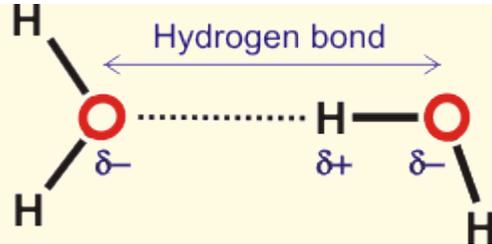


Hydrogen Bonding in Water



The hydrogen bond in water is a dynamic attraction between neighboring water molecules involving one hydrogen atom located between the two oxygen atoms.

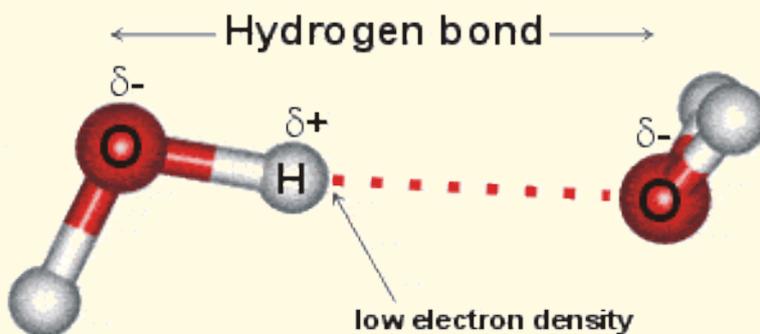
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'Water is life'

Audrey Hepburn

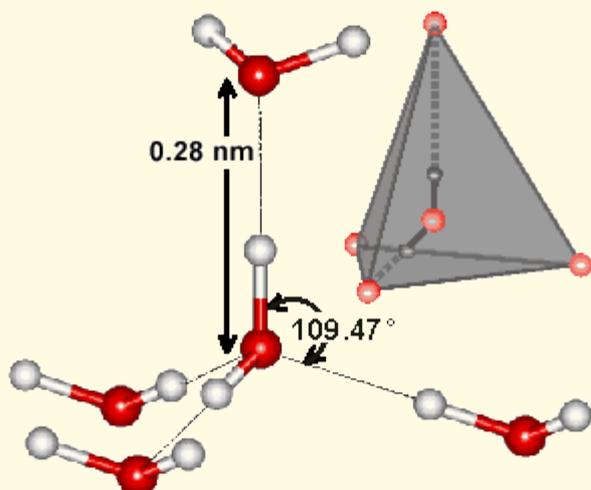
Introduction

Hydrogen bonding forms in liquid water as the hydrogen atoms of one water molecule are attracted towards the oxygen atom of a neighboring water molecule. In a [water molecule](#) (H_2O), the oxygen nucleus with +8 charges attracts electrons better than the hydrogen nucleus with its +1 charge. Hence, the oxygen atom is partially negatively charged and the hydrogen atom is partially positively charged. The hydrogen atoms are not only covalently attached to their oxygen atoms but also attracted towards other nearby oxygen atoms. This attraction is the basis of the 'hydrogen' bonds.



The water hydrogen bond is a weak bond, never stronger than about a twentieth of the strength of the O-H covalent bond. It is strong enough, however, to be maintained during thermal fluctuations at, and below, ambient temperatures. ^a The attraction of the O-H bonding electrons towards the oxygen atom leaves a deficiency on the far side of the hydrogen atom relative to the oxygen atom. The result is that the attractive force between the O-H

hydrogen and the O-atom of a nearby water molecule is strongest when the three atoms are in close to a straight line and when the O-atoms are closer than 0.3 nm.

