WATER STRUCTURES

Water Structures are Non-Polymeric: Although water scientists often speak of monomers, dimers, quadramers and other “mers”, water structures are not polymers. Polymers are usually long chain molecules composed of molecular fractions that are covalently bonded. Water structures (in their un-ionized forms, at least) are composed of whole molecules, not molecular fractions; and are primarily linked by hydrogen bonding, not by covalent bonding.

Nevertheless, we will continue to use the terminology of water science in referring to the various groupings as monomers, dimers, and so forth. It is both well established and convenient[1].

In water vapor and in liquid water, the most common of these forms is the simple monomer (one molecule, either unbonded or only ephemerally bonded). In ice, of course, the molecules are strongly bonded together into structures containing billions or more molecules. This is the crystalline form, and represents one endpoint in the eternal conflict between intermolecular attraction and intermolecular repulsion. Individual molecules of water vapor represent the other endpoint. Liquid water is in the middle, and is much more complex than either extreme.

Hydrogen Bonds

Because of the water molecule’s strongly polar nature, there exists a natural propensity for the molecule to form electrostatic bonds with other water molecules. The bond is formed between the covalently bonded hydrogen proton in one molecule (the donor molecule) and one of the lone pairs of electrons in another molecule (the acceptor molecule).

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[1] In this essay and in “Water Molecules” and “Water Ionization”, I am indebted to the superb series of summaries prepared and posted online by Martin Chaplin of the London South Bank University. No other source proved so useful or so cogent. See http://www.lsbu.ac.uk/water/index2.html

Structured Bonding: A single water molecule may thus be twice a donor and twice an acceptor. Similarly, each bonded molecule may in turn bond to three additional molecules. Any one of those three may be bonded to “family” molecules (A to B to C to A). This tends toward regular organized structures, such as tetrahedra.

Unstructured Bonding: Alternatively, a bonded molecule may bond to a “stranger” molecule (A to B to C to D). This tends toward a more amorphous bonding. Liquid water has been described as an infinitely-bonded mass with volumes of localized structures having significant durability, and volumes of unstructured and only ephemerally-bonded molecules.

Enhanced Bonding: A molecule that is bonded at one site is much more likely to bond at additional sites. This continues until all available sites are filled. This means that the growth of water structures is entirely natural and self-starting. It requires no catalyst. As we shall see later, however, it is greatly aided by the presence of ions.

Bonding Limitations: The limiting factor to structured growth in liquid water is the thermal agitation of the molecules. Kinetic energies of translation, rotation, vibration, and libration are all capable of breaking the relatively weak hydrogen bond. Thus, as the temperature increases intermolecular bonding weakens and structures become both less numerous and more ephemeral.

By molecular bonding standards, the hydrogen bond is neither particularly strong nor particularly weak. It is easily formed and equally easily broken. This makes it ideally suited to supporting life.

Bonding Longevity: These hydrogen bonds have greater or lesser longevity depending upon a host of factors—most importantly the temperature and the phase structure. Some hydrogen bonds may last only picoseconds or nanoseconds, as is common in both liquid water and water vapor. They may last into human time scales, as is common in water ice. The mathematics of probability makes it very likely that the longevity follows a distribution function that is strongly temperature dependent.

Water Structures

The configuration of the water molecule, with its two covalently bonded hydrogen protons, its two lone pairs of electrons, and its native bonding angles pretty well determines the possible configurations of any resulting structures. One result is that the ensuing structures almost always consist of an even number of molecules. Dimers, quadramers, and octamers are known to exist. Trimers and pentamers are far less common, and are usually only found as parts of larger even-numbered structures.

Structure Size: Structures range from the common water dimer (H_4O_2) to clusters as large as a million molecules. The tetrahedral (14 molecules) and the icosahedral (280 molecules, or 20 tetrahedra) are thought to be particularly stable. Clustering reduces the density of the clustered water as compared to the unclustered. This is most obvious in the case of common (hexagonal) ice. Clustering diminishes as the temperature increases. Recent studies using x-rays have shown that, at common atmospheric temperatures, the denser relatively less structured form of water is dominant, but that the tetrahedral form is abundant.

Structure Stability: As we have seen in the water molecule, stability is a relative concept. Moreover, we have to distinguish between the stability of a form and the stability of its elements. The water molecule is a stable form, even though some of its elements (the hydrogen protons) change several thousand times a second. In a similar fashion, the form of the water structures can be quite stable, even though the individual water molecules or even individual tetrahedra may be changing rapidly.

Structure Ionization: Structures may be un-ionized or ionized. Hydrogen ions (protons) seem to switch oxygen allegiances with abandon. In atmospheric water, cations (water molecules and molecular structures with an extra proton) are extremely common. Anions (water molecules and molecular structures missing a proton) are equally abundant. Ionization of water and its structures is discussed with more detail in *Water Ionization*.

Formation of Water Structures by Phase

Since structure formation in water is inversely proportional to the temperature, it would appear logical that water vapor would have both the fewest and least durable structures. Ice, on the other hand, should have both the greatest proportion of structures and the most durable. And so it is.

Structures in Water Vapor: At temperatures and pressures normally found in the troposphere, water molecules collide billions of time per second. However, the distribution function for relative collision speeds mandates that most collisions be of relatively low total energy. It is entirely possible (and even probable) that many such collisions result in impulse transfers that are less than the hydrogen bonding energy. In those circumstances, the two (or more) water molecules may readily bond together.

