Density functional theory used for the study of molecular interaction in water cluster: A review

Sanjay Panwar[1], Mirtunjai Mishra[2], Narinder Kumar[1]*, Devendra Singh[2], Devesh Kumar[2]

[1]Department of Physics, School of Applied & Life Sciences, Uttaranchal University, Dehradun, Uttarakhand-248007, INDIA

[2]Department of Physics, School for Physical & Decision Sciences, Babasaheb Bhimrao Ambedkar University, Vidya Vihar, Raebareli Road, Lucknow (U.P.) 226025 INDIA

*Corresponding author: knarinder7@gmail.com

Abstract: Due to the significance of "water clusters," groups of water molecules locked together by hydrogen bonds, in understanding cloud and ice formation, solution chemistry, and a wide range of biological activities, they have been the focus of several intensive experimental and theoretical research. There is an obvious need for chemists to have a better knowledge of how such aggregates affect the general structure of their surrounds. "Water clusters" can play a significant role in the stability of supramolecular systems both in solution and in the solid state.

INTRODUCTION

Water is a particular and uncommon form of material, which is why it is an essential part of all living things. Philosophers, naturalists, and scientists are all intrigued by the peculiar nature and qualities. Despite years of intensive research, scientists are still interested in water because of how little is known about it. Water's primary physical and chemical characteristics. Water has

several special qualities that are vital to life. Others have an impact on the living organism's size and shape, as well as how they function and the physical boundaries of their environment. The most recent field of computer simulation has also contributed since it has advanced to the point where it can interpret experimental data and stimulate qualities that are not directly accessible through experiment in the study of water. Many of the fundamental physical characteristics of water cannot be at least partially explained in terms of their molecular and structural makeup. The water molecule's molecular structure is H_2O. It's a very small, bent molecule. It is made up of two molecules of hydrogen and one molecule of oxygen that are joined by covalent bonds. Each molecule has a neutral electrical charge. It is a polar molecule because the centres of positive and negative charge are separated from one another.

Ten electrons are paired together in five orbitals when the molecule is created. The remaining two pairs are created by each of the two identical O-H covalent bonds, with one pair being tightly linked with the oxygen atom and the other two pairs being attached to it as outside electrons.

(a)   (b)

Figure 1: Lewis structure of water

Lone Pair

The O-H bond (covalent bond) is represented by the pair of electrons between O and H atoms, while the lone pair is represented by the other two pairs of electrons. Due to their attraction to one another, the electron pair's electron clouds form a tetrahedral arrangement around the oxygen nucleus. So, the bent structure of the water molecule comes from this (Lee, 1994).

Dipole Moment

The molecule of water is electrically neutral. Water is electrically polarised because oxygen has a significantly higher electro negativity than hydrogen and because of this, the electron dispersion is more concentrated near the former. Additionally, it exhibits a persistent dipole moment in the gas phase of 6 10(-30) cm. Due to the randomly ordered mutual polarisation of nearby water dipoles, the dipole moment is significantly bigger in liquid and ice. Each atom (hydrogen and oxygen) must be given a partial charge in order to replicate the net charge and dipole moment of the molecule and so depict the polarity of the molecule.

Due to the oxygen's high electro-negativity, all of the electrons are strongly attracted to it compared to the solitary positive charge on each hydrogen atom since the water molecule is bent and the carrier of the positive charge does not correspond with the centre of the negative charge.

In liquid water, a molecular dipole moment is produced by the dislocations of the centres of positive and negative charge. A unit positive charge (one electron) and a unit positive charge are separated by 0.061 nm at this dipole moment. The water molecule's polar character also develops as a result of the dipole moment.
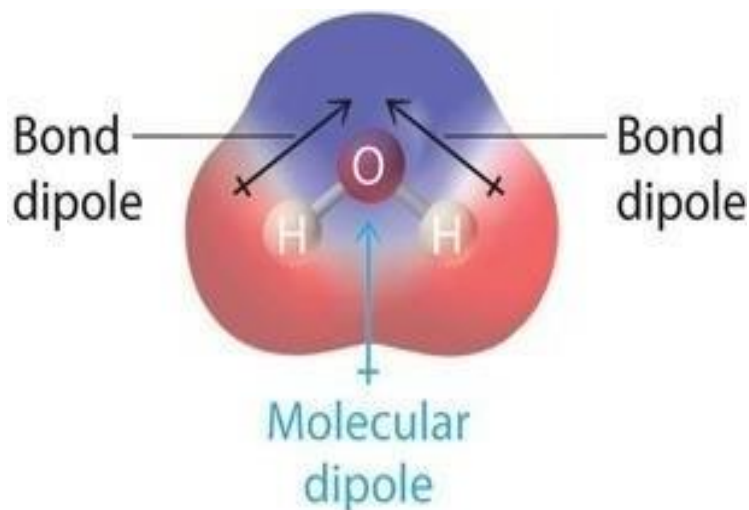

