Scientific Research Publishing

Journal of Biophysical Chemistry, 2018, 9, 15-21
http://www.scirp.org/journal/jbpc
ISSN Online: 2153-0378
ISSN Print: 2153-036X

Water Molecules in the Carbon C60 Confined Space

M. Baskar[1*], N. Sathyan[2,3], T. R. Gopalakrishnan Nair[4]

[1]Central Forensic Science Laboratory, Directorate of Forensic Science Services, Chandigarh, India
[2]RajaRajeswari College of Engineering, Visvesvaraya Technical University, Bangalore, India
[3]Humanity and Science Department, KG Reddy College of Engineering & Technology, Moinabad, Telangana, India
[4]RajaRajeswari Group of Institutions, Visvesvaraya Technical University, Bangalore, India
Email: *munubas@yahoo.com

How to cite this paper: Baskar, M., Sathyan, N. and Gopalakrishnan Nair, T.R. (2018) Water Molecules in the Carbon C60 Confined Space. *Journal of Biophysical Chemistry*, **9**, 15-21.
https://doi.org/10.4236/jbpc.2018.92002

Received: March 25, 2018
Accepted: May 28, 2018
Published: May 31, 2018

Abstract

Experimental scenario of the world being successful in planting water molecule at binary level in fullerene C70 is of utmost importance to pursue the theoretical properties of predictive triple water molecules and poly water molecules in Vander Waals confined space like fullerenes. Here, we present a paper in these lines of exploration of embedding triple water molecules in a Carbon confined space through the studies of behavior of three water molecules in Fullerene C60 by *ab-initio* methods. This heterogeneous system manifests cyclic hydrogen bonds which may be working with flipping actions. The unusual structural property of water trimers is reported. There exists a dipole moment of 0.9 ± 0.1 Debye which indicates the probable semiconductor properties.

Keywords

Endohedral, Fullerene C60, *Ab-Initio*, Water Trimer, Carbon Confined Space, Dipole

1. Introduction

Water in liberal space expresses bond formation exclusively directed by orbital interaction of oxygen and independent dual hydrogen atoms. But, within the proximity of Vander Waals fields encapsulating the liberty of water molecules as in the case of Fullerene, its behavior tends to change forming Dimers, Trimers or Polymers. This is a matter of great interest. There were few successful attempts in the recent past, in which C70 Buckminster Fullerenes was injected with dual water molecules and observed its features. Those Water molecules expressed ex-

ceptional properties in bond alignment and formations into a dimer inside a distance of 3.7 Å × 4.6 Å, a prolate C70 Fullerene. The endohedral C70 structure offered an opportunity to review the properties of embedded monomeric and dimeric water molecules with hydrogen bonding. X-ray diffraction provided insight into this formation. The property of the individual atoms and molecules tends to change when confined to a cage of atomic dimension. Some of the recent endohedral fullerene works show lots of promising in science and technology [1] [2] [3] [4] [5].

Fullerene C60 is truncated icosahedrons which resembles like football with 20 hexagons and 12 pentagons having the diameter of Van der Waals and nucleus to nucleus is 1.1 nm and 0.71 nm respectively. The discovery of fullerenes opened up by ways of constructing large atomic cluster of various shapes and sizes and research has been going on for the last three decades in discovering similar cage structure and modifying the known cage structures to yield materials with different characteristics. Fullerenes that have additional atoms, ions, or charges enclosed within their inner spheres are called as endohedral fullerene. The arrangement of water molecules in a cluster is known to depend on the environment.

Having studied fullerenes and water clusters one wonders about the shape of water cluster inside the confines of a fullerene cage. The fullerene cage is so stable and the space within is so limited, water cluster inside the fullerene cage forming unusual geometries. In this paper, the situation of embedding triple water molecule in fullerene C60 is presented. This pursuit was to increase the total charge available in the modulated fullerene with water and to achieve dipole movement of much higher than 0.5 Debye [6] realized through one water molecule encapsulation.

