

The bifurcated hydrogen-bond model of water and amorphous ice

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The existence of bifurcated hydrogen bonds (BHB) between three molecules as a major feature of the structure of liquid water was postulated recently to account for the remarkable effect of temperature on the O–H stretching bands in the Raman spectra. As a corollary, there should be two kinds of $\text{H}\cdots\text{O}$ distances in water: one, 1.85 Å, for the well-known linear bonds (LHB), prevalent in cold water, the other, 2.3 Å, for the weaker BHB. This is evident in the neutron diffraction studies of heavy water, which reveal important structural changes with temperature. For instance, the atom pair correlation functions, both in the first-order difference, and the isochoric temperature derivative methods, show two peaks at 1.8 and 2.3 Å, with inverse temperature dependence similar to that of the Raman bands at 3220 (LHB) and 3420 cm^{-1} (BHB). In the BHB the nearest-neighbor $\text{O}\cdots\text{O}$ distances are the same as in the LHB, but the apex angle is much smaller than the tetrahedral, between 95° and 100°. This allows slightly shorter second neighbor $\text{O}\cdots\text{O}$ distances, and a closer packing of the molecules. The increased average coordination of the H and O atoms creates an imbalance in the stoichiometry of hydrogen bonding. As a result, a few percent of the water molecules are left with one “free,” i.e., nonhydrogen-bonded OH group (NHB). The energy of the BHB is estimated at 2.5 kcal mol⁻¹, i.e., half that of the LHB, and its proportion in the liquid, at nearly 30% at 0 °C. Amorphous ice prepared from the vapor may also contain BHB according to x-ray and neutron diffraction data. The BHB appears as a common feature of hydroxylic compounds; e.g., hydrogen peroxide, alcohols, etc.

I. INTRODUCTION

More than half a century after Bernal and Fowler proposed their partially hydrogen-bonded model for liquid water,¹ there is still no agreement on the subject. Of the various models put forward,^{2–4} none can fit adequately both the physical properties and the available structural data. For instance, the so-called “continuum models,” featuring a uniform distribution of hydrogen bond energies and geometries, are incompatible with the thermodynamic anomalies of water, such as the density maximum at 4 °C, and the compressibility minimum at 45 °C. Furthermore, they cannot account for the remarkable effect of temperature on the intensity distribution in the 3 μ region of the Raman spectra.^{5–8} Indeed, the two main bands at about 3220 and 3420 cm^{-1} show a strong, inverse temperature dependence. Repeated attempts to explain this in terms of Fermi resonance between ν_1 , the symmetric O–H stretching, and $2\nu_2$, the overtone of the bending mode,^{7,9} are disproved by a number of experimental observations, as explained elsewhere.¹⁰ Particularly significant is the complete lack of correlation between the behavior of the very weak ν_2 band at 1640 cm^{-1} , and its presumed overtone band at 3220 cm^{-1} in response to variables such as temperature, the addition of electrolytes, etc. Likewise, the actual intensity distribution in no way resembles that typical of Fermi resonance: namely a splitting of the original level into two equal sublevels, equidistant from the original frequency. Moreover, a recent study¹¹ of the Raman spectrum of very pure water in the overtone region of the O–H stretching has revealed a band at 6160 cm^{-1} , which cannot reasonably be assigned to $4\nu_2$. *A priori*, one would not expect any clear feature from resonance between the fundamental vibrations of H_2O molecules in condensed phases because they

are so strongly perturbed by mechanical coupling with the intermolecular motions (hydrogen-bond bending and stretching). Therefore, the two temperature-dependent Raman bands must be due to OH oscillators in two different environments.