Figure 2: Dipole Moment

Structure
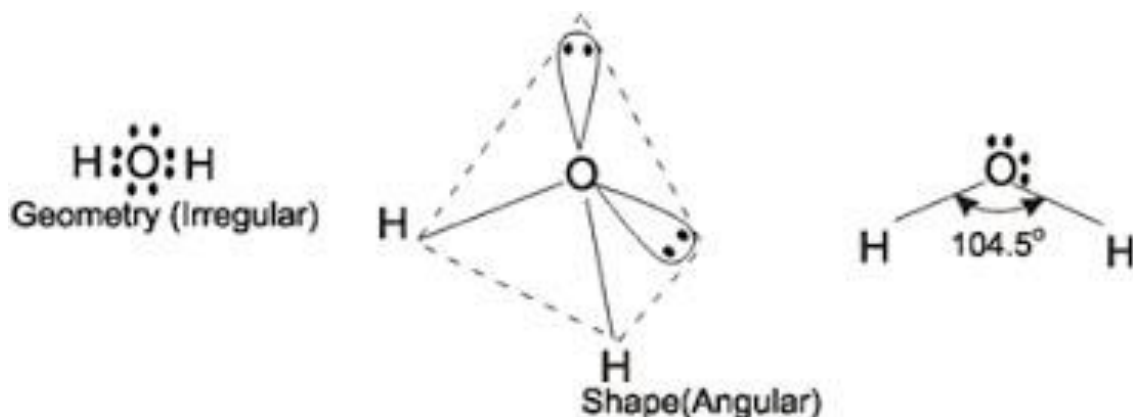
Figure 3: Geometry of water molecule

Fig. 3 provides an illustration of the water molecule's shape. It consists of two 0.096 nm long O-H bonds that are angled at 104.58 degrees. If two unconnected atoms are placed near enough to overlap their electron orbitals, they will strongly repel one another. The two atoms at greater distances have a modest attraction towards one another because of induced dipole-induced dipole (London dispersion) forces. Water is electrically neutral, but because oxygen has a far higher electronegativity than hydrogen does, the electron distribution is more concentrated near (Maheshwary, 2001).
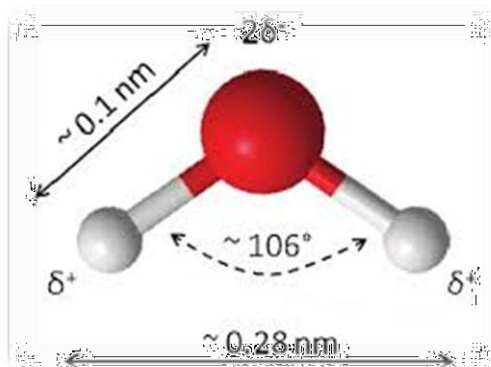
Figure 4: Water Dipole

The average H-O-H angle in water is 1060, and the O-H bond length is around 0.097 nm (0.1nm). Each positively charged hydrogen atom shares the neutralising charge with an average 70% negative charge on the oxygen atom's electron, depending on the energy and environment.

These properties will vary depending on the specific water molecule. Due to the opposing charges of oxygen and hydrogen atoms, different water molecules are attracted to one another. The attraction is strongest when the O-H bond from one water molecule directly attaches to neighbouring oxygen atoms in another water molecule, or when the three atoms O-H-O are arranged in a straight line. Hydrogen bonding occurs when the hydrogen atoms seem to cling on to the two oxygen atoms. They produce high molecular densities because of their tiny size and the attraction between nearby water molecules. The cohesive effect that results from the attraction of nearby molecules inside the liquid water is what gives it its liquid consistency at room temperature. Since nonmetallic liquid water has one of the greatest dielectric constants, it also has the unusual trait that both its high dielectric constant and expansion during freezing give liquid water its structural characteristics at the molecular level (Steve, 1994).

Intermolecular interactions

Water is a tiny solvent, taking up just around 0.03 nm^3 per molecule at normal temperature and pressure. Strong intermolecular interactions between the hydrogen and oxygen atoms give it a very cohesive character. Water has a high boiling point, a high surface tension, and a high intermolecular interaction (between hydrogen and oxygen). Additionally, water requires a lot of heat to evaporate. The intermolecular connection changes dramatically when one or both hydrogen atoms are changed, leading to a weakening of the intermolecular interaction. The following results also come from the strong to forceful contact with water (Estrin 1996):

1. High viscosity - Since a liquid must constantly break the contact between nearby molecules, or modify the intermolecular interaction, in order to move.

