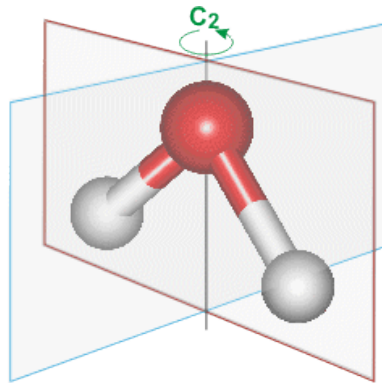


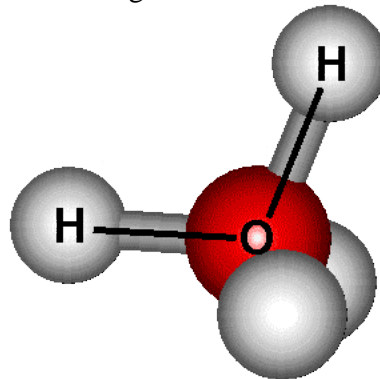
# Water Molecule Structure

- ◀ Water's molecular vibrations and absorptions
- ▼ Water's lone pairs
- ▼ Water electronic structure
- ▼ Water dimer
- ▼ Water models
- ▼ Water reactivity

Water molecules<sup>i</sup> are tiny and V-shaped with molecular formula  $\text{H}_2\text{O}$ <sup>a</sup> and molecular diameter about  $2.75 \text{ \AA}$ .<sup>g</sup> In the liquid state, in spite of 80% of the electrons being concerned with bonding, the three atoms do not stay together as the hydrogen atoms are constantly exchanging between water molecules due to protonation/deprotonation processes. Both acids and bases catalyze this exchange and even when at its slowest (at pH 7), the average time for the atoms in an  $\text{H}_2\text{O}$  molecule to stay together is only about a millisecond. As this brief period is, however, much longer than the timescales encountered during investigations into water's hydrogen bonding or hydration properties, water is usually treated as a permanent structure.



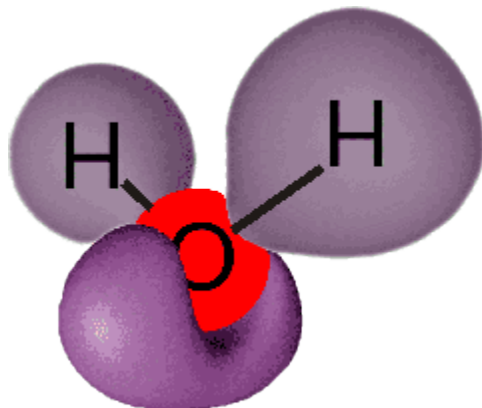
Water molecules ( $\text{H}_2\text{O}$ ) are symmetric (point group  $C_{2v}$ ) with two mirror planes of symmetry and a 2-fold rotation axis. The hydrogen atoms may possess parallel or antiparallel nuclear spin.<sup>h</sup> The water molecule consists of two light atoms (H) and a relatively heavy atom (O). The approximately 16-fold difference in mass gives rise to its ease of rotation and the significant relative movements of the hydrogen nuclei, which are in constant and significant relative movement.



Note. This cartoon of water does not represent its actual outline, which is more rotund (see below).

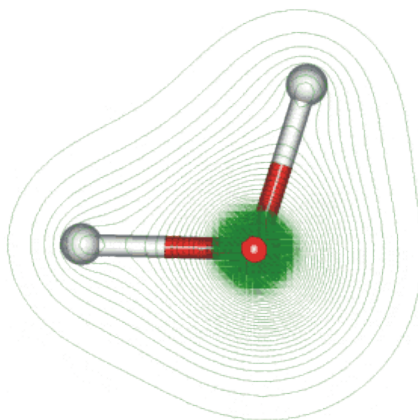
### Water's lone pairs?

