THE ATOMIC WEIGHT OF EUROPIUM

$EuCl_2$, g.	Ag, g.	Ratio $EuCl_2$:2Ag	At. wt. Eu
2.37131	2.29571	1.03293	151.95
3.08192	2.98364	1.03294	151.95
2.81855	2.72847	1.03301	151.97
4.88930	4.73350	1.03291	151.95
	Average	1.03295	151.95

Urbain and Lacombe [*Compt. rend.*, **138,** 627 (1904)] found 151.96; Jantsch [*ibid.*, **146,** 473 (1908)], 152.04; Aston [*Proc. Roy. Soc.* (London), **A146,** 46 (1934)] from the isotopic constitution, 151.90; Hopkins and Meyers [THIS JOURNAL, **57,** 241 (1935)], 152.30. The International value has been 152.0 for some time.

Summary

1. A concentrated solution of the chlorides of the rare earths containing 70% or more of europium gives upon reduction of the latter with zinc and treatment with concentrated hydrochloric acid a crystalline precipitate of europous chloride dihydrate, $EuCl_2 \cdot 2H_2O$, practically free from accompanying rare earths.

2. By means of this reaction about 500 g. of europium oxalate has been prepared, the high purity of which is shown by spectrograms by Dr. King.

3. An X-ray examination by Dr. Pauling has established the isomorphism of $EuSO_4$ and $BaSO_4$, and therefore also of $SrSO_4$.

4. Dr. Baxter and Mr. Tuemmler have completed the purification of europium and determined its atomic weight to be 151.95.

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RECEIVED APRIL 24, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Raman Spectrum and the Structure of Water

BY PAUL C. CROSS, JOHN BURNHAM AND PHILIP A. LEIGHTON

The tridymite-like structure of ice as regards the distribution of the oxygen atoms appears to be definitely established,[1] and Pauling's[2] explanation of the discrepancy between the third law and statistical entropies in ice leaves little doubt that the hydrogens are unequally spaced between the oxygens. Each four-coördinated oxygen nucleus, at 0°, has bonded at tetrahedral angles four oxygens at $d = 2.76$ Å., with a proton along each oxygen–oxygen axis; two chemically bonded at $d = 0.99$ Å. (see section III) and two "hydrogen bonded" at $d = 1.77$ A. Present theory, as developed by Bernal and Fowler[3] and modified by Katzoff[4] and others, considers liquid water at ordinary temperatures as having essentially a broken down ice structure, with a considerable amount of coördination still persisting through hydrogen bonding which, however, decreases with increasing temperature or addition of electrolytes. Little progress has been made beyond this qualitative picture, and to obtain further evidence on the nature and extent of coördination in water the authors have reinvestigated, using rather high dispersion, the Raman spectrum of water over a wide range of temperatures, of ice at 0°, and of deuterium oxide. The results are treated on the basis of a model consisting of coupled O—H oscillators perturbed by various types of coördination.

An empirical treatment of the perturbation forces leads to an estimate of the intermolecular frequencies which confirms their identification. For earlier measurements and their interpretation we refer to the review and bibliography of Magat[5] and to the recent paper of Hibben.[6]

I. Experimental Data

The Raman spectra were excited by the unreversed 2536.52 Å. line of a mercury–argon discharge lamp and photographed on a quartz spectrograph of 3.5 Å./mm. dispersion at 2650 Å. The water was placed in a fused silica tube of 30 mm. diameter for the work below 100°, while at higher temperatures the high pressures (up to 218 atm. at 375°) necessitated the use of a smaller bore; a 4-mm. tube with 1.1-mm. walls being employed. For frequency measurements each spectrum was partially overlaid with an iron arc spectrum. Wave lengths were corrected to vacuum.

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(1) Barnes, *Proc. Roy. Soc.* (London), **A125,** 670 (1929).

(2) Pauling, THIS JOURNAL, **57,** 2680 (1935).

(3) Bernal and Fowler, *J. Chem. Phys.*, **1,** 515 (1933).

(4) Katzoff, *ibid.*, **2,** 841 (1934).

(5) Magat, *Ann. phys.*, **6,** 108 (1936).

(6) Hibben, *J. Chem. Phys.*, **5,** 166 (1937).

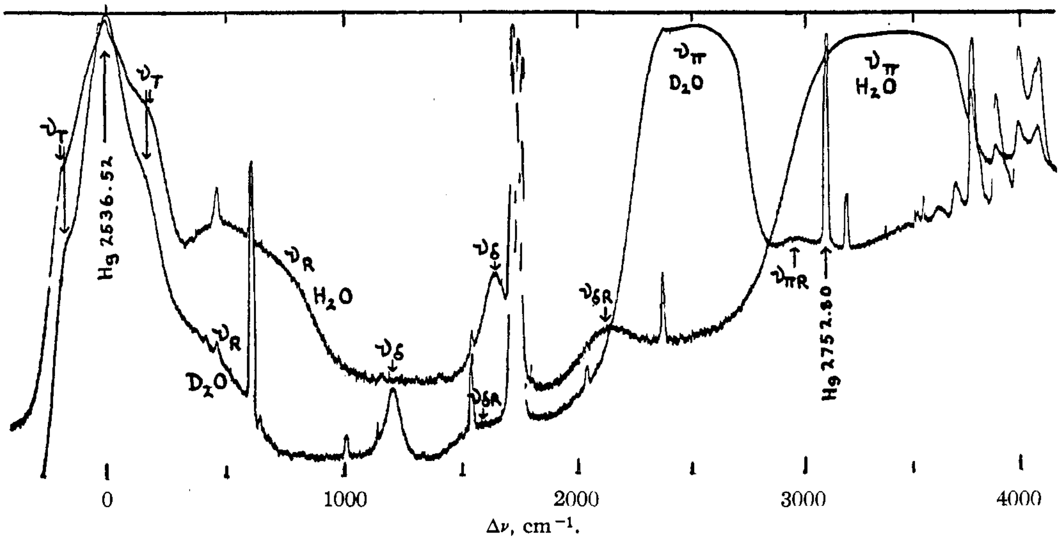

Fig. 1.—Comparison of the Raman spectra of H_2O (40°) and D_2O (50°).

In Fig. 1 are shown microphotometer records, obtained by use of the instrument described recently,[7] of the entire Raman spectrum of H_2O at 40° and D_2O at 50°. The main bands of each are overexposed in order to bring out the low frequencies. These low frequency bands are compared with greater linear magnification in Fig. 2, while in Fig. 3 the low frequency spectrum of melting ice at 0° is compared with that of water at 26 and at 80°. The exposures required to show these bands even to the small extent to which they appear in Fig. 3 were about twenty times greater than those required to give the main band the intensity shown in Figs. 4 and 5. Particularly noteworthy in Fig. 3 are the broadening in the neighborhood of the source line in liquid water as compared with ice; the sharp "hindered translation," ν_T, frequency in ice, observable both as a Stokes and anti-Stokes band; and the decrease in intensity of this frequency with increasing temperature in liquid water on the Stokes side as compared with its increasing intensity with increasing temperature on the anti-Stokes side. Frequencies of intensity maxima, taken from these figures, are given in Table I. Owing to the breadth and flatness of the ν_R (hindered rotation) band, which extends at least from 320 to 1020 cm.$^{-1}$ for H_2O and from 250 to 730 cm.$^{-1}$ for D_2O, no estimates of the maxima are attempted. The differences between the maxima of $\nu_{\delta R}$ and ν_δ are 511

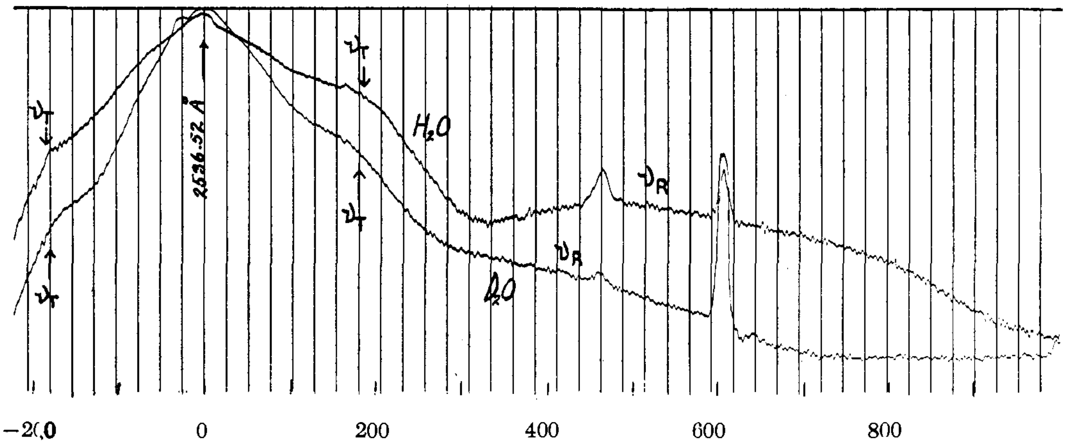

Fig. 2.—Low frequency Raman bands of H_2O (40°) and D_2O (50°).

