Hydrogen Bonding in Water

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Hydrogen bonds

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Hydrogen bonding occurs when an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them [99]. Typically hydrogen bonding occurs where the partially positively charged hydrogen atom lies between partially negatively charged oxygen and/or nitrogen atoms, but is also found elsewhere, such as between fluorine atoms in HF$_2^-$ (a very strong hydrogen bond at 163 kJ mol$^{-1}$) and between water and the smaller halide ions $\text{F}^-$, $\text{Cl}^-$ and $\text{Br}^-$ (for example, HO-H⋯Br$, [178, 1190]; the strength of hydrogen bonding reducing as the halide radius increases), and to a much smaller extent to $\text{I}^-$ [190] and even xenon [941], (a very weak hydrogen bond at 2 kJ mol$^{-1}$). Even very weak C-H⋯OH$_2$ hydrogen bonds (≈ 4 kJ mol$^{-1}$) are being increasingly recognized [1293]. In theoretical studies, strong hydrogen bonds even occur to the hydrogen atoms in metal hydrides (for example, LiH⋯HF; [217]). The current view of the hydrogen bond has been reviewed [1462]. Hydrogen bond strength is given by the weaker of the two interactions of the flanking atoms with the central hydrogen atom and is strongest when these interactions are equal [1653]. Hydrogen bonding is characterized by its preferred dimensions, molecular orientation, approximate linearity and changes in infrared frequency and intensity. [Back to Top]

Water hydrogen bonds

Liquid water is exceptional in having approximately as many hydrogen bonds as it has covalent bonds. In water's hydrogen bonds, the hydrogen atom is covalently attached to the oxygen of a water molecule (492.2148 kJ mol$^{-1}$ [350]) but has (optimally) an additional attraction (about 23.3 kJ mol$^{-1}$) [168]; almost 5 $\times$ the average thermal collision fluctuation at 25°C$^{32}$ to a neighboring oxygen atom of another water molecule that is far greater than any included van der Waals interaction.$^1$ Hydrogen bonds within heavy water are stronger.$^{33}$ Water's hydrogen bonding holds water molecules up to about 15% closer than if 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-$H_2O$, possessing no ground state spin, are stronger and last longer than hydrogen bonds between ortho-$H_2O$ [1150].

The hydrogen bond in water is part (about 90%) electrostatic and part (about 10%) covalent [96] and may be approximated by bonds made up of covalent HO-H⋯$\cdot\cdot\cdot$OH$_2$, ionic HO$^-$-H$^+\cdot\cdot\cdot$O$^-$H$_2$, and long-bonded covalent HO$^-$H—O$^+$H$_2$ parts with HO-H⋯$\cdot\cdot\cdot$OH$_2$ being very much more in evidence than HO$^-$H—O$^+$H$_2$, where there would be expected to be much extra non-bonded repulsion. Hydrogen bonding affects all the molecular orbitals even including the inner O1s ($1\alpha_1$) 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].

Clusters linked by extensive hydrogen bonding can be considered as being connected by extensive, but complementary, electron delocalization. As electrons are not held by individual molecules but are easily distributed amongst water clusters they can give rise to coherent regions [1691] interacting with local electromagnetic radiation. The water protons are also not held by individual molecules but may switch partners in an ordered manner within distinct networks [1699]. Over short hydrogen-bonded water wires (see right) there can be correlated movement of protons and electrons due to quantum fluctuations [2025] reinforcing the concept of water not being a molecular liquid.

X-ray spectroscopic probing indicates that the electron transitions between molecular orbitals (changing with the local hydrogen bonding topology) with differing such contributions may shift on a time scale of less than a femtosecond. Contributing to the strength and dynamics [1673] of water's hydrogen bonding are nuclear quantum effects (zero point vibrational energy) which bias the length of the O-H covalent bond longer than its 'equilibrium' position length (as the shorter HO-H⋯$\cdot\cdot\cdot$OH$_2$ hydrogen bonds are stronger), so also increasing the average dipole moment [554]. On forming the hydrogen bond, the donor hydrogen atom stretches away from its oxygen atom and the
acceptor lone-pair stretches away from its oxygen atom and towards the donor hydrogen atom [585], both oxygen atoms being pulled towards each other. The stronger the hydrogen bond, the longer lived and the less easy does the proton escape the two water molecules involved.