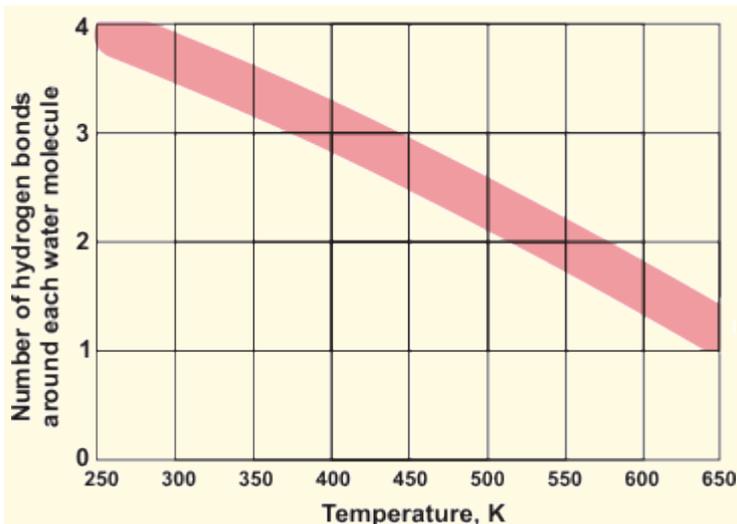


Each water molecule can form two hydrogen bonds involving their hydrogen atoms plus two further hydrogen bonds utilizing the hydrogen atoms attached to neighboring water molecules. These four hydrogen bonds optimally arrange themselves tetrahedrally around each water molecule as found in ordinary ice (see right). In liquid water, thermal energy bends and stretches and sometimes breaks these hydrogen bonds. However, the 'average' structure of a water molecule is similar to this tetrahedral arrangement. The diagram shows such a typical 'average' cluster of five water molecules. In the [ices](#) this tetrahedral clustering is extensive, producing crystalline forms. In liquid water, the tetrahedral clustering is only locally found and reduces with increasing temperature. However, hydrogen bonded chains still connect liquid water molecules separated by large distances.

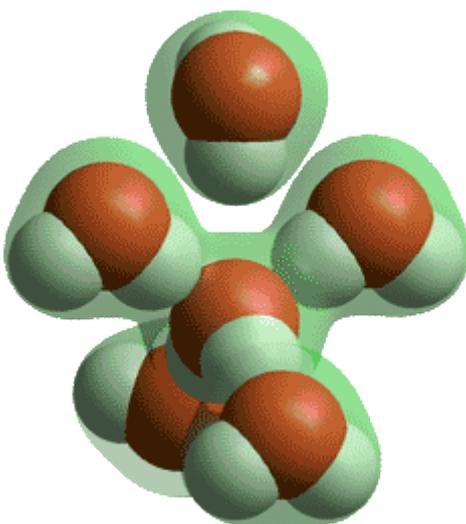
There is a balance between the strength of the hydrogen bonds and the linearity that strong hydrogen bonds impose on the local structure. The stronger the bonds, the more ordered and static is the resultant structure. The energetic cost of the disorder is proportional to the temperature, being smaller at lower temperatures. This is why the structure of liquid water is more ordered at low temperatures. This increase in orderliness in water as the temperature is lowered is far greater than in other liquids, due to the strength and preferred direction of the hydrogen bonds, and is the primary reason for water's rather unusual properties. [\[Back to Top ▲\]](#)

Water hydrogen bonds

In liquid water, all water molecules have at least one hydrogen bond to neighboring water molecules with effectively no free water molecules under ambient conditions (i.e. molecules with no hydrogen bonds). There are two main hypotheses concerning the hydrogen bonding of liquid water that divide water science; either (a) water forms an effectively continuous three dimensional network with the hydrogen bonds more or less distorted from their ideal three dimensional structures, or (b) water consists primarily of a mixture of clusters of water molecules with different degrees of hydrogen bonding in an equilibrium. Many properties of water are more easily explained using the latter model which is also supported by a number of experimental methods.



Water molecules in solid and low temperature liquid water are exceptional, amongst hydrogen-bonding molecules, in having approximately twice as many hydrogen bonds as covalent bonds around each molecule and averaging as many hydrogen bonds as covalent bonds. Shown left is the number of hydrogen bonds around each water molecule as the temperature rises with the line-width showing the approximate disparity between different experimental methods (data from [2264]). Although there are reports of water surrounded by more than four hydrogen bonds (for example 5 or 6) these hydrogen bonds cannot be spatially accommodated around the central water molecule without being sited significantly further from the central oxygen (see below) plus with one or more of the original four hydrogen bonds being substantially weakened.



Thus, they can be bifurcated bonds where the bond is essentially shared between the water molecules (for example, two half -bonds rather than one full bond). No stable water cluster (for example within a crystal structure) has been found with the central water molecule 5-coordinated by hydrogen bonding to five water molecules.

