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# An ab initio Study of Water Clusters in Gas Phase and Bulk Aqueous Media: $(\text{H}_2\text{O})_n$ , $n = 1\text{--}12$

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**ABSTRACT:** Geometries of several clusters of water molecules including single minimum energy structures of  $n$ -mers ( $n = 1\text{--}5$ ), several hexamers and two structures of each of heptamer to decamer derived from hexamer cage and hexamer prism were optimized. One structural form of each of 11-mer and 12-mer were also studied. The geometry optimization calculations were performed at the RHF/6-311G\* level for all the cases and at the MP2/6-311++G\*\* level for some selected cases. The optimized cluster geometries were used to calculate total energies of the clusters in gas phase employing the B3LYP density functional method and the 6-311G\* basis set. Frequency analysis was carried out in all the cases to ensure that the optimized geometries corresponded to total energy minima. Zero-point and thermal free energy corrections were applied for comparison of energies of certain hexamers. The optimized cluster geometries were used to solvate the clusters in bulk water using the polarized continuum model (PCM) of the self-consistent reaction field (SCRF) theory, the 6-311G\* basis set, and the B3LYP density functional method. For the cases for which MP2/6-311++G\*\* geometry optimization was performed, solvation calculations in water were also carried out using the B3LYP density functional method, the 6-311++G\*\* basis set, and the PCM model of SCRF theory, besides the corresponding gas-phase calculations. It is found that the cage form of water hexamer cluster is most stable in gas phase among the different hexamers, which is in agreement with the earlier theoretical and experimental results. Further, use of a newly defined relative population index (RPI) in terms of successive total energy differences per water molecule for different cluster sizes suggests that stabilities of trimers, hexamers, and nonamers in gas phase and those of hexamers and nonamers in bulk water would be favored while those of pentamer and decamer in both the phases would be relatively disfavored. © 2001 John Wiley & Sons, Inc. *Int J Quantum Chem* 81: 90–104, 2001

**Key words:** cluster; water; ab initio calculation; electronic structure; rotational constant

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## Introduction

Water is widely distributed in nature, has many interesting physicochemical properties, and is essential for life processes. In view of this reason, numerous efforts have been made in the past toward understanding the structure and electronic origin of different properties of water. In the recent years, several experimental [1–6] and theoretical [7–15] studies have been carried out to investigate the microscopic structure of water in terms of clusters of water molecules. Theoretical investigations of this problem have been carried out primarily using quantum chemical *ab initio* total energy minimization calculations as well as quantum Monte Carlo simulations. Experimental studies have been carried out on several water clusters using vibration-rotation tunneling (VRT) spectroscopy that yielded very precise rotational constants [1–6]. A comparison of the experimentally observed rotational constants with the theoretically calculated ones leads to confirmation of observed clusters [1]. It is now known that several clusters of water molecules  $(\text{H}_2\text{O})_n$  ( $n = 2\text{--}6$ ) are quite stable. In the dimer, the two water molecules lie in mutually perpendicular planes while the most stable forms of trimer, tetramer, and pentamer are cyclic [2–6]. There are several possible hexamer structures out of which two, i.e., cage and prism, are quite close in stability [1, 14, 16]. An interesting result obtained earlier [1] is that the cage form of hexamer, which is observed experimentally at low temperature in supersonic jets, is more stable than the prism form only if zero-point energy (ZPE) correction to electronic energies is applied. Some higher clusters of water molecules than hexamer have also been studied. Thus two symmetric octamer clusters have been found from Monte Carlo simulations and *ab initio* Hartree–Fock calculations [17], and Sadlej et al. [18] have studied certain heptamer to decamer clusters using symmetry considerations that also analyzed the OH stretch spectra in gas phase extensively. Water heptamer has been studied by Brudermann et al. [19] both experimentally and theoretically and by Kim et al. [20] using rigorous *ab initio* calculations. However, to the best of our knowledge, occurrence of higher clusters than hexamer has not yet been established convincingly experimentally. Various other interesting aspects of water have been investigated [21–36] by different workers using experimental and theoretical techniques.

The occurrence of different stable water clusters in gas phase gives rise to the question as to what role such clusters are likely to play with regard to the structure of bulk water including its interface with air. It appears quite likely that bulk water would also be made of clusters, an equilibrium would be established between the formation and dissociation of the clusters with a distribution of different cluster sizes in a given condition, and anionic and cationic clusters would play important roles in alkaline and acidic media, respectively, while neutral clusters would occur dominantly at neutral pH. The gas-phase results regarding the relative stability of different clusters may not be directly applicable to bulk water, though they may be applicable to the water–air interface. In other words, the distribution of cluster sizes in gas phase or at the water–air interface may be different from that inside bulk water. In order to be able to understand these aspects, it is necessary to carry out reliable quantum theoretical calculations on clusters of different sizes in gas phase, from monomer to fairly large ones, and subsequently to study the stability of the clusters in bulk aqueous media. There are ample experimentally measured physical properties of clusters, which can be used to test reliability of the chosen theoretical method. To the best of our knowledge, these aspects of water clusters have not been studied earlier. We present here the results obtained about these aspects using *ab initio* calculations.

## Method of Calculations

The geometry of a water molecule and those of different clusters of water molecules from dimer to decamer in gas phase were fully optimized. Initially the geometry optimization was performed using the *ab initio* restricted Hartree–Fock (RHF) method and the 3-21G basis set. Subsequently, geometry optimization was repeated at the RHF level using the 6-311G\* basis set. These optimized geometries were used to calculate total energies of the clusters in gas phase employing the B3LYP density functional method [37] and the 6-311G\* basis set. In these calculations, a single structure of each cluster up to pentamer, several structures of hexamer clusters, and two structural forms of different clusters from heptamer to decamer were considered. The gas-phase calculations were also extended to one particular (prism) form of each of 11-mer and 12-mer. MP2/6-311++G\*\* geometry optimization calculations were performed on water monomer

and three hexamer clusters, i.e., cage, prism, and cap. The cage and prism forms of hexamer were taken to be the starting structures for generating higher clusters. Locating the global minima of total energies of clusters where several different conformations or structures can occur is a rather difficult job [38, 39]. To minimize the difficulty in building successive higher clusters than hexamer, at each step, an additional water molecule was added to an optimized cluster structure using the criterion of lowest negative molecular electrostatic potential (MEP), as it is known that MEP is a good descriptor of hydrogen bonding [40]. No symmetry constraint was applied in optimizing geometries of clusters. Frequency analysis was carried out at the RHF level in all cases using the optimized cluster geometries. All the vibrational frequencies were found to be real in the different cases, including the 11-mer and 12-mer. The optimized cluster geometries were used to solvate the monomer and the clusters in bulk water using the polarized continuum model (PCM) of the self-consistent reaction field (SCRF) theory [41, 42], the 6-311G\* basis set, and the B3LYP density functional method. It is expected that solvation calculations employing the PCM model would yield relative total energies for the clusters of different sizes reliably. In our earlier studies on molecular electronic structure and spectra [43, 44], we found that the PCM model works satisfactorily to describe solvent effects and, therefore, preferred to use it here also. However, the solvation calculation using the PCM model did not converge for the 11-mer due to which only gas-phase results for 11-mer and 12-mer (prism form) are presented here. The 6-311G\* basis set employed here for the RHF and B3LYP calculations is quite moderate, but it was used since we undertook a computationally extensive study of the structures and stabilities of several clusters of different sizes both in gas phase and bulk aqueous media. The calculations were performed using the Windows version of the Gaussian 94 program [45].

