

Myths and Reality about Chemistry of Oxidane – The Wonder Liquid: A Review

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Abstract

About 71% of Earth's surface is covered by oxidane or water and the Oceans hold about 96% of all earth's water. Water also exists in the air as water vapour, in rivers and lakes, in ice caps and glaciers and in ground as soil moisture and also in aquifers. The water distribution on earth shows that most water in the Earth's atmosphere and crust comes from the world ocean's saline seawater, while freshwater accounts for only 2.5% of the total. Because the oceans that cover roughly 70% of the area of the Earth reflect blue light, the Earth appears blue from space, and is often referred to as the blue planet and the Pale Blue Dot. An estimated 1.5 to 11 times the amount of water in the oceans may be found hundreds of miles deep within the Earth's interior, although not exactly in liquid form. The total volume of water on Earth is estimated at 1.386 billion km³ (333 million

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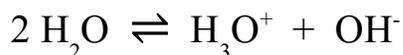
cubic miles), with 97.5% being salt water and 2.5% being fresh water. Of the fresh water, only 0.3% is in liquid form on the surface. In addition, the lower mantle of inner earth may hold as much as 5 times more water than all surface water combined (all oceans, all lakes, all rivers).

Keywords: *Water, molecular structure, water distribution, hydrogen bonding, oxidane.*

Introduction

Liquid water consists of a mixture of molecule and ions, including H_2O , HDO ($\sim 10^{-2}$ %), H_3O^+ and OH^- ($\sim 10^{-6}$ %), H_2O_2 ($\sim 10^{-7}$ %), CO_2 ($\sim 10^{-4}$ %), O_2 ($\sim 10^{-4}$ %) and N_2 ($\sim 10^{-3}$ %). ‘Pure liquid water’, which means consisting of just H_2O molecules, only exists in computer simulations. Even ‘just H_2O ’ consists of a mixture of ‘ortho’ and ‘para’ forms. Avoiding this complexity, ‘water’ is normally taken to mean H_2O molecules, without consideration over its magnetic state. H_2O is also known as ‘light water’ with D_2O being heavy water (D_2O density = 111% H_2O density, 25 °C) and T_2O being super heavy water (T_2O density = 122% H_2O density, 25 °C). The properties of H_2O , D_2O and T_2O 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 (^1H) only. Oxidane or hydrogen oxide or simply water (Leigh et. al) is a polar inorganic compound which is a tasteless, odourless liquid at room temperature with a tinge of blue colour. It is a

universal solvent due to its ability to dissolve many substances. The molecules of water are always in rapid random motion and constantly moving in relation to each other, and the hydrogen bonds are continually breaking and reforming at timescales faster than 200 femto - seconds (2×10^{-13} seconds). However, these bonds are strong enough to create many of the peculiar properties of water, some of which make it integral to life. It is a polar liquid that slightly dissociates disproportionately or self ionizes into an hydronium ion and hydroxide ion.



The dissociation constant for this dissociation K_w at 25 °C is 10^{-14} .

Historical Perspective

Henry Cavendish showed that water was composed of hydrogen and oxygen in 1781. The first decomposition of water into hydrogen and oxygen, by electrolysis, was done in 1800 by English chemist William Nicholson and Anthony Carlisle. In 1805, Joseph Louis Gay Lussac and Alexander von Humboldt showed that water is composed of two parts of hydrogen and one part of oxygen. Gilbert Newton Lewis isolated the first sample of pure heavy water in 1933. The properties of water have historically been used to define various temperature scales. Notably, the Kelvin, Celsius, Rankine, and Fahrenheit scales were, or currently are, defined by the freezing and boiling points of water. The less common scales of Delisle, Newton, Reaumur and Rømer were defined similarly. The triple point of water is a more commonly used standard point today.

Biological Aspect of Oxidane

Water is the most abundant inorganic compound in living systems. The water content of an organism is related to its age and metabolic activity. For example, water amount is highest in embryo (90-95%) and decrease progressively in adult and in the aged. It constitutes 70-90% of living cells. Nearly 90-95% of succulent plant body is water. In human, about two-third of the body composed of water and out of these, about 55 % (20-22 liters) is confined within cells as intracellular fluid (ICF) and the remaining 45% exist as extracellular fluid (ECF) like blood, lymph, tissue fluid etc. In the cell water exist in two forms i.e. in free and bound forms. Free water constitutes 95% of the total cellular water which is used as a natural solvent. Bound water represents just 4-5% of total cellular water which is loosely held to biomolecules by hydrogen bonds and other forces.