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 H_2O molecule). In \(^1\)H-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 \(^17\)O 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 H_2O\(^+\) 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 if the bond length is greater than 3.10 Å or the bond angle less than 146° [173],\(^c\) although \textit{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].
There is a trade-off between the covalent and hydrogen bond strengths; the stronger is the H⋯O bond, the weaker the O-H covalent bond, and the shorter the O⋯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 (~ GPa) the remaining hydrogen bonds (H⋯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 1016 times the hydrogen bond breaks.

The anomalous properties of liquid water may be explained primarily on the basis of its hydrogen bonding [1530].

**Hydrogen bond cooperativity**

When a hydrogen bond forms between two water molecules, the redistribution of electrons changes the ability for further hydrogen bonding. The water molecule donating the hydrogen atom has increased electron density in its 'lone pair' region [577], which encourages hydrogen bond acceptance, and the accepting water molecule has reduced electron density centered on its hydrogen atoms and its remaining 'lone pair' region [577], which encourages further donation but discourages further acceptance of hydrogen bonds. This electron redistribution thus results in both the cooperativity (e.g. accepting one hydrogen bond encourages the donation of another) and anticooperativity (for example, accepting one hydrogen bond discourages acceptance of another) in hydrogen bond formation in water networks. Cooperative hydrogen bonding increases the O-H bond length whilst causing a 20-fold greater reduction in the H⋯O and O⋯O distances [436]. The increase in bond length has been correlated with the hydrogen bond strength and resultant O-H stretch vibrations [1318]. Thus O⋯O distances within clusters are likely to be shorter than those at the periphery, in agreement with the icosahedral cluster model. If the hydrogen bond is substantially bent then it follows that the bond strength is weaker. The main criteria to determine the strength of hydrogen bonds are their (relatively inaccurately determined) intermolecular distances and the (more precise) wavenumbers of their stretching vibrational modes and those of the donor hydrogen covalent bond. Any factors, such as polarization, that reduces the hydrogen bond length, is expected to increase its covalency. There is still some dispute over the size of this covalency, however any covalency will increase the network stability relative to purely electrostatic effects. The hydrogen bond in water dimers is sufficiently strong to result in the dimers persisting within the gas state at significant concentrations [1977] (for example, ~0.1% H₂O at 25 °C and 85% humidity) to contribute significantly to the absorption of sunlight and atmospheric reaction kinetics [266]. The molecular orbitals involved in the hydrogen bonding between two water molecules and five water molecules in a cyclic pentamer are given on other pages.

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 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 \[818\].

The latest molecular parameters for water are given elsewhere. The O····O distance in ice Ih 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.

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 below. 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 \[1024\]. Even if the instantaneous hydrogen bonded arrangement is tetrahedral, distortions to the electron density distribution may cause the hydrogen bonds to have different strengths \[1979, 2095\].