2. Methods of Calculation

Computations of *ab-initio* calculations at the levels of STO-3G, 3-21G and 6-31G of Restricted Hartree-Fock (RHF) method by using the quantum computations package, Firefly [7] [8] and Avogadro [9], have been carried out at Raja-Rajeswari Collage of Engineering (RRCE), Bangalore-560074, India.

3. Results

The structure of endohedral fullerene in which three water molecules encapsulated in Carbon 60 is shown in **Figure 1**. The structure of different views and orientations of three encapsulated water molecules inside the fullerene is shown in **Figure 2**. The view of the three encapsulated water molecules and the end to end distance between two six memberring is as shown in **Figure 3(a)** and **Figure 3(b)**. All the *ab-initio* calculations were optimized at STO-3G, 3-21G and 6-31G levels by RHF method. Total energy inatomic units for the water trimer, bucky ball (C60) and endohedral fullerene encapsulating three water molecules are given in **Table 1**. It is noteworthy to identify that the trimer molecule of water orients inside C60 differently compared to free water trimer [10] molecules. The

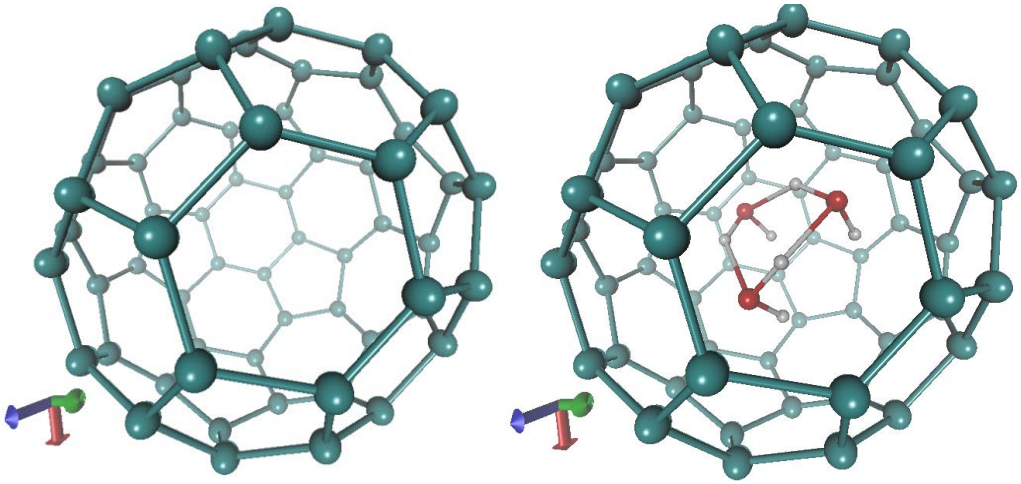


Figure 1. Structure of endohedral fullerene with 3 encapsulated water molecules.

