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Citation: *J. Chem. Phys.* **2**, 558 (1934); doi: 10.1063/1.1749530

View online: <http://dx.doi.org/10.1063/1.1749530>

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# Comparison of X-Ray Diffraction Curves of Water and Deuterium Oxide at 25°C

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(Received June 29, 1934)

The difference in freezing point temperatures, maximum densities and molecular volumes and other physical constants of water and deuterium oxide indicate that the molecular forces do not remain entirely invariant with the isotopic change in mass. A comparison of the diffraction of x-ray curves for the two substances at 25°C indicates

that the liquid structure of deuterium oxide is much like that of water. The peaks in the deuterium oxide curve are slightly sharper, apparently explicable in the fact that, at 25°C, this substance, compared with water, is nearer to its freezing point.

ONE would expect the forces in the water molecule to remain nearly invariant with the isotopic change of mass to deuterium oxide. Nevertheless, these two compounds differ in freezing points, boiling points, temperatures of maximum density<sup>1</sup> and molecular volumes.<sup>2</sup> It is of interest to ascertain if the liquid structure of these two compounds, as determined by the diffraction of x-rays, is noticeably different.

The deuterium oxide was supplied by Professor G. N. Lewis of the University of California and was 99 percent pure. The conductivity water was prepared by Professor J. N. Pearce of this University. The apparatus used is the same as that referred to in previous work.<sup>3</sup> The effect of Mo  $K\alpha$  radiation was obtained by differential readings with  $\text{SrCO}_3$  and  $\text{ZrO}_2$  screens. The liquids were placed in very thin-walled cylindrical glass containers, these being nearly of the same diameter, 6.8 and 6.6 mm, and same thickness of wall. The transmission for the Mo  $K\alpha$  radiation of the containers was found to be 0.81 and 0.79 percent. Corrections were made for the penetration and scattering of the Soller slits, the scattering from the glass container and the absorption of the liquid and container. No correction was made for the slight variation in effective thickness with angle of diffraction, for the beam was confined to a width of 2 mm by an additional single slit, thus making such a correction small. Nothing was to be gained by correcting for the incoherent scattering. The results of the observations are plotted in Fig. 1.

<sup>1</sup> Lewis and McDonald, *J. Am. Chem. Soc.* **55**, 3057 (1933).  $\text{D}_2\text{O}$  freezing point is 3.8°C, boiling point, 101.42°C and maximum density at 11.6°C.

<sup>2</sup> Luten, *Phys. Rev.* **43**, 161 (1933), gives the specific gravity as 1.1056 at 25°C. The value 1.111 would be required for no change in molecular volume.

<sup>3</sup> Stewart, *J. Chem. Phys.* **2**, 147 (1934).

The lower full line is that of water and the upper that of deuterium oxide, the zero for the ordinate being shifted for convenience. Approximately nine independent observations were made at each degree of angle of diffraction from 1° to 40° and 20° to 40°, and at each half degree from 10° to

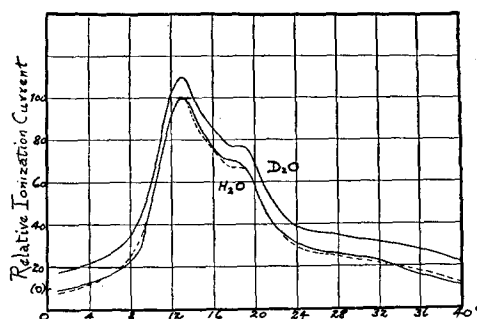


FIG. 1.

20°. These curves essentially agree with previous observations<sup>4</sup> on water.

Bernal and Fowler<sup>5</sup> have discussed the liquid structure of water as indicated by the position of the two peaks and the course of the diffraction curve. The consideration of the moment may therefore be limited to whether or not there is any significant differences in these curves of water and deuterium oxide. The variations between the two noticed, other than in the middle portion, are within the uncertainties of the experiments.

The experimental errors in the middle portion

<sup>4</sup> Meyer, *Ann. d. Physik* **5**, 701 (1930); Stewart, *Phys. Rev.* **37**, 9 (1931); Amaldi, *Phys. Zeits.* **32**, 914 (1931). The curve of Meyer matches the present one very closely throughout the middle portion, differing only in the end regions. The former curves of Stewart were taken with a zirconium filter only and general radiation was reduced to a small amount by a low voltage.

<sup>5</sup> Bernal and Fowler, *J. Chem. Phys.* **1**, 515 (1933).

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 found<sup>3</sup> 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  $D_2O$  are precisely what would be anticipated from these earlier experiments for the

$D_2O$  is nearer to its freezing point, as well as its temperature of maximum density. To use the new term of Bernal and Fowler,<sup>5</sup> 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

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(Received June 6, 1934)

Absorption percentages for the region 1–10 $\mu$  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 $\mu$  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/cm<sup>3</sup>, this somewhat larger value than usual arising from an excess of  $O^{18}$ .

### THE EXPERIMENTAL EQUIPMENT

For the region 2.5–10 $\mu$  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