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REGULAR ARTICLE

Water molecule encapsulated in carbon nanotube model systems: effect of confinement and curvature

**Naresh K. Jena · Manoj K. Tripathy ·
Alok K. Samanta · K. R. S. Chandrakumar ·
Swapan K. Ghosh**

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Abstract Water present in the nanoscale confined medium like the hydrophobic interior of the carbon nanotubes (CNT) is known to extol unique properties that depart largely from their behavior in the bulk form. Considering suitable model systems that structurally resemble single unit of the CNT, we demonstrate that two unique parameters namely the local nanoscale curvature and the confinement length are of cardinal importance in governing the structural and electronic properties of water molecule present inside CNT in a general manner. Water molecule encapsulated between the model systems that offer both the above two effects exhibits dramatic trend in the interaction energy with respect to the variation of these parameters. In relation to the curvature of the model system, we propose three different regimes where water molecule experiences a distinct trend in the stabilization energy. Similarly, a confinement distance of 6 Å also marks as a borderline for the distinct manifestations in the stabilization energy of the water molecule. These two parameters also play a key role in governing the significant variations in the structural parameters, Mulliken charges, and red and blue shift in the O–H vibrational frequencies of the encapsulated water molecule. There seems to be interplay between curvature and confinement in deciding the electronic properties of water in the nanoscale confinement.

Keywords Water under confinement · Carbon nanotube · Nanoscale curvature · Weak interaction

1 Introduction

Ubiquitous and indispensible as always, water in all its forms and manifestations has been the cynosure of innumerable scientific investigations for its distinctly unique properties. Behavior of water under the confined environment of nano-channels is a fascinating field of research as it extols some different new phenomena not witnessed for water in bulk systems. The role of water in the nonpolar cavities of proteins and other biological systems is of fundamental importance. Some recent studies have established the role of water as mediator for proton transfer through the nonpolar interior channels of biological importance [1, 2]. The dynamics of water permeation through membrane channel protein aquaporin has also been investigated by several groups [3–5]. In this case, a narrow hydrophobic channel has been shown to facilitate the facile single-file water transport through the core of protein. The energetics and thermodynamic aspects of water interaction in these cavities are very poorly understood avenues.

Carbon nanotube (CNT), in recent years, has emerged as a potential candidate for its applications to store or

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Dedicated to Professor Eluvathingal Jemmis and published as part of the special collection of articles celebrating his 60th birthday.

N. K. Jena · A. K. Samanta · K. R. S. Chandrakumar (✉) ·
S. K. Ghosh (✉)
Theoretical Chemistry Section, Bhabha Atomic
Research Centre, Mumbai 400085, India
e-mail: krsc@barc.gov.in

S. K. Ghosh
e-mail: skghosh@barc.gov.in

N. K. Jena · A. K. Samanta · S. K. Ghosh
Department of Atomic Energy,
Homi Bhabha National Institute, Mumbai, India

M. K. Tripathy
Research Reactor Services Division,
Bhabha Atomic Research Centre, Mumbai 400085, India

transport fluids in nanoscale precision, apart from its mechanical, optical, thermal, electrical, or biomedical applications. Some recent experiments [6, 7] have established that CNTs facilitate pressure driven transport of gas, ion, and water. These experiments also demonstrate significant enhancement of water flow inside the tube thereby widening the scope of using CNTs as obvious candidates for fabrication of nanopore structures. The hydrophobic interior of CNT can be considered as functionally similar to that of proteins. From these considerations, study of water interaction with the channel of CNT is an important problem to address. The initial reports by Hummer et al. [8] on the burst transmission of water in the hydrophobic channel of CNT have inevitably spurred an active research dealing with several aspects of water under the confinement of CNT [9, 10]. The experimental results of Holt et al. [7] reveal that flow rate of water through a CNT of radius 1–2 nm is more than three orders of magnitude faster than the conventional hydrodynamic flow. In addition, Ghosh et al. [11] have demonstrated that the flow of a liquid on single-walled CNT bundles can induce a voltage in the sample along the direction of the flow. Water inside nanotubes under the application of axial pressure has been shown to exhibit a first-order freezing transition to hexagonal and heptagonal ice nanotubes and a continuous phase transformation into solid-like square or pentagonal ice nanotubes [12]. It has also been conjectured that liquid confined in the nanotube can exhibit very interesting behavior like solid–liquid critical point beyond which the distinction between solid and liquid phases becomes difficult [13]. A recent review article highlights some of the recent advancements in our understating pertaining to this unique system viz. water inside nanotube [14].

Structurally, CNT can be thought of a rolled planar sheet of graphene. The building block of honeycomb graphene is none other than the six-membered carbon ring as present in, say benzene. On the contrary, if we examine meticulously, the repeating unit of CNT is not the simple benzene ring, but a bent counterpart of the benzene ring with some inherent degree of curvature. Some of the previous studies have demonstrated the influencing role of curvature in governing the reactivity and property of nanotubes [15–17]. The usefulness of this concept has been demonstrated in one of the studies by Chandrakumar et al. [18] for the rational design of carbon-based nanomaterials for hydrogen storage. Thus, it is also expected that the curvature and confinement due to the nanotube can influence the properties of water present inside CNT. However, investigations based on these two factors have not been addressed so far in the literature to describe the behavior of encapsulated water molecule in a generalized manner. The classical molecular dynamics simulations can essentially shed light on the dynamical aspects of water conduction in CNT. The electronic structure methods, on the other hand, can supplement with the nitty–gritty of structural and electronic properties that are essential for understanding the properties of the confined systems. However, first principles–based investigations [19–21] to explore the structural, electronic, and vibrational properties of confined water are rather scarce in the literature. In our present study, using density functional theory–based first principle methods, we have tried to explore the structural and electronic properties of water under the confinement of CNT.

