

# Small Clusters of Water Molecules Using Density Functional Theory

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The geometries, interaction energies, and harmonic vibrational frequencies of water clusters (with up to 8 molecules) have been studied using density functional theory (DFT) at the gradient corrected level. The water monomer and water dimer calculations have been used as benchmarks to investigate different choices for basis sets and density functionals. Our results for larger clusters agree with both available high-level ab initio calculations and experimental information. The calculations of the vibrational frequencies and IR absorption intensities for the larger clusters, for which no other reliable quantum-chemical calculation is available, are presented to facilitate the frequency assignment of experimental spectra.

## 1. Introduction

Small clusters of water molecules have been the subject of a large number of theoretical studies in the last 25 years.<sup>1–6</sup> Since the early ab initio computations,<sup>1</sup> it was clear that the larger the cluster, the larger the number of energetically closely spaced energy minima. For clusters with up to 6 water molecules, the combination of Monte-Carlo minimizations and ab initio computations with reliable basis sets pointed out<sup>1</sup> the existence of cyclic structures, which were assumed to be either the lowest or near to the lowest energy. Later,<sup>2</sup> the water clusters were revisited and it was confirmed that the cyclic structures correspond to the lowest energy minima for small clusters, at least up to 5 molecules, whereas for larger clusters clathrate-type structures have this characterization. Today, structural and vibrational determinations of water clusters are the object of studies, because of the importance of these systems for understanding hydrogen bonding, which plays a key role on many chemical and biological problems. Furthermore, additional motivations are (i) the existence of experimental information based on spectroscopic studies of clusters,<sup>7–9</sup> which complements the theoretical calculations through experimental–theoretical feedback; (ii) the development of models of liquid water based on the existence of discrete clusterlike structures in the bulk;<sup>10,11</sup> and (iii) the need of developing improved water–water interaction potentials, flexible enough to deal with situations ranging from the isolated molecule to the condensed phase.<sup>12</sup>

As it is now very well-known, accurate studies of the water–water interaction by means of ab initio techniques require the use of larger and flexible basis sets and methods which consider correlation effects.<sup>4,12–14</sup> Since high-level ab initio post-Hartree–Fock calculations are unfeasible because of their high computational cost for systems with many degrees of freedom, density functional theory (DFT), which is more economical from the computational point of view, has emerged as a powerful alternative.

Recently, several papers have appeared where the DFT method has been applied to hydrogen-bonded systems.<sup>15–19</sup>

In the present work, we present results of structural parameters, dipole moments, and vibrational frequencies for the water

monomer and dimer, using several basis sets of varying flexibility and two gradient corrected density functionals.

One gradient corrected density functional (labeled PP) is obtained by combining the gradient correction of Perdew and Wang<sup>20a</sup> for the exchange and that of Perdew<sup>20b</sup> for the correlation. The other one (labeled BP) is built by combining the exchange functional of Becke<sup>21</sup> and the Perdew<sup>20b</sup> functional for the correlation. In both density functionals the parameterization of the correlation energy of the homogeneous electron gas due to Vosko<sup>22</sup> was used.

Lee et al. have recently reported the binding energies for water clusters, with up to 20 molecules, evaluated with DFT with local and nonlocal functionals;<sup>19</sup> the reported<sup>19</sup> binding energies have not been corrected for BSSE or ZPE and the results are, in general, comparable to ours. However, we find no agreement in the most stable geometry of the clusters composed by 6 and 8 molecules; this will be remarked in the appropriate sections of this work.

In a recent work on the water monomer and dimer, it is shown that the density functional obtained by combining the new Becke's exchange potential<sup>23</sup> and the nonlocal correlation functional of Lee, Yang, and Parr<sup>24</sup> (labeled B3LYP) yields better results (particularly for the harmonic vibrational frequencies) than either the BP and the PP potentials. Unfortunately, the B3LYP functional requires the evaluation of the exact exchange matrix elements; therefore, for systems of the size we are interested in, it scales with about the fourth power of the number of the basis functions, and we lose the advantages of schemes, like PP and BP functionals, which scales nominally as the third power of the number of basis functions.

The results here reported for the clusters (H<sub>2</sub>O)<sub>n</sub>, n = 3–8, have been obtained using the PP functional and a moderate size basis set, which yields results close to very large basis sets for the water monomer and dimer.

## 2. Computational Methodology

The calculations reported in this study have been carried out with the Molecule-DFT program,<sup>25</sup> where the Kohn–Sham self-consistent procedure<sup>26</sup> is applied to obtain the electronic density and energy through the determination of a set of one-electron orbitals (the solution of the Kohn–Sham equations). Gaussian basis sets are used for the expansion of the one electron orbitals. The electronic density is also expanded in an additional gaussian basis set.<sup>27</sup> The coefficients for the fit of the electronic density are obtained by minimizing the error in the Coulomb repulsion

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**TABLE 1: Water Monomer: Distances (angstroms), Angles (degrees), Dipole Moments (debyes), and Frequencies (cm<sup>-1</sup>)**

	expt	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B
PP Potential											
<i>R</i> (O–H)	0.9572 <sup>a</sup>	0.984	0.981	0.981	0.981	0.977	0.976	0.972	0.971	0.972	0.971
∠HOH	104.52 <sup>a</sup>	104.22	103.35	103.25	103.30	103.59	103.66	104.67	104.73	104.56	104.72
$\mu$	1.855 <sup>b</sup>	1.824	1.854	1.952	1.966	2.009	2.022	1.855	1.867	1.853	1.864
$\nu_1$	3657 <sup>c</sup>	3561	3598	3632	3646	3628	3648	3664	3689	3661	3686
$\nu_2$	1595 <sup>c</sup>	1588	1606	1605	1615	1610	1620	1613	1623	1613	1621
$\nu_3$	3756 <sup>c</sup>	3664	3707	3722	3747	3723	3756	3752	3793	3751	3793
BP Potential											
<i>R</i> (O–H)	0.9572 <sup>a</sup>	0.982	0.980	0.979	0.977	0.975	0.974	0.970	0.969	0.971	0.969
∠HOH	104.52 <sup>a</sup>	103.25	103.34	103.44	103.63	103.75	103.83	104.40	104.56	104.43	104.63
$\mu$	1.855 <sup>b</sup>	1.843	1.863	1.952	1.964	2.007	2.021	1.857	1.869	1.854	1.866
$\nu_1$	3657 <sup>c</sup>	3607	3632	3667	3698	3660	3680	3692	3717	3687	3715
$\nu_2$	1595 <sup>c</sup>	1591	1601	1601	1607	1606	1616	1611	1620	1613	1620
$\nu_3$	3756 <sup>c</sup>	3705	3741	3761	3804	3759	3791	3783	3825	3777	3823

<sup>a</sup> Reference 33. <sup>b</sup> Reference 34. <sup>c</sup> Reference 51.

energy. The use of this fit reduces the integral evaluation process dependency from  $N^4$  to  $N^2M$  (where  $N$  is the number of functions in the orbital basis set and  $M$  is the total number of functions in the auxiliary basis, typically of comparable size to  $N$ ). It could be noted that this type of procedure has been proposed also for Hartree–Fock computational (see the “dynamical basis” in ref 28).

Matrix elements of the exchange-correlation potential are evaluated by a numerical integration scheme based on the grids and quadratures proposed by Becke.<sup>29</sup> In performing the numerical integration of the exchange-correlation potential matrix elements, in the SCF step, we have used a grid with 25 radial shells for the oxygen atoms, 20 for the hydrogen atoms, and 50 angular points per shell.<sup>25</sup> At the end of the SCF procedure, the exchange-correlation energy and its contribution to the gradients have been evaluated using an augmented grid, with 35 radial shells for the oxygen atoms, 30 for the hydrogen atoms, and 194 angular points per radial shell.

The geometry optimization has been performed by using a quasi-Newton minimization method in Cartesian coordinates with analytical energy gradients. The Cartesian force constants and dipole moment derivatives are calculated by numerical differentiation of the energy gradients and dipole moments using Cartesian displacements of 0.010 au. From the force constant matrix, vibrational frequencies and zero-point energies have been obtained. The infrared absorption intensities have been calculated by taking the numerical derivatives of the dipole moment and transforming them to the corresponding ones with respect to the normal modes.

