



Effect of nano-confinement on the structure and properties of water clusters: An *ab initio* study

MANOJ K TRIPATHY^{a,b}, DEVENDRA K MAHAWAR^c and K R S CHANDRAKUMAR^{b,d,*} 

^aResearch Reactor Services Division, Bhabha Atomic Research Centre, Mumbai 400 085, Maharashtra, India

^bHomi Bhabha National Institute, Mumbai 400 094, Maharashtra, India

^cDepartment of Chemistry, University of Rajasthan, Jaipur 302 004, Rajasthan, India

^dTheoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, Maharashtra, India

E-mail: krschandrakumar@gmail.com

MS received 17 May 2019; revised 13 August 2019; accepted 15 August 2019

Abstract. An *ab initio* investigation on water clusters confined to armchair carbon nanotubes (CNT) with varying diameters has been performed using the density functional theory-based calculations. Different parameters have been investigated including structure, hydrogen bonding pattern and vibrational spectra of water-CNT complexes. Our results reveal that one-dimensional water chain parallel to CNT axis is formed in narrow nanotubes CNT(4,4) and CNT(5,5), whereas in CNT(6,6), zigzag structure is observed. An increase in the CNT diameter results in more symmetric structures similar to the gas phase. The vibrational analysis shows a redshift in stretching frequency of the hydrogen bond assisted O–H in CNT(6,6) due to the reduction in O–O separation whereas a significant blue shift in stretching frequency mode is observed in highly confined CNT(4,4) and CNT(5,5). It implies that the hydrogen bond strength between water molecules is strongest in CNT(6,6). It is also observed that water cluster tends to be near CNT wall due to H $\cdots\pi$ interaction between water molecule and the π -electron cloud of CNT. An inverse relation between the electronic charge transfer (from CNT to water) and the diameter is also established. This study demonstrates that the degree of confinement is extremely important in deciding the properties of confined water molecules.

Keywords. Nanoconfinement; Water clusters; Carbon nanotubes; Density functional theory.

1. Introduction

Water has been recognized as the matrix of life.¹ It plays an invaluable role in governing the structure, stability, and function of biomolecules such as proteins and enzymes.^{2–7} It has been established that the long-range transfer of ions and metabolites along the bio-surfaces is possible only because of the presence of the spanning network of water. Water molecules are also found in rocks, zeolites and many other inorganic materials. In many of these systems, water molecules are present in small pores of dimension in nanoscale. The influence of these confined water molecules on the thermodynamics of the equilibrium process occurring in these systems can be very significant.

Water molecules in the bulk phase are bonded to each other through hydrogen bonds. Each water molecule accepts two hydrogen bonds and donates two hydrogen bonds to other water molecules. Thus, each

molecule is tetrahedrally coordinated to four other water molecules and water is considered as a highly structured liquid. The hydrogen bond network of water is extended in space in three dimensions. However, in a confined scenario, the arrangement is entirely different and a few earlier studies have shown that confinement in the nano regime brings stimulating phenomenon in the enclosed species.^{2–8} Therefore, the properties of water confined in nanometer-scale pores can differ significantly from the bulk as the hydrogen-bond network is modified in the confining geometries. The loss of hydrogen-bond energy should render the transfer of a single water molecule into a nonpolar environment energetically unfavorable.⁸ However, experimental evidence for water penetrating into weakly polar cavities in the protein interior has been obtained in recent years.^{8–12}

The exact behavior of water in these confined nanocavities remain as a challenge to the scientific community because of the difficulties in performing experiments in nanoscale and the limitation of

*For correspondence

computational facility to treat such large systems accurately. Thus, in the last decade, large number of studies have been performed on water in various kinds of model nanopores to understand water behavior in the real systems. Among these model studies, water in carbon nanotubes (CNTs) has been thoroughly investigated primarily because of two reasons. The hydrophobic interior of CNT resembles with the biomolecules¹³ and the tremendous potential of CNT for technological applications. The applications involving CNT-water system include hydroelectric power converters,^{14,15} desalination of seawater¹⁶ and drug delivery.¹⁷ When water is confined in sub-1.5 nm diameter CNTs, it can freeze to form ice-NTs,^{18–32} which has potential applications as nanoscale ferroelectric devices,^{26,30} gas nanovalves,²⁷ nanoscale flow sensors³³ and high-flux membranes.^{13,16,34–36}

The initial molecular dynamics (MD) report of Hummer and co-workers³⁷ indicated that water molecules can occupy the hydrophobic interior of CNT(6,6) which opened the door for the upsurge research in this particular topic. Their prediction of water occupying CNT has been confirmed through neutron diffraction,³⁸ NMR,²⁹ X-ray diffraction^{19,25} and IR spectroscopic studies.^{12,39} The important findings from these studies have been discussed in the review articles.^{5,40} Water molecules undergo molecular ordering to form a stacked-ring structure with a linear chain at the center of the nanotube.³⁹ There is a reduction in the number of hydrogen bonds for each water molecule inside the nanotube.⁴¹ But the weak interaction between water and CNT, and the tight hydrogen-bonding network leads to a pulse-like transport of water molecule in these CNTs^{13,24,35,37,42–44} which exceeds expectations from macroscopic hydrodynamics by several orders of magnitude. This high fluid velocity results from an almost frictionless interface at the carbon-nanotube wall.⁴⁵ In addition, phase transition,^{18,19} viscosity modification⁴⁶ and wetting-drying transition³⁷ have also been observed in these studies. *Ab initio*, as well as classical simulation studies on molecular mechanism and kinetics of hydronium and hydroxide ion migration along water chains of different dimensions and lengths in confinement, have been reported by Bankura *et al.*^{47,48} Kayal *et al.*, have recently reported molecular dynamics simulation studies to investigate spectral and dynamical properties of the confined water.^{49,50} Maiti and co-workers have recently written an account on the structure, dynamics and thermodynamics of confined water.⁵ More interestingly, their earlier results based on classical model potentials reveal that the water molecules inside the nanotube

show solid like ordering at room temperature, which they quantify by calculating the pair correlation function.⁴² According to the recent experimental study by Strano *et al.*,⁵¹ nanoconfined water stays frozen even above its boiling point.