As for the “mixture models,” which consider liquid water as a mixture, or solution, of a small number of molecular species distinguishable by the number of hydrogen bonds, they all imply the concept of “broken hydrogen bonds.” But the nature of these broken bonds has never been defined, and estimates of their concentration in water, based on various criteria, diverge over an excessively wide range.¹² Now, these difficulties can be overcome by introducing another kind of molecular interaction, intermediate between the usual linear hydrogen bond (LHB) and the “free” or nonhydrogen-bonded (NHB) OH group, as proposed recently.¹⁰

II. BIFURCATED HYDROGEN BONDS

There are only a few known examples of true BHB in crystalline hydrates,¹³ but none in liquids. Yet, the packing geometry in water is particularly favorable (Fig. 1), since in an approximately tetrahedral network the $\text{H}\cdots\text{O}$ distance (2.3 Å) is slightly shorter than the sum of the van der Waals radii (1.2 Å for H and 1.4 Å for O¹⁴), as per the accepted criterion. Then, the obvious way for thermal agitation to dislocate the strong tetrahedral lattice of ice on melting is by bending the hydrogen bonds. With sufficient amplitude this brings the OH group in an interstitial orientation, halfway between two adjacent O atoms. There, a minimum in the potential curve provides a moderately stable state, spectroscopically distinguishable. The higher energy of that state compared to the LHB is partly offset by the fact that it mini-

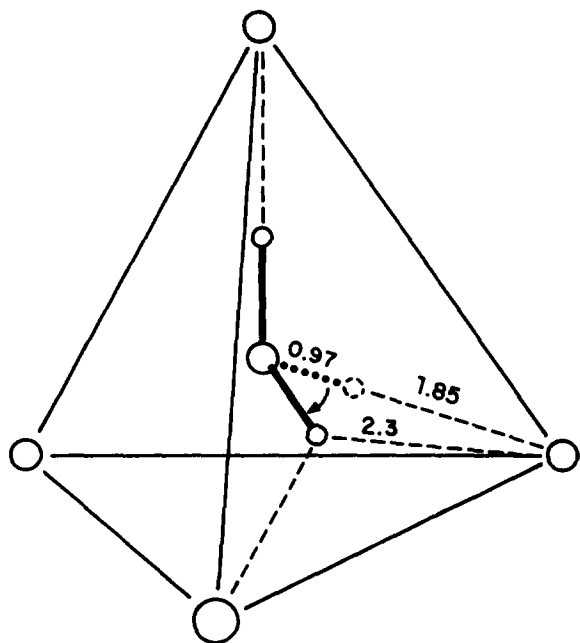


FIG. 1. Reorientation of one OH group from the LHB to the BHB configuration on melting ice. For simplicity the simultaneous rotation of the adjacent molecules is not shown (distances in Å).

mizes the van der Waals overlap (Fig. 2), which, in LHB, amounts here to about 1 Å^3 . Another stabilizing factor is the increase in the number of intermolecular contacts. Clearly, the BHB hypothesis is consistent with the Raman spectra. Both the relatively high frequency of the BHB band (3420 cm^{-1}) and its increasing intensity with temperature indicate a weaker hydrogen bond than the LHB.

A. Diffraction data

The coexistence of LHB and BHB in liquid water should be evident in diffraction patterns. For that purpose x rays are not very suitable because they are sensitive only to correlations of oxygen atoms, and the next-neighbor $\text{O}\cdots\text{O}$ distances are about the same in both cases; namely 2.82 Å ¹⁵ for the LHB, predominant in cold water, and $(2 \times 1.4 \text{ Å})$ for the van der Waals contacts expected for the BHB (cf. the 2.9 Å distance between nonbonded O atoms in the H_2O_2 crystal.)¹⁶ Still, the x-ray radial distribution functions for liquid water¹⁵ show that the first peak at 2.8 Å cannot fit a single Gaussian curve. The asymmetry towards longer distances increases with temperature, suggesting another overlapped $\text{O}\cdots\text{O}$ peak, and, therefore, a complex first coordination sphere of the water molecule. (As explained below, these two peaks are well resolved in the x-ray diffraction patterns of amorphous ice.)

