

Accurate Predictions of Water Cluster Formation, $(\text{H}_2\text{O})_{n=2-10}$

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An efficient mixed molecular dynamics/quantum mechanics model has been applied to the water cluster system. The use of the MP2 method and correlation consistent basis sets, with appropriate correction for BSSE, allows for the accurate calculation of electronic and free energies for the formation of clusters of 2–10 water molecules. This approach reveals new low energy conformers for $(\text{H}_2\text{O})_{n=7,9,10}$. The water heptamer conformers comprise five different structural motifs ranging from a three-dimensional prism to a quasi-planar book structure. A prism-like structure is favored energetically at low temperatures, but a chair-like structure is the global Gibbs free energy minimum past 200 K. The water nonamers exhibit less complexity with all the low energy structures shaped like a prism. The decamer has 30 conformers that are within 2 kcal/mol of the Gibbs free energy minimum structure at 298 K. These structures are categorized into four conformer classes, and a pentagonal prism is the most stable structure from 0 to 320 K. Results can be used as benchmark values for empirical water models and density functionals, and the method can be applied to larger water clusters.

Introduction

Given water's importance to all life and its incredibly odd and complex properties, a significant amount of research has been devoted to understanding all its features.¹ Despite all the effort, important questions still remain unsolved, and much experimental^{2–27} and theoretical^{7,28–57} research has been directed at this fundamental substance.^{1,58–70} More than 50 models of water⁷¹ have been developed since the first realistic interaction potential of water was proposed in 1933,⁷² and none of them have been able to reproduce all the properties of water accurately.⁷³ Although many of these models use empirical potentials that were fitted to experimental data, the increasing reliability of ab initio quantum mechanical methods and great improvement in computational power has enabled the use of potentials derived from first principles. Empirical models are indispensable for studying bulk water and molecular solvation, but they do not always provide accurate structures and energies for smaller water clusters. Most water models were developed to reproduce bulk liquid properties, such as the heat of vaporization and the diffusion coefficient. The results from classical simulations of water dynamics depend on the quality of the water models^{71,74–76} used and usually predict tetrahedral networks of hydrogen bonding.^{29,38,63} Quantum mechanical approaches generally result in a less symmetrical configuration of water building blocks.³⁶

In contrast to the inherent difficulties of studying the structure and dynamics of liquid water, where the experimentally correct answer is still being debated, studies of gas phase structures benefit from high-resolution experiments and high-level theoretical calculations.^{3,52,77–108} Over the past fifteen years, Xantheas and co-workers have completed extensive studies of water clusters using second-order Møller–Plesset perturbation theory (MP2) and have generated highly accurate estimates of the MP2 complete basis set (CBS) limit interaction energy.^{109–120} These

MP2/CBS limit energies can be used as benchmarks for other methods.⁶⁷ We have used Xantheas's MP2/CBS results for water clusters to examine the ability of density functional theory (DFT) methods developed specifically for improved descriptions of nonbonded interactions and water clusters to reproduce structures and energies of small water clusters, $(\text{H}_2\text{O})_n$, where $n = 2–6,8$.⁶⁷ These include X3LYP,^{121,122} PBE1W,^{123,124} and B971.¹²⁵ Using the optimal basis sets for water clusters for each method, we found that although these methods were excellent for water clusters with traditional hydrogen bonds, they failed to locate structures with substantial dispersion interactions.⁶⁷ This makes it difficult to rely on DFT methods to study larger water clusters in a systematic way. Also, density functionals like B3LYP vastly underestimate the two-body interactions that account for the majority of the binding energy of water clusters, and overestimate three-body interaction energies, which are far from negligible.^{122,126} Furthermore, an investigation of the ability of various popular density functionals to characterize stationary points on the potential energy surface of the water dimer has shown that most of them fail to properly identify and order the nature of these stationary points.¹²⁷ Considering the water dimer potential is used to build many models of water, it is not clear whether it will be possible to build reliable models using data derived from density functionals.

Of the many wave function methods, MP2 has been the method of choice for studying water clusters because it is the cheapest ab initio electron correlation method, and it captures all the important features of water clusters. Because of the absence of significant multireference character in the electronic structure of water clusters, benchmark MP2 binding energies have been shown to be virtually identical to their CCSD(T) analogs.^{117,119,128} Reliable MP2/CBS electronic binding energies are available for $(\text{H}_2\text{O})_n$, where $n = 2–6,8$,^{117,119} but not for $(\text{H}_2\text{O})_{n=7,9,10}$. For the purposes of applications such as atmospheric chemistry, electronic binding energies at 0 K are more useful after they are combined with thermal and entropic information to compute thermodynamic quantities such as

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enthalpies and free energies at finite temperatures and pressures. Systematic ab initio binding enthalpies and free energies for water clusters extending to $n = 10$ are rare. The computational cost and difficulty of calculating accurate intermolecular vibrational frequencies for hydrogen-bonded systems, along with difficulties in conformational analysis of the potential energy surfaces of the $n = 7, 9, 10$ clusters, has hampered the availability of thermodynamic data for these water clusters. Two noteworthy studies report MP2/DZP and MP2/TZ2P++ binding energies, enthalpies, and free energies,⁸⁹ and G3 and G3MP2 values.¹²⁹

As part of our ongoing effort to understand the thermodynamics of cluster formation in the atmosphere, we have used high level model chemistry methods to support the idea that water clusters up to $n = 6$ can exist on the troposphere in concentrations comparable to that of ambient aerosols.⁹⁴ In this work we extend our investigation to a systematic study of larger water clusters, $(\text{H}_2\text{O})_{n=7,9,10}$, using Xantheas's MP2 benchmarks and our own MP2/CBS calculations. These results reveal a lower cost way to validate empirical potentials and DFT methods.

Methods

We recently tested the B3LYP, X3LYP, PBE1W, and B971 density functionals for their ability to reproduce benchmark structures and energies of small water clusters, containing two to eight water molecules. This study employed the optimal basis set for each functional, which is crucial for maximizing the performance of each functional for water clusters.^{67,122,124,125} We found that while all the DFT methods capture the minimum energy structures for water tetramers and pentamers, and reproduce the energies well, they fail to locate certain structures where London dispersion forces are critical to the overall shape. Specifically, structures that are not composed of cyclic rings, such as the tetramer pyramid and the pentamer cage structures, are not minima on the DFT potential energy hypersurfaces. Because we do not know, *a priori*, which structures will be minima when we have numerous water molecules per cluster, we have chosen not to rely on current density functionals for a comprehensive study of the thermodynamics of water cluster formation. We have shown that the frozen core MP2/6-31G* geometries are surprisingly accurate when compared to available experimental data and MP2 benchmark calculations.^{98,99} We have therefore used a combination of molecular dynamics and MP2 quantum chemistry calculations using modest size basis sets to thoroughly assess the thermodynamics of pure water cluster formation in the gas phase for two to ten water molecules.

In the first part of this study, we have compared the benchmark MP2/CBS binding energies of Xantheas et al.^{117,119} with those computed using a cheaper scheme. Their MP2/CBS binding energies were calculated by extrapolating the MP2/aug-cc-pVNZ//MP2/aug-cc-pVTZ ($N = T - 5$) binding energies to the complete basis set limit using eq 1. Our cheaper alternative extrapolates MP2/aug-cc-pVNZ ($N = D - 5$) binding energies calculated at the MP2/6-31G* optimized geometry using eq 1. Dunning's aug-cc-pVNZ^{130,131} basis sets are referred to as aNZ in this work. Unless stated otherwise, all MP2 calculations invoke the frozen-core approximation. We have exploited the fact that MP2 geometries for small water clusters are fairly independent of basis set size past a double- ζ quality basis.^{98,99} For $(\text{H}_2\text{O})_{n=2-6,8}$ the large basis MP2 single point calculations, designated by MP2/aNZ//MP2/6-31G*, are used to calculate binding energies that are then extrapolated to the CBS limit by least-squares fitting to the equation

$$\Delta E_N = \Delta E_{\text{CBS}} + \frac{b}{(l_{\max} + 1)^4} + \frac{c}{(l_{\max} + 1)^5} \quad (1)$$

where ΔE_N is the MP2/aNZ//MP2/6-31G* binding energy, ΔE_{CBS} is the extrapolated MP2/CBS binding energy, l_{\max} is the largest angular momentum number for the aNZ basis set ($l_{\max} = 2, 3, 4, 5$ for $N = D, T, Q, 5$, respectively), and b and c are fitting parameters.^{113,132} As this least-squares fitting requires a minimum of three basis sets, we have explored different combinations ($N = D - Q$, $N = D - 5$, and $N = T - 5$) in an effort to evaluate the sensitivity of the extrapolation scheme.

In the second part of our study, we have developed an MP2 model chemistry that allows us to obtain accurate results for water clusters by combining MP2/aDZ//MP2/6-31G* calculations of energies with the same set of calculations corrected for basis set superposition error (BSSE) using the counterpoise (CP) correction.^{133,134} Because the CP correction always overestimates BSSE, we varied the contribution of BSSE until we discovered that for water clusters, $(\text{H}_2\text{O})_n$, $n = 2-6$ and 8, combining 1/3 of the CP correction with 2/3 of the uncorrected energy gave corrected MP2/aDZ//MP2/6-31G* values for formation of these water clusters that rivaled the MP2/CBS limit calculated by Xantheas.^{117,119}

The drastically reduced computational cost of our MP2 model chemistry, denoted as MP2/CBS-e, allows us to study larger water clusters ($n = 7, 9$, and 10) for which there are no benchmark quality ab initio data. One of the challenges of studying these larger water clusters is that the number of possible hydrogen bonding configurations, g_n , increases exponentially with the number of water molecules, n in the cluster.¹³⁵

$$g_n \cong 2^{N_2} 2.12^{N_3} 1.5^{N_4} \quad (2)$$

Here N_2 , N_3 , and N_4 are the number of 2-, 3-, and 4-coordinated water molecules in the cluster, respectively. For $n = 7, 9$, and 10, the possible number of hydrogen bonding configurations is 162, 820, and 1845, respectively. To capture all the relevant low energy configurations, it is essential that one perform adequate sampling of the vast potential energy hypersurface. Monte Carlo algorithms,^{136,137} molecular dynamics simulations,¹³⁸ genetic algorithms,^{137,139} and a host of other techniques¹⁴⁰⁻¹⁴² have been used to explore the configurational space of water clusters. In our case, we ran 10 ns constant temperature gas phase molecular dynamics simulations using AMBER 9¹⁴³ for $(\text{H}_2\text{O})_{n=7,9,10}$. Three water models (TIP3P, TIP4P, and TIP5P) have been evaluated to understand the strengths and weaknesses of each for generating viable cluster configurations. Preliminary results suggested that the TIP4P model is able to replicate MP2 geometries of water clusters better than the other two models, and we thus used. A study of the suitability of molecular mechanics empirical potentials in QM/MM simulations of water has also shown TIP4P to be most compatible with the QM methods like MP2.¹⁴⁴ To obtain starting structures, an energy minimization was performed on each of the three TIP4P water clusters ($n = 7, 9$, and 10) using the Sander subroutine until the root-mean-square deviation of the energy gradient was below 0.1 kcal/mol/Å. Starting with each structure, we ran a two-step gas-phase MD simulation. In the first step, the system was heated from 5 K to the reference temperature T_f over a period of 1 ns. In the second step, the temperature remained at T_f for a 9 ns production run. Simulations were very fast, and were repeated at various final temperatures until we reached a temperature where the cluster

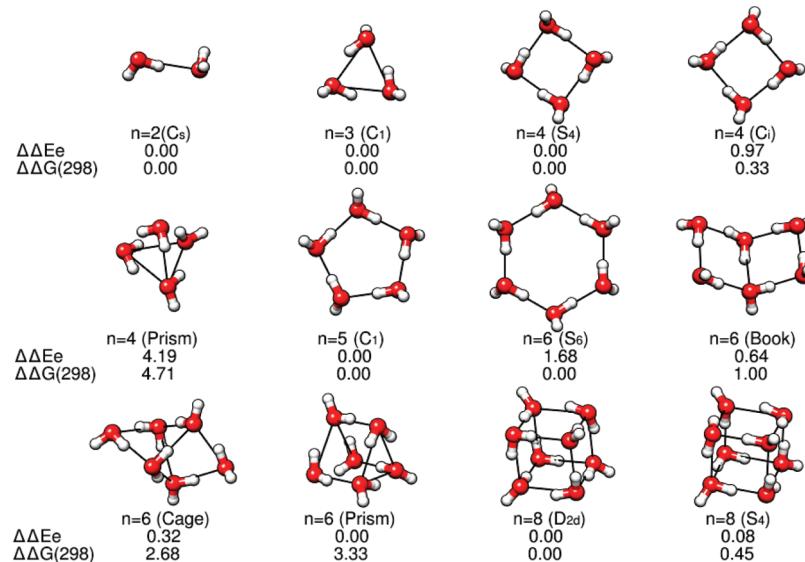


Figure 1. Minimum energy structures for $(H_2O)_n$, $n = 2–6$ and 8 and their relative electronic ($\Delta\Delta E_e$) and Gibbs free energies ($\Delta\Delta G_{298}$) calculated using the MP2/CBS-e model chemistry. See text for details.

dissociated. This temperature represents the point where too much energy is in the system to allow it to remain a cluster, and we used the next lowest temperature simulation to generate our structures for quantum mechanical calculations. That critical temperature was 250 K for $(H_2O)_7$ and $(H_2O)_9$ and was 200 K for $(H_2O)_{10}$. All MD simulations were performed with a nonbonded cutoff of 40 Å and weighting factors of 2.0 and 1.2 for the nonbonded and electrostatic interactions. The timesteps were set to 2 ps. From these simulations we extracted configurational “snapshots” of the clusters. These snapshots were used as starting models for MP2 free energy calculations. We extracted 200 structures for $(H_2O)_7$ and $(H_2O)_9$ and 300 structures for $(H_2O)_{10}$ at evenly spaced intervals, and these starting structures were used as inputs for MP2/6-31G* geometry optimizations with Gaussian 03, Revision D.01 and E.01.¹⁴⁵ Any configurations that did not converge after 200 geometry optimization cycles were discarded. The search ensured that unique configurations were sampled multiple times, reducing the likelihood of missing important configurations. For the configurations that converged in 200 cycles, MP2/6-31G* harmonic vibrational frequency calculations were performed to verify that the configurations were minima. To calculate thermodynamic corrections to the electronic energy, the MP2/6-31G* harmonic frequencies were scaled by 0.9676 to correct for inherent errors in MP2 theory as well as the anharmonic nature of the vibrational modes.^{103,133,146} Single-point energies were computed at the MP2/aDZ level on each stable MP2/6-31G* optimized structure. Finally, we corrected for basis set superposition error via an MP2/aDZ//MP2/6-31G* counterpoise correction calculation. We used the thermodynamic information from the MP2/6-31G* calculations along with the corrected MP2/aDZ//MP2/6-31G* electronic energies (E_e) to estimate the enthalpies (ΔH_{298}) and free energies (ΔG_{298}) of formation of the water clusters at 298 K. It should be noted that the reliability of the harmonic oscillator and rigid rotor approximations invoked in calculating the partition function and subsequent thermodynamic corrections is questionable, particularly at higher temperatures. Unfortunately, more rigorous treatments are computationally expensive at the moment. Previous work does suggest that the errors introduced by scaling frequencies for water clusters are relatively small.^{94,103}

TABLE 1: Comparison of Binding Energies Calculated Using G3 and CBS-APNO Model Chemistries with Benchmark MP2/CBS Values^a

	G3 ^b	CBS-APNO ^b	MP2/CBS ^c
$2H_2O \rightarrow (H_2O)_2$	-5.1	-5.1	-4.9
$3H_2O \rightarrow (H_2O)_3$	-15.8	-15.7	-15.8
$4H_2O \rightarrow (H_2O)_4$	-28.2	-27.8	-27.6
$5H_2O \rightarrow (H_2O)_5$	-37.3	-36.8	-36.3
$6H_2O \rightarrow (H_2O)_6$ cage	-47.7	-46.8	-45.8
$6H_2O \rightarrow (H_2O)_6$ prism	-48.2	-47.2	-45.9
$6H_2O \rightarrow (H_2O)_6$ cyclic S6	-46.0	-45.6	-44.8
$8H_2O \rightarrow (H_2O)_8$ D2d	-76.4	-74.8	-72.7
$8H_2O \rightarrow (H_2O)_8$ S4	-76.4	-74.7	-72.7

^a All energies are in kcal/mol. ^b See refs 94, 95, 98, and 99. ^c See refs 117 and 119.

Results and Discussion

Benchmark MP2/CBS values versus MP2/6-31G* Geometries. The minimum energy structures for small ($n = 2–6$) water clusters have been studied exhaustively and Figure 1 shows the optimized structures referenced in this work.^{94,95,98,99} MP2/6-31G* optimized geometries have proven to be reliable enough to serve as a basis for many model chemistries including the popular G3.^{133,147} These models rely on MP2/6-31G* geometries and aim to correct for basis set incompleteness and missing electron correlation effects through a series of single point energy calculations employing a variety of basis sets and MP2, MP4, and QCISD(T) energy calculations. For water, the overall performance of model chemistries like G2,¹⁴⁸ G3,¹⁴⁷ CBS-QB3,¹⁴⁹ and CBS-APNO¹⁵⁰ is reasonably good for small clusters,^{67,94,95,98,99} but the results degrade with increasing cluster size, as shown in Table 1. Although both G3 and CBS-APNO perform adequately in predicting the electronic binding energies of water clusters of sizes $n = 2–6$, their error increases to 2–4 kcal/mol relative to the MP2/CBS binding energies for the water octamer. These shortcomings of model chemistries necessitate the development of other schemes that can reproduce benchmark quality MP2/CBS binding energies^{117,119} at a reasonable computational cost.

The approach presented here exploits the use of MP2/6-31G* geometries to circumvent the need to perform more expensive MP2/aNZ (N = D, T) geometry optimizations. We approximate

TABLE 2: Comparison of the MP2/CBS Electronic Binding Energies wth MP2//aNZ//MP2/6-31G* and MP2/CBS-e Values for the Formation of Water Clusters^a

	binding energies					extrapolated binding energies				
	MP2/CBS ^b	MP2/aDZ//6-31G*[CP] ^c	MP2/aDZ//6-31G* ^d	MP2/aTZ//6-31G* ^d	MP2/aQZ//6-31G* ^d	MP2/a5Z//6-31G* ^d	MP2/CBS DTQ ^e	MP2/CBS DTQ ^f	MP2/CBS TQ5 ^g	MP2/CBS-e ^h
(H ₂ O) ₂	-4.9	-4.3	-5.1	-5.0	-4.9	-4.9	-4.8	-4.8	-4.8	-4.8
(H ₂ O) ₃	-15.8	-13.2	-15.8	-15.8	-15.6	-15.4	-15.3	-15.2	-15.3	-14.9
(H ₂ O) ₄	-27.6	-23.8	-28.3	-28.2	-27.7	-27.4	-27.2	-27.1	-27.1	-26.8
(H ₂ O) ₅	-36.3	-31.5	-37.3	-37.1	-36.5	-36.2	-35.8	-35.7	-35.6	-35.4
(H ₂ O) ₆ (Cage)	-45.8	-39.4	-47.8	-47.3	-46.4	-45.8	-45.7	-45.2	-45.1	-45.0
(H ₂ O) ₆ (Prism)	-45.9	-39.6	-48.2	-47.5	-46.6	-46.1	-45.5	-45.5	-45.4	-45.3
(H ₂ O) ₆ (S ₆)	-44.8	-39.5	-45.9	-45.6	-45.0	-44.5	-44.1	-44.0	-43.9	-43.6
(H ₂ O) ₈ (D _{2d})	-72.7	-63.4	-76.7	-75.5	-73.9	-73.0	-71.9	-71.9	-71.9	-72.3
(H ₂ O) ₈ (S ₄)	-72.7	-63.2	-76.6	-75.5	-73.9	-73.0	-71.9	-71.9	-71.9	-72.2
MAE ⁱ	5.5	1.7	1.2	0.5	0.2	0.5	0.6	0.6	0.6	0.6

^a All energies are in kcal/mol. ^b MP2 complete basis set limit estimates of Xantheas from refs 117 and 119. ^c MP2/aDZ//MP2/6-31G* with counterpoise correction. ^d MP2/aNZ//MP2/6-31G* where N = D, T, Q, 5. ^e MP2 complete basis set limit for MP2/aNZ//MP2/6-31G*, where N = D, T, Q. ^f MP2 complete basis set limit for MP2/aNZ//MP2/6-31G*, where N = D, T, Q, 5. ^g MP2 complete basis set limit for MP2/aNZ//MP2/6-31G*, where N = T, Q, 5. ^h 2/3*MP2/aDZ//MP2/6-31G* + 1/3*MP2/aDZ//MP2/6-31G*[CP] (eq 3)). ⁱ Mean absolute error relative to MP2/CBS^b.