In spite of such a large number of studies on water under carbon nanotubes, the molecular level understanding is still lacking. A density functional theory (DFT) based study of water clusters in CNT(6,6) by Wang *et al.*,⁵² predicted weak coupling between the molecular orbitals of the encapsulated water molecules and the delocalized π electrons of carbon nanotube. In another study, it has been shown that water-nanotube interaction influences water flow through CNT.⁵³ Investigation on water molecule in model carbon nanopores using MP2 and DFT method has shown the cardinal importance of pore separation distance in governing the properties of the encapsulated water molecule.⁵⁴ Although a study by Rojas and co-workers⁵⁵ has shed some light on this, an organized first principle study in this regard can give more insight into this particular problem. In the present work, we present the results obtained from the systematic study performed on water in CNT by DFT method. The main objective of the present study is to find out how the properties of water molecules vary as the degree of confinement changes. In particular, we have studied the structure, bonding and vibrational spectra of water clusters in carbon nanotubes (CNT) of diameter in the range of sub-nanometer. The effect of confinement on the properties of water cluster has been systematically investigated by varying the diameter of the CNT.

2. Computational details

The equilibrium structure of the water clusters are initially obtained in the gas phase and subsequently, these optimized water clusters are placed inside the CNTs and the complexes comprising of water clusters and CNTs have been optimized to get the minimum energy structure of the CNT-Water complexes. The structure of the CNT framework is in general observed to be least affected during the course of optimization. To investigate the effect of confinement on the properties of water molecules, several CNTs have been considered and the degree of confinement has been systematically varied. It can be mentioned that the smaller is the nanotube diameter, the higher is the degree of confinement and *vice versa*. We have considered the armchair CNTs from CNT(4,4) to CNT(8,8) with the corresponding diameter of 5.7 to 11.2 Å. Herein, the length of each carbon nanotube in

the present study is 12.5 Å. The length of the nanotube is not periodically replicated in the axial direction. However, the structural optimisations are carried out without any symmetry constraint and water molecules are free to move in all directions. The shortest distance between the hydrogen atom of water molecule and the open surface of CNT is nearly 2 Å. Since the electronegativity of hydrogen atom is comparable with that of carbon and it does not affect the electron delocalization inside the carbon ring, the terminal atoms of the CNTs are saturated with dangling hydrogen atoms to minimize the end effects.

All the calculations have been performed by employing density functional theory with B3LYP exchange-correlation hybrid functional as implemented in TURBOMOLE program.⁵⁶ The reliability of DFT calculations in describing the water clusters and other hydrogen-bonded systems has been already tested with respect to other schemes such as MP2 and CCSD, in earlier studies.⁵⁷ The correlation-consistent triple-zeta basis set augmented with diffuse basis functions (augCC-pvTZ) is used for water molecules, whereas for the nanotube framework, split valence with polarization (SVP) basis set is used. Dispersion correction is also incorporated in all the calculations.⁵⁸ The infra-red vibrational modes of the confined water molecules have been calculated by freezing the coordinates of the CNT framework and following the NumForce module of the TURBOMOLE program. A scaling factor of 0.97 has been used for the vibrational frequencies as recommended by Merrick and co-workers.⁵⁹ To get the electronic population on individual atoms, natural bond orbital (NBO) scheme has been adopted.

3. Results and Discussion

3.1 Structure and properties of gas-phase water clusters

Let us start with the structure and properties of water cluster in the gas phase. As a representative case, herein we have considered water clusters consisting of one to four water molecules $\{(H_2O)_n, n = 1 \text{ to } 4\}$. The optimized structures of these water clusters are presented in Figure 1. It can be seen from this figure that water molecules ($n < 5$) form a 2-dimensional cluster. The geometrical parameters of these optimized water clusters are presented in Table 1. The geometrical parameters and the interaction energy (IE) of the water cluster obtained in the present study using B3LYP/augCC-pvTZ method are quite close to the results available from experiment and other theoretical methods such as MP2 and CCSD.⁶⁰ For example, the interaction energy

value in the case of water trimer in the present study is -16.56 kcal/mol which is in good agreement with MP2/aug-cc-pVTZ value of -16.29 kcal/mol. Similarly, the O–H bond length of water monomer obtained in the present study is 0.962 Å and the available results from MP2 method⁶¹ is 0.959 Å. Thus, the B3LYP/augCC-pvTZ method can describe the water cluster with reasonable accuracy and validates the choice of our method for the current study. As the number of water molecules increases in a cluster, number of hydrogen bonds and hence the interaction energy value increases with the size of the cluster.

Let us discuss the vibrational frequency of the water clusters in the present case. In water clusters of finite size, in general, four major types of OH stretching modes are observed. These modes originate from the OH groups that belong to the following water species: free OH groups dangling from the surface ($3690\text{--}3720\text{ cm}^{-1}$), double H-atom donor-single O-atom acceptor ($3450\text{--}3550\text{ cm}^{-1}$), water molecules in a distorted tetragonal coordination ($3400\text{--}3450\text{ cm}^{-1}$), and single donor-double acceptor ($3050\text{--}3200\text{ cm}^{-1}$).^{62–65} The values given in parentheses correspond to the spectral region in which these modes are observed. Thus, the position of the OH stretching mode highly depends on the involvement of the OH group in the hydrogen-bond network. As mentioned earlier, the calculated vibrational frequencies are scaled by a factor of 0.97 according to the report of Merrick and co-workers⁵⁹ and the scaled frequency values are presented in Table 2. The stretching frequency of water molecule decreases with an increase in the number of water molecules in the cluster which can be attributed due to the strong hydrogen bonds in larger clusters. This is also supported by the reduction in H \cdots O hydrogen bond distance from 1.95 Å to 1.77 Å upon going from $(H_2O)_2$ to $(H_2O)_4$. The vibrational frequencies obtained in the present study are reasonably close to the results from other high-level correlated calculations.⁶⁷ In these water clusters, one of the hydroxyl groups (OH) is involved in the hydrogen bond formation whereas the other hydroxyl group dangles away from the cluster. Accordingly, the stretching mode which is dominated by the dangling OH bond appears at a higher frequency as compared to the other stretching modes.

3.2 Structure and properties of water molecules under the confinement of CNTs

The optimized structures of water molecules in CNTs (CNT-Water complex) are presented in Figure 2. It

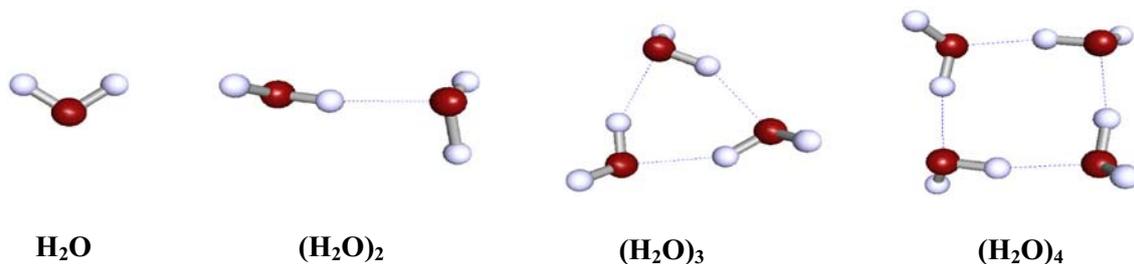


Figure 1. Structure of water clusters $\{(\text{H}_2\text{O})_n, n = 1 \text{ to } 4\}$ predicted from DFT/B3LYP method.