For the water molecule and the water dimer, five different basis sets have been used, combined with two different auxiliary basis sets. The first basis set (labeled 1), has a contraction pattern (5211/311/1) and (51/1) for oxygen and hydrogen, respectively, and it has been optimized for HF calculations.<sup>30</sup> The second set has a contraction pattern (5211/411/1) and (41/1) for oxygen and hydrogen, respectively, and has been optimized for DFT calculations<sup>31</sup> (labeled 2). The third one (labeled 3)<sup>30</sup> has a contraction pattern of (73111/521/1) and (721/1) for oxygen and hydrogen, respectively. The fourth set (labeled 4) is constructed by augmenting with two diffuse polarization functions (exponents 1.8 and 0.3 for oxygen and 1.4 and 0.3 for hydrogen) basis set 3. Finally, the fifth set (labeled 5) is an almost completely uncontracted basis set, with a contraction scheme of (7111111/1111111/111) and (7111/111) for oxygen and hydrogen, respectively. For the auxiliary basis sets, one (labeled A) has the contraction pattern (111111/11/1) and (111111/1) for oxygen and hydrogen, respectively, and the other (labeled B) has the pattern (1111111/111/111)

and (111111/1) for oxygen and hydrogen, respectively; both auxiliary basis are derived with slight modifications from basis found in literature.<sup>32</sup>

### 3. Results

**3.1. The Water Molecule.** The geometrical parameters, dipole moments, and harmonic vibrational frequencies have been evaluated with all the basis sets described previously, both with the PP and the BP functionals. The corresponding computed data and experimental results<sup>33–34</sup> are summarized in Table 1. The agreement with the experiments is acceptable, with exception of the computed O–H bond length, which remains too large. From Table 1, we can notice that the deviation of the computed values from the experimental results decrease while improving the basis set quality. In particular, a noteworthy improvement is observed for the dipole moment, a quantity known to be very sensitive to the choice of the basis set. The values of the OH bond length and the HOH bond angle are, for the larger basis sets, within 0.015 bohrs and 0.2 deg from the experimental one, for both the BP and the PP functionals.

It can be noticed that results obtained with basis sets 4 and 5 are very similar, an indication that basis set 4 is almost acceptable; we note also that the major variations for the computed changes, observed relative to the use of basis set 3 and basis set 4, are due to the additional of diffuse polarization functions. From Table 1, it can be seen, also, that the auxiliary basis sets have, on their own, noticeable effects in the predicted results. Calculations on the water monomer using DFT have also been reported by Sim et al.,<sup>15</sup> and Laasonen et al.<sup>16</sup> All in all, reasonable qualitative agreement is found between our results and those in ref 15, whereas our results disagree considerably with those reported in ref 16, probably due to additional approximation introduced in using pseudopotentials and plane waves.

The DFT results, obtained with the B3LYP potential by Kim et al.,<sup>18</sup> predict an HO bond length in better agreement with experiment than those reported in Table 1, and dipole moments and HOH angles of similar quality as the ones obtained with the BP and PP potentials.

Vibrational frequencies obtained with the PP and BP functionals are more similar to the anharmonic experimental values than the values calculated with the B3LYP potential; however, the latter better reproduces harmonic experimental frequencies.<sup>33</sup> Averaged deviations of the calculated values from the experimental ones are  $\approx 0.2$ , 0.7, and 3.7% for the PP/4A, BP/4A, and B3LYP/aug-cc-pVQZ<sup>18</sup> potentials, when considering an-

**TABLE 2: Water Dimer:<sup>a</sup> Distances (angstroms), Angles (degrees), Dipole Moments (debyes), Frequencies (cm<sup>-1</sup>), Energies (kcal/mol)**

	expt <sup>b</sup>	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B
PP Potential											
$R(\text{O}_1\text{H}_1)$		0.982	0.982	0.982	0.982	0.978	0.977	0.973	0.971	0.973	0.971
$R(\text{O}_1\text{H}_2)$		0.982	0.982	0.982	0.982	0.978	0.977	0.973	0.971	0.973	0.971
$R(\text{O}_2\text{H}_3)$		0.992	0.991	0.991	0.991	0.987	0.987	0.981	0.980	0.981	0.980
$R(\text{O}_2\text{H}_4)$		0.981	0.980	0.981	0.979	0.976	0.974	0.971	0.969	0.971	0.969
$R(\text{O}_1\text{O}_2)$	2.98	2.900	2.912	2.897	2.893	2.889	2.892	2.907	2.895	2.899	2.893
$\angle\text{H}_1\text{O}_1\text{H}_2$		103.71	104.05	104.23	104.18	104.76	104.58	105.21	105.24	105.09	105.22
$\angle\text{H}_3\text{O}_2\text{H}_4$		102.39	102.09	103.46	102.87	104.08	103.27	105.02	105.01	104.79	104.94
$\angle\text{O}_1\text{H}_3\text{O}_2$	$6 \pm 20$	3.74	4.97	5.68	1.37	3.99	1.43	6.19	6.42	6.47	6.41
$\mu$	2.60	2.740	2.871	3.312	2.856	2.867	2.942	2.617	2.654	2.621	2.644
$\Delta E$	$-5.44 \pm 0.7^c$	-5.23	-5.53	-5.51	-5.79	-5.84	-6.08	-5.90	-5.99	-5.79	-5.96
$\Delta E$ (BSSE)		-3.01	-2.87	-5.17	-5.49	-5.18	-5.45	-5.77	-5.90	-5.61	-5.80
$D_0$	$-3.59 \pm 0.5^c$	-0.79	-0.72	-2.91	-3.50	-2.92	-3.31	-3.53	-3.66	-3.43	-3.63
BP Potential											
$R(\text{O}_1\text{H}_1)$		0.981	0.979	0.981	0.979	0.976	0.975	0.971	0.970	0.971	0.970
$R(\text{O}_1\text{H}_2)$		0.981	0.979	0.981	0.979	0.976	0.975	0.971	0.970	0.971	0.970
$R(\text{O}_2\text{H}_3)$		0.990	0.989	0.989	0.989	0.986	0.985	0.980	0.979	0.980	0.979
$R(\text{O}_2\text{H}_4)$		0.981	0.980	0.979	0.977	0.974	0.973	0.970	0.968	0.970	0.968
$R(\text{O}_1\text{O}_2)$	2.98	2.913	2.914	2.903	2.926	2.864	2.903	2.921	2.917	2.919	2.913
$\angle\text{H}_1\text{O}_1\text{H}_2$		103.57	103.69	104.07	103.90	104.56	104.67	105.08	105.29	104.96	104.93
$\angle\text{H}_3\text{O}_2\text{H}_4$		102.29	102.27	103.92	103.69	104.26	104.10	104.79	104.57	104.50	104.70
$\angle\text{O}_1\text{H}_3\text{O}_2$	$6 \pm 20$	3.52	3.40	6.57	5.00	3.99	3.24	6.05	6.13	3.76	6.17
$\mu$	2.60	2.687	2.704	2.794	2.784	3.040	2.926	2.616	2.613	2.677	2.608
$\Delta E$	$-5.44 \pm 0.7^c$	-3.95	-4.17	-4.26	-4.44	-4.53	-4.72	-4.37	-4.54	-4.35	-4.53
$\Delta E$ (BSSE)		-1.97	-2.19	-3.97	-4.18	-4.05	-4.28	-4.28	-4.47	-4.18	-4.37
$D_0$	$-3.59 \pm 0.5^c$	0.34	0.29	-1.95	-2.21	-1.84	-2.08	-2.21	-2.31	-2.01	-2.31

<sup>a</sup> See Figure 1a for the atom labels.  $D_0$  is the binding energy corrected for ZPE and BSSE contributions. <sup>b</sup> Reference 51. <sup>c</sup> Reference 38.

harmonic experimental findings, while they are  $\approx 4.3$ , 3.7, and 0.9%, again for the PP/4A, BP/4A, and B3LYP/aug-cc-pVQZ<sup>18</sup> potentials, when considering harmonic corrections to the experimental values. In the overall, we safely can state that the B3LYP DFT potential yields structural results more accurate than both the PP and BP potentials. From the results in Table 1, as expected, the improvement on the quality of both orbital sets and auxiliary sets brings about closer agreement with experimental data. Finally, the results obtained with basis set 4 are almost identical to those obtained with the larger basis set 5.

**3.2. The Water Dimer.** Geometrical parameters, dipole moment, and binding energies for the water dimer have been evaluated with all basis sets described previously, and with both the PP and the BP functionals. The calculated results are summarized in Tables 2 and 3, where we report also the corresponding experimental data.<sup>35,36</sup> We refer to Figure 1a for the indexing scheme which identifies the atoms. Independently from basis set quality, the minimum geometry corresponds to the  $C_s$  structure, in agreement with ab initio calculations and microwave spectroscopy.<sup>36</sup>

As in the case of the water monomer, the computation of dimer improves compared with the experimental values, by adding flexibility to the basis set. It is apparent from the results obtained for both the BP and PP functionals that reasonable agreement with experimental data is reached when the basis set includes diffuse polarization functions. As for the water monomer, the computation for the dimer results agree qualitatively with those of Sim et al.<sup>15</sup> but are considerably different from those reported by Laasonen et al.<sup>16</sup>

In Table 2 we also present the results obtained for the binding energies, without ( $\Delta E$ ) and with basis set superposition errors ( $\Delta E(\text{BSSE})$ ), evaluated within the counterpoise scheme,<sup>37</sup> whereas the  $D_0$  values include both the BSSE and the zero-point energy (ZPE) corrections.  $D_0$  ranges from 0.29 to  $-2.31$  kcal/mol for the BP potential, and from  $-0.72$  to  $-3.66$  kcal/mol for the PP potential. Notice that basis set 1 yields a large BSSE value, which makes positive the value of the binding

energy (i.e., nonbonded dimer) for the BP functional. It must be noted that in ref 19 a value of  $\Delta E = -5.36$  kcal/mol is reported for the DFT-BP functional. This is outside the range of values we find for DFT-BP (see Table 2); however, our values are in agreement with those reported in ref 15 for the same functional. The true value of the water dimer binding energy is an issue still not completely settled. If we assume as reference the experimental value of  $-3.59 \pm 0.50$  kcal/mol from ref 38, then the BP underestimates the water dimer binding energy, and the PP potential overestimates it. However, the PP yields numerical values closer to those of ref 38. We will comment further on the binding energy issue, in this and following sections.

