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STRUCTURE OF VARIOUS POSSIBLE TETRAMER WATER CLUSTERS AND THEIR ROLE IN MOLECULAR SELF-ASSEMBLY – AN ab-initio COMPUTATIONAL STUDY AND CRYSTAL DATABASE ANALYSIS

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2.1 INTRODUCTION: WATER –STRUCTURE AND FUNCTION

Water is the most abundant substance on the Earth, very much essential for the existence of life – that's why the other name of water is 'life'. It is not only the matrix of life processes, it is also the commonest solvent for various chemical processes.

Bulk water is the most intriguing substance; it has a number of anomalous properties [1]. Water can exist in various possible phases with differing amount of order in its structure. The network of hydrogen bonded water molecules is nearly static in the solid ice [2] but in liquid water this network is a dynamic one [3]. In liquid phase the hydrogen bonded network of billions and billions of water molecules continuously changes where the hydrogen bonds between neighboring molecules make and break due to thermal fluctuations. At the smallest scale water molecules form cluster of nano dimensions. A water cluster is a group of small number of hydrogen bonded water molecules having a well defined network structure. The smallest possible water cluster is a hydrogen bonded system of two water molecules, called water dimer. Being the smallest water system, our knowledge regarding water dimer is most advanced compared to other smaller water clusters - namely water trimer, water tetramer, water pentamer, water hexamer etc. Structure and energetic aspects of water dimer have been explored through experimental [4] as well as computational [5] studies which show that it has a linear structure. The lowest energy structure of water trimer through pentamer is cyclic and nearly planar [4]. Water hexamer can exist in a number of isomeric forms [6] and similar is the case for other higher order clusters [7]. Bulk water is assumed to be a statistical mixture of these lower order water clusters – especially water dimer, trimer, tetramer, pentamer and hexamer. Various models of bulk water as superposition of lower order water clusters have been proposed [8] to explain various observed properties of bulk water. It has been found that besides the role of water dimer, the contribution of water tetramer, pentamer and hexamer is crucial [9].

Accurate understanding of the structure of small water clusters is not only important for understanding the properties of bulk water but also is essential for understanding the properties of confined water in pores of micro and nano dimensions. Biological function of water in processes such as protein folding is mainly controlled by interfacial waters which are of nano-dimensions [10]. At these length scales the concept of bulk water is no longer applicable; instead the structure and properties of small water cluster become crucially important. Relevance of small water clusters is also expected to be very important for the functioning of nano scale devices [11] which are ensemble of small number of molecular components. In summary, the understanding of the molecular level interaction of water is the exploration and understanding of the interaction of various small water clusters with themselves as well as with the relevant molecular ensemble.

Molecular self-assembly is a process in which a set of molecules organize themselves into a well defined pattern through intermolecular forces [12]. Molecular self-assembly process governs the assembly and growth of crystalline materials. It is often found that one or more solvent water molecules also join this assembly and results in a crystalline substance that contain water molecules within it. These materials are called crystal hydrates. A large proportion of crystalline materials fall in this class. When more than one water molecules take part in crystallization, the water molecules generally organize themselves in small water clusters. The crystal structures determined through X-ray crystallography also reveal the structure of these water clusters. Thus the exploration of the structure of crystalline materials has become another means of widening the knowledge regarding the structural aspect of small water clusters. In recent years, there are large number of reports of crystalline materials with water clusters of various nuclearity such as dimer, tetramer, pentamer, hexamer etc [13]. It is a general statistical observation that even order water clusters such as water dimer, tetramer and hexamer appear more often in the crystalline materials than their odd counterparts such as trimer, pentamer, heptamer etc. A CSD (Cambridge Structural Database) analysis reveals that it is the water tetramer that appears more often within crystal hydrates [14]. It is an interesting as well as intriguing information indeed! This should be related to the structural and energetic aspects of water tetramer. Present work is motivated by an urge to understand why water tetramer motif is a dominant one in the set of crystal hydrates. The approach adopted in the present work is to explore various possible water tetramer clusters besides the global minimum one which are obviously different local minima in the potential energy landscape. As water tetramer is a combination of two water dimer, we have searched for different initial configuration of tetramer from combinatorial approach where two water dimers have been combined to form various tetramers. This methodology has been explained in section 2.2. With these initial configurations we have computed the optimized geometries and energies of various possible tetramer isomers. This computational result has been presented in section 2.3. It has been seen that as compared to the previous belief water tetramer can exist in as many as twelve different possible isomeric forms. This indicates that tetramer isomers posses enough structural flexibility as well as moderate inter-isomer transition potential barrier. The perturbation energies needed for this inter-isomer transitions have been estimated. In section 2.4 we have analyzed the relevance of some of the water tetramer motifs in hydrated crystalline materials. In section 2.5 we conclude.

2.2 WATER MONOMER TO DIMER AND TETRAMER: A COMBINATORIAL ANALYSIS

2.2.1 Water Monomer

Water is the chemical substance with chemical formula **H_2O**: one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. O-H bond distance and H-O-H angle of water molecule are 95.84 pm and 104.45° (Figure 2.1).

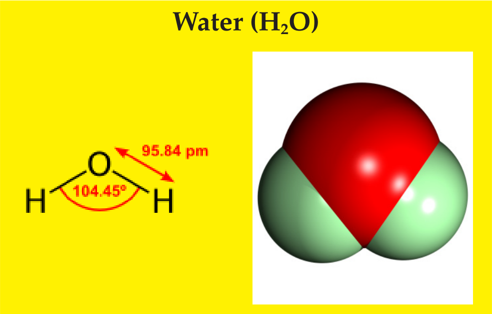


Figure 2.1: The structure of a water molecule.

In a water molecule, oxygen is covalently bound to two hydrogen atoms and also it has two lone pair of electrons which are generally unnoticed. So, it can accept two protons (Hydrogen) from neighboring water molecules and can donate two hydrogen atoms to nearby acceptors. As the hydrogen atoms and the lone pair of electrons are arranged in a tetrahedral fashion around the O atom, water molecules can act as a four-connecting node in hydrogen bonded network when it is maximally hydrogen bonded. This is the case in ice, which is a tetrahedral network where each water molecule is connected to four other water molecules. Generally the maximum no of coordination of a water molecule is four. In liquid water where the randomness is more, a water molecule is sparsely bonded as some of the donor and acceptor sites are not utilized.

2.2.2 Water Dimer

With regard to hydrogen bonded network of water molecules, a particular water molecule is primarily a 4-connecting node. With oxygen atom at the centre of a tetrahedron, two hydrogen atoms and two lone pairs are disposed around this oxygen atom in a tetrahedral manner. To graphically represent this and the network of water molecules we proceed to join these four connecting nodes by projecting these tetrahedrons on the plane of the paper. A single water molecule in this representation has been shown in Figure 2.2.

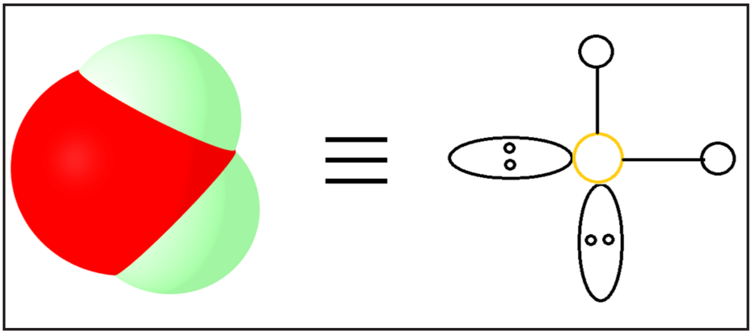
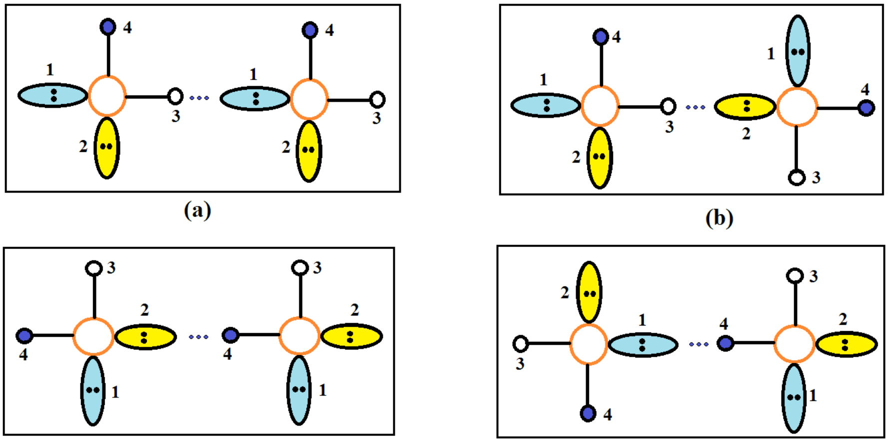


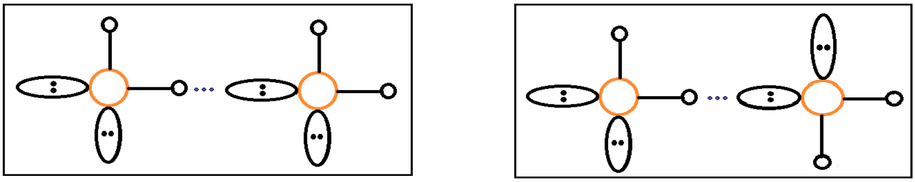
Figure 2.2: Schematic representation of a water molecule with the lone pairs shown.