The water molecule is often described in school and undergraduate textbooks of as having four, approximately tetrahedrally arranged,  $sp^3$ -hybridized electron pairs, two of which are associated with hydrogen atoms leaving the two remaining lone pairs. In a perfect tetrahedral arrangement the bond-bond, bond-lone pair and lone pair-lone pair angles would all be  $109.47^\circ$  and such tetrahedral bonding patterns are found in condensed phases such as hexagonal ice.

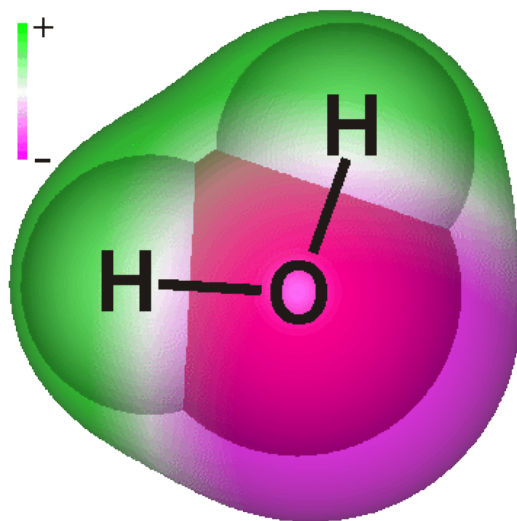


*Ab initio* calculations on isolated molecules, however, do not confirm the presence of significant directed electron density where lone pairs are expected. The negative charge is more evenly smeared out along the line between where these lone pairs would have been expected, and lies closer to the center of the O-atom than the centers of positive charge on the hydrogen atoms (as left).

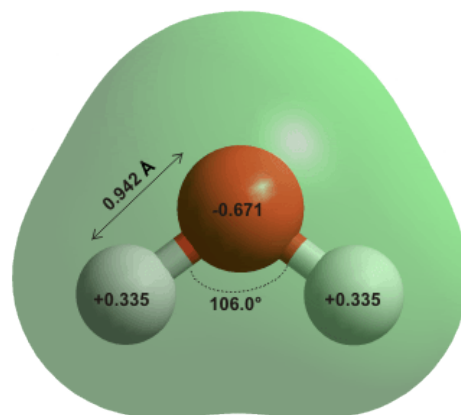
Early 5-point molecular models, with explicit negative charge where the lone pairs are purported to be, fared poorly in describing hydrogen bonding, but more recent models show some promise. Although there is no apparent consensus of opinion [116], such descriptions of substantial  $sp^3$ -hybridized lone pairs in the isolated water molecule should perhaps be avoided [117], as an  $sp^2$ -hybridized structure (plus a  $p_z$  orbital) is indicated. This rationalizes the formation of (almost planar) trigonal hydrogen bonding that can be found around some restricted sites in the hydration of proteins and where the numbers of hydrogen bond donors and acceptors are unequal.



Note that the average electron density around the oxygen atom is about 10x that around the hydrogen atoms.



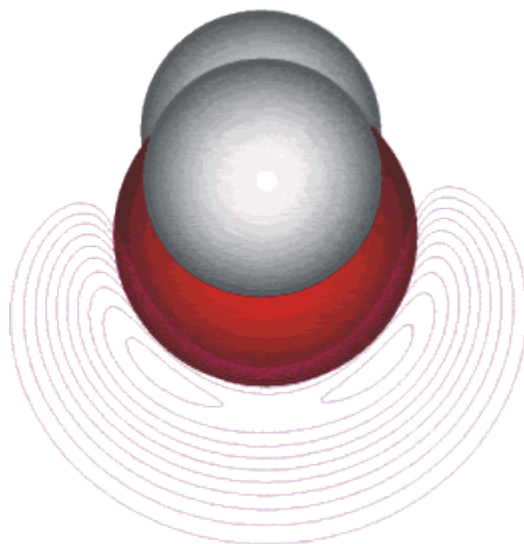
The approximate shape and charge distribution of water