2. Water is a little solvent with a tiny particle size. In contrast to other liquids, it therefore has a comparatively high specific heat and heat of vaporisation. When comparing other liquids, water has a higher level of intermolecular interaction.

Dielectric constant

The dielectric constant is a measurement of how quickly a material becomes polarised in relation to vacuum in the presence of an electric field. The degree of dielectric polarisation (dipole moment per unit volume) brought about by a unit field serves as its defining characteristic. The dielectric constant of water is over eighty times greater than that of vacuum. It is significantly more polarizable than the majority of organic solvents.

A polar liquid like water's dielectric constant depends on four main factors:

1. The molecule's permanent dipole moment

2. The dipole density

3. How quickly can one get orientated in the field's response?

4. How conscientious is this orientation?

A greater dipole moment exists in water. Due of its tiny size, it has many dipole moments per unit volume. They can be quickly and readily reoriented while they are liquid. Since water contains a lot of H-bonds, the polarisation response is positive. Water molecules can't just reorient themselves to their neighbour on their own. They successfully reposition themselves as a trio. The extraordinarily high dielectric constant factor of water is explained by the whole structure. Since it lessens the thermal fluctuation that prevents dipole alignment by an electrostatic field, lowering the temperature raises the dielectric constant. The dielectric constant of ice illustrates the significance of the influence of dipole reorientation across the six orders of magnitude longer time scale of reorientation order (Miyake, 2003).

Cluster

Clusters are tiny, multiple-atom particles in physics. Any particle with between 3 and 3 107 atoms is often regarded as a cluster. Sometimes, clusters are also thought to include two-atom particles. A molecule might also be a particle with two atoms (Leach, 2001).

Introduction of water cluster

A useful experimental platform for the study of the microscopic physics and chemistry of salvation is the water cluster. It is feasible to follow the development of intermolecular interactions from a solitary water molecule to a bulk cluster by keeping track of the features of water clusters as a function of the number of water molecules. Hydrogen bonds are used to hold together water clusters or collections of water molecules. Numerous theoretical and experimental studies have been conducted on it. Additionally, their significance in comprehending the chemistry of solutions, several biological processes, ice production, and cloud formation.

We focus our research on the interactions between O-H or hydrogen bonds in the cluster of water molecules. This seemingly straightforward interaction has proven to be one of the most fascinating and crucial for understanding the chemical and physical characteristics. Early studies on these bonds mainly focused on how hydrogen bonding appeared in condensed phases (Friesher, 2005).

The bonding patterns of the molecules involved in the H-bond might be observed changing through the use of infrared and Raman spectroscopy (Steve, 1994). The structure of liquid and solid water is generally difficult to describe at the molecular scale due to the vast hydrogen-bonding network present and its soft modes. The potential energy hyper surface of water clusters has a large number of local minima, and as the size of the cluster increases, so does the number of these hyper surfaces, making the search for global minima computationally challenging (Maheshwary, 2001). Recent years have seen significant advancements in our understanding of the structure of water clusters.

Theoretically, several models of water clusters have been investigated in order to comprehend the properties of hydrogen bonding. Research on small water clusters has been conducted both theoretically and experimentally. To get insight into the nature of these inter-water interactions in various contexts, it is crucial to have a thorough understanding of the many different conceivable water structures, aggregates, and their stabilities (Dorsett, 2007).

Water Cluster

A discrete arrangement of water molecules bound together by hydrogen bonds is known as a water cluster. These clusters have been observed experimentally or have been anticipated in silico (a computer programme or computer simulation), in ice, the crystal lattice, and bulk liquid water. The Water cluster explains a number of peculiar properties of water, including its

remarkably odd density-temperature relationship. Water clusters can reveal details on how specific supramolecular structures are stabilised. The oxygen to oxygen distance is shown to decrease with increasing cluster size; thus, due to a shift in charge distribution, the H-acceptor molecule becomes a better H-donor molecule as water molecule concentration rises (abdulsatter, 2012).
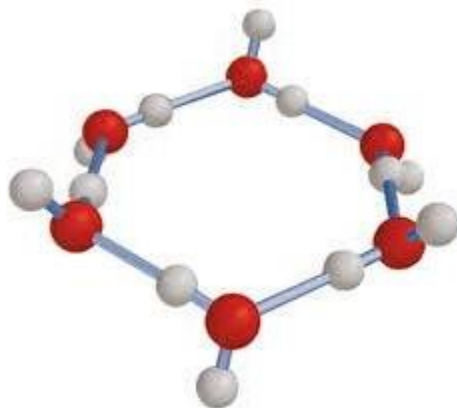
Figure 5: Water molecule cluster [hexamer,$(H_2O)_6$]