## Results and Discussion

### TOTAL ENERGIES OF CLUSTERS IN GAS PHASE AND AQUEOUS MEDIA

The computed total electronic and zero-point energies per water molecule in gas phase for the different water clusters (H<sub>2</sub>O)<sub>n</sub>, *n* = 1–12, obtained from RHF/6-311G\* calculations, relative to the corresponding quantities for the water monomer, are

presented in Table I. The total electronic energies for the different clusters in gas phase and bulk water obtained at the B3LYP/6-311G\* level, the energies in bulk water having been obtained using the PCM model of the SCRF theory, relative to the corresponding monomer energies, are also presented in Table I. These energies are given here in terms of “per water molecule” as this presentation enables a direct comparison of stabilities of different clusters. The data presented in Table I show that the magnitudes of total electronic energies as well as the zero point energies (ZPE) per water molecule increase rapidly in going from monomer to dimer to trimer. The increase in the electronic energy is also quite large in going from trimer to tetramer; but, from tetramer onward, the rates of change of total electronic energy and ZPE become relatively much smaller according to both the RHF and B3LYP calculations. In Table I, the hexamer cluster called “cap” has a conical cavitylike empty space while that called “ellipsoid” has a center of symmetry with the six water molecules sitting symmetrically on the surface of an ellipsoid. Our cap structure is similar to that called “bag” by Kim and Kim [16]. The optimized structures of cage, prism, cap, and ellipsoid forms of hexamer are given in Figure 1 where the hydrogen bond lengths are specified. According to the RHF/6-311G\* and B3LYP/6-311G\* results presented in Table I, the prism hexamer structure is more stable than cage in gas phase and bulk water. However, when MP2/6-311++G\*\* optimized geometry was used and the electronic energy calculated using the 6-311++G\*\* basis set employing the B3LYP method in gas phase, without considering ZPE, the two structures were found to be almost isoenergetic, as reported by other authors also [1].

The relative energies per water molecule of the different clusters in gas phase and bulk water obtained after making ZPE correction obtained in gas phase, with respect to the corresponding monomer energies (in cm<sup>-1</sup>) are presented in Table II. When the MP2/6-311++G\*\* optimized geometry was used and RHF energy including ZPE calculated using the 6-311++G\*\* basis set, the cage and prism hexamer clusters were found to be nearly isoenergetic (Table II). But according to the corresponding B3LYP energies, the cage is noticeably more stable than prism in gas phase with the ZPE correction. The importance of ZPE correction in this context has been discussed by other authors also earlier [1, 2]. The prism structure has one additional hydrogen bond than cage due to which the former appears to have a larger amount of ZPE

TABLE I

Total electronic and zero-point energies (eV) per water molecule in different water clusters obtained at the RHF and B3LYP levels using the 6-311G\* basis set in gas phase and bulk water.<sup>a</sup>

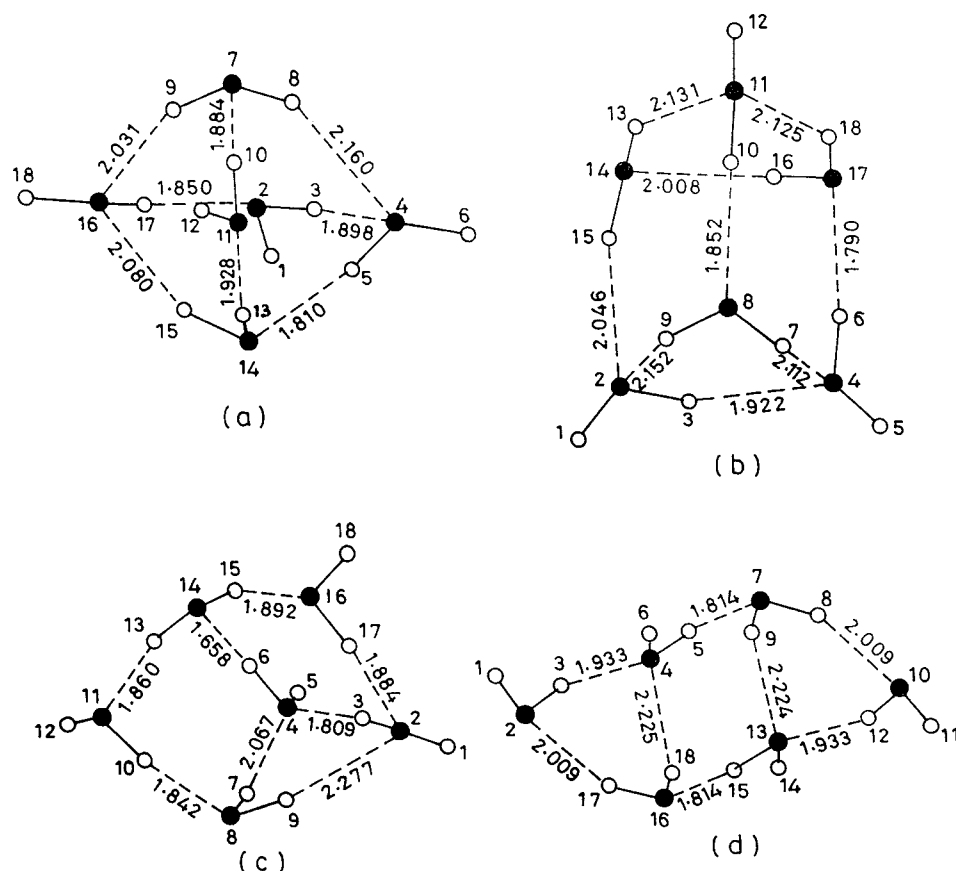
Sl. No.	Molecule/ cluster	RHF <sup>b</sup>		B3LYP <sup>c</sup>	
		Gas		Gas	Bulk water
1	(H <sub>2</sub> O) <sub>1</sub>	0.0	(0.0)	0.0	−0.3580
		[−6.5750]	[−0.0436]	[−0.6958]	[−0.9105]
2	(H <sub>2</sub> O) <sub>2</sub>	−0.1406	(0.0507)	−0.1812	−0.4911
3	(H <sub>2</sub> O) <sub>3</sub>	−0.2810	(0.0890)	−0.3777	−0.5843
4	(H <sub>2</sub> O) <sub>4</sub>	−0.3625	(0.1018)	−0.4807	−0.6493
5	(H <sub>2</sub> O) <sub>5</sub>	−0.3814	(0.1005)	−0.4992	−0.6522
6	(H <sub>2</sub> O) <sub>6</sub>	−0.3987	(0.1124)	−0.5383	−0.7120
	cage	[−6.9712]	(0.1187)	[−1.0508]	[−1.1690]
7	(H <sub>2</sub> O) <sub>6</sub>	−0.4043	(0.1159)	−0.5493	−0.7298
	prism	[−6.9731]	(0.1204)	[−1.0505]	[−1.1856]
8	(H <sub>2</sub> O) <sub>6</sub>	−0.3950	(0.1025)	−0.5129	−0.6634
	cyclic				
9	(H <sub>2</sub> O) <sub>6</sub>	−0.3933	(0.1086)	−0.5247	−0.6920
	book				
10	(H <sub>2</sub> O) <sub>6</sub>	−0.3796	(0.1051)	−0.5066	−0.6778
	boat				
11	(H <sub>2</sub> O) <sub>6</sub>	−0.3911	(0.1093)	−0.5261	−0.7000
	cap	[−6.9675]	(0.1173)	[−1.0464]	[−1.1644]
12	(H <sub>2</sub> O) <sub>6</sub>	−0.3774	(0.1060)	−0.5049	−0.6815
	ellipsoid				
13	(H <sub>2</sub> O) <sub>7</sub>	−0.4094	(0.1186)	−0.5596	−0.7440
	cage				
14	(H <sub>2</sub> O) <sub>7</sub>	−0.4092	(0.1147)	−0.5540	−0.7330
	prism				
15	(H <sub>2</sub> O) <sub>8</sub>	−0.4250	(0.1168)	−0.5723	−0.7345
	cage				
16	(H <sub>2</sub> O) <sub>8</sub>	−0.4138	(0.1137)	−0.5564	−0.7262
	prism				
17	(H <sub>2</sub> O) <sub>9</sub>	−0.4452	(0.1228)	−0.6027	−0.7665
	cage				
18	(H <sub>2</sub> O) <sub>9</sub>	−0.4536	(0.1223)	−0.6116	−0.7638
	prism				
19	(H <sub>2</sub> O) <sub>10</sub>	−0.4392	(0.1228)	−0.5961	−0.7583
	cage				
20	(H <sub>2</sub> O) <sub>10</sub>	−0.4282	(0.1181)	−0.5771	−0.7516
	prism				
21	(H <sub>2</sub> O) <sub>11</sub>	−0.4407	(0.1235)	−0.5974	NA <sup>d</sup>
	prism				
22	(H <sub>2</sub> O) <sub>12</sub>	−0.4541	(0.1247)	−0.6135	−0.7909
	prism				

