

# Ab initio investigation of the topology and properties of three-dimensional clusters of water (H<sub>2</sub>O)<sub>n</sub>

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## Abstract

Quantum mechanical studies were carried out in order to understand and describe the nature and strength of the hydrogen bond topology in three dimensional water cluster systems (H<sub>2</sub>O)<sub>n</sub>, in the size range 6–20 molecules. Optimal structures and vibrational frequencies of cage like water clusters are computed at the Hartree–Fock (HF) and the electronic density functional theory (DFT) level of theory with a detailed data analysis. Theoretical results are compared to experimental data when available. The general tendency is a decrease of the global minimum energy as the cluster size increases. The nearest neighbour separation between oxygen atoms decreases exponentially when the cluster size increases. The present work suggests that DFT results are in a good agreement with the corresponding HF data, however slight differences remain with regard to values of the nearest neighbour separation between oxygen atoms. The Morokuma's decomposition of the total interaction energy performed on two and three-dimensional clusters lead to a better understanding of the cluster formation with a strong polarization energy component.

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**Keywords:** Water clusters; Structure; Interactions; Quantum mechanical calculations

## 1. Introduction

Because of its importance in chemistry and biology, water and aqueous mixtures have been the subject of intense experimental and theoretical studies over the past few years, focusing efforts on elucidation of energetic considerations and structures of small water clusters (H<sub>2</sub>O)<sub>n</sub> ( $3 \leq n \leq 8$ ) (Choi, Pak, & Kim, 2006; Day, Kirschner, & Shields, 2005; Xantheas & Dunning, 1993), and concentrating on calculations of the binding energies for arranged symmetrical molecules which affect the stability and the structure of the cluster. The correlation of various properties of water molecule aggregates with the cluster size ( $n$ ) has been investigated using intensive ab initio calculations

(Myoung Lee, Suh, Yong Lee, Tarrakeshwar, & Kim, 2000). Most investigations have focused on binding energies, electronic, thermodynamics, and structural properties, either from different experimental techniques (Bjornelholm, Federman, Kakar, & Moller, 1999; Gross, Sharpe, Blake, Vaida, & Brault, 1999; Kim, Majumdar, Myoung Lee, & Kim, 1999; Rodriguez, Lavia, Marceca, & Estrin, 1999; Uchino & Yoko, 1999; Wang & Gunn, 1999; Geoffrey & Henrik, 1999) or theoretical approaches (Allen & Tildesley, 1989; Freeman & Doll, 1996; Millet, Moszynski, Wormer, & Van Der Avoird, 1999; Morokuma & Pedersen, 1968; Press, Teukolsky, Vetterling, & Flannery, 1992).

The contribution of the interaction energy of cyclic water clusters (H<sub>2</sub>O)<sub>n</sub> at their lower nuclear energy configuration has been estimated (Xantheas, 1994a, 1994b) showing the importance and effects of the three-body terms while building small water clusters. Electronic properties

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of water are poorly described at the HF level of theory (Xantheas, 1994a, 1994b; Dauchez, Peticolas, Debelle, & Alix, 2003). An electron correlation was suggested in order to have a better description of the structural and energetic binding of water cluster, however this alternative is very expensive and time consuming. In order to overcome this problem, the density functional theory (DFT) (Ziegler, 1991) is introduced and results for small water clusters were accurate enough when compared to those obtained at the MP2 (Møller–Plesset correlation energy correction, truncated at second-order) level of theory (Knochenmuss & Leutwyler, 1992; Myoung Lee et al., 2000; Ziegler, 1991). Ab initio studies indicate that the  $R_{O-O}$  distance decreases exponentially with an increase of the cluster size. An experimental  $R_{O-O}$  distance fit of the dimer and cyclic two-dimensional clusters yields to an expression of the form  $R_{O-O}$  (Å) =  $2.748 + 1.3e^{-(0.8644n)}$  (Liu, Brown, & Saykally, 1997).

Experiments have provided the signature of small water clusters including a bending frequency analysis. The vibration-rotation tunnelling (VRT) spectroscopy and the infrared spectroscopy (IR) developed by Saykally and co-workers, (Pugliano & Saykally, 1992), with quantum, mechanical methods were used to solve the enigma of water clusters. Several studies as it will appear in the following work, suggest that large clusters are rather in three-dimensional structures (Kim, Dupuis, Lie, & Clementi, 1986; Tsai & Jordan, 1991) starting with the water hexamer. Experimental investigations of water clusters are a complicated task, and the use of the theoretical approaches appears to be the preferential route to improve our understanding of the hydrogen bond arrangement. Nevertheless, advances on laser spectroscopy facilitate these kinds of investigations.