Xantheas's MP2/CBS estimates by extrapolating the MP2/aNZ single point energies computed on the MP2/6-31G* optimized geometries. Table 2 shows the MP2/aNZ//MP2/6-31G* binding energies of small water clusters in columns 4–7 and the MP2/CBS values extrapolated via least-squares fitting of the binding energies using eq 1 in columns 8–10.

As can be seen in columns 4–7 of Table 2, the MP2/aNZ//MP2/6-31G* binding energies converge monotonically toward the benchmark MP2/CBS values shown in the second column despite the fact that they are all using MP2/6-31G* geometries. The largest difference between the MP2/a5Z//MP2/6-31G* and MP2/CBS binding energy is only 0.4 kcal/mol for the case of the trimer. Extrapolating the MP2/aNZ//MP2/6-31G* binding energies using eq 1 for N = D–Q, N = D–5, and N = T–5 all give approximate MP2/CBS values that are within 1 kcal/mol of Xantheas's benchmark MP2/CBS numbers shown in column 2. Furthermore, the extrapolation is fairly independent of the series of basis sets one uses for the least-squares fitting, with the largest difference between the N = D–Q, N = D–5, and N = T–5 extrapolations being less than 0.6 kcal/mol. Thus, in large clusters where geometry optimizations using large basis sets are prohibitively expensive, it would be possible to get reliable binding energies for water clusters with MP2/6-31G* optimized geometries followed by extrapolations of single point energies employing a larger basis set.

Development of the MP2/CBS-e Model Chemistry. A more efficient way to approach Xantheas's MP2/CBS numbers can be derived from the realization that the counterpoise-corrected MP2 method underestimates the total binding energy for water clusters whereas the uncorrected method overestimates the binding energy by a smaller amount. The deviation of the two from MP2/CBS binding energies is relatively systematic, and it is possible to exploit it to construct an inexpensive but highly accurate scheme for calculating binding energies.

We have shown previously that for the formation of NH₄⁺(H₂O)_{n=2–10} clusters, BSSE is basis set dependent; MP2/CBS//MP2/6-31G* calculations extrapolate to the same CBS limit with and without including BSSE.¹⁵¹ Figure 2 illustrates that the error in the CP corrected MP2/aDZ//6-31G* binding energy is typically twice as large as that for the uncorrected analog, and the errors have opposite signs. Thus, taking 1/3 of the CP corrected and 2/3 of the uncorrected MP2/aDZ binding energies should give results that rival the MP2/CBS benchmarks. Our MP2/CBS energy estimate, E_{MP2/CBS-e} is defined as

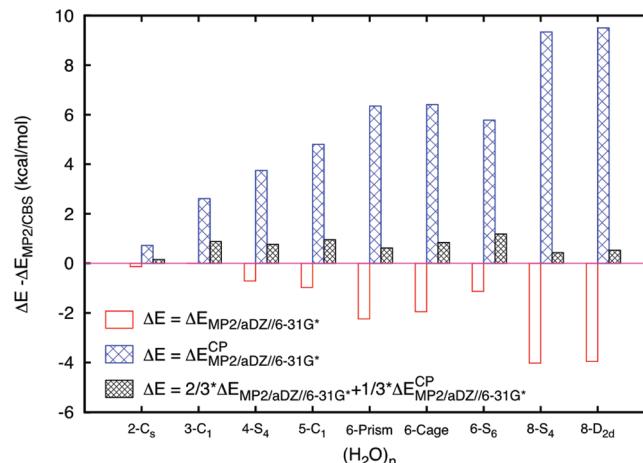


Figure 2. The error in counterpoise corrected and uncorrected MP2/aDZ//6-31G* binding energies relative to MP2/CBS binding energies for small water clusters. The magnitude of the error in the BSSE corrected binding energy is typically twice that of the uncorrected analog. See refs 117 and 119 for the MP2/CBS binding energies (where CP corrected and uncorrected MP2/CBS binding energies differ, an average of the two is used as the benchmark MP2/CBS value).

$$E_{\text{MP2/CBS-e}} = \frac{2}{3}E_{\text{MP2/aDZ//MP2/6-31G*}} + \frac{1}{3}E_{\text{MP2/aDZ//MP2/6-31G*}}^{\text{CP}} \quad (3)$$

Although it is common to combine 1/2 of the CP corrected energy with the uncorrected energies,^{89,152,153} significantly more accurate results can be achieved by including a higher portion of the uncorrected energy in this particular case. In our study, using 1/2 of the CP-corrected energy gave a mean absolute error (MAE) of 1.9 kcal/mol, in contrast to 0.6 kcal/mol when using 1/3 of the CP-corrected energy for (H₂O)_{n=2–10}.

The last column of Table 2 shows our MP2/CBS estimates, designated as MP2/CBS-e binding energies. The MAE of only 0.6 kcal/mol for this scheme is as accurate as the extrapolated MP2/aNZ//MP2/6-31G* binding energies using N = D–5. The reduced computational cost of the MP2/CBS-e scheme allows for the calculation of reliable binding energies and enthalpies for larger water clusters where good ab initio benchmarks are not available. Although small (*n* ≤ 6) water clusters have been studied extensively due to their size and importance, others like *n* = 8, 12, and 20 have garnered a lot of interest for their symmetry and potential resemblance to bulk water. We therefore focus our work on the less-studied water heptamer (H₂O)₇, nonamer (H₂O)₉, and decamer (H₂O)₁₀.

TABLE 3: The MP2/CBS-e Absolute and Relative Electronic (ΔE_e , $\Delta\Delta E_e$) and Gibbs Free (ΔG_{298} , $\Delta\Delta G_{298}$) Binding Energies for the Formation of Water Heptamers Displayed in Figure 3^a

	binding energies ^b		relative binding energies ^b	
	ΔE_e	ΔG_{298}	$\Delta\Delta E_e$	$\Delta\Delta G_{298}$
7H ₂ O → PR1	-56.69	13.68	0.00	1.36
7H ₂ O → PR2	-56.33	14.09	0.35	1.76
7H ₂ O → PR3	-56.09	13.90	0.60	1.57
7H ₂ O → CA1	-55.12	13.32	1.57	0.99
7H ₂ O → CA2	-54.08	14.20	2.61	1.87
7H ₂ O → CH1	-53.12	12.33	3.57	0.00
7H ₂ O → BI1	-52.56	13.65	4.13	1.33
7H ₂ O → CH2	-52.51	12.42	4.18	0.09
7H ₂ O → BI2	-52.41	13.40	4.27	1.07
7H ₂ O → BI3	-52.37	13.58	4.32	1.25
7H ₂ O → CH3	-52.09	13.26	4.60	0.94
7H ₂ O → HM1	-51.14	13.61	5.55	1.28
7H ₂ O → HM2	-51.01	13.79	5.67	1.47

^a All energies are in kcal/mol. ^b See eq 4 for definitions.

Hydrogen Bonding Topology. As represented by eq 2, the exponential increase in hydrogen bonding configurations with the number of water monomers makes it challenging to identify and classify different conformers into groups. In the absence of significant symmetry of high order for many conformers of (H₂O)_{7,9,10}, we devised a way to profile and categorize the different structures into conformer groups. The hydrogen bonding of each water molecule in a given cluster can be characterized as D (single donor), A (single acceptor), DD (double donor), AA (double acceptor), DA (single donor – single acceptor), DAA (single donor – double acceptor), DDA

TABLE 4: Hydrogen Bonding Topology, Types of Water Molecules (DA, DAA, DDA, DDAA), and Total Number of Hydrogen Bonds [n(HB)] in the Five Main Conformer Groups of (H₂O)₇

	DA	DAA	DDA	DDAA	HB topology	n(HB)
PR	1	3	3	0	1330	10
CA	3	2	2	0	3220	9
CH	5	1	1	0	5110	8
BI	6	0	0	1	6001	8
HM	5	1	1	0	5110	8

(double donor – single acceptor) or DDAA (double donor – double acceptor). Using hydrogen bonding cutoffs defined by Mills and Dean¹⁵⁴ and implemented in the Chimera package,¹⁵⁵ we used the hydrogen bonding topology information to categorize the different clusters into conformer groups. The D, A, DD, and AA types of waters are prominent in small water clusters, but are not featured in the lowest energy conformers of (H₂O)_{7,9,10}. Thus, we designate the each conformer group of (H₂O)_{7,9,10} by a number $N_{DA}N_{DAA}N_{DDA}N_{DDAA}$ where N_{DA} , N_{DAA} , N_{DDA} , and N_{DDAA} are the number of DA, DAA, DDA, and DDAA waters in each cluster, respectively.

(H₂O)₇. For (H₂O)₇, we found 13 configurations that can be classified into five conformer groups based on their hydrogen bonding topology. The five conformer groups denoted by PR (Prism), CA (Cage), CH (Chair), BI (Bicyclic), and HM (Hexamer+Monomer) in Table 3 and Figure 3 can be distinguished by their structural motifs, the number of hydrogen bonds they form and the donor–acceptor characteristic of each water monomer (see Table 4). Figure 3 shows the low energy configurations of (H₂O)₇ sorted by increasing binding electronic energy (ΔE_e). Our molecular dynamics simulation and subse-

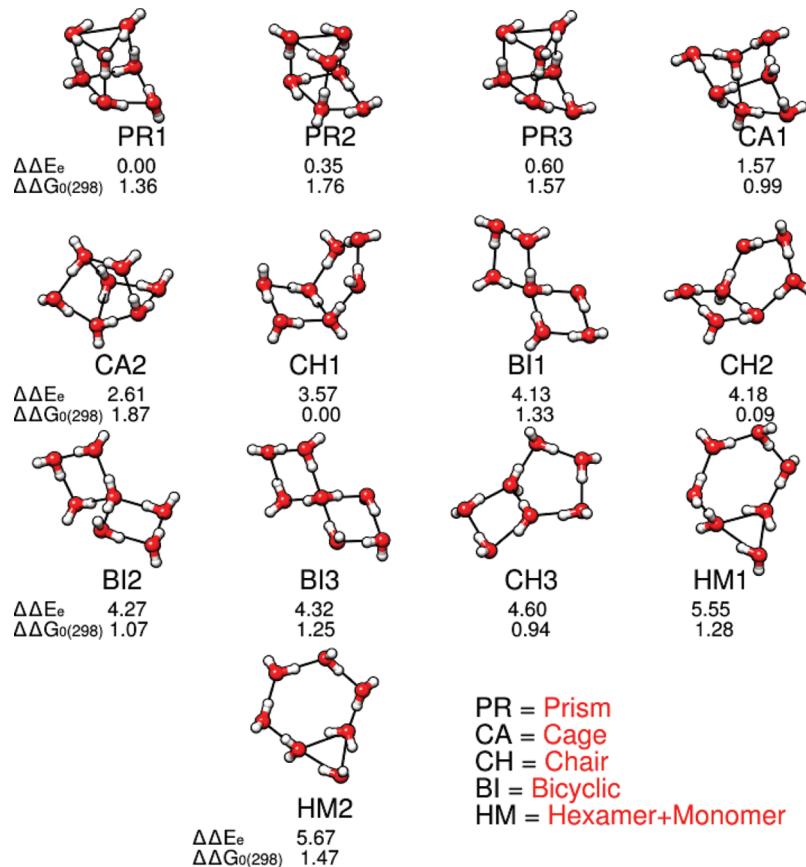


Figure 3. Low energy conformers of (H₂O)₇ ordered by increasing electronic conformational energy (ΔE_e) calculated using MP2/CBS-e (see refs 89 and 153 for other labels used to designate some of these structures).

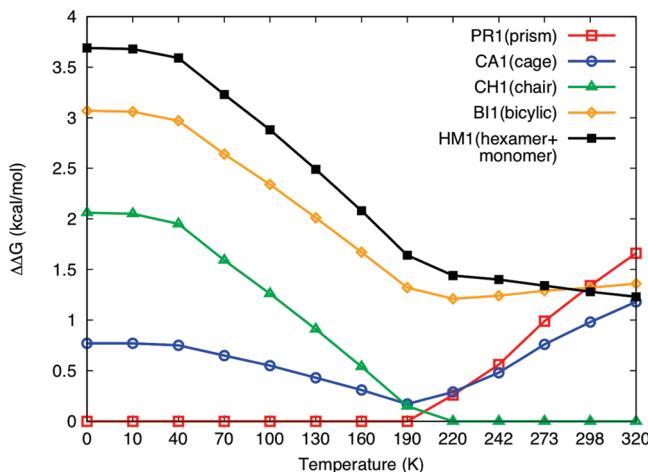


Figure 4. Relative Gibbs free energies (ΔG) of the most stable configurations of the main conformer classes of the water heptamer as a function of temperature. The PR1 (prism) conformer is favored at low temperatures from energetic considerations, and the CH1 (chair) becomes more favorable at higher temperatures because of entropic effects.

quent MP2/CBS-e calculations yielded 13 unique configurations that are within 2 kcal/mol of the global Gibbs free energy minimum structure (CH1) at 298 K (ΔG_{298}). The relative electronic ($\Delta \Delta E_e$) and free energies ($\Delta \Delta G_{298}$) of each minimum configuration are listed in Table 3. We note that because of the small differences, we have reported the numbers to a 100th of a kcal/mol in order not to lose information in the tenths of a kcal/mol; we expect the error bars in this method to be on the order of many 10ths of a kcal/mol. For the i th conformer of $(\text{H}_2\text{O})_n$, $\Delta E_e^{n_i}$, $\Delta \Delta E_e^{n_i}$, $\Delta G_{298}^{n_i}$, and $\Delta \Delta G_{298}^{n_i}$ are defined as

$$\begin{aligned}\Delta E_e^{n_i} &= E_e^{n_i} - nE_e^1 \\ \Delta \Delta E_e^{n_i} &= \Delta E_e^{n_i} - \min_i \{\Delta E_e^{n_i}\} \\ \Delta G_{298}^{n_i} &= G_{298}^{n_i} - nG_{298}^1 \\ \Delta \Delta G_{298}^{n_i} &= \Delta G_{298}^{n_i} - \min_i \{\Delta G_{298}^{n_i}\}\end{aligned}\quad (4)$$

The PR conformers have prism shape and this class consists of the most energetically stable heptamers because they form the most number of hydrogen bonds (10). The CA class of conformers is cage-like with nine hydrogen bonds per cluster. Although the three-dimensional PR and CA conformers are energetically favorable because of their large number of hydrogen bonds, they have substantially lower entropies than the quasi-planar CH, BI and HM conformers. As a result, the CH, BI and HM conformer classes are entropically more favorable at higher temperatures. Figure 4 shows the relative Gibbs free energy, ΔG as a function of temperature for the lowest energy structure of each conformer group. Conformer classes CH, BI and HM each have 0 K Gibbs free energies, $\Delta G(0)$, that are more than 2 kcal/mol higher than the $\Delta G(0)$ of the global minimum configuration of the water heptamer (PR1). These three classes become entropically favorable at higher temperatures since their structures are less constrained by hydrogen bonds. Conformer PR1 remains the Gibbs free energy minimum until about 200 K, at which point CH1 becomes the most stable structure. The interplay between the energetic and entropic effects of hydrogen bonds is evident in the case of the heptamer. Although a larger number of hydrogen bonds provide

energetic stability, the structural constraints they impose come at a considerable entropic cost.

Although the kinetic mechanisms of water cluster formation are beyond the scope of this paper, it is possible to comment on the structural relationship between certain clusters and those of a different size. The prism conformers have been referred to as “Prism34” in the literature^{89,153,156} to make note of the 3- and 4-sided faces that form their three-dimensional shape. PR1 and PR3 can be formed from an S_4 octamer (0440) by the removal of a DDA (0010) water, and PR2 can similarly be derived from an S_4 octamer by removing a DAA (0100) water. Brudermann et al.¹⁵⁷ have combined vibrational spectroscopy data and theoretical predictions to reach the conclusion that the prism structure of the heptamer is derived by the removal of a double donor or double acceptor water from the S_4 octamer. Buch and collaborators’s analysis of the vibrational spectrum of the hexamer caused them to reach a similar conclusion.¹⁵⁶

Alternatively, the PR class of conformers (1330) can be formed from a prism hexamer (0330) by adding a DA (1000) water to one of the trimer faces. Although determining the pathway for the formation of these clusters would require a careful look at energies of reaction, entropic changes and kinetic considerations, the above-mentioned pathways appear most sensible on the basis of the hydrogen bonding topologies. Conformers PR1 and PR3 differ in the positions of the dangling hydrogens in the tetramer face; PR1 has the dangling hydrogen of its DA water pointing away from the trimer face, whereas PR3’s hydrogen is directed unfavorably toward the trimer face.

CA1 (3220) and CA2 (3220) have cage-like structures and they can both be formed by adding a DA (1000) water to the cage hexamer (2220). CH1 (5110), CH2 (5110), and CH3 (5110) can be constructed from a book hexamer (4110) precursor by the addition of a DA (1000) water to the tetramer face with unidirectional or homodromic hydrogen bonds. Once again, the orientation of the dangling hydrogens determines the relative stability of these conformers within the class. Members of conformer class BI (6001) have a unique bicyclic structure made of two cyclic tetramers sharing a DDAA bridge water. Lastly, class HM (5110) conformers are derived from a cyclic hexamer (6000) by the addition of a DA (1000) water. The orientation of the dangling hydrogen of the DA water relative to the homodromic hydrogen bonds of the cyclic hexamer gives conformer HM1 stability over HM2.

Although the conformers labeled as PR1, PR2, and CH1 have been studied in the literature and referred to as W7:Prism34(n), W7:Prism34'(n), and W7:R5, respectively^{89,153} the others are unique to the current study. We did not consider any structures whose ΔG_{298} is more than 2 kcal/mol higher than that of the ΔG_{298} global minimum structure. As a result, our study does not include the cyclic heptamer (W7:Cyclic) and W7:J structures reported in other studies.^{89,153} Lee et al.⁸⁹ used MP2/DZP with 0.50%, and 100% BSSE correction and found the prism (PR) structure to be competitive with the chair (CH) in terms of zero-point energy (ZPE) corrected electronic energies (ΔE_0), enthalpies (ΔH_{298}), and free energies (ΔG_{50}). Their MP2/TZ2P++ energies, without BSSE correction, favor the prism as the global minimum structure. Du et al.¹²⁹ started with structures from Lee et al.⁸⁹ and calculated electronic energies, enthalpies, and entropies using G3MP2. They located seven unique structures within 2.57 kcal/mol of the relative electronic energy of the chair structure. In agreement with our data, they find the chair structure to be the global minimum even though their ordering of the other structures is markedly different.

