THE DIELECTRIC CONSTANTS OF HYDROGEN-BONDED SUBSTANCES[1]

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Evidence is presented to show that the abnormally high values for the dielectric constant of many hydrogen-bonded substances are probably due to the "atomic polarization" of the proton in the bond. A mechanism is suggested for the orientation of the dipoles in ice which depends upon the jumping of protons over the potential barrier in the hydrogen bond and not upon the rotation of the water molecules. The calculated activation energy for the process is in agreement with the experimental values obtained by Wentsch.

My discussion will be confined largely to two subjects: (*1*) the general effect upon the dielectric constant of small "atomic polarizations" due to proton displacements and (*2*) a mechanism for the orientation of the dipoles in ice which does not require a rotation of the molecules.

As an introduction, a brief review will be given of the status of the general problem of the dielectric properties of liquids. The Clausius–Mosotti equation, relating the dielectric constant and the distortion polarization, and the extension by Debye (1) to include the effect of permanent dipole account most satisfactorily for the behavior of gases and dilute solutions of polar molecules in non-polar solvents:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu}{3kT}\right) \qquad (1)$$

where ϵ is the dielectric constant, α the distortion polarization, N the number of molecules per cubic centimeter, and μ the permanent moment. Its application to liquids fails for the same general reason that the perfect gas law cannot be used to calculate pressure–volume relations in liquids. The problem of relating the dielectric constant of a liquid to the properties of the individual molecules is obviously highly complicated and doubtless not subject to exact formulation, but substantial progress has been made toward an approximate solution.

Wyman (15) observed that for non-associated liquids the dielectric constant is linearly proportional to the polarization per cubic centimeter calculated from the moment of the gas molecule and gave the equation:

$$(\epsilon + 1) = AP \qquad (2)$$

The data for ethyl formate and acetone in table 1 indicate the order of agreement which he found, with A equal to 8.5.

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Equation 2 does not hold for hydrogen-bonded liquids, as is illustrated by the data for water and formic acid.

Onsager (11) recognized the importance of Wyman's contribution. He wrote: "Wyman's relation implies quite simply that the polarization of the dielectric (by orientation) involves practically no change of the internal energy . . . . Such a discovery belies the pessimistic expectations of the 'association theory' and indicates that our theoretical understanding of polar liquids is capable of great advancement."

Onsager treated the molecule as a cavity of dielectric constant equal to the square of the optical refractive index of the liquid surrounded by a continuum of liquid of uniform dielectric constant. He introduced the concept of a reaction field which acts upon the dipole as a result of the electric displacements induced by its own presence and obtained the equation:

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)} = \frac{4\pi N\mu^2}{9kT} \tag{3}$$

TABLE 1

Comparison of Wyman's calculations with experiment

COMPOUND	P (FROM GAS)	ϵ_{exptl}	ϵ_{calcd}
Ethyl formate	1.21	8.6	9.4
Acetone	2.62	21.5	21.1
Water	4.24	78.5	35.0
Formic acid	1.08	62	8.2

For high values of ϵ this reduces approximately to the Wyman equation with

$$A = \frac{(n^2 + 2)^2}{2} \tag{4}$$

and the value of A equal to 8.5 corresponds to a reasonable average value of 1.46 for n. The Onsager equation also fails to account for the high dielectric constant of hydrogen-bonded liquids and would require that μ for the water molecule in the liquid be around 3×10^{-18}. Near the end of his paper Onsager makes the remark, "Incidentally our 'refractive index' should include the 'atomic polarization' due to elastic displacement of the atomic nuclei by the electric field." It is apparent from equations 2 and 4 that even small atomic polarizations will have a significant effect upon ϵ, since it enters the constant A. This point will be amplified later in more detail.

Kirkwood (7) has attacked the problem of the hydrogen-bonded liquids by assuming hindered rotation of the dipole due to short-range intermolecular forces. His treatment leads to the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \cdot V = \frac{4\pi N}{3}\left[\alpha + \frac{g\mu^2}{3kT}\right] \tag{5}$$

where V = molar volume, α = optical polarizability, μ = the dipole moment of the liquid, and g is given by the expression

$$g = [1 + Z\ (\cos \gamma)_{\text{av}}] \tag{6}$$

where Z is the average number of nearest neighbors and $(\cos \gamma)_{\text{av}}$ is the average value of the cosine of the angle between the given dipole and one of its neighbors.