Hydrogen Bonding

Two varieties of hydrogen bonding exist (Sotiris, 1993)

(i) Hydrogen bonds between molecules

(ii) hydrogen bonds within individual molecules

Intermolecular hydrogen bonding

Intermolecular hydrogen bonding is the word used to describe hydrogen bonds that occur between molecules of the same or distinct substances.

for instance, water, ammonia, etc.

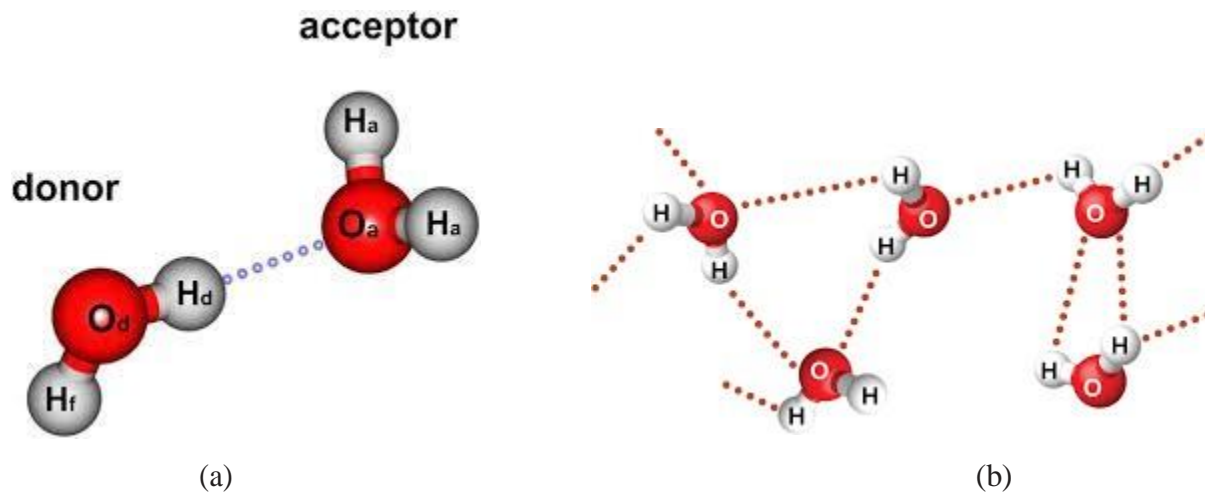### Intramolecular hydrogen bonding

Intermolecular hydrogen bonding is the term used to describe hydrogen bonds that occur between molecules.

nitro phenol, for instance

Hydrogen intermolecular bonds function in the water crystal. where two H atoms and the centre oxygen atom are joined covalently. A hydrogen bond is created by each H.

The core oxygen atom additionally establishes hydrogen bonds with the surrounding molecules in addition to these two. and in a way that several water clusters are created (tsai, 1993).

| (a) | (b) |

Figure 6 (a) represents the intermolecular hydrogen bonding and (b) represents the intramolecular hydrogen bonding

In this work we study only the water cluster upto four molecules.

    (i)   Water Monomer   (H_2O)

    (ii)   Water Dimer $(H_2O)_2$

    (iii)   Water Trimer $(H_2O)_3$

    (iv)   Water Tetramer $(H_2O)_4$

Monomer (single water molecule,H_2O)

It has no hydrogen bonds since there is just one water molecule in it. O-H bonds are separated by 0.991 nm, while the two hydrogen atoms are spaced apart by 1.568 nm. The two arms are at an angle of 1040.56.

The oxygen atoms in a water molecule are covalently joined to two hydrogen atoms, and it also possesses a pair of normally invisible electrons. As a result, it has the ability to give two hydrogen atoms to nearby acceptors and take two lone protons from surrounding water molecules. When water is maximally hydrogen bound, the hydrogen atoms and the lone pair of electrons are organised in a tetrahedral pattern around the O atom, allowing water molecules to