<sup>a</sup> MP2 energies obtained using 6-311++G\*\* basis set with geometry optimization at the same level are given in brackets. The B3LYP energies given in brackets were obtained using 6-311++G\*\* basis set and the MP2 optimized geometries.

<sup>b</sup> Zero-point energies (ZPE) are given in parentheses with reference to the monomer ZPE obtained at the RHF level, i.e., 0.6337 eV. RHF and MP2 gas-phase total energies are given with reference to the monomer RHF total energy, i.e., −2068.9629 eV. ZPE were obtained using the corresponding basis set.

<sup>c</sup> Total energies are given with reference to the monomer gas-phase energy, i.e., −2079.8609 eV in gas phase obtained at the B3LYP level.

<sup>d</sup> Not available.



**FIGURE 1.** Structures of four hexamer clusters as projected in the plane of the paper: (a) cage, (b) prism, (c) cap, and (d) ellipsoid. The hydrogen bond lengths (Å) are indicated.

than the latter. In bulk water, even after ZPE correction obtained in gas phase, the prism form of hexamer is more stable than the corresponding cage form. Among hexamers, the cap structure is third after cage and prism in the order of stability both in bulk water and gas phase. The cyclic, boat, and ellipsoid structures are less stable than even cap. It appears likely that higher clusters obtained from the prism and cage hexamers would be present in gas phase and bulk water. Thus, larger clusters than hexamer generated starting with only these two hexamer clusters (cage and prism) were studied here. We shall consider the higher clusters derived from hexamer cage and hexamer prism also as those of cage and prism type, respectively, for convenience of description. The optimized structures of both cage- and prism-type heptamer and octamer clusters are presented in Figure 2, while the corresponding structures of nonamer and decamer are presented in Figure 3. The optimized structures of prism-type 11-mer and 12-mer clusters are pre-

sented in Figure 4. The hydrogen bond lengths are indicated in the Figures 2–4. The energies obtained from B3LYP calculations (Table II) show that the cage forms of heptamer to decamer clusters are more stable than those of prism form in bulk water. The same order of stability of the cage and prism forms of higher clusters than hexamer is also found in gas phase according to the B3LYP results, except for nonamers, for which the reverse is true (Table II). The RHF results, however, do not follow the same trend as those obtained by the B3LYP method (Table II). There is no difficulty as to which of these RHF and B3LYP results should be considered to be more reliable since the latter method is established to be superior to the former [46, 47]. In certain earlier studies, cagelike water clusters from heptamer to decamer have been studied [17, 20].

The variation of relative total energies including ZPE in gas phase and bulk water per water molecule with respect to the water monomer obtained from RHF/6-311G\* and B3LYP/6-311G\* cal-



TABLE II

Relative total energies including the zero-point energies per water molecule with respect to the monomer in different water clusters calculated at the RHF and B3LYP levels using the 6-311G\* basis set, unless otherwise specified, in gas phase and bulk water.<sup>a</sup>