In water's hydrogen bonds, the hydrogen atom is covalently attached to the oxygen of a water molecule (492.2145 kJ mol⁻¹ [350]) but has (optimally) an additional attraction (about 23.3 kJ mol⁻¹ [168]). This is the energy (ΔH) required for breaking and completely separating the bond, and should equal about half the enthalpy of vaporization. On the same basis $\Delta S = 37 \text{ J deg}^{-1} \text{ mol}^{-1}$ [168]. (Lower enthalpies for the hydrogen bond have been reported [1369], varying between ~6-23 kJ mol⁻¹, with

entropies ~29-46 J deg⁻¹ mol⁻¹, depending on the assumptions made). Just breaking the hydrogen bond in liquid water leaving the molecules essentially in the same position requires only about 25% of this energy; recently estimated at 6.3 kJ mol⁻¹ [690] and only just over twice the average collision energy ^a If the hydrogen bond energy is determined from the excess heat capacity of the liquid over that of steam (assuming that this excess heat capacity is attributable to the breaking of the bonds) $\Delta H = 9.80 \text{ kJ mol}^{-1}$ [274]. A number of estimates give the equivalent ΔG at about 2 kJ mol⁻¹ at 25 °C [344]; however from the equilibrium content of hydrogen bonds (1.7 mol⁻¹) it is -5.7 kJ mol⁻¹. The hydrogen bonding in ice Ih is about 3 kJ mol⁻¹ stronger than liquid water (= 28 kJ mol⁻¹ at 0 K, from lattice energy including non-bonded interactions) and evidenced by an about 4 pm longer, and hence weaker, O-H covalent bond. However, the hydrogen bond strength in supercooled liquid water may be stronger than in ice [2020]. The hydrogen bond strength is almost five times the average thermal collision fluctuation at 25 °C^a to a neighboring oxygen atom of another water molecule and is far greater than any included van der Waals interaction.

Hydrogen bonds within heavy water are stronger. Unexpectedly for such an important parameter, there is some dispute as to whether the hydrogen bonds in D₂O and H₂O are longer or shorter or the same length. One report states (opposite to earlier conclusions [554]) that D₂O hydrogen bonds are longer (H···O 1.74 Å, D···O 1.81 Å at 23 °C [1485], but more linear; the weakening on lengthening being compensated by the strengthening on straightening) and D₂O hydrogen bonds being more asymmetric (with the hydrogen atom more displaced away from the center of the O-H···O bond), more tetrahedral, more plentiful and stronger than in H₂O [1485]. More recently the hydrogen bonds in D₂O and H₂O have been found to be about the same length due to compensatory quantum effects [1752]. Hydrogen bond in T₂O are expected to be stronger still. Thus given the choice, hydrogen bonds form with the preference

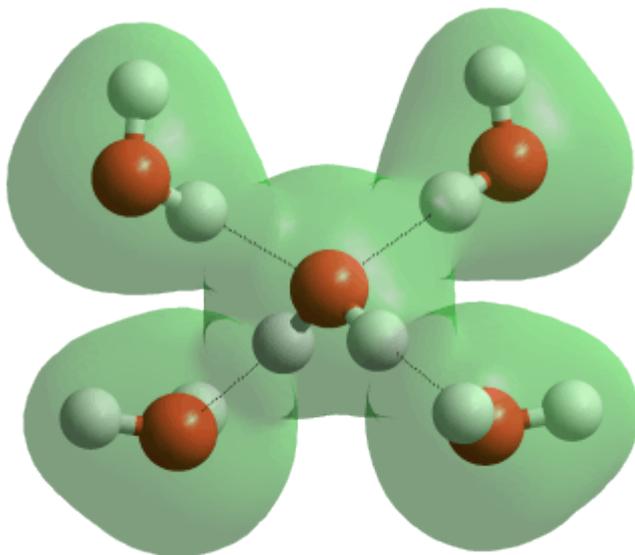


Water's hydrogen bonding holds water molecules up to about 15% closer than if water was a simple liquid with just van der Waals dispersion interactions. However, as hydrogen bonding is directional it restricts the number of neighboring water molecules to about four rather than the larger number found in simple liquids (for example, xenon atoms have twelve nearest neighbors in the liquid state. Formation of hydrogen bonds between water molecules gives rise to large, but mostly compensating, energetic changes in enthalpy (becoming more negative) and entropy (becoming less positive). Both changes are particularly large, based by per-mass or per-volume basis, due to the small size of the water molecule. This enthalpy-entropy compensation is almost complete, however, with the consequence that very small imposed enthalpic or entropic effects may exert a considerable influence on aqueous systems. It is possible that hydrogen bonds between *para*-H₂O, possessing no ground state spin, are stronger and last longer than hydrogen bonds between *ortho*-H₂O [1150].