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[7] Leighton, Smith and Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).

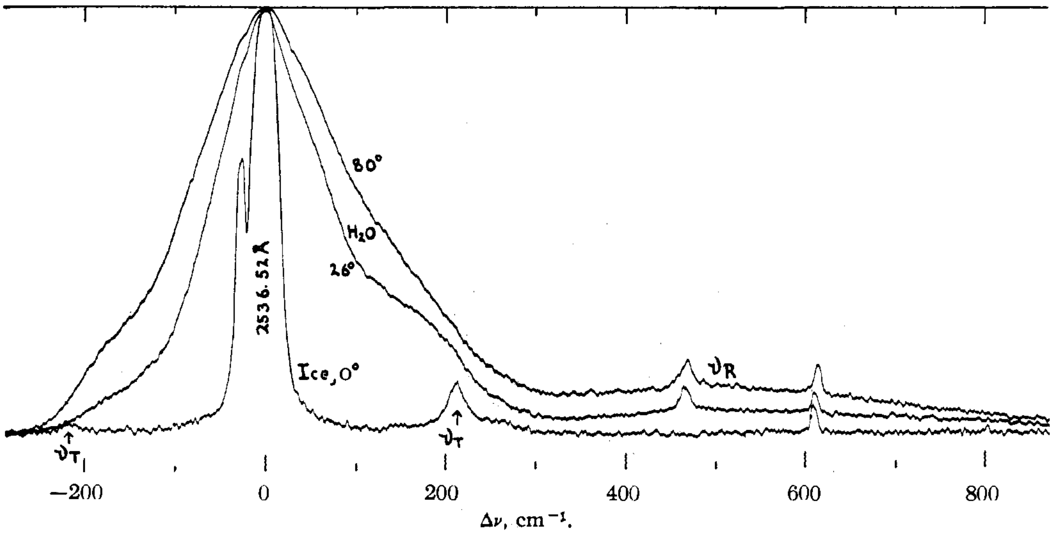

Fig. 3.—Low frequency Raman bands of ice at 0° and water at 26 and 80°.

and 392 cm.$^{-1}$ for H_2O and D_2O, respectively. All frequencies in D_2O, in accordance with theory, are approximately in the ratio of $2^{-1/2}$ to those in H_2O, with the exception of ν_T where the ratio, in agreement with the assignment of this frequency as a hindered translation, is $(20/18)^{-1/2}$.

The main band for melting ice at 0° is compared with that for water at two temperatures, 26 and 75°, in Fig. 4, and to facilitate comparison of shapes, the main bands of H_2O and D_2O at 40° are superimposed, using different frequency abscissas, in Fig. 5. The change in position and shape of the band with temperature in liquid water up to the critical temperature is shown in Fig. 6. The low intensity at 374° is due to an explosion of the cell before the exposure was completed, which shattered the discharge tube and terminated the experimental work. Although this band (as well as the ν_R band) is to be treated by a procedure which attaches minor significance to the precise positions of maximum intensity, such positions are recorded for reference in Fig. 7. Variations among different authors in the reported frequencies of the three apparent components,

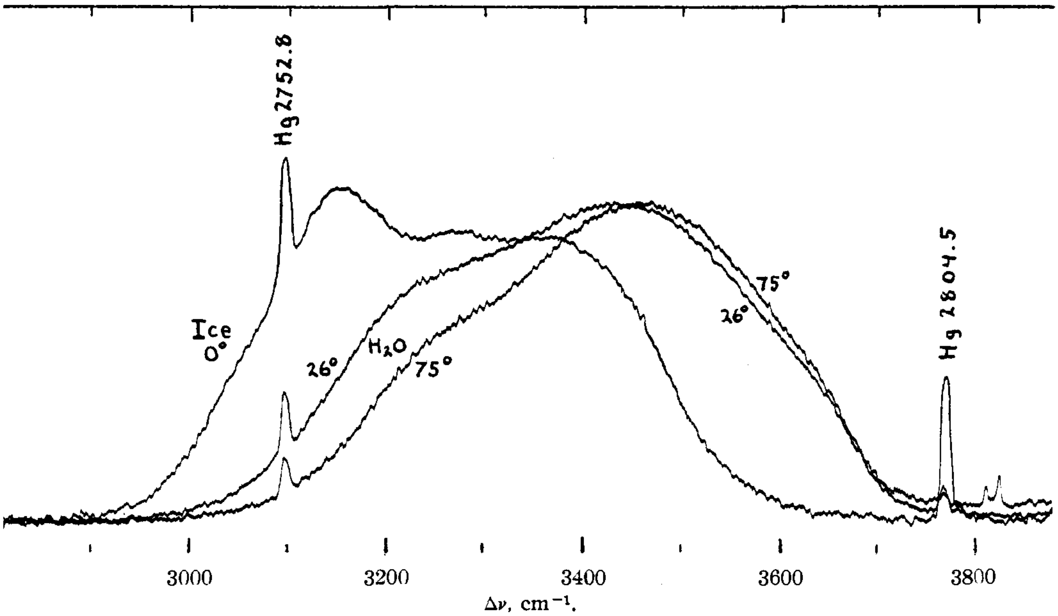

Fig. 4.—Main (ν_π) Raman band of ice at 0° and water at 26 and 75°.

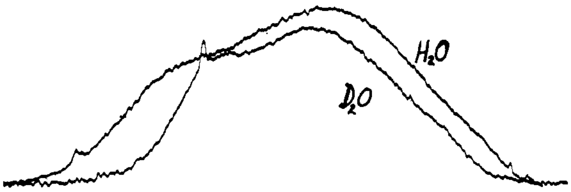

Fig. 5.—Main bands of H_2O and D_2O superimposed for comparison of shapes.

including the maximum, of the main band may be traced in part to temperature differences and in part to differences in the density of the photographic image obtained. The latter effect is illustrated in Fig. 8. Estimates, obtained from Figs. 4 and 8, of the positions of the principal components of the main band are given in Table II (notation from section II, 2).

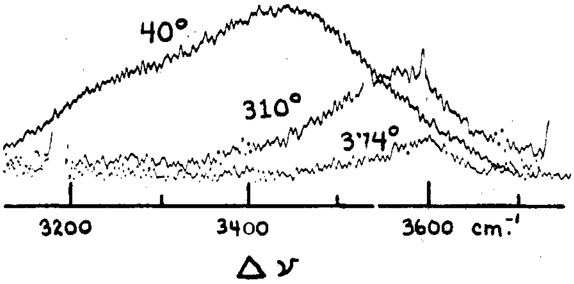

Fig. 6.—Shift in the main Raman band of water between 40° and the critical temperature.

TABLE I

FREQUENCIES OF INTENSITY MAXIMA

Band	Ice, 0°	H_2O, 40°	D_2O, 50°	Ratio ν_{D_2O}/ν_{H_2O}
ν_T	210 ± 2	200[a]	190[a]	0.95
ν_R	. . .	See Text		
ν_δ	. . .	1656 ± 2	1208 ± 2	.73
$\nu_{\delta R}$	. . .	2167 ± 5	1600[a]	.74
ν_π	3156 ± 3	3440 ± 5	2515 ± 5	.73
$\nu_{\pi R}$		4000[a]	2965 ± 5	.74

[a] No definite maximum; frequencies approximate.

II. Interpretation

1. The Hydrogen Bond and Coördination in Water.—The generally accepted theory of the structure of water is that formulated by Bernal and Fowler.[3] According to present views, the relatively open four-coördinated tridymite-like structure of ice is sufficiently broken down in liquid water to permit a closer packing of the water molecules than that in the ice crystal.