With this representation of a water molecule one can visualize four different possible water dimers if one considers two hydrogen atoms and the two lone pairs to be distinguishable or distinct. These have been depicted in Figure 2.3 where one of the hydrogen atoms is marked in light blue color and the other white. Similarly the two lone pairs have been differentiated by the light blue and yellow color of the lobes. Around the horizontal dimer axis established by a particular hydrogen and a lone pair there are four possible combinations of lone pairs and hydrogen atoms leading to four different possible water dimers. But in practice, as there is no way to distinguish the two hydrogen atoms and the two lone pairs among each other, one only gets two distinct water dimer. These are shown in Figure 2.4. In one of the dimers, two lone pairs and two hydrogen atoms are in the same side of the dimer axis (Figure 2.4a) and in the other one lone pair and one hydrogen atom are on either side of the dimer axis (Figure 2.4b). These two possibilities are the result of the rotational degrees of freedom around the dimer axis.



(a) (b) (c) (d)

Figure 2.3: There would have been four possible dimers if one could have distinguished the two hydrogen atoms and two lone pairs distinctly.



(a) (b)

Figure 2.4: Two possible distinct dimers when two hydrogen atoms and two lone pairs are considered indistinguishable.

2.2.3 Water Tetramers as a Combination of Water Dimer

Tetramer water cluster can be considered as the combination of two water dimer. As described in previous section, with reference to the hydrogen bond axis, two distinct water dimers are readily identifiable, dimer-(a) and dimer-(b) shown in Figure 2.4. It should be noted that both dimer-(a) and dimer-(b) can be assumed to have a preferred direction along their bonding axis which should be taken along the donor site (lone pair) to the acceptor site (hydrogen). Thus, both dimer-(a) and dimer-(b) are inherently directional. This leads to two obvious combination of each of these dimers, parallel and antiparallel.

In dimar-(a), as both the lone pairs and the hydrogen atoms are on the opposite side of the dimer axis, they can readily complement donor acceptor complimentarity by attaching with each other sidewise leading to two possible tetramers (Figure 2.5). The tetramer generated by unidirectional side wise combination of two dimer-(a) leads to tetramer named h22 and antiparallel side wise combination of two dimer-(a) leads to tetramer named h31.

2.2.3.1 Water tetramers - h22 and h31

In h22, starting from the water oxygen atom that donates both the hydrogen atoms (filled in green in Figure 2.5a), the sequence of donor (h) acceptor (l) sites in the clockwise direction is h···l-h···l–l···h–l···h. The middle water molecule situated opposite to the marked water molecule, uses both its lone pair to accept the proton from adjacent water molecules whereas two protons of this remain unused. The 'homodromicity', which is the continuation of the sequence of donor(h) and acceptor(l) sites is broken at the middle water of tetramer h22 and in Figure 2.5a this has been shown by two half-circled arrows one clockwise and the other anticlockwise. Considering the continuity of h···l–h···l sequence in a tetramer hydrogen bond circuit, h22 is symmetrically divided into two sections of half homodroicity, one clockwise and the other anticlockwise. This is the origin of the nomenclature h22 adopted here, which indicates twice repetition of h···l sequence in the clockwise direction and twice repetition of h···l sequence in the anticlockwise direction.

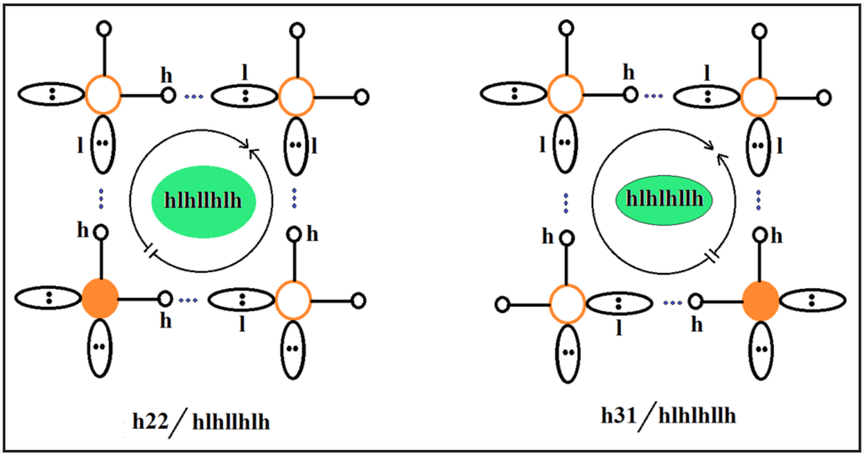


Figure 2.5: Two tetramers (h22 and h31) that are possible from self-association of dimer (a) shown in Figure 2.3.

On the other hand, in h31, starting from the water oxygen atom that donates both the hydrogen atoms (filled in green in Figure 2.5b), the sequence of donor (h) acceptor (l) sites in the clockwise direction is h···l–h···l–h···l–l···h. The repetition of h···l sequence in the clockwise direction is thrice whereas in the anticlockwise direction it appears only once. Thus clockwise homodromicity is ¾th and anti clockwise homodroicity is ¼th. Thus the nomenclature h31 indicates 3 times repetition of h···l sequence in the clockwise direction and one appearance of this in the anticlockwise direction. This has been indicated in Figure 2.5b by drawing the arrowed arcs in 3:1 proportion.

2.2.3.2 Water tetramers - h40 and h11

Combination of two water dimer-(b) shown in Figure 2.4b also lead to two possible water tetramers named here as h40 and h11. Dimer-(b) is also directional, but on both sides of the dimer axis, donor hydrogen atom site and acceptor lone pair site is present. This dimer is thus inversion symmetric with respect to the middle of the hydrogen bond. Two possible combination of dimer-(b) leading to tetramers h40 and h11 is depicted in Figure 2.6. It is interesting to note that no parallel sideway combination of dimer-(b) is possible due this inversion symmetry, only antiparallel combination of two dimer-(b) can lead to two possible tetramers. In tetramer h40, all water atoms contribute only one hydrogen atom and one lone pair in the hydrogen bonding circuit and the repetition of h···l sequence in the clockwise direction h···l–h···l–h···l–h···l and in the anticlockwise direction it does not appear. This is shown in Figure 2.6 by a clockwise arrowed circle.

On the other hand in tetramer h11 two of the water molecules contribute both the donor sites in the hydrogen bonding circuit and two provides both the acceptor sites. Thus as shown in Figure 2.6, h···l sequence is never repeated more than once in either clockwise or anticlockwise direction.

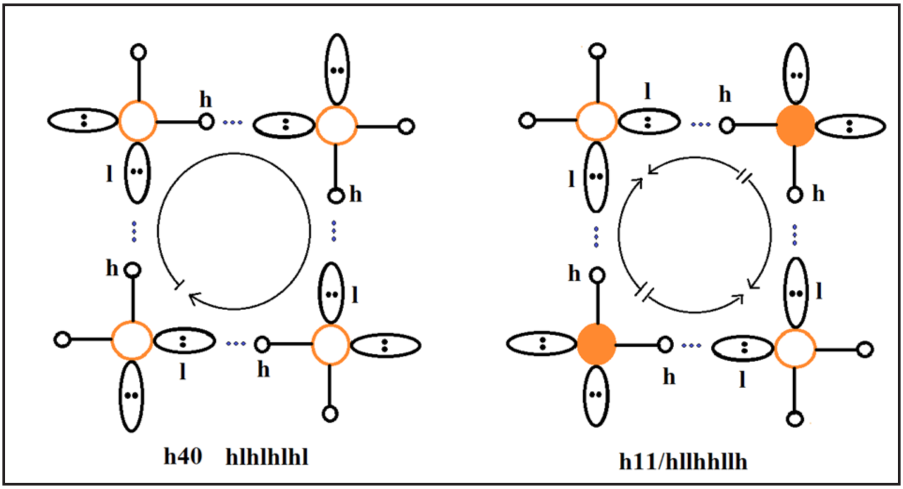


Figure 2.6: Two tetramers (h40 and h11) that arise from the combination of dimer (b) shown in Figure 2.4.