The hydrogen bond in water is part (about 90%) electrostatic and part (about 10%) electron sharing, that is covalent [96] (see [discussion](#)) and may be approximated by bonds made up of covalent HO-H^{δ-}···^{δ+}OH₂, ionic HO^{δ-}-H^{δ+}···O^{δ-}H₂, and long-bonded covalent HO··H—O⁺H₂ parts with HO-H^{δ-}···^{δ+}OH₂ being very much more in evidence than HO··H—O⁺H₂, where there would be expected to be much extra non-bonded repulsion. The movement of electrons from the oxygen atom to the O-H antibonding orbital on a neighboring molecule (HO-H^{δ-}···^{δ+}OH₂) both weakens the covalent O-H bond (so lengthening it) and reduces the HO-H··OH₂ 'hydrogen' bond. Hydrogen bonding affects all the molecular orbitals even including the inner O1s ([1a₁](#)) orbital which is bound 318 kJ mol⁻¹ (3.3 eV) less strongly in a tetrahedrally hydrogen bonded bulk liquid phase compared to the gas phase [1227]. [[Back to Top](#) ▲]

Water hydrogen bond length

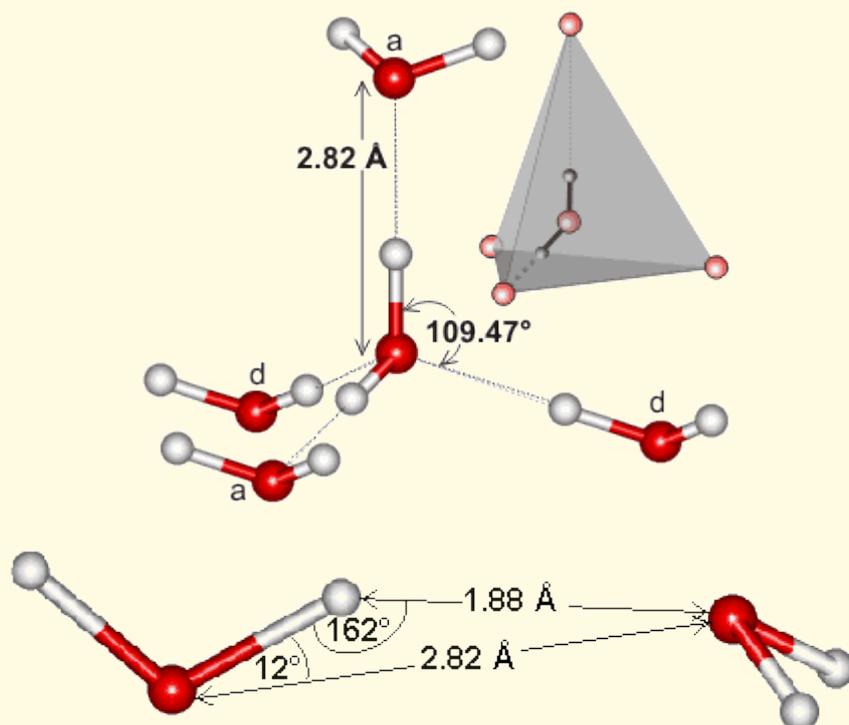
Although the hydrogen atoms are often shown along lines connecting the oxygen atoms, this is now thought to be indicative of time-averaged position only and unlikely to be found to a significant extent even in ice.



Liquid water consists of a mixture of short, straight [2405] and strong hydrogen bonds and long, weak and bent hydrogen bonds with many intermediate between these extremes. Short hydrogen bonds in water are strongly correlated with them being straighter [1083]. Proton magnetic shielding studies give the following average parameters for the instantaneous structure of liquid water at 4 °C; non-linearity, distances and variance; all increasing with temperature [458].

Note that the two water molecules below are not restricted to perpendicular planes and only a small proportion of hydrogen bonds are likely to have this averaged

structure.