The effectiveness of Kirkwood's treatment is indicated by the calculated and observed values of ϵ for water and the aliphatic alcohols summarized in tables 2 and 3. In making these calculations the dipole moment μ of equation 4 was calculated from the Onsager expression for the relationship between μ and μ_0 of the molecule as a gas:

TABLE 2

Dielectric constant of water

t	ϵ_{calcd}	ϵ_{obsd}
°C.		
0	84.2	88.0
25	78.2	78.5
62	72.5	66.1
83	67.5	59.9

TABLE 3

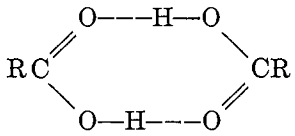
Dielectric constant of the aliphatic alcohols

ALCOHOL	ϵ_{calcd}	ϵ_{obsd}
Methyl alcohol	29.2	32.8
Ethyl alcohol	21.3	24.6
n-Propyl alcohol	17.3	19.5
n-Butyl alcohol	14.6	18.0
n-Amyl alcohol	12.6	15.8

$$\mu = \frac{2\epsilon + 1}{2\epsilon + n^2} \cdot \frac{n^2 + 2}{3} \mu_0 \tag{7}$$

ATOMIC POLARIZATION IN HYDROGEN-BONDED LIQUIDS

There is considerable evidence for a very appreciable contribution to the dielectric constant of hydrogen-bonded liquids by the "atomic polarization" of the proton in the hydrogen bond. Hobbs, Gross, and coworkers (9, 12) have studied the apparent moments of the carboxylic acids in organic solvents. The acids were present as equilibrium mixtures of the monomer and the symmetrical dimer,



Evaluation of the parameters by successive approximations gave the equilibrium constant and the apparent moments of the monomer and dimer. From their data they concluded that the symmetrical dimer had an atomic polarization of about 20 cc.

Coop, Davidson, and Sutton (2) found a similar moment in the formic acid dimer in the vapor phase. They showed that the moment was independent of the temperature and therefore not due to an orientation type of polarization.

Recently Collie, Hasted, and Ritson (1) have reported an extensive study of the dielectric constant of light and heavy water as a function of frequency. They analyzed their data in terms of the equation,

$$\epsilon - \epsilon_0 = \frac{\epsilon_s - \epsilon_0}{1 + j\omega\tau} \tag{8}$$

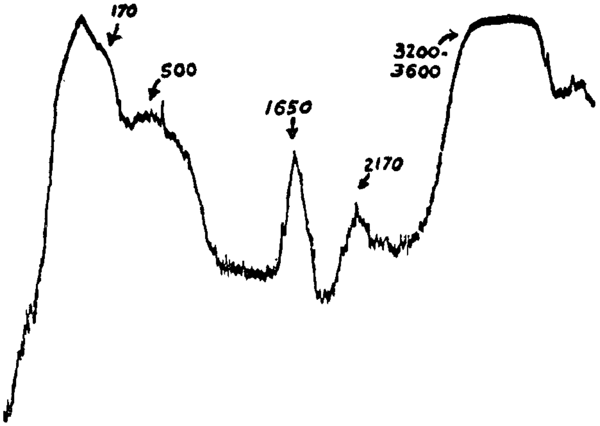


FIG. 1. Raman spectrum of water (from Hibben)

where τ is the relaxation time, ϵ the complex dielectric constant at angular frequency ω, ϵ_0 the electronic and atomic polarization, and ϵ_s the static dielectric constant. At constant temperatures equation 8 gives an accurate representation of their results with a constant value of τ. They find $\epsilon_0 = 5.5$ for both light and heavy water, a value which is considerably larger than the square of the index of refraction, and conclude that the atomic polarization in water is much higher than is generally assumed.

It seems likely that an atomic polarization of hydrogen-bonded substances is to be associated with a low-frequency vibration of the proton and it is therefore of interest to examine the infrared spectrum for such frequencies.