TABLE 5: MP2/CBS-e Absolute and Relative Electronic (ΔE_e and $\Delta \Delta E_e$) and Gibbs Free Energies (ΔG_{298} , $\Delta \Delta G_{298}$) for the Formation of Water Nonamers Displayed in Figure 5^a

	binding energy ^b		relative binding energy ^b	
	ΔE_e	ΔG_{298}	$\Delta \Delta E_e$	$\Delta \Delta G_{298}$
$9\text{H}_2\text{O} \rightarrow D_{2d}\text{DDh}$	-81.46	12.42	0.00	0.00
$9\text{H}_2\text{O} \rightarrow S_4\text{DAh-1}$	-81.16	12.89	0.30	0.47
$9\text{H}_2\text{O} \rightarrow S_4\text{DAh-2}$	-81.11	12.87	0.35	0.46
$9\text{H}_2\text{O} \rightarrow S_4\text{DDh-1}$	-81.00	12.96	0.46	0.54
$9\text{H}_2\text{O} \rightarrow S_4\text{DDh-2}$	-80.98	13.04	0.48	0.63
$9\text{H}_2\text{O} \rightarrow D_{2d}\text{DAh}$	-80.83	13.45	0.63	1.04
$9\text{H}_2\text{O} \rightarrow S_4\text{DAh-1}$	-80.76	13.44	0.70	1.03
$9\text{H}_2\text{O} \rightarrow S_4\text{DAh-2}$	-80.66	13.48	0.80	1.06

^a All energies in kcal/mol. ^b See eq 4 for definitions.

One of the notable features of the heptamer is that five different classes of structures are found to be within 2 kcal/mol of the ΔG_{298} minimum. Although the relative energy spectrum is sparse (13 unique structures spanning 5.69 kcal/mol in electronic energies), the free energy spectrum is significantly crowded, with all 13 structures within 2 kcal/mol of the free energy global minimum. Sadlej¹⁵⁶ studied the structure, binding, and vibrational spectrum of the water heptamers and observed that these heptamers are more strained and asymmetric than water hexamers and octamers. The asymmetry of hydrogen bonding configurations manifests itself in a complex vibrational spectrum with numerous OH peaks corresponding to different kinds of hydrogen bonds. The presence of 13 unique conformers belonging to five disparate conformer groups that are all within 2 kcal/mol of the ΔG_{298} global minimum structure are bound to complicate spectroscopic analysis of the water heptamer. The water hexamer has been studied extensively in the literature (see ref 158 for the latest) because it is the crossover point between 2D and 3D hydrogen bond networks of water. Our results clearly show that the same competition is very much in play for the heptamer. On the other hand, 3D hydrogen bonding topologies are clearly favored for the water octamer and larger clusters.

(H₂O)₉. Table 5 and Figure 5 show the low energy conformers of the nonamer and their relative conformational stability. All the nonamers have 13 hydrogen bonds with 1440 topology, and

they can be formed by adding a DA water to either the D_{2d} (0440) or S_4 (0440) octamers. The labels DD and DA are used in the literature to indicate that the extra water monomer donates a hydrogen bond to either a DD or DA water, respectively, in the D_{2d} or S_4 octamer. Since that water could be added to a face with either a homodromic or non-homodromic hydrogen bonds, the resulting structures are distinguished by adding an "h" or "nh" to the structure labels. All but the $S_4\text{DAh-1}$ and $S_4\text{DAh-2}$ have homodromic cyclic pentamer and S_4 tetramers stacked on top of each other. The way they stack and the orientation of the DA water relative to the homodromic faces determines the energetic stability of the clusters. Clearly, the presence of the homodromic faces is favorable, as the first six lowest energy conformers have that feature.

Just like the D_{2d} octamer, the $D_{2d}\text{DDh}$ is stabilized by the opposite helicities of the two homodromic hydrogen bond rings and it is the global minimum conformer. When forming a nonamer from a D_{2d} octamer, it is more favorable for the DA water to donate a hydrogen bond to a DD water, as can be seen in the energy difference between the $D_{2d}\text{DDh}$ and $D_{2d}\text{DAh}$. On the contrary, when forming a nonamer from an S_4 octamer, the structures where the added DA water donates to a DA water are more stable. This is revealed by the 0.1–0.2 kcal/mol difference in ΔE_e and ΔG_{298} between the $S_4\text{DAh}$ and $S_4\text{DDh}$ structures.

$S_4\text{DAh-1}$ and $S_4\text{DAh-2}$ differ in that the dangling hydrogen of the DA water in the homodromic pentagonal ring is parallel to the ring in the case of the $S_4\text{DAh-1}$ isomer and perpendicular for $S_4\text{DAh-2}$. Similarly, $S_4\text{DDh-1}$ and $S_4\text{DDh-2}$ differ only in the orientation of the dangling hydrogen of the DA water. Otherwise, both pairs of structures are enantiomers. The energetic and entropic impact of this difference is apparently very small.

The most stable structure at 0 K as well as 298 K is the $D_{2d}\text{DDh}$ conformer. Since all the conformers have the same number of hydrogen bonds and similar shapes and types of water monomers, their ordering by electronic (ΔE_e) and Gibbs free energy (ΔG_{298}) is very similar. Lee et al.,⁸⁹ Sadlej et al.,¹⁵⁶ and Du et al.¹²⁹ all find the $D_{2d}\text{DDh}$ conformer to be the global minimum structure with $S_4\text{DD}$ and $S_4\text{DA}$ within 1 kcal/mol both in terms of electronic and Gibbs free energy. Figure 6 shows the relative Gibbs free energy as a function of temperature for

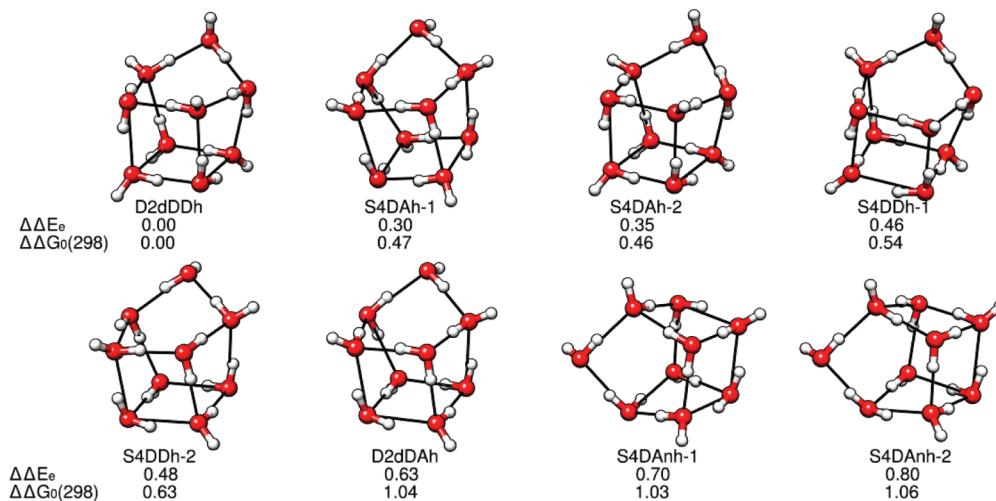


Figure 5. Relative electronic ($\Delta \Delta E_e$) and Gibbs free energies ($\Delta \Delta G_{298}$) for the formation of water nonamers calculated using MP2/CBS-e. The nonamers are formed by adding a DA water to a D_{2d} or S_4 octamer. The DD or DA labels indicate that the added monomer donates a hydrogen bond to a DD or DA water. The "h" or "nh" label indicates that the monomer is added to a homodromic or non-homodromic face. To facilitate comparison, the structures are oriented such that the homodromic faces are on the top and bottom.

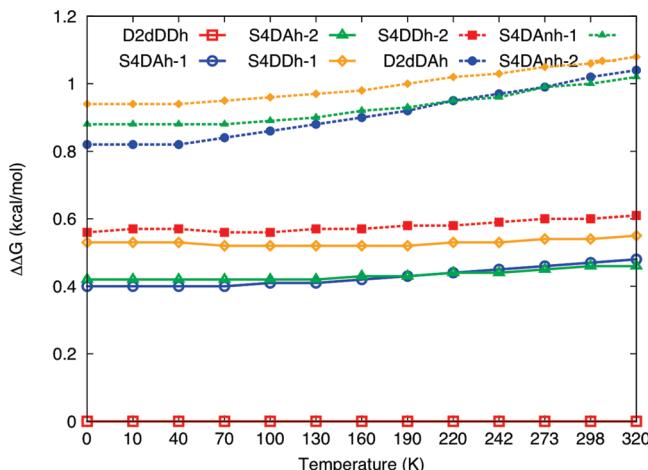


Figure 6. Relative Gibbs free energies of the water nonamer conformers as a function of temperature.

the nonamer conformers. Unlike the case of the water heptamer, ZPE corrections and entropic effects do not change the relative ordering of the conformers and the D_{2d} DDh structure is predicted to be the most stable nonamer at atmospherically relevant temperatures. All the low energy conformers of the nonamer have a stacked pentamer-tetramer shape, and all other motifs were found to be at least 3 kcal/mol higher in electronic and Gibbs free energy than the D_{2d} DDh minimum. Although the absence of other motifs may look peculiar, the water octamer,

(H_2O)₈, also displays similar behavior. A G3 study of 18 cubic (including the D_{2d} and S_4) and noncubic conformers found the D_{2d} and S_4 structures to be the most stable and all other conformers to be at least 2.81 and 1.13 kcal/mol higher in electronic and Gibbs free energy, respectively.⁹⁸

(H_2O)₁₀. The water decamer highlights the importance of performing a thorough sampling of the conformational space of water clusters. With more than 2000 possible hydrogen bonding topologies,¹³⁵ it is easy to miss important, low energy conformers of the decamer unless one performs reliable sampling. We extracted 300 structures from a 10 ns molecular dynamics simulation and performed MP2/6-31G* optimizations on each. A total of 183 of those structures converged to local minima in 200 optimization cycles, and our subsequent analysis yielded 30 unique conformations that were within 2 kcal/mol of the MP2/CBS-e global Gibbs free energy minimum structure. These 30 structures do not include any enantiomers.

The 30 conformers shown in Figure 7 can be categorized as four main classes based on the shape of their hydrogen bonding network. These four shapes are pentagonal prism (PP), open box (OB), distorted prism (DP), and cage (C). The conformer classes are unique not only in terms of their shape, but also in the types of waters involved in the hydrogen bonding networks. Table 6 shows the donor–acceptor nature of the waters involved in the different conformer classes. The pentagonal prism conformers only have three-coordinated waters with 5 DAA and 5 DDA waters in each cluster accounting for their 15 hydrogen bonds whereas the open box conformers also have 15 hydrogen

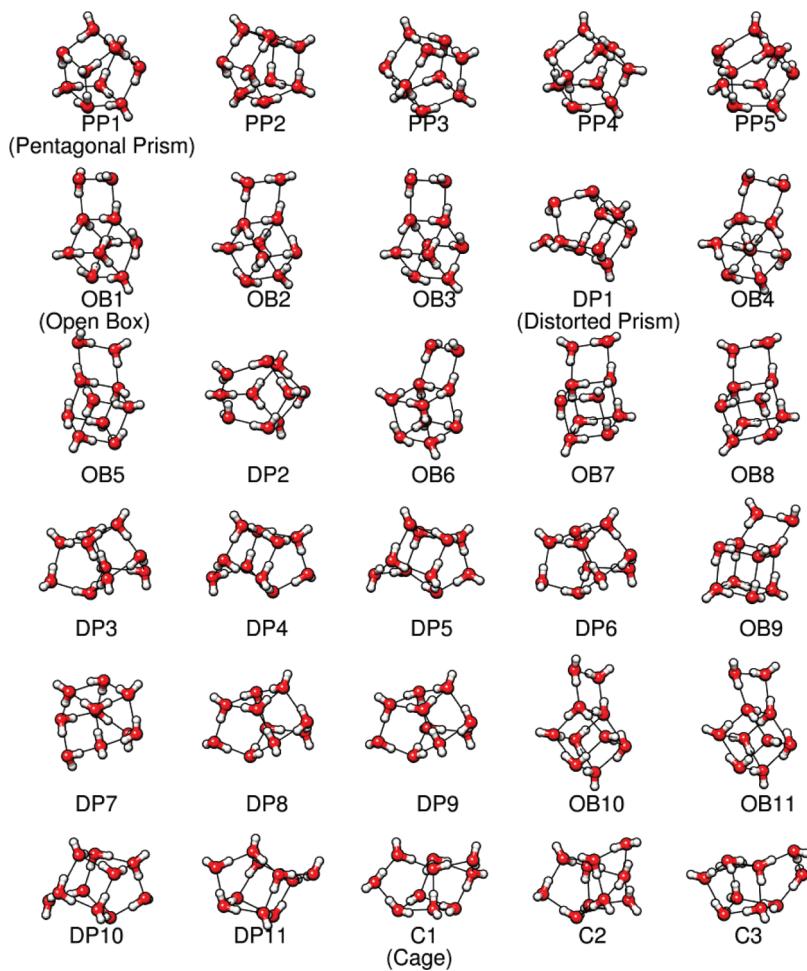


Figure 7. Structures for (H_2O)₁₀ that are within 2 kcal/mol of the MP2/CBS-e $\Delta\Delta G_{298}$ global minimum structure. The structures are ordered by increasing relative electronic energy ($\Delta\Delta E_e$). See Table 7 for energies.

TABLE 6: Types of Water Molecules (DA, DAA, DDA, DDAA) and Total Number of Hydrogen Bonds [n(HB)] in the Four Main Conformer Groups of $(H_2O)_{10}$

	DA	DAA	DDA	DDAA	HB topology	n(HB)
PP	0	5	5	0	0550	15
OB	2	3	3	2	2332	15
DP	2	4	4	0	2440	14
C	3	3	3	1	3331	14

TABLE 7: The MP2/CBS-e Absolute and Relative Electronic (ΔE_e , $\Delta\Delta E_e$) and Gibbs Free Energies (ΔG_{298} , $\Delta\Delta G_{298}$) for the Formation of Water Decamers Displayed in Figure 7^a

	binding energy ^b		relative binding energy ^b	
	ΔE_e	ΔG_{298}	$\Delta\Delta E_e$	$\Delta\Delta G_{298}$
$10H_2O \rightarrow PP1$	-92.90	13.78	0.00	0.00
$10H_2O \rightarrow PP2$	-92.77	13.84	0.13	0.06
$10H_2O \rightarrow PP3$	-92.19	14.74	0.71	0.96
$10H_2O \rightarrow PP4$	-92.12	14.75	0.78	0.96
$10H_2O \rightarrow PP5$	-92.07	14.83	0.83	1.04
$10H_2O \rightarrow OB1$	-91.24	14.95	1.66	1.17
$10H_2O \rightarrow OB2$	-91.09	15.08	1.81	1.30
$10H_2O \rightarrow DP1$	-91.08	15.10	1.82	1.31
$10H_2O \rightarrow OB3$	-90.78	15.12	2.12	1.34
$10H_2O \rightarrow OB4$	-90.72	15.61	2.17	1.83
$10H_2O \rightarrow OB5$	-90.71	15.00	2.18	1.22
$10H_2O \rightarrow DP2$	-90.67	15.18	2.23	1.39
$10H_2O \rightarrow OB6$	-90.64	15.60	2.26	1.81
$10H_2O \rightarrow OB7$	-90.54	15.68	2.35	1.90
$10H_2O \rightarrow OB8$	-90.52	15.74	2.38	1.96
$10H_2O \rightarrow DP3$	-90.32	13.96	2.58	0.18
$10H_2O \rightarrow DP4$	-90.14	13.99	2.76	0.21
$10H_2O \rightarrow DP5$	-90.04	14.28	2.86	0.50
$10H_2O \rightarrow DP6$	-89.94	14.42	2.95	0.64
$10H_2O \rightarrow OB9$	-89.80	15.54	3.09	1.76
$10H_2O \rightarrow DP7$	-89.79	14.44	3.11	0.66
$10H_2O \rightarrow DP8$	-89.69	15.24	3.21	1.46
$10H_2O \rightarrow DP9$	-89.69	14.62	3.21	0.84
$10H_2O \rightarrow OB10$	-89.67	15.46	3.23	1.67
$10H_2O \rightarrow OB11$	-89.62	15.26	3.28	1.48
$10H_2O \rightarrow DP10$	-89.62	14.71	3.28	0.92
$10H_2O \rightarrow DP11$	-89.50	14.84	3.40	1.06
$10H_2O \rightarrow C1$	-88.48	15.22	4.42	1.44
$10H_2O \rightarrow C2$	-88.48	15.13	4.42	1.34
$10H_2O \rightarrow C3$	-88.43	14.40	4.47	0.62

^a All energies are in kcal/mol. ^b See eq 4 for definitions.

bonds, but between 2 DA, 3 DAA, 3 DDA, and 2 DDAA water molecules. The distorted prism structures have 14 hydrogen bonds between 2 DA, 4 DAA, and 4 DDA molecules whereas the cage structures have 3 DA, 3 DAA, 3 DDA, and 1 DDAA waters bound by 14 hydrogen bonds.

The structures in Figure 7 are sorted by increasing MP2/CBS-e relative electronic energy, ΔE_e , and their binding (ΔE_e , ΔG_{298}) and conformational ($\Delta\Delta E_e$, $\Delta\Delta G_{298}$) energies are given in Table 7. The E_e and G_{298} global minimum structure for the water decamer is conformer PP1, which is composed of two stacked pentagonal faces. The two faces have homodromic hydrogen bonds, which typically have stabilizing effects in smaller cyclic water clusters. What distinguishes PP1 from PP2, the next lowest energy structure, is that for PP1 the homodromic hydrogen bonds within its two pentagonal faces circle in opposite directions, while they rotate in the same direction in PP2. The pentagonal faces of PP3–PP5 lack homodromic hydrogen bonds and they lie at least 0.5 kcal/mol higher in electronic conformational energy ($\Delta\Delta E_e$) relative to PP1.

The conformers with the most number of hydrogen bonds are expected to be energetically favorable, and that is indeed

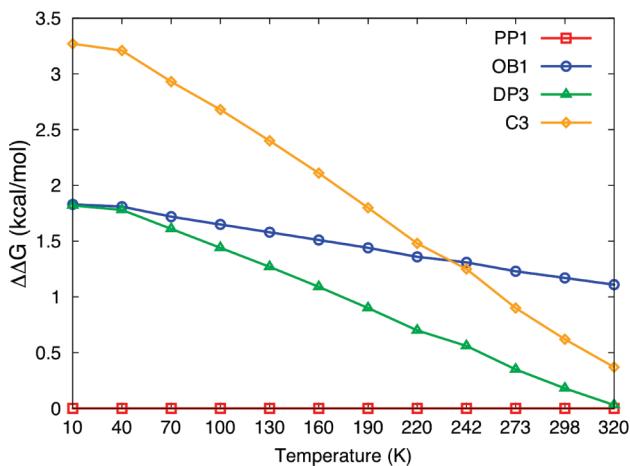


Figure 8. Relative Gibbs free energy of the water decamer conformers as a function of temperature. These four conformers have the lowest Gibbs free energy within their conformer classes at 298 K.

what we observe. The lowest energy conformers are the PP and OB structures with 15 hydrogen bonds each. The DP and C conformers have 14 hydrogen bonds each, and their electronic energy lies more than 1.8 kcal/mol higher than that of the PP conformers. The conformers with more hydrogen bonds, however, are more strained and less entropically favorable. Although the PP and OB conformers remain the more stable structures at 298 K, the more disordered DP and C conformer classes benefit from entropic effects, and their conformational Gibbs free energy at 298 K ($\Delta\Delta G_{298}$) is well below 2 kcal/mol of the PP global minimum. Figure 8 shows the conformational Gibbs free energy of the lowest G_{298} structures of each conformer class as a function of temperature. At all atmospherically relevant temperatures, the PP1 conformer remains the global minimum structure. Past 273 K, some of the DP and C conformers are within 1 kcal/mol of the PP1 global minimum, and they may be observed experimentally. At temperatures above 320 K, the DP3 and C3 conformers are favored over the PP1 conformer by virtue of entropic effects.