The optimized structures and vibrational frequencies of water monomer to the decamer were obtained at various levels of theory using different basis sets and significant dipole moments ( $\sim 2.0$  D) are observed in the monomer, hexamer, and nonamer by Myoung Lee et al. (2000). The global minimum of the water dimer is well understood, as it is well known that the global minimum of small water clusters  $(H_2O)_n$ , with  $n = 3-5$ , leads to cyclic structures. One can observe that frequencies calculated at the Hartree–Fock level are higher than those obtained from experimental studies, whereas frequencies calculated by the DFT/B3LYP method are lower than experimental frequencies.

Water–water interaction are of major importance both in the experimental front as well as for calculation purposes (Ferguson, 1995; Xantheas, 1994a, 1994b; Kim, Mhin, Choi, & Lee, 1992; Low & Kjaergaard, 1999). The most simple water–water system is the water dimer, its geometry, predicted by several calculations of molecular orbital theory (Xantheas, 1994a, 1994b; Ziegler, 1991; Knochenmuss & Leutwyler, 1992) was perfectly confirmed by experimental studies (Liu et al., 1997). Optimization of the water dimer structure obtained by ab initio calculations according to the two methods, Hartree–Fock and the electronic

density functional theory DFT, are compared to experimental values when available as shown in Table 1. The water hexamer case is more ambiguous since its preferential structure between the cyclic shape and the three-dimensional structure is still widely debated (Liu et al., 1996).

The topology of the hydrogen bond network of water clusters undergoes significant changes from simple cyclic structure to more complex three-dimensional systems. Several studies suggest that large clusters are rather in the three-dimensional structures (Kim et al., 1986; Tsai & Jordan, 1991) starting with the hexamer. Three-dimensional clusters may exist in different conformations of different symmetries (Kuo, Coe, Singer, Band, & Ojamäe, 2001, 2003; McDonald, Ojamäe, & Singer, 1998; Shi, Kais, & Francisco, 2005) and the hydrogen bond topology strongly affects the structure and chemistry of the cluster (Kuo, Ciobanu, Ojamäe, Shavitt, & Singer, 2003). The hypothesis of different water configurations as obtained from ab initio quantum calculations for a tetrahedral cluster was used in recent molecular dynamics calculations (Amrani, Sellou, Belhakem, Krallafa, & Bormann, 2003). The model used at low temperatures led to results in good agreement with experimental data. It is of great interest to understand the intermolecular interactions to develop state of the art molecular mechanics force fields for liquid mixtures and biomolecular simulations and modelling. Such route will improve our knowledge of the many body polarization terms into the potential energy function and will yield to faster computationally force fields.



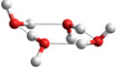
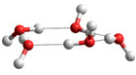
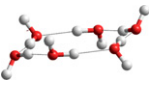
In this work accumulations of water molecules  $(H_2O)_n$ , ( $3 \leq n \leq 8$ ) were studied by ab initio computational method at the Hartree–Fock (HF) level of theory and the method of the electronic density functional theory (DFT) with a 6-31G(d) basis set, in order to seek for global minima in the potential energy surface.

On account of the size of the clusters, the chosen method is reliable enough to ensure acceptable calculated frequencies at low computational cost. The frequencies obtained for small clusters ( $n = 2, 3$ ) compare favourably well with experimental data. Structural properties and spectral trends are reported for most probable structures through the calculated force constant of the hydrogen bond, and the mean distance between oxygen atoms within a cluster is worked out. Moreover, an analysis of the disposition of water molecules within a cluster is performed and symmetries are reported. The decomposition of the total interaction energy into its specific components is of major importance in our understanding of the intermolecular interactions.

## 2. Methods and calculations

All calculations were performed at the Hartree–Fock and the density functional theory (DFT) level, with the 6-31G(d) basis set (Frisch et al., 2004 (Gaussian 98.)). For the choice of the functionals, we used the three parameter functional of Becke (1993) and the correlation functional

Table 1  
Optimal configurations of cyclic water clusters (H<sub>2</sub>O)<sub>n</sub>, n = 2–6, adjacent bond lengths R<sub>o–o</sub> (Å), and hydrogen bond frequencies (cm<sup>-1</sup>)