The electron density distribution for water is shown above right with some higher density contours around the oxygen atom omitted for clarity. The polarizability of the molecule is almost isotropic, centered around the O-atom ( $1.4146 \text{ \AA}^3$ ) with only small polarizabilities centered on the H-atoms ( $0.0836 \text{ \AA}^3$ ) [736]. Parameters using *ab initio* calculations with the 6-31G\*\* basis set are shown right.<sup>j</sup> For an isolated  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$  or  $\text{H}_2^{18}\text{O}$  molecule, the more exact calculated O-H length is  $0.957854 \text{ \AA}$  and the H-O-H angle is  $104.500^\circ$  ( $\text{D}_2^{16}\text{O}$ ,  $0.957835 \text{ \AA}$ ,  $104.490^\circ$ ) [836]. The charge distribution depends significantly on the atomic geometry and the method for its calculation but is likely to be about  $-0.7e$  on the O-atom (with the equal but opposite positive charge equally divided between the H-atoms) for the isolated molecule [778].<sup>d</sup> The experimental values for gaseous water molecule are O-H length  $0.95718 \text{ \AA}$ , H-O-H angle  $104.474^\circ$  [64].<sup>e</sup>

These values are not maintained in liquid water, where *ab initio* (O-H length  $0.991 \text{ \AA}$ , H-O-H angle  $105.5^\circ$  [90]) and diffraction studies (O-H length  $1.01 \text{ \AA}$ , O-D length  $0.98 \text{ \AA}$  [1485]; O-H length  $0.990 \text{ \AA}$ , O-D length  $0.985 \text{ \AA}$  [1884]; O-D length  $0.970 \text{ \AA}$ , D-O-D angle  $106^\circ$  [91])<sup>f</sup> suggest slightly greater values, which are caused by the hydrogen bonding weakening the covalent bonding and reducing the repulsion between the electron orbitals. These bond lengths and angles are likely to change, due to polarization shifts, in different hydrogen-bonded environments and when the water molecules are

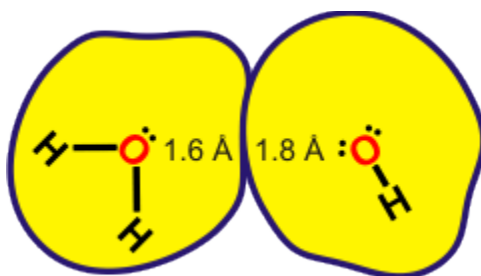
bound to solutes and ions. Commonly used molecular models use O-H lengths of between 0.957 Å and 1.00 Å and H-O-H angles of 104.52° to 109.5°. [Back to Top ▲]



### Water electronic structure

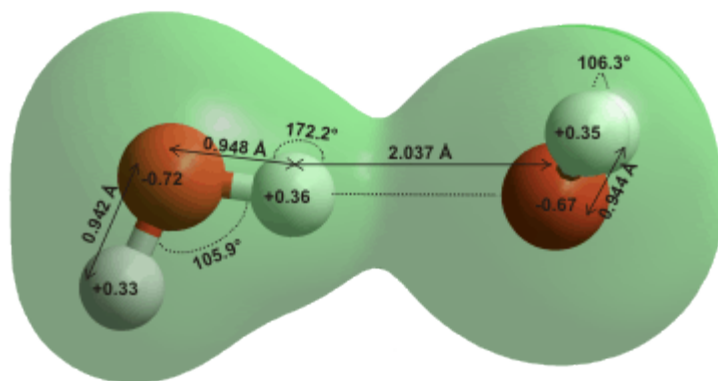
The electronic structure has been proposed as  $1s_{\text{O}}^{2.00} 2s_{\text{O}}^{1.82} 2p_{x\text{O}}^{1.50} 2p_{z\text{O}}^{1.12} 2p_{y\text{O}}^{2.00} 1s_{\text{H1}}^{0.78} 1s_{\text{H2}}^{0.78}$  [71], however it now appears that the 2s orbital may be effectively unhybridized with the bond angle expanded from the (then) expected angle of 90° due to the steric and ionic repulsion between the partially-positively charged hydrogen atoms (as proposed by Pauling over 50 years ago [99]). The molecular orbitals of water,  $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ , are shown on another page.