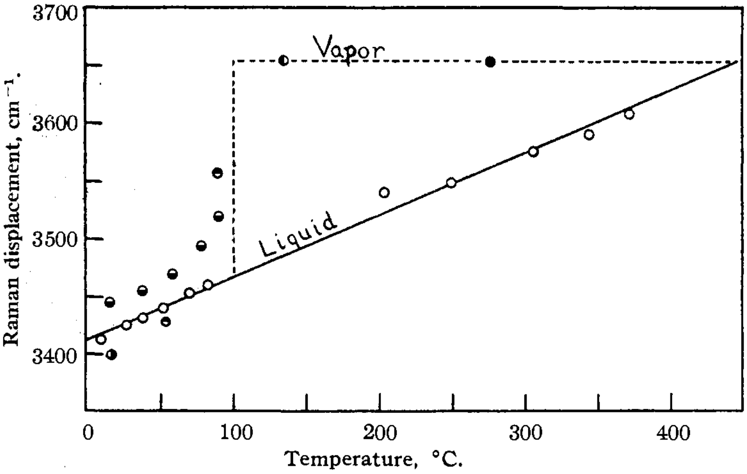

Fig. 7.—Frequency of maximum intensity in the main band (ν_π) as a function of temperature; ○, Authors; ⊖ Specchia; ◓, Meyer; ◑, Magat; ◐, Bender; ●, Johnston.

TABLE II

FREQUENCIES OF MAIN BAND COMPONENTS

Designation of component	Ice, 0°	Water, 40°	D_2O, 50°	Ratio ν_{D_2O}/ν_{H_2O}
$''\nu''_\pi$	3150	3190	2360	0.74
$'\nu''_\pi$	3270	. .	. .	
ν_π'' and $''\nu_\pi$	3390	3440	2515	.73
ν_π	. .	3650	2680	.73

Although little definite information as to the extent of the coördination of liquid water has been published, it is generally implied that, in the range 0 to 100°, a high percentage (50–80%) of the maximum coördination still persists.

The coördination of water may be considered as due to the formation of hydrogen bonds between the oxygens. Pauling[2] has shown that two of the four hydrogens which tetrahedrally surround a four-coördinated oxygen atom are probably bonded to that oxygen in much the same manner as in an isolated water molecule, while the other two hydrogens are at a greater distance from the oxygen and essentially bonded to other oxygen atoms.

The energy of sublimation of ice, plus the knowledge that water is unassociated in the gas phase, permits an estimate of the energy of the hydrogen bond in water as very small, certainly less than about 6 kcal. per mole. This suggests that the intramolecular vibrations of a coördinated water molecule could be represented as perturbed vibrations of the isolated water molecule. The authors are indebted to Professor Linus Pauling for suggesting the simplified procedure for carrying out this treatment as outlined in the following paragraphs.

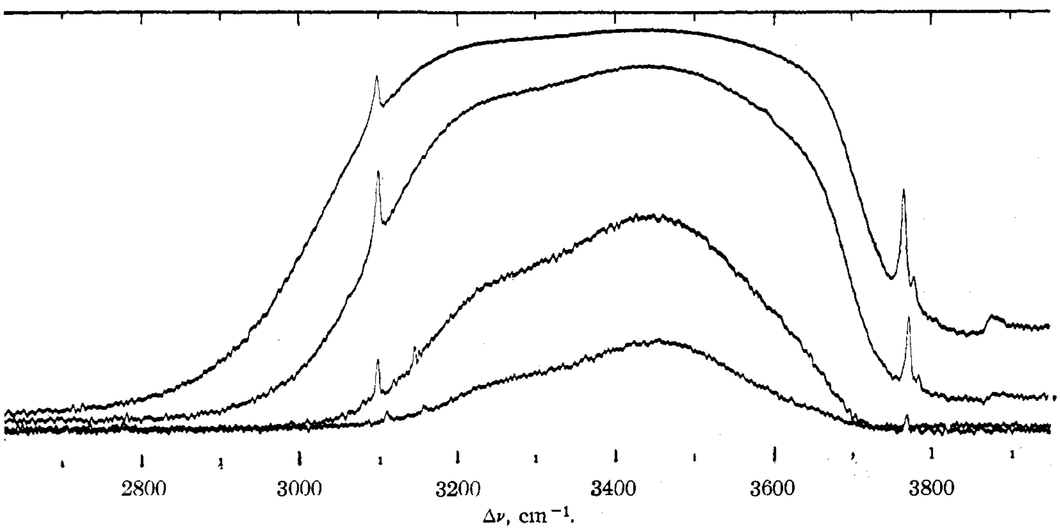

Fig. 8.—The main Raman band of water at 40°, as obtained with different times of exposure.

2. Model of Water Molecule for Perturbation Treatment.—By virtue of the large mass of the oxygen atom relative to the hydrogen atoms and the small value of the cross terms in the "valence force" representation of the potential energy of water, one may use as a satisfactory model for water, as far as the radial frequencies ν_σ and ν_π are concerned, simply two coupled O–H oscillators with a common oxygen atom, and each having a frequency ν_0.

A given water molecule has two possible types of perturbing hydrogen bonds:

I. Hydrogen bonds through the hydrogens of the molecule being considered. One may further assume that hydrogen bonds of this type perturb only the O–H oscillator of which the hydrogen is involved in the hydrogen bond, and that the perturbation is by an amount Δ cm.$^{-1}$, *i. e.*, ν_0 (perturbed) $= \nu_0 - \Delta$.

II. Hydrogen bonds through the hydrogens of molecules other than the one being considered. This type of perturbation may be assumed to affect equally both O–H oscillators by an amount δ cm.$^{-1}$. Furthermore, assuming that the interaction between the hydrogen bonds is negligible, two bonds of type II would shift the frequency of both O–H oscillators by 2δ cm.$^{-1}$. These two types of perturbation may combine to give nine varieties of perturbed water molecules, as shown in Fig. 9. The perturbation type is indicated by P with primes to the right for bonding through hydrogens of the molecule considered, type I, and primes to the left for bonding through hydrogens of neighboring molecules, type II. The secular equations and their solutions are given in equations (1) to (9). These equations are given in two groups, the first group of six including those which, according to our model, represent coupled identical oscillators and hence have symmetric and antisymmetric wave functions. The other three equa-

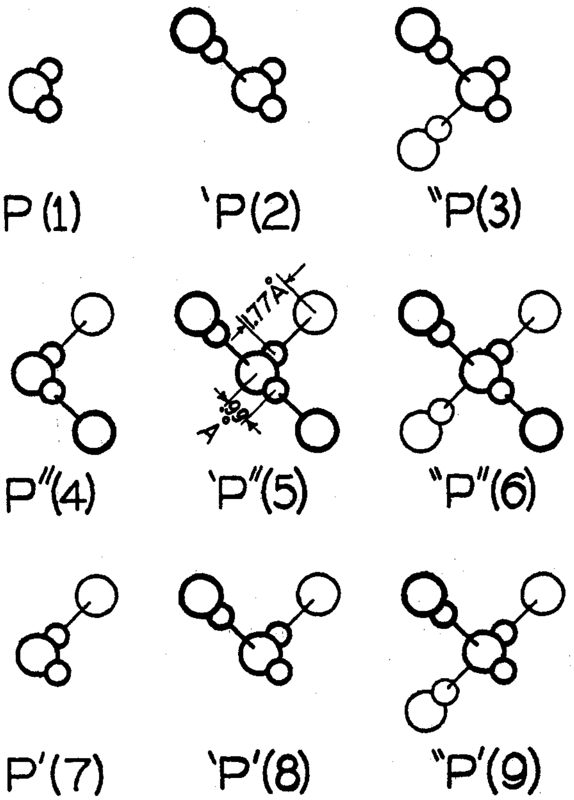

Fig. 9.—Types of coördinated water molecules, with numbers of the corresponding secular equations.

tions are for molecules having non-identical oscillators. Only approximate solutions are given for the latter.