Liquid water contains by far the densest hydrogen bonding of any solvent with almost as many hydrogen bonds as there are covalent bonds. These hydrogen bonds can rapidly rearrange in response to changing conditions and environments (for example, solutes). The hydrogen bonding patterns are random in water (and ice Ih); for any water molecule chosen at random, there is equal probability (50%) that the four hydrogen bonds (that is, the two hydrogen donors and the two hydrogen acceptors) are located at any of the four sites around the oxygen. Water molecules surrounded by four hydrogen bonds tend to clump together, forming clusters, for both statistical \[11\] and energetic reasons. Hydrogen bonded chains (that is, O-H····O-H····O) are cooperative \[379\]; the breakage of the first bond is the hardest, then the next one is weakened, and so on (see the cyclic water pentamer). Thus unzipping may occur with complex macromolecules held together by hydrogen bonding, for example, nucleic acids. Such cooperativity is a fundamental property of liquid water where hydrogen bonds are up to 250% stronger than the single hydrogen bond in the dimer \[77\]. A strong base at the end of a chain may strengthen the bonding further. The cooperative nature of the hydrogen bond means that acting as an acceptor strengthens the water molecule acting as a donor \[76\]. However, there is an anticooperative aspect in so far as acting as a donor weakens the capability to act as another donor, for example, O····H-O-H····O \[77\]. It is clear therefore that a water molecule with two hydrogen bonds where it acts as both donor and acceptor
is somewhat stabilized relative to one where it is either the donor or acceptor of two. This is the reason why it is suspected that the first two hydrogen bonds (donor and acceptor) give rise to the strongest hydrogen bonds [79]. An interesting way of describing the cooperative/anticooperative nature of the water dimer hydrogen bond is to use the nomenclature d'a'DAd''a'" where DA represents the donor-acceptor nature of the hydrogen bond, the d'a' represents the remaining donor-acceptor status of the donating water molecule and d"a'" represents the remaining donor-acceptor status of the accepting water molecule [852]. Individually, the most energetically favored donating water molecules have the structures 02D, 12D, 01D and 11D with 00D and 10D disfavored whereas the most energetically favored accepting water molecules have the structures A20, A21, A10 and A11 with A00 and A01 disfavored.

**Water hydrogen bonding**

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Using quantum chemical calculation of different clusters of water molecules has shown that the hydrogen bonding strength can vary for as much as 90% between extreme cases of cooperativity and anti-cooperativity with cooperativity increasing (~3 kJ mol$^{-1}$) the bond strength and reducing (~0.03 Å) the hydrogen bond length per added molecule and anti-cooperativity reversing these effects by the same amounts. The hydrogen bond strength is computed to vary for as much as 90% between extreme cases of cooperativity and anti-cooperativity [1829]. From this calculation, the difference in effect between the 2 anticooperative and 4 cooperative interactions in the above table would be ~18 kJ mol$^{-1}$ and ~0.18 Å.

Cations may induce strong cooperative hydrogen-bonding around them due to the polarization of water O-H by cation-lone pair interactions (Cation···O-H···O-H). Luck et al [78] introduced a cooperativity factor for this effect, which varied as the Hofmeister series from K$^+$ (1.08) to Zn$^{2+}$ (2.5). Total hydrogen bonding around ions may be disrupted however as if the electron pair acceptance increases (for example, in water around cations) so the electron pair donating power of these water molecules is reduced; with opposite effects in the hydration water around anions. These changes in the relative hydration ability of salt solutions are responsible for the swelling and deswelling behavior of hydrophilic polymer gels [317].

The substantial cooperative strengthening of hydrogen bond in water is dependent on long range interactions [98]. This cooperative effect may be stronger in chains of ortho-water molecules due to spin coupling [2041]. Breaking one bond generally weakens those around whereas making one bond generally strengthens those around and this, therefore, encourages larger clusters, for the same average bond density. The hydrogen-bonded cluster size in water at 0 °C has been estimated to be 400 [77, 1791]. Weakly hydrogen-bonding surface restricts the hydrogen-bonding potential of adjacent water so that these make fewer and weaker hydrogen bonds. As hydrogen bonds strengthen each other in a cooperative manner, such weak bonding also persists over several layers and may cause locally changed solvation. Conversely, strong hydrogen bonding will be evident at distance. The weakening of hydrogen bonds, from about 23 kJ mol$^{-1}$ to about 17 kJ mol$^{-1}$, is observed when many bonds are broken at superheating temperatures (> 100 °C) so reducing the cooperativity [173]. The breakage of these bonds is not only due to the more energetic conditions at high temperature but also results from a related reduction in the hydrogen bond donating ability by about 10% for each 100 °C increase [218]. The loss of these hydrogen bonds results in a small increase in the hydrogen bond accepting ability of water, due possibly to increased accessibility [218].