Accordingly, our standpoint to address this very important problem is, however, a bit different in the sense that instead of considering actual CNT, we have chosen suitable models that can mimic the effect of CNT. From the rationale followed in the preceding discussion that a bent benzene ring can be thought of as the single repeating unit of CNT, we have taken this model system to represent the CNT and proceeded further in our investigation of interaction with the water molecule. In this study, we envision that the curvature on the model systems, that is, benzene rings with a certain degree of curvature, has a direct correlation with the diameter of the CNT. For CNTs with smaller diameters, the curvature introduced on the model rings is higher and vice versa. As we approach from the planar benzene ring to its counterpart with some degree of curvature, essentially we start probing the effect of moving from planar graphene to the CNTs with increasing curvature or in other words decreasing diameter. The ways in which we define this curvature and model system have been explicitly mentioned in the following ("Models and methods") section. To gain insight into this effect of variation of curvature, we have considered model rings of different curvatures and studied its interaction with water molecule. More importantly, in order that the water molecule feels the effect of confinement, we have modeled our systems such that water molecules are sandwiched between two model rings where the confining distances as well as the curvatures are varied. These apparently two simplistic terms, confinement and curvature, can be two imperative parameters to decide the structural and electronic properties of water inside CNT. From our model system calculations, we are able to conclude the combined effect of confinement and curvature on the structure and electronic and vibrational properties of water molecule present inside CNT.

2 Models and methods

To mimic the effect of confinement, the model system that we have considered in our study is essentially two benzene rings separated by some distance which we treat as the confinement distance. While this can produce the effect of confinement, in order to really mimic the curvature effect of the hydrophobic surfaces, we have judiciously introduced some finite curvature on the benzene rings. The rationale for selecting this kind of curved benzene rings can be justified if we carefully have a zoom-in view of a single building block of CNT that has been demonstrated in part a of Fig. 1. The curved carbon rings in CNT are structurally similar to our model curved rings with the difference that in our model rings, the C-atoms are saturated with H atoms and the rings are not interconnected. Since the electronegativity of hydrogen atom is comparable with that of carbon and it does not affect the electron delocalization inside the carbon ring, hydrogen has been used to saturate the carbon ring. The way we define the two important parameters namely the confinement and the curvature in these model systems has been illustrated in part b of Fig. 1. Water molecule is placed between the two models rings marked as C1–C2–C3–C4–C5–C6 in the above figure. The confinement is defined by the distance between the base planes formed by C1–C2–C4–C5 atoms on both the rings. The curvature is defined here in terms of the acute angle between the base plane and the plane(s) formed by atoms C2–C3–C4 (C1–C5–C6). The curvature values considered here are 0°, 10°, 15°, 20°, 25°, and 30° in our calculations. This variation of curvature, interestingly, has direct correlation with the diameter of the CNT. For the CNT with smaller diameter, the model ring deviates significantly from the planarity and consequently the curvature is larger and vice versa. Hence, as we approach from the planar benzene ring to its counterpart with some degree of curvature, essentially we start probing the effect of moving from planar graphene to the CNTs with increasing curvature or in other words decreasing diameter. For our calculations, the confinement is varied from 4 to 8 Å. This situation is analogous to two diametrically opposite carbon rings in the real CNT where the distance between them represents the diameter. For simplicity, the effect of curvature and confinement on water with benzene rings is designated as W–DB–CV–CF, where W, DB, CV, and CF are referred as water, double benzene rings, curvature (°), and confinement length (Å), respectively. Similarly, the terminology, "W–SB–CV", denotes the system consisting of a water molecule and single benzene ring with varying curvature.

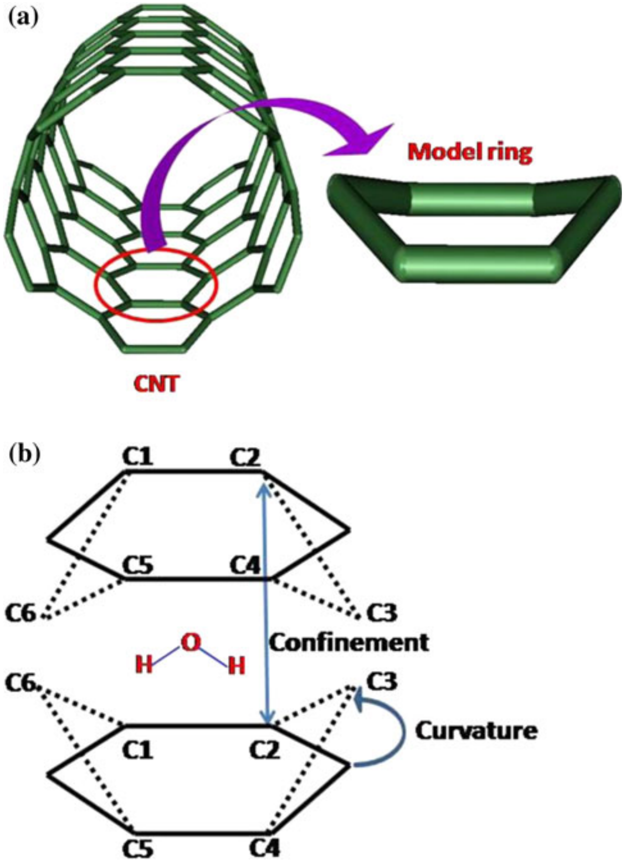

Fig. 1 **a** A zoom-in view of a single unit of CNT showing the model structure, **b** model ring depicting the confinement and curvature

All the calculations have been carried out with GAMESS [22] electronic structure package. The split–valence basis set with diffuse and polarization functions namely, 6-31+G(2d, 2p), have been used for all the atoms. We have employed the second-order Moller–Plesset (MP2) perturbation method for all the calculations. Apart from this, we have also employed the full Hartree–Fock exchange functional along with the Lee–Yang–Parr (LYP) correlation functional in the density functional calculations (HLYP method) as well as the popular hybrid functional B3LYP and the hybrid *meta*-GGA exchange–correlation functional M06 as proposed by Zhao and Truhlar [23] for comparison of performance of various methods and functionals. During optimization, the positions of the two model rings have been kept frozen so as to maintain the desired confinement and curvature value, and only the water molecule is subjected to geometry optimization. For some representative cases, the vibrational spectra of water have been computed using the turbomole [24] package at the level of BP86/def2-SV(P) with the already obtained MP2 optimized structures.