Table 1. Geometrical parameters and interaction energy of water clusters $\{(\text{H}_2\text{O})_n, n = 1 \text{ to } 4\}$ in gas phase.

System	$R_{(\text{O}-\text{H})}$ (Å)		$\Theta_{(\text{H}-\text{O}-\text{H})}$	Hydrogen Bond Parameters			IE kcal/mol
				$\Theta_{(\text{O}-\text{H}-\text{O})}$	$\delta_{(\text{O} \cdots \text{O})}$	$\delta_{(\text{H} \cdots \text{O})}$	
1W	0.962	0.962	105.09	–	–	–	–
2W	0.961	0.961	105.38	171.42	2.912	1.949	– 5.26
	0.963	0.963	105.50				
3W	0.961	0.976	106.13	151.60	2.795	1.897	– 16.56
	0.961	0.976	106.43	149.18	2.802	1.920	
	0.961	0.976	106.30	151.54	2.796	1.899	
4W	0.961	0.984	106.16	167.62	2.735	1.766	– 29.45
	0.961	0.984	106.24	167.69	2.735	1.766	
	0.961	0.984	106.17	167.64	2.735	1.766	
	0.961	0.984	106.18	167.66	2.736	1.766	

Table 2. Vibrational modes of water clusters $\{(\text{H}_2\text{O})_n, n = 1 \text{ to } 4\}$ in the gas phase.

Vibrational Frequency (cm^{-1})	1W	2W	3W	4W
Bending	1587	1576	1586	1591
		1595	1587	1602
			1611	1604
				1632
Symmetric Stretching	3696	3560	3415	3219
		3675	3478	3321
			3492	3322
				3358
Asymmetric Stretching	3756	3727	3737	3728
		3775	3746	3744
			3755	3745
				3749

can be seen from Figure 2 that the water molecules form a linear chain parallel to the nanotube axis in CNT(4,4) and CNT(5,5) irrespective of the number of water molecules present in the cluster. This is due to the steric hindrance offered by these two CNTs because of their small diameter. On the contrary, in CNT(7,7) and CNT(8,8), cyclic water clusters are formed in the case of three and four water molecules. The geometrical parameters of water clusters in these

two wider nanotubes are very much similar to that of gas-phase clusters. However, in the case of CNT(6,6), zigzag type of arrangement is observed. That means the structures formed in this particular nanotube is neither perfectly linear nor perfectly circular in nature. For example, in CNT(6,6)-4W, the oxygen atom of one water molecule is not exactly on the top of the other water molecule, but shifts slightly away in the axial direction. This introduces asymmetry in the structure of water cluster and two different O—O distances are observed. The radial O—O distance is slightly shorter in comparison to the axial O—O distance. The exact values of axial and radial O—O distance in the case of three water molecules in CNT(6,6) are 2.87 and 2.68 Å respectively (Table 3).

It may be interesting to note that the classical model potential based results reveal that water molecules encapsulated in CNT(6,6) form a linear structure. We, however, note that the local energy minimum values of these linear and zigzag structures obtained in CNT(6,6) do not favour the formation of linear structures. In other words, the zigzag structure in CNT(6,6) is found to be energetically more favourable by ~ 3 kcal/mol than that of linear structure. The distorted tetramer (Parallel-displaced) structure as

