Water Cluster Equilibria

At ambient temperatures, the icosahedral cluster equilibrium in water is shown rather idealistically in the equation (ES ⇌ CS). Clearly complete clusters, without any pendant hydrogen bonding, are likely to be rarely, if ever, found. It should be noted that such a five or six (complete) shell cluster has 86% or 89% hydrogen bonding (respectively), approximately in line with that estimated by some in water [465a]. A dynamic range of partial structures (reducing the % hydrogen bonding) is expected together with extensive links to pendant molecules and other clusters (increasing the hydrogen bonding). A model, using the significant liquid structure theory, estimates an average of 20 water molecules per flickering cluster gives the best fit over a range of temperatures (0-100 °C) [600]. As the hydrogen bonding flickers between arrangements, the stability of the expanded water dodecahedra (see below) will vary [435]. An effectively-infinite number of arrangements (even a dodecahedral $(H_2O)_{20}$ cluster has 30026 symmetry-distinct hydrogen bond arrangements differing in energy by up to the equivalent of 40% of the hydrogen bond energies [464]) will be found with an extraordinarily complex potential energy surface; lower energy (more symmetrically arranged with smallest net overall and partial-cluster dipoles being more stable [464])[d] arrangements tending to expand whereas higher energy forms (more asymmetric with largest net dipoles being least stable) will pucker, so leading to the cluster flickering phenomena. If the range of energies for the dodecahedral $(H_2O)_{20}$ cluster [464] is used for calculating the range of energies for the icosahedral $(H_2O)_{280}$ cluster, it is expected that differences in energy by up to the equivalent of 8% (40% x 60/20 x 20/280) of the hydrogen bond energies will be possible for differing hydrogen bond arrangements. As the temperature is lowered towards 0 °C and below, it is expected that a greater degree of cluster completion is to be found, flickering between structural forms (see animated gifs, 379 KB). There is likely to be a continuum of structures present. It is also possible that clusters can fuse together to form cylindrical clusters and cover surfaces.

The agreement of the CS structure with the radial distribution function indicates that it is by far the major contributor at 4 °C. Under pressure the collapsed structure (CS) may collapse further because only the one dodecahedron at the center has collapsed in the cluster model (CS), leaving three (12 quarters, icosahedrally arranged) mostly uncollapsed on the periphery. As the density of ES is 0.94 g cm^{-3} and that of CS (with a quarter of the dodecahedral voids collapsed) is 1.00 g cm^{-3} then the collapse of these other three (equivalent) dodecahedral voids (under pressure) will give a density of about 1.18 g cm^{-3}; similar to that of high-density amorphous ice when returned to ambient pressure; so offering explanation of the continuous nature of the LDA⟶HDA process that occurs without breaking the hydrogen bonds [394].

There are a number of changes to the structure of water that occur with increasing temperature. The water molecules gain energy, which is used to bend and break the hydrogen bonds. Due to the multiple nature of the hydrogen bonding around water molecules, central molecules in clusters are likely to resume unchanged hydrogen bonding after such breakage but peripheral molecules will be preferentially lost to other clusters, less structured environments and interstitial sites. On raising the temperature, the size of ordered clusters decreases, the number of smaller clusters increases, the number of hydrogen bonds decreases and the average distance between the water molecules increases.

$$(H_2O)_m \rightleftharpoons (H_2O)_n + (H_2O)_{m-n}$$
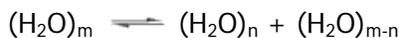
There is always considerable hydrogen bonding, however, and it is likely that almost all molecules will be linked to almost all others by at least one intact chain of hydrogen bonds. Some hydrogen

bonding, of the order of 1-2 hydrogen bonds per molecule dependent on the density, is evident even in supercritical water (>374 °C) [208].