Every hydrogen bond formed increases the hydrogen bond status of two water molecules and every hydrogen bond broken reduces the hydrogen bond status of two water molecules. The network is essentially complete at ambient temperatures; that is, (almost) all molecules are linked by at least one unbroken hydrogen bonded pathway. Hydrogen bond lifetimes are 1 - 20 ps [255] whereas
broken bond lifetimes are about 0.1 ps with the proportion of 'dangling' hydrogen bonds persisting for longer than a picosecond being insignificant [849]. Broken bonds are basically unstable [849] and will probably re-form to give same hydrogen bond (as shown by the slow ortho-water/para-water equilibrium process [410]), particularly if the other three hydrogen bonds are in place; hydrogen bond breakage being more dependent on the local structuring rather than the instantaneous hydrogen bond strength [833]. If not, breakage usually leads to rotation around one of the remaining hydrogen bond(s) [673] and not to translation away, as the resultant 'free' hydroxyl group and 'lone pair' are both quite reactive. Also important, if seldom recognized, is the possibility of the hydrogen bond breaking, as evidenced by physical techniques such as IR, Raman or NMR and caused by loss of hydrogen bond 'covalency' due to electron rearrangement, without any angular change in the O-H⋯O atomic positions. Thus, clusters may persist for much longer times [329] than common interpretation of data from these methods indicates. Evidence for this may be drawn from the high degree of hydrogen bond breakage seen in the IR spectrum of ice [699], where the clustering is taken as lasting essentially forever. [Back to Top ▲]

Hydrogen bonds and solubility
As is clear from the origin of the words used, water is a good solvent for hydrophilic solutes (such as alcohols) but a poor solvent for hydrophobic solutes (such as the noble gasses). The solubilities change significantly with temperature and these changes have been correlated with the hydrogen bonding donation (acidity) and acceptance (basicity) changes in the water. Both these factors reduce with increasing temperature but to different extents [1830]. At 300 °C the solvent properties of water to hydrophilic solutes are similar to those of nitrobenzene or acetonitrile at 25 °C but hydrophobic solutes remain poorly soluble [1830].

Rearranging hydrogen bonds
Water's hydrogen bonds only reorient when there is an available partner able to accept the bond, with the strength of the broken hydrogen bond playing little or no role [1135]. The molecular orbitals of water indicate that the two 'lone pairs' of electrons do not give distinct directed electron density in isolated molecules, with tetrahedral nature of water's hydrogen bonding due to four-coordination involving two donor and two acceptor hydrogen bonds. However trigonal (approximately planar) hydrogen bonding is also possible with two donor and one acceptor hydrogen bonds associated with individual water molecules. The lack of substantial tetrahedrally positioned 'lone pair' electrons may ease this process, at a cost of one hydrogen bond energy. Also the acceptor hydrogen bond in three coordinated but tetrahedral arrangements (two donor and one acceptor hydrogen bonds with one vacant acceptor site) can slide through a planar arrangement to
the vacant tetrahedral site without breaking. This flexibility in the hydrogen bonding topology facilitates hydrogen-bonding rearrangements. [Back to Top]

Bifurcated hydrogen bonds

Bifurcated hydrogen bonds (where both hydrogen atoms from one water molecule are hydrogen bonding to the same other water molecule, or one hydrogen atom simultaneously forms hydrogen bonds to two other water molecules) have just under half the strength of a normal hydrogen bond (per half the bifurcated bond) and present a low-energy route for hydrogen-bonding rearrangements [255]. They allow the constant randomization of the hydrogen bonding within the network. However, it should be noted that they require the breakage of two hydrogen bonds; one hydrogen bond to form the bifurcated arrangement and another to make way for a different hydrogen bond to form. Any necessary rotation may also involve bending or stretching other hydrogen bonds. Bifurcation of hydrogen bonds cannot cause their net breakage and only occur when a broken hydrogen bond releases a lone pair to accept the incoming hydrogen bond donor [1135]. Trifurcated hydrogen bonds (where one hydrogen atom simultaneously forms hydrogen bonds to three other water molecules, forming a tetrahedral face) may also form but only have about one sixth the strength of a normal hydrogen bond per third of the bifurcated bond [573], require free lone pairs on all three bound water molecules and the rest of local cluster must also be poorly hydrogen bonded. [Back to Top]
**Information transfer**

Hydrogen bonding carries information about solutes and surfaces over significant distances in liquid water. The effect is synergistic, directive and extensive. Thus, in the diagram opposite, strong hydrogen-bonding in molecule (1), caused by solutes or surfaces, will be transmitted to molecules 2 and 3, then to 5 and 6 and then as combined power to 8.