Physical Properties of Oxidane

1.	Molar mass	18.01528 g mol ⁻¹
2.	Density	0.9970474 g ml ⁻¹ at 25 °C (density varies with temperature)
3.	Flash Point	Non - inflammable
4.	Melting Point (mp)	0.0 °C
5.	Boiling Point (bp)	99.98 °C (373.13 K)

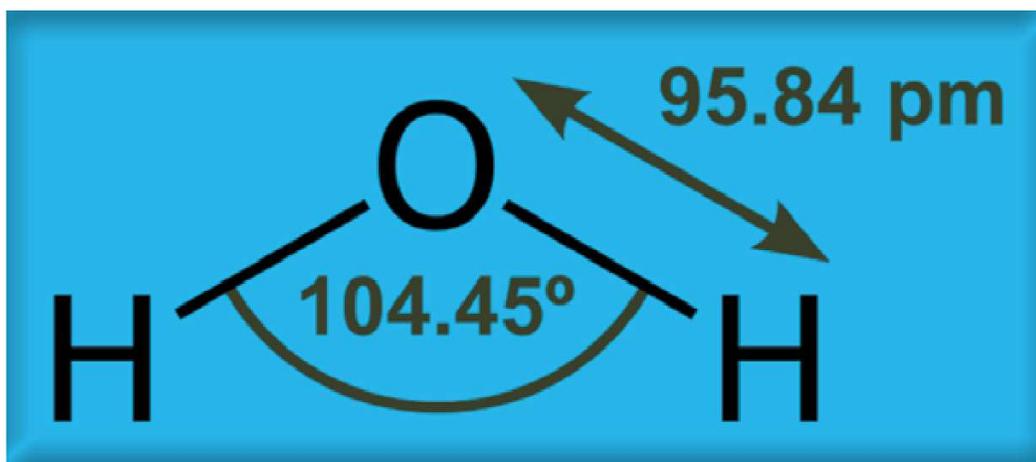
6.	Acidity (pKa)	13.995
7.	Basicity (pKb)	13.995
8.	Refractive index (μ)	1.333 (20 °C)
9.	Molecular Diametre	2.75 Å
10.	Bond angle in the ground state	104.5 °

Myths and Reality about Water

The water molecule is often described in school and undergraduate texts as having four, approximately tetrahedrally arranged, sp^3 -hybridized electron pairs, two of which are associated with covalent bonds to the 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° and such tetrahedral bonding patterns are found in condensed phases such as hexagonal ice. However, **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).

Molecular Structure of Oxidane

A drop of water contains trillions of water molecules held together by weak hydrogen bonds. The tendency of water molecules to bond is called cohesion. The fact that water molecules cohere or coalesce or cling using weak hydrogen bonds is what gives water its fluid consistency.



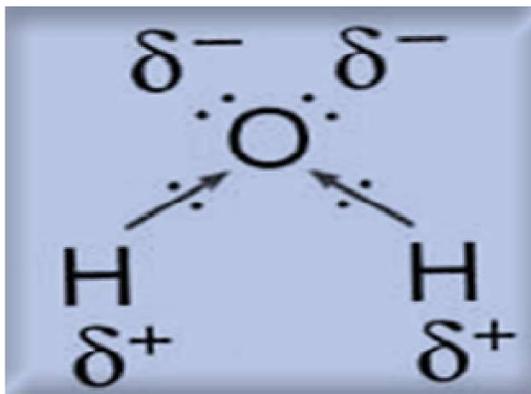
(Fig. 1)

(https://en.wikipedia.org/wiki/Properties_of_water)

Shape, Size, Geometry and Polarity of Oxidane Molecule

Oxidane or water (H_2O) molecule has a triangular geometry with O-H bond distance of 95.84 pm/0.0965 nm and the H-O-H bond angle is 104.45° . Although the water as a whole is electrically neutral, it behaves as an electrical dipole. This is because; oxygen atom is more electronegative than the hydrogen atoms, so it attracts electrons away from the hydrogen nuclei. This gives the oxygen atom two partial negative charges (\ominus), while each hydrogen atom carries a partial positive charge (\oplus).

