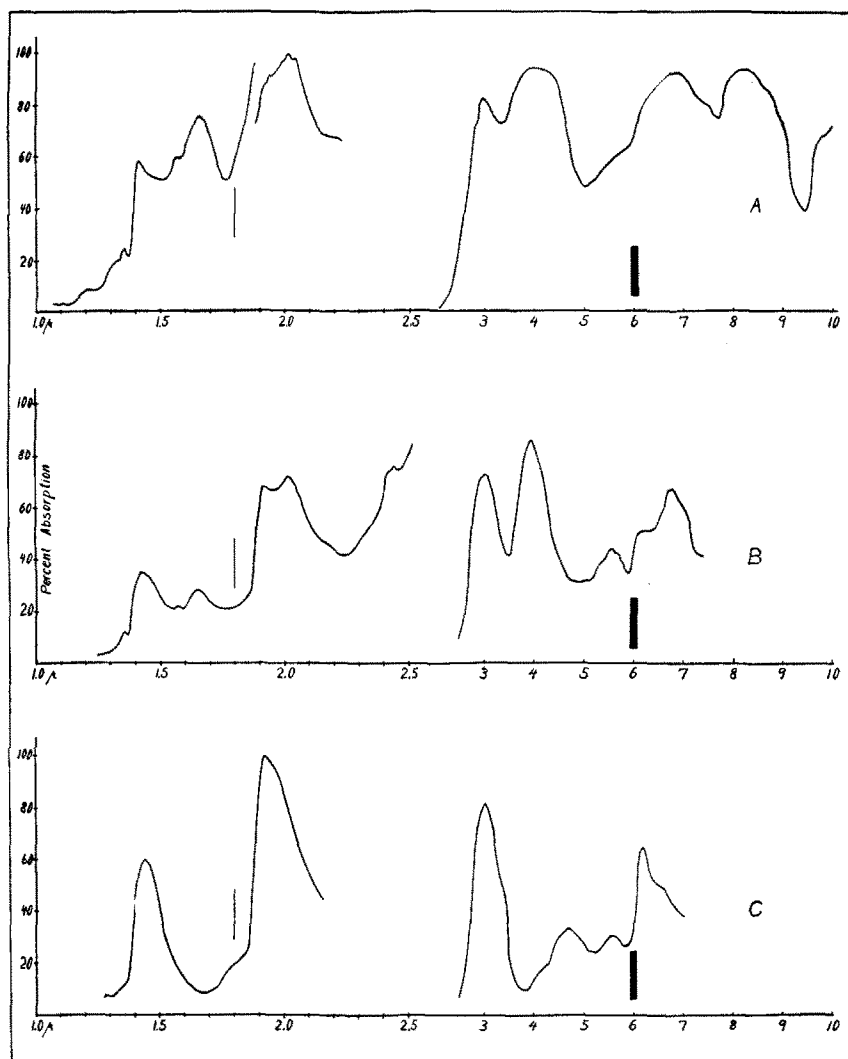


FIG. 1. *A*, percentage absorption through 99.5 percent deuterium oxide; *B*, water containing 60 percent deuterium; *C*, ordinary distilled water.

portion of the capsule. The single drop of water was later transferred to the mica cell and some days after the longer wave measurements were made it escaped by evaporation through a crack in the seal of this cell.

The record for the 99.5 percent sample of deuterium oxide is given in Fig. 1*A*. The maxima occur at 8.20, 6.85, 4.00, 2.95, 2.040, 2.015, 1.940, 1.655, 1.565, 1.415, 1.355, 1.310 and 1.20 μ . Absorption is increasing at 10 μ but the small deflections did not permit a complete study of this region. There is apparently absorption in the region of 5.6 μ but, since rocksalt cell windows were used, this can bear no relation to

similar absorption in Fig. 1*C*. The short wave record represents absorption by about 6 mm and 0.5 mm layers for the regions 1.0–1.9 μ and 1.9–2.2 μ , respectively. The former was obtained directly through the original cylindrical tube and the latter through a small drop enclosed in a capillary.