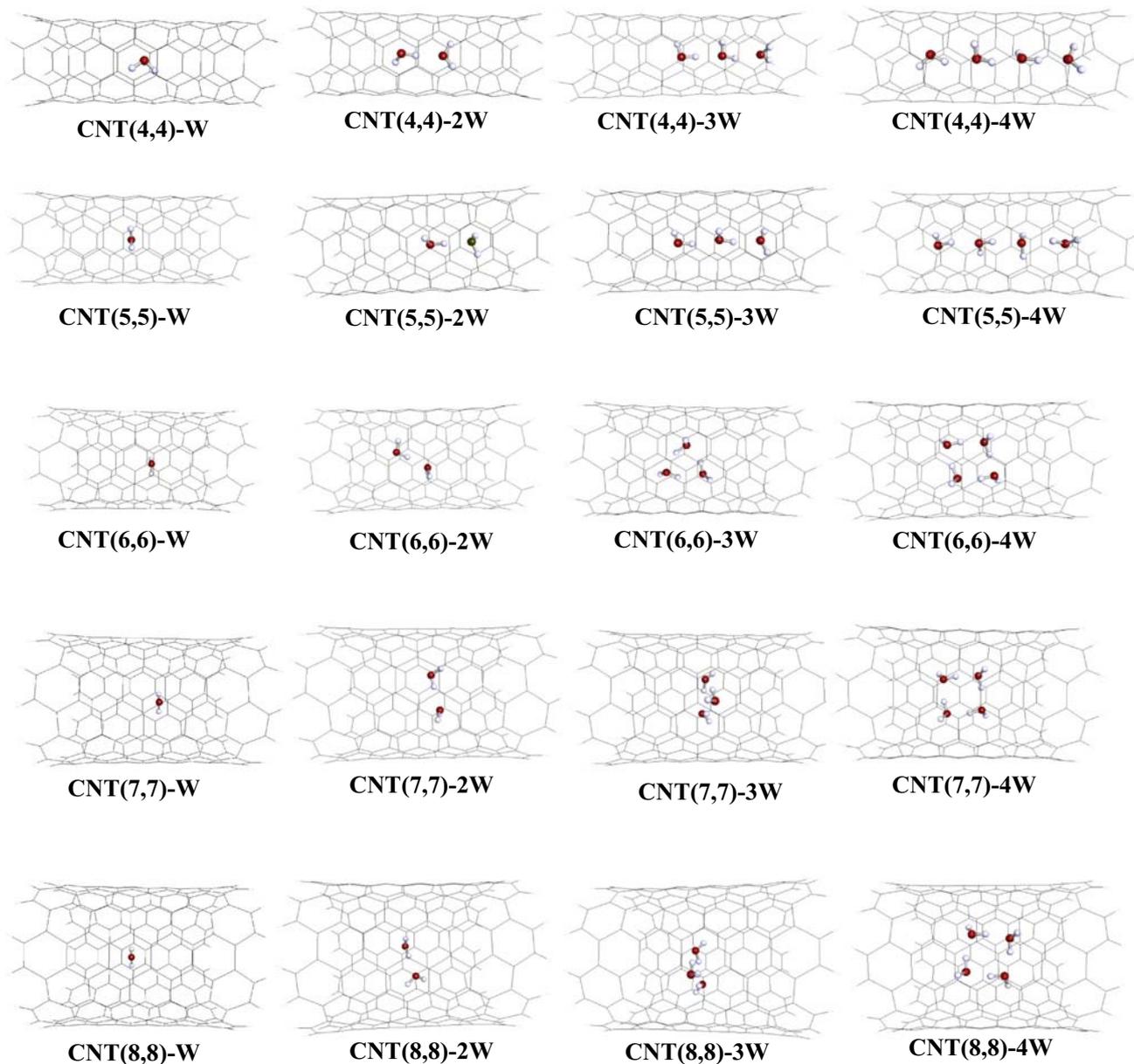


Figure 2. Optimized structures of CNT-Water complex.

obtained in the present study can be considered to be the onset for the transition of linear to layered types of structures. Therefore, the structure of water clusters in CNT largely depends on the diameter of the CNT. It may also be noted that thermal fluctuations can also cause changes in the structure and dynamics of the water molecules confined inside the nanotube. Bankura and Chandra have reported that water molecules encapsulated in CNT(6,6) are in a single-file arrangement with the average angle of the dipole vector of a molecule with the nanotube axis at about 35° .^{47,48} Interestingly, small changes in the Lennard-Jones parameters with polarizable and non-polarizable water models can also affect the structures of water

molecules in CNT.^{45,66} For example, the use of isotropic model potential usually leads to the formation of one-dimensional ordered water chain inside CNT(6,6) whereas, frequent chain ruptures are observed with medium to strongly anisotropic potentials. In the latter case, water molecules tend to form the compact denser clusters instead of linear one.⁴⁵

We have also analyzed the distance of nearest neighbor carbon atom from each atom of the water cluster. Interestingly, we observed that the hydrogen atoms are relatively closer to the carbon atom of CNT in comparison to the oxygen atom. This can be attributed to the hydrogen bonding between the H atom of the water cluster and the π -electron cloud of

Table 3. Geometrical parameters of water clusters confined under CNTs.

System	$R_{(O-H)}$ (Å)	$\Theta_{(H-O-H)}$	$\Theta_{(O-H-O)}$	$\delta_{(O-O)}$	$\delta_{(H-O)}$
CNT(4,4)-1W	0.956	0.957	105.39	–	–
CNT(4,4)-2W	0.951	0.969	106.03	171.03	2.795
	0.955	0.955	105.49		1.834
CNT(4,4)-3W	0.951	0.965	105.99	174.96	2.828
	0.952	0.968	103.44	158.64	1.865
	0.957	0.957	104.95	2.787	1.863
CNT(4,4)-4W	0.954	0.962	106.58	149.35	2.853
	0.953	0.966	103.69	156.86	1.983
	0.954	0.969	103.71	166.20	2.784
	0.957	0.957	105.23	2.780	1.834
CNT(5,5)-1W	0.962	0.962	104.65	–	–
CNT(5,5)-2W	0.961	0.972	104.84	176.39	2.869
	0.964	0.964	105.35		1.898
CNT(5,5)-3W	0.961	0.970	104.79	160.64	2.825
	0.962	0.973	103.80	164.08	1.892
	0.963	0.964	105.51	2.816	1.867
CNT(5,5)-4W	0.961	0.969	105.11	158.48	2.807
	0.962	0.969	103.91	146.97	1.883
	0.962	0.974	104.77	171.20	2.766
	0.964	0.964	105.33	2.819	1.902
CNT(6,6)-1W	0.963	0.963	104.44	–	–
CNT(6,6)-2W	0.961	0.971	105.13	175.96	2.884
	0.964	0.964	104.68		1.914
CNT(6,6)-3W	0.961	0.978	105.74	153.25	2.679
	0.961	0.974	106.00	148.38	1.769
	0.961	0.979	106.48	152.30	2.868
CNT(6,6)-4W	0.961	0.987	104.76	167.52	2.679
	0.961	0.987	106.59	166.17	1.773
	0.960	0.986	104.67	167.34	2.586
	0.961	0.987	106.41	166.40	2.699
	0.961	0.987	106.41	166.40	1.731
CNT(7,7)-1W	0.963	0.963	104.24	–	–
CNT(7,7)-2W	0.961	0.971	105.35	172.06	2.886
	0.963	0.963	104.99		1.922
CNT(7,7)-3W	0.961	0.976	106.41	149.77	2.786
	0.961	0.976	106.39	150.64	1.899
	0.961	0.976	106.10	151.55	2.793
CNT(7,7)-4W	0.961	0.984	106.97	166.67	2.787
	0.962	0.983	105.86	168.00	2.742
	0.961	0.984	106.80	166.80	2.749
	0.962	0.983	105.98	167.72	1.780
CNT(8,8)-1W	0.963	0.963	104.20	–	–
CNT(8,8)-2W	0.961	0.972	105.49	174.18	2.746
	0.964	0.963	104.19		1.778
CNT(8,8)-3W	0.961	0.976	106.59	151.79	2.796
	0.962	0.975	106.33	149.59	1.900
	0.962	0.974	106.66	147.94	2.803
CNT(8,8)-4W	0.961	0.985	106.39	168.66	2.823
	0.962	0.982	106.10	165.73	1.950
	0.961	0.985	106.42	168.28	2.730
	0.961	0.982	106.26	165.70	2.741
					1.757
					1.779
					1.755
					1.780

CNT.^{53,68–70} Due to this particular mode of interaction, water clusters get optimized close to the CNT surface and not at the centre of the nanotube. To get a clear picture of it, the radial view of the

optimized geometries of CNT(8,8)-4W is presented in Figure 3.

The interaction energy (IE) of the water molecules with CNT has been calculated using relation (1).

$$IE = E_{(CNT-W)} - [E_{(CNT)} + E_{(W)}] \quad (1)$$

where, $E_{(CNT-W)}$, $E_{(CNT)}$, and $E_{(W)}$ are the energy values of CNT-water complex, bare CNT and the water cluster respectively.