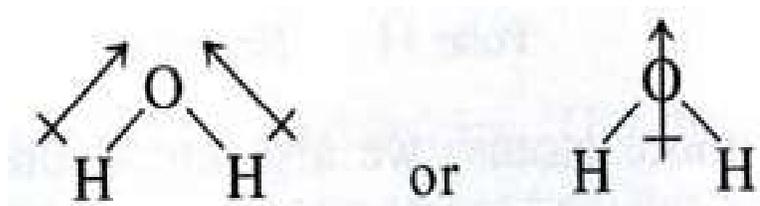
In pure liquid water, each H_2O molecule is hydrogen bonded to an average of 3.4 adjacent H_2O molecules, compared with 4 in ice. Hydrogen bond is a weak non-covalent bond, in which a hydrogen atom is shared by two other atoms i.e. hydrogen donor (tightly bound to hydrogen) and hydrogen acceptor. In biological systems, the hydrogen donor is an oxygen atom (as in water) or nitrogen atom (as in protein or in nitrogen base pairs). Oxygen has a higher electronegativity. Because of this difference in electronegativity, the electrons in the covalent bonds between oxygen and hydrogen get pulled slightly toward the oxygen. This leaves the hydrogens a little bit electron-deficient and thus slightly/partially positive. It is a type of weak electrostatic attraction (from positive to negative). Because each of the water molecules can form four hydrogen bonds, an elaborate network of huge water molecule is formed due to hydrogen bonding. Polarization and hydrogen bonding can be depicted as follows:



(Fig. 2)

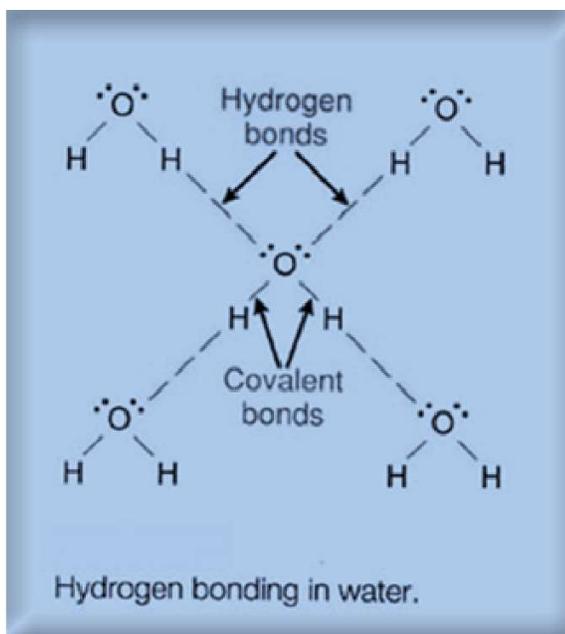
Image Source: “Chemistry in Context” Wm C Brown Publishers, Dubuque Iowa, 2nd edition, A project of the American Chemical Society, ed: A. Truman Schwartz et al., 1997, Chapter 5 “The Wonder of Water”

From a “net polarization” perspective, the molecule looks like as given below:



(Fig.3)

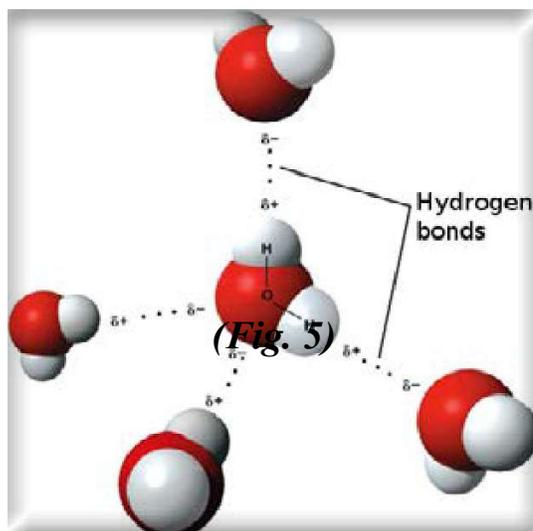
Image Source: “Chemistry and Life”, 4th Edition, John W. Hill, Dorothy M. Feigl, and Stuart J. Baum, Macmillan Publishing Company, New York, 1993.