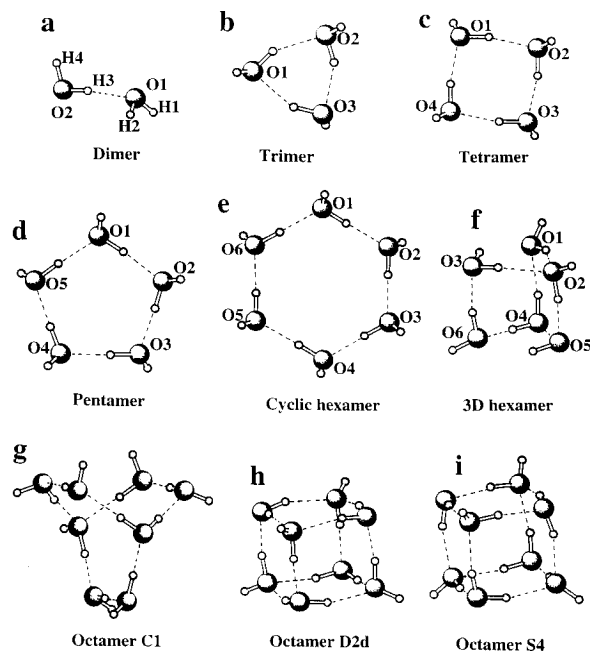
The computed harmonic vibrational frequencies of the water dimer are reported in Table 3. As for the water monomer, even if the intramolecular mode frequencies are underestimated, the overall agreement with experimental data for both the PP and the BP potentials is acceptable. Again, our results are similar to those reported by Sim et al.,<sup>15</sup> but differ considerably from those reported by Laasonen et al.<sup>16</sup> It can be observed that the basis set used in ref 15, even if it yields results in reasonable agreement with experimental values, is still not optimal, and a more flexible basis set with diffuse polarization functions seems to be needed for achieving better results, particularly for dipole moments and vibrational frequencies. In this respect, we must warn once again on the fact that we are comparing DFT *harmonic* vibrational frequencies with experimental *anharmonic* vibrational frequencies. In this light, the DFT results of this work are superior to MP2 results,<sup>13c</sup> which, in turn, seem to describe more accurately the *harmonic* vibrational behavior of the system; of course, this consideration is applicable only for those cases in which harmonic experimental informations can be obtained.

The water dimer has been studied in many theoretical works using different ab initio methods; in Table 4 we compare our results obtained with the PP functional and the 4A basis set

**TABLE 3: Water Dimer:<sup>a</sup> Vibrational Frequencies (cm<sup>-1</sup>)<sup>a</sup>**

mode <sup>b</sup>	expt <sup>c</sup>	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B
PP Potential											
acc asym str	3714	3687	3754	3713	3738	3712	3748	3746	3785	3745	3784
donor asym str	3698	3603	3694	3692	3720	3684	3723	3719	3759	3720	3757
acc sym str	3626	3567	3613	3625	3639	3609	3632	3659	3685	3659	3684
donor sym str	3548	3435	3408	3502	3503	3482	3495	3539	3555	3542	3554
donor and acc bend	1618	1615	1659	1630	1642	1631	1642	1636	1647	1635	1644
acc and donor bend	1600	1583	1583	1598	1607	1605	1610	1615	1624	1616	1625
O <sub>2</sub> H <sub>3</sub> O <sub>1</sub> bend	520 <sup>d</sup>	674	706	625	646	669	648	639	646	639	647
acc rot., donor wag	320 <sup>d</sup>	391	628	344	362	387	370	382	383	363	368
O—O str	243 <sup>d</sup>	255	205	218	228	222	221	232	238	231	235
acc and donor rock	—	214	192	162	170	189	188	166	164	162	160
acc rot., donor wag	155 <sup>d</sup>	181	143	157	123	162	153	159	156	144	150
acc and donor rock	—	165	63	152	100	138	93	135	124	119	116
BP Potential											
acc asym str	3714	3713	3753	3747	3780	3750	3782	3775	3815	3775	3818
donor asym str	3698	3671	3697	3725	3754	3722	3756	3750	3787	3749	3789
acc sym str	3626	3596	3627	3658	3682	3657	3678	3687	3712	3689	3718
donor sym str	3548	3450	3476	3513	3529	3490	3517	3551	3567	3545	3567
donor and acc bend	1618	1630	1641	1620	1633	1630	1643	1634	1647	1637	1645
acc and donor bend	1600	1588	1596	1604	1614	1607	1615	1615	1623	1617	1626
O <sub>2</sub> H <sub>3</sub> O <sub>1</sub> bend	520 <sup>d</sup>	695	693	641	638	683	674	637	645	640	642
acc rot., donor wag	320 <sup>d</sup>	422	420	357	366	388	390	383	387	380	376
O—O str	243 <sup>d</sup>	281	271	186	183	203	192	187	188	189	186
acc and donor rock	—	212	214	178	158	174	177	167	163	161	155
acc rot., donor wag	155 <sup>d</sup>	192	188	130	135	172	163	159	157	156	134
acc and donor rock	—	158	155	111	123	120	127	142	145	140	107

<sup>a</sup> See Figure 1a for atom labels. <sup>b</sup> Acc = acceptor water molecule, donor = donor water molecule, str = stretching, bend = bending, wag = wagging, rock = rocking, rot = rotation. <sup>c</sup> Reference 52. <sup>d</sup> Reference 46.

**Figure 1.** Water clusters studied in the present work.

(which will be used for all the calculations presented in the next sections) and selected results from literature, also obtained after systematic improvements of the basis set quality.<sup>18,39</sup> As is evident from the table, the DFT-PP results differ considerably from the other methods: it predicts too long OH bond lengths, and a too short O—O distance. Even if the  $D_0$  PP result is in agreement with the experimental value,<sup>38</sup> from the systematic study of Table 2 and equivalent studies in ref 39 for the MP2 method and in ref 18 for the MP2 and DFT-B3LYP, we do not rule out that DFT-PP overestimates the dimer binding energy.

**3.3. The Water Trimer.** All calculations performed on clusters larger than the water dimer have been performed with

**TABLE 4: Water Dimer: Comparison between Different Methods. Lengths (Å), Angles (deg) Dipole Moments (debyes), Binding Energies (kcal/mol)**

	DFT PP <sup>a</sup>	DFT B3-LYP <sup>b</sup>	MP2 <sup>b</sup>	MP2 <sup>c</sup>	CASSCF <sup>d</sup>	expt <sup>e</sup>
$d(\text{O}_1\text{H}_1)$	0.973	0.963	0.960		0.967	
$d(\text{O}_1\text{H}_2)$	0.973	0.963	0.960		0.967	
$d(\text{O}_2\text{H}_3)$	0.981	0.970	0.965	0.964	0.948	
$d(\text{O}_2\text{H}_4)$	0.971	0.961	0.958	0.964	0.943	
$d(\text{O}_1\text{O}_2)$	2.907	2.917	2.889	2.911	3.084	2.98
$\angle\text{H}_1\text{O}_1\text{H}_2$	105.2	105.5	104.7		104.3	
$\angle\text{H}_3\text{O}_2\text{H}_4$	105.0	105.4	104.7		105.9	
$\angle\text{O}_1\text{H}_3\text{O}_2$	6.2	5.2	5.0	4.5	0	$6 \pm 20$
$\mu$	2.617	2.637	2.653	1.977		2.60
$\Delta E$	-5.90	-4.57	-5.63	-5.44		$-5.44 \pm 0.7^f$
$D_0$	-3.53					$-3.59 \pm 0.5^f$

<sup>a</sup> This work; 4A basis set. <sup>b</sup> Reference 18; aug-cc-pVTZ basis set. <sup>c</sup> Reference 39; 6-311++G(2d,2p) basis set. <sup>d</sup> Reference 13c; aug-cc-pVDZ basis set. <sup>e</sup> Reference 51. <sup>f</sup> Reference 38.

the basis set labeled 4 and the auxiliary set labeled A (4A). This combination, in the cases of the water monomer and dimer, yields nearly converged results in the computed dipole moments, geometries, vibrational frequencies, and dimer binding energy. For the trimer and the bigger clusters, we have performed calculations only with the PP potential, since the water dimer binding energy seems to be more accurately described with this potential than with the BP potential.

The water trimer has been the subject of several experimental<sup>8,40–42</sup> and theoretical studies.<sup>1,13,43–45</sup> As is known, since the pioneering works of ref 1, the lowest energy corresponds to a cyclic structure; however, an accurate experimental geometry is not available.