Hibben (5) has given the Raman spectrum of water reproduced in figure 1. The bands at 500, 1650, and 3200–3400 cm.$^{-1}$ are hydrogen vibrations, since they are shifted by approximately $\sqrt{2}$ in deuterium water.
The 3200–3400 cm.$^{-1}$ band is ν_3 of figure 2, since the frequency is only slightly less than the corresponding O—H frequency in water vapor. The 176 cm.$^{-1}$ band has been attributed to ν_1 and the 500 cm.$^{-1}$ band to ν_2.

The polarizability, α, of a harmonic vibration of charge e, mass m, and frequency ν is given by the expression

$$\alpha = \frac{e^2}{4\pi^2 m\nu^2} \tag{9}$$

The molal polarization, P, is

$$P = N\tfrac{4}{3}\pi\alpha = \frac{Ne^2}{3\pi m\nu^2} \tag{10}$$

From equation 10 the polarization per mole of hydrogen for the 500 cm.$^{-1}$ frequency is 39 cc. The number of hydrogen bonds in water is indefinite; hence the number of proton vibrators in a given direction in water is not definitely known but the maximum polarization per mole, taking into account the two hydrogens and the two-dimensional vibration, would be of the order of magnitude $2 \times \frac{2}{3} \times 39$ or 52. Even if only one-third of the possible hydrogen bonds are formed in water, this would give a polarization of 17 cc. From the index of refraction and the Clausius–Mosotti equation the electron polarization is 3.7 cc. It is obvious that this equation cannot be used to calculate the dielectric constant for high values of the proton polarization, but a polarization of 17 cc. appears adequate to account for the value of ϵ_0 observed by Collie, Hasted, and Ritson. The polarization for a deuterium vibration would be the same, since the decrease in the frequency by the factor of the square root of 2 balances the increase in mass.

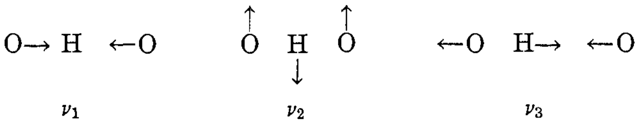


FIG. 2

As pointed out in the discussion of the Onsager equation, even a small value for the atomic polarization can thus produce a large change in ϵ_1, since it affects the proportionality constant between ϵ and P as indicated in equation 4. Indeed, the experimental value of ϵ_0 (5.5), obtained by Collie, Hasted, and Ritson for water, appears to be too high, as it would lead to a dielectric constant of at least 125. The contribution of the proton polarization will vary considerably from one hydrogen-bonded compound to another, depending upon the value for the vibrational frequency. In some compounds the frequency may be so high that the effect will be quite small. This may be true, for example, in KHF_2.

Hydrogen-bond formation also lengthens the X—H bond distance. From the change in Raman frequency, Sutherland (14) has calculated that the increase may be as large as 0.1 Å. for the O—H distance on association of two carboxyl groups. The dipole moment of a molecule such as water would then be appreciably increased over the value for the vapor, but in terms of the

Onsager equation, this effect on the dielectric constant of hydrogen-bonded liquid should not be as significant as the contribution from proton polarizations.

THE MECHANISM OF DIPOLE ORIENTATION IN ICE

An interpretation of the dielectric constant of ice must account for the following facts: The constant has a value of 75 at 273°C., and the relaxation time is between 10^{-5} and 10^{-6} sec. at that temperature but rapidly increases at lower temperatures. For comparison the relaxation time in water is around 10^{-10} sec. For frequencies greater than 10 kilocycles the dielectric constant falls to a small value (less than 10) at low temperatures, but there is evidence that the constant for infinite wave length does not decrease. Thus Murphy (10) charged an ice condenser for 1 hr. at −138.7°C. and by successive discharges collected about the same total charge as is obtained at 0°C. Also by rapidly cooling an ice condenser with liquid air, it is possible to freeze a permanent electric moment into the ice, which again indicates that a dipole must go over an appreciable