Symmetrically Perturbed Types.—

$$\psi_A = \psi_\sigma = 2^{-1/2}\,\psi_1 - 2^{-1/2}\,\psi_2 \text{ and } \psi_S = \psi_\pi = 2^{-1/2}\,\psi_1 + 2^{-1/2}\,\psi_2$$

(ψ_1 and ψ_2 refer to the wave functions of the respective OH oscillators, ψ_1 and ψ_2 refer to the antisymmetric combination, while ψ_S and ψ_π refer to the symmetric combination. ϵ is the coupling coefficient.)

$$\text{P,}\quad \begin{vmatrix} \nu - \nu_0 & \epsilon \\ \epsilon & \nu - \nu_0 \end{vmatrix} = 0 \tag{1}$$

$$\nu_\sigma = \nu_0 + \epsilon,\ \nu_\pi = \nu_0 - \epsilon$$

$$\text{`P,}\quad \begin{vmatrix} \nu - \nu_0 + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \delta \end{vmatrix} = 0 \tag{2}$$

$$\nu_\sigma = \nu_0 - \delta + \epsilon,\ \nu_\pi = \nu_0 - \delta - \epsilon$$

$$\text{``P,}\quad \begin{vmatrix} \nu - \nu_0 + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + 2\delta \end{vmatrix} = 0 \tag{3}$$

$$\nu_\sigma = \nu_0 - 2\delta + \epsilon,\ \nu_\pi = \nu_0 - 2\delta - \epsilon$$

$$\text{P'',}\quad \begin{vmatrix} \nu - \nu_0 + \Delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta \end{vmatrix} = 0 \tag{4}$$

$$\nu_\sigma = \nu_0 - \Delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - \epsilon$$

$$\text{`P'',}\quad \begin{vmatrix} \nu - \nu_0 + \Delta + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + \delta \end{vmatrix} = 0 \tag{5}$$

$$\nu_\sigma = \nu_0 - \Delta - \delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - \delta - \epsilon$$

$$\text{``P'',}\quad \begin{vmatrix} \nu - \nu_0 + \Delta + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + 2\delta \end{vmatrix} = 0 \tag{6}$$

$$\nu_\sigma = \nu_0 - \Delta - 2\delta + \epsilon,\ \nu_\pi = \nu_0 - \Delta - 2\delta - \epsilon$$

Unsymmetrically Perturbed Types.—

$$\psi_I = \frac{\Delta}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_1 - \frac{\epsilon}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_2 = \frac{\Delta + \epsilon}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_\sigma + \frac{\Delta - \epsilon}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_\pi$$

$$\psi_{II} = \frac{\epsilon}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_1 + \frac{\Delta}{(\Delta^2 + \epsilon^2)^{1/2}}\,\psi_2 = \frac{\epsilon - \Delta}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi_0 + \frac{\epsilon + \Delta}{(2\Delta^2 + 2\epsilon^2)^{1/2}}\,\psi\pi$$

$$\text{P',}\quad \begin{vmatrix} \nu - \nu_0 & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta \end{vmatrix} = 0 \tag{7}$$

$$\nu_I = \nu_0 + \epsilon^2/\Delta,\ \nu_{II} = \nu_0 - \Delta - \epsilon^2/\Delta$$

$$\text{`P'}\quad \begin{vmatrix} \nu - \nu_0 + \delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + \delta \end{vmatrix} = 0 \tag{8}$$

$$\nu_I = \nu_0 - \delta + \epsilon^2/\Delta,\ \nu_{II} = \nu_0 - \Delta - \delta - \epsilon^2/\Delta$$

$$\text{``P',}\quad \begin{vmatrix} \nu - \nu_0 + 2\delta & \epsilon \\ \epsilon & \nu - \nu_0 + \Delta + 2\delta \end{vmatrix} = 0 \tag{9}$$

$$\nu_I = \nu_0 - 2\delta + \epsilon^2/\Delta,\ \nu_{II} = \nu_0 - \Delta - 2\delta - \epsilon^2/\Delta$$

3. Numerical Results.—Before attempting an identification of the component frequencies of the main band in the Raman spectrum of water, one must accept certain views concerning the identification of the unperturbed frequencies in this region.

It is generally admitted that the 3654 cm.$^{-1}$ Raman band of water vapor corresponds to the symmetric or ν_π vibration. This appears to disagree with Mecke's analysis of the infrared spectrum, which suggests that ν_π should have a frequency of about 3600 cm.$^{-1}$.(8) Inasmuch as this treatment gives at best only an approximation to the frequency changes, the absolute values of the frequencies used are not of prime importance. Accordingly, we somewhat arbitrarily select $\nu_\sigma = 3750$ cm.$^{-1}$ and $\nu_\pi = 3650$ cm.$^{-1}$, the observed fundamental frequencies from the infrared and Raman spectra, respectively. This is largely a matter of convenience in that it enables direct comparison of calculated and observed values without any intermediate and uncertain extrapolation to frequencies at infinitesimal amplitude. An additional factor aids in the simplification of the comparison with experimental data, namely, the Raman scattering can be taken as nearly completely due to the excitation of the symmetric vibrations. Thus, in our calculations to follow, the Raman spectrum will be compared to the envelope of the frequencies having wave functions $\psi = a\psi_\pi + b\psi_\sigma$ in which $a \neq 0$. Similarly our results may be compared with infrared measurements on liquid water by considering the frequencies for which $b \neq 0$.(9)

Substituting the above values for ν_σ and ν_π in the equation for the unperturbed molecule gives $\nu_0 = 3700$ cm.$^{-1}$ and $\epsilon = 50$ cm.$^{-1}$. Assuming that the low frequency hump in ice, Fig. 4, is the ν_π vibration of the four-coördinated structure,

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(8) Mecke, *et al.*, *Z. Physik*, **81**, 313, 445, 465 (1933). It is possible that this disagreement is only apparent and that the difference is due to an unanticipated peculiarity in the intensity pattern of the accompanying rotational transitions of the Raman band. However, the authors do not subscribe to the exceedingly simple structure of the Raman band proposed by Rank, Larsen and Bordner [*J. Chem. Phys.*, **2**, 464 (1934)]. A similar explanation is necessary to account for ν^δ occurring at 1648 cm.$^{-1}$ [Johnston and Walker, *Phys. Rev.*, **39**, 535 (1932)] in the Raman effect, whereas Mecke gives 1595 cm.$^{-1}$ as the center of the infrared band. The frequency ν_σ is so weak as to be unobserved in the Raman spectrum unless one assigns it to Rank's band at 3804 cm.$^{-1}$, which is again about 50 cm.$^{-1}$ higher than Mecke gives from the infrared. Bender [*ibid.*, **47**, 252 (1935)], however, points out that the Raman band of D_2O falls approximately where it is expected from Mecke's analysis, and accordingly holds that the discrepancy can hardly be due to a peculiarity in the intensities of the rotational lines in water. Furthermore, Bender measures the band as only about 10 cm.$^{-1}$ wide, which favors its interpretation as being a *Q* branch. If so, the vibrational frequency should be slightly above 3654 cm.$^{-1}$ rather than much below.

(9) This comparison will be exceedingly difficult because liquid water absorbs so strongly that this region appears in infrared measurements as a band nearly a thousand wave numbers wide with only 0.02 mm. of liquid in the light path [Gordy, *J. Chem. Phys.*, **4**, 769 (1936)] and the maximum is probably shifted by an unsymmetrical enhancement of the wings. The shift of the Raman maximum to lower frequencies with increasing exposure, shown in Fig. 8, supports this view that the apparent maximum of the infrared absorption would shift to higher frequencies if measurements were made with still thinner absorbing layers. Infrared absorption in this region may be further complicated by the contributions of $2\nu_\delta$, the first overtone of the bending frequency.

and taking its maximum as 3150 cm.$^{-1}$, one obtains from equation (6)

$$\Delta + 2\delta = 500 \text{ cm.}^{-1} \qquad (10)$$

A study of the envelope produced by various selections of Δ and δ which satisfy equation (10) led to the final choice of Δ = 250 cm.$^{-1}$ and δ = 125 cm.$^{-1}$. This yields the frequency patterns shown in Fig. 10. Strictly speaking, these patterns for the water spectrum are valid only at or near 0°, because the values of Δ and δ change with increasing temperature due to the increasing distance between the oxygen atoms and the corresponding weakening of the perturbation forces. To compare these calculated frequencies with the experimental intensities of scattering at various temperatures, one must make allowances for two variable factors: first, the distribution of the molecules among the various perturbation types; and, second, the shift of the frequencies themselves due to variations of the magnitude of the perturbing forces. These factors lead one to predictions of the nature of the changes in the main band with increasing temperature which are confirmed by the experimental results.