There have been a few studies of some prominent conformers of the water decamer, namely the pentagonal prism and the butterfly structures, although no comprehensive study of the quantum chemical conformational space of the decamer has been reported. Du et al.¹²⁹ used the G3MP2 model chemistry on five conformers they found from the literature.^{159,160} They found the G_{298} global minimum to be a butterfly (C_2) structure, with a prism (our PP1), butterfly (C_s) and prism' (our PP2) all being within 0.09 kcal/mol of the global minimum butterfly (C_2) structure. An open box conformer they call B1, which is equivalent to our OB2 conformer, is the fifth structure they consider, and it lies 1.27 kcal/mol higher in free energy at 298 K. Deficiencies of the G3 method for as cluster size increases has been discussed earlier (Table 1). The counterpoise corrected MP2/DZ1P binding energy calculations of Sadlej et al.¹⁵⁶ revealed that pentagonal prism structures like D_{opp} (our PP1) and D_{same} (our PP2) are the most stable structures. A butterfly conformer (D_{bif}) in their study is only 1 kcal/mol higher in energy despite the fact that it has one less hydrogen bond than the pentagonal prism conformers D_{opp} (our PP1) and D_{same} (our PP2). Su et al.¹²² have benchmarked the ability of the X3LYP functional to predict structures and binding energies of water clusters including $(H_2O)_{10}$. Their X3LYP/aug-cc-pVTZ(-f) calculations on two pentagonal prism (PP1 and PP2) and one butterfly structure predicted that the pentagonal prisms are nearly isoenergetic with each other and more stable than the butterfly

TABLE 8: Total (top) and Stepwise (bottom) Changes in E_e , E_0 , H_{298} , G_{10} , and G_{298} for the Formation of an $(\text{H}_2\text{O})_n$ Cluster from n Water Monomers^a

$n(\text{H}_2\text{O})$	ΔE_e^b	ΔE_0^c	ΔH_{298}^d	ΔG_{10}^d	ΔG_{200}^d	ΔG_{298}^d
$n(\text{H}_2\text{O}) \rightarrow (\text{H}_2\text{O})_n$						
2	-4.82	-2.59	-3.06	-2.61	0.91	2.89
3	-14.92	-8.65	-10.55	-8.62	0.80	6.59
4	-26.83	-17.78	-20.55	-17.68	-2.77	5.99
5	-35.35	-24.2	-27.56	-24.03	-4.66	6.60
6	-45.31	-30.27	-34.67	-30.01	-4.83	9.51
7	-56.69	-38.24	-43.99	-38.26	-5.87	12.85
8	-72.27	-50.44	-57.56	-49.99	-11.17	11.53
9	-81.46	-57.54	-64.83	-57.00	-12.77	12.86
10	-92.90	-65.94	-74.11	-65.31	-14.87	14.36
$\text{H}_2\text{O} + (\text{H}_2\text{O})_{n-1} \rightarrow (\text{H}_2\text{O})_n$						
2	-4.82	-2.59	-3.06	-2.61	0.91	2.89
3	-10.1	-6.06	-7.50	-6.01	-0.11	3.70
4	-11.91	-9.13	-10.00	-9.06	-3.57	-0.60
5	-8.52	-6.43	-7.00	-6.35	-1.89	0.61
6	-9.96	-6.06	-7.11	-5.98	-0.17	2.91
7	-11.38	-7.97	-9.33	-8.25	-1.04	3.33
8	-15.58	-12.2	-13.57	-11.73	-5.30	-1.32
9	-9.18	-7.10	-7.27	-7.01	-1.59	1.33
10	-11.44	-8.40	-9.27	-8.31	-2.10	1.50

^a All energies are in kcal/mol. ^b ΔE_e for the global minimum structure. ^c ΔE_0 for the global minimum structure. ^d ΔH_{298} , ΔG_{10} , ΔG_{200} , and ΔG_{298} are all Boltzmann averaged over low energy conformers.

by at least 5 kcal/mol in terms of BSSE- and ZPE- corrected and uncorrected binding energies, as well as with Gibbs free energies at 50 K. Kim and co-workers⁸⁹ have performed a similar investigation of two pentagonal prism (Prism5 = PP1, Prism5'' = PP2) and one butterfly (Bfly(pn)) structure of the water decamer using MP2/DZP and MP2/TZ2P+++/MP2(FC)/TZ2P levels of theory. Their calculated binding energies, both including and excluding BSSE and ZPE corrections, indicate that the pentagonal prism structures are more stable than the butterfly structure by at least 1 kcal/mol up to temperatures of 50 K. Previous lower level studies of water clusters that include the decamer can also be found in the literature.^{137,159,161,162}

The four works discussed above all include the butterfly structure in their study of the water decamer, but no such structure appears in the 30 lowest energy conformers we report here. The Gibbs free energy (G_{298}) for the lowest butterfly structure is not within 2 kcal/mol of the global minimum conformer. We do find butterfly like structures in our conformational search, but they are more than 2 kcal/mol higher than the global minimum in free energy at 298 K. A thorough conformational sampling clearly indicates that there are many conformers that are much more energetically accessible than the butterfly that have not been published previously. Future work on water clusters where $n > 10$ would benefit substantially from comprehensive, quantum mechanical, conformational sampling.

Thermodynamics of Cluster Growth. To understand how these water clusters grow, it is necessary to examine energies associated with the formation of these clusters. The presence and concentration of water clusters at ambient temperatures in the atmosphere, as well as low-temperature ultrahigh vacuum experiments, depends on the free energy of formation of the clusters under the given conditions. Our comprehensive and systematic study provides reliable data about the thermodynamics of water cluster formation. The top part of Table 8 contains the total change in E_e , E_0 , H_{298} , G_{10} , G_{200} , and G_{298} as a result of the formation of water clusters from individual monomers.

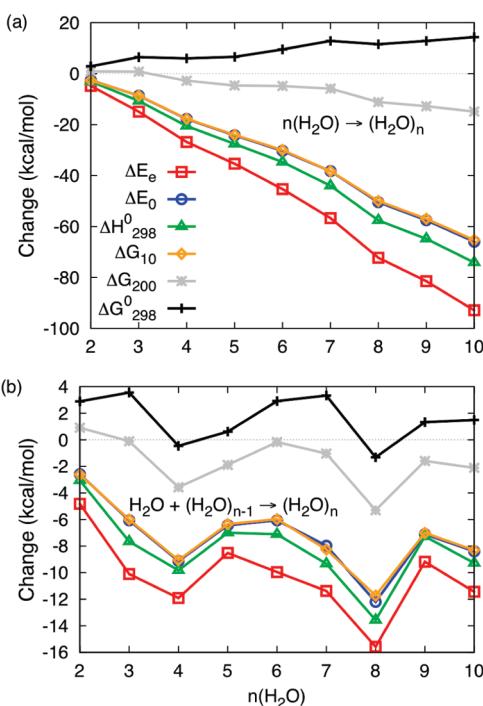


Figure 9. MP2/CBS-e total (a) and stepwise(b) energy changes associated with the formation of small water clusters. ΔE_e and ΔE_0 correspond to the global minima, and ΔH_{298} , ΔG_{10} , ΔG_{200} and ΔG_{298} are Boltzmann averaged over the low energy structures of each cluster.

The bottom of Table 8 lists the changes associated with growing water clusters by adding one water monomer to smaller clusters. Figure 9 shows the trends graphically. ΔE_e and ΔE_0 correspond to the electronic and ZPE-corrected binding energies of the global minimum structures. While the E_e global minimum structures are typically E_0 global minimum structures as well, they correspond to different structures for the case of $(\text{H}_2\text{O})_6$ where the prism and the book are the E_e and E_0 global minimum structures, respectively. The ΔH_{298} , ΔG_{10} , ΔG_{200} and ΔG_{298} values have been Boltzmann averaged over all the low energy structures of a given cluster size. E_e , E_0 , and G_{10} should be relevant for low temperature analysis, and the ΔH_{298} , ΔG_{200} and ΔG_{298} would be pertinent to water cluster growth at ambient temperatures.

Looking at Figure 9a, it is clear from the difference between the ΔE_e and ΔE_0 lines that the ZPE correction to the electronic energy is significant. As a percentage of ΔE_e , this correction ranges from 29% for $(\text{H}_2\text{O})_{10}$ to 46% for $(\text{H}_2\text{O})_2$. The thermal correction due to the population of vibrational and rotational modes is comparatively small up to 298 K. The difference between the ΔH_{298} and ΔE_0 trendlines can be attributed to thermal corrections. The significant overlap between ΔE_0 and ΔG_{10} results from negligible thermal and entropic corrections at 10 K. At higher temperatures, entropic effects become large and shift the ΔG line upward. The trends in ΔE_e , ΔE_0 , and ΔG_{10} indicate that the growth of water clusters is thermodynamically favorable at low temperatures, whereas ΔG_{298} points to an unfavorable process under standard state conditions at room temperature.

The changes due to the addition of a water monomer to a cluster of size $n-1$ to form a cluster of size n are shown in Figure 9b. The trends again point to a favorable stepwise growth of water clusters at low temperatures, but typically not at ambient temperatures. $(\text{H}_2\text{O})_4$ and $(\text{H}_2\text{O})_8$, however, have negative ΔG_{298}

values, indicating that they can be easily formed from $(\text{H}_2\text{O})_3$ and $(\text{H}_2\text{O})_7$ under standard state conditions.

Conclusions

For $(\text{H}_2\text{O})_n$ where $n = 7, 9$, and 10 , we have used a scheme combining molecular dynamics (MD) sampling with MP2 calculations to locate the global and many low lying local minima for each cluster. We estimate the MP2/CBS binding energy of these clusters using a scaled combination of the counterpoise corrected and uncorrected MP2 binding energies employing a modest basis, which we have called a MP2/CBS-e model chemistry. Comparison of MP2/CBS benchmark calculations for $(\text{H}_2\text{O})_n$ where $n = 2–6$ and 8 , which have been studied in great detail, reveals that the MP2/CBS-e procedure is efficient and accurate. This procedure combining MD simulations with MP2/CBS-e structures and energies allowed us to perform an exhaustive conformational sampling of the less-studied water heptamer, nonamer, and decamer. Our conformational search yielded many low energy conformers that have not previously been identified. The water heptamer has low energy conformers with five different structural motifs ranging from a 3D prism to a quasi-planar book structure. The prism structure is favored energetically at low temperatures, but the book structure is the global Gibbs free energy minimum past 200 K because of entropic effects. The water nonamers exhibit less complexity with all the low energy structures shaped like a prism. In contrast, we found 30 conformers for the decamer that are within 2 kcal/mol of the Gibbs free energy minimum structure at 298 K . These structures are categorized into four conformer classes based on their shapes, and the pentagonal prism is the most stable structure up to 320 K . The method outlined in this paper can be used as a benchmark method for comparing the ability of conformational search methods, empirical water potentials, and improved density functionals to adequately describe water clusters.

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Supporting Information Available: MP2/6-31G* optimized structures, counterpoise corrected and uncorrected MP2/aug-cc-pVDZ//MP2/6-31G* electronic energies, enthalpies and free energies for all the clusters reported in this paper, and a figure comparing ΔE_e and ΔG_{298} per water as well as per number of hydrogen bonds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information for:

Accurate Predictions of Water Cluster Formation, $(H_2O)_{n=2-10}$

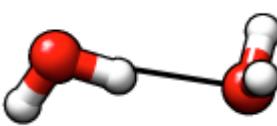
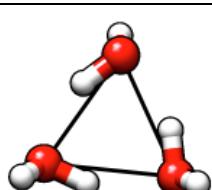
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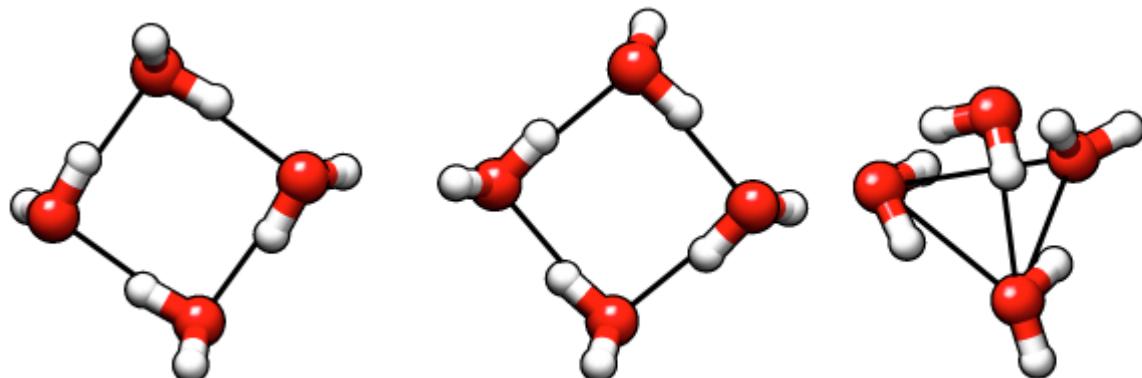
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Procedure for calculating estimates of E_{CBS} and G_{CBS}	<p>(A) For $(H_2O)_{n=2-6,8}$, start with structures from our previous papers-</p> <ol style="list-style-type: none"> (1) Day, M. B., Kirschner, K. N., & Shields, G. C. (2005). Pople's Gaussian-3 model chemistry applied to an investigation of $(H_2O)_8$ water clusters. <i>INT J QUANTUM CHEM.</i>, 102, 565–572. (2) Dunn, M. E., Evans, T. M., Kirschner, K. N., & Shields, G. C. (2006). Prediction of accurate anharmonic experimental vibrational frequencies for water clusters, $(H_2O)_n$, n=2-5. <i>Journal Of Physical Chemistry A</i>, 110(1), 303–309. (3) Dunn, M. E., Pokon, E. K., & Shields, G. C. (2004). <i>The ability of the Gaussian-2, Gaussian-3, Complete Basis Set-QB3, and Complete Basis Set-APNO model chemistries to model the geometries of small water clusters</i> (Vol. 100). (4) Dunn, M. E., Pokon, E. K., & Shields, G. C. (2004). Thermodynamics of forming water clusters at various temperatures and pressures by gaussian-2, gaussian-3, complete basis set-QB3, and complete basis Set-APNO model chemistries; Implications for atmospheric chemistry. <i>J. Am. Chem. Soc.</i>, 126(8), 2647–2653. (5) Kirschner, K., & Shields, G. (1994). <i>Quantum-Mechanical Investigation Of Large Water Clusters</i>. (6) Shields, G. C., & Kirschner, K. N. (2008). The limitations of certain density functionals in modeling neutral water clusters. <i>Synthesis And Reactivity In Inorganic Metal-Organic And Nano-Metal Chemistry</i>, 38(1), 32–36. <p>(B) For $(H_2O)_{n=7,9,10}$, structures were computed using the procedure outlines below (1)-(3)</p> <ol style="list-style-type: none"> (1) Run a constant volume minimization on TIP4P waters (2) Using the minimized structure, heat the system from 5 K to the reference temperature (250 K for $n=7,9$ and 200 K for $n=10$) in 1 ns time. (3) Run a constant temperature gas phase MD simulation for 10 ns and pick out about 200-300 structures at regular intervals along the trajectory (4) Perform MP2/6-31G* geometry optimization on those 200-300 structures <p>(E) For all the structures that converged to a local minimum within 200 optimization cycles, MP2/6-31G* frequency calculations and MP2/aug-cc-pVDZ//MP2/6-31G* single point energies were performed</p> <p>(F) Frequencies were scaled by 0.9676 before computing thermodynamic quantities like G, H, S</p> <p>(G) Counterpoise correction was performed on the optimized structures at MP2/aug-cc-pVDZ//MP2/6-31G*</p> <p>(H) The MP2/CBS electronic energies are approximated by summing the scaled counterpoise corrected and uncorrected energies:</p> $E_{MP2/CBS} = 0.67 * E_{MP2/aug-cc-pVDZ//MP2/6-31G^*} + 0.33 * E_{MP2/aug-cc-pVDZ//MP2/6-31G^*}^{CP}$ <p>(I) $G_{MP2/CBS}(298) = E_{MP2/CBS} + G_{corr}(298)[MP2/6-31G^* \text{ freqs scaled by } 0.9676]$</p>
Sorting of structures	The structures are sorted by their electronic energy E_e

All clusters are optimized using MP2/6-31G*

H2O	3 H2O H -0.584628 -1.061660 -0.130984 O -1.464518 -0.657805 -0.097603 H -1.860489 -1.025949 0.706191	
(H2O)2	6 (H2O)2 H -0.586116 -0.853488 0.212116 O -1.483751 -0.596919 0.493801 H -2.056167 -1.275768 0.109314 O 1.339429 -0.992624 -0.116698 H 1.512052 -0.105163 -0.470219 H 1.667025 -0.953220 0.796259	
(H2O)3	9 (H2O)3 min H -0.578400 -1.061891 -0.138056 O -1.472126 -0.652686 -0.093810 H -1.873835 -1.017331 0.709277 O 1.311636 -0.934602 -0.102722 H 1.196451 0.042157 -0.061379 H 1.788313 -1.158405 0.710917 O 0.160256 1.595763 0.119018 H -0.631715 1.011392 0.096164 H 0.101062 2.116272 -0.696804	

(H ₂ O) ₄		
.....
Cyclic_S₄	Cyclic_C_i	Pyramid
.....
12	12	12
(H ₂ O) ₄ S ₄	(H ₂ O) ₄ C _i	(H ₂ O) ₄ Pyramid
H -0.215184 -2.447418 -0.780809	H 2.358989 -0.787453 0.701556	H 1.42013 0.25452 0.03907
O -0.088111 -1.942280 0.036669	O 1.881106 -0.522682 -0.098825	O 1.52873 -0.54195 0.60383
H 1.296949 -0.839555 -0.048259	H 1.108548 1.065104 0.067233	H -0.42463 0.13759 1.67595
H -0.839555 -1.296909 0.048201	H 1.093587 -1.121253 -0.134636	H 2.47959 -0.72719 0.62870
O 1.942324 -0.088119 -0.036643	O 0.530304 1.867973 0.103410	O -1.21580 0.43500 1.19216
H 2.447394 -0.215239 0.780870	H 0.774125 2.375877 -0.685053	H -1.38248 -0.32360 0.58693
H 0.839599 1.296924 0.048317	H -1.093649 1.121355 0.134711	H -0.38249 1.30473 -0.13690
O 0.088155 1.942293 0.036731	O -1.881168 0.522785 0.098912	O 0.25974 1.39821 -0.88659
H 0.215288 2.447428 -0.780739	H -2.359075 0.787570 -0.701450	H 0.31581 2.34668 -1.07760
H -1.296889 0.839569 -0.048294	H -1.108614 -1.065002 -0.067165	H -0.62077 -0.64377 -1.48032
O -1.942268 0.088134 -0.036716	O -0.530367 -1.867868 -0.103341	O -0.76226 -1.39889 -0.88241
H -2.447334 0.215215 0.780806	H -0.774192 -2.375776 0.685118	H 0.11147 -1.48793 -0.45172



kcal/mol	S₄	C_i	Pyramid
$\Delta\Delta E_e$	0.00	0.97	4.19
$\Delta\Delta G_{298}$	0.00	0.33	4.71

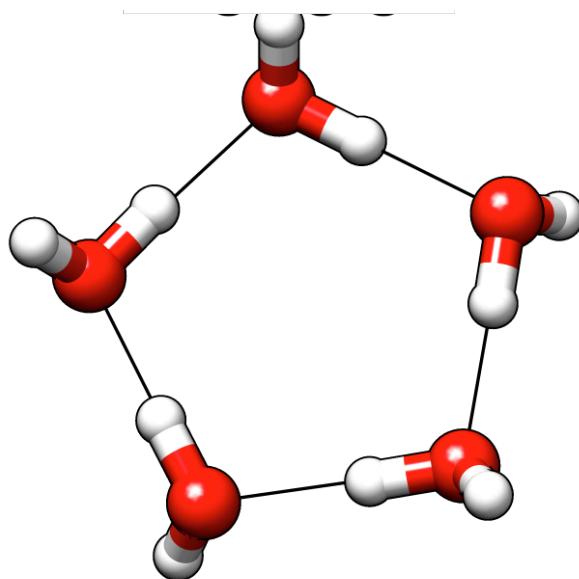
(H₂O)5

.....
Cyclic
.....