Interesting phenomena, in the (interfacial) vicinal water that occurs at solid surfaces, are the apparent transitions in physical properties at the 'Drost-Hansen' temperatures (~15 °C, ~30 °C, ~45 °C, ~60 °C and ~75 °C) [205]. It is possible that these transitions are caused by the breakage of hydrogen bonds due to the increasing difference between the potential of the ordered vicinal and disordered bulk phases. This would then cause an incremental loss of order and restructuring of the water clusters and explain the pronounced thermal hysteresis in the effects. Note that the properties of bulk water have similar turning points (for example, complex permittivity analysis shows a discontinuity at about 30 °C [1045], specific heat has a minimum at about 36 °C, compressibility has a minimum at about 46.5 °C and the speed of sound has a maximum at about 73 °C) and gaseous solutes can create other turning points (for example, the presence of equilibrated air creates a turning point at 44 °C for the proton spin-lattice relaxation time in water, T_1 [294]), so it is not unreasonable that the changes in the clustering of water creates these transitions within the interfaces.[c] Other transitions occur in many ionic solutions on increasing their concentration to about molal concentrations [518], when the preferred (low concentration) water clustering starts to overlap at higher concentrations and indicating that at least 20 water molecules are associated with each ion's cluster.

Dodecahedral $(H_2O)_{20}$ clusters are at the center of the icosahedral water clusters. These are expanded when the hydrogen bonding is dominant and collapsed when the van der Waals dispersion interactions dominate. Under normal conditions there will be equilibrium between these forms.
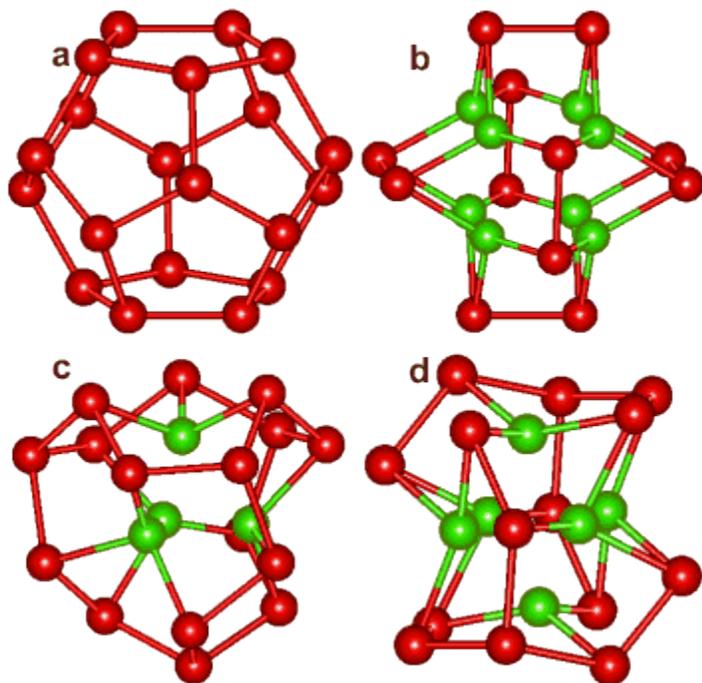
The central $(H_2O)_{20}$ dodecahedron of water molecules (a) in a water cluster can collapse in a number of ways.[a] Their oxygen atoms are depicted above showing a collapse with 8 (b), 4 (c) or 6 (d) inner molecules (shown as yellow) producing cubic, tetrahedral or octahedral cavities respectively.

Other collapsed structures are also possible (for example, with two inner molecules similar to that occurring with the oxygen atoms in CO_2 clusters).