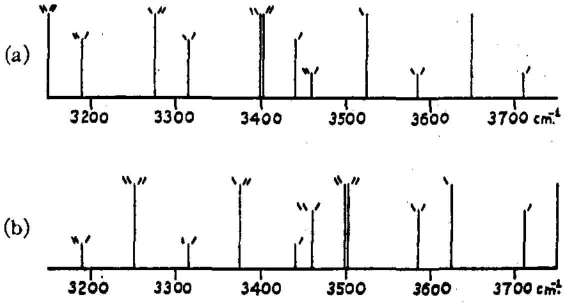

Fig. 10.—Calculated frequency patterns at 0°: (a) strong Raman components. Height of line proportional to a^2 ($\psi = a\psi_\pi + b\psi_\sigma$). (b) Strong infrared components. Height of line proportional to b^2 ($\psi = a\psi_\pi + b\psi_\sigma$).

Consider first the spectrum of ice. As expected, an intense maximum occurs at 3150 cm.$^{-1}$, due to four-coördinated water molecules. However, our picture shows maxima of unexpectedly high intensity at 3270 and 3390 cm.$^{-1}$, which should be assigned to three-coördinated and two-coördinated structures, respectively (see Table II).

If our interpretation is correct, this means that in ice which has been stored under conditions which permit slow melting, several per cent. of the molecules do not show the maximum coördination. Our experiment on ice is not conclusive since the ice was melting rapidly during the exposure, but we interpret the weakness of the scattering near 3600 cm.$^{-1}$ as an indication of relatively little contribution from water. Sutherland's[10] results on ice at −183° are in excellent accord with the idea that there is practically complete four-coördination at that temperature, giving a very sharp maximum at 3090 cm.$^{-1}$, 60 cm.$^{-1}$ below the corresponding maximum of our spectrum at 0° due to the temperature shift of the component "ν_π", which we estimate as about 3150 cm.$^{-1}$. More experiments on ice at and below 0° are very desirable before any definite statements regarding the deviation from complete four-coördination can be made. Our evidence is that hydrogen bonds are being broken before ice melts, and that it is probable that two-coördinated structures are slightly favored over three-coördinated structures,[11] an observation made necessary by the high intensity of the 3390 cm.$^{-1}$ component relative to the 3270 cm.$^{-1}$ component. The latter statement is, of course, based upon the assumption that the perturbations have no appreciable effect upon the intensity of Raman scattering.

When considering the main band of water at 26°, we have to permit a shift of the frequency pattern of Fig. 10 toward 3650 cm.$^{-1}$ by roughly 10% of the difference between 3650 and each component frequency. This gives the four-coördinated maximum at 3200 cm.$^{-1}$ to account for the hump observed at 3190 cm.$^{-1}$. The double frequency corresponding to the two types of symmetrical two-coördination would occur at 3425 cm.$^{-1}$ and account chiefly for the intense maximum of the Raman band at 3440 cm.$^{-1}$. Also, the slight indication of a high frequency component can be attributed to some free water molecules. We make no effort to observe regions specifically assigned to the unsymmetrically perturbed types because their number and lower intensity probably result in their contribution being more or less like a continuous background. The distribution of the molecules among the various perturbation structures has changed so that two-coördination is dominant. It appears from the Raman band intensities that water at 26° averages slightly more than two hydrogen bonds per molecule. Continuing the above considerations

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[10] Sutherland, *Proc. Roy. Soc.* (London), **A141**, 535 (1933).

[11] This result may be expected because the entropy of the two-coördinated structures will be considerably larger than that of the three-coördinated structures on account of the low-frequency pendulum-like oscillation which is introduced on forming the former from the latter.

to higher temperatures one can nicely account for all the features of the observed spectrum. We thus agree with Rao[12] that there are three components of the band (our "ν_π", ν_π" and "ν_π together, and ν_π) which are observable above the background, but we admit many other indistinguishable components, and we consider the component frequencies as well as their intensities to shift with temperature. Needless to say, the considerations upon which our treatment is based attach little or no significance to the existence of definite polymolecular structures such as $(H_2O)_2$, $(H_2O)_3$, etc., so frequently postulated to account for the components of the main band in liquid water.

The measurements near the critical temperature probably represent scattering predominantly due to single water molecules. The slight shift from 3650 may be accounted for by some coördination, or it may be due to factors which we have neglected, especially since these experiments were made at such high pressures (> 200 atmospheres).

The structure of the main band of heavy water readily may be seen to conform to the same interpretation as that of ordinary water. All the frequencies are roughly in the ratio of $2^{-1/2}$/ to those of ordinary water, and the band is correspondingly narrower, as clearly evidenced by Fig. 5. The relatively greater intensity of the "ν_π" component in liquid D_2O, indicating relatively more four-coördination as compared with H_2O, is in conformity with other properties indicating higher coördination, *e. g.*, the higher temperature of maximum density, the sharper maxima in x-ray scattering, and the fact that the relative magnetic susceptibility of D_2O liquid/D_2O solid is less than that of H_2O liquid/H_2O solid.

III. Representation of the Perturbation Forces

In the preceding paragraphs perturbations have been invoked to obtain the effective displacements of the vibration frequencies of the water molecule necessary to explain the observed Raman spectrum. In this section it is proposed to give briefly some empirical calculations designed to represent semiquantitatively the perturbation forces. The results will be used later in the discussion of the low frequency bands of liquid water and heavy water.

The simplest function which gives a fair representation of the forces and energies accompanying bond formation as a function of the nuclear separation, r, of the atoms forming the bond is the well-known Morse function

$$V = D(1 - e^{a(r_0 - r)})^2 - D \qquad (11)$$

where D is the dissociation energy of the bond, r_0 the equilibrium separation of the nuclei, and a is a constant related to the vibration frequency of the bond. ($2Da^2 = 4\pi^2c^2\mu\nu^2 = k$, the force constant in the harmonic approximation to the vibration.) Assuming the uncoupled O–H oscillator of the preceding section to have a dissociation energy of one-half that of the water molecule, an equilibrium nuclear separation the same as the O–H separation in the normal state of the water molecule, and a vibration frequency of 3700 cm.$^{-1}$, one obtains the Morse function

$$V_{\text{O—H}} = 110(1 - e^{2.23(0.97 - r)})^2 - 110 \qquad \text{(kcal. per mole)} \quad (12)$$

Since the "hydrogen bond" is also formed between hydrogen and oxygen atoms, it may further be assumed that its energy is represented by a function of the type

$$V_{\text{H---O}} = \beta V_{\text{O-H}} = 110\beta(1 - e^{2.23(0.97 - r)})^2 - 110\beta \quad (13)$$

with β to be determined from some experimentally measured property of the bond. Selecting as that experimental property the perturbation of the vibration frequency, Δ, due to hydrogen bonding through the hydrogen of the oscillator being considered, β may be determined as a function of the distance between the oxygens.

Combining the two functions represented by equations (12) and (13) to represent the energy of the hydrogen in the hydrogen bond O—H---O as a function of the distance r from the oxygen to which the hydrogen is chemically bonded, and taking the O–O separation, $d_0 = 2.76$ Å. at 0°, one obtains

$$\begin{aligned} V_{\text{O—H---O}} &= -2De^{a(r_0 - r)} + De^{2a(r_0 - r)} \\ &\quad -2\beta De^{a(r_0 - d_0 + r)} + \beta De^{2a(r_0 - d_0 + r)} \qquad (14) \\ &= -1910e^{-2.23r} + 8320e^{-4.46r} \\ &\quad - 4.06\beta e^{2.23r} + 0.0375\beta e^{4.46r} \end{aligned}$$

Expanding this function in the vicinity of $r = r_0$ one may determine r'_0, the perturbed O–H distance at equilibrium, and β by the restrictions that the linear term must vanish at r'_0, and the quadratic term must give the proper force constant $k = 4\pi^2c^2\mu(\nu_0 - \Delta)^2$. The results are $\beta = 0.25$ and $r'_0 = 0.98_6$ Å.

IV. Calculation of the Intermolecular Frequencies and Other Properties

The potential function $V_{\text{O—H—O}}$ of equation (14), with the value of $\beta = 0.25$ just determined,

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[12] Rao, *Proc. Roy. Soc.* (London), **145**, 489 (1934).

may be used to calculate various other properties of the hydrogen bond. It must be understood that the use of such simple representations of the inherently complicated interactions of chemical bond formation can at best lead to results that are only qualitative.