Shown opposite is the electrostatic potential associated with the water structure. Although the lone pairs of electrons do not appear to give distinct directed electron density in isolated molecules, there are minima in the electrostatic potential in approximately the expected positions.



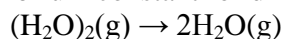
Van der Waals radii [206]

The mean van der Waals diameter of water has been reported as identical with that of isoelectronic neon (2.82 Å) [112]. Molecular model values and intermediate peak radial distribution data indicates however that it is somewhat greater (~3.2Å). The molecule is clearly not spherical, however, with about a ±5% variation in van der Waals diameter dependent on the axis chosen; approximately tetrahedrally placed slight indentations being apparent opposite the (putative) electron pairs. [Back to Top ▲]



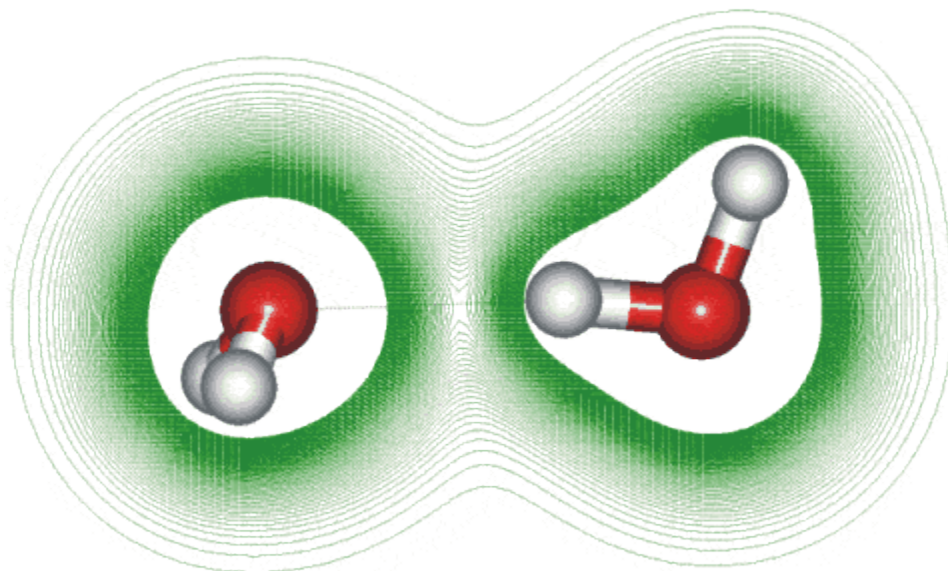
### Water dimer

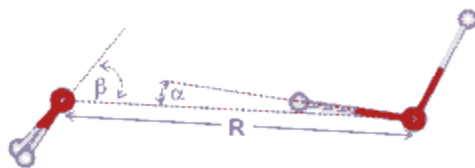
Much effort has been expended on the structure of small isolated water clusters. Typically, in the ambient atmosphere there is over one water dimer for every thousand free water molecules rising to about one in twenty in steam. The equilibrium constant for dimer formation



is  $0.0501 \text{ bar}^{-1}$  at 298.15 K [2052]. The thermochemical properties of the dimer have been determined [2052].

The most energetically favorable water dimer is shown right using *ab initio* calculations with the 6-31G\*\* basis set.<sup>j</sup> It is also shown below with a section through the electron density distribution (high densities around the oxygen atoms have been omitted for clarity). This shows the tetrahedrality<sup>b</sup> of the bonding in spite of the lack of clearly seen lone pair electrons; although a small amount of distortion along the hydrogen bond can be seen. This tetrahedrality is primarily caused by electrostatic effects (that is, repulsion between the positively charged non-bonded hydrogen atoms) rather than the presence of tetrahedrally placed lone pair electrons. The hydrogen-bonded proton has reduced electron density relative to the other protons [222]. Note that, even at temperatures as low as a few kelvin, there are considerable oscillations (< ps) in the hydrogen bond length and angles [591]. The potential energy surface [1668] and wagging vibration [1743] of the water dimer have been described and molecular orbitals of the water dimer are shown on another page.