The effect is reinforced by additional polarization effects and the resonant intermolecular transfer of O-H vibrational energy, mediated by dipole-dipole interactions and the hydrogen bonds [142]. Reorientation of one molecule induces corresponding motions in the neighbors.

Thus solute molecules can 'sense' (for example, affect each other's solubility) each other at distances of several nanometers and surfaces may have effects extending to tens of nanometers. This long range correlation of molecular orientation has recently been confirmed using hyper-Rayleigh light scattering [152] and is a reason for the high dielectric constant of water and the consequent reduction in this dielectric constant as the temperature is raised and the number of hydrogen bonds is reduced [239]. Where water molecules are next to flat hydrophobic surfaces, and unable to form extensive clathrate structuring, some hydrogen bonds must be broken and the water molecules will tend to change orientation, from one hydrogen bond directed orthogonally away from the surface (as in clathrates) to one hydrogen bond directed orthogonally towards the surface, in order to minimize the energy requirement. Also the water molecules tend to collapse into their shallow energy minima due to increased non-bonded interactions. Although there may be a consequentially increased density in the first water layer, the second and subsequent water shells compensate by forming stronger hydrogen bonds and a less dense structure. Consequences of this include differential solvation properties affecting surface absorption.

![Diagram](image)

Hydrogen bonding rearrangement offers a low energy pathway for the transfer of hydrogen atoms during tautomerism, in a way similar to Grothuss mechanism for hydrogen ion transport. Shown opposite is adenine tautomerism that can give rise to Adenine - Cytosine (mutation producing) pairing, which uses the rare tautomer on the left.

**Footnotes**

\(^{a1}\) 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 ΔS = 37 J deg\(^{-1}\) 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 (see below). 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 \( \Delta G \) 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 \( \text{Ih} \) 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]. [Back]

\(^{a2}\) The average molecular linear translational energy is \( RT/2 \). The average collision energy is \( (2.479 \text{ kJ mol}^{-1} ) \). 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]

\(^{a3}\) Unexpectedly for such an important parameter, there is some dispute as to whether the hydrogen bonds in \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) are longer or shorter or the same length. One report states (opposite to earlier conclusions [554]) that \( \text{D}_2\text{O} \) 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 \( \text{D}_2\text{O} \) 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 \( \text{H}_2\text{O} \) [1485]. More recently the hydrogen bonds in \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) have been found to be about the same length due to compensatory quantum effects [1752]. Hydrogen bond in \( \text{T}_2\text{O} \) are expected to be stronger still. Thus given the choice, hydrogen bonds form with the preference O-T····O > O-D····O > O-H····O. [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 (\( T_1 \), \( \sim 3.6 \text{ s, 25 °C} \)) 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 \( 10^{-13} \text{ s} \)) 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]. [Back]

\(^{c2}\) 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····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····O bond lengths has also been suggested where water's hydrogen bond gives a difference with fluctuations around 0.75 Å (with bond angles ~155° - 180°) and the bond can be considered broken with O-H H····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····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]

d There is still some controversy surrounding this partial covalency with both for (for example, [411] gives the 3a1 orbital most responsible for the hydrogen bonding via orbital mixing), against (for example, [437] favors 'antibonding' rather than bonding due to the charge transfer and neutral [438] in the recent literature. If the water hydrogen bond is considered within the context of the complete range of molecular hydrogen bonding then it appears most probable that it is not solely electrostatic [447]; indeed the dissociation of water, the formation of the symmetrical 'Zundel' H$_2$O$_2^+$ ion, the continuous transformation of ice VII to ice X and the lower ionization potential for liquid water relative to water vapor would all seem to indicate a continuity of electron sharing between water molecules. Although N-H····N and N-H····O hydrogen bonds are known to be weaker than the O-H····O hydrogen bonds in water, there is clear evidence for these bonds' covalent natures from NMR. In nucleic acids, inter-nucleotide N-H····N coupling ($^3J_{NN}$ using $^{15}$N nuclei) confirms some covalent nature in the N-H····N hydrogen bond [779]. Also, 3-bond NMR ($^3J_{NC}$) splitting has been found through peptide N-H····O=C hydrogen bonds in proteins, confirming some covalent nature in the N-H····O hydrogen bond [780]. The current definition for a hydrogen bond (see h below) involves the necessity of evidence for bond formation which necessarily requires electron delocalization. [Back]