TABLE 4

ΔE and ΔS for the dipole orientation activation in ice

EXPERIMENTER	ΔE	ΔS
	kcal./mole	*cal./degree/mole*
Wentsch	9.3	0
Murphy	14.4	17
Smyth and Hitchcock	12.2	13

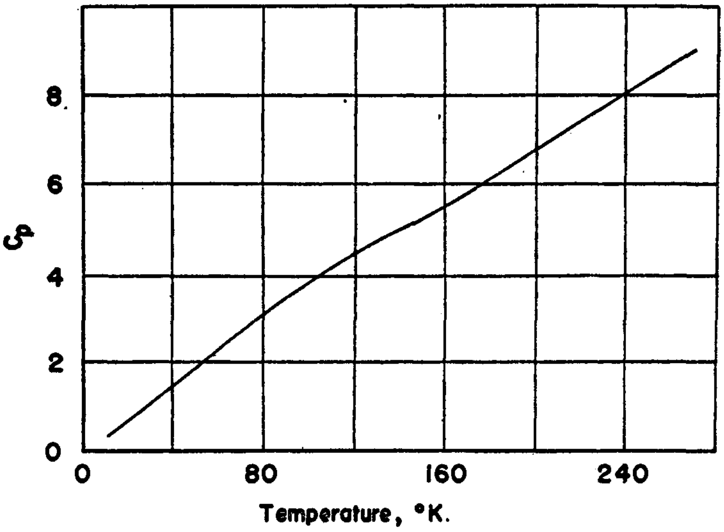


FIG. 3. Heat capacity of ice; C_p in calories per degree per mole

barrier in returning to its normal position. Quantitative information on the activation energy of the orientation barrier can be obtained from the temperature coefficient of the relaxation time. Kauzmann (6; see also 13) has calculated the values summarized in table 4. The specific heat curve obtained by Giauque and Stout (4) is given in figure 3. Around 120°K. the curve looks as though it would extrapolate to a value of $C_p = 6$, which would correspond to the equipartition value for the oxygen, and then it rises in almost a straight line to the value of 9, or 1.5 cal. per hydrogen higher. This rise is not the sort of curve one expects with the acquisition of rotational energy.

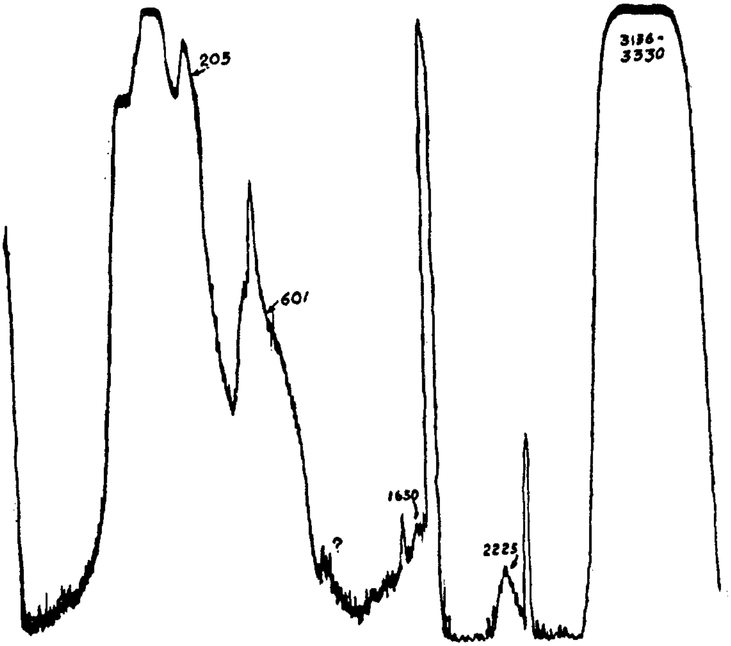


FIG. 4. Raman spectrum of ice (from Hibben)