In contrast, neutron diffraction in liquid heavy water provides information on the orientational correlation between pairs of molecules. The first measurements were carried out at one temperature only, 25°C .¹⁷ From the correlation functions, the contributions of different atom pairs were separated assuming an exact tetrahedral model. According to that model the feature at 2.3 Å (Table I) was assigned to the nearest intermolecular $\text{D}\cdots\text{D}$ distances. However, subsequent studies as a function of temperature

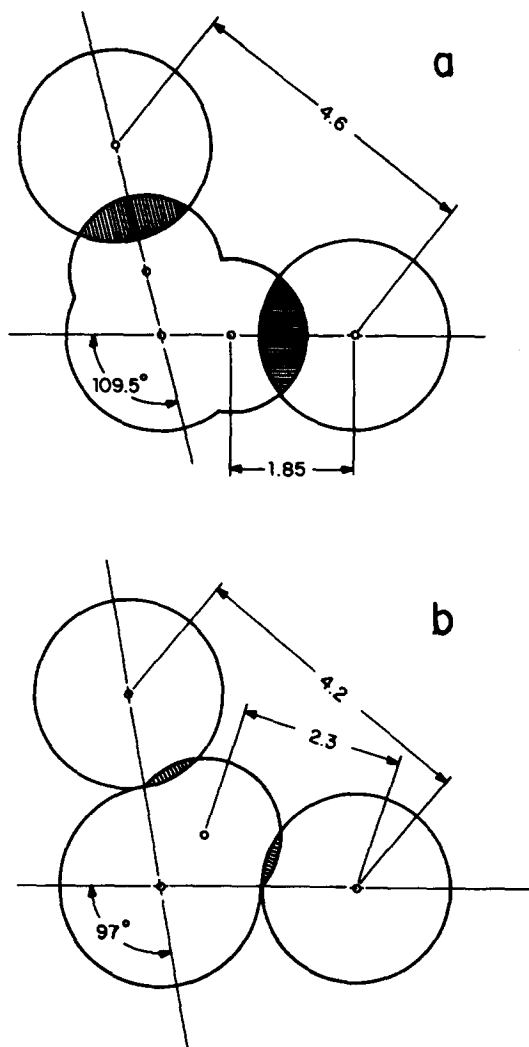


FIG. 2. Compared geometry of the LHB (a) and the BHB (b) in liquid water. The shaded areas represent the van der Waals overlap.

disprove that interpretation. Indeed, both the difference functions (Dore *et al.*¹⁹⁻²¹) and the isochoric derivative of the structure factor (Egelstaff *et al.*²²⁻²⁵) show clearly that relatively small temperature changes produce significant structural variations. In particular, the feature at 2.3 Å increases on warming, while that at 1.85 Å decreases at the

TABLE I. $\text{O}\cdots\text{D}$ distances of the BHB from neutron diffraction in D_2O .

Physical state	Temperature ($^\circ\text{C}$)	Analytical function ^a	$r_{\text{O}\cdots\text{D}}$ (Å)	Refs.
Liquid	25	ATC	2.4	17
Liquid	25	ATC	2.29	18
Liquid	11-79	TDF	2.3	19,20
Liquid	-14.5	TDF	2.3	21
Liquid	-1-23	ITD	2.3	22-25
Amorphous ice	-263	ATC	2.26	26
Amorphous ice	-263	ATC	2.30	27
Amorphous ice	-263	ATC	2.31	28

^a ATC: atom pair correlation; TDF: temperature difference function; ITD: isochoric temperature derivative.

same rate. This is exactly the opposite of what one would expect from the above assignment, which implies more local order at higher temperature. Much more logical is the present model which considers the 2.3 Å feature as characteristic of the BHB. For example, the various temperature difference curves (Fig. 3), when superimposed, all intersect at the same point, analogous to the isosbestic point in spectroscopy,²⁹ a recognized symptom of two species in equilibrium.