e The O-H vibrational frequency does not follow the O····O hydrogen bond length exactly due to dispersion of the hydrogen bond O-H····O angle [439]. [Back]

f However note that some hydrogen bonds may distort a hydrogen bonded cluster such that when such a bond breaks the detached cluster may form a more optimum tetrahedrally bonded arrangement with lower energy and thus reclaiming some or most of the energy lost by bond breakage. [Back]

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$_{OC}$≤3.2Å) 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
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]

A recent historical review of hydrogen bonding is available [1950]. The hydrogen bond in water was first suggested by Latimer and Rodebush in 1920 [789]. Hydrogen bonds are different from van der Waals dispersion interactions, but this difference is blurred in some instances. The key to the difference is that hydrogen bonding usually involves partial covalent bond formation and a mutual penetration of atoms within their van der Waals radii. The IUPAC definition is 'The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.' [1702]. The most important criteria for a hydrogen bond are: (i) the H in the X–H group is more electropositive than X and (ii) the physical forces involved in hydrogen bonding should include attractive electrostatic forces, i.e. it should not be primarily dispersive forces [1461].

Hydrogen bonds in other molecules, such as DNA, also possess considerable covalent character [1867]. [Back]

The van der Waals dispersive attraction has been estimated as high as about 5.5 kJ mol⁻¹ [548] based on isoelectronic molecules at optimal separation, but is likely to be repulsive within a hydrogen bond due to the close contact (see for example, [736]). Separating the hydrogen bond components, as below, helps our understanding, although in reality these components are combined.

<table>
<thead>
<tr>
<th>Hydrogen bond contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Attraction/repulsion</strong></td>
</tr>
<tr>
<td>++  electrostatic attraction</td>
</tr>
<tr>
<td>long range interaction (&lt; 30 Å) based on point charges, or on dipoles plus quadrupoles, and so on. They may be considered as varying with distance.</td>
</tr>
<tr>
<td>++  polarization attraction</td>
</tr>
<tr>
<td>due to net attractive effects between charges and electron clouds (&lt; 8 Å), which may increase cooperatively dependent on the local environment. They may be considered as varying with distance. This net attractive effect may contain a small repulsive element due to slightly increased electron cloud overlap.</td>
</tr>
<tr>
<td>+    covalency attraction</td>
</tr>
<tr>
<td>highly directional and increases on hydrogen bonded cyclic cluster formation. It is very dependent on the spatial arrangement of the molecules within the local environment (&lt; 6 Å)</td>
</tr>
<tr>
<td>+    dispersive attraction</td>
</tr>
<tr>
<td>interaction (&lt; 6 Å) due to coordinated effects of neighboring electron clouds. They may be considered as varying with distance.</td>
</tr>
<tr>
<td>--  electron repulsion</td>
</tr>
<tr>
<td>very short range interaction (&lt; 4 Å) due to electron cloud overlap. They may be considered as varying with distance.</td>
</tr>
</tbody>
</table>

In an unstrained tetrahedral network (such as ice Ih) only the six structures below can arise without 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 Ih 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 Ih unit cell.

\[\text{Energy}\]

\[\text{Strongest}\]

\[\text{Weakest}\]

\[^{k}\] The approximate bond energies (kJ mol\(^{-1}\)) as derived from DO-H\(\cdots\)OD\(_2\) in D\(_2\)O [1932]. The steps in H\(_2\)O are likely to be closer to 5 kJ mol\(^{-1}\). [Back]

Source: [http://www1.lsbu.ac.uk/water/hbond.html](http://www1.lsbu.ac.uk/water/hbond.html)