WATER MOLECULES

This essay is entitled "Water Molecules" rather than "The Water Molecule" because water in not made up of a single kind of molecule, but of many kinds of molecules. There are at least two different species of water, differing from one another in having either parallel or anti-parallel nuclear spin of the hydrogen atoms. There are eighteen different isotopes, each having physical and chemical properties that differ to a greater or lesser degree from one another. Water molecules usually exist as monomers, but also form dimers and polymers. These structures often move about and otherwise act as units. Finally, water is self-ionizing. This results in a wide variety of ions, each having physical and chemical properties that differ to a greater or lesser degree from one another[1].

Water molecules thus differ widely in their size, their shape, and their physical and chemical properties. Pure water—that is, water consisting only of un-ionized monomers of a single isotope—exists only in computer simulations and other scholarly fantasies. Real water consists of a mixture of isotopes; of a mixture of monomers, dimers, and polymers; and of a mixture of ions and un-ionized molecules. In addition, real atmospheric water enjoys the addition of a wide variety of substances in solution and other substances in suspension.

It should be noted that each of these water molecules has its own individual electromagnetic spectrum of allowable emission and absorption energies and wavelengths. This is important in understanding the role that water plays in the earth's heat budget (see *Water and the Earth's Heat Budget*).

We will look at most of these variations, but we will start with the simplest and most common type of water molecule—the un-ionized monomer of the most common isotope.

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[1] In this essay and the succeeding "Water Structures" 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

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The Basic Water Molecule: Let us start with a molecule of the most common isotope (99.73%) of water, ^1H-^{16}O-^1H. This molecule is composed of a single oxygen atom and two hydrogen atoms. The oxygen atom has a nucleus containing eight proton-neutron pairs. This is what makes it ^{16}O. Other isotopes of oxygen contain nine (^{17}O) or ten (^{18}O) neutrons, but still only eight protons. Each hydrogen atom has a nucleus consisting of a single proton, with no neutron. Deuterium (^2H) has a single neutron to match the single proton in its nucleus, while tritium (^3H) has two neutrons, but still only the one proton. These six atomic isotopes combine to form the eighteen possible isotopes of natural water.

Molecular Structure: This atom of oxygen has a full complement of two electrons (one pair) in its inner or K shell. It has three pairs of electrons in its outer or L shell. This leaves it one pair short of a full complement for that shell. Each hydrogen atom has only a single electron in its K shell, leaving it one electron shy of a full set. These individual atomic lacks are fulfilled in the chemical combination of the two hydrogen atoms with the single oxygen atom to form a single molecule of water (H_2O).

In the water molecule thus formed, the two hydrogen atoms take up station in the outer shell of the oxygen atom, sharing electrons in a covalent bond. Each hydrogen atom’s K shell now has a full pair of electrons and the oxygen atom’s L shell has a full set of four pairs of electrons. Two of those four pairs are covalently bonded with the two hydrogen atoms and the oxygen atom, leaving two “lone pairs” bonded only to the oxygen atom.

This topologic arrangement is what gives the water molecule its strong electrostatic polarity. The two lone pairs of electrons at the one end of the molecule give that end an unsaturated negative charge. The two bonded protons at the other end still have some residual unsaturated positive charge. The water molecule thus has a dipolar electrostatic moment.

This means that each of the bonded hydrogen atoms can form additional hydrogen bonds with a lone pair of electrons on an adjacent water molecule; and each of the lone pairs of electrons can form similar hydrogen bonds with the bonded protons on a neighboring water molecule. In this fashion a single water molecule can form hydrogen bonds with four other nearby water molecules. Moreover, it appears that forming one such hydrogen bond makes a water molecule even more likely to form others. We will look at this hydrogen bonding more closely in *Water Structures*.

Sometimes, a water molecule can actually capture a hydrogen atom (proton) from another water molecule, forming a positively charged ion (cation). The process is called protonation. Sometimes a water molecule can capture a free hydroxide ion (OH^-) to form a negatively charged ion (anion). The process is called hydration. We will look at both of these processes and the wide variety of ions thus produced in *Water Ionization*.

It should be noted that the hydrogen proton is extremely fickle. In the liquid water molecule, each hydrogen nucleus (proton) changes its oxygen partner some thousand times or more each second.