Cluster types symmetry	Donor–acceptor configuration	Number of conformations symmetry	R <sub>o–o</sub> (Å)		Hydrogen bond frequency (cm <sup>-1</sup> )		
			HF/ 6-31G(d)	DFT/B3LYP 6-31G(d)	HF/ 631G(d)	DFT/B3LYP 6-31G(d)	Experiment
	1(D–A)	01 C <sub>s</sub>	2.971	2.860	3585	3514	3718 <sup>a</sup> 3550 <sup>a</sup> 1574 <sup>b</sup>
	3(D–A)	06 06 <sup>a</sup> C <sub>1</sub>	2.858	2.742	3521	3237	3517 <sup>b</sup> 3516 <sup>c</sup> 3525 <sup>b</sup> 3612 <sup>b</sup>
	4(D–A)	05 S <sub>4</sub> 02 <sup>a</sup> C <sub>i</sub> C <sub>4</sub> C <sub>4h</sub>	2.826	2.703	3443 3496(2) 3521	3050 3192(2) 3248	–
	5(D–A)	01 C <sub>1</sub>	2.815 2.813 2.818 2.819 2.831	2.700 2.693 2.689 2.689 2.694	3430 3474 3478 3507 3513	3021 3145 3150 3355 3225 3229	–
	6(D–A)	01 S <sub>6</sub>	2.813	2.690	3430 3469(2) 3502(2) 3515	3152 3030 3134(2) 3215(2) 3241	–

<sup>a</sup> Fredin, L., Nelander, B., & Ribbergard, G. (1977). *Journal of Chemical Physics* 66, p. 4065.; Nelander, B. (1978). *Journal of Chemical Physics* 69, p. 3870.

<sup>b</sup> Bentwood, R. M., Barnes, A. J., & Orville-Thomas, W. J. (1980). *Journal of Molecular Spectroscopy* 84, p. 391.

<sup>c</sup> Engdahl, A., & Nelander, B. (1987). *Journal of Chemical Physics* 86, p. 4831.

of Lee, Yang and Parr (Lee, Yang, & Parr, 1998). Harmonic vibrational frequencies were computed in order to verify whether the located stationary point is a minimum or a saddle point on the potential energy surface. Initially, all possible structures are fully optimized taking into account the positions of hydrogen atoms within the cluster. Water aggregates are built on a step by step basis starting from the dimer (n = 2) and up to the dodecahedron (n = 20). The total interaction energy for a complex AB is defined as:

$$\Delta E_{\text{int}} = E_{(\psi_{\text{AB}})} - (E_{(\psi_{\text{A}})} + E_{(\psi_{\text{B}})}) + \Delta E_{(\text{BSSE})}$$

where (ψ<sub>AB</sub>) is the optimized wave function of the complex AB, (ψ<sub>A</sub>) and (ψ<sub>B</sub>) are respectively the wave functions of monomers A and B, ΔE<sub>(BSSE)</sub> is the correction term in conjunction with the basis set superposition error and obtained using the Boys and Bernardi counterpoise method (Boys & Bernardi, 1970). The Kitaura–Morokuma scheme (Kitaura, K. and Morokuma, K., 1976, 1981) is used for the decomposition of the total intermolecular interaction energy and can be expressed in terms of four components:

$$\Delta E_{\text{int}} = \Delta E_{\text{electrostatic}} + \Delta E_{\text{exchange repulsion}} + \Delta E_{\text{polarization}} + \Delta E_{\text{charge transfer}}$$

### 3. Results and discussion

From sets of possible structures most investigations led to the conclusion that water clusters can be classified into two categories, two-dimensional rings or cyclic clusters for n ≤ 6 (Table 1) and three-dimensional cages when n ≥ 6 (Tables 2–4). The case of the hexamer is still widely debated with a controversy between the cyclic and the cage like architecture most likely to occur (Kim et al., 1986; Millet et al., 1999; Tsai & Jordan, 1991). Our calculations at the Hartree–Fock level give a preferential form to the cage like structure for the hexamer in agreement with the cage bound by 8 hydrogen jumps suggested by (Liu et al., 1996; Liu, Cruzan, & Saykally, 1996) as shown in Table 2. Our results ensure that the cage structure yields to energy slightly lower (2.1 kcal mol<sup>-1</sup>) than the cyclic structure whatever the level of theory is used. When extended to larger clusters the calculations show that data obtained at the Hartree–Fock level are in good agreement with experiment as shown in Fig. 1.