Negative interaction energy values are obtained for all the water clusters in CNT(5,5), CNT(6,6), CNT(7,7) and CNT(8,8). However, in CNT(4,4), IE value is negative only for water monomer and dimer and turns on to positive value for water trimer and tetramer. This clearly suggests that CNT(4,4) cannot accommodate water clusters containing more than two water molecules in an energetically favourable manner. Another interesting observation is the non-monotonic variation of IE with CNT diameter (Figure 4). Irrespective of the number of water molecules present in the cluster, maximum IE value is obtained in the case of CNT(5,5). This strongly suggests that the strongest interaction between CNT-Water interaction in CNT(5,5) is possible in spite of the significant reduction in hydrogen bonding in CNT(4,4) and CNT(5,5).

Let us now discuss the electronic properties of the water clusters under the confinement of CNTs. The electron population analysis has been done following the NBO method. In general, it is observed that the intramolecular charge separation for each water molecule increases under the confinement of CNT as compared to the water molecule in the gas phase. For example, the charge on oxygen and hydrogen atom of a water molecule is increased from its gas phase value of -0.93 , 0.46 to -1.55 and 0.67 a.u. inside CNT(4,4). It is also observed that electrons are transferred from CNT to the water cluster. A plot of the electronic charge transfer as a function of confinement length (diameter of CNT) is presented in Figure 5. A small amount of charge transfer is an indication of weak coupling between CNT and the water cluster. It can be seen from Figure 5 that the charge transfer from CNT to the water cluster in the case of CNT(4,4) is highest among all the CNTs and gradually decreases with the increase in the diameter of CNT.

Let us now discuss the vibrational frequency of the water molecules under the confinement of CNTs. As mentioned earlier, vibrational spectroscopy is a great tool to identify the water structures in a confined environment.^{12,39,71} For example, Byl *et al.*,³⁹ observed two different stretching modes corresponding to inter and intra ring water molecules in a CNT(10,10). In the present study, the system is quite large and comprises of more than 200 atoms in some cases. Therefore, the vibrational frequencies of the

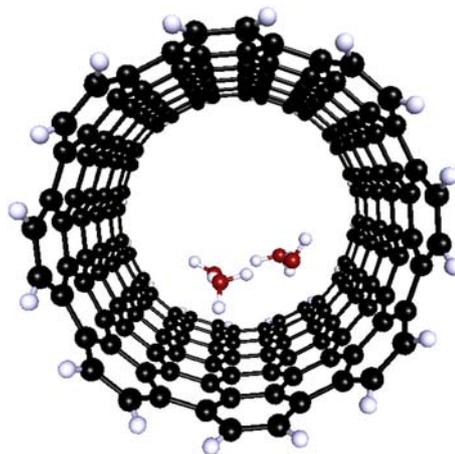


Figure 3. Radial view of the optimized geometry of CNT(8,8)-4W complex.

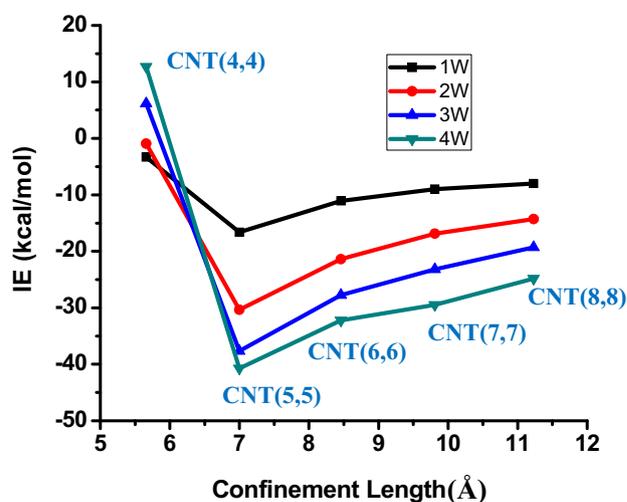


Figure 4. Interaction energy of water molecules and CNT as a function of confinement length (diameter of CNT).

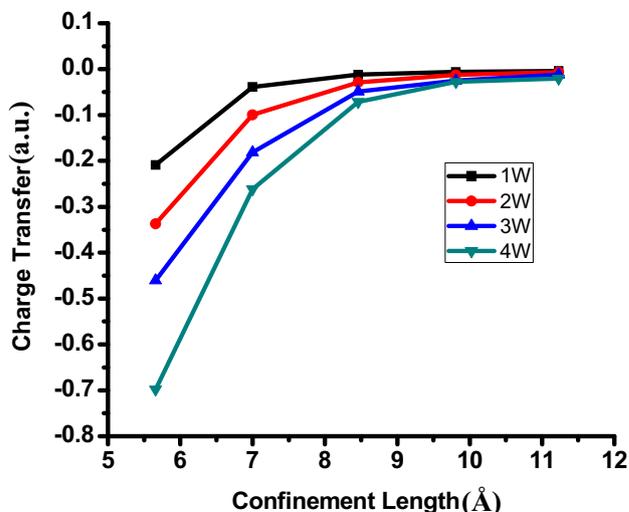


Figure 5. Electronic charge transfer as a function of confinement length (diameter of CNT).

water clusters have been calculated by following the NumForce module of the Turbomole program. After the geometry optimization is done, the CNT coordinates are fixed while computing the vibrational modes in the NumForce module. These results are presented in Table 4. In a highly confined scenario such as CNT(4,4), a significant blue shift in the stretching frequency mode is observed. For instance, stretching frequencies of water monomer in CNT(4,4) are blue-shifted to 3734 and 3823 cm^{-1} from the corresponding gas-phase value of 3696 and 3756 cm^{-1} respectively. The primary reason for this blue shifting is the reduction on the O–H bond length in CNT(4,4) (Table 3). As the diameter of the CNT increases, the amount of blue shifting is sharply reduced and in larger diameter CNTs, the stretching frequency values of water monomer are quite close to the gas phase values. Water trimer and tetramer form a linear chain structure in CNT(4,4) and CNT(5,5) in contrast to the 2-dimensional structure in gas phase. Thus, the stretching modes associated with the O–H bond that is involved in hydrogen bonding are drastically affected in case of water trimer and tetramer.

More importantly, H...O hydrogen bond distance and O–O separation distance increases from their original gas-phase value in highly confined CNTs due to the linear chain formation (Tables 1 and 3). This causes the reduction in hydrogen bond strength between water molecules and blue shifting in hydrogen-bonded stretching modes. It may be noted that a significant change in the stretching modes of water molecule is not observed for the case of wider nanotubes, [CNT(7,7) and CNT(8,8)]. On the other hand, the stretching modes in CNT(6,6) are in general red-shifted as compared to the gas phase cluster. The vibrational modes analysis in CNT(6,6) reveals that the redshifting is predominant in stretching frequencies due to the reduction in the bond length of donor-acceptor oxygen atoms in CNT(6,6) which are associated with the hydrogen-bonded O–H groups. While discussing the structural parameters of water clusters in nanotube, we have highlighted that the oxygen atoms which are not present in the axial direction come closer to each other in CNT(6,6). As a result, the H–O and O–O distance become shorter for these water molecules in comparison to the axial O–O distance. Therefore, it can be concluded from these results that the hydrogen bond strength between the confined water molecules is strongest in CNT(6,6). These finding indirectly support the burst transmission of water molecules in CNT(6,6) reported in the earlier studies.³⁴ Strong hydrogen bonding between water molecules is recognized as the main reason for this particular phenomenon.