2.2.4 Four Possible Tetramers Together

As discussed in the previous section, combination of two distinguishable water dimers leads to four possible water tetramers. From the consideration of donor acceptor sequence in the hydrogen bonded circuit these are named h40, h31, h22 and h11. Here h is used to denote unidirectionality or homodromicity, the first index denotes how many times the donor (h) ···acceptor (l) sequence is repeated in the clockwise direction in succession and the second index denotes that in the anticlockwise direction. So h40 possesses highest homodromicity and ranked first in the scale of homodromicity, h31 is ranked second in this sequence, h22 is ranked third and h11 is least homodromic ranking fourth in the descending sequence of homodromicity. In a sense h11 is antihomodromic. Both h40 and h11 are more symmetric than h31 and h22. This ranking and sequence is depicted in Figure 2.7 together for four possible tetramers. The tetramer h40 is most symmetric, it possesses a four fold rotational symmetry, whereas h11 has a two fold symmetry axis. Tetramer h11 also possesses mirror symmetry along its diagonal.

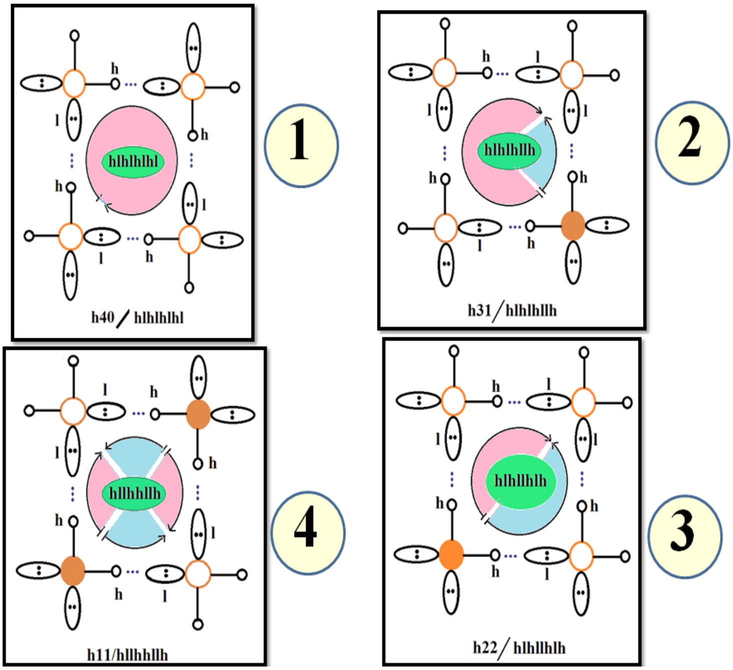


Figure 2.7: Four possible tetramers. In (1) the ring current extends over all four water molecules in the clockwise direction. In (2) ring current in the clockwise direction extends over the three water molecules and over two water molecules in the anticlockwise direction. In (3) the ring current is equally extended over two water molecules in clockwise as well as anticlockwise direction. In (4), the ring current is divided into four equal segments.

2.2.5 Optimized Geometries and Energies of Various Possible Water Tetramers from ab-initio Computation

To determine the stability of the four possible water tetramers conceived and described in section 2.2, as well as to find whether other possible water tetramers exists or not, an ab-inition computational approach was adopted. Different tetramer assemblies described in the previous section is only topologically distinct planar water tetramer motifs. These are not the optimized geometries of the water tetramers. To find out the optimized geometries and the energies corresponding to these clusters, geometry optimization was carried out using quantum chemical ab-initio computations. These initial water tetramers configurations were generated by developing an algorithm implemented in C-languages which produces four possible tetramers and these were adopted as input to the ab-initio computation in the GAMESS package [15]. All calculations have been performed using restricted Hartree-Fock theory with 63-11G(d,p) basis set.

2.3 OPTIMIZED STRUCTURES OF VARIOUS POSSIBLE WATER TETRAMERS

Besides the four possible tetramer configurations conceived in section 2.2, which are possible planar isomers of water tetramer, eight other water tetramers have been found which are obtained by randomizing the initial inputs to GAMESS [15] by a suitable C-program. In the following section we first report the optimized structures of the water clusters from the input prepared according to the topological structure of tetramers described in section 2.2.

The aim of the computation is also to verify the expected sequence of stability of these clusters from the homodromicity considerations. It is expected that the h40 water tetramer which is most homodromic should be most stable.

2.3.1 Planar Tetramers

2.3.1.1 Optimized geometry of h40 water tetramer

The optimized energy of the tetramer h40 is -304.1407601004 Hartree. The optimized configuration for this tetramer has been depicted in Figure 2.8. The hydrogen bond distances and angles have been given in Table 2.1. From the data presented in the table, it is immediately clear that for this cluster all the O···O, H···O distances and OH···O angles are equal. This indicates that all the water molecules play equal role in the hydrogen bonding assembly and the system is electronically homogeneous. This is also evident from the electrostatic potential plot and symmetry of HOMO and LUMO depicted in

Figure 2.9. All four oxygen atoms lie in the same plane. Maximum deviation of any of the oxygen atoms from the mean plane passing through them is not more than 0.026Å. Alternate unbound hydrogen atoms dangle up and down over this mean plane. In the literature this is known as the udud arrangement [16]. Diagonal O1–O3 and O2–O4 distances are respectively 3.996Å and 4.009Å. Four angles O1–O4–O3, O1–O2–O3, O2–O3–O4 and O2–O1–O4 are respectively 89.81°, 89.80°, 90.16°, 90.15°. So h40 water tetramer slightly deviates from perfect square geometry.

Table 2.1: Hydrogen bonding parameters for the h40 tetramer water cluster shown in Figure 2.8

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H2···O4	0.95	1.89	2.8302	167
O2-H4···O1	0.95	1.89	2.8315	167
O3- H6···O2	0.96	1.89	2.8303	167
O4-H7···O3	0.96	1.89	2.8309	167

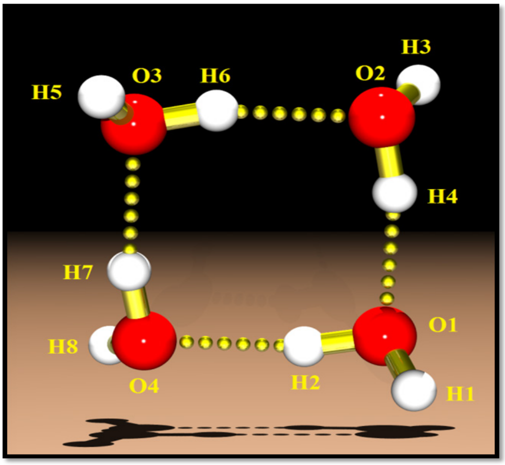


Figure 2.8: Optimized geometry of h40 water tetramer.

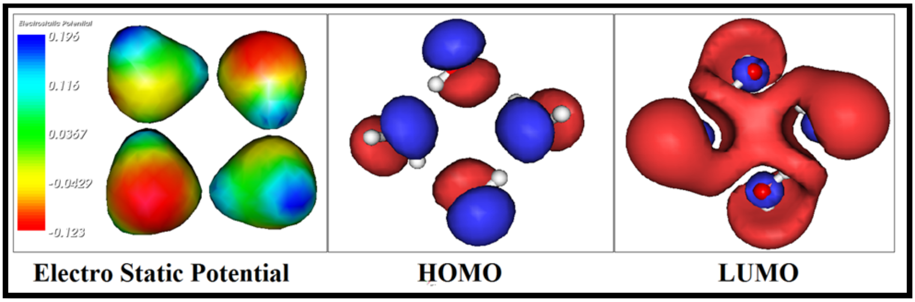


Figure 2.9: Electrostatic potential surface, HOMO and LUMO of h40 water tetramer shown in Figure 2.8.

2.3.1.2 Optimized geometry of h40(a) water tetramer

The optimized configuration of the h40(a)tetramer has been shown in Figure 2.10 and corresponding energy of the tetramer is -304.1354183181 Hartree. The hydrogen bond distances and angles have been given in Table 2.2. Like h40, h40(a) also have all the O···O, H···O distances and OH···O angles equal. For this cluster also all water molecules play equal role in the hydrogen bonding assembly. The distinctly different geometrical features of h40(a) compared to h40 is that here all the non-bonded dangling h atoms lie in the same plane of the four water oxygen atoms. Comparison of Table 2.1 and Table 2.2 reveal that for h40(a) O···O and H···O distances are slightly larger whereas the OH···O angle is 3° smaller compared to h40. All O atoms lie perfectly in the same plane. Diagonal O1-O4 and O2-O3 distances are respectively 4.010Å and 4.008Å. Four angles O1–O2–O4, O1–O3–O4, O3–O1–O2 and O3–O4–O2 are respectively 90.03°, 90.03°, 89.97°, 89.97°. So, h40a water tetramer has near perfect square geometry. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.11, which also shows the equal contribution from all four water molecules and symmetric nature of these surfaces.