CALCULATION OF THE FUNDAMENTAL FREQUENCIES OF THE MOLECULES DOD AND HOD IN THE LIQUID STATE

Mecke's⁴ analysis of the vibration-rotation spectrum of ordinary water vapor leads him to

⁴ Mecke, *Zeits. f. Physik* **81**, 313 (1933).

the choice of 6.269, 2.8 and 2.663 μ as the wavelength values associated with the three fundamental frequencies of the vapor HOH molecule. In liquid water we associate absorption bands at 6.20 and 3 μ with the 6.269 and the 2.8, 2.663 μ bands, respectively. More detailed information about the 3 μ region is obtained from the Raman spectrum,⁵ which usually yields three components, the average of the maxima being approximately 3.11, 2.92 and 2.80 μ . Since the 3.11 band disappears or diminishes greatly in intensity with the addition of nitric acid and with a rise in temperature, we choose the remaining two as corresponding to Mecke's 2.8 and 2.663 μ bands, respectively. The shift in wave-length for the liquid state is not surprising, especially since many of the molecules contributing to these bands are doubtless parts of polymer molecules.

$$\delta^2(\pi) + \nu^2(\pi) + \nu^2(\sigma) = \left[\frac{f}{\mu_{12}} + \frac{f}{\mu_{23}} + \frac{d}{\mu_4} \right] \left[\frac{1}{2\pi c} \right]^2$$

$$\delta^2(\pi)\nu^2(\pi) + \delta^2(\pi)\nu^2(\sigma) + \nu^2(\pi)\nu^2(\sigma) = \left[\frac{f^2}{\mu_{12}\mu_{23}} \left(1 - \frac{\mu_{12}\mu_{23}}{m_2^2} \cos^2 \phi \right) + \frac{fd}{\mu_{12}\mu_4} \left(1 - \frac{\mu_{12}\mu_4}{m_2^2} \sin^2 \phi \right) + \frac{fd}{\mu_{23}\mu_4} \left(1 - \frac{\mu_{23}\mu_4}{m_2^2} \sin^2 \phi \right) \right] \left[\frac{1}{2\pi c} \right]^4$$

$$\delta^2(\pi)\nu^2(\pi)\nu^2(\sigma) = \left[\frac{f^2 d}{\mu_{12}\mu_{23}\mu_4} \left(1 - \frac{\mu_{12}\mu_{23}}{m_2^2} \right) \right] \left[\frac{1}{2\pi c} \right]^6$$

in which $\phi = (\pi - \theta)$, $c = 3 \times 10^{10}$ and

$$\begin{aligned} 1/\mu_{12} &= 1/m_1 + 1/m_2; & 1/\mu_{23} &= 1/m_2 + 1/m_3; \\ 1/\mu_4 &= 1/\mu_{12} + 1/\mu_{23} + (2/m_2) \cos \phi. \end{aligned}$$

When $m_1 = m_3$, as is the case for HOH and DOD, these expressions simplify considerably.

The values for f , d and θ obtained are

$$\begin{aligned} f &= 6.80 \times 10^5 \text{ dynes/cm} \\ d &= 6.92 \times 10^4 \text{ dynes/cm} \\ \theta &= 136^\circ. \end{aligned}$$

No great accuracy should be attached to this value of the valence angle as it is very sensitive to slight changes in the choice of fundamental

Assuming that the HOH molecule in the liquid state retains a symmetrical triangular shape, even though it couples with other molecules to form a polymer, and that the potential energy of the molecule can be written in terms of valence and bending force coefficients, f and d , respectively, a calculation of these two constants as well as the valence angle θ has been made. Values for the three possible normal frequencies have been taken as follows, using Mecke's⁴ notation: $\delta(\pi)$, 1610 cm^{-1} , 6.20 μ ; $\nu(\pi)$, 3420 cm^{-1} , 2.92 μ ; $\nu(\sigma)$, 3560 cm^{-1} , 2.80 μ . In this calculation the general theory outlined by Lechner⁶ for triangular molecules has been followed.