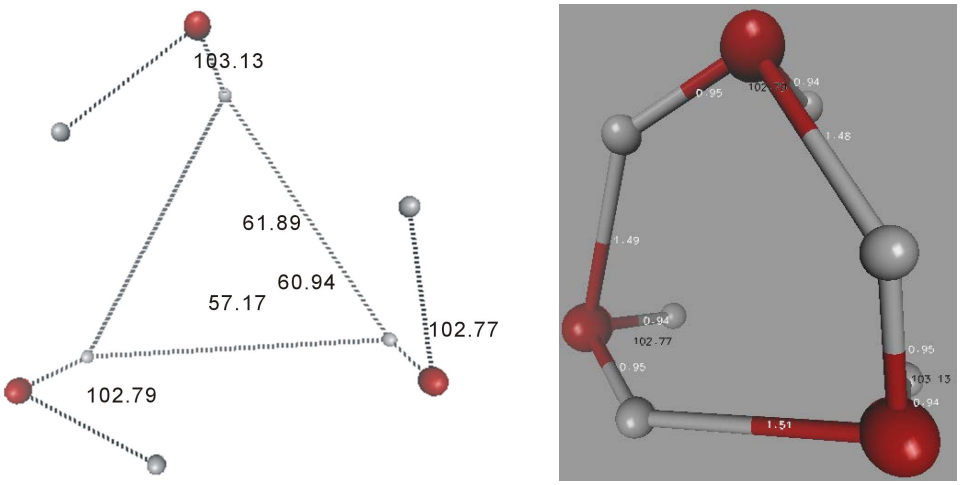
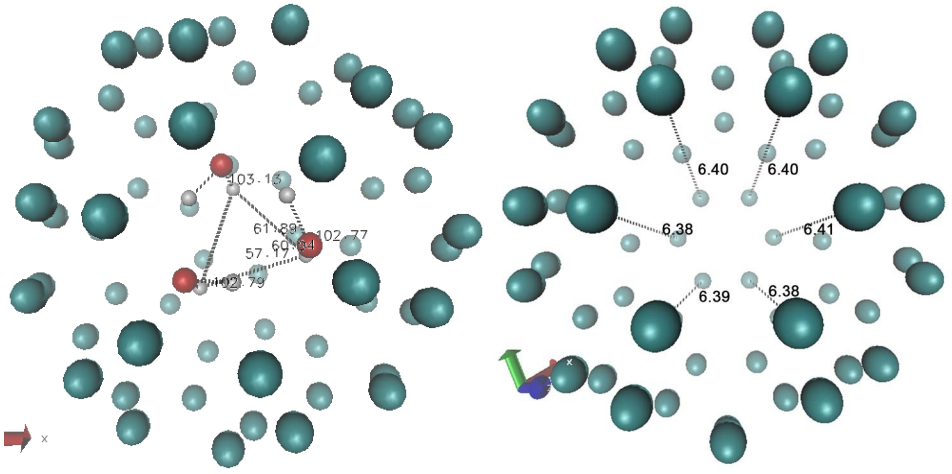


Figure 2. Orientations of water molecules in the endohedral fullerene. Bond length in Å and Bond angles in degrees.



(a) (b)

Figure 3. (a) Encapsulated water molecules and (b) End to end distance between two six member carbon ring.

Table 1. Total energy of the molecules in atomic units.

Molecules	Total Energy in Atomic Units		
	STO-3G	3-21G	6-31G
Water trimer	−224.83473	−226.73388	−227.91756
Fullerene (C60)	−2244.22124	−2259.04767	−2270.97756
Water trimer encapsulated fullerene	−2468.91043	−2485.66234	−2498.68282

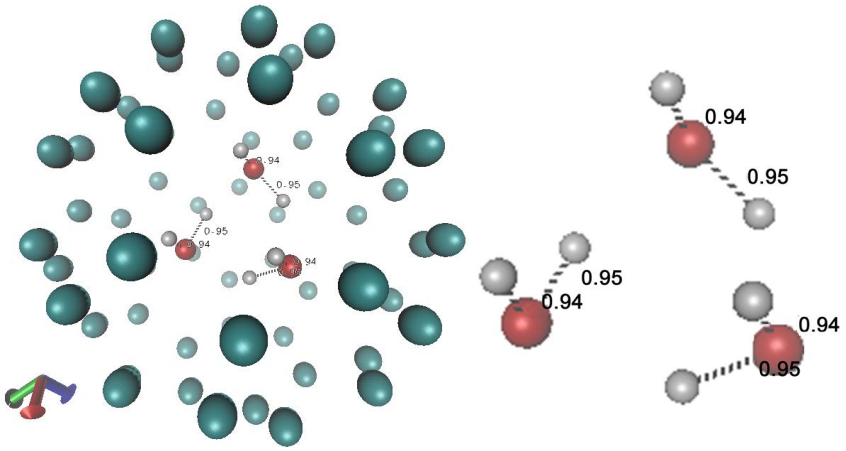
hydrogen bond length between the oxygen atoms of the water molecules in the trimer of the endohedral fullerene is found to be 2.21 Å at STO-3G and 2.28 Å at 3-21G and 6-31G optimized structures, which is the indication of strong hydrogen bonds in encapsulation against the free water trimer molecules forming cyclic hydrogen bonds of 2.8 Å as reported [11]. Water trimer in the encapsulated fullerene shows a strange behavior of forming ortho meta stable state which was discussed for one water molecule in C60 [12]. This result is in line with our earlier works on hydrogen bonded dimers involving linear and circular hydrogen bonds [13] [14] [15] [16]. This study shows the importance of high end computations as we reported [17].