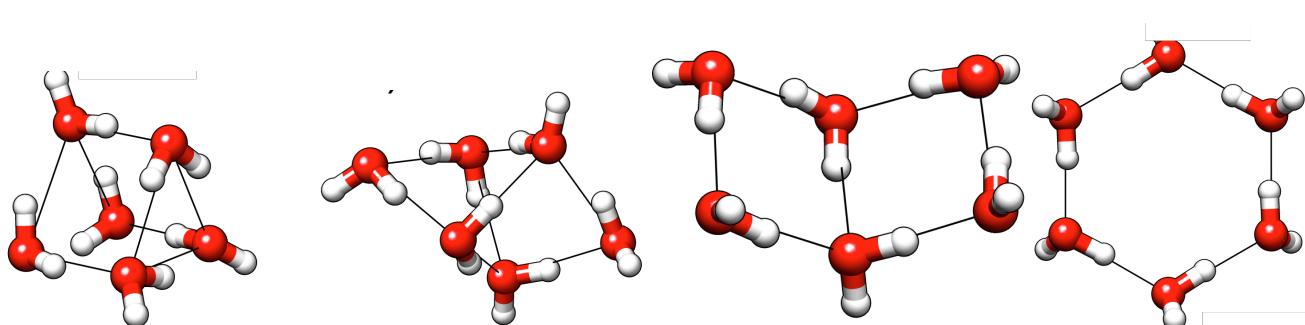
15

(H₂O)5 Cyclic

H	-0.976098	-1.670678	0.027772
H	2.586991	-1.244628	0.797861
O	-0.221668	-2.313473	0.011992
O	-2.287920	-0.513039	-0.033895
H	-1.935308	0.411273	-0.085374
H	-2.825368	-0.529412	0.771884
O	-1.178836	2.005715	-0.091977
H	-1.377787	2.606032	0.641794
H	-0.191861	1.916016	-0.073380
O	1.547425	1.742939	0.048267
H	1.781909	0.779735	0.069448
H	1.978262	2.074232	-0.754271
O	2.143835	-0.930610	-0.004691
H	1.297223	-1.445873	-0.034637
H	-0.361330	-2.824381	-0.799654

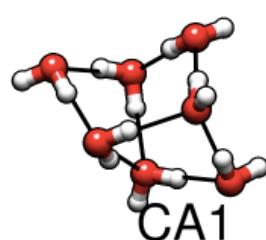
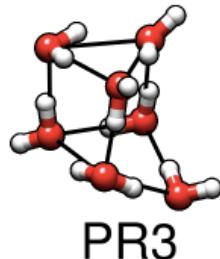
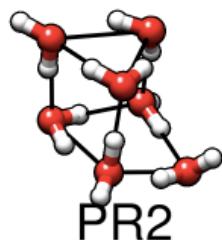
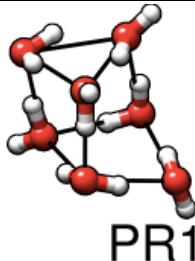


(H ₂ O) ₆			
Prism	Cage	Book	Cyclic
18 (H ₂ O) ₆ Prism	18 (H ₂ O) ₆ Cage	18 (H ₂ O) ₆ Book	18 (H ₂ O) ₆ Cyclic
H 0.309536 -1.159959 -1.486115	H 0.081314 1.347845 -0.551623	O 0.097619 1.521194 0.802041	H -0.834068 2.203626 0.038578
O 1.264770 -1.252931 -1.296357	O 0.613510 1.714078 0.218533	H 0.949600 1.485530 0.283055	O 0.000000 2.738219 0.012580
H 1.577796 -0.328064 -1.245346	H 0.482781 2.674855 0.199296	H 0.285574 2.088806 1.565481	H -0.096011 3.286402 -0.780636
H -0.411599 -0.636609 1.537713	H 2.186936 0.830805 0.082696	O -0.024281 -1.368435 0.966542	H 1.491362 1.824138 -0.038578
O -1.392180 -0.435272 1.437638	H -1.639935 0.281889 -1.203574	H -0.035941 -0.402608 1.119240	O -2.371367 1.369109 -0.012580
H -1.821502 -0.813170 2.220478	O 2.808121 0.064146 0.063357	H -0.846547 -1.527555 0.447204	H -2.894113 1.560054 0.780636
H 1.315144 -1.326990 0.564354	H 1.617352 -1.166100 -0.347092	O -2.414823 1.408560 -0.429428	H -2.325431 0.379489 -0.038578
O 1.230399 -0.906025 1.454297	H 3.105077 -0.025611 0.982509	H -1.543240 1.556314 0.002600	O -2.371367 -1.369109 0.012580
H 1.604730 -0.021176 1.267712	O 0.783718 -1.686753 -0.485619	H -2.326976 1.804713 -1.309445	H -1.491362 -1.824138 0.038578
H -2.274801 -1.208588 -1.706207	H 1.065052 -2.577484 -0.745110	O -2.439433 -1.379963 -0.460475	H -2.798103 -1.726349 -0.780636
O -1.573411 -0.687640 -1.285968	H -0.309679 -0.439408 -1.525273	H -2.523275 -0.398938 -0.519010	O 0.000000 -2.738219 -0.012580
H -1.672632 -0.821585 -0.313260	H -0.187540 -1.061849 1.089745	H -3.169518 -1.650235 0.116905	H 0.096011 -3.286402 0.780636
H -1.348407 1.296444 -0.870739	O -0.773053 0.412919 -1.656671	O 2.447931 1.201195 -0.478763	H 0.834068 -2.203626 -0.038578
O -1.039904 1.883283 -0.153048	O -0.635075 -0.432660 1.691415	H 2.513025 0.207382 -0.462470	O 2.371367 -1.369109 0.012580
H -1.300655 1.373540 0.640861	H -2.196098 -0.170093 0.825641	H 2.485430 1.428749 -1.420366	H 2.325431 -0.379489 0.038578
H 0.703688 1.662763 -0.180816	H -0.212797 0.421044 1.465771	O 2.284985 -1.500412 -0.440607	H 2.894113 -1.560054 -0.780636
O 1.653545 1.373906 -0.171756	O -2.868179 0.011416 0.122824	H 1.404581 -1.570840 0.021607	O 2.371367 1.369109 -0.012580
H 2.172957 2.180820 -0.30709	H -3.424800 -0.781068 0.096296	H 2.898070 -1.983600 0.133950	H 2.798103 1.726349 0.78063



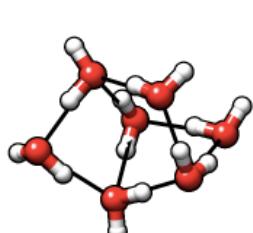
kcal/mol	Prism	Cage	Book	Cyclic
$\Delta\Delta E_e$	0.00	0.33	0.64	1.69
$\Delta\Delta G_{298}$	3.32	2.67	1.00	0.00

(H ₂ O)7			
PR1 21 (H ₂ O)7 O 1.06787 -1.28330 -1.37572 H 0.27791 -1.57300 -0.81931 H 1.15306 -1.94906 -2.07538 O 2.49959 -0.01306 0.68281 H 2.29739 -0.70908 0.02282 H 2.36350 0.79769 0.15480 O 0.17841 -0.10120 2.09939 H 1.08124 -0.07317 1.67877 H 0.33430 -0.12984 3.05597 O -0.96928 -1.89342 0.20844 H -0.68931 -1.43736 1.02954 H -1.72056 -1.34438 -0.12579 O -1.12665 1.83827 0.45089 H -0.38918 1.89512 -0.19143 H -0.74965 1.30171 1.17894 O -2.78118 -0.01454 -0.69667 H -3.64707 0.04766 -0.26606 H -2.25956 0.74455 -0.32592 O 1.10089 1.46310 -1.31893 H 1.21090 1.94781 -2.15132 H 0.97985 0.51457 -1.56719	PR2 21 (H ₂ O)7 O -0.89266 -1.32371 -1.56888 H -1.66877 -1.23566 -0.98035 H -0.19582 -1.67661 -0.97864 O -0.99568 1.43708 -1.31198 H -0.80477 0.52401 -1.63946 H -1.79559 1.26546 -0.77399 O -0.38948 -0.13655 2.03597 H 0.14703 -0.85943 1.64685 H 0.08782 0.67055 1.75197 O 2.77936 0.11651 -0.49567 H 2.25513 0.86808 -0.12776 H 2.70922 0.21751 -1.45807 O 0.90743 1.88521 0.49034 H 1.01138 2.83921 0.63138 H 0.19057 1.78571 -0.20955 O 1.14088 -1.87088 0.37354 H 1.82475 -1.22444 0.05243 H 1.62318 -2.68437 0.58759 O -2.56970 -0.12191 0.41351 H -1.83569 -0.13455 1.08684 H -3.38959 -0.24148 0.9160	PR3 21 (H ₂ O)7 O -0.96140 -1.87207 0.08802 H -0.70382 -1.46911 0.94400 H -1.74516 -1.33884 -0.19250 O 1.17665 1.49345 -1.26928 H 1.09369 0.55544 -1.56607 H 1.40054 2.01115 -2.05763 O 2.47909 -0.04163 0.76433 H 2.28520 -0.71526 0.07922 H 2.35479 0.78533 0.25919 O 0.10783 -0.16759 2.09509 H 0.21013 -0.23308 3.05702 H 1.03034 -0.12422 1.72369 O -1.12468 1.82452 0.44162 H -0.37324 1.86373 -0.18414 H -0.77711 1.28249 1.18001 O 1.12391 -1.23920 -1.40403 H 0.30441 -1.52069 -0.88409 H 1.27275 -1.93753 -2.05976 O -2.91165 -0.01162 -0.54376 H -3.10132 0.20646 -1.46815 H -2.36917 0.74721 -0.20663	CA1 21 (H ₂ O)7 O -1.37227 0.41410 -1.64512 H -2.08114 0.22505 -0.98455 H -0.79028 -0.37076 -1.59654 O 1.38987 0.94350 1.38643 H 1.60451 1.50013 2.15091 H 0.90853 1.53686 0.74000 O 2.85827 -0.63068 -0.33628 H 2.50592 -0.06526 0.39130 H 3.23607 -0.00489 -0.97304 O -2.94376 -0.16447 0.56330 H -3.56921 -0.90427 0.57198 H -2.15411 -0.49784 1.05959 O 0.02663 2.35926 -0.41953 H -0.54210 1.68612 -0.89418 H 0.44979 2.86994 -1.12534 O 0.46255 -1.74377 -1.04568 H 1.37527 -1.39102 -0.88193 H 0.58664 -2.62628 -1.42742 O -0.58517 -1.17203 1.56333 H -0.26508 -1.56621 0.72613 H 0.04612 -0.43888 1.71150

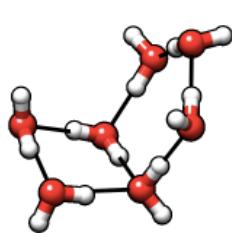


kcal/mol	PR1	PR2	PR3	CA1
$\Delta\Delta E_e$	0.00	0.35	0.60	1.57
$\Delta\Delta G_{298}$	1.35	1.76	1.57	0.99

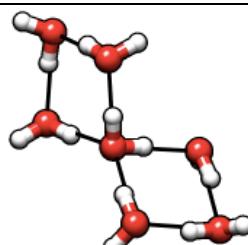
... (H ₂ O)7				
CA2		CH1	BI1	CH2
21		21	21	21
(H ₂ O)7		(H ₂ O)7	(H ₂ O)7	(H ₂ O)7
O -2.77257 -0.57180 0.70154		O -2.14533 -1.70684 -1.04952	O -0.01052 0.41538 0.10362	O -2.97596 1.30410 -0.52664
H -3.23538 -0.03573 1.36151		H -1.71270 -1.66826 -1.91558	H -0.47114 -0.28095 -0.43381	H -2.91720 0.35576 -0.78654
H -1.94145 -0.87427 1.14505		H -2.53771 -0.80944 -0.93284	H 0.53710 -0.09626 0.75581	H -3.76923 1.35600 0.02739
O 1.37997 1.06749 1.27100		O 1.16039 2.35659 -0.19175	O -3.83307 -0.37313 -0.27017	O 3.12312 0.25272 -0.80603
H 1.95244 1.50168 1.92278		H 0.85383 2.72152 -1.03613	H -4.29812 -0.90973 0.38978	H 2.57813 1.02336 -0.49213
H 1.99684 0.58547 0.65389		H 1.82252 1.65889 -0.44806	H -3.40323 0.34760 0.25595	H 3.14032 0.35222 -1.77004
O -0.25860 2.56362 -0.48322		O -2.98976 0.89755 -0.52056	O -2.34824 1.45320 1.15371	O 2.02420 -2.07552 0.04265
H -0.90075 3.04130 0.06298		H -2.29939 1.13736 0.13930	H -1.44783 1.14458 0.88135	H 2.40855 -1.23370 -0.32441
H 0.34514 2.13013 0.15958		H -3.82242 0.90168 -0.02433	H -2.40153 2.36662 0.83424	H 2.69066 -2.38035 0.67676
O -1.42709 0.25065 -1.59401		O 2.24208 -1.83511 0.37239	O 2.14137 1.36557 -1.34869	O -0.45084 -1.54886 0.96939
H -2.06468 0.03791 -0.87376		H 1.30112 -1.76067 0.69367	H 1.30488 1.07885 -0.90279	H -0.53526 -2.02090 1.81199
H -1.05375 1.12456 -1.33845		H 2.27042 -2.66983 -0.11812	H 2.24583 2.29448 -1.09301	H 0.46140 -1.77209 0.62856
O -0.25971 -1.30874 1.57997		O -0.34588 -1.54628 1.11944	O -1.50028 -1.47825 -1.21086	O -2.52856 -1.42248 -0.91870
H 0.00453 -1.64438 0.69789		H -0.96246 -1.74321 0.37834	H -1.52376 -1.39774 -2.17661	H -3.15751 -2.14044 -0.75683
H 0.25243 -0.47948 1.66479		H -0.50452 -0.59891 1.30529	H -2.39985 -1.18933 -0.91283	H -1.78844 -1.57661 -0.29034
O 2.81930 -0.44526 -0.45874		O -0.85302 1.28932 1.23146	O 3.80232 -0.44449 -0.07145	O -0.69203 1.32983 1.11603
H 2.04387 -0.87234 -0.90037		H -0.85801 1.77777 2.06916	H 4.54534 0.04889 0.30723	H -0.58031 0.35810 1.14473
H 3.27241 -1.17835 -0.01350		H -0.10361 1.68666 0.70165	H 3.31551 0.21272 -0.62761	H -1.48087 1.45735 0.54016
O 0.43333 -1.57718 -1.18253		O 2.93959 0.43966 -0.93045	O 1.73425 -1.03370 1.65115	O 1.54414 2.32619 -0.04973
H 0.26658 -2.29765 -1.81026		H 3.81086 0.63032 -0.55064	H 2.55151 -0.87448 1.11606	H 1.90560 2.90677 0.63641
H -0.25527 -0.86910 -1.40431		H 2.67749 -0.42294 -0.50984	H 1.55866 -1.98182 1.54762	H 0.69166 1.98678 0.33867



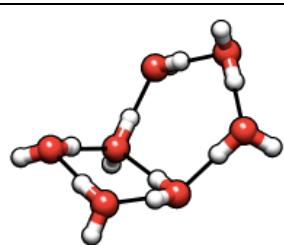
CA2



CH1



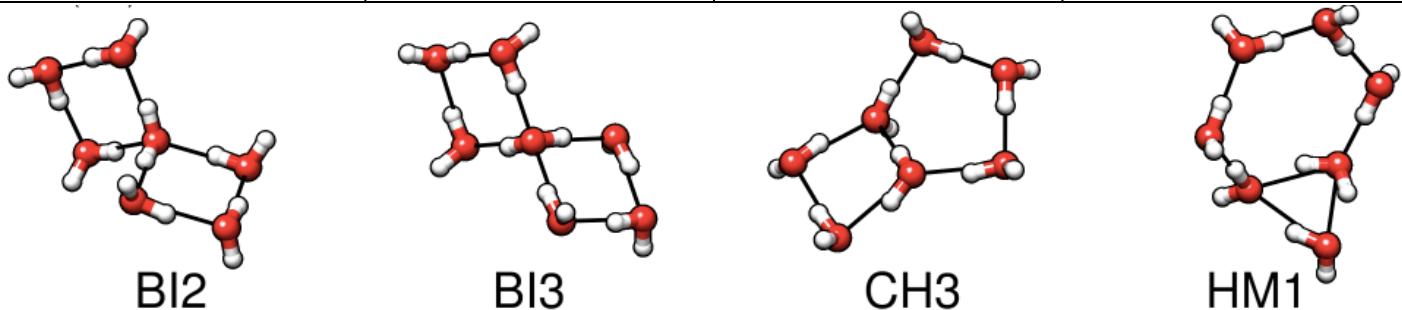
BI1



CH2

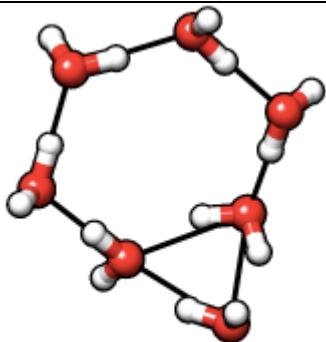
kcal/mol	CA2	CH1	BI1	CH2
$\Delta\Delta E_e$	2.61	3.57	4.14	4.18
$\Delta\Delta G_{298}$	1.87	0.00	1.33	0.09

... (H ₂ O)7			
BI2	BI3	CH3	HM1
21	21	21	21
(H ₂ O)7	(H ₂ O)7	(H ₂ O)7	(H ₂ O)7
O -2.39716 1.43531 1.16528	O 2.13163 -1.32681 1.39212	O -3.20248 1.52221 -0.04129	O 2.99021 -1.13488 0.14901
H -1.48316 1.10754 0.97381	H 1.30133 -0.84862 1.14311	H -3.51886 1.81516 -0.90975	H 2.17362 -1.69089 0.05432
H -2.40959 2.34444 0.82985	H 1.96463 -2.24846 1.14133	H -3.30601 0.54190 -0.06925	H 3.36795 -1.41982 0.99485
O 3.80523 -0.14697 -0.18975	O 1.69345 1.49956 -1.26932	O -3.17879 -1.27174 -0.19003	O -1.80715 1.25269 -0.80571
H 4.10466 -0.87919 -0.74929	H 1.84143 2.42303 -1.01534	H -2.24305 -1.47097 0.03401	H -2.13392 1.76178 -1.56323
H 3.25610 -0.57249 0.51586	H 2.53313 1.03181 -1.03107	H -3.69972 -1.75829 0.46631	H -1.03743 1.78298 -0.45970
O -0.02194 0.29687 0.32999	O 3.81690 0.02520 -0.31223	O -0.41877 1.22729 -0.29824	O -3.31464 -0.19429 1.10939
H 0.58094 0.82231 -0.25592	H 4.47642 0.45600 0.25205	H -1.34255 1.53100 -0.15227	H -2.92303 0.49991 0.53690
H -0.44896 -0.37080 -0.26672	H 3.29580 -0.54492 0.30771	H -0.42206 0.30855 0.03815	H -4.23377 -0.26688 0.81039
O 1.96313 -1.16622 1.58922	O -0.00793 0.09052 0.36597	O 3.43074 0.02272 -0.18671	O 0.25288 2.76981 0.05744
H 1.18824 -0.63981 1.27108	H 0.52729 0.67052 -0.23490	H 4.07687 -0.00642 0.53489	H 1.13558 2.31514 0.05230
H 1.68079 -2.08917 1.50036	H -0.49806 -0.52469 -0.23991	H 2.90943 0.85185 -0.01786	H 0.14997 3.07677 0.97098
O 1.88115 1.49799 -1.25243	O -3.82322 -0.20458 -0.31311	O 1.89355 -2.22529 -0.31446	O -1.57708 -1.59689 -0.64886
H 2.15637 2.39095 -0.99425	H -4.27888 0.42257 -0.89452	H 1.92582 -2.47059 -1.25170	H -1.45715 -0.67957 -0.96579
H 2.63616 0.92092 -0.97140	H -3.36324 0.36497 0.35339	H 2.45667 -1.40833 -0.25257	H -2.19292 -1.45503 0.10007
O -1.42571 -1.51117 -1.19596	O -2.26282 1.31373 1.37727	O -0.50231 -1.48698 0.65412	O 2.69912 1.58031 0.17566
H -2.33503 -1.22006 -0.92996	H -1.38662 0.96588 1.07412	H -0.33995 -1.51972 1.60992	H 2.74639 0.58926 0.18229
H -1.38930 -1.34250 -2.15012	H -2.32333 1.04289 2.30616	H 0.33725 -1.83788 0.24192	H 3.29684 1.84335 -0.53991
O -3.78599 -0.39078 -0.35240	O -1.56830 -1.49661 -1.24019	O 1.97715 2.27472 0.35889	O 0.79623 -2.75228 0.04003
H -3.38829 0.32949 0.19928	H -2.45435 -1.13616 -0.98515	H 2.13448 2.93667 -0.33188	H -0.07296 -2.31174 -0.15106
H -4.29861 -0.92190 0.27592	H -1.47332 -1.28291 -2.18100	H 1.03883 1.98371 0.20183	H 0.86423 -3.44101 -0.63801



kcal/mol	BI2	BI3	CH3	HM1
$\Delta\Delta E_e$	4.28	4.33	4.61	5.56
$\Delta\Delta G_{298}$	1.07	1.25	0.94	1.28