Table 4. Vibrational modes of water molecules confined under CNTs. The first row inside each column represents the bending modes whereas the second row corresponds to the stretching modes. All the frequency values are in cm^{-1} .

Conf. Medium	1W	2W	3W	4W
CNT(4,4)	1576 3734, 3823	1542, 1592 3546, 3734, 3780, 3833	1572, 1588, 1645 3552, 3611, 3711, 3770, 3811, 3848	1563, 1572, 1614, 1640 3525, 3594, 3649, 3713, 3767, 3770, 3789, 3817
CNT(5,5)	1574 3676, 3760	1573, 1623 3520, 3655, 3735, 3743	1568, 1600, 1620 3496, 3556, 3657, 3710, 3737, 3744	1569, 1595, 1605, 1633 3475, 3551, 3582, 3652, 3717, 3728, 3729, 3748
CNT(6,6)	1574 3666, 3750	1577, 1601 3536, 3657, 3733, 3748	1582, 1599, 1612 3348, 3419, 3495, 3716, 3728, 3737	1590, 1595, 1623, 1645 3116, 3222, 3261, 3310, 3723, 3726, 3728, 3732
CNT(7,7)	1578 3667, 3752	1577, 1602 3548, 3665, 3743, 3745	1582, 1586, 1605 3414, 3477, 3477, 3725, 3729, 3734	1584, 1595, 1602, 1626 3241, 3317, 3338, 3371, 3724, 3725, 3732, 3734
CNT(8,8)	1582 3669, 3753	1586, 1607 3517, 3668, 3745, 3751	1576, 1583, 1605 3435, 3490, 3510, 3732, 3735, 3749	1583, 1597, 1605, 1632 3231, 3296, 3352, 3374, 3723, 3727, 3743, 3743

The model classical model potential based results on the vibrational frequencies of encapsulated water molecules reveal that the highly condensed water molecules in nanobubbles are found to have significantly red-shifted OH frequencies arising from the strong hydrogen bonds.⁴⁹ Gordillo and Marti have observed significant shifts in the positions of the spectral bands of water confined in CNT which has been directly related to the tube radii.⁴¹ In one of the recent experimental studies, it has been observed that the presence of intense high-frequency components between 3500 and 3700 cm^{-1} differentiate between water confined in CNTs and free water system.¹² The blue-shifted frequency is attributed as a signature of loosely bound water molecules, due to the effect of strong confinement. It is gratifying to note that the above experimental results are in close comparison with our results obtained by the *ab initio* methods as discussed above.

4. Conclusions

From the interaction energy values calculated by the dispersion corrected DFT method, it is confirmed that water can occupy the interior of narrow nanotube such as CNT(4,4). As the number of water molecule increases to three, the interaction energy attains a positive value for CNT(4,4). In CNT(4,4) and CNT(5,5), 1-dimensional water chains parallel to the CNT axis is formed whereas in CNT(6,6), the zigzag structure is formed with radial O—O distance shorter than that of axial O—O distance. Relatively more symmetric structures similar to the gas phase clusters are predicted in larger diameter CNTs. It is also observed that the water cluster gets stabilized close to the CNT wall due to H- π electron interaction between the water molecule and the π -electron cloud of CNT. In a highly confined medium like CNT(4,4), a significant reduction in the O—H bond length of water molecule compared to the gas phase geometry is observed. An inverse relation between the electronic charge transfer (from CNT to water) and the CNT diameter is also established. It is found that the intramolecular charge separation for each water molecule increases under confinement. Irrespective of the number of water molecules, the highest tube-water interaction energy is achieved in CNT(5,5) (diameter ~ 7 Å). Under the highly confined scenario, blue shift in the stretching modes of water molecule is observed which can be due to the reduction in O—H bond length. In CNT(6,6), a red shifting in stretching frequency of the hydrogen bond assisted O—H is observed due to the reduction in O—O separation

distance and hence strengthening of the hydrogen bond. Our results also support some of the earlier findings such as burst transmission in CNT(6,6). The important findings from this study suggest that the degree of confinement (diameter of carbon nanotube) is extremely important in deciding the properties of confined water molecules. The conclusions drawn from this work can motivate further investigations in porous media and can give valuable insights to understand the properties of water confined in sub-nanometer scale.

Acknowledgements

KRSC and MKT gratefully acknowledge the support and encouragement of Dr. T. K. Ghanty and Dr. P. V. Varde and Dr. R. S. Sharma, respectively. The computer Centre of BARC is acknowledged for providing supercomputing facilities. DKM is thankful to IUAC and University of Rajasthan. The fellowship provided by Indian Academy of Sciences through Summer Research Fellowship Programme is gratefully acknowledged by DKM.

References

1. Ball P 2001 In *Life's Matrix: A Biography of Water* (Berkeley, California: University of California Press)
2. Schlichting I, Berendzen J, Chu K, Stock A M, Maves S A, Benson D E, Sweet R M, Ringe D, Petsko G A and Sligar S G 2000 The Catalytic Pathway of Cytochrome P450 cam at Atomic Resolution *Science* **287** 1615
3. Taraphder S and Hummer G 2003 Protein Side-Chain Motion and Hydration in Proton-Transfer Pathways. Results for Cytochrome P450 cam *J. Am. Chem. Soc.* **125** 3931
4. de Groot B L 2001 Water Permeation Across Biological Membranes: Mechanism and Dynamics of Aquaporin-1 and GlpF *Science* **294** 2353
5. Chakraborty S, Kumar H, Dasgupta C and Maiti P K 2017 Confined Water: Structure, Dynamics, and Thermodynamics *Acc. Chem. Res.* **50** 2139
6. Tripathy M K and Chandrakumar K R S 2017 The exemplary role of nanoconfinement in the proton transfer from acids to ammonia *Phys. Chem. Chem. Phys.* **19** 19869
7. Bagchi B 2013 In *Water In Biological And Chemical Processes: From Structure and Dynamics to Function* (Cambridge, UK: Cambridge University Press)
8. Wolfenden R and Radzicka A 1994 On the probability of finding a water molecule in a nonpolar cavity *Science* **265** 936
9. Pal S K, Peon J and Zewail A H 2002 Biological water at the protein surface: dynamical solvation probed directly with femtosecond resolution *Proc. Natl. Acad. Sci. U.S.A.* **99** 1763
10. Ernst J A, Clubb R T, Zhou H X, Gronenborn A M and Clore G M 1995 Demonstration of positionally disordered water within a protein hydrophobic cavity by NMR *Science* **267** 1813