3 Results and discussions

In this section, the interaction of water molecule with single and double benzene rings with different curvature as well as confinement is discussed separately. Let us first consider the interaction of a water molecule with single benzene ring and its curved counterparts. The interaction energy of the system W–SB–CV (CV is curvature in degree) evaluated by the MP2 method has been presented in Fig. 2. In our model system, the water molecule is

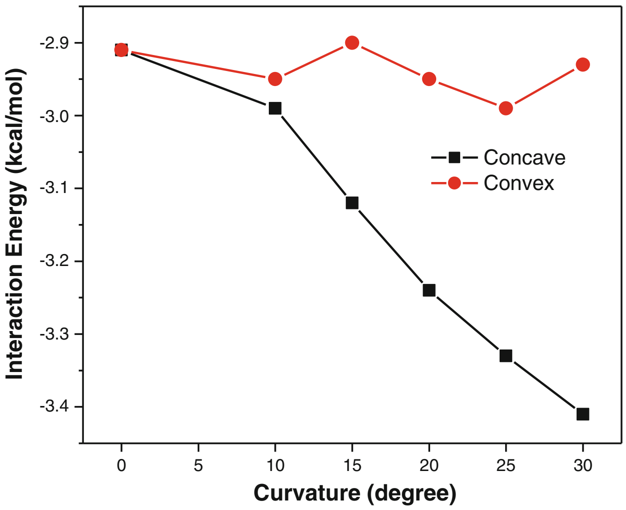

Fig. 2 Trend of interaction energy of water with variation of curvature (W–SB system)

placed on the concave side of the model ring as we vary the curvature. Herein, it may be noted that the water molecule experiences the effect of only the curvature on the ring, and there is no confinement effect. The most important point about the water and benzene system is that it exemplifies an ideal case of hydrogen bonding interaction to the π-acceptor (benzene ring in this case) and such type of systems have been addressed in great details by both the theoretical and experimental methods [25–29]. Moreover, for this kind of systems, the correlated ab initio methods like MP2 are known to describe the binding energies in a fairly accurate manner [30]. Both the hydrogen atoms of the water molecule are always found to orient toward the π-electrons of the carbon ring with the concave surface, and the minimum distance between center of mass of the carbon ring and hydrogen is 3.06 Å. We have also studied the water molecular interaction with convex surface of the curved carbon ring, and the corresponding energy values are presented in Fig. 2. Herein, we note that the interaction energy does not vary significantly with respect to the curvature of the carbon ring, and the increment in the interaction energy is only ~3 % whereas for the concave surface is ~17 %. As the curvature is introduced in the carbon ring, the effect of π-electron density due to the four carbon atoms (C1–C2–C4–C5) lying on the convex surface experienced by the incoming water molecule is not altered significantly. In addition, only one of the hydrogen atoms of water molecule is found to interact with the carbon atom of the convex surface, and the shortest carbon-hydrogen distance also does not change appreciably. Hence, it appears that the convex surface is less interactive than the concave surface due to the above reasons.

For the case of planar benzene–water system, the experimental distance [27] and the CCSD(T)/CBS [30] values are 3.35 and 3.21 ± 0.03 Å, respectively. The estimate of the interaction energy of flat benzene (curvature = 0°) with water is found to be ~2.9 kcal/mol, and the previous reported benchmark calculation [30] with MP2/IB (infinite basis set limit) predicts the same to be 3.66 kcal/mol. The lesser magnitude of interaction energy in our case can be attributed mainly to (1) smaller basis set and (2) the fact that here the geometries of benzene ring and its curved counterparts are frozen and only the water is allowed to be optimized. In a related study, Jenness and Jordan [31] employed density functional theory–symmetry-adapted perturbation theory for studying the interaction of water molecules with different sizes of aromatic benzene rings, and their results revealed that the interaction energy of water with benzene is found to be −3.14 kcal/mol and it is gradually reduced to −2.48 kcal/mol with respect to increase in the number and size of the aromatic benzene rings. More interestingly, the energy decomposition analysis revealed that there is a 50 % reduction in the electrostatic energy term and 10 % increase in the dispersion energy term due to the increase in the number of π-hydrogen bond interactions. Similarly, Prakash et al. [29] have studied the interaction of water clusters with benzene ring, and they predicted that the presence of π-hydrogen bond interaction in all the clusters that add to the stability of water clusters. These results clearly signify the effect of the inclusion of more number of water molecules and benzene rings on the binding strength of water with planar benzene ring, and the results exhibit a noticeable variation in the binding strength.

Let us now discuss the effect of curvature on the interaction of water molecule with the curved carbon ring. It can be seen from Fig. 2 that the magnitude of interaction energy of W–SB increases with increase in the curvature on the ring; however, the increment is interestingly significant. The binding energy of the W–SB system corresponding to curvature of 30° is ~3.4 kcal/mol. The difference in interaction energy between truly flat benzene and the one with highest degree of curvature amounts to be ~20 %. Since the present system is an ideal case of weakly interacting systems, the increment observed in this case should be considered to be very significant. The important rationale from this observation is that the variation of curvature can have significant influence on the interaction of water with the surface of carbon nanomaterials having inherent curvature associated with different types of carbon ring networks. In general, such systems are controlled by the π-hydrogen bonding involving the dispersion, electrostatic, polarization (induction), and charge transfer interactions. Especially, the long-range dispersion interaction contributes significantly to the interaction energy of water and carbon rings. Based on our results, we indeed find that for the W–SB case, the electronic and geometric properties of water molecule like the H–O–H bond angle, O–H bond length, and Mulliken charge on O and H atoms for the W–SB system change marginally with respect to the different values of curvature.