We have optimized the structure of the water trimer, and the results are given in Table 5. The numbering of the atoms is in accordance with Figure 1b. The structure we found, a ring with two O—H<sub>free</sub> bonds pointing on one side of the ring plane and a third O—H<sub>free</sub> bond on the opposite side, agrees with MP2

**TABLE 5: Water Trimer: Distances (Å), Angles (deg) (See Figure 1b for the Atom Labels), Energies (kcal/mol)**

	this work	MP2 <sup>b</sup>	MP2 <sup>c</sup>	CCSD <sup>d</sup>	expt <sup>e</sup>
$d(\text{O}_3-\text{O}_1)$	2.784		2.789	2.825	
$d(\text{O}_1-\text{O}_2)$	2.780	2.800–2.798	2.801	2.837	2.94–2.97–2.97
$d(\text{O}_2-\text{O}_3)$	2.781		2.793	2.828	
$d(\text{O}_1-\text{H}_{b1})$	0.990	0.977	0.970	0.976	
$d(\text{O}_2-\text{H}_{b2})$	0.990	0.978	0.970	0.977	
$d(\text{O}_3-\text{H}_{b3})$	0.989	0.978	0.970	0.976	
$d(\text{O}_1-\text{H}_{f1})$	0.971	0.964	0.958	0.966	
$d(\text{O}_2-\text{H}_{f2})$	0.971	0.964	0.958	0.966	
$d(\text{O}_3-\text{H}_{f3})$	0.971	0.965	0.959	0.967	
$d(\text{O}_1-\text{H}_{b3})$	1.872	1.901	1.915	1.943	
$d(\text{O}_2-\text{H}_{b1})$	1.879	1.920	1.939	1.970	
$d(\text{O}_3-\text{H}_{b2})$	1.870	1.901	1.915	1.944	
$\Phi(\text{H}_{b1}-\text{O}_1-\text{H}_{f1})$	106.2	105.3	105.2	105.4	
$\Phi(\text{H}_{b2}-\text{O}_2-\text{H}_{f2})$	106.2	105.3	105.0	105.3	
$\Phi(\text{H}_{b3}-\text{O}_3-\text{H}_{f3})$	105.8	105.0	104.9	105.2	
$\delta(\text{O}_1-\text{H}_{b1}-\text{O}_2)$	150.0	148.4	146.8	146.7	150
$\delta(\text{O}_2-\text{H}_{b2}-\text{O}_3)$	151.8	151.3	149.2	149.4	153
$\delta(\text{O}_3-\text{H}_{b3}-\text{O}_1)$	151.9	151.1	148.5	148.9	152
$\text{H}_{b1} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	-5.5	-16.0	0	0	0
$\text{H}_{b2} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	0.1	-0.6	0	0	0
$\text{H}_{b3} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	0.4	1.8	0	0	0
$\text{H}_{f1} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	72.3	57.3		41.0	
$\text{H}_{f2} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	78.4	50.9		40.2	
$\text{H}_{f3} \angle(\text{O}_1-\text{O}_2-\text{O}_3)$	-77.9	-62.6		-47.6	
$\Delta E$	-12.71	-8.50	-10.6	-9.79	

<sup>a</sup> Reference 16 reports the O–O distances in the range 2.77–2.81 Å and the  $\delta$  angle in the range 150–154°. Ref 13c reports the O–O distance at 2.807 Å, from MP4 calculations. <sup>b</sup> Reference 13c; aug-cc-pVDZ basis set. <sup>c</sup> Reference 13b; 6-311+G(d,p) basis set. <sup>d</sup> Reference 45; DZP-diff basis set. <sup>e</sup> Reference 7a.

**TABLE 6: Vibrational Frequencies of the water trimer (cm<sup>-1</sup>) and Infrared Intensities (km/mol) (in Parentheses)**

mode	this work	pwDFT-BP <sup>a</sup>	MP2 <sup>b</sup>	CCSD <sup>c</sup>	expt
$\nu_3$	3727 (43)	3710	3898 (97)	3957	
$\nu_3$	3727 (44)	3680	3896 (107)	3953	3707, <sup>e</sup> 3703, <sup>e</sup> 3695 <sup>e</sup>
$\nu_3$	3720 (41)	3650	3892 (105)	3951	
$\nu_1$	3418 (637)	3280	3641 (459)	3769	3356, <sup>c</sup> 3400 <sup>c</sup>
$\nu_1$	3412 (652)	3200	3632 (492)	3762	3366, <sup>d</sup> 3340 <sup>d</sup>
$\nu_1$	3336 (5)	3200	3573 (11)	3692	3525, <sup>e</sup> 3517, <sup>e</sup> 3516 <sup>f</sup>
$\nu_2$	1644 (22)		1660 (10)	1729	1632 <sup>e</sup>
$\nu_2$	1625 (38)		1635 (65)	1671	1620 <sup>e</sup>
$\nu_2$	1623 (89)		1632 (90)	1667	1602 <sup>e,f</sup>
	951 (8)		863 (10)	941	
	710 (279)		667 (291)	664	
	641 (190)		571 (148)	536	
	485 (130)		444 (132)	443	
	386 (6)		351 (37)	356	
	375 (74)		343 (95)	331	
	268 (15)		235 (35)	264	
	248 (42)		218 (4)	208	
	232 (54)		193 (85)	195	
	226 (38)		185 (29)	186	
	211 (61)		173 (84)	177	
	185 (107)		158 (79)	170	

<sup>a</sup> Reference 16a, planewaves DFT, Becke exchange, Perdew correlation. <sup>b</sup> Reference 13c, aug-cc-pVDZ basis set. <sup>c</sup> Reference 45, DZP+diff basis set. Reference 41, gas phase. <sup>d</sup> Reference 42, gas phase. <sup>e</sup> Reference 6, solid Ar. <sup>f</sup> Reference 47, Kr and Ar matrices.

structures reported in the literature,<sup>13c,43b</sup> and with a recent coupled cluster (CC) investigation.<sup>45</sup> The structural parameters reported by the planewave-DFT calculation of ref 16 also show a reasonable agreement with the present results. The values of the O–O distances in our case range from 2.780 to 2.784 Å, and are reported as varying from 2.798 to 2.800 Å in MP2 calculations,<sup>13c</sup> and from 2.825 to 2.837 Å in coupled cluster calculations.<sup>45</sup> The proposed experimental values<sup>8</sup> ranging from 2.94 to 2.97 Å are at variance with both the calculated DFT, MP2, and CC results. Tentatively, one can ascribe this discrepancy to the fact that perhaps the deduction of the

experimental structure of the trimer from a single set of rotational constants cannot be unique. In comparing the geometrical results obtained for the water dimer with the same basis set and same PP potential, we found for the trimer a considerable shortening of the O–O distance, pointing out the importance of nonadditive and dispersive contributions beyond a two-body approach. A collection of geometrical parameters selected from literature is presented in Table 5.

No experimental indications on the trimerization binding energy have been reported so far. We calculated a value of  $D_0 = -12.71$  kcal/mol when both ZPE and BSSE corrections are included.

The vibrational frequencies for the water trimer are reported in Table 6. Our results agree well with experimental frequencies (uncorrected for anharmonicity),<sup>41,42</sup> and are considerably better than the corresponding frequencies obtained using HF calculations<sup>44</sup> (even when scaling procedures are used). As for the water dimer case, DFT frequencies match experimental results better than MP2 frequencies;<sup>13c</sup> in particular, our results agree with the experimental gas-phase assignment<sup>41,42</sup> of the absorption bands around 3357 and 3400 cm<sup>-1</sup> and around 3340–3366 cm<sup>-1</sup>, assignment which has been contested<sup>13c</sup> on the basis of MP2 calculations and on solid and matrix measurements.<sup>46,47</sup> Again, the comparison with the planewaves-DFT results<sup>16</sup> show considerable differences, probably because of limitations in the planewaves approach when dealing with localized systems. CC calculations<sup>45</sup> yield values far from the experimental anharmonic findings.

**3.4. The Water Tetramer.** Very few theoretical and experimental information is available for the water tetramer. We find, at the energy minimum, a flat ringlike structure, with H bonds shorter than in the trimer case. We have also explored 3D structures, but all resulted to be higher in energy than the ring structure. Geometrical parameters are reported in Table 7. This minimum energy structure shows O–O distance ranging from 2.723 to 2.737 Å; as expected, they are considerably shorter than the O–O distances in the trimer. Deviation of H bonds from linearity is reduced, with respect to the trimer, to

**TABLE 7: Water Tetramer (Distances in Å, Angles in deg)**

structure <sup>a</sup>	this work	pwDFT-BP <sup>b</sup>	MP2 <sup>c</sup>
$d(\text{O}-\text{O})$	2.737–2.73	2.667–2.699	2.880
$d(\text{O}-\text{H}_b)$	0.997–0.999		0.985
$d(\text{O}-\text{H}_f)$	0.971		0.965
$\angle(\text{O}-\text{H}_b-\text{O})$	168.1–168.7	165	167.7
$\angle(\text{H}_b-\text{O}-\text{H}_b)$	105.9–106.4		105.0
$\angle\text{H}_b(\text{OOO})$	1.8–2.2		0.4
$\angle\text{H}_f(\text{OOO})$	110.1–111.2		112.4

<sup>a</sup> H<sub>b</sub> refers to bonded hydrogen atoms, H<sub>f</sub> to free hydrogen atoms.