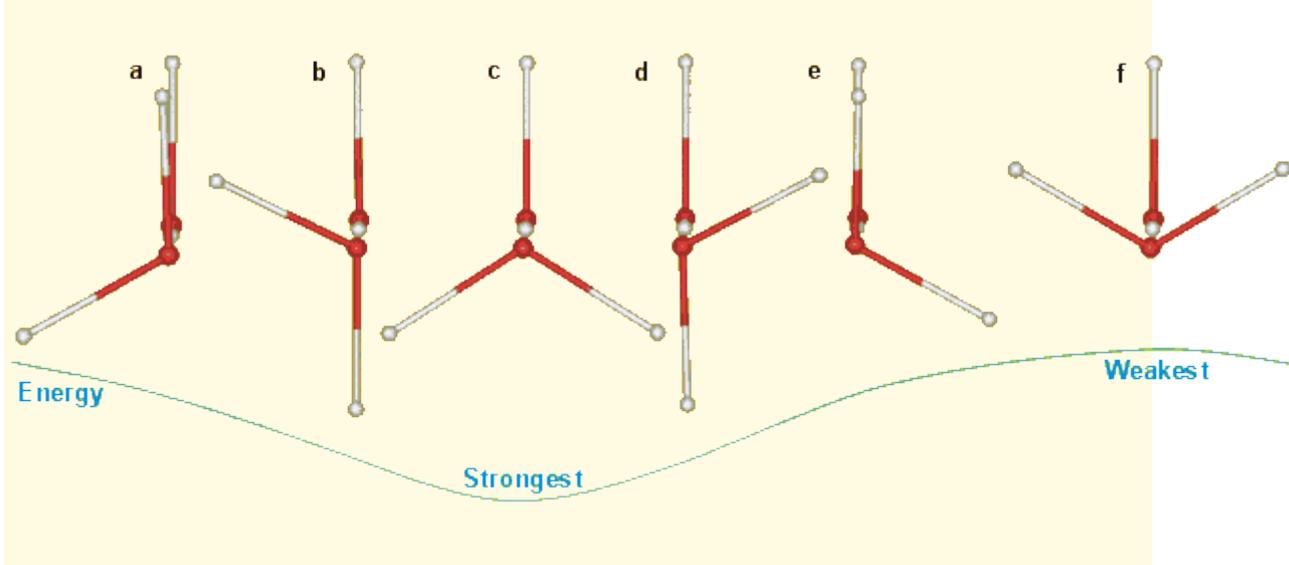


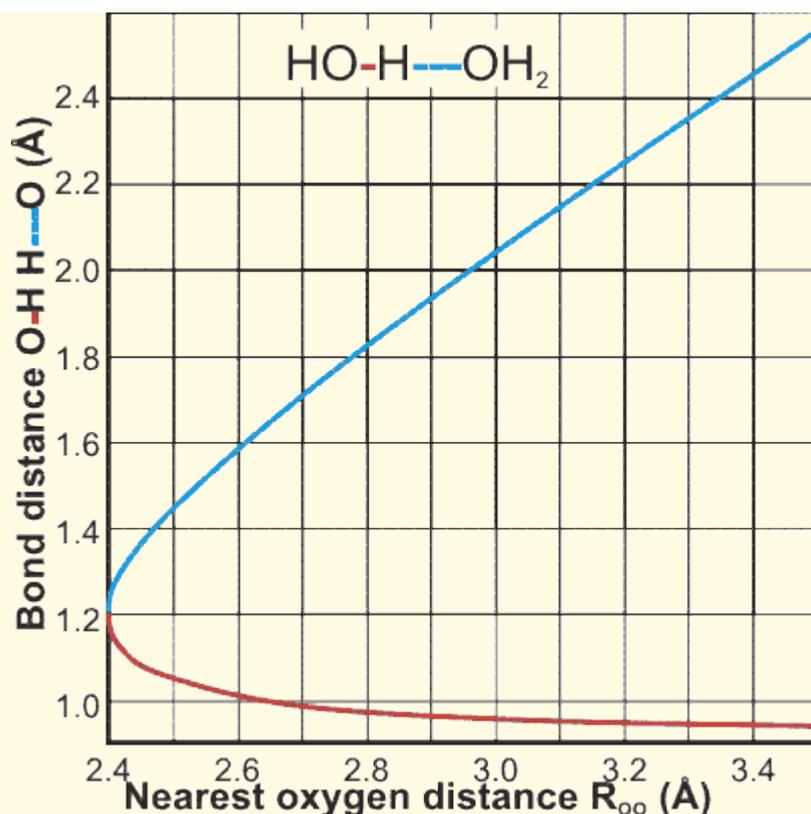
The hydrogen bond length of water varies with temperature and pressure. As the covalent bond lengths vary much less with temperature and pressure, most of the densification of ice Ih due to reduced temperature or increased pressure must be due to reduction in the hydrogen bond length. This hydrogen bond length variation can be shown from the changes in volume of ice Ih [818]. As hydrogen bond strength depends almost linearly on its length (shorter length giving stronger hydrogen bonding), it also depends almost linearly (outside extreme values) on the temperature and pressure [818].