(Fig.4)

Image Source: “Chemistry in Context” Wm C Brown Publishers, Dubuque Iowa, 2nd edition, A project of the American Chemical Society, ed: A. Truman Schwartz et al., 1997, Chapter 5 “The Wonder of Water”.

3D Oxidane hydrogen bonds



(https://en.wikipedia.org/wiki/Properties_of_water)

Thus we can say that:

Crystal structure = Hexagonal

Molecular shape = Bent

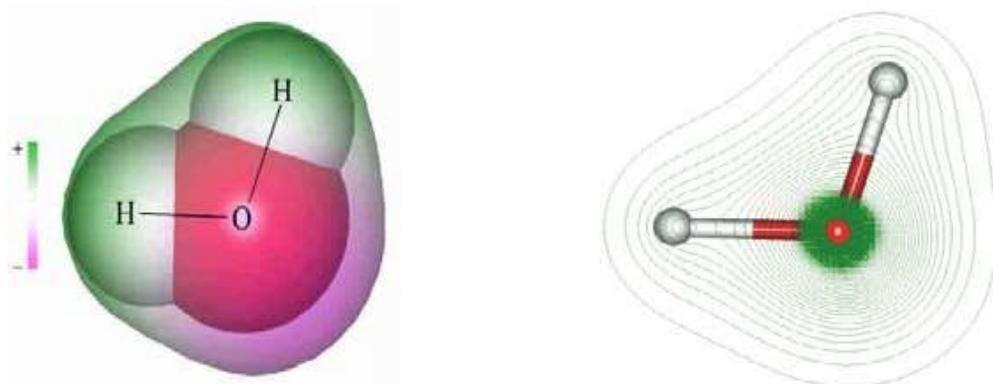
Point group = C_{2v}

Dipole moment = $1.8546 \text{ D}^{[14]}$

Structure of Oxidane in Different Forms

The structure of water varies considerably, depending on its physical state. In all forms, water is a polar molecule with electron-poor hydrogen atoms and electron-rich oxygen. It is this that leads to the hydrogen bonding interaction between water molecules.

Oxidane Vapour



(Fig.6)

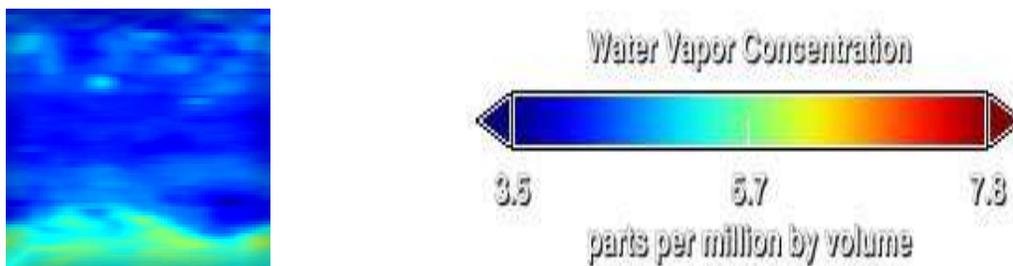
(Approximate size & charge distribution)

Water structure and science

http://www1.lsbu.ac.uk/water/water_molecule.html

Oxidane in the gas phase consists of isolated molecules of H_2O . Each molecule is bent with a bond angle of $\sim 105^\circ$. The negative charge is concentrated around the oxygen atom. The protons have a partial positive charge. The electron density map (above right) shows that the electron density is approximately 10 times greater around oxygen than around the hydrogen atoms.

Water vapor can be identified and quantified through its **IR** spectrum and through its **microwave** spectrum. Water vapor is concentrated close to the surface of the Earth in the troposphere. This shows water vapor in the upper troposphere and stratosphere through the summer season of 2004. It was obtained by the **Microwave Limb Sounder (MLS)** instrument on **NASA's Aura satellite**. MLS can simultaneously measure several trace gases and ozone-destroying chemicals the upper atmosphere.