<sup>b</sup> Reference 16a, planewaves DFT, Becke exchange, Perdew correlation.

<sup>c</sup> Reference 13c, Aug-cc-pVDZ basis set.

**TABLE 8: Vibrational Frequencies of the Water Tetramer (cm<sup>-1</sup>) and Infrared Intensities (km/mol) (in Parentheses)**

mode	this work	HF <sup>a</sup>	MP2 <sup>b</sup>
$\nu_3$	3725 (40)	3747	3887 (0)
$\nu_3$	3723 (36)	3746	3887 (126)
$\nu_3$	3721 (41)	3746	3887 (126)
$\nu_3$	3720 (31)	3745	3886 (102)
$\nu_1$	3286 (55)	3348	3522 (20)
$\nu_1$	3245 (1549)	3306	3484 (1349)
$\nu_1$	3238 (1554)	3306	3484 (1349)
$\nu_1$	3124 (6)	3211	3391 (0)
$\nu_2$	1660 (0)	1703	1683 (0)
$\nu_2$	1632 (42)	1664	1653 (47)
$\nu_2$	1630 (41)	1664	1653 (47)
$\nu_2$	1615 (88)	1659	1637 (81)
	1043 (0)		996 (0)
	859 (165)		826 (166)
	856 (161)		826 (166)
	756 (130)		754 (171)
	466 (21)		451 (39)
	465 (23)		451 (40)
	462 (21)		435 (21)
	422 (0)		403 (0)
	284 (1)		291 (0)
	272 (42)		261 (0)
	268 (167)		255 (199)
	266 (145)		255 (197)
	255 (66)		237 (59)
	254 (125)		237 (61)
	231 (24)		211 (0)
	221 (0)		200 (46)
	89 (2)		79 (2)
	50 (0)		51 (0)

<sup>a</sup> Reference 44. HF/4-31G. Frequencies are scaled by an empirical factor equal to 1.0898. <sup>b</sup> Reference 13c. Aug-cc-pVDZ basis set.

about 12°. Similar structures have been found with HF,<sup>1,44</sup> MP2,<sup>13c</sup> and DFT<sup>16,19</sup> calculations. Also for the water tetramer, there is no experimental binding energy value to compare with. We find a binding energy of -24.6 kcal/mol. We will comment later on this result.

Vibrational intramolecular frequencies are reported in Table 8; we compare our results with those obtained either from MP2 calculations<sup>13</sup> or from HF/4-31G, scaled with an empirical parameter.<sup>44</sup> From the values reported in Table 8, we notice, in general, that our values are closer to the HF/4-31G-scaled results. We must point out, once more, that harmonic DFT frequencies are close to anharmonic (experimental) frequencies than MP2 harmonic values. Unfortunately, no experimental information is available for this system to judge the quality of the results obtained with the various methodologies. The high IR intensity of two  $\nu_1$  stretching modes in the region around 3240 cm<sup>-1</sup> seems to be characteristic of the tetramer and may be used in order to detect these clusters using IR techniques.

**3.5. The Water Pentamer.** We have investigated the ring geometry of the water pentamer; the optimized geometrical parameters are reported in Table 9. As observed in the smaller

**TABLE 9: Water Pentamer (Distances in Å, Angles in deg)<sup>a</sup>**

$d(\text{O}_1-\text{O}_2) = 2.717$	$d(\text{O}_1\text{H}_{b1}) = 1.000$	$d(\text{O}_1\text{H}_{f1}) = 0.970$
$d(\text{O}_2-\text{O}_3) = 2.713$	$d(\text{O}_2\text{H}_{b2}) = 1.000$	$d(\text{O}_2\text{H}_{f2}) = 0.970$
$d(\text{O}_3-\text{O}_4) = 2.716$	$d(\text{O}_3\text{H}_{b3}) = 1.000$	$d(\text{O}_3\text{H}_{f3}) = 0.971$
$d(\text{O}_4-\text{O}_5) = 2.712$	$d(\text{O}_4\text{H}_{b4}) = 1.000$	$d(\text{O}_4\text{H}_{f4}) = 0.971$
$d(\text{O}_5-\text{O}_1) = 2.711$	$d(\text{O}_5\text{H}_{b5}) = 0.999$	$d(\text{O}_5\text{H}_{f5}) = 0.971$
$\angle\text{O}_1\text{H}_{b1}\text{O}_2 = 175.3$	$\angle\text{O}_2\text{H}_{b2}\text{O}_3 = 177.9$	$\angle\text{O}_3\text{H}_{b3}\text{O}_4 = 177.25$
$\angle\text{O}_4\text{H}_{b4}\text{O}_5 = 177.2$	$\angle\text{O}_5\text{H}_{b5}\text{O}_1 = 176.8$	
$\angle\text{H}_{b1}(\text{O}_4\text{O}_5\text{O}_1) = -125.5$	$\angle\text{H}_{b2}(\text{O}_5\text{O}_1\text{O}_2) = -118.7$	$\angle\text{H}_{b3}(\text{O}_1\text{O}_2\text{O}_3) = 116.1$
$\angle\text{H}_{b4}(\text{O}_2\text{O}_3\text{O}_4) = -119.5$	$\angle\text{H}_{b5}(\text{O}_3\text{O}_4\text{O}_5) = 116.0$	

<sup>a</sup> See Figure 1d for the atom labels. H<sub>b</sub> refers to bonded hydrogen atoms, H<sub>f</sub> to free hydrogen atoms.

**TABLE 10: Vibrational Frequencies of the Water Pentamer (cm<sup>-1</sup>) and Infrared Intensities (km/mol) (in Parentheses)**

	this work	HF <sup>a</sup>
asym stretchings $\nu_3$	3733 (43)	3752
	3725 (39)	3745
	3723 (38)	3744
	3718 (33)	3743
	3713 (25)	3742
sym stretchings, $\nu_1$	3246 (45)	3296
	3238 (25)	3295
	3183 (2392)	3238
	3171 (2366)	3234
	3063 (9)	3145
bendings, $\nu_2$	1680 (15)	1722
	1665 (30)	1693
	1647 (54)	1686
	1631 (15)	1675
	1618 (80)	1672
intermolecular modes	1028 (4)	1051
	927 (124)	975
	892 (106)	952
	811 (149)	918
	730 (21)	829
	568 (72)	611
	486 (14)	502
	459 (2)	496
	442 (26)	480
	429 (46)	458
	315 (36)	332
	308 (6)	330
	306 (1)	280
	292 (206)	267
	263 (197)	263
	243 (56)	224
	241 (51)	207
	231 (23)	192
	225 (55)	185
	180 (1)	101
	69 (2)	82
	65 (0)	77
	40 (0)	53
	30 (3)	22

<sup>a</sup> Reference 44. HG/4-31G. Frequencies are scaled by an empirical factor equal to 1.0898.

clusters, the O–O distances follow the trend of decreasing with the cluster size, with values ranging from 2.711 to 2.717 Å. All free OH bonds point out of the ring plane, with alternate directions; two adjacent O–H<sub>free</sub> bonds are therefore pointing in the same direction, and this symmetry breaking causes one oxygen atom to be slightly out of the plane. Differently from the HF/6-31G\* structure,<sup>48</sup> no O–H<sub>free</sub> bond is found lying on the ring plane. The predicted binding energy is  $D_0 = -32.13$  kcal/mol.

The results from the harmonic vibrational analysis are reported in Table 10. To our knowledge, these are the only results at a correlated level, and thus we compare them only with scaled HF values.<sup>48</sup>

**TABLE 11: Water Hexamer: Cyclic Structure (Distances in Å, Angles in deg)<sup>a</sup>**

$d(\text{O}_1-\text{O}_2) = 2.703$	$d(\text{O}_1\text{H}_{b1}) = 1.000$	$d(\text{O}_1\text{H}_{f1}) = 0.971$
$d(\text{O}_2-\text{O}_3) = 2.707$	$d(\text{O}_2\text{H}_{b2}) = 1.000$	$d(\text{O}_2\text{H}_{f2}) = 0.971$
$d(\text{O}_3-\text{O}_4) = 2.705$	$d(\text{O}_3\text{H}_{b3}) = 1.000$	$d(\text{O}_3\text{H}_{f3}) = 0.970$
$d(\text{O}_4-\text{O}_5) = 2.702$	$d(\text{O}_4\text{H}_{b4}) = 1.000$	$d(\text{O}_4\text{H}_{f4}) = 0.971$
$d(\text{O}_5-\text{O}_6) = 2.707$	$d(\text{O}_5\text{H}_{b5}) = 1.000$	$d(\text{O}_5\text{H}_{f5}) = 0.971$
$d(\text{O}_6-\text{O}_1) = 2.706$	$d(\text{O}_6\text{H}_{b6}) = 1.000$	$d(\text{O}_6\text{H}_{f6}) = 0.970$
$\angle\text{O}_1\text{H}_{b1}\text{O}_2 = 177.4$	$\angle\text{O}_2\text{H}_{b2}\text{O}_3 = 177.5$	$\angle\text{O}_3\text{H}_{b3}\text{O}_4 = 177.8$
$\angle\text{O}_4\text{H}_{b4}\text{O}_5 = 177.4$	$\angle\text{O}_5\text{H}_{b5}\text{O}_6 = 177.5$	$\angle\text{O}_6\text{H}_{b6}\text{O}_1 = 177.7$
$\angle\text{O}_1(\text{O}_2\text{O}_3\text{O}_5\text{O}_6) = -16.1$	$\angle\text{O}_4(\text{O}_2\text{O}_3\text{O}_5\text{O}_6) = 16.1$	

<sup>a</sup> See Figure 1a for the atom labels. H<sub>b</sub> refers to bonded hydrogen atoms, H<sub>f</sub> to free hydrogen atoms.