1. The Shift of the Component Frequencies in the Main Band with Temperature.—The shift of the frequencies contributing to the main band may readily be determined as a function of d_0, the O–O separation, with the assumption that $\Delta = 2\delta$. Thus, from the density of ice, d_0 = 2.76 Å. at 0° and 2.735 Å. at −183°, and we may estimate the frequency of the main component of ice ("ν_π") to shift toward lower frequencies by 30 cm.$^{-1}$ on cooling from 0 to −183°. This is in satisfactory agreement with the observed shift of 60 cm.$^{-1}$, from the frequency of maximum intensity of ice at 0°, 3150 cm.$^{-1}$, to Sutherland's value of 3090 cm.$^{-1}$ at −183°. Our value at 0° is undoubtedly high due to the overlapping of components of higher frequency, causing the maximum to shift upward from the true value of "ν_π".

Determinations of the observed frequency shifts with temperature in the liquid state are very difficult because no one perturbation type predominates, as in ice, and because the changing distribution of types masks the effect of frequency shift. The large shift which we postulated in order to account for the observed main band of water at 26° (*e. g.*, Δ "ν_π" = 50 cm.$^{-1}$) indicates either that there is an abrupt increase of the O–O distance in the coördinated bond on melting or, more likely, that our function represents too small a change in frequency with O–O separation. The qualitative facts, both theoretical and experimental, are that the components of the main band are all shifted toward higher frequencies with increasing temperature (excepting the unperturbed ν_π, which, to our approximation, remains constant).

2. The Frequency of "Hindered Rotation."—As we pointed out in discussing the experimental results, the region from 320 to 1020 cm.$^{-1}$ represents an appearance of continuous scattering, and measurements of the "maximum" have little significance. Its structure is even more complicated than that of the main band, since most of the nine types of perturbed molecules have ratios of restoring force/moment of inertia which vary with the axis of rotation. The absence of any sufficiently strong components to be evident above the continuous background renders impractical any attempt to treat this band in the same manner in which the main band was treated.

Only one type of associated molecule, P″, lends itself to a convenient calculation of the frequency of hindered rotation from our potential function. In this case, bonds of type II (through hydrogens of neighboring molecules) are absent and no uncertain estimate of their directive forces is necessary. Justifiable approximations which simplify the calculation of the hindered rotation frequency of P″ molecules due to the hydrogen bonding of type I are:

(a) The center of rotation is taken at the oxygen atom.

(b) The O–H chemical bond is considered rigid, $r'_0 = 0.99$ Å.

(c) The force acting on the hydrogen is obtained from the linear term of the potential function $V_{\mathrm{H---O}}$, which represents the energy of the hydrogen as a function of the distance from the oxygen of the neighboring hydrogen-bonded water molecule.

$$V'_{\mathrm{H---O}}\,(r'_0) = 2a\beta D[-e^{a(r_0 - d_0 + r_0')} + e^{2a(r_0 - d_0 + r'_0)}] \quad (15)$$

(d) The force restoring the rotated O–H bond to its equilibrium orientation is the component of the above force along the tangent to the arc of motion of the hydrogen atom.

(e) The force constant, $k = 4\pi^2c^2\mu\nu^2$, for the calculation of the frequency (in cm.$^{-1}$) is obtained from the quadratic term of the expansion of the integral of the restoring force as a function of the displacement of the hydrogen atom along the arc of motion. μ may be taken as the mass of the hydrogen atom.

(f) The frequency of hindered rotation of the P″ molecule is independent of the axis of rotation and is equal to the frequency of oscillation of a single hydrogen-bonded hydrogen perpendicular to the line joining the oxygens. This holds for our approximation because the forces on the hydrogens act from points on the extended equilibrium bond directions.

From these considerations the frequency of hindered rotation, for infinitesimal amplitude, becomes

$$\nu = (2\pi c)^{-1}\,(1.56\,V'_{\mathrm{H---O}}\,(r_0')/r_0'\mu)^{1/2} \sim 570 \text{ cm.}^{-1} \quad (16)$$

This falls very nearly in the center of the region described as due to "hindered rotation." If the potential function represents these restoring forces accurately, this result requires that the type II bonds do exert an appreciable directive action in order to account for the existence of scattering up to *ca.* 1020 cm.$^{-1}$. Others have postulated a combination frequency of hindered rotation and hindered translation (see following paragraph) to account for scattering around 700 cm.$^{-1}$, but we consider this unnecessary. Our view is supported by the fact that the upper limits of scattering for D_2O and H_2O are in approximately the ratio of $730/1020 = 0.715 \sim 2^{-1/2}$, whereas a combination of hindered rotation and hindered translation would have an upper limit with a ratio considerably greater than $2^{-1/2}$ (due to the larger ratio of the hindered translation frequencies of D_2O and H_2O $(20/18)^{-1/2}$). Our results indicate that the "hindered rotation" frequency of water molecules in the ice crystal should be of the order of 700 to 900 cm.$^{-1}$, considerably higher than that calculated by Bernal and Tamm.[13] Hibben's recent article[6] indicates that the scattering of ice in this region shows a considerable drop in intensity from that of water on the low frequency side, while the intensity of the high frequency side is enhanced. It is likely that the maximum of the entire region is not far from the component due to P″ type molecules, while the band variously reported to exist between 700 and 800 cm.$^{-1}$, and noticeable as a component near 800 cm.$^{-1}$ on Hibben's microphotometer record for ice, may be due to the contribution of the "P" type molecules.

3. **The Frequency of Hindered Translation.**—It has recently been suggested that much of the low frequency scattering of liquids is due to hindered translational oscillations rather than to rotational scattering.[14] In the case of water, it is quite certain that hindered translation is largely responsible for the observed scattering near 200 cm.$^{-1}$. This scattering is the water analog of the ice line at 210 cm.$^{-1}$. Here again we see the possibility of a very complex structure in the actual scattering spectrum. However, at this low frequency range, the absolute separation of the components with large relative separation may be too small to be noticeable under ordinary dispersion, hence the apparent sharpness of the ice line in spite of our previous conclusion that there were appreciable amounts of three- and two-coördinated molecules present during the time of our exposure.

The frequency of oscillation of a water molecule about its equilibrium position in the ice lattice may be estimated by an empirical treatment similar to that used in the previous calculations. Here again some assumptions are necessary to give reasonably simple equations.

(a) The O–H chemical bond is considered rigid, $r'_0 = 0.99$ Å.

(b) The energy of the hydrogen bond as a function of the O–O distance, d, is represented by the potential function

$$V_{\text{O---O}} = -55e^{2.23(1.96-d)} + 27.5e^{4.46(1.96-d)} -2\gamma Ee^{b(s_0-d)} + \gamma Ee^{2b(s_0-d)} \qquad (17)$$

where the first two terms are from the function $V_{\text{H---O}}$ of section III as a function of d, with $\beta = {}^1/_4$, and the last two terms represent an O–O Morse function with an arbitary coefficient γ, to be determined from the equilibrium position $d_0 =$ 2.76 Å. (at 0°). A closer examination of the last two terms in Equation (17) reveals that in the vicinity of $d_0 = 2.76$ Å., d is so large relative to $s_0 \sim 1.32$ Å.[15] that the final term may be ignored and the O–O repulsion represented by $-2\gamma\cdot Ee^{bs_0}\cdot e^{-bd}$. Furthermore, since γ is an arbitrary multiplier, $-2\gamma Ee^{bs_0}$ may be set equal to an arbitrary multiplier γ', and the Morse function representation of the oxygen–oxygen repulsion reduces, for our purpose, to the simple exponential form, $\gamma e'^{-bd}$, giving

$$V_{\text{O---O}}(d) = -4351e^{-2.23d} + 172100e^{-4.46d} + \gamma' e^{-bd} \qquad (18)$$

$$V_{\text{O---O}}(d_0) = -8.47 + \gamma' e^{-bd_0} = -D_{\text{OHO}} \quad \text{(kcal. per mole)} \qquad (19)$$

$$V'_{\text{O-- O}}(d) = 9703e^{-2.23d} - 767600e^{-4.46d} - b\gamma' e^{-bd} \qquad (20)$$

$$V'_{\text{O---O}}(d_0) = 17.1 - b\gamma' e^{-bd} \qquad (21)$$

$$V''_{\text{O---O}}(d) = -21640e^{-2.23d} + 3424000e^{-4.46d} + b^2\gamma' e^{-bd} \qquad (22)$$

$$V''_{\text{O---O}}(d_0) = -30.5 + b^2\gamma' e^{-bd_0} = k_{\text{OO}} \quad \text{(kcal. per mole per Å.}^2\text{)} \qquad (23)$$

D_{OHO} is the dissociation energy of the hydrogen bond and k_{OO} is the force constant for the harmonic approximation to the vibration frequency of the hydrogen-bonded water molecules against each other. Various estimates of b are given below.