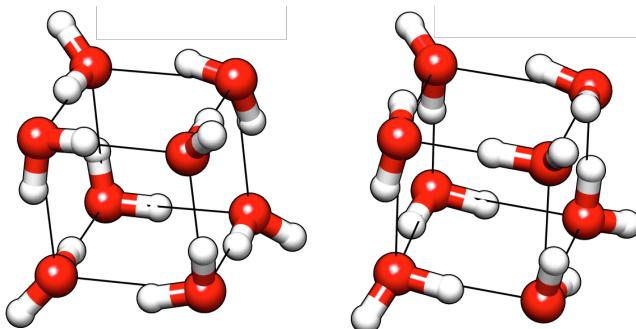
... (H ₂ O)7			
HM2 21 (H ₂ O) ₇ O -0.19162 2.77277 0.06345 H 0.54934 2.19792 -0.26750 H -0.20184 3.51898 -0.55489 O 3.35150 -0.09704 1.04975 H 2.94054 0.05716 1.91406 H 2.80351 -0.79982 0.63945 O 1.82743 1.24546 -0.93279 H 1.52829 0.32371 -1.06744 H 2.53107 1.11333 -0.26316 O -0.81447 -2.77211 -0.00483 H -0.87696 -3.22974 0.84693 H -1.58495 -2.14602 -0.00267 O -2.96575 -1.10821 0.13412 H -3.58088 -1.21237 -0.60718 H -2.79557 -0.13175 0.17433 O 1.54816 -1.57881 -0.56592 H 0.68102 -2.00042 -0.31854 H 1.91900 -2.15973 -1.24797 O -2.65550 1.60447 0.20510 H -1.74685 1.99107 0.10529 H -2.96384 1.94547 1.05813			



HM2

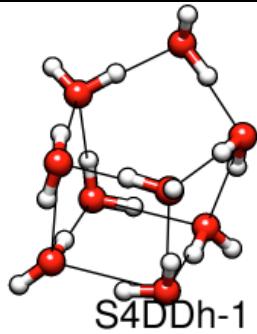
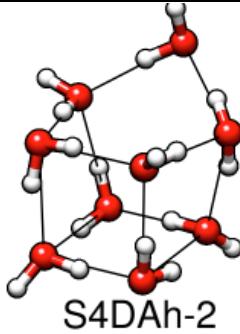
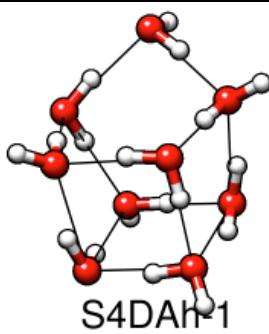
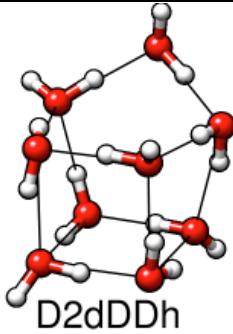
kcal/mol	HM2			
$\Delta\Delta E_e$	5.68			
$\Delta\Delta G_{298}$	1.47			

(H ₂ O)8							
D_{2d}			S₄				
.....						
24			24				
(H ₂ O)8 D2d			(H ₂ O)8_S4				
H	2.086834	0.191270	0.351019	H	-1.291629	-0.803232	1.478752
O	1.992921	0.193697	-1.334112	O	-0.051576	-1.941178	1.421467
H	1.348931	0.909534	-1.526426	H	0.758589	-1.405745	1.56600
H	1.492169	-0.626752	-1.534675	H	0.259886	-2.664519	-2.023778
O	-0.192659	1.981872	-1.348304	O	1.951230	0.051576	1.400650
O	0.178137	-1.969667	-1.365830	O	-1.951230	-0.051576	1.400650
O	1.984614	0.176209	1.348393	H	-2.664519	-0.259886	2.023778
H	-1.508532	0.640380	-1.515321	H	-2.173303	0.008670	-0.468128
H	-0.196801	2.084833	-0.350904	H	-0.758589	1.405745	1.566007
H	-0.278707	2.878271	-1.708138	O	0.051576	1.941178	1.421467
H	0.260576	-2.862844	-1.734405	H	0.008670	2.173303	0.468128
H	-1.364792	-0.895882	-1.521211	H	1.291629	0.803232	1.478752
H	0.192847	-2.081429	-0.369465	O	1.941178	-0.051576	-1.421467
H	2.881392	0.256853	1.708534	O	-1.941178	0.051576	-1.421467
H	0.907648	-1.363459	1.515351	H	-1.405745	-0.758589	-1.566007
H	0.645108	1.492222	1.526675	H	-0.259886	2.664519	-2.023778
O	0.191325	-2.004908	1.316511	O	0.051576	-1.951230	-1.400650
H	-2.082799	-0.194575	0.369344	H	-0.008670	-2.173303	0.468128
H	-0.891402	1.349690	1.534776	H	0.803232	-1.291629	-1.478752
O	-0.177253	1.993021	1.334200	H	2.173303	-0.008670	-0.468128
H	-0.628929	-1.505497	1.521206	H	2.664519	0.259886	2.023778
O	-1.970090	-0.188409	1.365693	O	-0.051576	1.951230	-1.400650
O	-2.007055	-0.181884	-1.316653	H	-0.803232	1.291629	-1.478752
H	-2.863073	-0.272055	1.734466	H	1.405745	0.758589	-1.566007



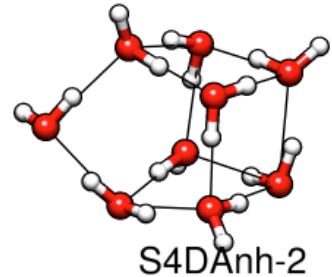
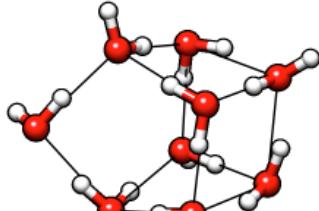
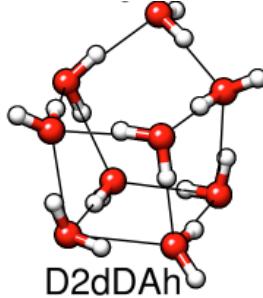
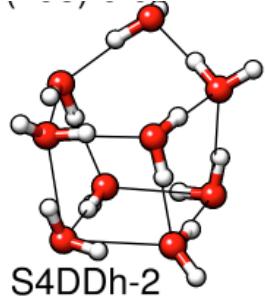
kcal/mol	D2d	S4
$\Delta\Delta E_e$	0.00	0.08
$\Delta\Delta G_{298}$	0.00	0.45

(H ₂ O) ₉			
D2dDDh	S4DAh-1	S4DAh-2	S4DDh-1
.....
27	27	27	27
(H ₂ O) ₉			
O -0.42490 1.08658 -2.04989	O -0.49417 1.52622 1.83073	O 2.36629 -1.38855 -0.15919	O 3.31957 0.09629 -0.20605
H 0.31469 1.45595 -1.51957	H -1.30189 1.59921 1.27743	H 1.72569 -1.51255 -0.89414	H 2.75971 -0.73068 -0.17262
H -1.22361 1.31780 -1.52874	H 0.22355 1.83425 1.23546	H 1.83533 -1.59224 0.64155	H 3.90109 0.02721 0.56629
O -0.32301 -1.09160 2.06929	O 3.36330 0.09064 0.02380	O 2.46767 1.27759 -0.08348	O -2.46489 1.29780 0.02515
H -0.30434 -0.09057 2.02022	H 2.73981 0.84428 -0.09078	H 2.53243 0.27565 -0.11085	H -3.20478 1.89046 -0.17899
H -0.35840 -1.30643 3.01419	H 3.77237 0.23859 0.88974	H 3.37889 1.60400 -0.14195	H -1.84538 1.34901 -0.76314
O -2.40405 -1.36054 0.17957	O 1.54185 -2.02941 0.06373	O -1.50947 -2.02937 -0.05129	O 1.47178 2.03728 -0.19190
H -1.84344 -1.62818 -0.58146	H 1.02481 -1.80940 0.86752	H -2.23482 -1.37333 0.07201	H 2.19750 1.34842 -0.18273
H -1.79609 -1.43955 0.94695	H 2.26436 -1.35952 0.03503	H -0.94409 -1.93620 0.74548	H 1.91563 2.87875 -0.38030
O -0.41095 -1.58518 -1.80093	O 1.39371 2.06049 -0.21597	O 0.19015 -1.32804 -1.95882	O -0.47069 -1.53199 -1.82328
H -0.45074 -1.98208 -2.68479	H 0.76479 1.73994 -0.93538	H 0.07133 -1.92271 -2.71557	H -1.20283 -1.59576 -1.14076
H -0.36226 -0.59546 -1.95168	H 1.64744 2.95689 -0.48776	H -0.50662 -1.60412 -1.28517	H -0.71699 -2.14961 -2.52956
O 1.53889 2.00943 -0.21682	O -0.39608 1.22483 -1.99283	O -1.43000 2.04464 0.08867	O -0.64623 1.28559 -1.93212
H 2.01082 2.83028 -0.42634	H -0.31216 0.25115 -2.10467	H -1.64140 2.98888 0.01907	H -0.51629 0.32467 -2.09036
H 2.24378 1.30229 -0.15070	H -1.23606 1.33234 -1.49588	H -0.83007 1.84618 -0.69455	H 0.16096 1.57014 -1.45018
O -2.46623 1.30005 -0.11346	O -0.27421 -1.57817 -1.81779	O 0.28907 1.48142 -1.86475	O -0.20687 -1.20729 2.02171
H -3.37502 1.63599 -0.15169	H -0.16044 -2.22201 -2.53410	H 0.20975 0.52334 -2.07209	H -0.21191 -0.20451 2.02694
H -2.54426 0.30584 -0.00378	H 0.46736 -1.76829 -1.16345	H 1.14573 1.54486 -1.38837	H -0.21433 -1.47270 2.95435
O 3.31891 0.01188 -0.08276	O -2.32478 -1.44413 0.11274	O 0.44219 -1.42982 1.90664	O -2.29391 -1.51636 0.14316
H 3.87680 -0.04420 0.70781	H -1.72675 -1.52141 0.88790	H 0.43428 -0.43226 2.00004	H -2.59287 -0.58123 0.13984
H 2.72961 -0.79354 -0.03113	H -1.74024 -1.65759 -0.64804	H 0.49389 -1.77583 2.81104	H -1.68876 -1.56029 0.91568
O -0.40598 1.57669 1.79169	O -0.27997 -1.14220 2.04734	O 0.54286 1.25362 1.98343	O 1.64994 -2.00909 0.01559
H -1.21128 1.66821 1.23760	H -0.31363 -0.14079 2.02256	H -0.21674 1.59868 1.46594	H 1.09028 -1.82956 0.80096
H 0.32329 1.84448 1.19140	H -0.32556 -1.38160 2.98589	H 1.31590 1.42974 1.40500	H 1.01499 -1.96092 -0.73090
O 1.57802 -2.03019 0.17164	O -2.50685 1.21050 -0.11717	O -3.37259 0.04166 0.20643	O -0.35728 1.46653 1.89276
H 0.97171 -2.01719 -0.59974	H -3.42864 1.50278 -0.18970	H -2.76389 0.81536 0.20578	H -1.19160 1.56605 1.38476
H 0.99309 -1.80066 0.92481	H -2.54150 0.21095 -0.02839	H -3.89478 0.13736 -0.60428	H 0.33429 1.78049 1.27049



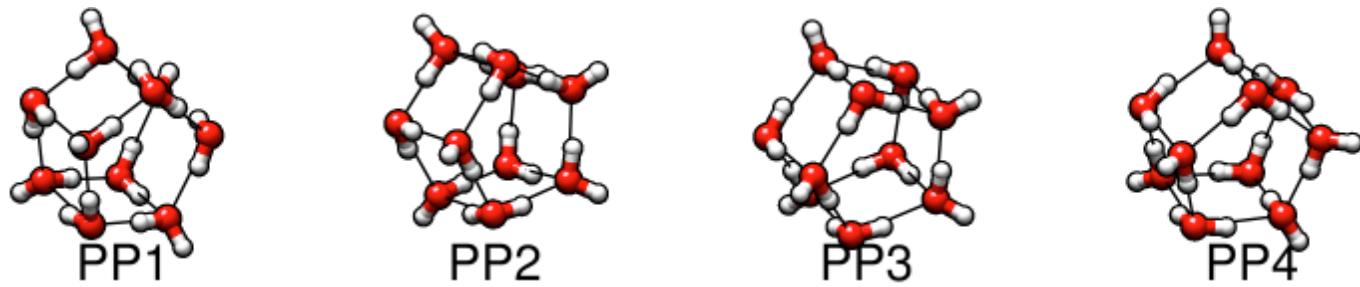
kcal/mol	D2dDDh	S4DAh-1	S4DAh-2	S4DDh-1
$\Delta\Delta E_e$	0.00	0.31	0.35	0.47
$\Delta\Delta G_{298}$	0.00	0.47	0.47	0.56

(H ₂ O)9			
S4DDh-2 27 (H ₂ O) ₉ O -3.32533 0.17427 -0.02722 H -2.78613 -0.66659 -0.05273 H -3.85080 0.14945 -0.84138 O 0.27407 -1.63017 1.79759 H 0.29034 -2.04115 2.67581 H 0.26988 -0.64102 1.96316 O -1.69420 -1.96345 -0.22040 H -1.07545 -1.74502 -0.94971 H -1.11287 -1.98474 0.56988 O 0.40902 1.03010 2.07890 H 1.23757 1.22755 1.59148 H -0.29065 1.43843 1.52330 O 0.35103 -1.12599 -2.03142 H 0.54486 -1.62718 -2.83924 H 1.10624 -1.33375 -1.40285 O 0.25873 -1.53901 -0.20023 H 2.57691 -0.62589 -0.03036 H 1.70241 -1.74286 0.58359 O 0.65557 1.66652 -1.70848 H -0.13293 1.89934 -1.17182 H 0.48440 0.74656 -2.00797 O -1.43139 2.05954 0.17268 H -2.17196 1.39365 0.07465 H -1.86671 2.90301 0.37185 O 2.49652 1.24432 0.18882 H 1.87407 1.47076 -0.56461 H 3.24877 1.85043 0.10514	D2dDAh 27 (H ₂ O) ₉ O 0.79482 1.60709 -1.73397 H 0.56867 0.69282 -2.01461 H 0.01465 1.90232 -1.21634 O 0.38562 1.15411 2.02333 H 0.23490 0.18598 2.11103 H 1.26164 1.21803 1.58561 O 2.14394 -1.65578 -0.11878 H 2.51687 -0.76184 0.04036 H 1.56251 -1.80818 0.65854 O -1.69865 -1.93697 -0.14566 H -1.13687 -1.73852 -0.92464 H -2.36971 -1.21474 -0.12890 O 0.31156 -1.16739 -2.01250 H 0.50931 -1.68089 -2.81164 H 1.03553 -1.40604 -1.35894 O -3.35694 0.31050 -0.14083 H -3.72361 0.48283 -1.02123 H -2.67781 1.01198 -0.01093 O 2.56027 1.10984 0.22302 H 1.97501 1.36133 -0.55091 H 3.35808 1.65535 0.14494 O -1.25357 2.12780 0.16589 H -0.68101 1.75732 0.90738 H -1.47200 3.03017 0.44866 O 0.08413 -1.63127 1.80239 H -0.64729 -1.76708 1.12433 H -0.09826 -2.26437 2.51406	S4DAnh-1 27 (H ₂ O) ₉ O 3.35498 0.22379 -0.09975 H 2.69984 0.95637 -0.15721 H 3.81252 0.36488 0.74269 O 1.64572 -1.98362 -0.02902 H 2.32930 -1.27467 -0.07632 H 1.15846 -1.80573 0.80312 O -2.17415 -1.60008 0.28153 H -2.52144 -0.68755 0.17650 H -1.66643 -1.75181 -0.54615 O 1.29687 2.11090 -0.17687 H 1.47778 3.06375 -0.15233 H 0.69185 1.93329 0.60661 O -0.17714 -1.21984 2.02005 H -0.96136 -1.42037 1.42479 H -0.33554 -1.72611 2.83240 O -2.51792 1.17714 -0.04620 H -1.89621 1.23893 -0.83271 H -3.30426 1.69117 -0.28655 O -0.28740 -1.57827 -1.81102 H 0.49423 -1.74448 -1.19909 H -0.17956 -2.20293 -2.54502 O -0.42305 1.58468 1.79418 H -1.28004 1.57811 1.31452 H -0.29048 0.64255 2.04319 O -0.69552 1.20177 -1.99702 H 0.08877 1.56881 -1.53506 H -0.49655 0.24412 -2.10032	S4DAnh-2 27 (H ₂ O) ₉ O 2.51610 1.21285 0.01607 H 1.86542 1.37331 0.76250 H 3.28325 1.77521 0.20428 O 0.47140 1.32554 -1.92503 H 1.31165 1.39150 -1.42168 H 0.36751 0.36085 -2.08447 O 2.22392 -1.59247 0.00823 H 1.65084 -1.63100 0.80549 H 2.55518 -0.66825 0.00965 O 0.60413 1.47958 1.87025 H 0.39907 0.53770 2.06334 H -0.15260 1.78975 1.32791 O -1.33547 2.08826 -0.12069 H -1.56432 3.00386 -0.34691 H -0.69889 1.79679 -0.84432 O 0.32781 -1.49339 -1.88228 H 1.08338 -1.60419 -1.23154 H 0.53841 -2.07390 -2.63036 O 0.18387 -1.30728 1.94339 H 0.05612 -1.88039 2.71524 H -0.55043 -1.55575 1.30042 O -1.62531 -1.97671 0.11593 H -1.09162 -1.92527 -0.70564 H -2.32248 -1.28761 0.00886 O -3.38541 0.18451 -0.09437 H -3.85221 0.31461 0.74498 H -2.72659 0.91579 -0.12986