**3.6. The Water Hexamer.** As of today, the most stable geometry for the water hexamer has not been characterized by experimental techniques. What seems to be clear is that there are several possible minimum structures, with energies differing one each other by 1 kcal/mol at most (see, for example, ref 14). In this work, we have investigated the ring structure, and a 3D prismatic structure which is found to be the absolute minima in the extended MP2 analysis on water hexamers of ref 14.

Optimizing the ring structure, we have obtained an hexagonal chairlike geometry, with O–H<sub>free</sub> bonds pointing alternatively in opposite directions. Four oxygen atoms lie on a plane, while the remaining two are out of plane by about  $\pm 16.1^\circ$ . This highly symmetric structure leads to a nonpolar cluster.

The O–O distances range from 2.702 to 2.707 Å and are smaller, as was expected, than O–O distances of the smaller clusters. The optimized parameters are given in Table 11. We found a binding energy of  $D_0 = -39.88$  kcal/mol.

The optimized 3D prismatic structure is also a real minimum (i.e., no imaginary values in the harmonic vibrational frequencies); its energy is lower by 1.4 kcal/mol than the energy of the cyclic structure when no corrections are applied, confirming the findings of ref 14. However, the zero-point energy correction is larger than the value for the cyclic structure, and by including also the BSSE correction, we find  $D_0 = -38.02$  kcal/mol. Unfortunately, in ref 14, the zero-point energy correction is not taken into account, and therefore it cannot be ruled out that the hexagonal chairlike geometry is the most stable. As noted in ref 19, different DFT functionals can yield different minimum geometries. Since different structures are found within a narrow range of energies, all possible corrections must be taken into account to determine properly the relative energy between these structures at finite temperature.

The structure, shown in Figure 1f is ideally obtained by stacking two cyclic trimers; it presents nine hydrogen bonds: two of them, the one between water 1 and water 3 and the one between water 5 and water 6, are particularly weak (and they are not highlighted in Figure 1f), their lengths being 2.184 and 2.140 Å, respectively. Selected structural parameters are reported in Table 12.

The results of the harmonic normal-mode analysis for the two structures are reported in Table 13 for the intramolecular modes; no correlated ab initio results are available in literature. From the results of Table 13, it is evident that the two structures present different vibrational characteristics; in particular, the most IR intense modes have very different vibrational frequencies, around 3160 cm<sup>-1</sup> for the cyclic structure and at 2887 cm<sup>-1</sup> for the prismatic structure. Ideally, the question of the lowest hexamer structure could thus be answered experimentally by IR spectroscopy.

**3.7. The Water Octamer.** We have investigated three structures for the water octamer, reported in the literature as

**TABLE 12: Water Hexamer: 3D Structure (Distances in Å, Angles in deg)<sup>a</sup>**

$d(\text{O1}-\text{O2}) = 2.750$	$\angle\text{O}_1\text{H}_{b1}\text{O}_2 = 153.8$	
$d(\text{O2}-\text{O3}) = 2.807$	$\angle\text{O}_2\text{H}_{b2}\text{O}_3 = 149.4$	
$d(\text{O3}-\text{O1}) = 2.965$	$\angle\text{O}_3\text{H}_{b3}\text{O}_1 = 135.6$	
$d(\text{O4}-\text{O5}) = 2.774$	$\angle\text{O}_4\text{H}_{b4}\text{O}_5 = 156.0$	
$d(\text{O5}-\text{O6}) = 2.908$	$\angle\text{O}_5\text{H}_{b5}\text{O}_6 = 133.9$	
$d(\text{O6}-\text{O4}) = 2.855$	$\angle\text{O}_6\text{H}_{b6}\text{O}_4 = 149.9$	
$d(\text{O1}-\text{O4}) = 2.886$	$\angle\text{O}_1\text{H}_{b4}\text{O}_4 = 158.5$	
$d(\text{O2}-\text{O5}) = 2.637$	$\angle\text{O}_2\text{H}_{b2}\text{O}_5 = 170.0$	
$d(\text{O3}-\text{O6}) = 2.749$	$\angle\text{O}_3\text{H}_{b6}\text{O}_6 = 169.4$	
$\angle\text{H}-\text{O1}-\text{H} = 105.6$	$d(\text{O1}-\text{H}_{f1}) = 0.972$	$d(\text{O1}-\text{H}_{b1}) = 0.992$
$\angle\text{H}-\text{O2}-\text{H} = 106.2$	$d(\text{O2}-\text{H}_{f2}) = 0.971$	$d(\text{O2}-\text{H}_{b2}) = 1.016$
$\angle\text{H}-\text{O3}-\text{H} = 101.9$	$d(\text{O3}-\text{H}_{b3-\text{O1}}) = 0.980$	$d(\text{O3}-\text{H}_{b3-\text{O2}}) = 0.987$
$\angle\text{H}-\text{O4}-\text{H} = 103.1$	$d(\text{O4}-\text{H}_{b4-\text{O1}}) = 0.984$	$d(\text{O4}-\text{H}_{b4-\text{O6}}) = 0.985$
$\angle\text{H}-\text{O5}-\text{H} = 101.2$	$d(\text{O5}-\text{H}_{b5-\text{O6}}) = 0.981$	$d(\text{O5}-\text{H}_{b5-\text{O4}}) = 0.997$
$\angle\text{H}-\text{O6}-\text{H} = 105.9$	$d(\text{O6}-\text{H}_{f6}) = 0.971$	$d(\text{O6}-\text{H}_{b6}) = 1.000$

<sup>a</sup> See Figure 1f for the atom labels. H<sub>f</sub> refers to free hydrogen atoms, H<sub>b</sub> to bonded hydrogen atoms.

**TABLE 13: Intramolecular Vibrational Frequencies of the Water Hexamers (cm<sup>-1</sup>) and Infrared Intensities (km/mol) (in Parentheses)**

cyclic structure		3D structure	
asym stretchings, $\nu_3$	3726 (68)	asym stretchings, $\nu_3$	3720 (40)
	3725 (6)		3712 (32)
	3721 (64)		3705 (29)
	3720 (9)		3580 (169)
	3718 (70)		3571 (137)
	3713 (1)		3512 (364)
sym stretchings, $\nu_1$	3250 (160)	sym stretching, $\nu_1$	3469 (263)
	3231 (0)		3461 (262)
	3225 (0)		3336 (447)
	3161 (3092)		3261 (369)
	3154 (3025)		3185 (843)
	3058 (0)		2887 (1022)
bendings, $\nu_2$	1678 (0)	bendings, $\nu_2$	1706 (61)
	1659 (68)		1688 (126)
	1657 (70)		1676 (35)
	1624 (0)		1657 (75)
	1622 (0)		1646 (53)
	1609 (99)		1637 (110)

among the most stable ones, i.e., two cubic structures, of  $D_{2d}$  and  $S_4$  symmetries, and the trilobate structure proposed by Stillinger et al.<sup>6b</sup> Cyclic structures have been reported to be less stable, even if a recent work<sup>49</sup> has pointed out that entropic effects may have a great influence on the relative stability of water octamers and stabilize cyclic structures at higher temperatures. Our results indicate (Table 14) that the two cubic structure are almost equally stable, their binding energies differing by a few tenths of kcal/mol. This result is very much in agreement with the three structures C, C' and C'' proposed as the lowest octamer structures by Kim et al.<sup>2</sup> Our energetic result agrees with MP2//HF/DZP data;<sup>49</sup> it should be noticed, however, that at MP2//HF/DZP,  $D_{3d}$  octamer is 0.08 kcal/mol more stable than the  $S_4$  octamer, while in our DFT results, the order is the opposite. The DFT calculations of ref 19 find the  $D_{2d}$  octamer slightly more stable than the  $S_4$  octamer, either with local and nonlocal functionals; as mentioned before, these data do not include ZPE and BSSE corrections.