function as a four-connecting node in the hydrogen linked network. This is true of ice, which is made up of a tetrahedral network of four water molecules bonded to one another. A water molecule can coordinate up to four times at once. A water molecule is sparsely bound when it is in liquid form because part of the donor and acceptor sites are not being used.
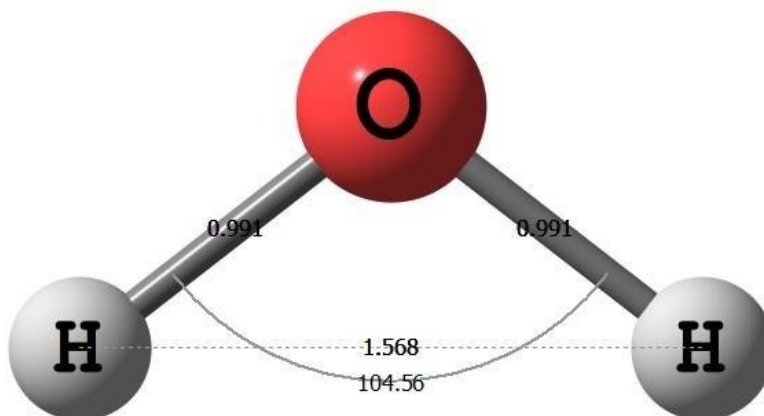

Figure 7: Single water molecule

Water Dimer $(H_2O)_2$

It has two water molecules within that are only weakly connected by hydrogen bonds. The smallest water cluster is this one. It has been the subject of several theoretical investigations because it is the most straightforward model system for examining hydrogen bonds in water. The two water molecules' binding energy is thought to be 5–6 kcal/mol. Experimental measurements place the O-O distance of the vibrational ground state at around 2.98; the hydrogen bond is essentially linear, although the angle with the acceptor molecule's plane is about 57°. The linear water dimer is the name of the vibrational ground-state (Lia, 1996).
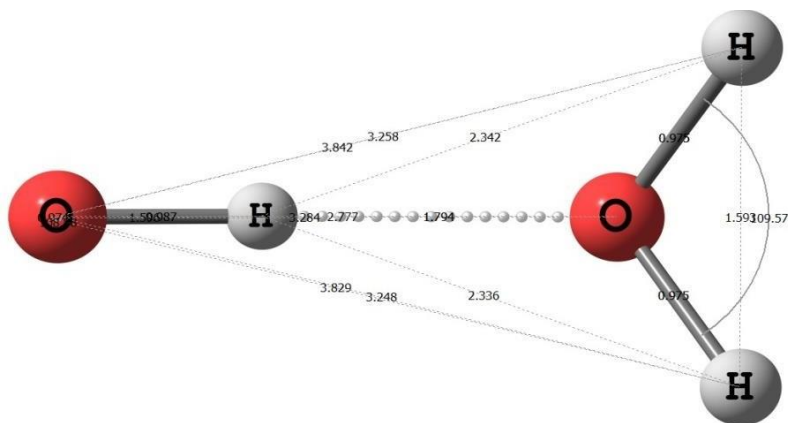
Figure 8: Water dimer

A specific water molecule is primarily a 4-connecting node in the hydrogen-bonded network of water molecules. Two hydrogen atoms and two lone pairs are arranged tetrahedrally around the oxygen atom in the centre of the tetrahedron. If two hydrogen atoms and the two lone pairs are assumed to be recognisable or distinct from one another, one can imagine four different potential water dimmers. Now, in figure.6, one hydrogen atom is highlighted in light blue, while the other hydrogen atom is highlighted in white. Similar to how the two lone pairs are distinguished, the labels are yellow and light blue in hue. There are now four distinct combinations of lone pairs and hydrogen atoms across the horizontal axis of the dimer established specific hydrogen and a lone pair, resulting in four different water dimers.
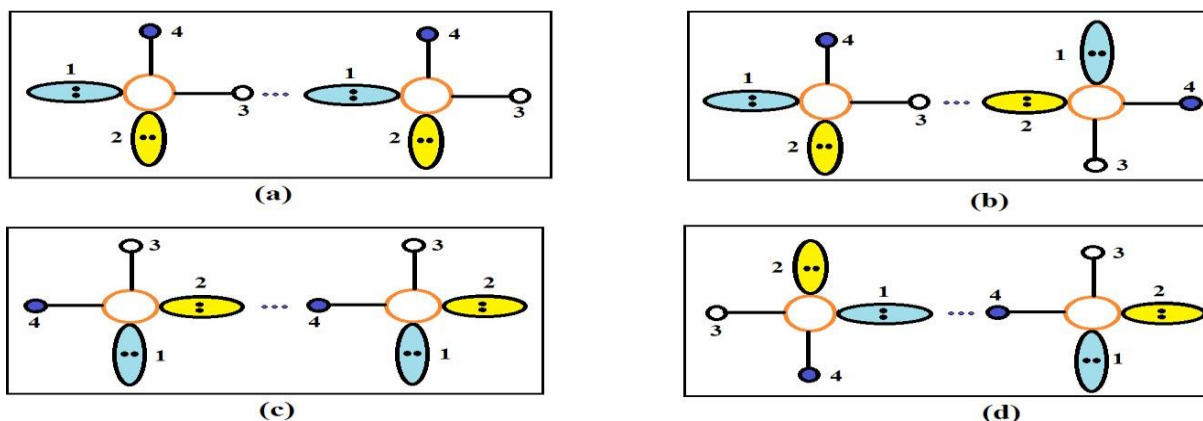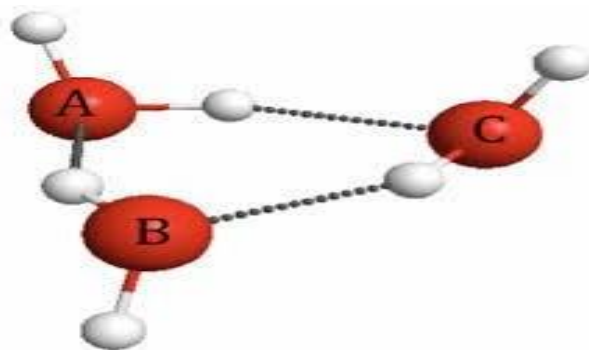