Besides the temperature dependence of these two diffraction peaks, the BHB concept is also consistent with their similar contour. Indeed, the nonbonded intermolecular $D\cdots D$ distances cannot possibly have the same distribution as the strongly bonded $O\cdots D$ distances. Finally, there is no conceivable way in which a decrease in the number of OD pairs could bring about an equal increase in DD pairs. From all indications, neutron scattering by DD pairs in D_2O is very diffuse. For instance, there is no clear evidence of the intramolecular $D\cdots D$ distances around 1.56 Å.^{17,18} Then, no significant feature at 2.3 Å has been reported in the correlation functions of D_2O ice I, which definitely rules out assignment of the major peak in the liquid to DD pairs. Not surprisingly, repeated efforts to separate the partial OD and DD pair functions using the basic tetrahedral coordination model have not yet succeeded (cf. Dore³⁰ for a recent review). Likewise, molecular dynamics calculations based on a pair potential model have revealed significant discrepancies with experimental data.²²⁻²⁴

B. Geometry of the BHB

The diffraction feature at 2.3 Å, combined with the O-H bond length (0.97 Å) and the near-neighbor $O\cdots O$ distance (2.82 Å) in cold water,¹⁸ means an apex OOO angle of about 97°, much smaller than the tetrahedral, and a second-neighbor $O\cdots O$ distance shorter than 4.6 Å (Fig. 2). This allows a closer packing of the molecules and a density increase; first on melting ice, despite the 2% increase in near-neighbor $O\cdots O$ distances, then in the liquid up to the maximum at 4 °C (11.2 in D_2O). It is worth noting here that according to Egelstaff and Root,²⁴ the isothermal density derivative of liquid D_2O follows a sigmoid curve, similar to the isochoric temperature derivative of the structure factor. The greater number of contacts in the BHB agrees with the conclusion from x-ray diffraction of a higher coordination number (4.4 on the average) than the tetrahedral value.¹⁵ True, there is no clear sign in the correlation functions of an $O\cdots O$ distance slightly shorter than 4.6 Å, but this is due to overlapping, which gets worse at longer distances and higher temperatures. Obviously, the $LHB \leftrightarrow BHB$ reorientation is a cooperative process (not shown in Fig. 1, for simplicity), resulting in ring structures made of OH groups linked similarly through either LHB or BHB. Of course, there are no discrete rings in a continuously hydrogen-bonded milieu, as each H_2O molecule is part of at least four rings.

The BHB model recognizes three major species of water molecules distinguished by their environment, previously labeled LL, BB, and LB.¹⁰ Thus, intermixing occurs at the level of individual molecules, and there is no need for such vague concepts as "icebergs" or "flickering clusters" or "patches" sometimes used to describe "mixture" models. In

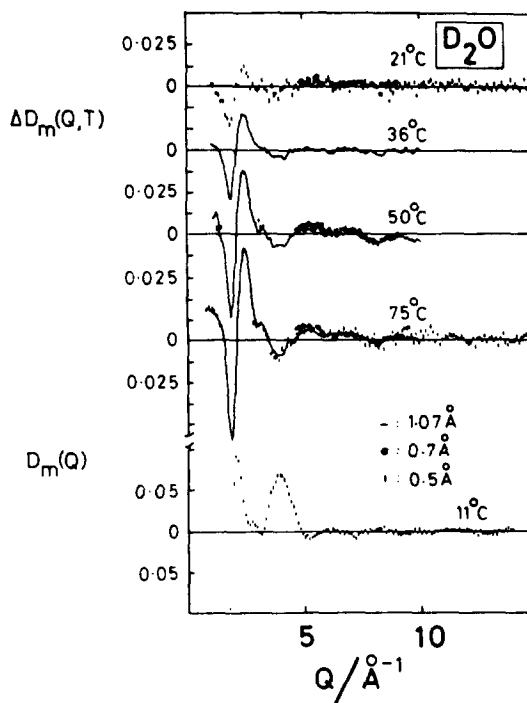


FIG. 3. The difference function $\Delta D_m(Q, T)$ for liquid D_2O relative to a reference temperature of 11 °C; the form of the $D_m(Q)$ function at the reference temperature is also shown. Reproduced from Gibson and Dore (Ref. 20) with permission.