Dipole moment values indicate the role of charges in conductivity. This pursuit was to increase the total charge available in the modulated fullerene with water and to achieve dipole movement of much higher than 0.5 Debye [6] realized through one water molecule encapsulation in C60. Water trimer is actively involved in flipping and circular activities inside the endohedral buckyball. It provides an opportunity to investigate further results in the domain of conductivity and molecular encapsulations. Our *ab-initio* calculations on the three water molecule embedded in C60 shows the dipole moment of 0.8Debye at STO-3G, 0.9 Debye at 3-21G and 1.0 Debye at 6-31G levels. This is the indication of structural distortion and the starting point of conductivity. Because of ortho meta stable state water trimer inside the endohedral fullerene magnetism may arise.

4. Discussion

One hydrogen atom of all the three water molecules (H-O-H) encapsulated in the endohedral fullerene is anchored with respect to H-O- in a triangle among themselves in an angle H-H-H is 57.17˚, 60.94˚ and 61.89˚ respectively. On the other hand, the other hydrogen atom is deflected in all the three water molecules with respect to -O-H and the angle between the deflected hydrogen is 60.26, 59.84 and 59.90 respectively. The bond length of the deflected hydrogen atom of one water molecule and the oxygen of the second water molecule, deflected hydrogen of second water molecule and the oxygen of the third water molecule and deflected hydrogen of third water molecule and the oxygen of the first water molecule have been observed respectively as 1.499 Å, 1.477 Å and 1.510 Å respectively. The *ab-initio* calculations of Fullerene C60, Water trimer and Water

trimer encapsulated fullerene in three different levels of basis sets, STO-3G, 3-21G and 6-31G, using RHF have been taken place and their optimized and the total energy for stabilizing the molecules is presented as shown in the Table 1. Water molecules in the endohedral fullerene adopt an angle is 102.8˚, 102.8˚ and 103.1˚ and their bond length as defined in Figure 4 and Table 2. The angles of each of the water molecules and their bond lengths are having little deviation



(a) (b)

Figure 4. Geometry of the trimer water molecule adopted in the endohedral fullerene.

Table 2. Bond angle and bond length.

Water Molecule	Bond Angle/Bond Length in Å
H_{11}-O_1-H_{12}	102.8˚ 0.936 0.949
H_{21}-O_2-H_{22}	102.8˚ 0.952 0.936
H_{31}-O_3-H_{33}	103.1˚ 0.952 0.936
O_1-O_2-O_3	60.00˚ 2.282 2.283
O_2.O_3-O_1	60.02˚
O_3-O_1	2.283
O_3-O_1-O_2	59.90˚
O_1-H_{21}	1.490
O_2-H_{31}	1.477
O_3-H_{11}	1.510
H_{12}-H_{22}-H_{33}	57.17˚ 2.162 2.186
H_{22}-H_{33}-H_{12}	60.94˚ 2.084
H_{33}-H_{12}-H_{22}	61.89˚

from their corresponding experimental values for gas phase, O-H length is 0.95718 Å and the H-O-H angle is 104.474˚ [18] and liquid water, O-H length 0.991 Å, H-O-H angle 105.5˚ [19] and 106.0˚ [20]. The final diameter of the fullerene is about 7.12 Å. However, the end to end length of the six member ring is closed to 6.52 Å. The hydrogens and oxygens of all the three water molecules are stabilized by maximally interacting with five member and six member rings of the fullerene molecule. Graphical representations of the molecule are referred by Visual Molecular Dynamics software Package [21].

5. Conclusion

The water molecules in the confined space of Carbon inside fullerene provide the opportunity for conductivity due to the presence of dipole moment. The unusual arrangement of circular hydrogen bonded water trimer molecules with flipping action shows ortho meta stable state is interesting and to be investigated further for applications in the field of conductivity and magnetism.

Acknowledgements

The authors are acknowledging the support rendered by Central Forensic Science Laboratory, Sector-36A, Chandigarh, India, RRCE management, Bangalore-74, India and KGRCET Management, Telangana, India.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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