Figure 9: Four possible dimmers when distinguished the two hydrogen atoms and two lone pair distinctly.

However, in reality, one only obtains two unique water dimers since it is impossible to discriminate between the two hydrogen atoms and the two lone pairs. Figure 9 shows two possibilities that result from the rotational degree of freedom around the dimer axis: in one dimer, two hydrogen atoms and two lone pairs are on the same side of the dimer axis (Fig. 9a), and in the other, one lone pair and one hydrogen atom are on either side of the dimer axis (Fig. 9b).

Figure 10: Two possible distinct dimers when two hydrogen atoms and two lone pairs are considered indistinguishable.
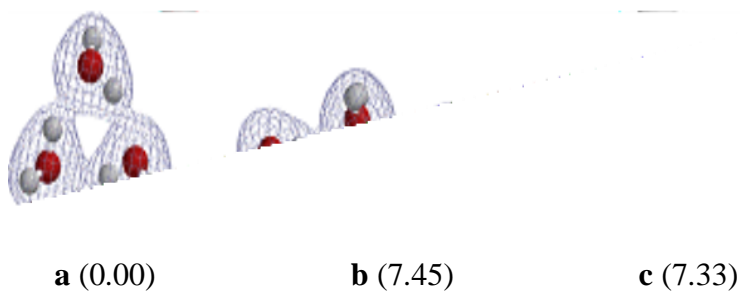
Trimer ($(H_2O)_3$)

Three water molecules make up a trimer, which are kept together or joined by a hydrogen bond. The hydrogen of one molecule connects or bonds with the oxygen of another molecule to produce a ring-like shape or compact structure. A six-member minimal energy cyclic water trimer that is chiral and goes through two different forms of degraded structural rearrangement has been constructed through theoretical calculations. Three hydrogen bonds form an equilateral angular shape in the water trimer. Above and below the plane that the oxygen atoms form are positioned free atoms. Compounds develop chiral compound properties as a result of this arrangement. Every monomer in a water trimer functions as both a donor and an acceptor of hydrogen, making it a special kind of stricture.

Figure 11: Water trimer

Every monomer that makes up a water trimer functions as both a donor and an acceptor of the hydrogen bond, and it also contains one free and one bound hydrogen atom. This makes it a special kind of structure. The hydrogen bond in the water trimer is shorter than in the water dimer, with an average length of 0.1926 nm. The hydrogen bond is strengthened as a result of the decrease in the O-O distance (0.2797 nm). Since just one hydrogen bond needs to be broken for a dimer to dissociate, the energy required to make a trimer is twice as great as that required to form a dimer. The three hydrogen bonds must be broken in order for the trimer to disintegrate into a monomer (anant, 2005, lee,1995).


a (0.00)   **b** (7.45)   **c** (7.33)

Figure 12: Geometries and electron density surfaces of water trimers.

Tetramer $(H_2O)_4$

Tetramers are made up of four water molecules that have formed a closed structure and are joined or bonded to one another by hydrogen bonds.