Bonding Angles and Bonding Lengths: The two hydrogen atoms in the water molecule are not evenly spaced in a linear H-O-H alignment. Instead, the centers of the hydrogen protons are connected to the center of the oxygen nucleus by axial lines that form an angle of 104.500° for isolated vapor molecules, and a bond length of 95.7854 pm (picometers, a trillionth of a meter). This angle and distance is flexible, and varies with circumstances. We will look at some of these circumstances later.

Electron Probability Cloud Configuration: The ten electrons that serve a single water molecule are not fixed in any position. They move about in "orbits" that are subject to strict quantum considerations. The term "orbit" is probably misleading, although in common usage. The easiest way to describe the configuration is to assume that the ten electrons "flesh out" the molecular nuclear skeleton with a cloud of probabilities. The probability of an electron being in any particular part of this cloud at any particular time is subject to a complex mathematical function. An electron is about ten times more likely to be a specific distance from the oxygen nucleus than it is from either of the hydrogen protons.

The end result of all of this is that a simple water monomer is roughly spherical in shape—give or take about five percent. There will be slight convex roundings where the two hydrogen atoms are situated and slight concave indentations where the two lone pairs of electrons are located.

Size of the Water Molecule: The question of molecular "size" can be approached in a variety of ways—all of which return different values. If we take the packing density of the densest form of water (liquid natural water at a temperature of 3.984°C), we get a molecular diameter of some 310 pm.

Recent x-ray spectroscopy of vapor molecules suggests a value closer to 320 pm, but other studies have placed the values as low as 282 pm. Different measurement methods produce different values, and the prudent scholar might be justified in responding to the question of how big the water molecule is by saying, “it depends”. In calculating the collision frequency and mean free path of the vapor molecule, we have used the value of 310 pm.

The whole matter of size must be considered in the knowledge that the molecule of water is not quite spherical in shape and is generally in constant thermal movement—rotating, spinning, and vibrating. On the macroscopic level, the volume of a mass of either liquid water or ice will vary with the phase, with the temperature, and with the ambient pressure. Real size thus becomes less important than “effective” molecular volume under the circumstances.

Nevertheless, of the hundreds of thousands of substances currently known to man, the water molecule is the third smallest. Only the hydrogen molecule (H_2) and hydrogen fluoride molecule (HF) are smaller.

Isotopic Variations: Water occurs as eighteen isotopes. These isotopes have different boiling points, different melting points, and different specific heat capacities. The mean velocities with which they move from place to place differ from one another whenever the masses differ; as do their rotational and vibrational characteristics. They absorb and emit radiation at different wavelengths from one another.

It should be noted that tritium is radioactive and unstable. It is found in atmospheric water only in trace amounts. This reduces the number of common water isotopes to twelve. Symmetry further reduces this number to only nine common isotopes. (^{1}H-^{16}O-^{2}H is functionally identical to ^{2}H-^{16}O-^{1}H.) **Table WMO01** shows the natural abundance of these isotopes.

Water “Species”: We now know that water consists of two magnetic “species”. These two species are differentiated on the basis of the magnetic or nonmagnetic “spin” of the hydrogen atoms. The *para* species has a parallel magnetic nuclear spin and a magnetic moment of one, the *ortho* species has an anti-parallel nonmagnetic nuclear spin and a magnetic moment of zero. It appears that the *ortho* species is more readily adsorbed to certain substances and passes through organic membranes more easily than does the *para* species. The *ortho* species also appears to form stronger and longer lasting structures and clusters than does the *para* species. In forming these structures, it appears that *ortho* molecules only bond with other *ortho* molecules, and *para* molecules only bond with other *para* molecules.

As temperatures approach 0°K, all of the molecules will be of the *para* species. As temperatures increase, the proportion of the *ortho* species increases dramatically. At the relatively cold temperature of 50°K, the *ortho* species have established a three to one preponderance.

It has been postulated that the two species have differing physical and chemical properties. However, since pure samples of either have yet to be produced and tested, this hypothesis remains conjectural.