Note that in liquid water, the hydrogen bonded arrangement of most molecules is not as symmetrical as shown here. In particular, the positioning of the water molecules donating hydrogen bonds to the accepting positions on a water molecule (that is, the water molecules behind in the diagram above, labeled 'd') are likely to be less tetrahedrally placed, due to the lack of substantial tetrahedrally positioned 'lone pair' electrons, than those water molecules that are being donated to from that water molecule (that

is, the water molecules top and front in the [diagram above](#), labeled 'a' [1224]. Also, the arrangement may well consist of one pair of more tetrahedrally arranged strong hydrogen bonds (one donor and one acceptor) with the remaining hydrogen bond pair (one donor and one acceptor) being either about 6 kJ mol⁻¹ weaker [573], less tetrahedrally arranged [373, 396] or bifurcated [573]; perhaps mainly due to the anticooperativity effects mentioned [elsewhere](#). Such a division of water into higher (4-linked) and lower (2-linked) hydrogen bond coordinated water has been shown by modeling [1349]. [X-ray absorption spectroscopy](#) confirms that, at room temperature, 80% of the molecules of liquid water have one (cooperatively strengthened) strong hydrogen bonded O-H group and one non-, or only weakly, bonded O-H group at any instant (sub-femtosecond averaged and such as may occur in [pentagonally hydrogen bonded clusters](#)), the remaining 20% of the molecules being made up of four-hydrogen-bonded tetrahedrally coordinated clusters [613]. There is much debate as to whether such structuring represents the more time-averaged structure, which is understood by some to be basically tetrahedral [1024].^f Even if the instantaneous hydrogen bonded arrangement is tetrahedral, distortions to the electron density distribution may cause the hydrogen bonds to have different strengths [1979, 2095].

The latest molecular parameters for water are given [elsewhere](#). The O···O distance in [ice lh](#) varies between 2.75 Å (0 K) and 2.764 Å (253 K). The energy of a linear hydrogen bond depends on the orientation of the water molecules relative to the hydrogen bond. In an unstrained tetrahedral network (such as [ice lh](#)) only the six structures below can arise with no structures at intermediate angles. The hydrogen bond energy depends particularly on the angle of rotation around the hydrogen bond, as below, due to the interaction between the molecular dipoles. Note that the hydrogen bonds in the structure pairs (a) and (e), and (b) and (d) have identical energies. In [ice lh](#) with no net dipole moment, the configurations with extreme *cis/trans* ratios have 56.3% *cis* (i.e. a+e+f) or 64.7% *trans* (that is, b+c+d) but the calculated difference in energies was only 0.12% (0.06 kJ mol⁻¹) [858]; much lower than the expected (several kJ mol⁻¹) difference in energy between the limiting *trans* and *cis* structures c and f. As a, c and e involve protons in hydrogen bonds parallel to the c-axis, their increased strength relative to b, d and f may be causative to the (0.3%) shortened c-axis in the [ice lh](#) unit cell.





There is a trade-off between the covalent and hydrogen bond strengths; the stronger is the H \cdots O hydrogen bond, the weaker the O-H covalent bond, and the shorter the O \cdots O distance [1928] (see right). Interestingly, this means that the O-H covalent part of the hydrogen bonds gets shorter as the temperature of the water increases. The weakening of the O-H covalent bond gives rise to a good indicator of hydrogen bonding energy; the fractional increase in its length determined by the increasing strength of the hydrogen bonding [217]; for example, when the pressure is substantially increased (\sim GPa) the remaining hydrogen bonds (H \cdots O) are forced shorter [655] causing the O-H covalent bonds to be elongated. Hydrogen bond strength can be affected by electromagnetic and magnetic effects. Dissociation is a rare event, occurring only twice a day that is, only once for every 10^{16} times the hydrogen bond breaks.