The tetramer, like its trimer, has a cyclic structure in which hydrogen free atoms alternate over and beneath the location of the ring O-O-O-O to produce a structure with a S 4-symmetry component. Every monomer in the tetramer cluster functions both as a donor and an acceptor, similar to the trimer. However, because they have an even number of oxygen atoms as part of the ring, they do not have the enantiomeric feature that the water trimer has. The O-O bond length (0.2748 nm) and the strength of the hydrogen bond both exhibit an exponential trend in the tetramer (0.1719nm).
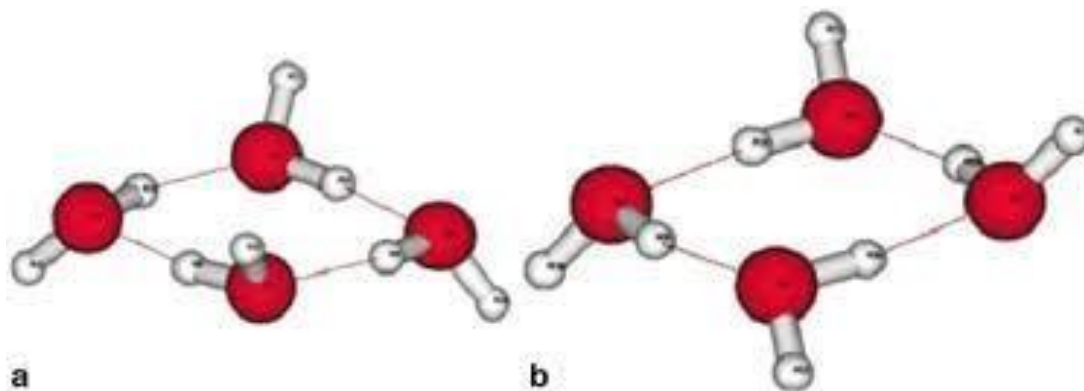
Figure 13: Tetramer structure of water

Two water dimer clusters together form a tetramer water cluster. Two different water dimers, dimer-(a) and dimer-(b), illustrated in Fig. 13, are easily distinguishable in relation to the hydrogen bond axis. Both dimer (a) and dimer (b), it should be emphasised, can be considered to have a preferential orientation along their bonding axis that should be followed along the donor site (lone pair) to the acceptor site (hydrogen). As a result, dimer (a) and dimer (b) are both directed by nature. This results in the two obvious combinations of parallel and antiparallel dimers for each of these dimers.


(a)   (b)
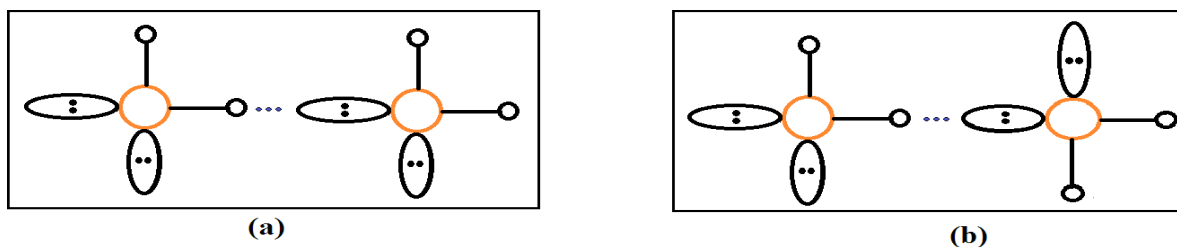
Figure 14:   dimer-(a)   dimer-(b)

As the hydrogen atoms and lone pairs in Fig. 14 Dimar-(a) lie on the opposite side of the dimer axis, they may easily complement each other by joining side by side, creating two potential tetramers. Two dimer-(a) are produced by the unidirectional side-wise combination of tetramers, while two dimer-(b) are produced by the antiparallel side-wise combination of tetramers (a).

In contrast to the less stable cyclic tetramer e, the electron density in the H-bond region is fairly high in the more stable cyclic tetramer d. It appears that a stable H-bond pattern is one in which there are more arrows (the directions of the H-bonds) pointing in the same direction (david, 2005).

d (0.0) **e** (12.4)   **f** (6.81)   **g** (6.49)   **h** (4.89)
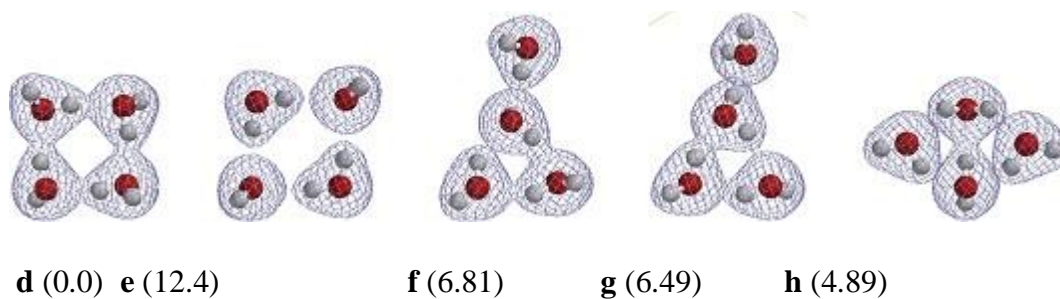
Figure 15: Geometries and electron density surfaces of water tetramers.