We will now discuss about the structure and electronic properties of water molecule placed between two benzene rings that we refer as Water–Di-Benzene (W–DB) system. In particular, the effect of two important parameters namely the confinement and curvature on the properties of encapsulated water has been focused. Also, results pertaining to MP2 as well as various DFT methods have been discussed to firmly establish our arguments. The MP2-optimized geometries of W–DB–CV–CF (CV = curvature in degree and CF = confinement distance in Å) systems have been presented in Fig. 3. From this figure, we observe that, as we increase the confinement distance between the two rings, keeping the curvature fixed, the water molecule changes from an initial position where the molecular plane is parallel to the base plane (horizontal) of the benzene rings to a position (vertical) where the two H atoms are pointing toward the ring. This observation suggests that when the confinement is more, water molecule is forced to adopt a horizontal orientation with respect to the rings, and as the confinement gradually decreases, it adopts a vertical structure. The interplay between confinement and curvature seems to govern the structure and orientation of water molecules. More interestingly, where the effect of confinement predominates and the curvature is larger, for instance in case of W–DB-25-04 and W–DB-30-04 systems, the water molecule is in a dissociated form with significant lengthening of O–H bond. However, on slight increase of the confinement distance as in the cases of W–DB-25-05 and W–DB-30-05, the water molecule attains regular geometry. An important rationale that we can derive from this observation is that, if the water molecule is placed in between highly confining hydrophobic surfaces where the surface is also curved, water molecule can be dissociated. This kind of dissociated structure of water molecule, in turn, can also affect the dynamical properties of water like diffusion as well as the strength and orientation of the hydrogen bonding. In the biological environment, the way water is transported in membrane proteins like aquaporin where the water molecules pass through a narrow constriction, our result can shed some light into the understanding of its behavior. Very interestingly, it has been demonstrated that in the protein channel of aquaporin 1, the narrowest part (~5–8 Å in diameter) of pore that is formed by aromatic and arginine residues has a decisive role in maintaining single-file flow of water molecules across the pore [3]. Moreover, we can also extend our argument to the case of water inside CNT and argue that if water is allowed to pass through extremely narrow diameter ~4–5 Å, the properties can exhibit a marked difference with the water confined in larger diameter CNTs.

In furtherance of our discussion, we now elaborate on the energetics of the water molecule placed between two model rings. The variations of interaction energy of the water molecule with curvature have been presented in Fig. 4a–e for different confinement distances ranging from 4 to 8 Å. Apart from the MP2 results, the results for different functionals have also been superimposed on these figures. From Fig. 4a, we observe that when the confinement is more prominent (CF = 4 Å), the interaction energy of water varies drastically. Up to curvature 10°, the water molecule is unfavorably bound as the interaction energy is positive. However, with a slight variation of curvature from 10° to 15°, there is a significant dip in the interaction energy, revealing the discerning role of curvature in stabilizing the encapsulated water molecule. This variation in interaction energy of water is as high as ~80 kcal/mol for the MP2 method. DFT methods HLYP, B3LYP, and M06 predict even larger variations in interaction energy (~100 kcal/mol) as we move from curvature 10°–15°. The water molecule attains its most energetically favorable orientation for curvatures 15°–20° where the interaction energy is negative, and then, it again shoots up for higher curvatures. This observation is indeed fascinating from the perspective that under highly confining media, although the water molecule experiences energetically a highly unfavorable situation, a miniscule variation of one parameter, namely, the curvature of the ring brings about a remarkable change in the stabilization energy of the water molecule. A change in energy of ~80–100 kcal/mol (depending upon the methods chosen) itself emphatically reflects this fact. Now, we move to a case where the confinement distance is 5Å (Fig. 4b). It is expected that as the confinement effect tends to disappear gradually, the stability of the water molecule can be enhanced in a significant manner. The results obtained by different methods in this case show some discrepancy in the trend of the interaction energy. The MP2 method predicts the water interaction energy to be positive, varying within a range of 5 kcal/mol across all the curvatures. However, the DFT methods predict trends similar to the case of confinement within 4 Å. As was the situation with the previous case, here also for initial smaller curvatures, the interaction energy is positive (but with lower magnitude than the 4 Å case) indicating that the water molecule is unbound. The water molecule attains minimum energy configuration with negative interaction energy for curvature beyond 15°. In this case, the variation in interaction energy shows a sudden dip in the curve with values between 15 and 25 kcal/mol. This observation is in the same spirit as seen for the 4 Å case highlighting the effect of curvature on the energetics of water molecule for smaller confinement lengths.