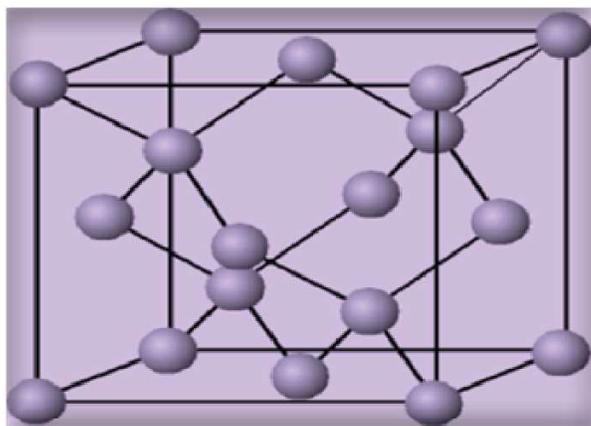


(Fig. 7)

(Structure of water, Lectute series, Prof. Patricia Shapley, University of Illinois, 2010)

Ice

Unlike water vapor, in the solid phase the oxygen atoms in water are in a tetrahedron of hydrogen atoms. Below is a diagram showing the position of the oxygen atoms of water in a cubic close packed lattice (CCPL). In the center of the lines connecting each oxygen atom to another is a hydrogen atom. The bonds are rigid within the ice structure.

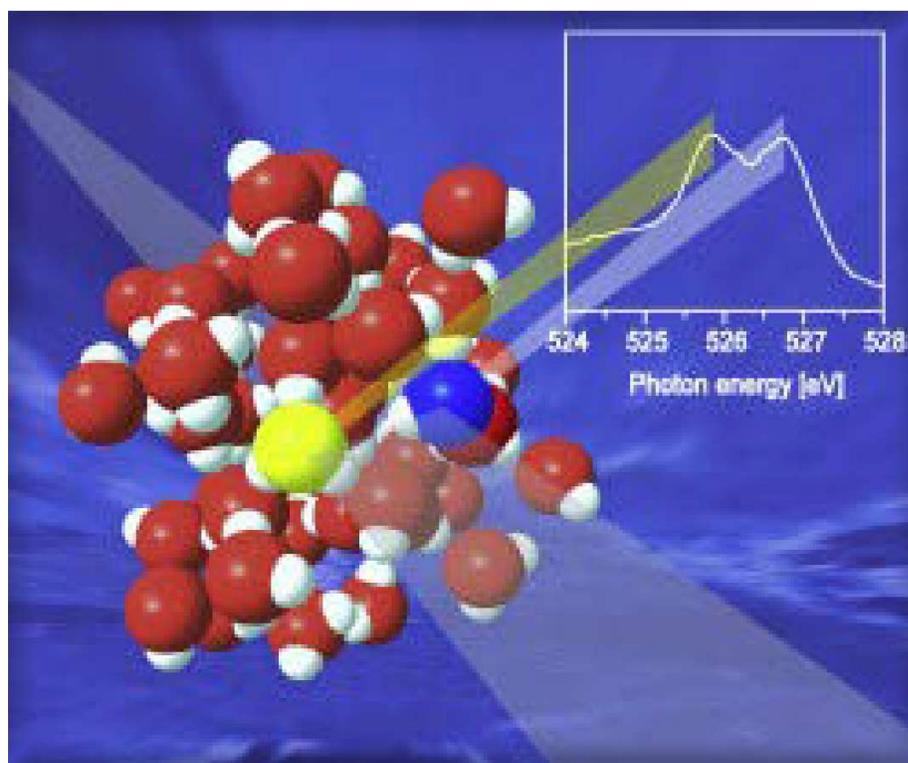


(Fig. 8)

(Structure of water, Lectute series, Prof. Patricia Shapley, University of Illinois, 2010)

Liquid Oxidane

But despite its prevalence and importance, liquid water is not as well understood in the other phases. In the recent study, Nilsson and colleagues probed the structure of liquid water using X-ray Emission Spectroscopy (**XRES**) and X-ray Absorption Spectroscopy (**XRAS**). These techniques use X-rays, generated by a synchrotron light source, to excite electrons within a water molecule's single oxygen atom. Tuning the X-rays to a specific range of energies can reveal with precision the location and arrangement of the water molecules.