Table 2.2: Hydrogen bonding parameters for the h40(a) tetramer water cluster shown in Figure 2.10

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H2··· O2	0.95	1.91	2.8346	164
O2 -H3···O4	0.95	1.91	2.8347	164
O3 -H6···O1	0.95	1.91	2.8347	164
O4 -H7···O3	0.95	1.91	2.8346	164

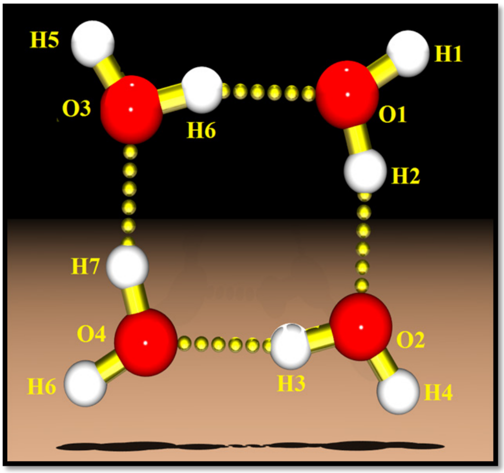


Figure 2.10: Optimized geometry of h40(a) water tetramer.

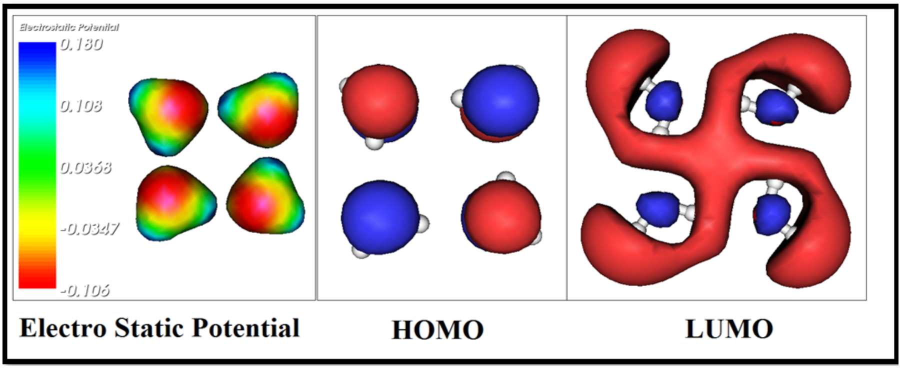


Figure 2.11: Electrostatic potential surface, HOMO and LUMO of h40(a) water tetramer shown in Figure 2.10.

2.3.1.3 Optimized geometry of h40(b) water tetramer

The optimized energy of the tetramer h40(a) shown in Figure 2.12 is -304.1391060764 Hartree. Among four dangling hydrogen atoms two are directed downwards of the ring plane and two hydrogen atoms are directed upward. The tetramer has a uudd configuration. Hydrogen bond distances and angles for this tetramer have been presented in Table 2.3. Two opposite parallel arms of the tetramer along the up down (ud) hydrogen direction is 0.0125 Å shorter than the opposite parallel arms along uu and down down (dd) hydrogen direction. O4–O2–O1 angle is 89.93° and O1–O3–O4 angle is 89.93°. On the other hand O2–O4–O3 angle is 90.07° and O3–O1–O2 angle is 90.07°. O2–O3 and O1–O4 diagonal distances are 4.016Å and 4.011Å respectively. Maximum deviation of any of the oxygen atoms from the mean plane passing through them is not more than 0.01Å. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.13.

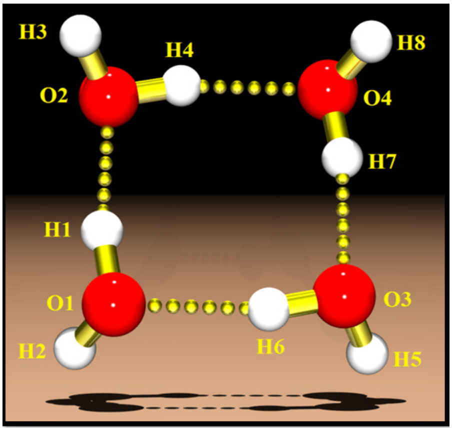


Figure 2.12: Optimized geometry of h40(b) water tetramer.

Table 2.3: Hydrogen bonding parameters for the h40(b) tetramer water cluster shown in Figure 2.12

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H1···O2	0.96	1.89	2.8314	168
O2 -H4···O4	0.95	1.91	2.8439	165
O3 -H6···O1	0.95	1.91	2.8439	166
O4 -H7···O3	0.95	1.89	2.8314	168

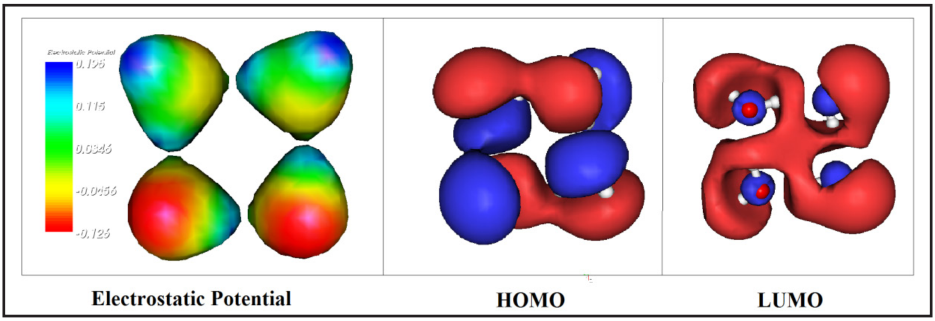


Figure 2.13: Electrostatic potential surface, HOMO and LUMO of h40(b) water tetramer shown in Figure 2.12.

2.3.1.4 Optimized geometry of h40(c) water tetramer

The optimized energy of the tetramer h40(c) shown in Figure 2.14 is -304.1362587475 Hartree. The hydrogen bond distances and angles have been given in Table 2.4. For this tetramer all dangling hydrogen atoms all are directed along the same downward direction of the mean plane passing through four hydrogen atoms. All O···O distances are very nearly equal, differ only by 0.001Å. All O–H···O angles are also same, 166°. O4–O2–O1 angle is 90.05° and O1–O3–O4 angle is 90.04°. On the other hand O2–O4–O3 angle is 89.94° and O3–O1–O2 angle is 89.97°. O2–O3 and O1–O4 diagonal distances are 4.022Å and 4.025Å. This shows that h40(c) has near perfect square geometry. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.15.

Table 2.4: Hydrogen bonding parameters for the h40(c) tetramer water cluster shown in Figure 2.14

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1 - H1···O2	0.95	1.91	2.8441	166
O2 - H4···O4	0.95	1.91	2.8457	166
O3 - H6···O1	0.95	1.91	2.8452	166
O4 - H7···O3	0.95	1.91	2.8449	166

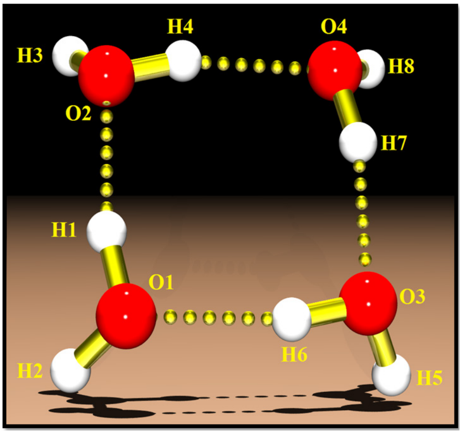
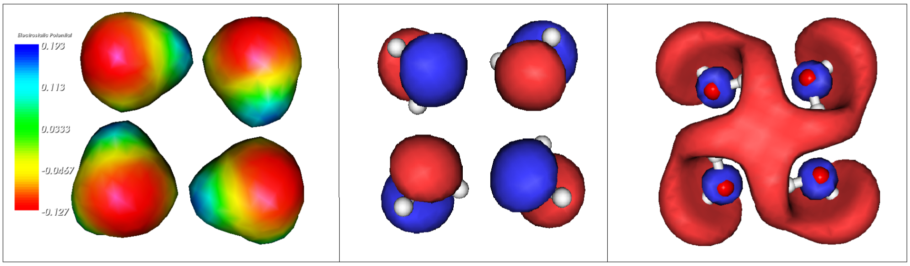


Figure 2.14: Optimized geometry of h40(c) water tetramer.



Electrostatic Potential **HOMO** **LUMO**

Figure 2.15: Electrostatic potential surface, HOMO and LUMO of h40(c) water tetramer shown in Figure 2.14.