The  $D_{2d}$  structure consists of two square tetramers, placed on parallel planes at a distance of 2.668 Å, with alternate double hydrogen donor and double hydrogen acceptor water molecules (see Figure 1h); this arrangement gives a very regular structure, with the sides of the tetramers having an average length of 2.830 Å. The  $S_4$  structure can be viewed as the superimposition of two tetramers of the kind presented in section 3.4; each water molecule is both single hydrogen acceptor and single hydrogen donor. In the superimposition, the two tetramers are stretched along perpendicular directions, resulting in a slightly distorted

**TABLE 14: Water Octamers (Distances in Å, Angles in deg)**

$C_1$		$S_4$		$D_{2d}$	
$R(O-O)$	$R(O-H)$	$R(O-O)$	$R(O-H)$	$R(O-O)$	$R(O-H)$
	H bonded	intratetramer	H bonded single donors	intratetramer	H bonded single donors
2.805	0.990	2.843	1.009	2.830	1.010
2.771	0.993	2.682	1.009	2.830	1.010
2.804	0.991	2.843	1.009	2.830	1.010
		2.681	1.009	2.830	1.010
2.802	0.990				
2.776	0.992	2.682	H bonded double donors	2.829	H bonded double donors
2.793	0.991	2.843		2.831	
		2.681	0.987	2.830	0.987
2.644	1.015	2.843	0.987	2.829	0.986
2.645	1.012		0.987		0.987
2.635	1.017	intertetramer	0.987	intertetramer	0.986
	free		0.987		0.986
	0.971	2.855	0.987	2.667	0.987
	0.972	2.852	0.987	2.668	0.986
	0.971	2.851	0.987	2.668	0.987
	0.971	2.853		2.667	
	0.970		free		free
	0.972		0.971		0.971
			0.971		0.971
			0.971		0.971
			0.971		0.971

**TABLE 15: Intramolecular Vibrational Frequencies of the Water Octamers ( $\text{cm}^{-1}$ ) and Infrared Intensities ( $\text{km/mol}$ ) (in Parentheses)**

	$C_1$		$S_4$		$D_{2d}$
single-donor, asym str, $\nu_3$	3725 (41)	single-donor, asym str, $\nu_3$	3719 (47)	single-donor, asym str, $\nu_3$	3701 (48)
	3724 (34)		3718 (39)		3701 (34)
	3719 (36)		3718 (56)		3700 (57)
	3718 (53)		3716 (2)		3698 (1)
	3714 (49)				
	3712 (18)				
	3710 (36)	double-donor, asym str, $\nu_3$	3488 (1146)	double-donor, asym str, $\nu_3$	3456 (1236)
			3472 (626)		3455 (1236)
			3472 (632)		3419 (8)
			3434 (7)		3412 (0)
double-donor, asym str, $\nu_3$	3394 (656)	double-donor, sym str, $\nu_1$	3443 (1)	double-donor, sym str, $\nu_1$	3393 (30)
sym str, $\nu_1$	3388 (248)		3428 (245)		3393 (14)
	3371 (318)		3427 (242)		3390 (392)
	3350 (854)		3425 (376)		3390 (359)
	3306 (1728)				
	3271 (84)				
	3029 (509)				
	2928 (2687)	single-donor, sym str, $\nu_1$	3034 (1751)	single-donor, sym str, $\nu_1$	3010 (3845)
	2817 (1053)		3030 (1737)		2932 (12)
			2996 (23)		2932 (12)
			2967 (4)		2899 (0)
bendings, $\nu_2$	1695 (4)				
	1678 (36)				
	1668 (24)		1699 (31)	bendings, $\nu_2$	1701 (0)
	1651 (23)		1675 (50)		1686 (1)
	1645 (57)		1674 (51)		1656 (16)
	1632 (77)		1669 (0)		1656 (15)
	1628 (35)		1634 (0)		1640 (0)
	1623 (70)		1623 (61)		1633 (4)
			1623 (60)		1631 (178)
			1614 (186)		1631 (181)

cube. The trilobate structure of symmetry  $C_1$ , when proposed by Stillinger<sup>6b</sup> using his polarizable water model, was supposed to be the most stable arrangement of eight water molecules; quantum-mechanical calculations do not support this conclusion: HF/4-31G calculations<sup>48</sup> demonstrated that this structure is not a minimum, while our calculation, HF/DZP<sup>49</sup> and the planewaves-DFT<sup>16</sup> results yield this geometry as a true minimum, but not as the most stable minimum. Nevertheless, this local minimum structure is interesting, since it can be thought of having the same structure of an octamer in the hexagonal-ice lattice.

The normal mode analysis is obviously richer in three-dimensional than in two-dimensional structures. Single-donor

and double-donor water molecules have substantially different stretching frequencies, so two new groups of fundamental modes appear, characterizing the  $\nu_1$  mode and the  $\nu_3$  mode of double-donor molecules, with frequencies in the 3443–3306  $\text{cm}^{-1}$  range for the former and in the 3488–3394  $\text{cm}^{-1}$  range for the latter (Table 15).

#### 4. Discussion

**4.1. Geometries.** We have optimized 10 different structures for the clusters  $(\text{H}_2\text{O})_n$ , with  $n = 1$  to  $n = 8$ , obtaining local minima; i.e., each optimized structure is characterized by not having imaginary frequencies in the harmonic vibrational



TABLE 16: Binding Energies of Water Clusters (kcal/mol)<sup>a</sup>

	h-bonds	DFT-PP <sup>b</sup>	pwDFT-BP <sup>c</sup>	SCF <sup>d</sup>	MP2 <sup>d</sup>	MP4 <sup>d</sup>	expt <sup>e</sup>
(H <sub>2</sub> O) <sub>2</sub>	1	-3.53 <sup>b</sup> (-5.90)	-4.38	-1.78 (-3.92)	-2.29 (-5.34)	-2.23 (-5.38)	-3.59 ± 0.5
(H <sub>2</sub> O) <sub>3</sub>	3	-12.71	-15.43	-6.17	-8.50	-8.27	
(H <sub>2</sub> O) <sub>4</sub>	4	-24.18	-28.87	-11.70	-16.05	-15.52	
(H <sub>2</sub> O) <sub>5</sub>	5	-32.13		-16.29			
(H <sub>2</sub> O) <sub>6</sub> 3D	9	-38.02			-40.22 <sup>f</sup>		
(H <sub>2</sub> O) <sub>6</sub> cyclic	6	-39.88	-45.52	-20.59	-39.75 <sup>f</sup>		
(H <sub>2</sub> O) <sub>8</sub> (C <sub>1</sub> )	9	-55.18	-67.34	-53.89 <sup>f</sup>	-62.42 <sup>g</sup>		
(H <sub>2</sub> O) <sub>8</sub> (D <sub>2d</sub> )	12	-63.51	-76.01	-59.76 <sup>f</sup>	-70.55 <sup>g</sup>		
(H <sub>2</sub> O) <sub>8</sub> (S <sub>4</sub> )	12	-64.06		-59.68 <sup>f</sup>	-70.47 <sup>g</sup>		

<sup>a</sup> All the results include ZPE and BSSE corrections, except otherwise indicated. Results for the water dimer, not corrected for ZPE and BSSE contributions, are given in parentheses. <sup>b</sup> This work. Value of  $\Delta H(T=298\text{ K})$  for the water dimer, in the rigid rotor approximation, is  $\Delta H_{T=298\text{ K}} = -3.99$  kcal/mol. The ZPE corrections in kcal/mol are (H<sub>2</sub>O)<sub>2</sub> = 2.24; (H<sub>2</sub>O)<sub>3</sub> = 5.81; (H<sub>2</sub>O)<sub>4</sub> = 8.19; (H<sub>2</sub>O)<sub>5</sub> = 10.27; (H<sub>2</sub>O)<sub>6</sub> (3D) = 14.39; (H<sub>2</sub>O)<sub>6</sub>(cyclic) = 12.08; (H<sub>2</sub>O)<sub>8</sub> (C<sub>1</sub>) = 17.20; (H<sub>2</sub>O)<sub>8</sub>(D<sub>2d</sub>) = 20.75; (H<sub>2</sub>O)<sub>8</sub>(S<sub>4</sub>) = 20.32. <sup>c</sup> Reference 16a. Planewaves-DFT, Becke exch., Perdew corr. These results are not corrected for zero-point contribution. <sup>d</sup> Reference 13d. aug-cc-pVDZ basis set. MP4 results use ZPE/MP2 corrections. <sup>e</sup> Reference 38.  $T = 298\text{ K}$ . <sup>f</sup> Reference 14. Values corrected for BSSE but not for ZPE contributions. <sup>g</sup> Reference 49. DZP basis set. MP2 results obtained at HF geometries and with ZPE/HF corrections.

spectrum. For five structures (i.e., for the systems with 1, 2, 3, 4, and 5 water molecules) we are confident to have obtained absolute minima, guided not only by our experience, but also by the numerous results available in the literature. We have investigated also some other structures, as the closed dimer and the open trimer, and a 3D tetramer, but no minimum has been found for those structures.

Some trends in the cyclic cluster's geometrical parameters can be observed: O–O distances decrease as the number of molecules increases, from a value of 2.907 Å in the dimer to a value of 2.705 Å in the cyclic hexamer. On the contrary, O–H<sub>bonded</sub> lengths increase with increasing number of molecules, from 0.981 Å in the dimer to 1.000 Å in the cyclic hexamer. Both these trends appear to be very near to convergence for the cyclic hexamer, and thus we expect no further modifications for these parameters in larger cyclic water clusters. In all the clusters under consideration in this work, the O–H<sub>free</sub> length has constantly the value of 0.971 Å. All these trends have been already reported for HF and MP2 calculations<sup>13c</sup> and are in qualitative agreements with our results.