Arrangement of water molecules within a cluster seems to obey a number of rules as shown in Tables 1–4. In the case of two-dimensional clusters, the arrangement of water molecules within a cluster is of type D–A (i.e. 1 Donor

Table 2  
Optimal configurations of cage water clusters (H<sub>2</sub>O)<sub>n</sub>, n = 6–12, bond angle, oxygen charge, and dipole moment (Debye)

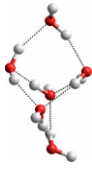
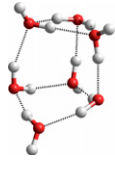
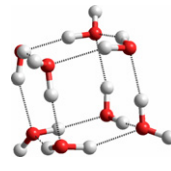
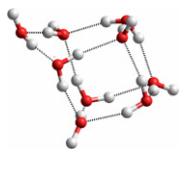

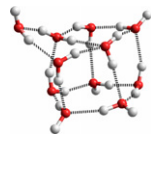
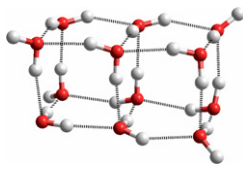
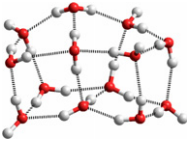
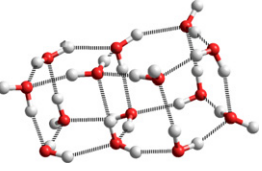
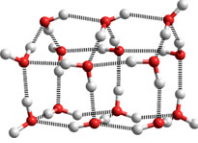
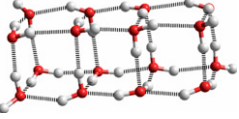
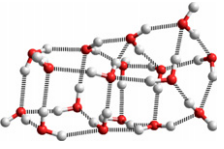
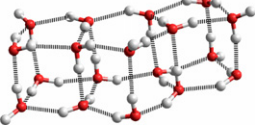
Cluster types symmetry	Donor–acceptor configuration	Number of conformations symmetry	$\phi_{[H-O-H]}$	$q_o$	Dipole moment (D)
	2(D–A)	01	106.0(D–A)	–0.9443	2.184
	2(D–AA)	Ring (S <sub>6</sub> )	106.7(D–AA)	–0.9616	
	2(DD–A)	Book (C <sub>1</sub> )	104.8(DD–A)	–0.9748	
		Cage (C <sub>1</sub> )		–0.9671	
		Prism (C <sub>1</sub> )		–0.9363	
				–0.9536	
	3(D–A)	12	105.4(D–A)	–0.9500	1.395
	2(D–AA)	12 <sup>*</sup> C <sub>1</sub>	106.4(D–AA)	–0.9767	
	2(DD–A)		105.1(DD–A)	–0.9874	
				–0.9738	
				–0.9443	
				–0.9482	
			–0.9568		
	4(D–AA)	02	106.6(D–AA)	–0.9632(4)	0.00
	4(DD–A)	01 <sup>*</sup> S <sub>4</sub>	105.2(DD–A)	–0.9793(4)	
		01 <sup>*</sup> D <sub>2d</sub>			
	1(D–A)	02	105.9(D–A)	–0.9605	1.710
	4(D–AA)	02 <sup>*</sup> C <sub>1</sub>	106.4(D–AA)	–0.9616	
	4(DD–A)		105.1(DD–A)	–0.9885	
				–0.9855	
				–0.9629	
				–0.9638	
				–0.9794	
				–0.963	
			–0.9852		
	5(D–AA)	01	105.0(DD–A)	–0.9512	2.683
	5(DD–A)	01 <sup>*</sup> C <sub>1</sub>	106.3(D–AA)	–0.9699	
				–0.9917	
				–0.9638	
				–0.9872	
				–0.9642	
				–0.9877	
				–0.9674	
				–0.9910	
				–0.9757	
			–0.9527		
	1(D–A)	02	106.2(D–A)	–1.0068	3.760
	4(D–AA)	02 <sup>*</sup> C <sub>1</sub>	106.4(D–AA)	–0.9695	
	2(DD–AA)		105.2(DD–AA)	–0.9959	
	4(A–DD)		105.0(DD–A)	–0.9724	
				–0.9527	
				–0.9809	
				–0.9679	
				–0.9958	
			–0.9609		
	4(D–AA)	01	106.6(D–AA)	–0.9642(4)	0.000
	4(DD–AA)	01 <sup>*</sup> C <sub>2</sub>	105.4(DD–AA)	–0.9771(4)	
	4(DD–A)		105.2(DD–A)	–1.0011(4)	

Table 3  
Optimal configurations of cage water clusters (H<sub>2</sub>O)<sub>n</sub>, n = 13–18, bond angle, oxygen charge, and dipole moment (Debye)