(Fig.9)

*(Structure of water, Lecture series, Prof. Patricia Shapley,
University of Illinois, 2010)*

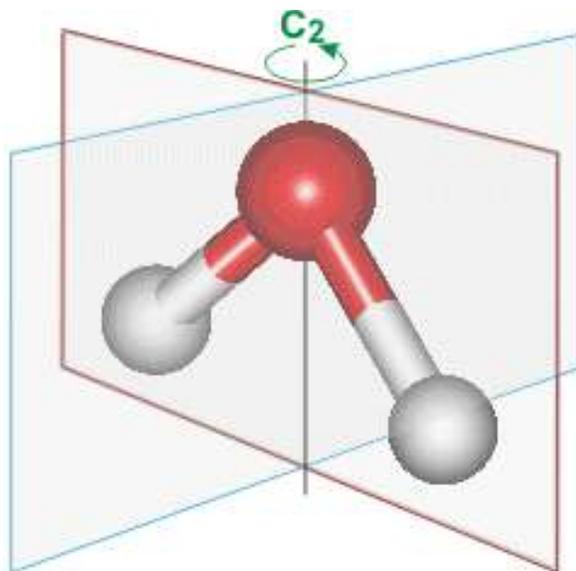
The researchers found that water is mostly made up of tetrahedral groups, as in ice, but there is also a less defined structure that seems to be like a distorted, hydrogen-bonded form of water vapor. The oxygen atoms in distorted water molecules have 2 strong bonds to hydrogen and 2 weak ones. The oxygens in tetrahedral, ice-like water have 4 equivalent bonds to hydrogen. Even in its tetrahedral form, liquid water is different from ice because the bonds are constantly breaking, the molecules of water moving, and more bonds forming. Water is denser than ice because water molecules are held within the holes of the cubic close packed lattice (CCPL).

Quantum Tunneling of Oxidane

The quantum tunneling dynamics in water was reported as early as 1992. At that time, it was known that there are motions which destroy and regenerate the weak hydrogen bond by internal rotations of the substituent water monomers. But in 2016, it was reported that the hydrogen bond can be broken by quantum tunneling in the water hexamer. Unlike previously reported tunneling motions in water, this involved the concerted breaking of two hydrogen bonds. Later in the same year, the discovery of the quantum tunneling of water molecules was reported. Water molecules are tiny, electrically neutral and V-shaped with molecular formula H_2O and molecular diameter about 2.75 Å. Water is much smaller than almost all other molecules. For example, it has a smaller volume, and is much lighter, than the four other common atmospheric molecules, oxygen (O_2), nitrogen

(N₂), argon (Ar) and carbon dioxide (CO₂); the density of water vapor being just 62% the density of dry air.

In the liquid state, in spite of 80% of the electrons in H₂O being concerned with bonding, the three atoms do not stay together as the H 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 H₂O 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.



(Fig. 10)

(Water structure and science

http://www1.lsbu.ac.uk/water/water_molecule.html)

Water molecules (H₂O) 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. 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 even at a temperature of absolute zero (0 K). Due to the relatively large positive charge on the oxygen atom nucleus (8+) and the closeness of its electrons, the oxygen atom attracts electrons much more strongly (i.e. is much more electronegative) than the hydrogen atoms (1+). This results in a charge transfer from the hydrogen atoms towards the oxygen atom and, hence, the polarity of the water molecule.

IR spectra of two types of large water-containing clusters, phenol-(H₂O)_n ($n < \sim 50$) and H⁺(H₂O)_n ($n \leq 221$), measured in the OH stretching vibrational region have clearly shown hydrogen bond networks in the bulk and interior crystallisation of the clusters. [x] Size dependence of the observed spectra was interpreted in terms of coordination numbers of water molecules, ring sizes of hydrogen bond networks.

Phase-sensitive sum-frequency vibrational spectroscopy was used to obtain the OH and OD stretch spectra of the imaginary part of the nonlinear susceptibility, $\text{Im } \chi S^{(2)}(\omega_{\text{IR}})$, for H₂O/vapor, D₂O/vapor, and 2:1 H₂O–D₂O/vapor interfaces that explicitly characterized their resonances. They all exhibit a positive and a

negative resonance band in the bonded-OH region, clearly different from those deduced from fitting of the $|\chi S^{(2)}(\omega IR)|^2$ spectra, and from MD simulations. The broad continuum is characteristic of inhomogeneously broadened resonances associated with interfacial water species of various hydrogen-bonding geometries and strengths. Spectral changes due to excess ions at the interfaces support the picture.