CONCLUSION

In this study, it was discovered that all water molecule clusters are caused by the O-H interaction. The water molecule's monomer, dimer, and trimer are polar compounds, but the tetramer is a non-polar substance by definition. O-H interaction causes two water molecules to form linear geometry, three water molecules to form triangular geometry, and four water molecules to form square geometry.

ACKNOWLEDGMENT

REFERENCES

1. http://crystal.med.upenn.edu/sharp-lab-pdfs/sharp_EncLifeSci.pdf

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

3. Lee C., Chen H., and Fitzgerald G., (1994)Structures of the water hexamer using density functional methods; The Journal of Chemical Physics 101, 4472.

4. https://en.wikipedia.org/wiki/Cluster_(physics)

5. Maheshwary S., Patel N., Sathyamurthy N., Kulkarni AD. and Shridhar R. Gadre; (2001) Structure and Stability of Water Clusters (H2O)n, n) 8-20: An Ab Initio Investigation; J. Phys. Chem. A , 105, 10525-10537

6. Steve Scheiner; (1994) Ab Initio Studies Of Hydr.Ogen Bonds: The WaterDimer Paradigm; Annu. Rev. Phys. Chern. 45: 23-56

7. D. A. Estrin, L. Paglieri, G. Corongiu and E. Clementi; (1996) Small Clusters of Water Molecules Using Density Functional Theory; J. Phys. Chem., 100, 8701-8711

8. https://en.wikipedia.org/wiki/Water_cluster

9. T. Miyake and M. Aida; (2003) Hydrogen Bonding Patterns in Water Clusters: Trimer, Tetramer and Pentamer ; Internet Electron. J. Mol. Des., 2, 24–32

10. Andrew R. Leach; (2001)Molecular Modeling Principle and Applications;2 , 233-345.

11. Richard A. Friesner; (2005) Ab initio Quantum Chemistry: Methodology and Applications, 5, 22-33.

12. Dorsett; H.E; (2007) A review of quantum chemical studies of energetic materials; DCTO Technical Report, 5, 785- 795.

13. Abdulsatter; Mudar A; (2012) SiGesuperlattice nanocrystal infrared and Raman spectra: density functional theory study. J.Appl.Phys;111, 635-640.

14. Sotiris S. Xantheas and Thom H. Dunning Jr.; Ab initio studies of cyclic water clusters (H2O) n , n=1–6. I. Optimal structures and vibrational spectra; The Journal of Chemical Physics 99, 8774 (1993)

15. Sotiris S. Xantheas; (1995) Ab initio studies of cyclic water clusters (H2O) n , n=1–6. III. Comparison of density functional with MP2 results; The Journal of Chemical Physics 102, 4505

16. C.J. Tsai and K.D. Jordan; (1993) Theoretical study of the (Hz0)6 cluster; CHEMICAL PHYSICS LETTERS; 213, 1,2

17. Thomas R. Dyke, Kenneth M. Mack, and J. S. Muenter; (1977) The structure of water dimer from molecular beam electric resonance spectroscopy; The Journal of Chemical Physics, 66, 498.

18. K.Lia; J.D.Cruzan; R.J.Saykslly; (1996) Water Cluster; Science.New Series, 241, 5251

19. K. Kim and K. D. Jordan; (1994) Comparison of Density Functional and MP2 Calculations on   the Water Monomer and Dimer ; J. Phys. Chem.,98, 10089-10094

20. https://www.worldofmolecules.com/solvents/water.htm

21. Anant D. Kulkarni, Rajeev K. Pathak and Libero J. Bartolotti; (2005) Structures, Energetics, and Vibrational Spectra of H2O2…(H2O)n, n) 1-6 Clusters: Ab Initio Quantum Chemical Investigations; J. Phys. Chem. A, 109, 4583-4590

22. Chengteh Lee, Han Chen, and George Fitzgerald; (1995) Chemical bonding in water clusters; J. Chem. Phys. 102, 1266

23. David Prendergast, Jeffrey C. Grossman, and Giulia Galli; (2005) The electronic structure of liquid water within density-functional theory; J. Chem. Phys. 123, 014501