(c) Since definite information is lacking as to the type of vibrational motion concerned in the Raman excitation of the 210 cm.$^{-1}$ frequency of ice, the following calculations are made for two different assumed modes of vibration which are intended to represent approximate extremes of frequencies magnitude as far as Raman excitation is concerned, type II appearing more likely than type I.

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(13) Bernal and Tamm, *Nature*, **135**, 229 (1935).

(14) Gross and Vuks, *J. phys. radium*, **7**, 113 (1936).

(15) Pauling and Huggins, *Z. Krist.*, **A87**, 205 (1934).

I. The four-coördinated water molecule is vibrating about its equilibrium position against the remainder of the crystal, considered rigid and of infinite mass. In this case the effective force constant can be shown to be approximately twice that of the hydrogen bond, k. Thus

$$2k = 4\pi^2C^2\mu\nu^2 = 1.054\nu^2 \tag{24}$$

where μ is the mass of the water molecule.

II. Two four-coördinated molecules are vibrating against each other along the direction of their common hydrogen bond, each being restrained also by its remaining three hydrogen bonds to the remainder of the crystal, considered rigid and of infinite mass. In this case, it can be shown that

$$3k = 4\pi^2c^2\mu\nu^2 = 1.054\nu^2 \tag{25}$$

From eq. (21) and the criterion of equilibrium, $V'_{\text{O---O}}(d_0) = 0$, one obtains

$$b\gamma' e^{-bd_0} = 17.1 \tag{26}$$

Hence, from eq. (19)

$$D_{\text{OHO}} = 8.47 - \gamma' e^{-bd_0} = 8.47 - 17.1/b \tag{27}$$

and from eq. (23)

$$k_{\text{OO}} = -30.5 + b^2\gamma' e^{-bd_0} = -30.5 + 17.1\ b \tag{28}$$

(k, the force constant of the hydrogen bond, in the usual units of dynes per cm., is equal to 0.69 k_{oo}).

The O–O Morse function was estimated by various means with resulting b values ranging from 2.5 to 3.0. The extreme values give, respectively, the limits 125 and 165 cm.$^{-1}$ for the frequency of vibration of the water molecule against the remainder of the crystal, type I, and the limits 155 and 200 cm.$^{-1}$ for the mutual vibration of two water molecules, type II. The corresponding dissociation energies of the hydrogen bond are 1.6 kcal. per mole for $b = 2.5$ and 2.8 kcal. per mole for $b = 3.0$. While all these values are of the proper order of magnitude to leave little doubt as to the correctness of the present interpretations of the nature of the low frequency Raman scattering of ice and water, they are definitely low, suggesting that a better representation of the oxygen–oxygen repulsion might be obtained by the use of larger b values.

4. The Energy of Dissociation of the Hydrogen Bond.—By using the experimental data to fit both the linear and quadratic term of the potential function $V_{\text{O---O}}$ a somewhat better approximation to the energy of dissociation of the hydrogen bond should be obtained. The values of b corresponding to vibrations of types I and II are 3.75 and 3.1, respectively. The corresponding limits of the dissociation energy of the hydrogen bond are 3.9 and 3.0 kcal. per mole. Since Raman excitation of the type II motion appears more plausible we favor the latter value. These values are in the range one expects from the comparison of the heat of sublimation of ice with those of the similar solids SO_2 and H_2S. Assuming intermolecular bond formation in the latter two to be negligible compared to that in H_2O, one finds that about half the energy of sublimation of ice is probably due to interactions other than those of hydrogen bond formation, giving approximately 3 kcal. per mole per hydrogen bond broken. Of course, in our calculation the hydrogen bond has been so represented as to imply that it was the only factor responsible for interaction of the molecules, and we should accordingly compare the calculated value of about 3 kcal. per mole per bond to the observed value of 5.9 kcal. per mole per bond. On the other hand, liquids in which the hydrogen bond is absent show very small perturbations of the intramolecular frequencies in the liquid state. Hence it may be significant that the calculated value, based primarily on the perturbation of the molecular vibrations by hydrogen bond formation, comes out with the proper order of magnitude to represent the energy of the hydrogen bond exclusive of the factors which contribute to intermolecular energy in systems where bond formation is of minor importance.

5. Perturbation of ν_δ by Hydrogen Bond Formation.—For the purpose of studying the perturbations of the symmetrical bending frequency, ν_δ, of the water molecule, a sufficiently accurate dynamical model is obtained by considering a harmonic oscillator with a force constant

$$2k/r^2 = 4\pi^2c^2\mu\nu_\delta^2 \tag{29}$$

where $(^1/_2)k(\Delta\phi)^2$ gives the potential energy as a function of the valence angle, ϕ, and μ is the mass of a hydrogen atom. Using again the observed frequency in preference to the extrapolated frequency at infinitesimal amplitude, and ignoring the deviation of water angle from the tetrahedral angle, one obtains

$$2k/r^2 = 0.0585(1595)^2 = 1.49 \cdot 10^5 \tag{30}$$

As in the case of hindered rotation, we can most conveniently calculate the perturbation of the P″ type of coördinated molecule, in which case the above restoring force is reduced by the ratio $(0.97/0.99)^2$ because of the stretching of the chemical O–H bond by the formation of the hydrogen bond H---O, and augmented by the amount 1.56 $V'_{\mathrm{H---O}}(r_0')/r'_0 = 0.186 \times 10^5$ (eq. 16), giving

$$4\pi^2c^2\mu(\nu''_\delta)^2 = 1.62 \times 10^5, \ \nu''_\delta = 1665 \text{ cm.}^{-1} \quad (31)$$

This value of ν''_δ, which is shifted toward higher frequencies from ν_δ by 70 cm.$^{-1}$, is in agreement with the maximum of the observed Raman band of water at 1656 cm.$^{-1}$, thus falling at about the same relative position in this band as did the ν''_R and ν''_π components in their respective bands. Hibben's curve for ice shows the maximum of this band to be shifted to still higher frequencies due to the presence of relatively more four-coördinated molecules. The calculation of the perturbed ν''_δ at a *higher* frequency than the unperturbed ν_δ is a striking confirmation of the essential correctness of the entire treatment.

6. **Combination Frequencies.**—The only feature of the Raman spectrum of water below 3700 cm.$^{-1}$ which remains to be accounted for is the band with a maximum at 2170 cm.$^{-1}$. This has usually been designated as a combination of ν_δ and ν_R the frequency of hindered rotation, a designation with which we agree. In fact, there is no other obvious way to account for this band. It is much wider than the ν_δ band, indicating the plausibility of the very wide ν_R being involved in its assignment. The frequency of maximum intensity is considerably less than the sum of the maxima of ν_δ and ν_R (1656 + 610 = 2266), but this is exactly what one might expect from the combination of two frequencies having such large amplitudes, especially in view of the very low maximum in the potential energy function which "hinders" the rotation of the water molecule. The harmonic approximation to the potential energy is naturally poor under these conditions and the interaction terms may well be very large. This same factor no doubt contributes to the unusual intensity of this band, considered as a combination frequency, for the usual treatment which predicts low intensity for combination and overtone frequencies is strictly applicable to only harmonic or nearly harmonic oscillations.[16]

Various bands have been reported at frequencies greater than 3700 cm.$^{-1}$. Some of the confusion which exists in the location of these high frequencies is probably due to the same factors we cited to account for the apparent disagreements at lower frequencies. Bands of frequency higher than the main band should be overtones or combinations of the frequencies we have already described.

V. Concluding Remarks

The calculations using modified Morse functions are subjected to many approximations which required the resulting deductions to appear in classical rather than quantum mechanical form.[17] Attention might be called to the fact that the oxygens are oscillating over relatively large amplitude. Even for $n_O = 0$[17] the classical amplitude of the O–O oscillation would permit the oxygen–oxygen separation to vary over a range of more than ±0.1 Å. from the mean value of 2.76 Å. This is undoubtedly important to remember when interpreting X-ray diffraction curves such as those of Katzoff.[4] The maximum of the density distribution curve for liquid water at 2.9 Å. is interpreted by the authors to represent the scattering due to oscillating hydrogen-bonded water molecules plus that due to the "contacting" non-bonded water molecules. Even if close-packed water molecules were separated by more than 3 Å., X-ray measurements would still be unable to resolve their contribution from that of the coördinated structures. Thus Katzoff's maximum at 2.9 Å. may indicate that the close-packed structure in liquid water has a mean water molecule separation of over 3 Å., or at least considerably greater than the mean separation of the hydrogen-bonded oxygens. A similar explanation holds for the second maximum of Katzoff's density–distribution curve. The near-doubling at 3.9–4.5 A. in the distribution at 3° may possibly be due to the fact that molecules oscillating through large amplitudes (with high quantum numbers) tend to spend most of their time near the extremums. (Vibrations which most affect the separations of non-bonded or non-contacting water molecules would have very low frequency and hence appear with high quantum

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[16] Our calculations of the hindered rotation frequency are also subject to this same poor approximation, but the order of magnitude is, of course, unaffected.