Dimers (two bonded molecules) are known to exist in atmospheric water vapor. One study found that at a temperature of 25°C and an 85% relative humidity, dimers made up 0.1% of the vapor molecules. Both common sense and the mathematics of probability tell us that if dimers are found in water vapor, then larger structures must be possible (and even probable) as well.

Both dimers and larger structures have significantly different electromagnetic absorption spectra from water vapor monomers. Indeed, recent studies have shown that these structures may very well account for most—if not all—of the anomalous shortwave absorption in atmospheric studies. This gives water an even larger role in the Earth's heat budget than its already overwhelmingly dominant position.

Structures in Ice: In ice, the water molecules are more or less permanently bonded into hexagonal crystalline structures[2]. These structures may be initiated and seeded both by extraneous icing nuclei and by the hexagonal hydrogen bonding of the hydronium ion:

$$\mathbf{H_3O^+ + 6\,H_2O \rightleftarrows H_{15}O_7^+} \qquad \text{WSC01}$$

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[2] Although cubic crystalline ice (I_c) is found under high pressures in glacial ice, it is not found in the free atmosphere.

This “icing ion” is not saturated, and readily tessellates throughout a water system whenever temperatures allow for icing. Indeed, in plant tissues, in the presence of proteins that are strongly hydrophilic, this ion may initiate freezing at temperatures as high as 4°C.

It should not be assumed that a mass of atmospheric ice represents a single bonded mass. Under ordinary circumstances, the ice will have numerous discontinuities, shear lines, and fractures. In addition, it will contain solutes, bubbles, and solid impurities.

As the ice temperature rises toward the melting point, the relatively rigid and durable intermolecular bonds stretch, bend, and otherwise weaken. There may be localized breaking of bonds and the formation of quasi-liquid systems. At the melting point, the time frame of this disruption increases exponentially, and the ice melts to form liquid water.

Structures in Liquid Water: There is strong evidence of many types of structures in liquid water. These range from simple dimers of two molecules to complex icosahedral clusters of 280 molecules (twenty bonded tetrahedra of fourteen molecules each). These latter clusters are spherical, link readily, are capable of tessellation, and show exceptional promise as a modeling tool. This is because they can be used to explain most of water’s anomalous properties—something that other models do not do anywhere near as well.

Surface Tension as a Bonded Structure: The most common example of water structuring is the virtually instantaneous formation of a structured monolayer on any exposed surface of liquid water. This monolayer usually goes by the name of “surface tension”. It appears to consist of water molecules bonded to one another by hydrogen bonding at all four bonding points to form a reticulated structure. If water molecules bond so readily on the surface of a droplet and with such a high degree of systematic order, it is logical to assume that they bond at least as readily within the droplet and with a similarly high degree of order.

Summary: Water molecules have a natural and unforced attraction for one another. They bond together spontaneously, without any assistance from either ionic forces or hygroscopic forces—although these forces can and do greatly facilitate bonding. This native bonding force (the hydrogen bond) is strong enough to almost instantly shape a falling raindrop into a sphere (surface tension), and to force water to climb a tube against the force of gravity (capillary action). It is certainly strong enough to attract wandering vapor molecules toward a liquid or solid water surface; molecules that might not otherwise impact on that surface.

In short, water can and does exert a strong attractive force in its immediate vicinity. This force can and does overcome the repulsive forces of thermal agitation in the lower ranges of the thermal term. It is this force and this force alone that makes spontaneous condensation and freezing possible.

It must be admitted, however, that water occasionally needs a little help in accomplishing these processes. Luckily, this help—ionic attraction and hygroscopic attraction—is usually readily available in the free atmosphere.

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The individual water structures in the following table have lifespans that range from picoseconds to millennia. It is likely that each form has its own temporal frequency distribution.

Even though the structure may be persisting, the individual water molecules that make up the structure may be changing. Moreover, even though the molecule is persisting, the hydroxyl ion and the hydronium ion that make up the common dimer may be changing. In addition, the hydrogen proton skips from one ion or molecule to an adjoining molecule or ion a thousand or more times each second. Finally, the hydrogen bonds that link one liquid water molecule to an adjoining water molecule fracture and reform even more frequently.

The keynote to all water molecule forms seems to be a strange combination of persistence and mutability.

TABLE WST01

SOME WATER STRUCTURES

STRUCTURE	FORMULA	COMMENTS
Monomer	H_2O	Not a structure, but the essential molecular building block of all water structures.
Dimer	H_4O_2	The most common water structure. It is found in atmospheric water vapor. It ionizes readily into hydroxide (OH^-) and hydronium (H_3O^+) ions.
Quadramer	H_8O_4	Very common in liquid water. It ionizes readily into one Zundel cation ($H_5O_2^+$) and one anion ($H_3O_2^-$).
Pentamer	$H_{10}O_5$	Most common in its cyclic form of five molecules bonded so as to form a five-sided ring.
Octamer	$H_{16}O_8$	Usually found in its bi-cyclic form of two parallel and bonded quadramers. Thirty-five of these bicyclo-octamers may combine to form an icosahedron.
Decamer	$H_{20}O_{10}$	Usually found in its complex tri-cyclic form. Decamers may combine with cyclic pentamers to form icosahedra.
Tetrahedron	$(H_2O)_{14}$	A very common and stable structure. Twenty of these may combine to form an icosahedron. It replicates easily and tessellates readily.
Icosahedron	$(H_2O)_{280}$	The most common and most stable of the larger clusters. It tessellates readily.

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