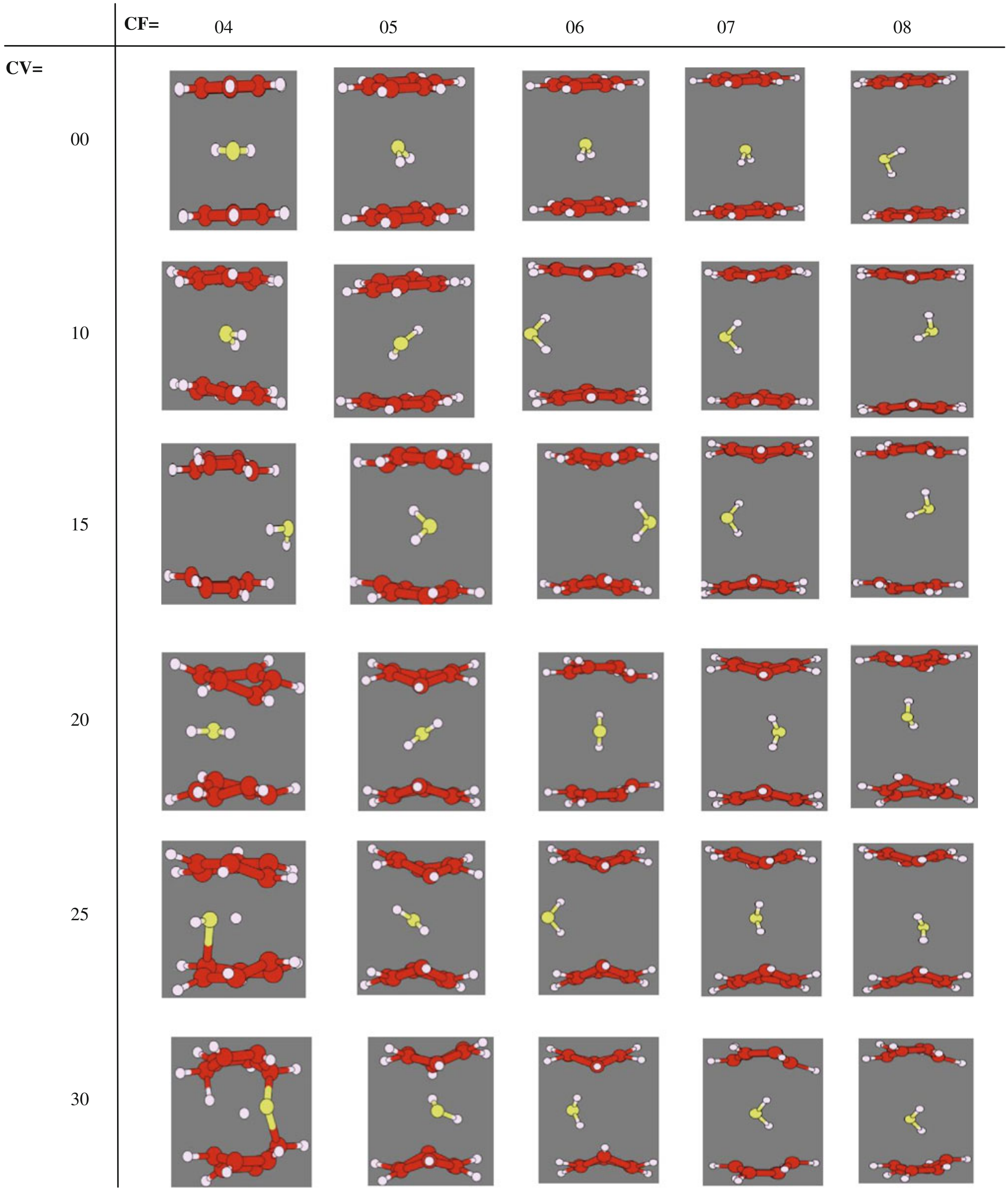

Fig. 3 MP2 optimized geometries of water molecule with different curvature and confinement values, W–DB–CV–CF system

More strikingly, on further increase in the confinement distance to 6 Å (Fig. 4c), it is observed that the interaction energy of the water molecule is always negative across the variation of curvature. This suggests that the water molecule is now in an energetically favorable environment with confinement being eased up leading to a net stabilization energy. Focusing on the results obtained by different DFT methods, a linear trend is observed for the