Cluster types symmetry	Donor–acceptor configuration	Number of conformations symmetry	$\phi_{[H-O-H]}$	$q_o$	Dipole moment (D)	
	5(D-AA)	01	106.3(D-AA)	-0.9768	2.278	
	3(DD-AA)	01* C <sub>1</sub>	105.8(DD-AA)	-0.9628		
	5(DD-A)		105.0(DD-A)	-0.9885		
						-1.0129
						-0.9596
						-1.0082
						-0.9666
						-0.9725
						-0.9791
						-0.9648
				-0.9965		
			-0.9651			
			-0.9852			
	5(D-AA)	01	106.4(D-AA)	-0.9636	2.615	
	4(DD-AA)	01* C <sub>1</sub>	105.2(DD-AA)	-0.9834		
	5(DD-A)		105.2(DD-A)	-1.0041		
						-1.0122
						-0.9767
						-1.0104
						-1.0118
						-0.9518
						-0.9659
						-0.9894
						-0.9669
						-0.9793
						-0.9634
				-0.9762		
	5(D-AA)	01	106.2(D-AA)	-0.9664(5)	4.538	
	5(DD-AA)	01* C <sub>1</sub>	105.2(DD-AA)	-1.0054(5)		
	5(DD-A)		105.3(DD-A)	-0.9708(5)		
						-0.9844(5)
	4(D-AA)	01	107.0(D-AA)	-1.0212(4)	0.000	
	8(DD-AA)	01* C <sub>1</sub>	105.8(DD-AA)	-1.0163(4)		
	4(DD-A)		105.7(DD-A)	-0.9724(4)		
						-0.9920(4)
	5(D-AA)	01	106.4(D-AA )	-1.0072(7)	2.710	
	7(DD-AA)	01* C <sub>1</sub>	105.7(DD-AA)	-0.9672(5)		
	5(DD-A)		105.2(DD-A)	-0.9838(5)		
	5(D-AA)	01	106.5(D-AA )	-1.0062(8)	2.508	
	8(DD-AA)	01* C <sub>1</sub>	105.2(DD-AA)	-0.9774(5)		
	5(DD-A)		105.3(DD-A)	-0.9642(5)		

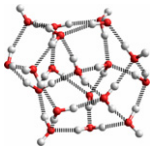
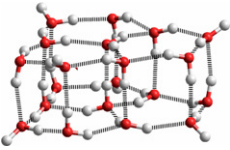
molecule “D”–1 Acceptor molecule “A”), whereas for three-dimensional clusters, this arrangement is either DD–A (2 Donor–1 Acceptor) or D–AA or DD–AA. On the basis of the calculated frequencies of the symmetric hydrogen bond stretching mode as reported in Fig. 2, sev-

eral comments could be made. The frequencies can be divided into four groups of hydrogen bond stretching modes. Frequencies of the symmetric mode of the hydrogen bond in the low range spectrum ( $\bar{\nu} < 3866 \text{ cm}^{-1}$ ) corresponding to DD–A group, those in medium range of the



Table 4

Optimal configurations of cage water clusters  $(\text{H}_2\text{O})_n$ ,  $n = 19\text{--}20$ , bond angle, oxygen charge, and dipole moment (Debye)

Cluster types symmetry	Donor–acceptor configuration	Number of conformations symmetry	$\phi_{[\text{H-O-H}]}$	$q_{\text{O}}$	Dipole moment ( $D$ )
	8(D-AA)	01	106.5(D-AA)	-1.0024 (8)	3.865
	5(DD-AA)	01* $C_1$	105.2(DD-AA)	-0.9664(5)	
	6(DD-A)		105.3(DD-A)	-0.9824(6)	
	6(D-AA)	01	106.1(D-AA)	-1.0075(8)	0.271
	8(DD-AA)	01* $C_1$	105.5(DD-AA)	-0.9655(6)	
	6(DD-A)		105.3(DD-A)	-0.9856(6)	

spectrum ( $\bar{\nu} > 3720 \text{ cm}^{-1}$ ) of the DD-AA group, followed by the vibrational mode of the D-AA group.

In the highest frequency region, we find the frequencies of the D-A group of molecules as shown in Fig. 2. According to Table 2, we notice that the cage like structure of water hexamer contains various types of water monomers, two water molecules (DD-A), two molecules (D-AA), and two molecules (D-A). Therefore, the hydrogen bond stretching modes can be classified according to the nature of the monomer. This spectrum is a good indicator of the force constant of the hydrogen bond network, which increases according to the nature of the water molecules involved in the cluster, and is not sensitive to the size of the cluster as shown in Fig. 3. This result lets us assume that changes and rearrangement of molecules within a cluster involve the contribution of the DD-A type of molecules, i.e. in cage structures with the relatively weak H-bond structures. These results on the force constants calculated by the two methods HF and DFT (Fig. 3a and b) show that among the four types of hydrogen bonds, the strongest result from D-A (donor–acceptor) molecular arrangement. Values of the force constant decrease with an increase in the size of the cyclic water clusters when  $n \leq 6$ , and undergo no significant changes in the case of three-dimensional ones. Hydrogen bonds for water molecules which are in D-AA, DD-AA molecular arrangement, are less stronger, but are, nevertheless in a medium range, followed by weak bonds which are DD-A. These three interconnection types vary little with the increase in the size of the three-dimensional water clusters as shown in Fig. 3.