$R = 2.976 (+0.000, -0.030) \text{ \AA}$ ,  $\alpha = 6 \pm 20^\circ$ ,  $\beta = 57 \pm 10^\circ$  [648];  $\alpha$  is the donor angle and  $\beta$  is the acceptor angle. The dimer (with slightly different geometry) dipole moment is 2.6 D [704]. Although  $\beta$  is close to as expected if the lone pair electrons were tetrahedrally placed ( $= 109.47^\circ/2$ ), the energy minimum ( $\sim 21 \text{ kJ mol}^{-1}$ ) is broad and extends towards  $\beta = 0^\circ$ .

It has been noted that dimers of more distant water molecules ( $\sim 1 \text{ nm}$ ) show synchronous behavior due to their interacting electric fields [2086].

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### Water models

Simplified models for the water molecule have been developed to agree with particular physical properties (for example, agreement with the critical parameters) but they are not robust and resultant data are often very sensitive to the precise model parameters [206]. Models are still being developed and are generally more complex than earlier but they still appear to have poor predictive value outside the conditions and physical parameters for which they were developed. [Back to Top ▲]

### Water reactivity

Although not often perceived as such, water is a very reactive molecule available at a high concentration. This reactivity, however, is greatly moderated at ambient temperatures due to the extensive hydrogen bonding. Water molecules each possess a strongly nucleophilic oxygen atom that enables many of life's reactions, as well as dissociating to produce reactive hydrogen and hydroxide ions. Reduction of the hydrogen bonding at high temperatures, or due to electro-magnetic fields, results in greater reactivity of the water molecules. [Back to Top ▲]

### Footnotes



<sup>a</sup> Water's composition (two parts hydrogen to one part oxygen) was discovered by the London scientist Henry Cavendish (1731-1810) in about 1781. He reported his findings in terms of phlogiston (later the gas he made was proven to be hydrogen) and dephlogisticated air (later this was proven to be oxygen). Cavendish died (1810) in his Laboratory just 30 minutes' walk from the present site of London South Bank University.



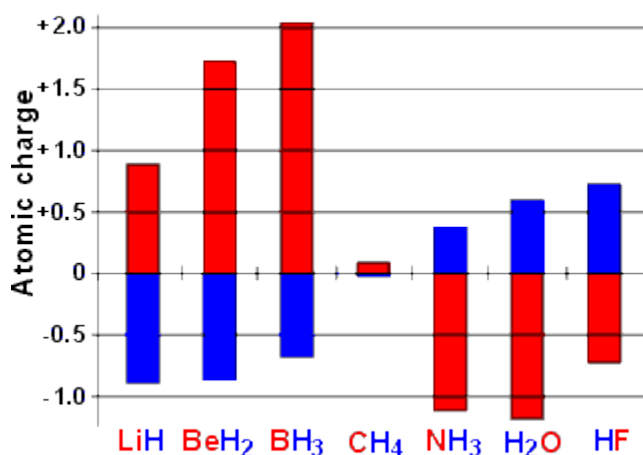
It has been suggested that  $H_{1.5}O$  may better reflect the formula at very small (attosecond) timescales when some of the H-atoms appear invisible to neutron and electron interaction [515]. The experimental results have since been questioned [630] and described as erroneous [796], but have been more recently confirmed and thought due to a failure of the Born-Oppenheimer approximation (this assumes that the electronic motion and the nuclear motion in molecules can be separated) [1134]. Thus the formula  $H_{1.5}O$  is incorrect but such suggestions do, however, add support to the view that observations concerning the structure of water should be tempered by the timescale used. [Back]