[17] To call attention to one of these in particular, consider the variation of the frequency of the components in the main band with temperature. A better approximation than the one we used would be obtained by considering the O—H—O linear oscillator which would have two internal degrees of freedom with energy levels specified by two quantum numbers, n_H and n_O corresponding roughly to the modes of vibration $\cdot \leftarrow \quad \cdot$ and $\leftarrow \quad \leftarrow \quad \rightarrow$, respectively. Our treatment attempted to determine the effect upon the observed transition $n_H = 0 \longrightarrow 1$ of allowing n_O to have different distributions through $n_0 = 0, 1, 2, \ldots$ etc. Thus each of the many components we give for the main band of water is split into subcomponents depending upon n_0 and the classical calculation of the shift of the maximum with temperature must necessarily be only a rough approximation.

numbers, even at 0°.) Katzoff's results, as well as ours, indicate that relatively small changes in the structure of water take place in the range 0–100°.

Estimates of the number of hydrogen bonds broken by fusion cannot very well be made from the latent heat of fusion. Holding the water molecules in a tetrahedral lattice necessarily involves some strain energy since the hydrogens in free water molecules tend to orient at less than the tetrahedral angle. This strain energy may be estimated as not over 300 cal. per mole. However, the breaking of only a small percentage of the hydrogen bonds appears to cause a collapse of the tridymite structure, and may relieve practically all the strain. This would cancel much of the energy effects of dissociating the first few bonds. Exclusive of the many other factors which influence energy of fusion, the effects of strain indicate that the coördination of water at 0° is less than that indicated by the heat of fusion. New experiments on ice and water just below and above 0° should yield interesting information concerning the role of the hydrogen bond in the fusion process.

An empirical treatment with Morse functions would appear from our results to be superior numerically to any straightforward theoretical treatment so far applicable to such complex systems. The approximate agreements which were obtained with experimental values in the empirical calculations presented here are interpreted by the authors as a tribute to the usefulness of the Morse function in representing interactions of atomic and molecular systems for which straightforward theoretical procedures are hopelessly cumbersome.

The general acceptance of the structure of water upon which this treatment of the Raman spectrum of water was based seems now to be assured. The success of our attempts to explain the complex experimental data here presented and analyzed can be taken not only as a new confirmation of prevailing ideas, but also as a satisfactory application of a new method of studying quantitatively the effects of hydrogen bond formation and association in liquids.

The authors wish to acknowledge their indebtedness to Professor Linus Pauling for helpful discussion of the material presented.

Summary

The Raman spectrum of liquid water over a wide range of temperatures, of ice at 0°, and of deuterium oxide were measured with high dispersion. Excitation was almost exclusively due to the 2537 Å. line of the mercury argon discharge lamp and the spectra are presented in the form of microphotometer records.

The results are discussed on the basis of the prevailing notion of a broken-down ice structure for liquid water. The perturbations of the radial vibration frequencies of the nine types of coördinated water molecules possible in such a structure are calculated from two experimentally determined constants: Δ, the perturbation of an OH oscillator due to hydrogen bonding through its hydrogen to another oxygen, and δ, the perturbation of the OH oscillator due to hydrogen bonding through its oxygen to the hydrogen of another oscillator. The resulting frequency patterns satisfactorily explain the structure and variations with temperature of the main band of ice and water.

Semi-quantitative estimates are made of the relative amounts of the different coördination types of water molecules. Water appears to average slightly more than two-coördinated in the range 25 to 90°, and is slightly less coördinated than is deuterium oxide. The two-coördinated structures predominate in both liquids. In ice at 0° the four-coördinated structure predominates but appreciable amounts of the three- and two-coördinated molecules were found to be present.

An empirical treatment of the perturbing potentials in terms of Morse functions gives the means of estimating the intermolecular frequencies. The results confirm already existing identifications for the "hindered translation" and "hindered rotation" frequencies. It is not necessary to postulate a combination of the two to account for all the data. The "hindered translation" was measured in ice as a sharp band with maximum at 210 cm.$^{-1}$. The bending frequency of water is shown to be shifted toward higher frequencies by the perturbations of the coördinated structures, in agreement with the observed Raman band.

The assignment of the band with maximum at 2170 cm.$^{-1}$ as a combination of the bending frequency with the hindered rotation frequency is discussed and accepted.

This analysis covers all the major features of the liquid water Raman spectrum and is confirmed both qualitatively and quantitatively by the

Raman spectrum of liquid heavy water and of ice.

The empirical treatment of the perturbing potentials as modified Morse functions leads to an estimate of the energy of the hydrogen bond in water as about 3 kcal. per mole per bond.

The essential agreement of the results of this analysis with X-ray data on liquid water is discussed and the usefulness of Raman spectra as tools for further studies of associated liquids is suggested.

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NOTES

The Molecular Structures of the 2,3-Epoxybutanes: a Correction

By L. O. Brockway and Paul C. Cross

In the recently published report of the electron diffraction investigation of the 2,3-epoxybutanes[1] it was incorrectly stated that the identification of the geometric isomers was the same as that found in the chemical[2] investigation. Because of this misapprehension the electron diffraction investigation has been repeated and extended, and the consideration of new molecular models has led to the assignment supported by the chemical investigation.

The original preparations were refractionated and samples were taken having the boiling point ranges, 52.9–53.7 and 59.3–59.9°, respectively, at 746 mm. For each substance the new electron diffraction photographs have a lighter background, the diffraction pattern is more distinct and measurements of the ring diameters are more reliable than on the earlier photographs. The same characteristic features appear as before, however; and although the photographs of the two substances again look very much alike, the chief distinguishing feature is still observed, *i. e.*, photographs of the low boiling modification show a well-defined shoulder on the inside of the second strong maximum near $s = 10$ (see Fig. 1, reference 1).

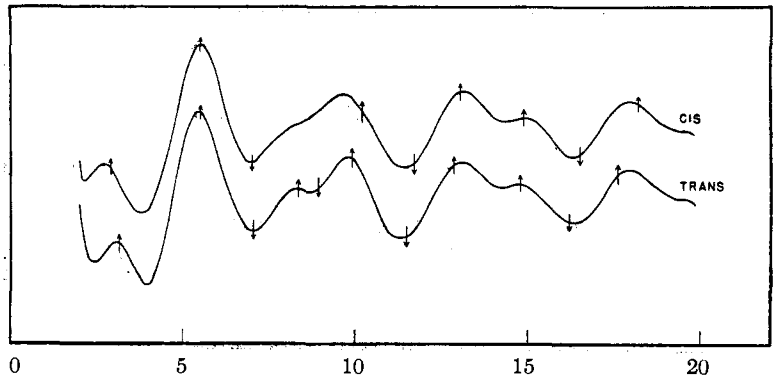

Fig. 1.—Theoretical electron scattering curves for models of the *cis* and *trans* 2,3-epoxybutanes in which five bond angles on each of the central carbon atoms divide equally the strain due to the formation of the three membered ring. The arrows represent maxima and minima observed on the photographs.

In the models previously considered it was assumed that the strain introduced in the bond angles on each of the central carbon atoms by the formation of the three-membered ring was distributed only among the angles involving the carbon–oxygen bond. Of the six angles between the four bonds the angle in the ring is 57°26′, the other two strained angles are 125°10′, and the three remaining angles have the value 109°28′. It seems probable that the strain is more widely distributed; and accordingly new curves have been calculated on the basis of models in which the strain of the small angle is divided among four other angles and also on models in which all five of the other angles divide the strain. These curves are very similar, and the pair corresponding to a small angle of 57°26′ and five equal angles of 117°20′ is reproduced in Fig. 1. It will be observed that the inner

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(1) L. O. Brockway and Paul C. Cross, This Journal, **58**, 2407 (1936).

(2) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).