2.3.1.5 Optimized geometry of h31 water tetramer

The optimized geometry presented in Figure 2.16 has been achieved by constraining the coordinates of O2 water oxygen atom and the H4 hydrogen atom attached to it. When the positions of these two atoms were allowed to change the optimum geometry obtained is that of h40 shown in Figure 2.8. So it appears that interaction between two lower water molecules (O1 and O2) in Figure 2.12 is crucial for the stability of this tetramer. Further investigation regarding this is currently under progress. The optimized energy of the tetramer h31 subject to two constraints mentioned above is -305.7128101707 Hartree. The hydrogen bond distances and angles have been given in Table 2.5. The longer O1···O2 bond distance (4.420Å) is not included in Table 2.5. The O2–H3···O1 angle is 169.79°. For this tetramer all dangling hydrogen atoms lie in the mean plane passing through four oxygen atoms. O···O distances as well as all O-H···O angles have a wide variation. O4–O2–O1 angle is 78° and O1–O3–O4 angle is 114.75°. On the other hand O2–O4–O3 angle is 99.24° and O3–O1–O2 angle is 67.91°. O2–O3 and O1–O4 diagonal distances are 4.258Å and 4.723Å respectively. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.17.

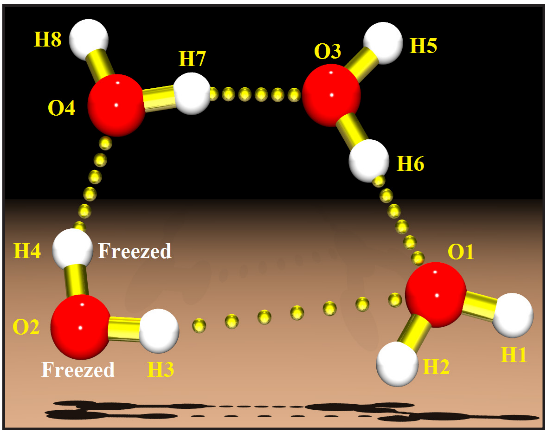
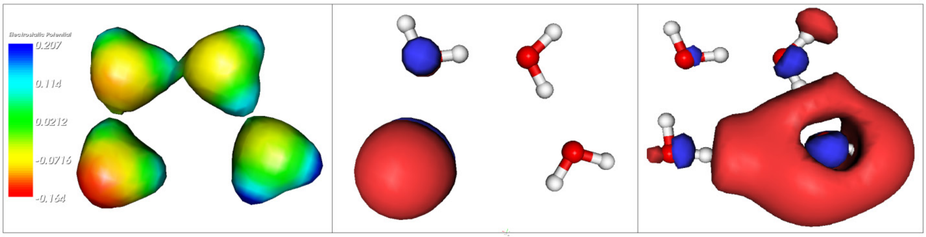


Figure 2.16: Optimized geometry of h31 water tetramer subject to two restraints where O2 and H4 were not allowed to move.

Table 2.5: Hydrogen bonding parameters for the h31 tetramer water cluster shown in Figure 2.16

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O2-H4···O4	0.95	1.91	2.8094	156
O3-H6···O1	0.97	1.85	2.8276	177
O4-H7···O3	0.98	1.81	2.7804	170



Electrostatic Potential **HOMO** **LUMO**

Figure 2.17 Electrostatic potential surface, HOMO and LUMO of h31 water tetramer shown in Figure 2.16.

2.3.1.6 Optimized geometry of h22 water tetramer

The optimized energy of the tetramer h22 is -304.1230408593 Hartree. The optimized geometry is shown in Figure 2.18. The hydrogen bond distances and angles have been given in Table 2.6. Data presented in the Table 2.3 shows that for this cluster though all the O···O distances vary with 0.02Å, H···O distances fluctuate little more (0.07Å). Though O1–H2···O3 and O4–H7···O3 angles are same (168°), other two bond angles differ by

1°. This indicates that all the water molecules do not play equal role in the hydrogen bonding assembly. All the four oxygen atoms lie nearly in the same plane. Maximum deviation of any of the oxygen atoms from the mean plane passing through them is not more than 0.001Å. The tetramer has a preferred symmetry axis along the joining line of O2 and O3. Two dangling hydrogen atoms of O3 orient in a plane which is perpendicular to the tetramer plane. Two other dangling hydrogen atoms, H1 and H8 orient respectively downwards and upwards of the mean plane passing through the four O atoms. Diagonal O4–O1 and O2–O3 distances are respectively 3.955Å and 4.582Å. Four angles O1–O3–O4, O1–O2–O4, O2–O1–O3 and O2–O4–O3 are respectively 81.81°, 81.39°, 98.42°, 98.38°. So h22 water tetramer has a parallelogram geometry. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.19.

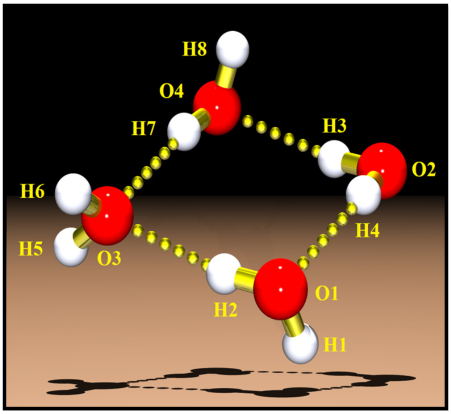


Figure 2.18: Optimized geometry of h22 water tetramer.

Table 2.6: Hydrogen bonding parameters for the h22 tetramer water cluster shown in Figure 18.

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H2···O3	0.95	2.09	3.0202	168
O2 -H3···O4	0.95	2.16	3.0338	153
O2-H4···O1	0.95	2.16	3.0319	154
O4-H7···O3	0.95	2.09	3.0197	168

2.3.1.7 Optimized geometry of h11 water tetramer

The optimized energy of the tetramer h11 shown in Figure 2.20 is -304.1215665559 Hartree. The optimized configuration of the cluster has been depicted in Figure 2.20. The hydrogen bond distances and angles have been given in Table 2.7. Hydrogen bonding data presented in the Table 2.4, reveal that for this cluster all the O···O, H···O distances and OH···O angles are equal. This indicates that all the water molecules play equal role in the

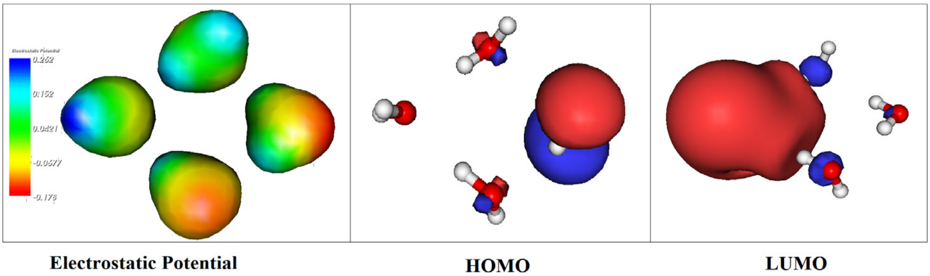


Figure 2.19: Electrostatic potential surface, HOMO and LUMO of h22 water tetramer shown in Figure 2.18.

hydrogen bonding assembly and the system is electronically homogeneous. All the four oxygen atoms lie in the same plane. Unbonded hydrogen atoms attached to O1 and O3 orient them in a plane perpendicular to the mean plane of the tetramer passing through the O atoms. O3–O4–O1 angle is 94.82° which is same as that of O3–O2–O1. O4–O1–O2 angle is 85.18° which is same as that of O4–O3–O2. The lengths of all opposite arms of the tetramer are equal. O2–O3 = 3.085 Å = O1–O4 and O3–O4 = 3.084Å = O1–O2. So the h11 tetramer has a parallelogram geometry. All O atoms lie nearly in the same plane. O1 deviates from mean plane by 0.0005 Å. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.21.

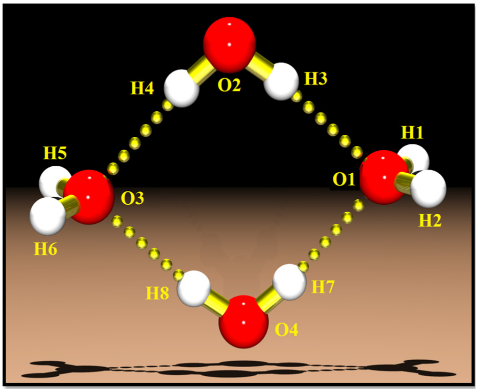
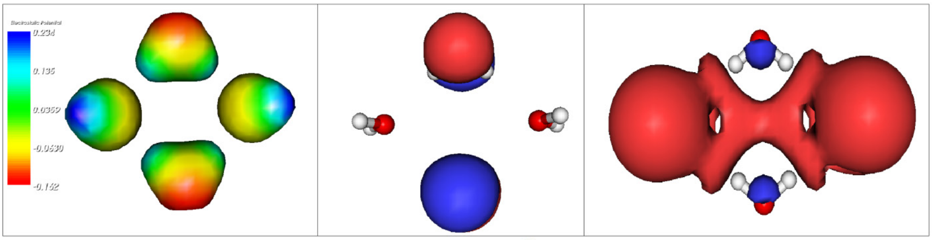


Figure 2.20: Optimized geometry of h11 water tetramer.