**4.2. Binding Energies.** The binding energies, including BSSE and ZPE corrections for all the clusters studied, are collected in Table 16. As often pointed out, it is apparent from the results that nonadditive effects are very important, since the results deviate strongly from linearity. In the same table we also report results from accurate calculations found in the literature. As expected, different energies result from different methods, and it is difficult to draw conclusive arguments about their relative accuracy. In addition, for a given method different basis sets can yield very different energies. From Table 16, the DFT-PP seems to overestimate the binding energies for the water dimer, trimer, and tetramer, with respect to MP2 and MP4 results, but, at the same time, it yields lower (in absolute value) binding energies than MP2/HF for the three octamers. This inconsistent trend can be ascribed in part to the sensitivity of MP2 results to the basis set quality and to the use of geometries optimized only at the HF level. Indeed, results under the column marked MP2 are not fully consistent, since different basis sets have been used for different cluster sizes. The sensitivity of MP2 binding energies to basis set size can be underlined by taking into account additional results not reported in Table 16. For example, for the D<sub>2d</sub> octamer, ref 10b, a MP2 calculation performed with Dunning double- $\zeta$  basis set plus polarization, at HF geometry yields a value of  $D_0 = -51.05$  kcal/mol which is 19.5 kcal/mol higher than the MP2/HF value<sup>49</sup> reported in Table 16, also obtained with a double- $\zeta$  with polarization basis set and at HF geometry.

For the water dimer binding energy, results obtained at the SCF, MP2 and MP4 level are reported. The values in Table 16 point out that the DFT-PP dimer binding energy, corrected with ZPE and BSSE contributions, agree with the experimental value better than any other correlated ab initio calculation. This agreement is maintained when the enthalpy change at  $T = 298\text{ K}$  is estimated by using the harmonic oscillator–rigid rotor model, as reported in note *a* of the same table; indeed, this should be the value to be properly compared with the experimental value, which is measured at 298 K. The B3LYP potential, which looks to be superior for geometry and frequency data, seems to yield a too weak interaction energy value<sup>18</sup> ( $-4.71$  kcal/mol with the aug-cc-pVDZ basis set without ZPE and BSSE corrections; the latter is expected<sup>18</sup> to be  $\sim 0.6$  kcal/mol, bringing the interaction energy to  $\sim -4.1$  kcal/mol). We must point out that accurate calculations with very large basis sets at the equilibrium geometry<sup>50</sup> estimate the dimer interaction energy at  $\sim 4.8$  kcal/mol, without ZPE correction. If we consider this as the most accurate result available, then the DFT-PP, MP2 and MP4 results of Table 16 are all off by 0.5–1.0 kcal/mol.

The trimer binding energy predicted by the DFT-PP potential is  $-12.71$  kcal/mol; this value is considerably larger (2–4 kcal/mol) than the one predicted by MP2 and MP4 calculations.<sup>13d</sup> In ref 45 several values for the trimer binding energy have been obtained at different levels of theory; their “best value”, i.e., the value obtained at the higher level of theory, is  $\Delta E = -14.80$  kcal/mol at CCSD/TZ2P+diff, evaluated for a geometry optimized with CCSD/DZP+diff, which, when corrected for ZPE obtained at SCF/TZ2P+diff, gives a  $D_0$  of  $-9.79$  kcal/mol. The energy spread reported in literature for the water tetramer shows how sensitive the binding energy is with the level of theory used: HF/DZP calculations<sup>10b</sup> give a value for  $D_0$  of  $-17.7$  kcal/mol, while HF/6-31G\*<sup>44</sup> calculations give  $D_0 = -20.77$  kcal/mol. With a MP2/DZP<sup>10b</sup> technique a value of  $D_0 = -25.6$  kcal/mol is obtained, and our DFT-PP value is of  $D_0 = -24.6$  kcal/mol. BSSE corrections, however, change significantly the MP2 results. More recent calculations with MP2/aug-cc-pVDZ<sup>13d</sup> technique report a value of  $D_0 = -20.84$  kcal/mol (and  $D_0 = -16.05$  with BSSE corrections) and MP3/aug-cc-pVDZ,<sup>13d</sup> at MP2/aug-cc-pVDZ geometry, yields a  $D_0 = -20.74$  kcal/mol (and  $D_0 = -15.52$  with BSSE corrections). From all the above results, it is clear that the “true value” of the tetramer binding energy cannot be settled.

The spread in the binding energy results is more evident for cluster sizes 5, 6, and 8. Regarding  $n = 5$ , the best HF results are at the HF/6-31G\* level<sup>48</sup>, which give  $D_0 = -27.58$  kcal/mol, and at the HF/aug-cc-pVDZ level,<sup>13d</sup> which gives  $D_0 =$

–17.67 kcal/mol ( $D_0 = -16.29$  kcal/mol with BSSE correction). DFT-BP/TZVP<sup>19</sup> gives  $\Delta E = -42.40$  kcal/mol, in good agreement with our uncorrected value  $\Delta E = -42.93$  kcal/mol. Our DFT-PP binding energy is larger than the other available theoretical results. However, the HF results are probably underestimated, since correlation effects seems to be important for this kind of systems.

For the water cyclic hexamer, the planewaves-DFT simulation<sup>16</sup> yields  $D_0 = -45.52$  kcal/mol and the HF/aug-cc-pVDZ<sup>13d</sup>  $D_0 = -20.59$  kcal/mol, to be compared with  $D_0 = -39.88$  kcal/mol from DFT-PP. The binding energy for the 3D hexamer structure is  $D_0 = -38.02$  kcal/mol with DFT-PP, while in ref 14 is reported a value of  $-40.22$  kcal/mol for a BSSE-corrected computation with MP2/aug-ccpVDZ\*, at the geometry of MP2/6-31+G\*\*; no ZPE has been taken into account. Since the ZPE correction is a large contribution to the  $D_0$  value ( $-14.38$  kcal/mol for the DFT/PP approximation), the  $D_0$  MP2 value is expected to be much higher than the DFT/PP value.

Finally, for the water octamers, even if the absolute value of the binding energies are quite different, the present DFT-PP, the SCF<sup>13b</sup>, and MP2<sup>13d</sup> results seem to agree in finding the  $S_4$  and  $D_{2d}$  structures almost degenerate in energy and the  $C_1$  structure much less stable.

**4.3. Vibrational Analysis.** Harmonic vibrational data compare well with experimental anharmonic results, when available. These DFT results can be used as a guide in assigning IR experimental findings and could contribute to the detection of larger clusters (we recall that up to now only the dimer and the trimer have been experimentally observed.) Following the trends observed in some geometrical parameters, vibrational frequencies show themselves regular shifts, when passing from small to large clusters. The asymmetric stretching mode,  $\nu_3$ , calculated to have a frequency equal to  $3752\text{ cm}^{-1}$  for the isolated water molecule, shows an increasing red shift, with increasing number of molecules, and for the hexamer the average value of the six  $\nu_3$  intramolecular modes is  $3720\text{ cm}^{-1}$ . Furthermore, this mode loses, upon clusterization, the character of “asymmetric stretching”, resulting in a more and more pronounced stretching of the O–H<sub>free</sub> bond solely. Analogously, the  $\nu_1$  symmetric stretching mode transforms itself in a O–H<sub>bonded</sub> stretching and reduces its frequency from the value of  $3664\text{ cm}^{-1}$  for the water monomer, to an average value of  $3180\text{ cm}^{-1}$  in the hexamer; differently from the  $\nu_3$  modes, as can be observed from the tables, the values of the  $\nu_1$  stretchings are spread over a large interval, while the  $\nu_3$  frequencies are restricted to a much smaller range of values, indicating possibly a different degree of coupling between the vibrations. The bending modes,  $\nu_2$ , suffer upon cyclic clusterization a blue shift of several  $\text{cm}^{-1}$  and the values cover a range wider and wider, up to an interval of  $\approx 70\text{ cm}^{-1}$  for the hexamer. Analogous modifications can be found in the octamers’ vibrational frequencies, in addition, as already pointed out for the octamer, the frequencies corresponding to vibrational modes of the double hydrogen donor molecules appear.

As a consequence of these shifts, if we consider all the clusters at once, the modes with the highest IR intensities (usually of  $\nu_1$  type) are not superimposed on each other in frequency; this should help in the experimental detection of these clusters.

## 5. Conclusions

The Gaussian-based DFT approach seems to provide a reasonable cost–benefit approach for a qualitative study of the structural, energetics and potential energy surfaces of water clusters. However, the results presented in this paper do not claim to be quantitatively accurate, especially for binding

energies, which, in our opinion, are systematically overestimated; the proposed geometrical parameters are sometimes a bit overestimated and, other times, somewhat underestimated. The vibrational frequencies seem, in general, to agree well with experimental data, better than those obtained from HF and MP2 computations. However, as pointed out in the paper, we find agreement between computed harmonic frequencies and experimental anharmonic frequencies, therefore pointing to cancellations of errors.

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