11. Yu B, Blaber M, Gronenborn A M, Clore G M and Caspar D L 1999 Disordered water within a hydrophobic protein cavity visualized by x-ray crystallography *Proc. Natl. Acad. Sci. U.S.A.* **96** 103
12. Bernardina S D, Paineau E, Brubach Jean-Blaise, Judeinstein P, Rouzière S, Launois P and Roy P 2016 Water in Carbon Nanotubes: The Peculiar Hydrogen Bond Network Revealed by Infrared Spectroscopy *J. Am. Chem. Soc.* **138** 10437
13. Holt J K, Park H G, Wang Y, Stadermann M, Artyukhin A B, Grigoropoulos C P, Noy A and Bakajin O 2006 Fast mass transport through sub-2-nanometer carbon nanotubes *Science* **312** 1034
14. Zhao Y C, Song L, Deng K, Liu Z, Zhang Z X, Yang Y L, Wang C, Yang H F, Jin A Z, Luo Q, Gu C Z, Xie S S and Sun L F 2008 Individual water-filled single-walled carbon nanotubes as hydroelectric power converters *Adv. Mater.* **20** 1772
15. Yuan Q and Zhao Y P 2009 Hydroelectric voltage generation based on water-filled single-walled carbon nanotubes *J. Am. Chem. Soc.* **131** 6374
16. Corry B 2008 Designing carbon nanotube membranes for efficient water desalination *J. Phys. Chem. B* **112** 1427
17. Singh R, Pantarotto D, Lacerda L, Pastorin G, Klumpp C, Prato M, Bianco A and Kostarelos K 2006 Tissue biodistribution and blood clearance rates of intravenously administered carbon nanotube radiotracers *Proc. Natl. Acad. Sci. U.S.A.* **103** 3357
18. Koga K, Gao G T, Tanaka H and Zeng X C 2001 Formation of ordered ice nanotubes inside carbon nanotubes *Nature* **412** 802
19. Maniwa Y, Kataura H, Abe M, Suzuki S, Achiba Y, Kira H and Matsuda K 2002 Phase transition in confined water inside carbon nanotubes *J. Phys. Soc. Jpn.* **71** 2863
20. Takaiwa D, Hatano I, Koga K and Tanaka H 2008 Phase diagram of water in carbon nanotubes *Proc. Natl. Acad. Sci. U.S.A.* **105** 39
21. Bai J, Wang J and Zeng X C 2006 Multiwalled ice helices and ice nanotubes *Proc. Natl. Acad. Sci. U.S.A.* **103** 19664
22. Koga K, Parra R D, Tanaka H and Zeng X C 2000 Ice nanotube: What does the unit cell look like? *J. Chem. Phys.* **113** 5037
23. Kyakuno H, Matsuda K, Yahiro H, Inami Y, Fukuoka T, Miyata Y, Yanagi K, Maniwa Y, Kataura H, Saito T, Yumura M and Iijima S 2011 Confined water inside single-walled carbon nanotubes: global phase diagram and effect of finite length *J. Chem. Phys.* **134** 244501
24. Mann D J and Halls M D 2003 Water alignment and proton conduction inside carbon nanotubes *Phys. Rev. Lett.* **90** 195503
25. Maniwa Y, Kataura H, Abe M, Udaka A, Suzuki S, Achiba Y, Kira H, Matsuda K, Kadowaki H and Okabe Y 2005 Ordered water inside carbon nanotubes: formation of pentagonal to octagonal ice-nanotubes *Chem. Phys. Lett.* **401** 534
26. Mikami F, Matsuda K, Kataura H and Maniwa Y 2009 Dielectric properties of water inside single-walled carbon nanotubes *ACS Nano* **3** 1279
27. Maniwa Y, Matsuda K, Kyakuno H, Ogasawara S, Hibi T, Kadowaki H, Suzuki S, Achiba Y and Kataura H 2007 Water-filled single-wall carbon nanotubes as molecular nanovalves *Nat. Mater.* **6** 135
28. Shiomi J, Kimura T and Maruyama S 2007 Molecular dynamics of ice-nanotube formation inside carbon nanotubes *J. Phys. Chem. C* **111** 12188
29. Ghosh S, Ramanathan K V and Sood A K 2004 Water at nanoscale confined in single-walled carbon nanotubes studied by NMR *Europhys. Lett.* **65** 678
30. Luo C, Fa W, Zhou J, Dong J and Zeng X C 2008 Ferroelectric ordering in ice nanotubes confined in carbon nanotubes *Nano Lett.* **8** 2607
31. Pascal T A, Goddard W A and Jung Y 2011 Entropy and the driving force for the filling of carbon nanotubes with water *Proc. Natl. Acad. Sci. U.S.A.* **108** 11794
32. Kumar H, Mukherjee B, Lin S-T, Dasgupta C, Sood A K and Maiti P K 2011 Thermodynamics of water entry in hydrophobic channels of carbon nanotubes *J. Chem. Phys.* **134** 124105
33. Ghosh S, Sood A K and Kumar N 2003 Carbon nanotube flow sensors *Science* **299** 1042
34. Lee C Y, Choi W, Han J H and Strano M S 2010 Coherence resonance in a single-walled carbon nanotube ion channel *Science* **329** 1320
35. Striolo A 2006 The mechanism of water diffusion in narrow carbon nanotubes *Nano Lett.* **6** 633
36. Walther J H, Ritos K, Cruz-Chu E R, Megaridis C M and Koumoutsakos P 2013 Barriers to superfast water transport in carbon nanotube membranes *Nano Lett.* **13** 1910
37. Hummer G, Rasaiah J C and Noworyta J P 2001 Water conduction through the hydrophobic channel of a carbon nanotube *Nature* **414** 188
38. Kolesnikov A I, Zanotti J M, Loong C K, Thiyagarajan P, Moravsky A P, Loutfy R O and Burnham C J 2004 Anomalous soft dynamics of water in a nanotube: a revelation of nanoscale confinement *Phys. Rev. Lett.* **93** 035503
39. Byl O, Liu J C, Wang Y, Yim W L, Johnson J K and Yates J T Jr. 2006 Unusual hydrogen bonding in water-filled carbon nanotubes *J. Am. Chem. Soc.* **128** 12090
40. Alexiadis A and Kassinos S 2008 Molecular simulation of water in carbon nanotubes *Chem. Rev.* **108** 5014
41. Gordillo M C and Marti J 2000 Hydrogen bond structure of liquid water confined in nanotubes *Chem. Phys. Lett.* **329** 341
42. Mukherjee B, Maiti P K, Dasgupta C and Sood A K 2007 Strong correlations and Fickian water diffusion in narrow carbon nanotubes Strong correlations and Fickian water diffusion in narrow carbon nanotubes *J. Chem. Phys.* **126** 124704
43. Joseph S and Aluru N R 2008 Why are carbon nanotubes fast transporters of water? *Nano Lett.* **8** 452
44. Ohba T, Kaneko K, Endo M, Hata K and Kanoh H 2013 Rapid water transportation through narrow one-dimensional channels by restricted hydrogen bonds *Langmuir* **29** 1077
45. Pérez-Hernández G and Schmidt B 2013 Anisotropy of the water-carbon interaction: molecular simulations of water in low-diameter carbon nanotubes *Phys. Chem. Chem. Phys.* **15** 4995
46. Thomas J A and McGaughey A J 2008 Reassessing fast water transport through carbon nanotubes *Nano Lett.* **8** 2788