Conclusion

Thus we can see that the structure of water is too complex to be dismissed easily and needs further spectroscopic and otherwise studies/probe so that its structure as well as its properties are fully understood. Till then it continues to be the wonder liquid and elixir of life.

Reference

- A Brief History of Temperature Measurement. *Home.comcast.net*. Retrieved on 24.09.2017.
- Alexander I. Kolesnikov, Reiter, G. F., Choudhury, N., Prisk, T. R., Mamontov, E., Podlesnyak, A., Ehlers, G., Seel, A. G., Wesolowski, D. J., & Lawrence M. A. (2016). Quantum Tunneling of Water in Beryl: A New State of the Water Molecule, *Phys. Rev. Lett.* **116**, pp. 167802.

Braun, C. L. & Smirnov, S. N. (1993). Why is water blue? *Journal of Chemical Education*, **70** (8): pp. 612.

“Enterprise and electrolysis...” Royal Society of Chemistry, (2003).
Retrieved on 24. 09.2017.

Fujii, A. & Mizuse, K. (2013). Infrared spectroscopic studies on hydrogen-bonded water networks in gas phase clusters, *International Reviews in Physical Chemistry Vol. 32* (2), pp. 266 – 307.

G. J. Leigh, H. A. Favre & W.V. Metanomski (1998). *Principles of chemical nomenclature: A guide to IUPAC recommendations*, Edited by G.J. Leigh, Blackwell Science Ltd, UK, p. 34.

Greenwood, N. N. & Earnshaw, A. (1997). *Chemistry of the Elements* (2nd edn.) Butterworth-Heinemann. p. 620.

Greenwood, N. N. & Earnshaw, A. (1997). *Chemistry of the Elements* (2nd edn.) Butterworth-Heinemann. p. 601.

Joseph Louis Gay-Lussac, French chemist (1778–1850), (1902), Encyclopedia. Footnote 122-1. *Retrieved on 24. 09. 2017.*

Lewis, G. N., MacDonald, R. T. (1933). Concentration of H₂ Isotope, *The Journal of Chemical Physics*. **1** (6): p. 341.

Lide, D. R. (2003). Dissociation Constants of Inorganic Acids and Bases, *CRC Handbook of Chemistry and Physics, 84th Edition*. *CRC Handbook*. CRC Press, Chap. 8, pp. 1 – 2616.

Lide, D. R. (2003). Concentrative Properties of Aqueous Solutions: Density, Refractive Index, Freezing Point Depression, and Viscosity, *CRC Handbook of Chemistry and Physics, 84th Edition*. *CRC Handbook*. CRC Press - 8.

- Lide, D. R. (2003). Dipole Moments, *CRC Handbook of Chemistry and Physics, 84th Edition. CRC Handbook. CRC Press – Chap. 9 . pp. 1 - 2616.*
- Linstrom, P. J. & Mallard W. G. (eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, *National Institute of Standards and Technology, Gaithersburg (MD), <http://webbook.nist.gov> (Retrieved On 24.09.2017)*
- Pugliano, N. (1992). Vibration-Rotation-Tunneling Dynamics in Small Water Clusters, *Lawrence Berkeley Lab., CA (United States): 6. doi:10.2172/6642535.*
- Richardson, J. O., Pérez, C., Lobsiger, S., Reid, A. A., Temelso, B., Shields, G. C., Kisiel, Z., Wales, D. J. & Pate, B. H. (2016). Concerted hydrogen-bond breaking by quantum tunneling in the water hexamer prism, *Science, 351 (6279), p. 1310–1313.*
- Smith, J. D., Christopher D. C., Kevin R. W., Ronald, C. C., Phillip L. G. & Richard J. Saykally (2005). Unified description of temperature-dependent hydrogen bond rearrangements in liquid water, *Proc. Natl. Acad. Sci. USA. 102 (40): pp. 14171–14174.*
- Tian, C. S. & Shen, Y. R. (2009). Sum-frequency vibrational spectroscopic studies of water/vapor interfaces, *Chemical Physics Letters, Vol. 470 (1 – 3), pp 1 – 6.*
- U.S. Geological Survey’s (USGS) (2017). Water, the Universal Solvent. *Water Science School, USA.*