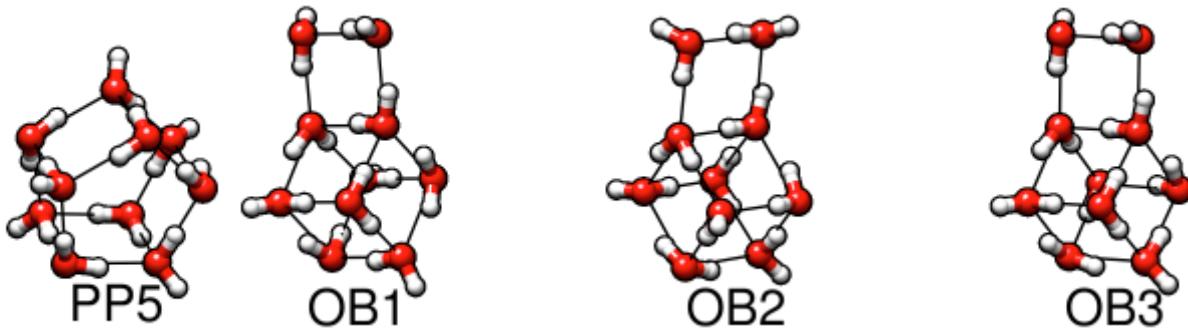
kcal/mol	S4DDh-2	D2dDAh	S4DAnh-1	S2DAnh-2
$\Delta\Delta E_e$	0.49	0.64	0.71	0.80
$\Delta\Delta G_{298}$	0.63	1.04	1.08	1.06

(H ₂ O)10			
PP1 30 (H ₂ O)10 O -0.76042 2.36745 -1.19303 H -1.12472 3.11770 -1.68728 H -1.40765 1.62572 -1.30385 O 1.88895 1.36362 -1.42170 H 1.00206 1.77992 -1.46841 H 2.12400 1.42238 -0.46899 O -2.43354 0.19709 -1.24266 H -3.22798 0.07991 -1.78660 H -1.89168 -0.64316 -1.37661 O 1.68469 -1.28739 -1.69145 H 1.75480 -0.28638 -1.66665 H 2.29695 -1.57482 -2.38636 O 2.11394 1.09576 1.36586 H 2.07158 0.09321 1.35602 H 2.86177 1.31947 1.94120 O 1.98722 -1.56212 1.11741 H 1.07917 -1.86904 1.33572 H 2.02856 -1.64204 0.14046 O -2.19571 -0.04595 1.61617 H -2.51269 0.08521 0.69986 H -1.62342 0.74728 1.77937 O -0.73271 -2.24053 1.34573 H -1.09357 -2.91397 1.94306 H -1.26846 -1.40597 1.52584 O -1.01520 -2.03336 -1.44095 H -0.08185 -1.82967 -1.67345 H -0.96317 -2.31982 -0.50182 O -0.51453 2.14112 1.68450 H 0.41033 1.81746 1.72302 H -0.61566 2.43108 0.75657	PP2 30 (H ₂ O)10 O -1.70735 -1.37952 1.61637 H -2.03545 -1.46466 0.69869 H -1.74075 -0.40281 1.78367 O -2.13460 -1.25848 -1.23148 H -2.12582 -0.27094 -1.31615 H -2.90647 -1.56341 -1.73262 O 0.53287 -2.23570 -1.45779 H -0.41036 -1.97307 -1.51304 H 0.66487 -2.43790 -0.50464 O 0.56979 2.23488 -1.41088 H 1.14153 1.47308 -1.65442 H 0.79395 2.40126 -0.46792 O 2.11970 -0.10015 -1.68676 H 1.51174 -0.89881 -1.67839 H 2.77595 -0.28061 -2.37758 O 0.78510 -2.23170 1.34270 H 0.90465 -2.99263 1.93208 H -0.14683 -1.89402 1.52673 O -1.95639 1.47128 -1.20325 H -0.99948 1.75845 -1.34441 H -2.49137 2.10067 -1.71162 O 2.52470 -0.03064 1.12371 H 1.99698 -0.83072 1.34292 H 2.60393 -0.06816 0.14639 O 1.00556 2.15058 1.36253 H 1.47477 2.79096 1.91948 H 1.57921 1.32672 1.35967 O -1.71876 1.37872 1.68346 H -1.96579 1.54228 0.75164 H -0.79026 1.69015 1.73053	PP3 30 (H ₂ O)10 O -1.18496 -2.02717 1.38106 H -1.35007 -2.16617 0.42218 H -0.20740 -2.05772 1.45636 O 2.30071 0.75475 1.18556 H 2.29848 0.84911 0.17310 H 3.15876 1.10612 1.47247 O 1.64864 -1.90800 1.22384 H 1.94298 -0.96787 1.33148 H 2.27515 -2.44707 1.73053 O -0.28139 2.37566 -1.29880 H -0.19177 2.46887 -0.30399 H -0.36427 3.28041 -1.63889 O -2.09191 0.47292 1.65754 H -1.74121 -0.46695 1.63091 H -2.77003 0.47727 2.35078 O -0.03172 2.37341 1.36946 H 0.79671 1.86272 1.49421 H -0.75069 1.75512 1.62733 O 1.39145 -1.71761 -1.66147 H 0.41593 -1.79048 -1.73081 H 1.57437 -1.98207 -0.73865 O -1.44108 -1.84700 -1.41371 H -1.83609 -0.92502 -1.39930 H -2.01248 -2.36549 -2.00115 O -2.47878 0.60530 -1.15080 H -2.55415 0.65172 -0.17342 H -1.78171 1.26582 -1.35950 O 2.15053 0.91937 -1.42820 H 1.90570 -0.01043 -1.67153 H 1.33987 1.44896 -1.58799	PP4 30 (H ₂ O)10 O -1.39474 -1.86313 -1.40364 H -1.81032 -0.94947 -1.39243 H -1.93964 -2.38873 -2.00963 O 1.43367 -1.77053 -1.46810 H 1.69072 -0.83718 -1.68203 H 0.46497 -1.81663 -1.62170 O -2.09687 0.45421 1.65664 H -2.77526 0.45816 2.34960 H -1.73953 -0.48324 1.63635 O -0.05776 2.37488 1.34460 H 0.78320 1.88752 1.47460 H -0.76352 1.74619 1.61306 O -0.33071 2.36693 -1.31669 H -0.22987 2.45909 -0.32240 H -0.42330 3.27191 -1.65353 O -1.16786 -2.04091 1.39916 H -0.18841 -2.03348 1.46516 H -1.33345 -2.18840 0.44177 O 2.10056 0.89964 -1.61348 H 1.28394 1.43742 -1.68615 H 2.36275 1.00857 -0.67818 O 1.65361 -1.81000 1.13855 H 2.23367 -2.54422 1.39623 H 1.60365 -1.85119 0.12259 O -2.48965 0.56188 -1.15276 H -1.80984 1.23870 -1.36757 H -2.56447 0.61389 -0.17561 O 2.33434 0.83951 1.28116 H 2.15340 -0.13266 1.34835 H 3.12465 1.00388 1.81804



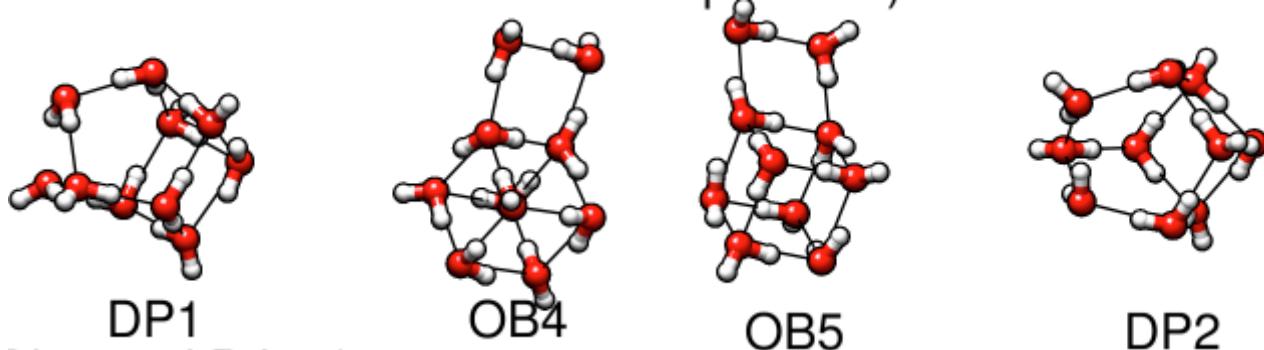
kcal/mol	PP1	PP2	PP3	PP4
$\Delta\Delta E_e$	0.00	0.13	0.71	0.78
$\Delta\Delta G_{298}$	0.00	0.05	0.96	0.96

...-(H ₂ O)10			
PP5 30 (H ₂ O)10 O -2.21165 0.99428 -1.34761 H -1.39146 1.51606 -1.47747 H -1.97320 0.08049 -1.61809 O 0.09403 2.29278 1.59474 H 0.12603 2.53877 0.64902 H -0.74393 1.78978 1.67135 O -1.36387 -1.68942 -1.58413 H -1.87986 -2.36904 -2.04608 H -1.51808 -1.85775 -0.60321 O 1.15753 -1.98493 1.42883 H 1.51336 -1.05256 1.56992 H 1.63126 -2.54067 2.06706 O 2.16234 0.46384 1.59959 H 1.45220 1.14162 1.73767 H 2.44819 0.61600 0.67631 O 0.26320 2.39844 -1.29615 H 1.04651 1.79827 -1.38236 H 0.46651 3.18119 -1.83082 O 1.44377 -1.86519 -1.36370 H 0.48945 -1.86011 -1.60072 H 1.44320 -2.10978 -0.41122 O -1.62831 -1.98091 1.04938 H -1.92768 -1.08892 1.33229 H -0.69028 -2.03600 1.33896 O 2.35473 0.62384 -1.26848 H 3.15897 0.65726 -1.80967 H 2.00663 -0.31760 -1.36507 O -2.29362 0.74293 1.32406 H -2.34790 0.87628 0.33220 H -3.13510 1.07144 1.67759	OB1 30 (H ₂ O)10 O 0.91704 -1.20451 2.05110 H 0.89196 -1.49618 2.97585 H 0.88027 -0.19810 2.07857 O 1.01932 -1.46837 -1.86968 H 1.07440 -1.87727 -2.74752 H 0.99339 -0.47393 -2.03131 O -3.76555 -1.31101 0.12519 H -4.12160 -1.81027 -0.62509 H -2.80093 -1.50670 0.12315 O -0.97809 -1.50531 0.05124 H -0.37090 -1.68152 -0.70531 H -0.40500 -1.57300 0.85099 O 3.00626 -1.23636 0.14012 H 2.42024 -1.40035 0.90992 H 2.45543 -1.50028 -0.62798 O 0.94400 1.18335 -2.07586 H 1.69184 1.46445 -1.50574 H 0.14719 1.41293 -1.54324 O -3.81638 1.45862 -0.13941 H -4.17822 1.79575 0.69430 H -3.91692 0.47846 -0.07287 O 2.89088 1.44746 -0.03789 H 3.04004 0.46035 0.03096 H 3.77276 1.85059 -0.04396 O 0.82269 1.45196 1.89208 H 0.06643 1.59329 1.27574 H 1.60902 1.65787 1.34195 O -1.05924 1.30055 -0.14998 H -1.08271 0.31678 -0.08799 H -2.01416 1.55596 -0.18573	OB2 30 (H ₂ O)10 O -2.93021 -1.30810 -0.18838 H -3.13887 -0.35300 -0.08735 H -2.41768 -1.52077 0.62145 O 1.04877 1.29445 0.13616 H 1.07292 0.31111 0.06440 H 2.00386 1.55123 0.15327 O 0.97850 -1.50867 -0.05985 H 0.38360 -1.68663 0.70593 H 0.39425 -1.58300 -0.85096 O -2.83519 1.49089 0.04834 H -3.50044 2.18163 -0.09600 H -2.16377 1.59909 -0.69034 O -1.00303 -1.47845 1.88080 H -0.97098 -0.48464 2.04913 H -1.06292 -1.89208 2.75611 O -0.91681 1.57947 -1.81413 H -0.89600 0.65183 -2.12950 H -0.11808 1.64790 -1.24043 O -0.91578 1.16712 2.10302 H -1.66948 1.44630 1.53914 H -0.12505 1.39654 1.56129 O 3.80509 1.46352 0.07891 H 4.15414 1.79745 -0.76152 H 3.91012 0.48345 0.01731 O 3.76592 -1.30775 -0.16116 H 2.80188 -1.50576 -0.15300 H 4.12522 -1.79388 0.59619 O -0.97707 -1.27367 -2.01180 H -1.17950 -1.85844 -2.75879 H -1.76458 -1.33872 -1.39155	OB3 30 (H ₂ O)10 O 1.06708 -1.48546 -1.85874 H 1.82145 -1.47786 -1.19492 H 1.31608 -2.13834 -2.53159 O 1.01898 1.37546 -1.97058 H 0.18722 1.51273 -1.45979 H 1.00336 0.41938 -2.18469 O -0.97791 -1.50942 0.01556 H -0.41587 -1.60383 0.82029 H -0.36136 -1.66818 -0.73748 O 0.91243 -1.26746 2.03011 H 0.87003 -0.26228 2.09092 H 0.90726 -1.58815 2.94559 O -1.04858 1.29814 -0.10763 H -1.07115 0.31285 -0.07320 H -2.00345 1.55283 -0.15384 O 0.81259 1.38928 1.95825 H 1.59929 1.60494 1.41169 H 0.05701 1.54994 1.34589 O -3.80519 1.46034 -0.14281 H -3.91012 0.47893 -0.10744 H -4.18241 1.77417 0.69320 O 2.83694 1.49036 -0.01366 H 3.51087 2.16237 -0.20000 H 2.20302 1.51583 -0.79233 O 2.93173 -1.31675 0.04780 H 3.13930 -0.35609 0.05718 H 2.38555 -1.44427 0.85346 O -3.76721 -1.31599 0.03156 H -2.80282 -1.51184 0.04888 H -4.10023 -1.78100 -0.75070



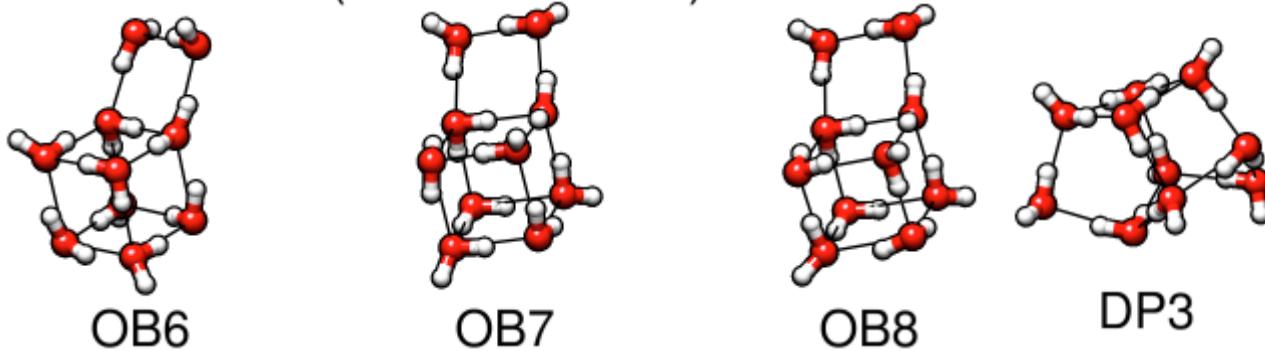
kcal/mol	PP5	OB1	OB2	OB3
$\Delta\Delta E_e$	0.83	1.66	1.81	2.12
$\Delta\Delta G_{298}$	1.04	1.17	1.30	1.34

DP1	OB4	OB5	DP2
... 30 (H ₂ O)10 O 1.38682 1.95611 1.18040 H 1.65978 2.82179 1.52176 H 0.90919 2.14525 0.31278 O 1.33808 -2.01852 1.15088 H 1.60591 -2.89487 1.46791 H 0.85107 -2.17905 0.28740 O -2.51370 0.02359 1.45373 H -1.59409 0.01349 1.86638 H -3.12932 0.00762 2.20251 O -0.09503 -0.01426 2.52783 H 0.39634 -0.79148 2.18212 H 0.41165 0.75649 2.18623 O 3.02683 -0.03456 0.05457 H 2.65410 0.74025 0.53058 H 2.63643 -0.80178 0.52677 O 0.13877 -2.28988 1.21985 H 0.58059 -1.57448 -1.72865 H -0.80285 -2.01643 -1.17257 O -2.44934 1.57353 -0.95061 H -2.55509 1.34328 -0.00594 H -2.54172 0.69994 -1.37383 O 1.53221 -0.03017 -2.17278 H 2.16750 -0.02738 -1.39622 H 2.09232 -0.01788 -2.96478 O 0.23013 2.30672 -1.17834 H -0.74001 2.12259 -1.14967 H 0.61381 1.56955 -1.69856 O -2.51544 -1.34057 -0.91552 H -2.58884 -1.02950 0.02059 H -3.26149 -1.94335 -1.05724	... 30 (H ₂ O)10 O 1.10205 -1.66944 -1.72343 H 1.37617 -2.36069 -2.34608 H 1.83331 -1.61066 -1.03820 O 0.83199 -1.16915 2.14206 H 0.11387 -1.34549 1.47731 H 0.62278 -1.71406 2.91630 O 2.82287 1.46122 -0.08660 H 3.52318 2.08909 -0.32292 H 2.21094 1.42381 -0.88070 O 2.91155 -1.32926 0.22115 H 2.35420 -1.39092 1.02577 H 3.10760 -0.36848 0.14995 O -3.75096 -1.35649 -0.13626 H -4.10033 -1.76617 0.66978 H -2.78129 -1.53410 -0.10541 O -3.73374 1.42825 -0.02190 H -3.84776 0.44715 -0.04624 H -4.17268 1.74417 -0.82631 O -0.96974 -1.37976 0.09808 H -0.99658 -0.38928 -0.04490 H -0.38793 -1.69333 -0.63375 O -1.00237 1.29535 -0.23680 H -0.50399 1.59416 0.57042 H -1.95487 1.54369 -0.13109 O 0.72457 1.69769 1.82458 H 0.77815 0.78095 2.16335 H 1.54344 1.79110 1.29287 O 1.06478 1.17135 -2.08990 H 1.05040 0.19743 -2.20055 H 0.22348 1.36356 -1.61744	... 30 (H ₂ O)10 O -0.98039 -1.46426 -1.87322 H -0.97181 -1.87367 -2.75262 H -0.94578 -0.46971 -2.03343 O -0.97211 -1.20643 2.05071 H -1.01264 -1.49451 2.97594 H -0.93027 -0.20013 2.07766 O 3.75583 -1.31747 -0.04040 H 2.79225 -1.51220 -0.00911 H 4.14384 -1.85081 0.66861 O 0.97026 -1.51558 0.09280 H 0.38139 -1.58607 0.87984 H 0.37672 -1.67834 -0.67815 O -3.01409 -1.22933 0.08166 H -2.45386 -1.49645 -0.67858 H -2.43975 -1.39484 0.85979 O -0.86432 1.45018 1.90085 H -1.63682 1.65810 1.33172 H -0.09289 1.59434 1.30426 O 3.82512 1.47226 -0.12743 H 3.94872 0.49366 -0.13542 H 4.19015 1.75935 0.72315 O -2.88519 1.45519 -0.07651 H -3.03837 0.46792 -0.02047 H -3.76557 1.86073 -0.10270 O -0.88953 1.18733 -2.06948 H -0.10546 1.40739 -1.51432 H -1.65026 1.47136 -1.51866 O 1.06692 1.29165 -0.09062 H 1.08935 0.30830 -0.02241 H 2.02094 1.54730 -0.14199	... 30 (H ₂ O)10 O 0.18082 -1.22086 2.24784 H 0.57332 -0.32260 2.27556 H -0.78635 -1.07715 2.10998 O -2.49049 -0.73196 1.60800 H -2.57826 -1.08868 0.70157 H -2.58080 0.22569 1.44831 O 0.16294 2.60710 -0.09437 H -0.78157 2.34009 -0.10197 H 0.55071 2.18008 -0.88888 O 3.01220 -0.01280 -0.12009 H 2.67854 0.46609 0.67041 H 2.63635 -0.91553 -0.01815 O 1.45805 1.28351 1.84313 H 1.75196 1.91517 2.51753 H 0.93876 1.82247 1.17617 O 1.37773 -2.28671 0.14431 H 1.66031 -3.18348 0.38193 H 0.87777 -1.93959 0.94916 O -2.48986 -0.85169 -1.25163 H -3.10046 -1.25683 -1.88645 H -1.56795 -1.08945 -1.58210 O -2.49861 1.62938 -0.09887 H -2.55523 0.83627 -0.68716 H -3.22690 2.21200 -0.36357 O -0.05955 -1.44881 -2.11847 H 0.42939 -1.89489 -1.39072 H 0.43111 -0.60737 -2.24696 O 1.42273 0.96581 -2.02676 H 2.08997 0.62170 -1.35754 H 1.95163 1.29214 -2.77182