Sl. No.	Molecule/ cluster	RHF (cm <sup>-1</sup> ) <sup>b</sup>	B3LYP (cm <sup>-1</sup> ) <sup>c</sup>	
		Gas	Gas ( <i>P<sub>g</sub></i> )	Bulk water ( <i>P<sub>w</sub></i> )
1	(H <sub>2</sub> O) <sub>1</sub>	0	0 (0.0)	–2888 (0.0)
2	(H <sub>2</sub> O) <sub>2</sub>	–724	–1052 (5.1)	–3553 (3.2)
3	(H <sub>2</sub> O) <sub>3</sub>	–1548	–2329 (6.1)	–3997 (2.1)
4	(H <sub>2</sub> O) <sub>4</sub>	–2103	–3057 (3.5)	–4417 (2.0)
5	(H <sub>2</sub> O) <sub>5</sub>	–2250	–3205 (0.7)	–4434 (0.1)
6	(H <sub>2</sub> O) <sub>6</sub>	–2309	–3435 (1.1)	–4838 (1.9)
	cage	[–1886] <sup>c</sup>	[–1553] <sup>d</sup>	[–2508] <sup>d</sup>
7	(H <sub>2</sub> O) <sub>6</sub>	–2325	–3496 (1.4)	–4952 (2.5)
	prism	[–1889] <sup>c</sup>	[–1538] <sup>d</sup>	[–2629] <sup>d</sup>
8	(H <sub>2</sub> O) <sub>6</sub>	–2359	–3311 (0.5)	–4525 (0.4)
	cyclic			
9	(H <sub>2</sub> O) <sub>6</sub>	–2296	–3357 (0.7)	–4708 (1.3)
	book			
10	(H <sub>2</sub> O) <sub>6</sub>	–2213	–3237 (0.2)	–4621 (0.9)
	boat			
11	(H <sub>2</sub> O) <sub>6</sub>	–2273	–3362 (0.7)	–4767 (1.6)
	cap	[–1868] <sup>c</sup>	[–1530] <sup>d</sup>	[–2484] <sup>d</sup>
12	(H <sub>2</sub> O) <sub>6</sub>	–2189	–3217 (0.1)	–4644 (1.0)
	ellipsoid			
13	(H <sub>2</sub> O) <sub>7</sub>	–2345	–3557 (0.6)	–5046 (1.0)
	cage			
14	(H <sub>2</sub> O) <sub>7</sub>	–2375	–3544 (0.2)	–4990 (0.2)
	prism			
15	(H <sub>2</sub> O) <sub>8</sub>	–2486	–3673 (0.6)	–4984 (–0.3)
	cage			
16	(H <sub>2</sub> O) <sub>8</sub>	–2420	–3571 (0.1)	–4942 (–0.2)
	prism			
17	(H <sub>2</sub> O) <sub>9</sub>	–2600	–3871 (1.0)	–5192 (1.0)
	cage			
18	(H <sub>2</sub> O) <sub>9</sub>	–2671	–3947 (1.8)	–5175 (1.1)
	prism			
19	(H <sub>2</sub> O) <sub>10</sub>	–2552	–3818 (–0.3)	–5126 (–0.3)
	cage			
20	(H <sub>2</sub> O) <sub>10</sub>	–2501	–3702 (–1.2)	–5111 (–0.3)
	prism			
21	(H <sub>2</sub> O) <sub>11</sub>	–2558	–3822 (0.6)	NA <sup>e</sup>
	prism			
22	(H <sub>2</sub> O) <sub>12</sub>	–2656	–3943 (0.6)	–5374
	prism			

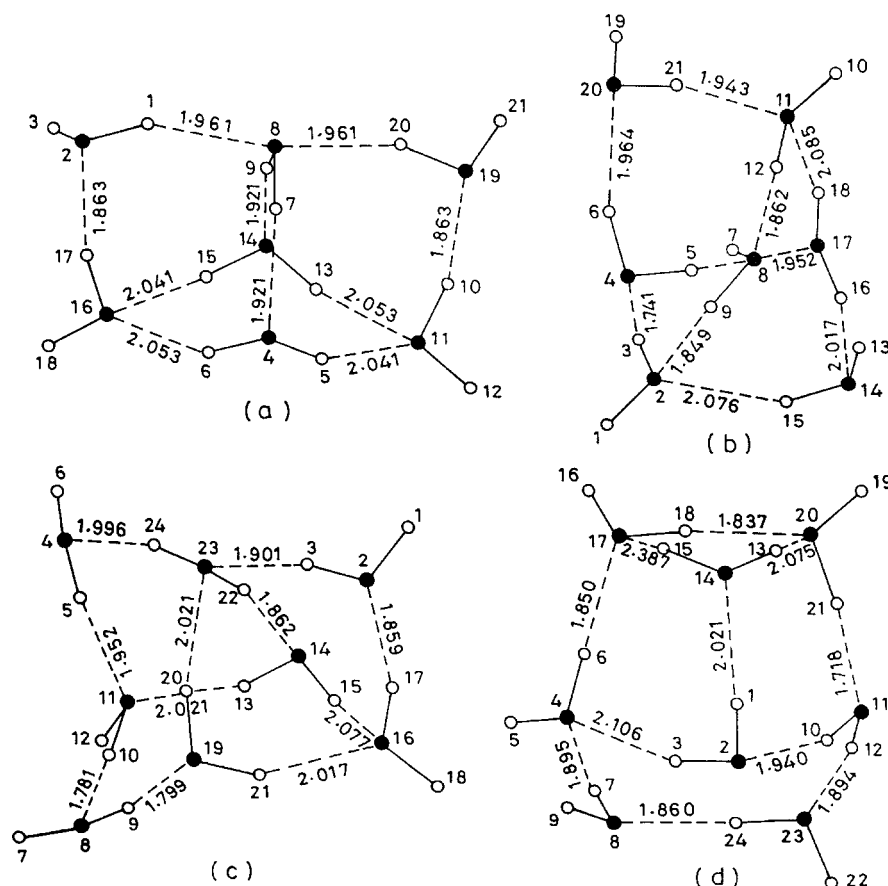
<sup>a</sup> Values of the relative population index (RPI) are given in parentheses.

<sup>b</sup> The monomer total energy corrected for ZPE (–16685212 cm<sup>-1</sup> at the RHF level and –16685214 cm<sup>-1</sup> at the B3LYP level) is taken as reference. The same reference is used for both gas phase and bulk water.

<sup>c</sup> Geometry optimized and energy calculated at MP2/6-311++G\*\* level. The reference energy in these cases is –16738604 cm<sup>-1</sup>.

<sup>d</sup> Obtained using MP2/6-311++G\*\* optimized geometry. The reference energy in these cases is 16779091 cm<sup>-1</sup>.

<sup>e</sup> Not available.