Several observations might be underlined from these results. The topology of the hydrogen bond in water clusters in the condensed phase is favourable to three-dimensional clusters strongly bound by their hydrogen bond network. The process of three-dimensional clusters growth is favourable to a nanostructure form of water molecules obtained from the stacking and aggregate of two-dimensional clusters. Recent calculations (Kuo et al., 2003) have

shown that several isomers for the dodecahedron cluster  $(\text{H}_2\text{O})_{20}$  are possible and the authors suggested that nearest neighbours dangling hydrogen's are strongly disfavoured. Our calculations for the most stable dodecahedron isomer (Kuo et al., 2003) and the cluster  $(\text{H}_2\text{O})_{20}$  resulting from the stacking of pentamers lead to an energy difference of  $14.36 \text{ kcal mol}^{-1}$  in favour of the later, with 6 dangling hydrogen's.

The mean charge on oxygen atoms increases with the size of the cluster Tables 1–4. This is consistent with the Morokuma's analysis (Morokuma, 1977) of the total interaction energy  $\Delta E_{\text{int}}$  reported in Fig. 4. Indeed, we observe that the main component is the electrostatic energy  $\Delta E_{\text{electrostatic}}$  and charge transfer energy  $\Delta E_{\text{charge transfer}}$  responsible in the stability of large clusters. In both cases, these components decrease with an increase of the cluster size. The calculated correction term  $\Delta E_{(\text{BSSE})}$  is of the order of magnitude of the polarization energy  $|\Delta E_{\text{polarization}}|$  (Fig. 4), this term increases with the size of the cluster.

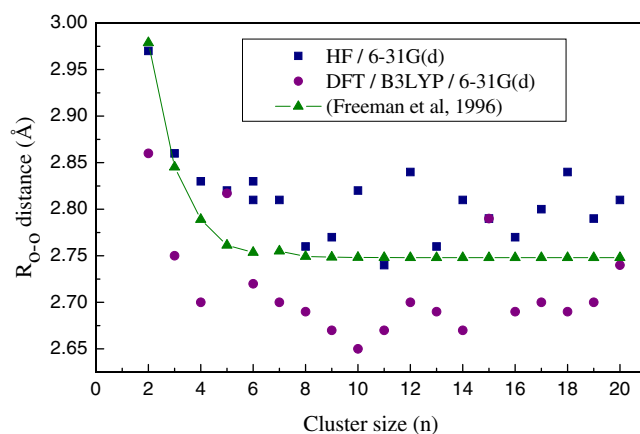


Fig. 1. Mean  $R_{\text{o-o}}$  distance between adjacent oxygen atoms vs. the cluster size ( $n$ ).