Structures and Clusters: Water molecules, in all three of their phases, naturally form polymers of various sizes and configurations. These polymers are composed of water molecules in a systematic arrangement, held together by covalent hydrogen bonds that are relatively more stable and longer lasting than the ephemeral electrostatic hydrogen bonds that simply bind the molecules of liquid water together. Ice is one end product of this structuring, but structures are present in both liquid water and water vapor at all temperatures.

We will be dealing with this tendency of water molecules to form structures and clusters in greater detail in *Water Structures*.

Molecular Masses: The nine common isotopes of the water monomer enjoy five different masses. When it comes to polymers and ions, it is difficult to decide just what arrangements of hydrogen atoms and oxygen atoms constitute a molecule of water.

Dimers (H_4O_2) are found in all three phases of water, and the hydrogen atoms in this dimer are equally covalently bonded to the oxygen atoms. Does this constitute a single molecule? What about polymers and other water structures? When they move about the atmosphere as a single unit, are they single molecules or groups of molecules?

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The hydronium ion (H_3O^+) and the hydroxyl ion (OH^-) are relatively stable ions and are found in all three phases of water. When moving about in a gas, should we accept them as molecules?

All of these questions are valid questions, and should be addressed at some time. For the nonce, however, we shall simply adopt the VSMOW value of $2.99150512 \times 10^{-26}$ kilograms for the mean molecular mass of the natural water monomer; and a value of $2.99144976 \times 10^{-26}$ kilograms for the mean impulse mass of the water monomer.

TABLE WMO01

COMMON WATER ISOTOPES

ISOTOPE	MASS NUMBER	MOLECULAR MASS	RELATIVE ABUNDANCE
		x 10^{-26} kilograms	
$^{1}\mathrm{H} - {}^{16}\mathrm{O} - {}^{1}\mathrm{H}$	18	2.98897	0.997340572092863
$^{1}\mathrm{H} - {}^{16}\mathrm{O} - {}^{2}\mathrm{H}$	19	3.15503	0.000229414714274
$^{2}\mathrm{H} - {}^{16}\mathrm{O} - {}^{2}\mathrm{H}$	20	3.32108	0.000000013192863
$^{1}\mathrm{H} - {}^{17}\mathrm{O} - {}^{1}\mathrm{H}$	19	3.15503	0.000379912605026
$^{1}\mathrm{H} - {}^{17}\mathrm{O} - {}^{2}\mathrm{H}$	20	3.32108	0.000000087389949
$^{2}\mathrm{H} - {}^{17}\mathrm{O} - {}^{2}\mathrm{H}$	21	3.48713	0.000000000005026
$^{1}\mathrm{H} - {}^{18}\mathrm{O} - {}^{1}\mathrm{H}$	20	3.32108	0.002049528527111
$^{1}\mathrm{H} - {}^{18}\mathrm{O} - {}^{2}\mathrm{H}$	21	3.48713	0.000000471445778
$^{2}\mathrm{H} - {}^{18}\mathrm{O} - {}^{2}\mathrm{H}$	22	3.65319	0.000000000027111

Mean molecular mass of a water molecule (VMSOW) = 29.9150512 x 10^{-26} kg.

Mean molecular impulse mass of a water molecule with VMSOW isotopic composition = 29.9144976 x 10^{-26} kg.

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INTERNAL REFERENCES: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

[11] ***Molecular Masses*** – This paper defines the molecular mass parameters ($\bar{m}, \bar{m}_i$) and shows how their values were calculated.

[35] ***Water Structures*** – This is a more detailed discussion of water structures and molecular clusters. Topics include: how structures are non-polymeric, hydrogen bonding, bonding limitations and longevity, the basic nature of water structures, structures in water vapor, structures in ice, structures in liquid water, and the nature of surface tension.

[36] ***Water Ionization*** **–** Discussions include: ionization mechanisms, ionic variations, the perfidious proton, and the ionization of water clusters.

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GENERAL REFERENCES: These are works by other authors that contain general treatments of kinetic gas theory, statistical mechanics and thermodynamics, atmospheric physics, and other scientific fields that are used in the current paper. They primarily contribute conceptual frameworks; but offer specific scientific data on occasion.

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Computational System: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3). The reader should be alerted to the fact that this computational system used fifteen significant figures for all calculations—whether or not such precision was warranted by the accuracy of the data. For areas under the normal curve, the NORMSDIST function was used and the ERF and ERFC functions were not used.

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