The connectivity map of the convex dodecahedron (a) is shown below with the most-stable positioning (red or blue circles) of outwards-oriented donor hydrogen atoms in an isolated cluster[b], having just three nearest neighbor double-donor and double-acceptor pairs [186]. The favored directions of (one set of) the hydrogen-bonded hydrogen atoms are also shown as short red lines [1441].
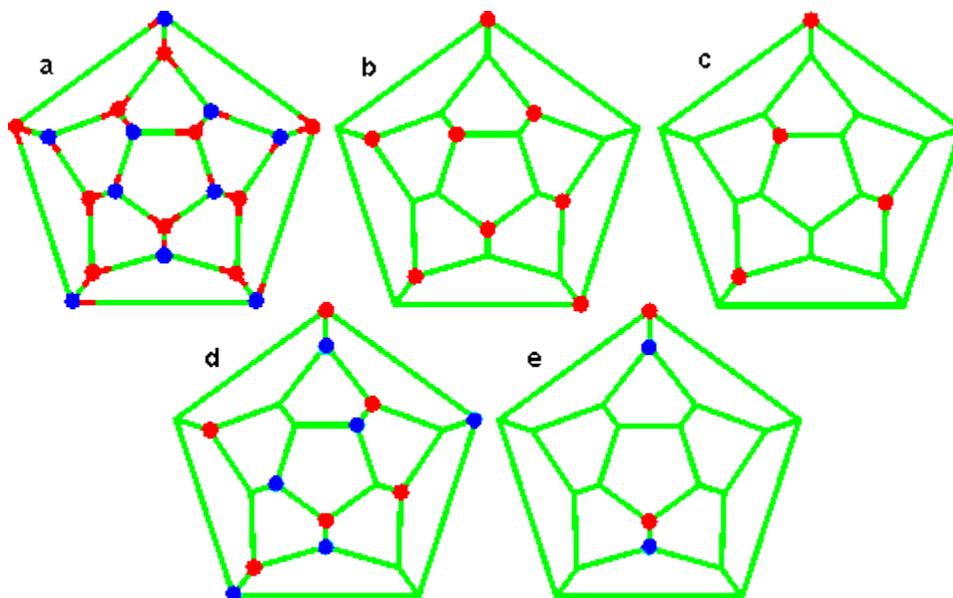
Also shown are the connectivity maps of the dodecahedra showing the collapsed positions (red or blue circles) for 2 (e), 4 (c), 6 (d) and 8 (b) molecules. Alternative structures (with redundancy in map b) may be formed from all of these connectivity maps by rotation and reflection. In water it is expected that the more-central water molecules will be constantly changing and there will be a range of collapsed structures although some may clearly be more stable than others; structure (b) was favored by molecular modeling. The figures (above) show the maximum amount of puckering that occurs when the non-bonded distance between the inner molecules (the edges of the holes) is the same as the bonded distance between two neighbors. In practice a lesser degree of puckering is expected. With this maximal puckering the central cavities have radii 1.71 Å, 2.01 Å, and 2.42 Å for tetrahedral, octahedral and cubic cavities respectively. Interactive structures are available using Jmol. The cavities may be occupied by ions which interact with the puckered water molecules in some cases forming magic number cluster ions.


Footnotes

[a] It is also possible that dodecahedra can fuse together to form tubes and cover surfaces. [Back]

[b] Although the difference in stability between hydrogen-bonding arrangements of the water central dodecahedron (($H_2O)_{20}$) within an icosahedral structure (($H_2O)_{280}$) will be much smaller than for the isolated water dodecahedron, modeling studies show that a similar order of relative stability against puckering remains. The least stable hydrogen bond arrangement in the central dodecahedron is that

with the greatest symmetry (S_{10}), where the ten outward-facing hydrogen bonds are contributed by two oppositely-positioned cyclic pentamers. [Back]

[c] An interesting, if not fully convincing, alternative explanation involves thermal quantum effects depending on the effective size of the molecules and the free volume space [724]. [Back]