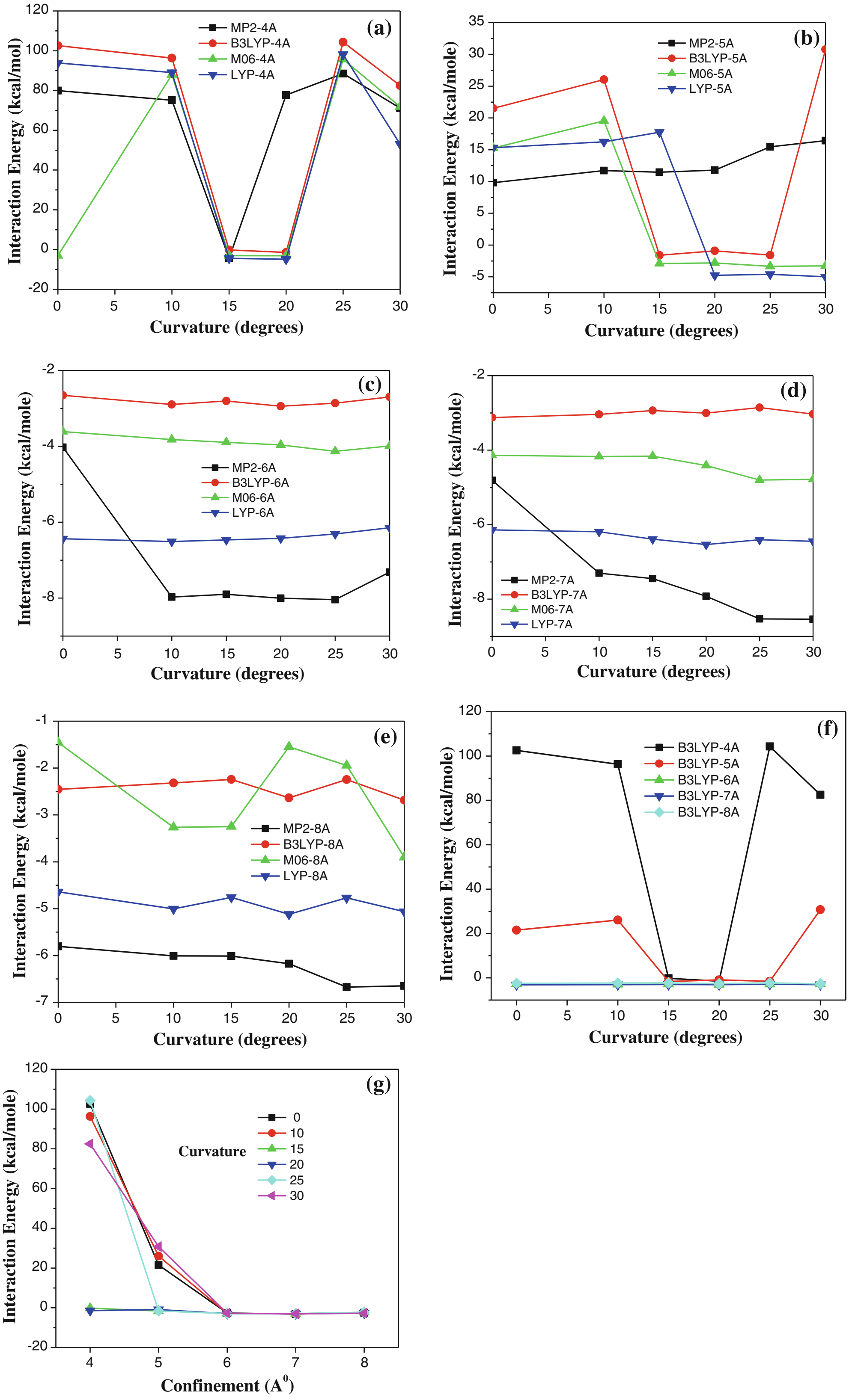

Fig. 4 **a**–**e** Variation of interaction energy of water as a function of curvature for W–DB system for different confinement distances 4–8 Å. **f** Interaction energy as a function of curvature for different confinement distances and **g** interaction energy as a function of confinement distances for all the curvatures

stabilization energy of water as the curvature changes. This observation suggests that the effect of curvature practically becomes irrelevant as there is almost no variation in the interaction energies with change in the curvature. Only the MP2 method predicts that as we move from curvature 0°–10°, the stabilization energy changes by ~4 kcal/mol and remaining nearly constant thereafter. Figure 4d and e represent the cases where the confinement is 7 and 8 Å, respectively. These two plots also show qualitatively similar behavior as in the 6 Å case. The stabilization energy is always negative, and this has minimal effect from variation of curvature.

To have a better illustration of the combined effect of interplay between confinement and curvature on the water interaction energy, we have presented the trend of variation of the latter as a function of confinement and curvatures in Fig. 4f and g. For the sake of clarity, we have presented only the B3LYP results as the results based on other methods have similar qualitative nature. We are able to make some important observations. There seem to be three regimes, viz., 0–15°, 15–25°, 25–30° of curvatures wherein the water molecule experiences the effect of curvature in a distinct way, and there is a noticeable change in the energetics of the water molecule. For the two extreme regimes (lower and higher), the stabilization energies of water molecule under highly confining regions especially below a confinement distance of 6 Å are found to be highly positive. Strikingly, there is an abrupt decline in stabilization energy for the intermediate curvature regime, 15–25°, and this sharp downward jump is as high as 100 kcal/mol. Beyond 6 Å confinement distance, the variation of stabilization energy changes marginally with curvature and it is also noted that the water molecule is always stabilized for all the curved structures. The important rationale that we derive from this observation is that for smaller and larger curvature cases, confinement indeed can be a factor of paramount importance. A confinement distance of 6 Å is believed to be at the borderline below which the water molecule interaction is energetically highly unfavorable (for the two extreme regimes), with the stabilization energy depending significantly on the curvature and beyond which the water interaction energy remains almost unchanged and curvature has a minimal effect on it. Secondly, for intermediate range of curvatures (15°–20°), the effect of confinement becomes insignificant as there is negligible change in the stabilization energy of water as is evident from the above two figures. However, this curvature range significantly induces the stabilization energy favorably inside the nanotube, implying that the water molecule prefers these curvatures for an energetically stable conformation thereby nullifying another important parameter of confinement that governs the energetics of water for rest of the curvature values.

Apart from the interaction energy of the water molecule, other structural and electronic properties like H–O–H bond angle, O–H bond distance, and Mulliken charges on O and H atoms (q_{O}, q_{H1}, and q_{H2}) of water molecule under confinement can provide important information on the nature of water molecule under nano-confinement. These essential properties have been presented in Table 1 (MP2 results) for all values of confinement and curvatures. As we have already mentioned, there are some cases where the water molecule undergoes dissociation (marked as DIS in the table) and the H–O–H bond angle and O–H bond distance become insignificant. The H–O–H bond angle for the free water molecule is 104.30° that almost matches with the experimental value [32] of 104.45, thus validating the present level of theory. One of the most note-worthy observations is that the bond angle for the confined water either shrinks or expands and the value varies between 101–105°. In cases where the interaction energy is positive, it is observed that the H–O–H bond angle shrinks (101°–102°) as compared to that of the isolated water molecule. In majority of the cases where the stabilization energy of water is favorable (negative), the bond angle marginally changes as compared to the free water molecule. Exception to this general trend is the case of W–DB-00-06 and W–DB-00-07 wherein the bond angle is ~101° with the net stabilization of energy being −4.02 and −4.81 kcal/mol, respectively. This deviation of ~3° from the usual bond angle suggests that, in fact, the confinement can have a pertinent role in deciding the structure and bonding of nano-confined water molecules. In our calculations, we have obtained the O–H bond distance for the free water molecule as 0.957 Å that is in good agreement with the experimental value [32] of 0.958 Å. On careful observation of the O–H bond length, we find that in almost all cases, the bond distance is increased from its initial value (free water) of 0.957 to ~0.960 Å for the encapsulated water molecule. The increment of about 0.014 Å in bond distance, although seems to be negligibly small, can have pronounced effect on the vibrational spectra of water. For encapsulated water, vibrational spectroscopy [33–38] is a sensitive indicator to probe the confinement effect as well as the strength and orientation of hydrogen bonding. It is well known that lengthening of the bond leads to a decrease in the stretching frequency, and thus, it is expected that the O–H stretching frequency in confined water will have a red shift as compared to that of the free water molecule. This red shifting of O–H stretching frequency, in principle, can act as a direct probe for the water under confinement. To quantify the above arguments, we have calculated the vibrational spectra of water for three representative cases, the free water molecule, W–DB-00-06 and W–DB-20-06 model systems. For the latter two cases, the stabilization energy is negative indicating the systems to be energetically stable.