<sup>b</sup> 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  $\psi_{jk}$  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 ( $\pm 0.5$  SD) for random arrangements, with a minimum value of -3. The density order parameter is described elsewhere. [Back]

<sup>c</sup> *ortho*-H<sub>2</sub>O rotates in its ground state with energy 23.79 cm<sup>-1</sup> [1150]. [Back]

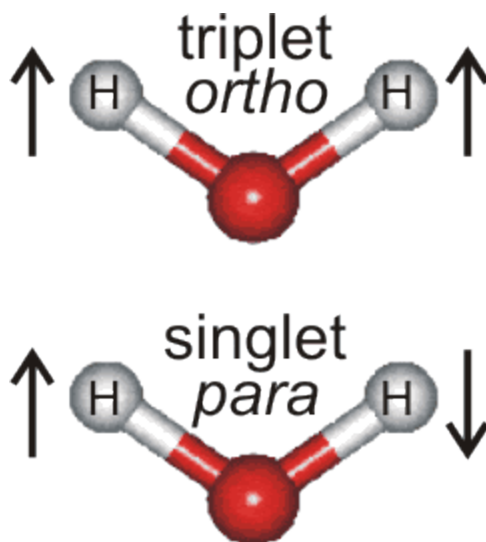


<sup>d</sup> The charge on the hydrogen atoms across the periodic table are shown opposite [820]. The hydrogen atom charges are blue and the charges on the other atoms are indicated red. [Back]

<sup>e</sup> The actual values depend on the vibrational state of the molecule with even values of 180° being attainable during high order bend vibrations ( $\nu_2 \geq 7$ ,  $\lambda < 900$  nm) for the H-O-H angle [860]. Vibrations are asymmetric around the mean positions. In the ground state, the bond angle (104.5°) is much closer to the tetrahedral angle than that of the other Group VI hydrides, H<sub>2</sub>S (92.1°), H<sub>2</sub>Se (91°) or H<sub>2</sub>Te (89°). [Back]

<sup>f</sup> The H-O-H angle and O-H bond length in ice Ih are reported as  $106.6^\circ \pm 1.5^\circ$  and 0.985 Å [717] respectively, whereas recent modeling gives H-O-H angle values of  $108.4^\circ \pm 0.2^\circ$  for ice Ih and  $106.3^\circ \pm 4.9^\circ$  for water [1028]. [Back]

<sup>g</sup> The atomic diameter can be determined from interpolation of the effective ionic radii of the isoelectronic ions (from crystal data) of O<sup>2-</sup> (2.80 Å), OH<sup>-</sup> (2.74 Å) and H<sub>3</sub>O<sup>+</sup> (2.76 Å) [1167]. Coincidentally, this diameter is similar to the length of a hydrogen bond. The water molecule (bond length 0.96 Å) is smaller than ammonia (bond length 1.01 Å) or methane (bond length 1.09 Å), with only H<sub>2</sub> (bond length 0.74 Å) and HF (bond length 0.92 Å) being smaller molecules. [Back]