For the special geometrically symmetrical triangular molecule made up of particles of masses m_1 , m_2 and m_3 with valence distances $s_{12} = s_{23} = s$, and $f_{12} = f_{23} = f$ the three normal frequencies can be readily expressed by

frequencies. If the vapor molecule value of θ , 107°, worked out from rotational structure by Mecke,⁴ is used in place of 136°, the values of f and d become, respectively,

$$\begin{aligned} f &= 7.76 \times 10^5 \text{ dynes/cm} \\ d &= 7.56 \times 10^4 \text{ dynes/cm}. \end{aligned}$$

This shows, therefore, in the calculations which follow, that the choice of θ introduces no large errors in the predicted approximate locations of the fundamental absorption bands. It seemed advisable, however, in working with the HOH molecule to fit the observed data to three constants rather than to two, i.e., rather than to use the vapor value for θ .

The calculation of the three fundamental frequencies for the molecules DOD and HOD is

⁶ Lechner, Monatshefte für Chemie 61, 385 (1932).

⁵ See K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, p. 129, for a summary of the measurements on water in this region.

HOH. The fact that this band does not appear as a doublet in Fig. 1*B* is probably because of a further superposition of a band arising from HOD.

The 8.20μ band is interpreted as $\delta(\pi)$ and 4.00μ as $\nu(\pi)$ and $\nu(\sigma)$ unresolved. Bands near these positions should be found for heavy water vapor. The strong band at 6.85μ is assumed to be a polymer band corresponding to 4.70 in ordinary water. It occupies a position intermediate between 4.0 and 8.2μ , just as 4.70 occupies such an intermediate position between 6.2 and 3.0μ . The relatively great intensity of the 6.85μ band suggests a greater degree of polymerization in deuterium oxide than in ordinary water. That this may be expected to be the case has been suggested by Bernal⁹ on the basis of diminished molecular rotation.

All of the other bands of Fig. 1*A* can be regarded as overtones and combinations of four fundamentals. The assignments of quantum numbers V_1 , V_2 , V_3 and V^* are shown in Fig. 2*C*. In this figure, also, the frequency positions for the three calculated fundamentals are shown by dotted lines.

R. W. Wood¹⁰ found a 2517 cm^{-1} Raman band which he assigned to the molecule DOD. This agrees well with our 2500 cm^{-1} band.

Wood also found a 2623 cm^{-1} Raman band which he assigned to HOD. We have included this frequency in Fig. 2*B* rather than our absorption value under the assumption that it may represent a value less influenced by other bands than the infrared maximum.

The band at 2.44μ , and perhaps the one at 1.915μ , represent the only features of the spectrum in Fig. 1*B* which may be credited to the unsymmetrical HOD molecule, representing $V_2 + V_3$ and $2V_2$, respectively. Other predicted combinations and overtone bands would be superposed upon bands also belonging to DOD.

It is believed that the agreement between

observed wave-number values in Fig. 2 and values anticipated on the basis of the quantum assignments are as good as could be expected in consideration of the widths and the overlapping of bands which exist.

During the course of this experiment there appeared a brief paper by Casselman¹¹ giving his results on a sample of heavy water comparable to our 60 percent water. There is a great similarity between his record and our Fig. 1*B* although we believe there are considerable errors in wavelength determination in Casselman's record. There is apparently a broad false minimum in his curves around 5.6μ which might be explained on the basis of failure properly to orient mica windows, an effect opposite to that which we have outlined above but which could be explained by the same mechanism. It is not stated whether mica windows were used but the termination of his spectrum near 7μ would indicate that they were.

CONCLUSION

The fair agreement between the observed frequency values for heavy and intermediate water with those resulting from an isotopic shift calculation with light water data, should not be construed to indicate with certainty the existence in the liquid state of molecules HOH, HOD and DOD similar to those in the vapor state. Realizing that H atoms in a vast variety of molecules always give rise to absorption and Raman bands near 3μ and $6-7\mu$, it is possible that the degree of agreement obtained in this experiment might still be obtained even though there is in the liquid state as radical a departure from the vapor molecule configuration as the model of Kinsey and Sponsler¹² requires. The one thing which the experiment does definitely show, we believe, is a large degree of polymerization in pure deuterium oxide, apparently a larger degree than in ordinary water.

⁹ Bernal, Proc. Roy. Soc. **A144**, 24 (1934).

¹⁰ Wood, Phys. Rev. **45**, 732 (1934).

¹¹ Casselman, Phys. Rev. **45**, 221 (1934).

¹² Kinsey and Sponsler, Proc. Phys. Soc. **45**, 768 (1933).