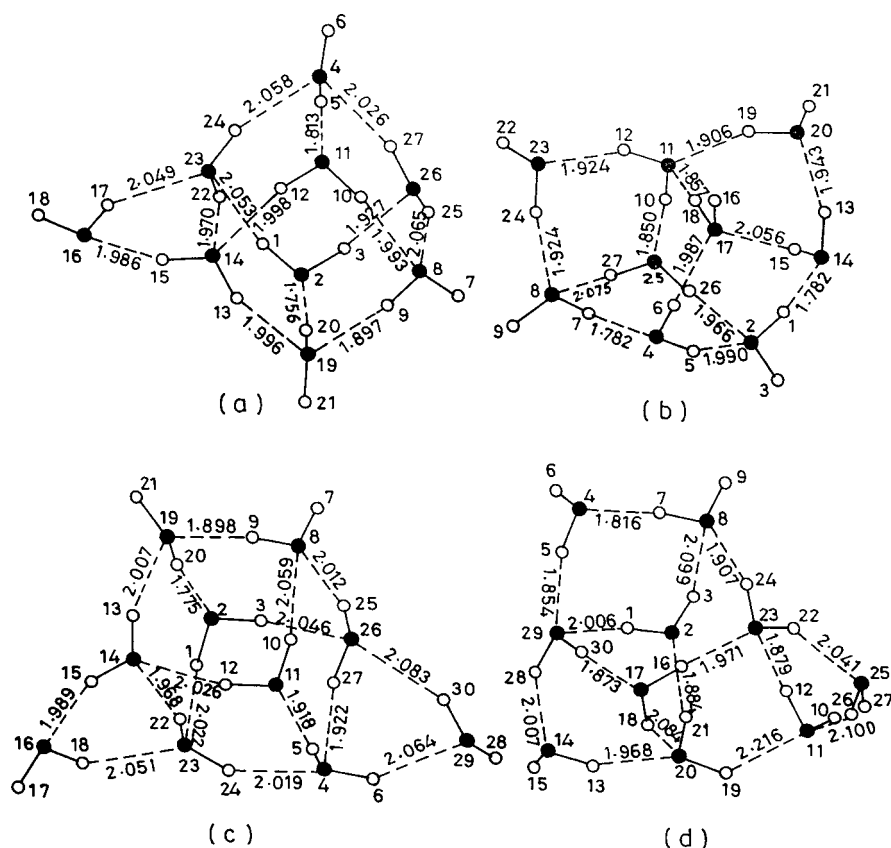


**FIGURE 2.** Structures of two heptamer clusters: (a) cage and (b) prism, and two octamer clusters: (c) cage and (d) prism, as projected in the plane of the paper. The hydrogen bond lengths (Å) are indicated.

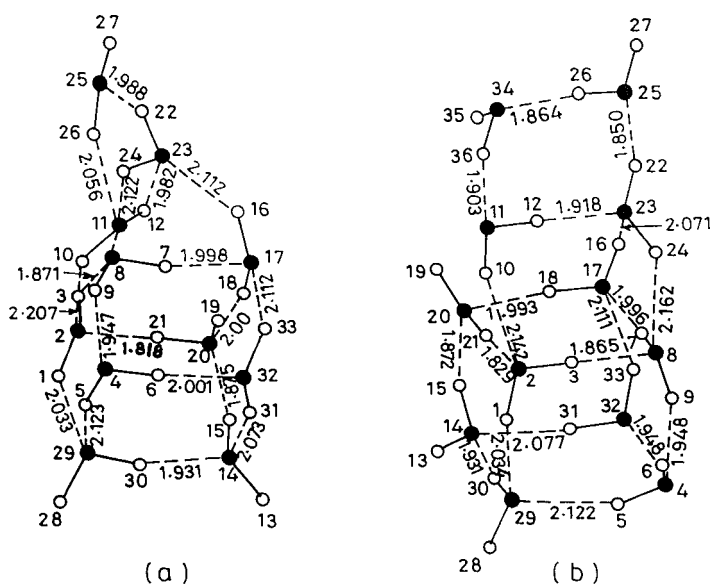
culations with the number of water molecules in the different cage-type clusters upto decamer is shown in Figure 5(a) while the corresponding variation of relative energies for the prism-type clusters is shown in Figure 5(b). The average variation of the relative energies of cage- and prism-type clusters up to decamer with the number of water molecules is shown in Figure 5(c). We find that the gas-phase relative total energy magnitudes per water molecule are appreciably increased in going from the RHF to B3LYP level, and the corresponding B3LYP energy magnitudes in bulk aqueous media calculated with respect to the gas-phase monomer total energy are much more than those of the corresponding gas-phase RHF and B3LYP energies. As the relative total energies per water molecule for different clusters are appreciably smaller in gas phase than the corresponding ones in bulk water, there appears to be a higher probability of formation of clusters in the latter case than that in the former. We can use the B3LYP energies in preference to the RHF ones in

view of a higher reliability of the former than those of the latter to discuss occurrence of different possible cluster sizes. The thermal fluctuation energy (kT) near the room temperature ( $\sim 300$  K) would be around  $208 \text{ cm}^{-1}$ . Therefore, it would be appropriate to consider that only those clusters can occur as stable entities near room temperature, the total energies of which per water molecule differ from that of next lower order cluster by a larger amount than this value. The clusters that do not satisfy this criterion would be expected to be formed and dissociated rapidly near room temperature. However, the clusters that do not satisfy this criterion can also be stabilized by appropriate cooling, e.g., in a supersonic jet [1–6]. In supersonic jets, VTR spectra are studied at quite low temperatures. For example, the experimental study in which the rotational constants of the cage hexamer were obtained was performed at 6 K [1]. At such low temperatures, the total energy difference required per water molecule between a cluster and other clusters with the same