<sup>h</sup>As is found in molecular hydrogen ( $H_2$ ), the hydrogen atoms in water ( $H_2O$ ) may possess parallel (paramagnetic *ortho*- $H_2O$ , magnetic moment = 1; the high spin state with three symmetric spin states  $+1$ ,  $0$ ,  $-1$ ; this spin state always rotates with the lowest state  $23.794352\text{ cm}^{-1}$   $H_2^{16}O$ , [607c],  $23.773510\text{ cm}^{-1}$   $H_2^{17}O$  [607a] or  $23.754902\text{ cm}^{-1}$   $H_2^{18}O$  [607a]) or antiparallel (nonmagnetic *para*- $H_2O$ , magnetic moment = 0; the low spin state with one antisymmetric spin state  $0$ ; some of these will not be rotating even at room temperature) nuclear spin. The equilibrium ratio of these nuclear spin states in  $H_2O$  is all *para* at zero Kelvin, where the molecules have no rotational spin in their ground state, shifting to the most stable ratio [1694] of 3:1 *ortho:para* at less cold temperatures ( $>50\text{ K}$ );<sup>c</sup> the equilibrium taking months to establish itself in ice (or gas) and nearly an hour in ambient water [410]. It is now thought that the ratio lies far from equilibrium and much closer to 1:1 in liquid water due to hydrogen bond formation [2076]. This means that liquid  $H_2O$  effectively consists of a mixture of non-identical molecules and the properties of pure liquid *ortho*- $H_2O$  or *para*- $H_2O$  are unknown. The differences in the properties of these two forms of water are expected to be greater in an electric field [1186], which may be imposed externally, from surfaces or from water clustering itself. Many materials preferentially adsorb *para*- $H_2O$  due to its non-rotation ground state [410, 835]. The apparent difference in energy between the two states is a significant  $1\text{--}2\text{ kJ mol}^{-1}$ , far greater than expected from spin-spin interactions ( $< \mu\text{J mol}^{-1}$ ) [835]. It has been suggested that structural rearrangements may be induced by *ortho*- $H_2O$  : *para*- $H_2O$  conversion [1430], as 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]. It is thus possible that *ortho*- $H_2O$  and *para*- $H_2O$  form separate hydrogen bonded clusters [1150] with *para*- $H_2O$  being preferred in the low density tetrahedrally coordinated clusters and *ortho*- $H_2O$  being preferred in the high density clusters [2070], where their rotation is more easily accommodated.

Due to deuterium's nuclear spin of 1 (compare  $1/2$  for H's spin; *ortho*  $D_2O$  has two spin states  $2$  and  $0$ ; *para*  $D_2O$  has one spin state  $1$ ), the lowest energy form of  $D_2O$  is *ortho*.  $D_2O$  converts to a 2:1 *ortho:para* ratio at higher temperatures. The difference in energy between the lowest *ortho* state and the lowest *para* state is  $12.1170191\text{ cm}^{-1}$  ( $D_2^{16}O$ ),  $12.098600\text{ cm}^{-1}$  ( $D_2^{17}O$ ) and  $12.082026\text{ cm}^{-1}$  ( $D_2^{18}O$ ) [607d].

HDO, having non-equivalent hydrogen atoms, does not possess an *ortho/para* distinction.  $T_2O$  behaves similarly to  $H_2O$  as tritium also possesses a nuclear spin of  $1/2$ . [Back]



<sup>i</sup> Liquid water consists of a mixture of molecules [1377] and ions, including H<sub>2</sub>O, HDO, H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>. A 'standard' water (Vienna Standard Mean Ocean Water) has been proposed. 'Pure liquid water', meaning consisting of just H<sub>2</sub>O molecules, only exists in computer simulations. Even 'just H<sub>2</sub>O' consists of a mixture of 'ortho' and 'para' forms. Avoiding this complexity, 'water' is normally taken to mean H<sub>2</sub>O molecules, without consideration over its magnetic state. H<sub>2</sub>O is also known as 'light water' with D<sub>2</sub>O being heavy water (D<sub>2</sub>O density = 111% H<sub>2</sub>O density, 25 °C) and T<sub>2</sub>O being super heavy water (T<sub>2</sub>O density = 122% H<sub>2</sub>O density, 25 °C). The properties of H<sub>2</sub>O, D<sub>2</sub>O and T<sub>2</sub>O are different. Even though the amount of deuterium in commonly-found water is low (~16 mM) the properties of such water are different to water containing protium (<sup>1</sup>H) only [2063]. [Back]

<sup>j</sup> More exact parameters are given in the text. These parameters are given mainly for comparison with the hydrogen and hydroxide ions. [Back]

Source:<http://www1.lsbu.ac.uk/water/molecule.html#bi>