Table 1 Interaction energy, H–O–H bond angle, O–H bond length, and Mulliken charges for water molecule with different curvature and confinement values, W–DB–CV–CF system

System name	ΔE (kcal/mol)	H–O–H (°)	O–H (Å)	Charge (Mulliken) (a.u.)		
				q_{O}	q_{H1}	q_{H2}
H_2O		104.304	0.957 0.957	−0.496	0.248	0.248
W–DB-00-04	79.93	103.231	0.943 0.943	−0.315	0.180	0.184
W–DB-00-05	9.81	102.473	0.957 0.957	−0.364	0.209	0.205
W–DB-00-06	−4.02	101.765	0.961 0.961	−0.390	0.214	0.215
W–DB-00-07	−4.81	101.951	0.961 0.961	−0.421	0.223	0.223
W–DB-00-08	−5.80	104.699	0.959 0.962	−0.466	0.235	0.249
W–DB-10-04	75.10	103.235	0.950 0.954	−0.352	0.181	0.229
W–DB-10-05	11.72	103.905	0.958 0.960	−0.367	0.198	0.218
W–DB-10-06	−7.97	104.752	0.962 0.962	−0.460	0.244	0.243
W–DB-10-07	−7.30	105.427	0.961 0.961	−0.448	0.241	0.240
W–DB-10-08	−6.00	104.604	0.962 0.959	−0.454	0.248	0.229
W–DB-15-04	−4.40	104.572	0.962 0.959	−0.417	0.223	0.225
W–DB-15-05	11.45	102.654	0.962 0.960	−0.364	0.224	0.198
W–DB-15-06	−7.89	104.587	0.962 0.962	−0.462	0.241	0.246
W–DB-15-07	−7.44	105.549	0.961 0.962	−0.438	0.236	0.240
W–DB-15-08	−6.01	104.570	0.959 0.963	−0.461	0.231	0.259
W–DB-20-04	77.69	101.090	0.972 0.989	−0.267	0.238	0.268
W–DB-20-05	11.79	102.707	0.962 0.961	−0.308	0.194	0.190
W–DB-20-06	−8.00	104.567	0.962 0.962	−0.460	0.242	0.241
W–DB-20-07	−7.92	105.264	0.963 0.962	−0.444	0.241	0.237
W–DB-20-08	−6.17	104.879	0.959 0.963	−0.455	0.23	0.263
W–DB-25-04	88.50	DIS	DIS	−0.271	0.247	0.297
W–DB-25-05	15.45	102.175	0.967 0.961	−0.312	0.218	0.186

Table 1 continued

System name	ΔE (kcal/mol)	H–O–H (°)	O–H (Å)	Charge (Mulliken) (a.u.)		
				q_O	q_{H1}	q_{H2}
W–DB-25-06	−8.04	104.511	0.962 0.962	−0.452	0.239	0.235
W–DB-25-07	−8.52	104.876	0.963 0.963	−0.439	0.238	0.243
W–DB-25-08	−6.67	104.669	0.960 0.964	−0.451	0.232	0.249
W–DB-30-04	71.11	DIS	DIS	−0.123	0.133	0.253
W–DB-30-05	16.43	102.544	0.961 0.974	−0.321	0.194	0.253
W–DB-30-06	−7.31	104.821	0.961 0.965	−0.420	0.224	0.224
W–DB-30-07	−8.53	104.813	0.963 0.964	−0.429	0.241	0.236
W–DB-30-08	−6.64	104.667	0.965 0.960	−0.451	0.249	0.231

Furthermore, the W–DB-00-06 system represents the case of only confinement with H–O–H bond angle and O–H bond distance both appreciably deviating (101.765° and 0.961 Å, respectively) and the W–DB-20-06 system represent the case of both confinement and curvature with only sizeable change of bond length (0.961 Å) with the bond angle 104.567° remaining practically unaffected from that of isolated water molecule case. For the free water molecule, we have obtained three normal modes of vibration as 3,811 cm^{-1} (symmetric stretching), 3,932 cm^{-1} (asymmetric stretching), and 1,539 cm^{-1} (bending) that are in close agreement with the reported experimental values [39] of 3,832, 3,943, and 1,648 cm^{-1} for the three modes, respectively. For the W–DB-20-06 system, our calculated vibrational frequencies are 3,772, 3,874, and 1,546 cm^{-1}, respectively, for the above mentioned three modes. In this case, the bond angle hardly changes from that of the free water molecule case that is also reflected in minimal change in the frequency for bending mode (1,546 against 1,539 cm^{-1} for free water). However, the O–H bond length increases for the W–DB-20-06 model system and correspondingly the symmetric stretching and asymmetric stretching frequencies decrease by 39 and 58 cm^{-1}, respectively. On the other hand, for the W–DB-00-06 case, our results 3,799, 3,888, and 1,567 cm^{-1} clearly demonstrate the effect of change in bond angle and bond lengths on the vibrational frequencies of water due to the confinement. Our analysis of vibrational frequencies of O–H stretching mode indicates a red shift of the frequency for the encapsulated water molecule as compared to free water molecule. This observation is in good agreement with the result obtained by Wang et al. [19] for water chains encapsulated in a CNT, thereby justifying the suitability of our model systems.

In a related study, Shameema et al. [40] have demonstrated that confinement induced by C_{60} fullerene cage leads to blue shift of the O–H frequency. It may, however, be noted that we also observe blue shift in O–H frequency for model systems where the confinement effect felt by the water molecule is very large and the stabilization energy is positive. To demonstrate this, we have considered three cases namely, W–DB-00-04, W–DB-00-05, and W–DB-10-04, where the net stabilization energy of the water molecule is positive. The calculated symmetric stretching, asymmetric stretching, and bending frequencies for the above three cases are as follows: 4,007, 4,105, 1,593; 3,848, 3,931, 1,572; and 3,829, 3,976, 1,539 in cm^{-1} units, respectively. From these values, it is clearly evident that the blue shift in the symmetric and asymmetric frequencies is relatively much larger for the case of highly confined water with the confinement length 4 Å. A slight increase in the confinement length from 4 to 5 Å is found, the observed blue shift is found to be reduced, and the symmetric frequency shifts from 4,007 to 3,848 cm^{-1}, which is higher than that of the free water molecule. Upon further increase in the confinement length beyond 6 Å, as we discussed earlier, red shift in the vibrational frequency is observed. From the above results, it appears that the molecule initially goes through a blue shift by shortening the O–H bond length, and thereafter, further increase in confinement length leads to the red shift. Comparing the result of Shameema et al. [40] for the real system, the blue shift due to the fullerene molecule whose diameter is ~6 Å is in good agreement with our results corresponding to the case of model case, W–DB-00-05. Hence, it is inferred that the blue or red shift in the vibrational frequencies of encapsulated water is governed by a fine balance between the curvature and confinement length.