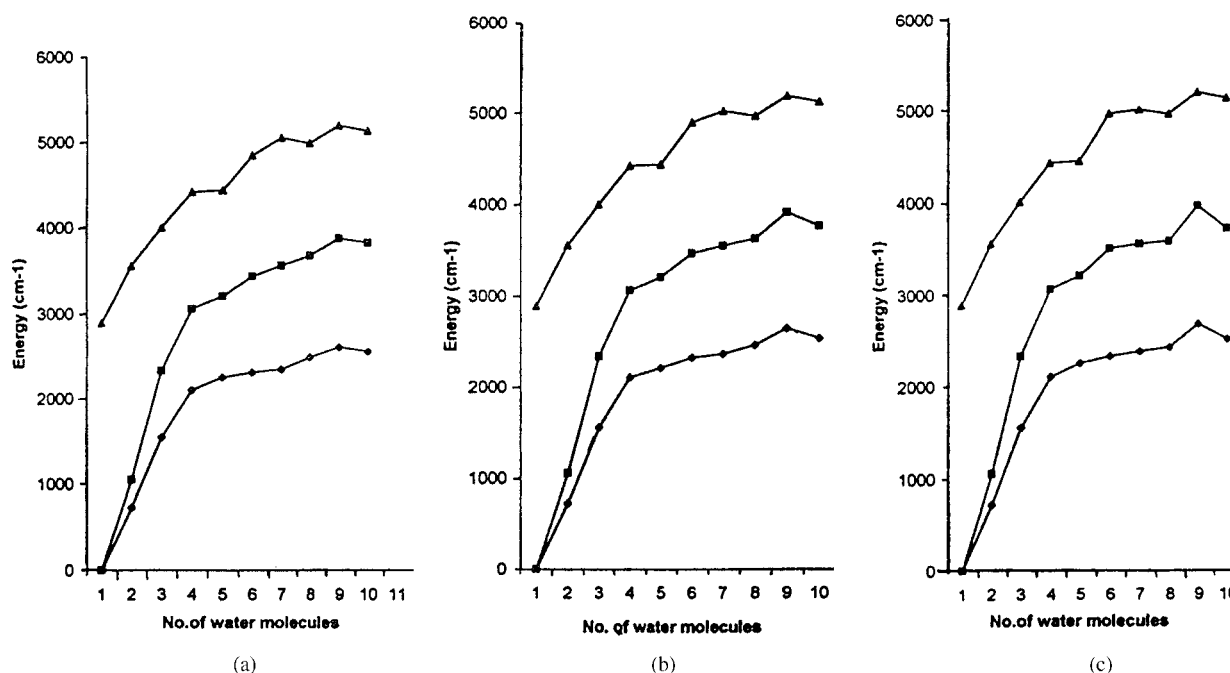




**FIGURE 3.** Structures of two nonamer clusters: (a) cage and (b) prism, and two decamer clusters: (c) cage and (d) prism, as projected in the plane of the paper. The hydrogen bond lengths (Å) are indicated.



**FIGURE 4.** Structures of 11-mer and 12-mer clusters (prism type): (a) 11-mer and (b) 12-mer, as projected in the plane of the paper. The hydrogen bond lengths (Å) are indicated.

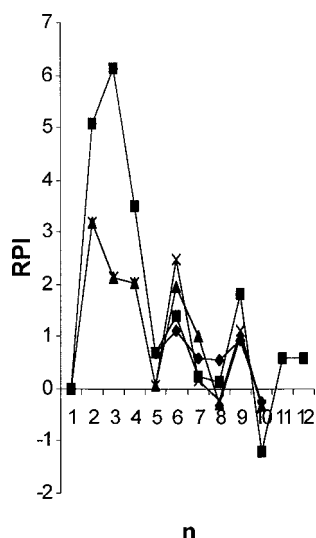


**FIGURE 5.** Variation of relative total energies ( $\text{cm}^{-1}$ ) including ZPE per water molecule with respect to the monomer in gas phase and bulk water obtained from RHF/6-311G\* and B3LYP/6-311G\* calculations with the number of water molecules in the different types of clusters upto decamer (Table II): (a) relative energies of cage-type clusters, (b) relative energies of prism-type clusters, and (c) average of the relative energies of the cage- and prism-type clusters. In (a), (b), and (c), the lowest curve corresponds to RHF/6-311G\* calculation, the middle curve corresponds to B3LYP/6-311G\* calculation in gas phase, and the uppermost curve corresponds to B3LYP/6-311G\* calculation in bulk water. The reference energies are specified in the footnote of Table II.

or one less number of water molecules would be only a few reciprocal centimeters ( $\text{cm}^{-1}$ ).

In view of the above discussion, we can define a relative population index (RPI) denoted by  $P$  for the different clusters in thermal equilibrium at room temperature as follows. Let  $\Delta E$  ( $\text{cm}^{-1}$ ) represent the differences between the relative total energies per water molecule of the different successive clusters from monomer to pentamer, the differences between the relative total energies per water molecule of the different hexamer clusters and that of the pentamer, and the differences between the relative total energies per water molecule of different successive clusters of prism type from hexamer to 12-mer (or cage type from hexamer to decamer). The quantity  $\Delta E/208$ , in view of the above discussion, would represent  $P$ . For gas phase and bulk water,  $P$  may be labeled by  $P_g$  and  $P_w$ , respectively. If the value of  $P$  is greater than 1, it would imply that out of the two clusters in question, the one of the higher order would have a larger population in thermal equilibrium than that of the lower order, and vice versa. Small positive or negative values of  $P$  would

indicate a lower population of the higher order cluster as compared to that of the next lower order. The values of  $P_g$  and  $P_w$  corresponding to the B3LYP relative total energies of Table II for the different clusters are given in the same table (in parentheses). The variation of RPI with the total number of water molecules ( $n$ ) in the different prism-type clusters from hexamer to 12-mer and cage-type clusters from hexamer to decamer is shown in Figure 6 both in gas phase and bulk water, where the variation of RPI in gas phase and bulk water with  $n$  for different clusters from monomer to pentamer is also shown. The following interesting information is revealed by the variation of RPI with  $n$  (Table II, Fig. 6): (i) in gas phase,  $P_g$  has peaks at  $n = 3, 6$ , and  $9$  and low positive ( $<1$ ) or negative value at  $n = 5$  and  $10$ . The values of  $P_g$  for  $n = 8$  are positive but appreciably smaller than those for  $n = 7$  and  $9$ . The value of  $P_g$  for the prism form of 11-mer is much larger (considering the signs) than the corresponding value for decamer while its value for the prism form of 12-mer is somewhat larger than that of the corresponding form of 11-mer. (ii) In bulk water, peaks



**FIGURE 6.** Variation of relative population index (RPI) with the number of water molecules ( $n$ ) in different clusters. From monomer to pentamer, each cluster has one form, while from hexamer to decamer each cluster has two forms, one cage and the other prism. Further for  $n = 11$  and 12 (in gas phase) each cluster has only one (prism) form. The symbols on the different curves are as follows: (■) gas phase for  $n = 1-5$  and gas phase prism form for  $n = 6-12$ , (◆) gas phase for  $n = 1-5$  (overlapping with ■) and gas phase cage form for  $n = 6-10$ , (×) bulk water for  $n = 1-5$  and bulk water prism form for  $n = 6-10$ , and (▲) bulk water for  $n = 1-5$  (overlapping with ×) and bulk water cage form for  $n = 6-10$ .

of  $P_w$  are seen at  $n = 6$  and  $n = 9$  while  $P_w$  decreases at each step in going from  $n = 2-5$ . Further,  $P_w$  has small positive or negative values at  $n = 5$  and 10. As  $P_w$  has a strong peak at  $n = 6$ , hexamers appear to be a major constituent of bulk water and on the same basis, it appears that nonamers would be the other higher sized clusters that would occur abundantly. Hexamer clusters have been suggested to occur dominantly in other studies also [48, 49].