[d] This can also be visualized as the form with the least number possible of free (non-hydrogen bonded) H atoms on adjacent (hydrogen-bonded) water molecules. Of the ten free H-atoms in the most stable dodecahedral water cluster, $(H_2O)_{20}$ isomer, four are isolated and six are contained in three isolated pairs of adjacent (hydrogen-bonded) water molecules, as shown above (a). [Back]
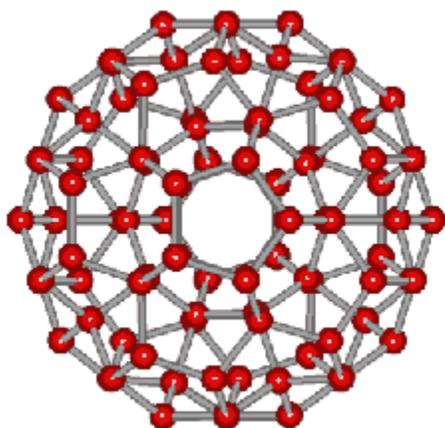
An icosahedral water cluster consisting of 280 water molecules has a central puckering dodecahedron. Only the oxygen atoms are shown. A full cluster also has 12 potential 100-water-molecule clusters surrounding the central 100 water molecule core. The puckering occurs with drops in the hydrogen bond energy (below left). Puckering not only changes the central dodecahedron but will flicker between new (surrounding) and old centers with the clusters disassembling and reforming as required, and as indicated in the animated figure below right. Thus, the cluster is self-replicating as any one cluster also contains the seeds for the formation of up to 12 further clusters.
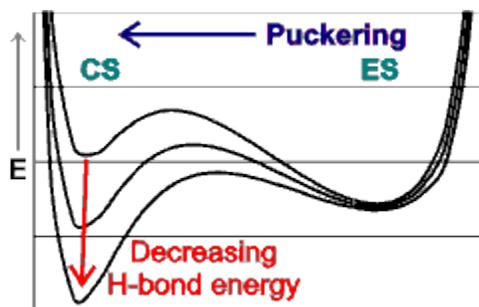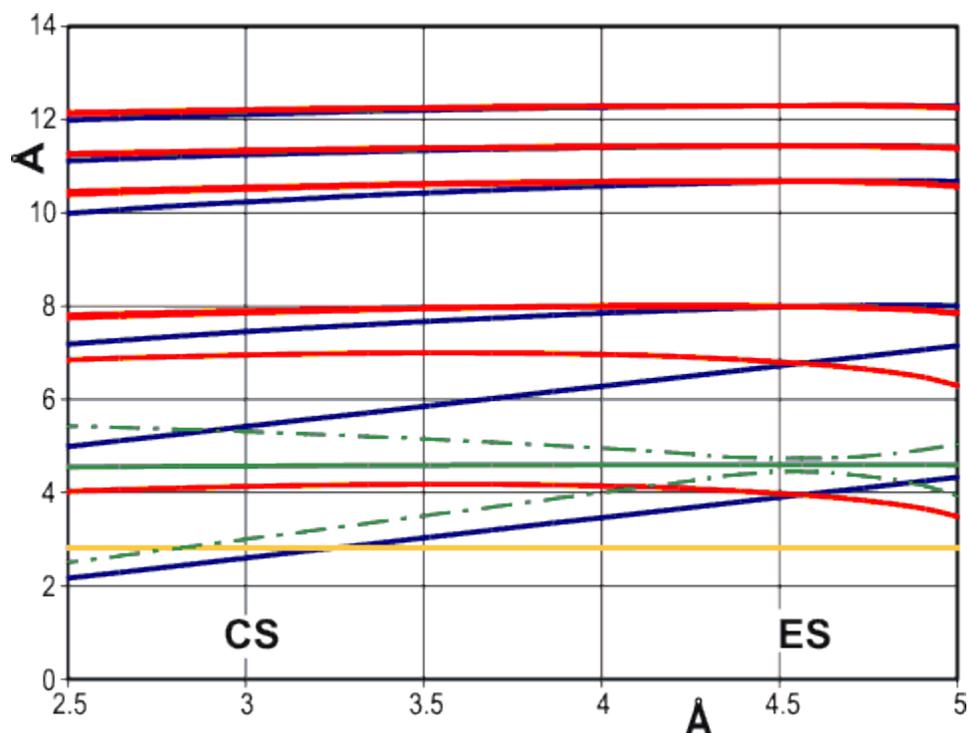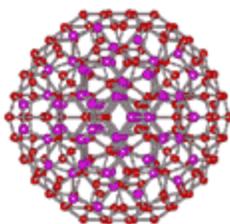
Puckering can occur with relatively small consequential distortion to the cluster as a whole. On the right is a graph showing the radial positions (vertical axis, ▬ eight cubically arranged 14-molecule tetrahedra;▬ remaining twelve 14-molecule tetrahedra) in the six radial positions from the center (containing 1, 1, 3, 3, 3, 3 molecules respectively) with the non-bonded cubic box length of the puckered water (horizontal axis). To generate this graph all hydrogen-bonded distances were held at 2.8 Å (▬); also shown are the mean 2nd neighbor distances (▬) and their range (▬·▬).

As the 8 cubically arranged 14-molecule tetrahedra pucker inward (blue lines, moving to the left), the remaining 12 14-molecule tetrahedra (red lines) first expand slightly before being dragged in. It is clear that the large movement in the inner two puckering water molecules (lowest two blue lines) is severely attenuated in the remaining molecules in the cluster. The spherical angle coordinates (θ, φ) of all the molecules also vary little (S.D. 0~3°, average 0.33°) during the puckering. The total volume (indicated by the surface positions given by the outer three blue and red lines) reduces throughout the puckering. The ES structure corresponds to about the 4.6 Å horizontal position when all 14-molecule tetrahedra are equivalent and the CS structure corresponds close to 3 Å where the inner cubically-arranged puckered water molecules are at their minimum permissable non-bonded distance apart.

Source : http://www1.lsbu.ac.uk/water/equil2.html