Table 2.7: Hydrogen bonding parameters for the h11 tetramer water cluster shown in Figure 2.20.

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O2-H3···O1	0.94	2.15	3.0844	172
O2-H4···O3	0.95	2.15	3.0849	172
O4-H7···O1	0.95	2.15	3.0849	172
O4-H8···O3	0.94	2.15	3.0844	172



Electrostatic Potential **HOMO** **LUMO**

Figure 2.21: Electrostatic potential surface, HOMO and LUMO of h11 water tetramer shown in Figure 2.20.

2.3.1.8 Optimized geometry of h11(a) water tetramer

The energy corresponding to the optimized energy of the h11(a) tetramer is -304.1142855254 Hartree. The corresponding iptimim configuration is depicted in Figure 2.22. The hydrogen bond distances and angles have been given in Table 2.8. Hydrogen bonding data presented in the Table 2.8, reveal that for this cluster all the O···O, H···O distances and OH···O angles are equal. OH···O angle is 176°. This indicates that all water molecules play equal role in the hydrogen bonding assembly and the system is electronically homogeneous. The specialty of this tetramer cluster is that all the atoms including the dangling hydrogen atoms lie in the same plane. O3–O4–O2 angle is 68.89° which is same as that of O2–O1–O3. O1–O3–O4 angle is 111.11° which is same as that of O2–O1–O3. The lengths of all arms of the tetramer are same. O1–O3 = O1–O2 = O3–O4 = O2–O4 = 3.177Å. So the h11(a) tetramer has a rhombic geometry. All O atoms lie nearly in the same plane. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.23.

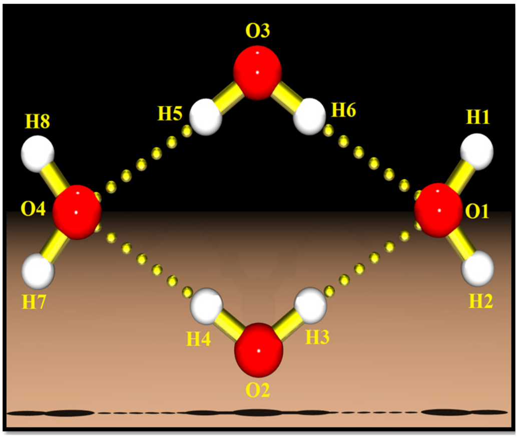
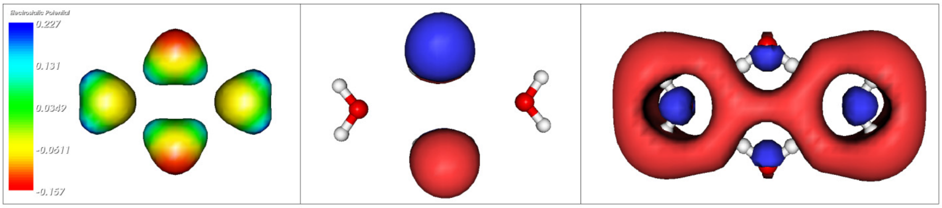


Figure 2.22: Optimized geometry of h11(a) water tetramer.

Table 2.8: Hydrogen bonding parameters for the h11(a) tetramer water cluster shown in Figure 2.22.

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O2-H3···O1	0.94	2.23	3.177	176
O2-H4···O4	0.94	2.23	3.177	176
O3-H5···O4	0.94	2.23	3.177	176
O3-H6···O1	0.94	2.23	3.177	176



Electrostatic Potential **HOMO** **LUMO**

Figure 2.23: Electrostatic potential surface, HOMO and LUMO of h11(a) water tetramer shown in Figure 2.22.

2.3.1.9 Linear zig-zag tetramer

The optimized energy of the linear zig-zag tetramer shown in Figure 2.24 is -304.1224985410 Hartree. The hydrogen bond distances and angles have been given in Table 2.9. Hydrogen bonding data presented in the Table 2.9, reveal that for this cluster the middle H···O distance is shorter (1.95Å) compared to two terminal H···O distances (1.99Å). All the OH···O geometry is near linear as the angles deviates maximum 1° from linearity. O1 and O4 distance is 8.182Å, O1 and O3 distance is 5.441Å and O2 and O4 distance is 5.340 Å. The zig zag angle <O1–O2–O3 is 137.44° and <O2–O3–

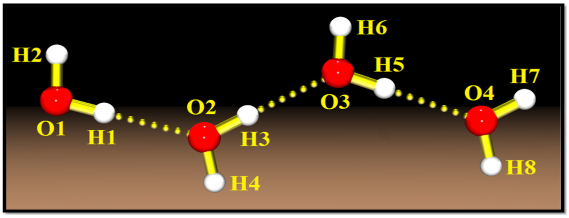
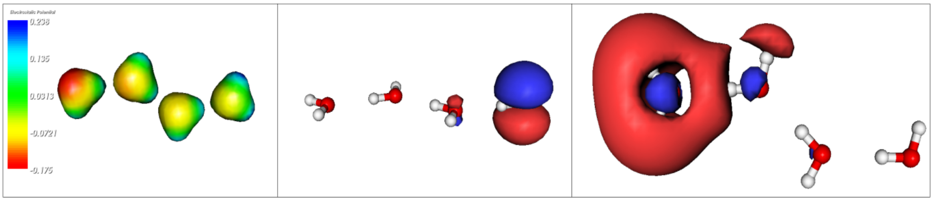


Figure 2.24: Optimized geometry of zig-zag linear water tetramer.

Table 2.9: Hydrogen bonding parameters for the linear zig-zag tetramer water cluster shown in Figure 2.24

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H1···O2	0.95	1.99	2.9421	179
O2 -H3··· O3	0.95	1.95	2.8971	179
O3 -H5 ···O4	0.95	1.99	2.9353	180

O4 is 132.58°. It is interesting to note that all the atoms of the cluster lie in the same plane. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.25.



Electrostatic Potential **HOMO** **LUMO**

Figure 2.25 Electrostatic potential surface, HOMO and LUMO of zig-zag-linear water tetramer shown in Figure 2.24.

2.3.2 Non-Planar Tetramers

2.3.2.1 Open-book tetramer

The optimized energy of the open book water tetramer is -304.1332373157 Hartree. The optimized configuration has been depicted in Figure 2.26. The hydrogen bond distances and angles are given in Table 2.10. The cluster has an open book like geometry with an additional hydrogen bond along the middle. This O1–H2···O2 hydrogen bond is distinctly shorter than the other hydrogen bonds in the assembly. This also forms the fold line of the book shaped tetramer whose two pages are the two trimers. Water molecules that lie on the fold line have tri coordination whereas other two have di-coordination. The values of the hydrogen bond angles reveal that O1O4 is the symmetry line of the tetramer. Hydrogen bond angle of O1 with O2 and O3 is the same (146°) and that of O4 with O2 and O3 is also same (143°). The torsion angle between the two planes is 103.77°. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.27.

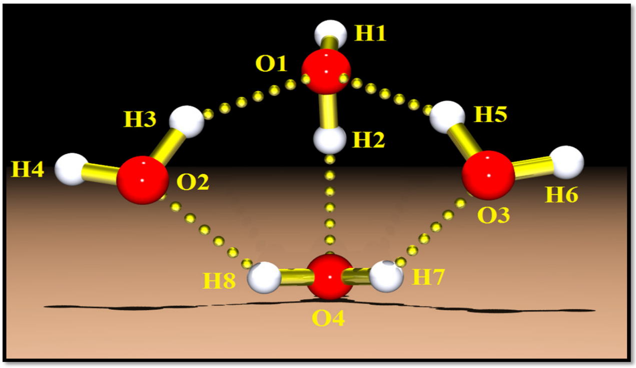
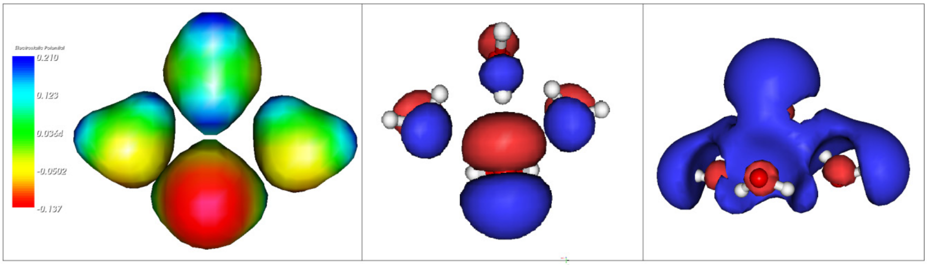


Figure 2.26: Optimized geometry of open book water tetramer.