The above results suggest that stabilities of the clusters of cage and prism type may be particularly favored for multiples of  $n = 3$  while those of the clusters corresponding to multiples of  $n = 5$  may be relatively disfavored. It should be noted that though the values of  $P_w$  in bulk water are quite high for each of dimer, trimer and tetramer (Table II, Fig. 6), these clusters would not exist in this medium near room temperature abundantly since the energy lowering is going from dimer to trimer, trimer to tetramer, and tetramer to hexamer (via pentamer or directly) is much more than  $208 \text{ cm}^{-1}$ . Thus hexam-

ers appear to be the lowest order stable clusters in bulk water. Though these results regarding the relatively favored and disfavored cluster sizes are interesting, they should be considered to be tentative, and more extensive and rigorous treatments would be needed to verify their validity. Further,  $P_g$  and  $P_w$  would be measures of relative abundance of water clusters in thermal equilibrium only, and it may be possible to stabilize clusters of a chosen specific size, particularly in gas phase, by creating appropriate conditions, e.g., cooling at a specific pressure. An obvious limitation of the above analysis is that it is based on RPI for prism- and cage-type clusters only. In certain studies, other types of cluster structures (e.g., symmetric octamers) have been investigated while in some cases, cagelike clusters were found [18, 19].

The possible significance of the above results relating to stabilities of the different clusters in bulk water needs to be examined. In bulk water, there would be a dynamic and extended network of hydrogen bonds. Thus hydrogen bonds would be forming and breaking and the lifetime of a hydrogen bond would be extremely short, of the order of picoseconds or even smaller. An important question in this context is whether there would be some preferred geometrical arrangements of water molecules at different instants of time where the water molecule would occur as an independently hydrogen bonded entity, or there would be clusters of water molecules that would occur as identifiable units. Since stable water clusters occur in gas phase [1-6] and definite arrangements of water molecules involving multiple hydrogen bonds occur in ice [50, 51], there is a reason to believe that clusters of water molecules would also occur in bulk water. Thus, if snapshots of the water structure could be taken at different instants of time, it might show distributions of clusters. It is obvious that occurrence of clusters would be governed by their relative stabilities, and a study of the present type can predict to a limited extent the clusters that would be likely to occur in such distributions. Even if the clusters would not be stable, knowledge about them would be useful from the point of view of understanding the overall behavior of water, say as a solvent or as a medium that can facilitate fast chemical reactions, e.g., tautomerism of biomolecules in the ground and excited states [43, 44].

As discussed earlier, when ZPE correction is applied, hexamer cage becomes more stable than prism, which agrees with experiment [1, 2]. We also applied (unscaled) thermal energy, thermal en-

**TABLE III**  
**Total energies per water molecule with different corrections for cage, prism, and cap hexamer clusters in gas phase taking  $-16690000\text{ cm}^{-1}$  as reference.<sup>a</sup>**

Sl. No.	Cluster	$E(\text{RHF})$	$E(\text{RHF}) + \text{ZPE}$	$E(\text{RHF}) + \text{Th. En.}$	$E(\text{RHF}) + \text{Th. Enth.}$	$E(\text{RHF}) + \text{Th. free energy}$
1	Cage	-6854	-785	-354	-320	-2140
2	Prism	-6860	-778	-350	-315	-2119
3	Cap	-6828	-771	-336	-302	-2136

<sup>a</sup> These results were obtained at the RHF level using 6-311++G\*\* basis set and MP2/6-311++G\*\* optimized geometries.

thalpy, and thermal free energy corrections corresponding to the normal temperature and pressure along with ZPE correction to the total RHF electronic energies obtained using the 6-311++G\*\* basis set and MP2/6-311++G\*\* optimized geometries of three hexamer clusters, i.e., cage, prism, and cap. The corrected energies per water molecule thus obtained for the three hexamer clusters are presented in Table III. We find that thermal free energy correction plays an important role since with this correction, the stabilities of the three clusters are found to be in the order cage > cap > prism while the order is found to be cage > prism > cap without this correction. Thus the cage form is most stable among the three hexamer clusters with or without the thermal free energy correction. However, consideration of both ZPE and thermal free energy corrections stabilizes the cage form over the prism form appreciably (Table III). If scaling is applied in relation to the thermal free energy correction [49], the energy differences would be somewhat modified, but the qualitative picture would remain unaffected. Thus it appears quite likely that the prism and cap hexamer clusters would also occur in a significant abundance each along with the cage form under thermal fluctuations, though not at as low temperatures as a few kelvins at which VRT spectra were studied [1].

**ROTATIONAL CONSTANTS AND AVERAGE O-O DISTANCES IN HEXAMERS**

The present calculated gas-phase rotational constants of the different hexamer clusters, those computed by other authors for these clusters using ab initio and quantum Monte Carlo methods as well as the experimental ones [1, 14] are presented in Table IV. A comparison of the rotational constants obtained in the different studies is quite informative as follows: (i) It is found that the identification

or nomenclature of the present calculated different hexamer clusters is in agreement with those reported in the literature since the rotational constants obtained in the present and the earlier work [1] agree reasonably well. (ii) The present calculated rotational constants  $B$  and  $C$  obtained using the MP2/6-311++G\*\* approach are in a very good agreement with the observed ones [1], the agreement being better than that obtained in the other theoretical studies [1] (Table IV). The agreement between our MP2/6-311++G\*\* calculated value of the rotational constant  $A$  and the corresponding experimental value is also good but somewhat inferior to that between the quantum Monte Carlo value of  $A$  and the experimental one [1]. (iii) The observed rotational constants agree satisfactorily only with those calculated for the cage hexamer cluster, showing that it is the cage structure that is observed experimentally. This point has also been discussed previously by other authors [1]. (iv) The rotational constants obtained in the present work at the RHF/6-311G\* level agree with those obtained at the MP2/6-311++G\*\* level for the cap and prism hexamer clusters satisfactorily, but the two sets of constants, particularly the two values of the constant  $A$ , obtained at the two levels of calculations for the cage structure are quite different. Thus when the computational accuracy is enhanced from RHF/6-311G\* level to MP2/6-311++G\*\* level, it is the rotational constant  $A$  of the cage structure that is affected most.

The average O-O distances in the cage and cyclic hexamers obtained using the RHF/6-311G\* approach in the present work were found to be 2.848 and 2.764 Å, respectively. The values of these distances in cage and cyclic hexamers were found experimentally to be 2.85 Å (in liquid water) and 2.76 Å (in ice), respectively [50–52], and the same values were also found in the earlier theoretical

**TABLE IV**  
**Calculated and experimentally observed rotational constants (MHz) of different forms of water hexamer clusters.**

Sl. No.	Molecule/ cluster	Rot. const.	Present results		Ref. [1]		Expt. value <sup>a</sup>
			RHF/6-311G*	MP2/6-311++G**	Ab initio	DQMC <sup>b</sup>	
1	Cyclic	A	1210		1269	1211	
		B	1210		1250	1211	
		C	620		636	598	
2	Book	A	1803		1984	1798	
		B	1097		1173	1078	
		C	810		866	802	
3	Boat	A	1850		2015	1733	
		B	1049		1067	1125	
		C	969		999	1054	
4	Ellipsoid	A	2323				
		B	975				
		C	805				
5	Cap	A	1640	1699			
		B	1326	1342			
		C	1092	1118			
6	Prism	A	1674	1707	1752	1607	
		B	1367	1388	1504	1355	
		C	1332	1350	1421	1256	
7	Cage	A	1650	2264	2345	2136	2163.61
		B	1049	1134	1195	1096	1131.20
		C	966	1064	1145	1043	1068.80

<sup>a</sup> From Ref. [1].