addition to the three major species, there is a minor one (only a few percent, labeled BN^{10}) of water molecules with one OH group free, i.e., nonhydrogen bonded (NHB).³¹ A consequence of an imbalance in the stoichiometry of hydrogen bonding, their existence is manifest in the shoulder at high frequency on the O-H Raman bands. It is clear that the "ice rule" of one lone pair per hydrogen bond does not hold in the liquid. Since the electron density of the H_2O molecule in the lone-pair region is nearly spherical, according to quantum mechanics,³² the details of hydrogen bonding are governed mainly by the packing geometry. Because of the increased coordination numbers in the BHB (from 2 to 3 for H atoms and from 4 to 5, and even 6, for the O atoms), no significant structure remains beyond a couple of molecular diameters, again in perfect agreement with the x-ray data.¹⁵ The distribution of these various species in the liquid is an incredibly complex problem of molecular dynamics. Also, it must always be remembered that the average lifetime of a water molecule in any given species is only of the order of 10^{-11} s because of the extreme mobility of the H atoms. Most likely, the proton jump via the H_3O^+ and OH^- ions³³ plays a key role in the $LHB \rightarrow BHB$ reorientation.

C. Thermodynamics of the BHB

An important parameter of the BHB in water is its energy relative to that of the LHB. As a first indication, the semiempirical relationship between hydrogen bond energy and O-H frequency shift³⁴ leads to a ratio of exactly 1/2; that is, 3220 and 3420 cm^{-1} for ν_1 of LL and BB molecules,

respectively, and 3620 cm^{-1} for the free OH group (NHB).¹⁰ Coincidentally, the same ratio is obtained from calculations of the damping force acting on the O–H oscillator in the LHB and BHB, using a simple model of Coulomb interactions between point charges located at the H and O atoms. Since the energy of the LHB in ice is about 5 kcal mol^{-1} , and that in the liquid a little less,¹⁴ this means an enthalpy change of some $2.3\text{--}2.5\text{ kcal mol}^{-1}$ between the LHB and BHB states. Again, this agrees with the ΔH^0 values derived from various data on either bulk properties of the liquid,² or Raman band intensities.³⁵ It is noteworthy that the same value of ΔH^0 is obtained from the temperature dependence of the peak intensities at 1.85 and 2.3 Å in the neutron diffraction of liquid D_2O (Fig. 3), a further confirmation of the present interpretation. Another significant parameter is the percentage of BHB in water as a function of temperature. The first estimate made by Pauling, based on the ratio of the enthalpy of fusion to the enthalpy of sublimation of ice, gave a value of slightly less than 15% of so-called “broken” hydrogen bonds; that is, 28%–30% of BHB formed on melting ice. This is in fair agreement with the ratio of $1/3$ between the intensities of the BHB band at 3420 cm^{-1} and that of the LHB band at 3220 cm^{-1} in the Raman spectra.⁵ Likewise, it agrees with the fraction 0.65 of “the number of O atoms seen at $\sim 1.9\text{ Å}$ from an H atom,” based on the area of the OH peak in the structure factor curve at the reference temperature (11.2°C) in the neutron diffraction of liquid D_2O .²³

From the above value of the van't Hoff ΔH^0 it follows that another one third, approximately, of the LHB in liquid water are converted into BHB over the normal $0\text{--}100^\circ\text{C}$ range, in agreement both with the estimate from Raman band intensities and the configurational contribution to the increase in heat capacity,² as explained before.¹⁰ As for supercooled water, the proportion of BHB should decrease regularly with decreasing temperature. On the assumption of a linear relationship, zero concentration would be achieved around -45°C , the limiting temperature of thermodynamics singularities.³⁶ This simple model could explain the exponential increase in heat capacity, as well as the observation that the extrapolated density curve crosses that of ice I at that limiting temperature. However, it does not agree with conclusions from recent spectroscopic³⁷ and neutron diffraction studies²¹ which favor, instead, a continuity of state with amorphous ice.