Table 2.10: Hydrogen bonding parameters for the open book tetramer water cluster shown in Figure 2.26

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H2···O4	0.96	1.90	2.7875	153
O2-H3···O1	0.95	2.14	2.9748	146
O3-H5···O1	0.95	2.14	2.9762	146
O4-H7···O3	0.95	2.12	2.9398	143
O4-H8···O2	0.95	2.13	2.9429	143



Electrostatic Potential **HOMO** **LUMO**

Figure 2.27: Electrostatic potential surface, HOMO and LUMO of the open book water tetramer shown in Figure 2.26.

2.3.2.2 Boat-form water tetramer

The optimized energy of the boat form water tetramer shown in Figure 2.28 is -304.1362587475 Hartree. The hydrogen bond distances and angles are given in Table 2.11. In this cluster four water molecules assemble in the form of an inverted boat. Two triangular flaps are formed by O2–O3–O1 and O2–O3–O4 with a fold line passing through O2 and O3. The fold angle between the planes of the triangles is 92.87°. O2···O3 distance is 3.25Å. O4···O1 distance is 3.22Å. O4···O2 and O4···O3 distances are relatively longer than

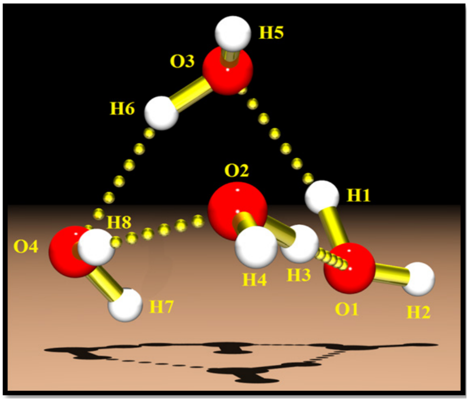
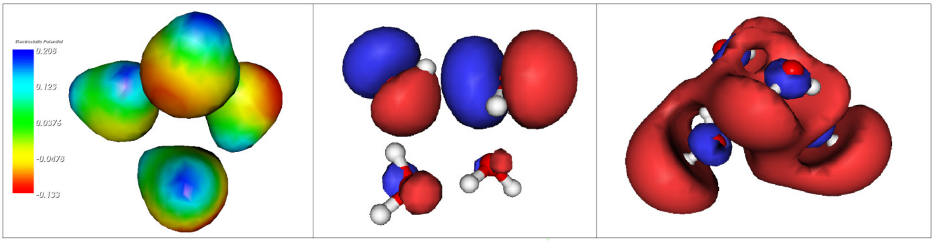


Figure 2.28: Optimized geometry of boat form water tetramer.

that of O1···O2 and O1···O3 distances. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.29.

Table 2.11: Hydrogen bonding parameters for the inverted boat form water cluster shown in Figure 2.28.

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H1···O3	0.95	1.92	2.8204	156
O2-H3···O1	0.95	1.97	2.8372	151
O3-H6···O4	0.95	2.02	2.8832	149
O4-H8···O2	0.95	2.05	2.9099	149



Electrostatic Potential **HOMO** **LUMO**

Figure 2.29: Electrostatic potential surface, HOMO and LUMO of boat-form water tetramer shown in Figure 2.28.

2.3.2.3 Plough like tetramer

The optimized energy of the plough like water tetramer shown in Figure 2.30 is -304.1306980387 Hartree. The tetramer consists of a cyclic trimer to which another water molecule is attached. Hydrogen bond distances and angles for this tetramer are given in Table 2.12. O3–H5···O2 hydrogen bond angle is 175°, indicating straightness of this bond. The hydrogen bond angles within the trimer ring vary in the range 146° to 156°. Deviation from the mean plane for the trimer O atoms (O1, O4, O3) is 0.00Å which indicates that it is perfectly planar. Electrostatic potential, HOMO and LUMO for this cluster is depicted in Figure 2.31.

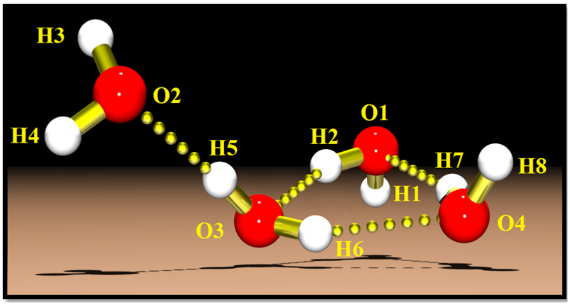
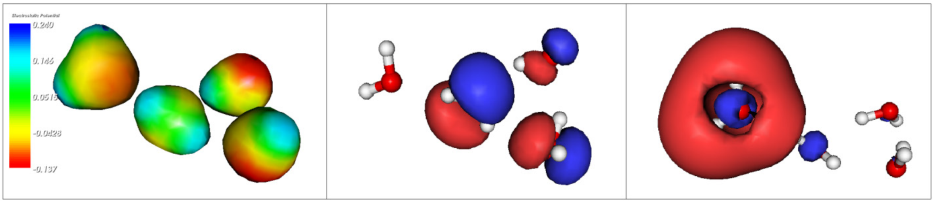


Figure 2.30: Optimized geometry of plough like water tetramer.

Table 2.12: Hydrogen bonding parameters for the plough like water cluster shown in Figure 2.30.

O–H···O	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O1-H2···O3	0.95	1.94	2.8311	156
O3-H5···O2	0.95	2.01	2.9595	175
O3-H6···O4	0.95	2.10	2.9429	146
O4-H7···O1	0.95	2.01	2.8914	154



Electrostatic Potential **HOMO** **LUMO**

Figure 2.31: Electrostatic potential surface, HOMO and LUMO of the plough like water tetramer.

2.3.3 Rank of Tetramers

Optimized energies of all tetramers together have been presented in Table 2.13. This shows that h40 tetramer which has the highest homodromicity is the most stable one. Other h40 tetramers in this class with same homodromicity lie closely in energy with h40 and rank within 1 to 5. The inverted boat form water tetramer occupies the 4th rank which has a 3D optimized geometry. As expected uudd tetramer is more stable than uuuu where all dangling hydrogen atoms aim upward of the tetramer ring plane. The configuration in which all the dangling hydrogen atoms also lie in the same plane of the tetramer is ranked 5th. Interestingly h11 tetramer which is observed frequently within crystal hydrates is ranked 10th. h22 tetramer is ranked 8th. Two other 3D tetramers, open book and plough form are ranked 6th and 7th respectively. From the data presented in Table 2.13 it can be inferred that planar homodromic tetramers are relatively more stable compared to three 3D tetramers which assume the middle positions of the ranked table. Other planar tetramers like h22 and the linear zig-zag tetramer have higher energies and the antihomodromic h11 and its close partner h11(a) posses the highest energy. So different water tetramer isomers form a class and span an energy range of 0.026474575 Hartree which correspond to 16.61 kcal/mole. In the following section we show that within the crystal hydrates one observes h40 tetramer water cluster as well as h11 tetramer water clusters. Thus through the crystal engineering methodology it should be possible to obtain all the tetramers presented here.

Table 2.13: Energies of all the tetramers and their ranks.

S.No.	Name of the water tetramer	Energy (in Hartree)	Rank (Lowest energy to highest)
		Planar Tetramers	
1	h40 (udud)	-304.1407601004	1
2	h40(a) (0000)	-304.1354183181	5
3	h40(b) (uudd)	-304.1391060764	2
4	h40(c) (uuuu)	-304.1366574148	3
5	h31	-305.7128101707	(Optimized under two constraints)
6	h22	-304.1230408593	8
7	h11	-304.1215665559	10
8	h11(a)	-304.1142855254	11
9	Linear zig-zag	-304.1224985410	9
		3D tetramers	
10	Open Book	-304.1332373157	6
11	Inverted Boat form	-304.1362587475	4
12	Plough like	-304.1306980387	7

2.4 CRYSTAL HYDRATES AND ROLE OF WATER TETRAMERS

At present the Cambridge Structural Database (CSD version 5.36 November 2014) contains 686,944 crystal structures, among which 118483 are hydrated crystals containing at least one water molecules. The role played by water molecules in hydrated crystal structures has been contemplated by the scientific community over a long time. A general view previously held by many is that water molecules merely occupy the void spaces within a solid material [17]. This view is somewhat true for porous materials of first generation. This class of crystalline materials is often called host crystals where guest water molecules are accommodated within the interstices. With the progress in time, as more and more crystal structures were obtained, it became clear that water molecules in many cases play more active role than just passively occupying the void spaces within the pores. In the area of crystal engineering, Prof. Gautam Desiraju, introduced the concept of synthon [18] which is a recurrent molecular aggregation pattern appearing across a set of molecular crystals. Especially in small molecular organic crystals it has been seen that in many cases one or more water molecules actively take part in crystallization to saturate or complete a molecular synthon, thereby enhancing the stability of molecular crystals. In this kind of crystals, water molecules strongly influence the molecular packing pattern and the stability of the crystals. It has been often seen that water molecules generally organize themselves as small water clusters through hydrogen bonding among themselves. These clusters have some particular topology or hydrogen bonding pattern. It is very interesting to note that even though water molecules satisfy the self-organization requirement of the organic molecular components forming the crystals, in many cases water molecules themselves try to achieve the regular water cluster geometry simultaneously. In many of the hydrated crystals the active role played by water molecules is evident from dependence of physical properties upon the presence and absence of water [19]. A class of crystalline materials shows reversible water re and dehydration. Recently we have reported crystalline to amorphous to another crystalline material transformation when water of crystallization is expelled by heating and the resulting material is recrystallized [20]. Motherwell et. al, have analyzed the Cambridge structural database and have shown various water motifs present within hydrated crystalline materials. Among these, clusters of four water molecules, namely water tetramer is a predominant water cluster motif that appears more often than the other water cluster motifs. This observation motivated us to look into the role of tetramer water cluster more closely. It appeared to us that water tetramer cluster may possess a number of isomeric forms among which only one is the global minimum structure but other ones are various local minima structures. Satisfying the constrains of the requirement of the molecular aggregation pattern, the water tetramers also accommodates itself into suitable isomeric form and coexist with the organic molecular partners or sometimes even with inorganic coordination complexes (Figure 2.32) [21].