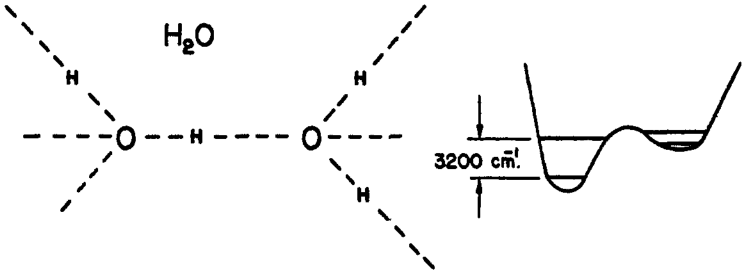


FIG. 5. Potential diagram for the proton in the hydrogen bond in ice

The Raman spectrum, again from Hibben, is given in figure 4. It has the same general characteristic as the water spectrum but the 500 cm.$^{-1}$ bond is located at 600 cm.$^{-1}$ and is sharper. Presumably it is due to the hydrogen vibrations at right angles to the bonds. At 273°K. such a two-dimensional vibration with $\omega/T = 2.2$ would have a specific heat of 1.8 cal. per gram-atom of hydrogen, which is approximately the excess over 6 noted above.

If the water molecules in ice are not rotating, the question arises as to how it is possible to obtain the dipole orientation which is required for the high dielectric constant. In answer to this question the following mechanism is suggested. The frequency of the first vibrational state, ν_3 of figure 2, is 3200 cm.$^{-1}$ from the Raman spectrum. This corresponds to 9100 cal./mole. Protons in this state should be able to cross the barrier, as is indicated in figure 5. While the population of molecules in the resulting H_3O^+ and OH^- states will be quite small, the rate at which such ion pairs are forming and disappearing will be quite rapid. This process provides a mechanism for dipole reorientation, since in the H_3O^+ ion there is the possibility of any one of the three protons jumping off and on the OH^- the possibility of any one of three protons returning to form the neutral molecule. As illustrated in figure 6, if the H_2O gains a proton at X and loses one at a, the dipole is reoriented. Likewise a loss at y and a gain at b produce a similar orientation. Ordinarily the same proton which jumped over will jump back, but there certainly will be conditions on the neighboring molecules which will permit the optional process and under the influence of an

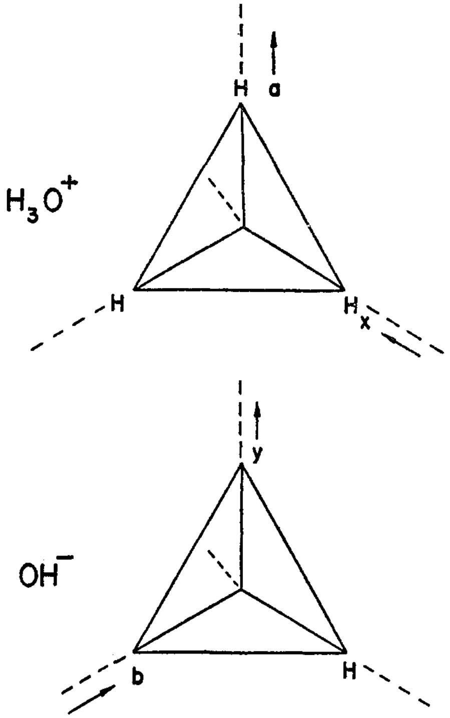


FIG. 6. Mechanism for the dipole orientation

electric field a certain amount of orientation in the direction of the field will occur. The value of 9100 cal. for the vibrational excitation agrees with the experimental value of Wentsch (9300 cal., table 4) and such a process would have a very small entropy change. It would be difficult to account for an entropy of activation as high as 17 cal./degree, which was calculated from the work of Murphy, since the total entropy of an ice molecule at 273°K. is only 9.1 cal./degree.

SUMMARY

In 1920 Latimer and Rodebush (8), in their paper in which they introduced the idea of the hydrogen bond, made the suggestion that the displacement of the proton in the bond was doubtless related to the high dielectric constant. This relationship may now be summarized.

1. An appreciable displacement of the proton along the direction of the bond increases the permanent moment of the molecule.
2. A small atomic polarization of the proton in an electric field results in a big change in the dielectric constant, as indicated by the Onsager equation.
3. A transfer of the proton over the barrier offers a mechanism for the orientation of the dipoles by an electric field in ice and probably other solids.

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