The anomalous properties of liquid water may be explained primarily on the basis of its hydrogen bonding [1530]. [[Back to Top](#) ▲]

Water hydrogen bond direction

An important feature of the hydrogen bond is that it possesses direction; by convention this direction is that of the shorter O-H (\rightarrow) covalent bond (the O-H hydrogen atom being donated to the O-atom acceptor atom on another H₂O molecule). In ¹H-NMR studies, the chemical shift of the proton involved in the hydrogen bond moves about 0.01 ppm K⁻¹ upfield to lower frequency (plus about 5.5 ppm further upfield to vapor at 100 °C); that is, becomes more shielded with reducing strength of hydrogen bonding [222, 1935] as the temperature is raised; a similar effect may be seen in water's ¹⁷O NMR, moving about 0.05 ppm K⁻¹ upfield plus 36-38 ppm further upfield to vapor at 100 °C. ^b Increased extent of hydrogen bonding within clusters results in a similar effect; that is, higher NMR chemical shifts with greater cooperativity [436], shorter hydrogen bonded O-H \cdots O distances [1616], smaller atomic volume of the hydrogen atom, greater positive charge on the hydrogen atoms and greater negative charge on the oxygen atoms. The bond strength depends on its length and angle, with the strongest hydrogen bonding in water existing in the short linear proton-centered H₅O₂[±] ion at about 120 kJ mol⁻¹. However, small deviations from linearity in the bond angle (up to 20°) possibly have a relatively minor effect [100]. The dependency on bond length is very important and has been shown to exponentially decay with distance [101]. Some researchers consider the hydrogen bond to be broken ^a if the bond length is greater than 3.10

Å or the bond angle less than 146° [173],^d although *ab initio* calculations indicate that most of the bonding energy still remains and more bent but shorter bonds may be relatively strong; for example, one of the hydrogen bonds in *ice-four* (143°). Similarly O \cdots H-O interaction energies below 10 kJ mol⁻¹ have been taken as indicative of broken hydrogen bonds although they are almost 50% as strong as 'perfect' hydrogen bonds and there is no reason to presuppose that it is solely the hydrogen bond that has been affected with no contributions from other interactions. Also, the strength of bonding must depend on the orientation and positions of the other bonded and non-bonded atoms and 'lone pair' electrons [525]. [Back to Top ▲]

Footnotes

^a The average molecular linear translational energy is $RT/2$. The average collision energy is RT (2.479 kJ mol⁻¹). 2% of collisions have energy greater than the energy required to break the bonds (9.80 kJ mol⁻¹, [274]) as determined by excess heat capacity. [Back]

^b Unfortunately this is difficult to use as a tool, however, due to the averaging of the shift and the complexity of the system. The spin-lattice relaxation times (T_1 , ~ 3.6 s, 25°C) of the water protons is also a function of the hydrogen bonding, being shorter for stronger bonding. The effect of solutes, however, shows the chemical shift and spin-lattice relaxation time are not correlated, as solutes may reduce the extent of hydrogen bonding at the same time as increasing its strength [281]. The spin-lattice relaxation time has been found to be two or three times greater than the spin-spin relaxation time, suggesting the presence of supramolecular structuring in the water [1664]. [Back]

^c Whether a hydrogen bond is considered broken or just stretched and/or bent should be defined by its strength but, as the isolated bond strength may be difficult to determine, this often remains a matter of an arbitrary definition based on distances and angles. An arrangement with strained geometry is very unlikely to last long. It may, however, occur during the breakage, formation or partner-switching (that is, bifurcation) of a hydrogen bond or arise transiently, due to thermal effects or other molecular interactions, in a long-lived hydrogen bond. The lifetime of a hydrogen bond (if more than 10^{-13} s) presents another measure of hydrogen bond formation but this also suffers from uncertainties in the definition of its geometry. Broken hydrogen bonds do not last long enough to present a free hydroxyl (O-H) infrared spectrum [1687]. Many hydrogen bonding definitions involve theoretically unsupported sharp cutoffs separating hydrogen-bonded from non-bonded molecules. Often these involve considerable transient breakage, which should be treated as an artifact of the definition employed [2417]. [Back]