47. Bankura A and Chandra A 2012 Hydroxide Ion Can Move Faster Than an Excess Proton through One-Dimensional Water Chains in Hydrophobic Narrow Pores *J. Phys. Chem. B* **116** 9744
48. Bankura A and Chandra A 2015 Proton transfer through hydrogen bonds in two-dimensional water layers: A theoretical study based on *ab initio* and quantum-classical simulations *J. Chem. Phys.* **142** 44701
49. Kayal A and Chandra A 2017 Infrared Spectral and Dynamical Properties of Water Confined in Nanobubbles at Hybrid Interfaces of Diamond and Graphene: A Molecular Dynamics Study *J. Phys. Chem. C* **121** 23455
50. Kayal A and Chandra A 2015 Exploring the structure and dynamics of nano-confined water molecules using molecular dynamics simulations *Mol. Simulation* **41** 463
51. Agrawal K V, Shimizu S, Drahushuk L W, Kilcoyne D and Strano M S 2017 Observation of extreme phase transition temperatures of water confined inside isolated carbon nanotubes *Nat. Nanotechnol.* **12** 267
52. Wang J, Zhu Y, Zhou J and Lu X H 2004 Diameter and helicity effects on static properties of water molecules confined in carbon nanotubes *Phys. Chem. Chem. Phys.* **6** 829
53. Li X, Shi Y, Yang Y, Du H, Zhou R and Zhao Y 2012 How does water-nanotube interaction influence water flow through the nanochannel? *J. Chem. Phys.* **136** 175101
54. Jena N K, Tripathy M K, Samanta A K, Chandrakumar K R S and Ghosh S K 2012 Water molecule encapsulated in carbon nanotube model systems: Effect of confinement and curvature *Theor. Chem. Acc.* **131** 1205
55. Hernández-Rojas J, Calvo F, Bretón J and Gomez Llorente J M 2012 Confinement Effects on Water Clusters Inside Carbon Nanotubes *J. Phys. Chem. C* **116** 17019
56. Ahlrichs R, Bar M, Haser M, Horn H and Kolmel C 1989 Electronic-Structure Calculations on Workstation Computers - the Program System Turbomole *Chem. Phys. Lett.* **162** 165
57. Bryantsev V S, Diallo M S, van Duin A C and Goddard W A 3rd 2009 Evaluation of B3LYP, X3LYP, and M06-Class Density Functionals for Predicting the Binding Energies of Neutral, Protonated, and Deprotonated Water Clusters *J. Chem. Theory Comput.* **5** 1016
58. Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction *J. Comput. Chem.* **27** 1787
59. Merrick J P, Moran D and Radom L 2007 An evaluation of harmonic vibrational frequency scale factors *J. Phys. Chem. A* **111** 11683
60. Xantheas S S, Burnham C J and Harrison R J 2002 Development of transferable interaction models for water. III. Reparametrization of an all-atom polarizable rigid model (TTM2-R) from first principles *J. Chem. Phys.* **116** 1493
61. Xantheas S S and Dunning T H Jr 1993 *Ab initio* studies of cyclic water clusters (H₂O)_n, n = 1–6. I. Optimal structures and vibrational spectra *J. Chem. Phys.* **99** 8774
62. Rowland B, Kadagathur N S, Devlin J P, Buch V, Feldman T and Wojcik M J 1995 Infrared-Spectra of Ice Surfaces and Assignment of Surface-Localized Modes from Simulated Spectra of Cubic Ice *J. Chem. Phys.* **102** 8328
63. Pribble R N and Zwier T S 1994 Probing hydrogen bonding in benzene-(water)_n clusters using resonant ion-dip IR spectroscopy *Faraday Discuss.* **97** 229
64. Andersson P, Steinbach C and Buck U 2003 Vibrational spectroscopy of large water clusters of known size *Eur. Phys. J. D* **24** 53
65. Pribble R N and Zwier T S 1994 Size-Specific Infrared Spectra of Benzene-(H₂O)_n Clusters (n = 1 through 7): Evidence for Noncyclic (H₂O)_n Structures *Science* **265** 75
66. Kumar H, Dasgupta C and Maiti P K 2015 Structure, Dynamics and Thermodynamics of Single File water under Confinement: Effects of Polarizability of Water Molecules *RSC Adv.* **5** 1893
67. Dunn M E, Evans T M, Kirschner K N and Shields G C 2006 Prediction of accurate anharmonic experimental vibrational frequencies for water clusters, (H₂O)_n, n = 2-5 *J. Phys. Chem. A* **110** 303
68. Suzuki S, Green P G, Bumgarner R E, Dasgupta S, Goddard W A and Blake G A 1992 Benzene forms hydrogen bonds with water *Science* **257** 942
69. Rozas I, Alkorta I and Elguero J 1997 Unusual Hydrogen Bonds: H...π Interactions *J. Phys. Chem. A* **101** 9457
70. Maheshkumar R, Elango M and Subramanian V 2010 Carbohydrate-Aromatic Interactions: The role of curvature on X H... π Interactions *J. Phys. Chem. A* **114** 4313
71. Sharma M, Donadio D, Schwegler E and Galli G 2008 Probing properties of water under confinement: Infrared spectra *Nano Lett.* **8** 2959