III. BHB IN AMORPHOUS ICE

The metastable phase, known as amorphous ice, obtained by slow condensation of the vapor on a cold surface has been much studied as a means of furthering our knowledge of the structure of the liquid. Because of the low temperature at which it is prepared, the contribution of thermal disorder is greatly reduced, so that structural disorder is more clearly observed. On the negative side, the actual form of the material (high density vs low density) seems to depend critically on the details of the preparation method; hence the results from different measurements are not always comparable. A first spectroscopic study in the far infrared³⁸ indicated that the average strength of the hydrogen

bonds in amorphous ice is somewhat lower than that in crystalline ice. Then a Raman study³⁹ led to the conclusion that the material “resembles liquid water more than it does ice, as the water molecules effectively experience at least two, and possibly three, distinguishable environments,” corresponding the LL, BB, and LB species of the present model. In contrast, infrared spectra in the O–H stretching region provide little structural information,⁴⁰ as in the case of the liquid.

More specific information comes from diffraction studies. For example, according to the x-ray diffraction patterns (Narten *et al.*²⁷), there are at least two forms of amorphous ice made by slow condensation of the vapor on a cold surface; one obtainable exceptionally at 10 K , with an estimated density of 1.1 g/cm^3 , the other of lower density 0.94 g/cm^3 , made at 77 K . In both, the nearest-neighbor $\text{O}\cdots\text{O}$ distances give rise to a sharp peak at 2.76 Å , exactly the same value as in ice I, but with larger variation, indicating a wider distribution of local distances. Likewise, the second-neighbor $\text{O}\cdots\text{O}$ distances give a peak at 4.4 Å , as in ice, but again with a broader distribution. More significant are the two extra features at shorter distances, not found in ice I. The first one, a shoulder at about 4.0 Å , corresponds to the 4.2 Å distance between second neighbors in the BHB model of liquid water [Fig. 2(b)]. The other is a fairly sharp peak at 3.3 Å , resolved in the 10 K amorph, but barely detectable in the low-density amorph (77 K). That feature, which also appears in the analysis of the x-ray radial distribution curves of the liquid,⁴¹ has never received a satisfactory explanation. Narten *et al.*²⁷ have suggested two possible models; one, an “interstitial” model, which requires as many as 19% of interstitial molecules located on the c axis in the cavities of the hexagonal lattice of ice I, while the other is based on a random network derived from the ice II and ice III lattices, the parentage of which has never been derived.

In contrast, the BHB affords a suitable definition. As may be checked on a hand-built model, 3.3 Å is the distance between two second-neighbor molecules linked to a third one having its two OH engaged in BHB. As for neutron diffraction studies of amorphous ice,^{26–28} in all cases the atom pair correlation functions show a peak at 2.3 Å . By analogy with liquid water it was usually attributed to intermolecular DD pairs. Here again this is ruled out by the fact that no such feature has been reported yet in the correlation functions of ice I. One difficulty with the BHB model in this case is the intensity of that peak, comparable to that of the LHB peak at 1.8 Å , and contrary to that of the features at 3.3 and 4.0 Å in the x-ray correlation functions. Clearly, more work is needed to elucidate that discrepancy. It may be that a continuous series of low-pressure amorphs can exist, with varying structure (i.e., content of BHB), depending on the variables of the preparation method.

IV. CONCLUSIONS

The BHB model of water is not only compatible with the bulk properties of the liquid and the structural data, it is also more defined than any of the previous ones. The BHB concept rests on two experimental criteria; (a) in the Raman spectra, a relatively high-frequency O–H band (around 3400

cm^{-1}) and (b) in the neutron diffraction data, a peak at 2.3 \AA in the correlation functions of OD pairs. Alternative interpretations based (a) on Fermi resonance with the OH bending mode and (b) on intramolecular DD pairs are disproved by the strong temperature dependence observed.

If the BHB concept is correct it should also apply to other situations. Indeed, even in steam there is an attractive force between three molecules that is not present between two, according to a comparison of the second and third virial coefficients.² In solids, besides the few crystalline hydrates already mentioned,¹³ BHB may be predicted in clathrate compounds. Other hydroxylic compounds also contain BHB, such as hydrogen peroxide⁴² and alcohols, in agreement with neutron diffraction data⁴³ and a recent spectroscopic study of liquid methanol.⁴⁴

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