^d Other workers use more generous parameters; for example, in [848], the hydrogen bond length must be less than 3.50 Å and the bond angle greater than 120° , whereas others suggest hydrogen bonding based on nearest neighbors [1432]. The importance of choosing a correct definition for the hydrogen bonds has been examined [1240]. The simple distance criterion of 2.50 Å for the H \cdots O distance was found very useful and cheapest in computational terms whereas methods based on energy proved poor. Adding further criteria, such as the bond angles, proved of marginal use [1240]. Six different hydrogen bond definitions are described in [1555] where they all gave the same qualitative picture of the spectroscopy. Using simulations, it has been proposed that purely geometric and energetic definitions are inaccurate as they may overestimate the connectivity and lifetime of hydrogen bonds and cannot distinguish improper relative orientations [1335]. Such overestimates may, however, be balanced by underestimates due to the cut-off parameters.

The difference between the O-H and H \cdots O bond lengths has also been suggested where water's hydrogen bond gives a difference with fluctuations around 0.75 Å (with bond angles $\sim 155^\circ - 180^\circ$) and the bond can be considered broken with O-H H \cdots O bond length differences varying with the bond angle (180° 1.67 Å; 135° 1.53 Å; 90° 1.40 Å), or more simply for hydrogen bonds of significant strength (covering about 99% of water hydrogen bonds) as where the O-H H \cdots O bond length difference is less than 1.25 Å [2025]. Some of the methods for defining water's hydrogen bond have been compared and reviewed [2028]. [Back]

^e The tetrahedral angle is $180 - \cos^{-1}(1/3)^\circ$; $109.47122^\circ = 109^\circ 28' 16.39''$. Tetrahedrality (q , the

$$q = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2$$

orientational order parameter) may be defined as , where ψ_{jk} is the angle formed by lines drawn between the oxygen atoms of the four nearest and hydrogen-bonded water molecules [169]. It equals unity for perfectly tetrahedral bonding (where $\cos(\psi_{jk}) = -1/3$) and averages zero (± 0.5 SD) for random arrangements, with a minimum value of -3. The density order parameter is [described elsewhere](#) and these and other geometric order parameters characterizing the local structure of liquid water and its tetrahedral arrangement have been described and compared. [\[Back\]](#)

^f The interpretation of the structure of water in terms of strands and rings of doubly-linked hydrogen-bonded molecules [613] was not confirmed by a Compton scattering study [1083] where the data was consistent with 3.9 hydrogen bonds ($R_{oo} \leq 3.2\text{\AA}$) around each water molecule, and has been disputed by another X-ray absorption spectroscopic study [690a], which presents a case for the 'non-, or only weakly, bonded O-H groups' to form the majority of O-H groups present and that these groups are more strongly bonded. Also, Bowron challenges the above interpretation (that is, [613]) in the Discussion included in [746] and a Raman study supports the fully tetrahedrally hydrogen bonded model [875]. This dispute was thought to have been resolved by an *ab initio* molecular dynamics study [832] that shows 170 fs fluctuations of 2.2-fold strength between the two donor hydrogen bonds from each water molecule whilst the overall geometric connectivity is retained, in line with the hypothesis first presented above. However this study [832] has attracted serious criticism [1159], leaving its conclusions seemingly unproven. Recent *ab initio* calculations of the x-ray cross section of liquid water shows only 20% broken hydrogen bonds are present [1059], other *ab initio* calculations show primarily tetrahedral coordinated water molecules [1654] and a novel force field for water, developed from first principles, gives 3.8 shared tetrahedrally coordinated hydrogen bonds per water molecule [1189]. Also, an *ab initio* quantum mechanical/molecular mechanics molecular dynamics simulation study shows that although the time averaged hydrogen bonding is about four shared hydrogen bonds per water molecule, the instantaneous value is significantly lower at about 2.8 shared hydrogen bonds per water molecule [922]. Tetrahedrally-coordinated water seems most accepted at the present time [2095], but it is clear that a mixture of a minority of higher (4-linked) and a majority of lower (2-linked) hydrogen bond coordinated water can be fitted equally well with the experimental data [1350]. [\[Back\]](#)