Finally, we will now discuss the Mulliken charges on the O and H atoms of the encapsulated water molecule, and all the values of charges are presented in Table 1. As an illustrative case, the plot for the variation of atomic charge on oxygen atom due to the curvature and confinement is presented in Fig. 5. It is clear from the Fig. 5 that for highly confined regions with high curvature (CV and CF are 30° and 4 Å, respectively), the charge on the oxygen atom is found to be very less, −0.123 a.u. while for the case of free water molecule is −0.496 a.u. Such remarkable charge separation is accompanied by the dissociation of water molecule. As we have discussed earlier for the case of stabilization energy for which the confinement distance of 6 Å seems to be at the borderline, following the same line of arguments, the charge separation also varies dramatically below 6 Å and above this border line, the variation is marginal with respect to curvature. Another striking result is that the magnitude of the charge on oxygen atom is not same as the sum of the charges on hydrogen atoms in water. This result reveals that there is a significant amount of charge transfer from the water molecule to the carbon rings, and hence, the encapsulated water molecule exists with a small amount of partial positive charge. Further, it is also evident from Table 1 that the charge on both the hydrogen atoms is not necessarily the same (unlike to the case of free water molecule), and the difference between the charge on the two hydrogen atoms becomes prominent for the case of highly confined and curved model systems. Considering the remarkable variation in the geometrical parameters and atomic charges of the confined water molecule, we can conclude that the hydrogen bonding characteristics of water under confinement will also differ to a large extent. Concomitantly, this observation is also in support of the different properties that the nano-confined water may exhibit as compared to free water. The preceding discussions lead us to conclude that nano-confinement and also curvature are two crucial parameters that can influence the structure and electronic properties as well as vibrational properties of water.

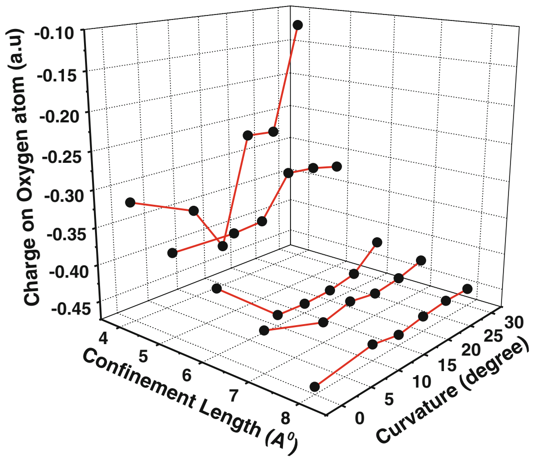

Fig. 5 Variation of Mulliken charge of oxygen atom of the encapsulated water molecule as a function of curvature with different confinement distances 4–8 Å

4 Conclusion

In summary, our ab initio theoretical studies attempt to explore the behavior of water molecule under confinement. Considering model systems that represent a single unit of CNT, a curved 6-membered carbon ring, we have investigated the structural, electronic, and vibrational properties of water molecule encapsulated in the model system. The interaction of a water molecule with a single model structure (W–SB) with inherent curvature reveals that the stabilization energy of the water molecule increases with increasing curvature. Similarly, for the case of confined system (W–DB), we note that although the water molecule is held in an energetically unfavorable situation, a slight change in curvature can bring about significant change in the interaction energy of water (~100 kcal/mol for 4 Å case) leading to an favorable configuration. For lower (0°–15°) and higher (20°–30°) curvature values, the interaction energy shows drastic variation with the confinement distance. However, for the curvature values ranging from 15° to 20°, the interaction energy is almost constant over the variation of the confinement distance and the energy is negative suggesting a favorable interaction. Another important outcome of the present study is that the confinement distance of 6 Å seems to mark a borderline below which the curvature has a pronounced effect on the stabilization energy of water. Beyond the confinement distance of 6 Å, curvature plays a lesser significant role, and for these cases, the behavior of water is similar to free water (gas phase). It is therefore inferred that water molecule can be favorably encapsulated between two moderately curved surfaces of curvature 15°–20°. The dissociation of water is also observed for higher values of curvature and lower values of confinement distance that is worth mentioning. In addition, we have demonstrated that the two parameters, curvature and confinement, play a key role in governing the significant variations in the structural parameters, Mulliken charges, and vibrational frequencies of the encapsulated water molecule. Encapsulation leads to slight elongation or shortening of the O–H bond length that in turn is reflected in the red or blue shift in the O–H stretching mode depending on the two important parameters, that is, the amount of curvature and confinement length. This kind of observation is in corroboration with some of the earlier results for water inside CNT or fullerene systems [19, 40]. Hence, we conclude that the conjunction of the two important factors namely the confinement distance and the curvature of the model system seems to manifest very interesting trend on the nature of confined water molecule. The interplay between these two parameters in deciding the electronic properties of water in the nanoscale confinement is of paramount importance.

Our model structures, at the most structurally primitive level, can be thought of representing the hydrophobic confinement medium like the interior of the CNT or water conducting channel proteins like aquaporin wherein the interaction is dominantly driven by weak hydrogen bonding types of interaction. Our calculations can provide some valuable insights into our understanding of the behavior of water under confined medium at the fundamental level.

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