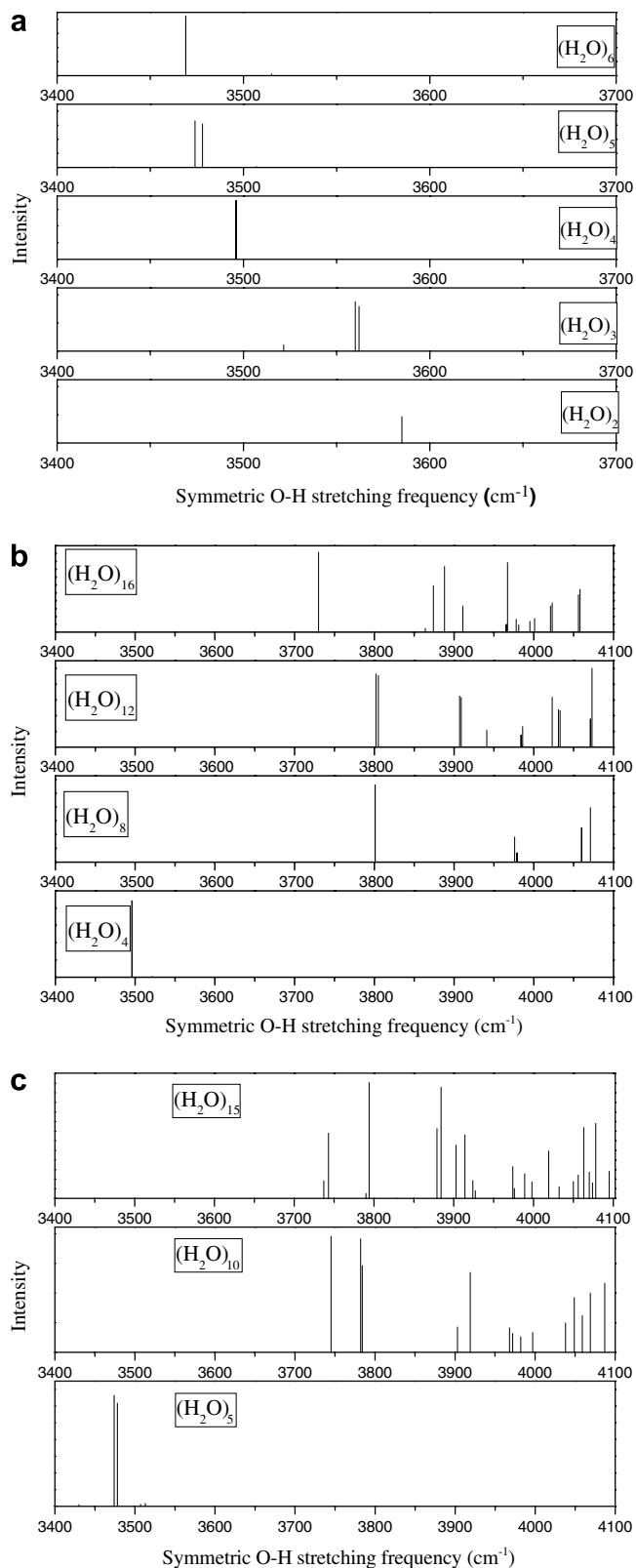


Fig. 2. Uncorrected calculated spectra of the hydrogen symmetric stretching mode of water clusters (a) cyclic water clusters  $(\text{H}_2\text{O})_n$ ,  $(n \leq 6)$ , (b) cubic water clusters  $(\text{H}_2\text{O})_n$ ,  $n = 4, 8, 12,$  and  $16$ , (c) cage water clusters  $(\text{H}_2\text{O})_n$ ,  $n = 5, 10,$  and  $15$ , (d) cage water clusters  $(\text{H}_2\text{O})_n$ ,  $n = 6, 7, 9, 11, 13, 14, 17, 18, 19,$  and  $20$ .

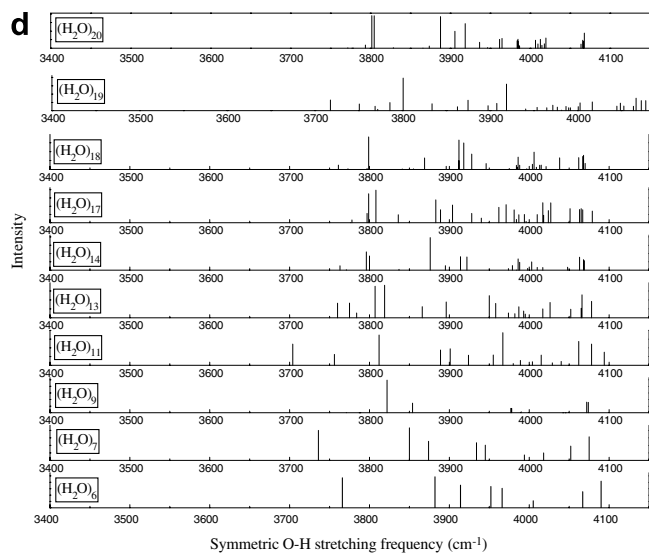


Fig. 2 (continued)