<sup>b</sup> DQMC stands for diffusion quantum Monte Carlo.

study [1]. Thus there is a close agreement between the present calculated O–O distances and those obtained earlier experimentally or theoretically [1, 50–52]. In the prism, cap, book, boat, and ellipsoid hexamers, the average O–O distances were found to be 2.870, 2.850, 2.817, 2.844, and 2.850 Å, respectively. Thus the average O–O distance has almost the same value in the cage, cap, and ellipsoid hexamers.

### DIPOLE MOMENT

The present calculated dipole moments of the different clusters along with those obtained by other authors are presented in Table V. It is noted that the RHF/6-311G\* and B3LYP/6-311G\* values of dipole moments of the clusters in gas phase are very similar. Dipole moments were also obtained for four cases, i.e., monomer, by cage prism and cap hexamers, using MP2/6-311++G\*\* calculations. It is found that the MP2 values of dipole moments are smaller than the RHF and B3LYP val-

ues for three cases, while for the fourth case, i.e., for the cage hexamer, the reverse is true. Thus we find that the MP2 correlation correction affects the calculated results for the cage hexamer differently than for the other cases. The agreement between the present and earlier [2] calculated dipole moment values is usually satisfactory. The experimental value of the dipole moment of water monomer is 1.855 debyes [2, 53]. Our calculated value using the B3LYP/6-311++G\*\* method and the MP2/6-311++G\*\* optimized geometry (2.18 debyes) is somewhat larger than this value. We find that in going from gas phase to bulk water, the dipole moments of the monomer as well as those of all the clusters are increased appreciably. This is broadly in agreement with the results obtained in other studies where the dipole moment of a water molecule is found to be appreciably enhanced with respect to the gas-phase value, lying between 2.4 and 2.6 debyes [54–56].

**TABLE V**

**Dipole moments (debye) of different water clusters obtained using RHF and B3LYP methods and 6-311G\* basis set, unless otherwise specified.**

S1. No.	Molecule/ cluster	RHF		B3LYP	
		Gas <sup>a</sup>		Gas	Bulk water
1	(H <sub>2</sub> O) <sub>1</sub>	2.31	[1.868]	2.23	2.54
		(2.26) <sup>b</sup>		(2.18) <sup>c</sup>	(2.42) <sup>c</sup>
2	(H <sub>2</sub> O) <sub>2</sub>	3.35	[2.683]	3.36	3.65
3	(H <sub>2</sub> O) <sub>3</sub>	1.21	[1.071]	1.17	1.33
4	(H <sub>2</sub> O) <sub>4</sub>	0.00	[0.000]	0.00	0.00
5	(H <sub>2</sub> O) <sub>5</sub>	0.77	[0.927]	0.74	0.89
6	(H <sub>2</sub> O) <sub>6</sub>	0.00	[0.000]	0.00	0.00
	cyclic				
7	(H <sub>2</sub> O) <sub>6</sub>	1.69	[1.904]	1.75	1.96
	cage	(2.18) <sup>b</sup>		(2.12) <sup>c</sup>	(2.47) <sup>c</sup>
8	(H <sub>2</sub> O) <sub>6</sub>	3.13	[2.701]	3.10	3.61
	prism	(2.91) <sup>b</sup>		(2.81) <sup>c</sup>	(3.34) <sup>c</sup>
9	(H <sub>2</sub> O) <sub>6</sub>	2.91		2.89	3.27
	book				
10	(H <sub>2</sub> O) <sub>6</sub>	0.86		0.83	1.26
	boat				
11	(H <sub>2</sub> O) <sub>6</sub>	4.30		4.25	4.75
	cap	(4.13) <sup>b</sup>		(3.95) <sup>c</sup>	(4.50) <sup>c</sup>
12	(H <sub>2</sub> O) <sub>6</sub>	0.00		0.00	0.00
	ellipsoid				
13	(H <sub>2</sub> O) <sub>7</sub>	1.41		1.39	1.62
	cage				
14	(H <sub>2</sub> O) <sub>7</sub>	5.69		5.65	6.35
	prism				
15	(H <sub>2</sub> O) <sub>8</sub>	2.39		2.35	2.70
	cage				
16	(H <sub>2</sub> O) <sub>8</sub>	6.64		6.59	7.46
	prism				
17	(H <sub>2</sub> O) <sub>9</sub>	2.54		2.56	3.00
	cage				
18	(H <sub>2</sub> O) <sub>9</sub>	2.66		2.59	2.95
	prism				
19	(H <sub>2</sub> O) <sub>10</sub>	2.74		2.75	3.31
	cage				
20	(H <sub>2</sub> O) <sub>10</sub>	3.48		3.47	4.05
	prism				
21	(H <sub>2</sub> O) <sub>11</sub>	6.63		6.63	NA <sup>d</sup>
	prism				
22	(H <sub>2</sub> O) <sub>12</sub>	6.34		6.30	7.46
	prism				

<sup>a</sup> Theoretical values from Ref. [2] obtained using MP2/aug-cc-VDZ calculations are given in brackets.

<sup>b</sup> Geometry optimized and dipole moment calculated at MP2/6-311++G\*\* level.

<sup>c</sup> Calculated using MP2/6-311++G\*\* optimized geometry and B3LYP/6-311++G\*\* method.

<sup>d</sup> Not available.



## Conclusions

We arrive at the following conclusions from this study:

1. The cage form of water hexamer cluster is found to be most stable in gas phase among all the hexamer clusters. This is in agreement with the earlier theoretical and experimental results and shows reliability of the computational approach adopted in the present work.
2. The prism and cap forms of hexamer clusters appear to be stable enough to occur under thermal fluctuations along with the cage form in gas phase. However, the prism and cap forms of hexamer clusters are not expected to be formed at the low temperatures achieved in supersonic jet experiments.
3. The relative total energy per water molecule for any cluster is appreciably increased in going from gas phase to bulk water, and the difference between the two relative total energies per water molecule increases appreciably in going from smaller to larger clusters.
4. Values of a newly defined relative population index (RPI) in terms of successive differences between relative total energies per water molecule suggest that in gas phase water trimers, hexamers, and nonamers (and in bulk water hexamers and nonamers) would be preferentially stabilized while formation of pentamers and decamers would be relatively much less favored.

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