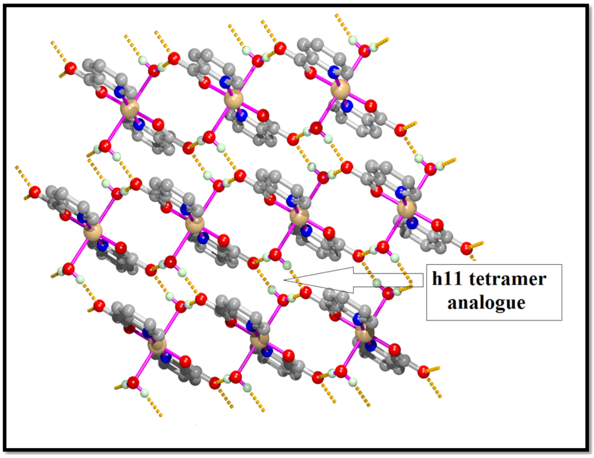


Figure 2.32: h11 water tetramer analogue shown here in uniting the Cu (pyridine-carboxylate) 22- complexes [21] into a supramolecular sheet where one of the pyridine carboxylate o atoms act as acceptor for two coordinated water molecules.

As has been discussed in section 2.3, h40 tetramer cluster motif is the global minimum among various possible water tetramers and this cluster has been seen to be present in many of the crystals that posses tetramer water clusters. This is often seen to form a spirocyclic or flip-flop one dimensional chain (Figure 2.33) [22].

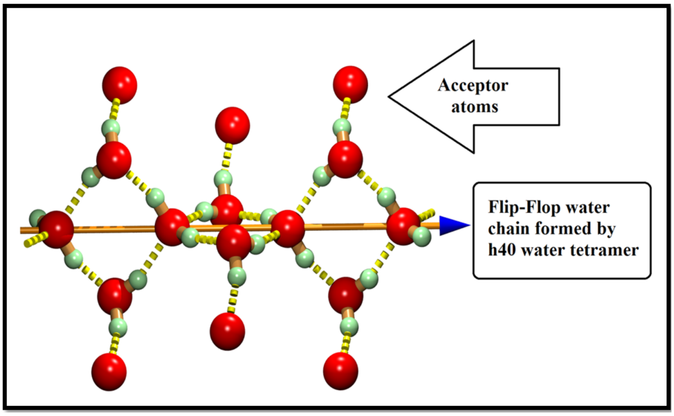


Figure 2.33: Flip-flop 1D chain formed by h40 water tetramers [22]. Successive h40 tetramers share the water molecules at a corner and planes of adjacent tetramers are twisted with respect to each other.

Other more frequently observed tetramer motif is the h11 cluster which can exist even if the water is coordinated to metal centers as is usually the case for transition metal complexes. Here is an example form a series of recently reported crystals structures containing metal malonate coordination complexes (Figure 2.34) [23].

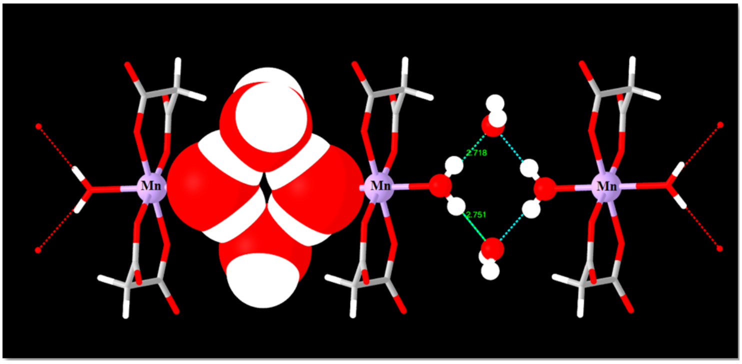


Figure 2.34: h11 water tetramer shown here unites Mn(malonate)22– coordination complexes [23] into supramolecular chains. The h11 water tetramer is observed when one water molecule is coordinated.

In many cases h11 tetramer mimics appear when two water molecules are replaced by a symmetry related pair of acceptor atoms (O or N generally) which are contributed by the organic molecular components (Figure 2.35) [24].

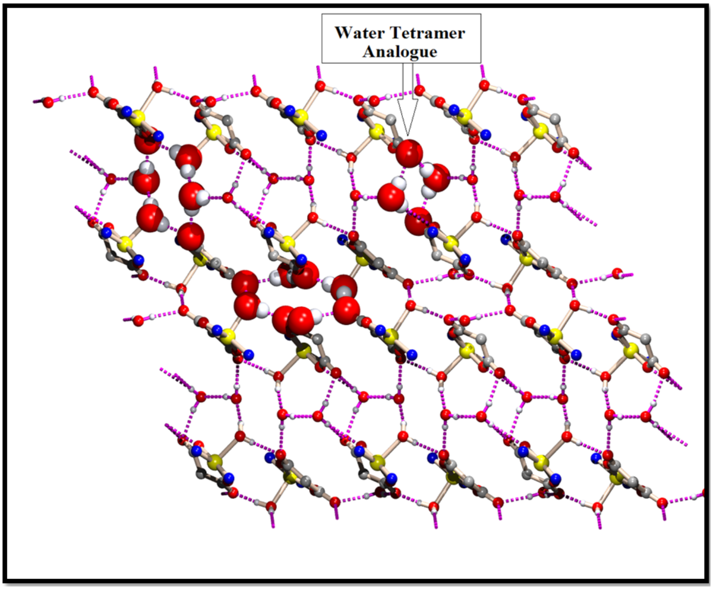


Figure 2.35: h11 water tetramer mimic shown here unites Cu(malonate) 22- complexes [24] into a supramolecular two dimensional sheet. A water hexamer analogue is also present.

Crystalline materials in a sense can be assumed to be functioning like filters of different water clusters as bulk water is considered to be mixture of various possible water clusters. Recently we have shown that through the control of pH of the solution it is possible to tune the inclusion or exclusion of the tetramer cluster motif. Tetramer also sometimes appears in combination with the hexamer water cluster.

2.5 CONCLUSIONS

Tetramer water clusters can be considered as the combination of two water dimer. From a simple combinatorial approach, it has been shown that four different tetramer water cluster is possible from the combination of two water dimers which differ from each other in the proportion of their homodromicity. Homodromicity is the successive appearance of hydrogen atom and lone pair in the hydrogen bonded circuit of four water molecules. In h40 the homodromicity is highest and h11 is most antihomodromic. Besides the global minimum tetramer geometry h40, eleven other local minimum isomers of water tetramers have been presented here which may be considered as the different excited states of the hydrogen bonded assembly of four water molecules. Computed energy of the tetramers is in accordance with the graphical analysis of homodromicity except the h31 cluster, which could not be optimized freely to its local minimum structure. The optimized structure for this could be obtained in the presence of two constrains.

In many of the hydrated crystalline materials tetramer water cluster is present and in many cases it actively takes part in assembling the molecular components into suitable organization in accordance with its own structural constraint. Both h40 and h22 are particularly amenable for crystal hydrates, the later one being found mostly in coordination complexes where besides hydrogen bonding water molecules also coordinate to metal centers. In many of the functional materials water is crucial for the functional property shown. Some cases the role of water is so important that once dehydrated through heating the material again reabsorbs that water molecule to regain its original structure. This imparts dynamism to the crystalline material. In summary, in most cases water molecules do not just play space filling role, rather it actively organizes molecular components into suitable molecular assembly where its role is essential. In the absence of water molecules the organization collapses. Besides, the studies of discrete as well as infinite chains of hydrogen-bonded water molecules in organic and metal-organic framework structures facilitate our understanding of the liquid. At present along with crystal engineering of organic and metal-organic materials the controlled production of water clusters in different environments by varying the size will lead to investigation about the nano scale liquid water itself.

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