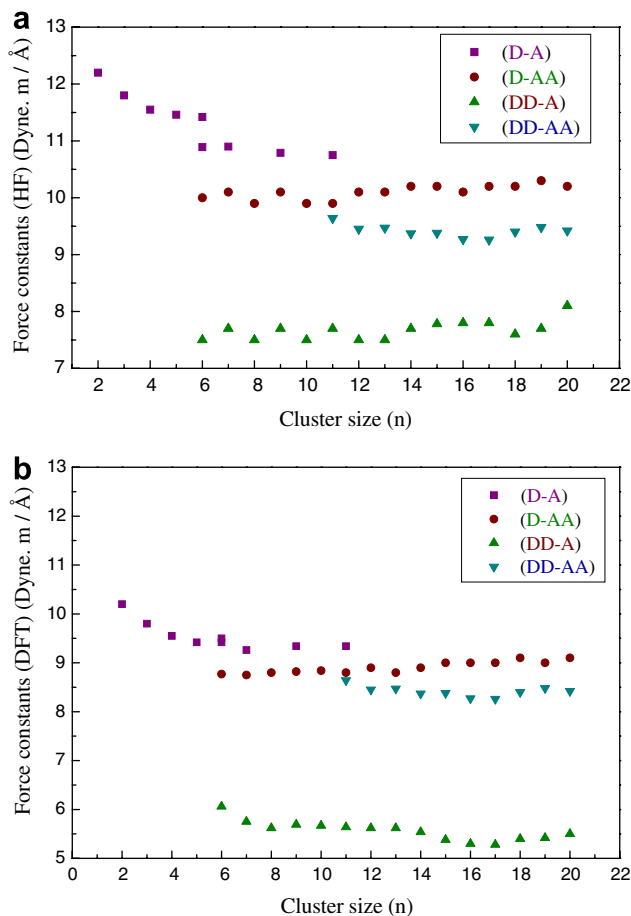


Fig. 3. Calculated force constant according to the molecular type vs. the cluster size ( $n$ ), (a) is results obtained from HF calculations and (b) data from DFT calculations.

In liquid water, the dipole moment of a single water molecule is more difficult to determine, recently (Silvestrelli & Parrinello, 1999) find that the average dipole moment of water molecule in liquid should be about 3.0 D. The studies

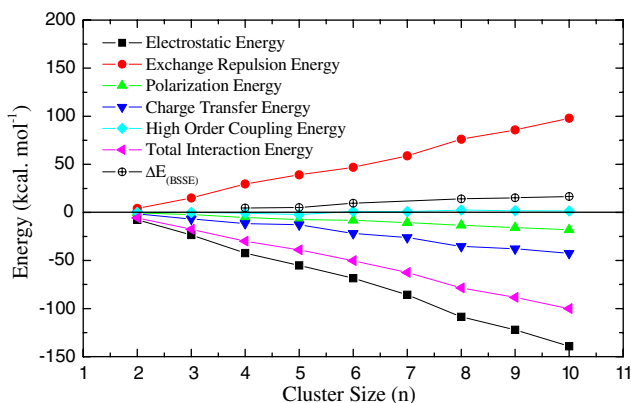


Fig. 4. Morokuma's analysis of the total interaction energy.

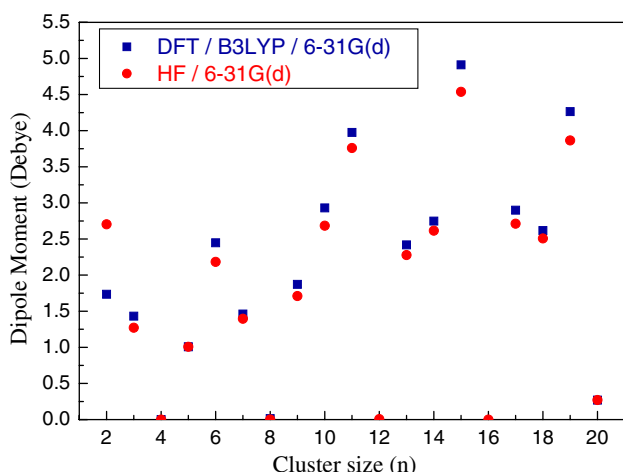


Fig. 5. Variation of dipole moment with the cluster size.

of water clusters by (Gregory, Clary, Liu, Brown, & Saykally, 1997) show that the average dipole moment of a water molecule increases from 2.1 to 2.7 D as the size of the cluster increases from the dimer up to the hexamer. Results obtained from the present calculations over the dipole moment of different clusters are illustrated in Fig. 5. We can notice that the variation of the dipole moment increases as the size of the cluster increases whereas this value is zero in the case of symmetrical clusters with even numbers ( $n$ ) ( $\text{H}_2\text{O}$ ) $_n$ ,  $n = 4, 6, 8, 10, 12$ , and 16 as expected.

#### 4. Conclusion

In this work, a quantum mechanical study of structural properties and the H-bond strength of water clusters ( $\text{H}_2\text{O}$ ) $_n$  is performed at the Hartree–Fock (HF) level of theory and the electronic density functional theory. The frequencies of the hydrogen bond stretching modes obtained for small clusters ( $\text{H}_2\text{O}$ ) $_n$ ,  $n \leq 6$  are in good agreement with experimental data. An analysis of the strength of the hydrogen bond network with the topology and arrangement of water type molecules of large clusters seems to follow a D–AA and DD–AA combination for three-dimensional clusters. These results strongly suggest that arrange-

ment of water molecules is strongly in favour of a stacking process of two-dimensional clusters.

Results and observations achieved from these calculations will enable us to perform and investigate the solvation of small molecules, hydrocarbons and peptides isolated from large macromolecular systems, such as the elastin.

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