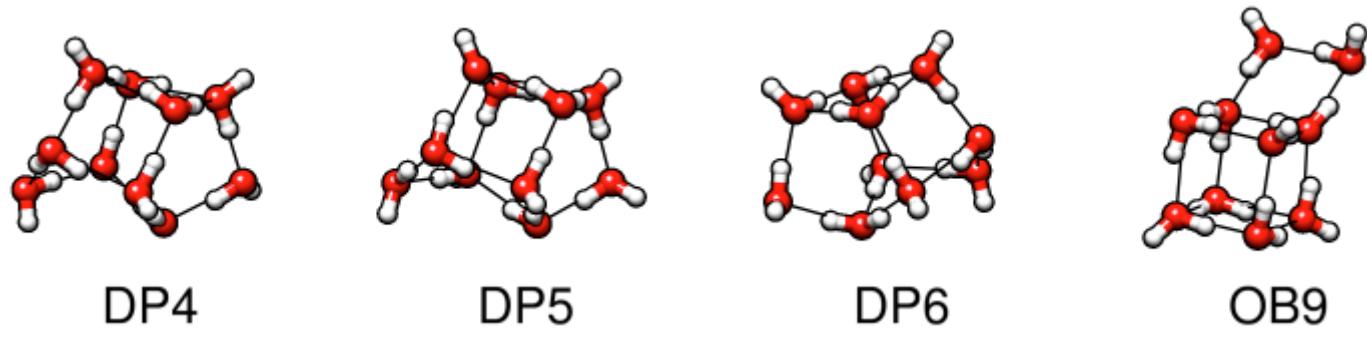
kcal/mol	DP1	OB4	OB5	DP2
$\Delta\Delta E_e$	1.82	2.17	2.18	2.23
$\Delta\Delta G_{298}$	1.31	1.83	1.22	1.40

... OB6	... OB7	... OB8	... DP3
30 (H2O)10 O -1.21997 1.81531 -1.56620 H -1.56037 2.54138 -2.11172 H -1.89421 1.68466 -0.83408 O -0.68201 0.98539 2.23251 H -0.01968 1.22519 1.53025 H -0.41174 1.46484 3.03096 O -2.80920 -1.46505 -0.07656 H -3.51730 -2.08393 -0.31335 H -2.25455 -1.35611 -0.90508 O -2.88093 1.29031 0.46907 H -2.27734 1.29069 1.24223 H -3.08190 0.33768 0.33402 O 3.74433 1.36389 0.04166 H 2.77466 1.54012 0.07036 H 4.04949 1.79205 -0.77272 O 3.71459 -1.41087 -0.21483 H 3.83459 -0.43395 -0.13054 H 4.04649 -1.77216 0.62104 O 0.95670 1.36902 0.08624 H 0.95851 0.39633 -0.14973 H 0.34222 1.75957 -0.57777 O 0.98554 -1.26442 -0.48517 H 0.52756 -1.62226 0.32149 H 1.94310 -1.50859 -0.42649 O -0.58881 -1.83832 1.66132 H -0.61939 -0.95267 2.07765 H -1.44399 -1.89387 1.18388 O -1.20465 -0.99160 -2.17289 H -1.19339 -0.01176 -2.19668 H -0.32743 -1.22631 -1.79482	30 (H2O)10 O 0.76006 -1.76744 -1.65344 H 0.73310 -2.30162 -2.46254 H 0.79250 -0.80830 -1.95795 O -3.71495 1.43827 -0.11017 H -3.98674 1.80659 -0.96476 H -2.74079 1.60908 -0.06843 O 0.85507 0.83464 -2.22996 H 1.67421 1.12828 -1.77542 H 0.13753 1.18832 -1.65354 O -3.69586 -1.30902 0.04102 H -3.79526 -0.32769 -0.06421 H -4.25247 -1.52758 0.80387 O 2.85961 -1.36966 0.21812 H 2.24660 -1.70935 -0.46892 H 2.31183 -1.34381 1.03144 O 0.93136 -0.90557 2.26292 H 0.83293 -1.37853 3.10368 H 0.13346 -1.13680 1.72323 O 1.03186 1.91579 1.60841 H 1.79245 1.86270 0.99152 H 1.04030 1.04656 2.05747 O 2.95533 1.24943 -0.39037 H 3.86644 1.56462 -0.49480 H 3.02538 0.27669 -0.16727 O -1.00558 -1.34624 0.41588 H -0.55187 -1.70234 -0.38249 H -1.98297 -1.48959 0.30964 O -0.97124 1.39118 -0.17541 H -0.34601 1.76421 0.50260 H -0.97591 0.42752 0.0409	30 (H2O)10 O -0.95449 1.39730 -0.07453 H -0.34312 1.70317 0.64810 H -0.96939 0.41784 0.05372 O 0.81806 -1.68499 -1.74609 H 1.59257 -1.67486 -1.10773 H 0.99999 -2.40423 -2.37082 O 2.92582 1.30759 -0.27213 H 2.24869 1.31314 -1.01255 H 3.64959 1.87967 -0.57097 O -1.02245 -1.37503 0.28421 H -1.99955 -1.50387 0.15594 H -0.56039 -1.66962 -0.53378 O 2.76733 -1.47079 0.08135 H 2.26834 -1.46457 0.92577 H 3.05484 -0.53662 -0.02317 O -3.70802 -1.29497 -0.10563 H -3.80038 -0.30773 -0.13363 H -4.27053 -1.57008 0.63430 O 1.01277 1.75478 1.79323 H 1.78836 1.75927 1.19315 H 1.01265 0.84710 2.15869 O 0.97334 1.15202 -2.09764 H 0.88431 0.18408 -2.22406 H 0.20277 1.38141 -1.52690 O 0.89288 -1.10740 2.19339 H 0.10249 -1.28805 1.62451 H 0.77504 -1.63977 2.99515 O -3.70028 1.45619 -0.05741 H -3.94989 1.88091 -0.89239 H -2.72612 1.61516 0.01670	30 (H2O)10 O 0.18982 0.11181 2.28480 H -0.13066 -0.72893 1.83299 H 0.16729 -0.08158 3.23483 O -0.64576 -2.09357 1.05677 H -1.59872 -2.00093 0.82233 H -0.18516 -2.14249 0.19086 O 0.71078 -1.87991 -1.41403 H 0.56907 -2.50533 -2.14206 H 0.38919 -0.99298 -1.76520 O 2.57178 0.89815 0.96452 H 1.84770 0.58799 1.55011 H 2.91715 0.07982 0.53603 O -3.26899 -1.53888 0.26483 H -3.86562 -1.34330 1.00292 H -3.11877 -0.67026 -0.17425 O -0.17609 0.46439 -2.30724 H 0.36227 1.18210 -1.90520 H -0.107194 0.60143 -1.93008 O -2.56616 0.92836 -0.83064 H -0.207064 1.43496 -0.11450 H -3.21044 1.55630 -1.19374 O -1.10023 2.23201 0.95710 H 3.32178 -2.22517 0.33843 H 2.40118 -1.68553 -0.77902 O 1.15464 2.36732 -0.72137 H 1.67456 3.13966 -0.99292 H 1.76445 1.82584 -0.12861



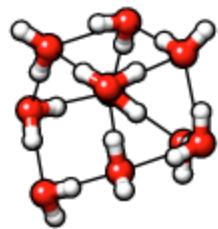
kcal/mol	OB6	OB7	OB8	DP3
$\Delta\Delta E_e$	2.26	2.35	2.38	2.58
$\Delta\Delta G_{298}$	1.81	1.90	1.96	0.18

...(<chem>H2O</chem>)10			
DP4 30 (<chem>H2O</chem>)10 O 0.24123 0.55733 -2.30905 H 1.11496 0.76622 -1.91445 H -0.36979 1.21667 -1.91004 O -0.35460 0.11460 2.28840 H 0.13311 0.89316 1.88345 H -0.26832 0.23324 3.24751 O 3.35203 -1.17820 0.46604 H 2.47761 -1.56602 0.75493 H 3.78162 -1.88803 -0.03471 O -2.74164 0.71656 0.86874 H -2.98473 -0.13055 0.42622 H -2.04029 0.46376 1.50674 O 0.79323 2.20729 1.07631 H 0.07347 2.46485 0.45965 H 1.50576 1.88232 0.48397 O -3.06876 -1.75629 -0.38578 H -3.06160 -2.45882 0.28227 H -2.18936 -1.82490 -0.82388 O 2.58802 1.06136 -0.79823 H 2.92684 0.22284 -0.37212 H 3.37687 1.56894 -1.04391 O 0.88981 -2.11254 1.04788 H 0.42172 -2.11322 0.18578 H 0.43906 -1.41233 1.56928 O -1.33975 2.28078 -0.75564 H -1.93709 1.69893 -0.19079 H -1.89501 3.02085 -1.04611 O -0.47797 -1.84797 -1.43613 H -0.21931 -0.93607 -1.77642 H -0.33830 -2.44523 -2.18774	DP5 30 (<chem>H2O</chem>)10 O -3.25270 -1.49728 -0.35955 H -3.59318 -2.10929 0.31076 H -3.12025 -0.63798 0.13225 O -0.77266 -1.98925 -1.25064 H -1.71319 -1.85866 -0.93453 H -0.82090 -2.68352 -1.92641 O 1.02400 2.29006 0.99169 H 0.27576 2.56653 0.41838 H 1.68603 1.93210 0.36148 O 2.59584 0.91373 -0.91210 H 3.33119 1.23891 -1.45418 H 2.91856 0.05838 -0.50622 O -0.12858 0.21028 2.22427 H 0.35423 0.98417 1.80542 H -0.06414 0.35950 3.18074 O -1.18334 2.38886 -0.74898 H -1.51222 3.08456 -1.33901 H -0.77684 1.69450 -1.34884 O -2.66419 0.74590 1.01984 H -2.33272 1.42307 0.39199 H -1.86526 0.51751 1.54191 O 3.31962 -1.42987 0.17137 H 2.44478 -1.78820 0.49615 H 3.87881 -1.39691 0.96238 O 0.88519 -2.17423 1.05253 H 0.31383 -2.23815 0.25758 H 0.53227 -1.39683 1.53758 O 0.08637 0.54148 -2.20018 H 1.00184 0.61018 -1.85269 H -0.21507 -0.35727 -1.94074	DP6 30 (<chem>H2O</chem>)10 O -0.32518 0.56756 -2.28088 H 0.24589 1.24853 -1.86083 H 0.10434 -0.29001 -2.06448 O -3.19793 -1.50223 0.48318 H -3.58413 -1.16783 1.30692 H -3.08249 -0.70164 -0.07919 O 0.79936 -1.86686 -1.38809 H 0.26527 -2.04603 -0.55098 H 0.65748 -2.63965 -1.95748 O 0.14874 0.10534 2.24845 H 0.04887 0.23183 3.20501 H -0.39158 0.83886 1.82796 O 3.34039 -1.35072 -0.34978 H 2.49609 -1.58693 -0.79879 H 3.50774 -2.08471 0.26073 O -1.14274 2.12027 1.03757 H -0.41392 2.45515 0.46931 H -1.79801 1.77324 0.39445 O 2.55578 0.96581 0.99340 H 1.84262 0.60365 1.56111 H 2.93743 0.17899 0.53704 O -0.53875 -2.25915 0.86264 H -1.50687 -2.12339 0.73309 H -0.27514 -1.51591 1.44799 O 1.06864 2.40925 -0.66661 H 1.70287 1.88671 -0.08464 H 1.56198 3.19479 -0.94954 O -2.61874 0.79760 -0.97605 H -1.77724 0.66238 -1.51517 H -3.25800 1.18712 -1.59316	OB9 30 (<chem>H2O</chem>)10 O 0.91426 -1.46904 -0.07333 H 0.32794 -1.56603 -0.87147 H 0.31657 -1.65581 0.70159 O -2.97413 -1.25621 -0.08518 H -3.88937 -1.57627 -0.10031 H -3.03520 -0.26011 -0.01650 O 1.02321 1.22821 0.04943 H 1.99006 1.45264 0.07223 H 1.01606 0.22881 0.01093 O -2.86841 1.42710 0.09747 H -2.28761 1.63843 -0.66418 H -2.28765 1.55153 0.87811 O -0.83651 1.55144 -1.88864 H -0.65882 2.23147 -2.55646 H -0.06204 1.56195 -1.26562 O 3.66923 -1.41188 0.06862 H 4.04551 -1.96615 -0.63075 H 2.69835 -1.58691 0.03872 O -0.94283 -1.33394 -2.07207 H -1.74595 -1.46257 -1.52326 H -0.93540 -0.37008 -2.24142 O 3.75561 1.35038 0.08406 H 3.86657 0.36737 0.11953 H 4.18414 1.61479 -0.74397 O -0.96070 -1.56289 1.89794 H -0.93769 -0.62325 2.17157 H -1.76182 -1.61956 1.33482 O -0.80690 1.32271 2.05128 H -0.03980 1.40714 1.42587 H -0.58642 1.86562 2.82390

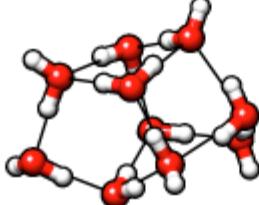


kcal/mol	DP4	DP5	DP6	OB9
$\Delta\Delta E_e$	2.76	2.86	2.96	3.09
$\Delta\Delta G_{298}$	0.21	0.50	0.64	1.76

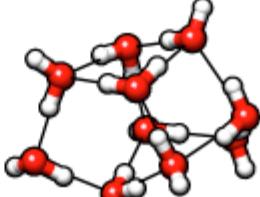
DP7 ...(H ₂ O)10	DP8 ... (H ₂ O)10	DP9 ... (H ₂ O)10	OB10 ... (H ₂ O)10
30 (H ₂ O)10 O 2.38545 -0.44491 1.36546 H 1.53234 -0.47660 1.84835 H 2.38550 0.44802 0.95786 O -2.21276 -1.94339 1.48631 H -1.86824 -2.84589 1.55788 H -1.52914 -1.37740 1.91482 O -2.35555 -0.93322 -1.11462 H -2.38540 -1.34342 -0.21883 H -1.50594 -1.22807 -1.50450 O 2.27820 -2.23514 -0.65278 H 2.37865 -1.57837 0.09286 H 2.25989 -3.10090 -0.21876 O 0.24821 -1.38325 -2.18895 H 0.38762 -1.78428 -3.06101 H 0.97208 -1.75575 -1.61010 O -0.22542 -0.28305 2.53824 H -0.25163 -0.14430 3.49874 H -0.41956 0.62641 2.14836 O 0.55516 1.44400 -2.13392 H -0.36307 1.67225 -1.87009 H 0.52624 0.46824 -2.24475 O -1.97484 1.68674 -0.91364 H -2.76920 2.14205 -1.23320 H -2.18906 0.70413 -0.96164 O 1.86641 2.04160 0.11504 H 2.49673 2.75394 -0.07389 H 1.45102 1.80829 -0.76846 O -0.59041 2.13002 1.49105 H 0.28989 2.30448 1.09170 H -1.19443 2.07181 0.71708	30 (H ₂ O)10 O 2.74388 0.63977 0.98070 H 1.97180 0.40757 1.54025 H 2.38712 1.32857 0.37996 O -0.15662 0.69227 -2.26303 H -1.06183 0.77262 -1.89320 H 0.12148 -0.22351 -2.03895 O 0.63206 -1.88440 -1.37566 H 0.69446 -2.57190 -2.05729 H 1.56748 -1.77891 -1.03344 O -3.37585 -1.28710 0.31441 H -2.50792 -1.65935 0.64096 H -3.72661 -1.96972 -0.27744 O -0.89114 2.20056 1.12953 H -1.57365 1.87146 0.50470 H -0.15902 2.49581 0.54571 O 3.13644 -1.60197 -0.45945 H 3.09514 -0.74291 0.04965 H 3.38372 -2.26277 0.20595 O -2.58356 1.01669 -0.81577 H -3.36521 1.50384 -1.11906 H -2.93193 0.17139 -0.41051 O 0.26334 0.07626 2.27510 H 0.20150 0.18114 3.23770 H -0.22326 0.86789 1.89436 O -0.92182 -2.16769 1.00505 H -0.40696 -2.16474 0.17002 H -0.50964 -1.45720 1.54374 O 1.23879 2.36376 -0.70307 H 0.77819 1.74905 -1.34766 H 1.58110 3.09657 -1.23798	30 (H ₂ O)10 O 0.26286 0.04969 2.29155 H 0.18459 0.14865 3.25359 H -0.22679 0.83753 1.90748 O 2.74130 0.61384 0.99684 H 2.39211 1.31486 0.40580 H 1.97098 0.38999 1.56237 O 0.60945 -1.87049 -1.40070 H 1.55387 -1.80469 -1.07252 H 0.63054 -2.54999 -2.09285 O -0.92409 -2.17420 0.99067 H -0.41296 -2.15793 0.15373 H -0.50470 -1.47651 1.54061 O 3.11146 -1.60517 -0.48472 H 3.06518 -0.75689 0.04208 H 3.38290 -2.27498 0.16164 O 1.25680 2.37021 -0.66617 H 0.80304 1.76485 -1.32419 H 1.59867 3.11422 -1.18555 O -2.57453 1.02775 -0.83746 H -3.35875 1.52453 -1.11768 H -2.92110 0.17465 -0.44789 O -3.37024 -1.26108 0.31620 H -3.75132 -1.95710 -0.24014 H -2.50386 -1.64169 0.63729 O -0.13047 0.72843 -2.26243 H -1.04001 0.81568 -1.90568 H 0.13344 -0.19249 -2.04352 O -0.89158 2.17150 1.14234 H -0.15521 2.47502 0.56828 H -1.56827 1.84844 0.50810	30 (H ₂ O)10 O -1.14053 0.49953 2.26406 H -1.31178 0.50608 3.21854 H -1.25527 -0.45965 1.98097 O -0.49527 1.94852 -1.41908 H -0.25194 2.54120 -2.14743 H -0.48054 1.01594 -1.80356 O 3.74923 1.15525 0.18322 H 2.83761 1.33718 0.50334 H 4.33667 1.53599 0.85208 O 1.04990 1.40293 0.80580 H 0.56335 1.76243 0.02567 H 0.36325 1.25737 1.49545 O -2.79067 1.43084 0.14228 H -2.32926 1.26346 0.99198 H -2.10278 1.83199 -0.43074 O -0.51154 -0.58559 2.19551 H -1.40810 -0.88773 -1.93633 H 0.07667 -0.98863 -1.51293 O 3.59580 -1.54844 -0.47915 H 3.78282 -0.59238 -0.32337 H 4.14243 -2.01617 0.16956 O -2.95719 -1.05979 -0.86208 H -3.00552 -0.12304 -0.51430 H -3.84390 -1.26952 -1.19350 O -1.45305 -1.99625 1.34997 H -0.57833 -2.07065 0.90754 H -2.08826 -1.88576 0.60966 O 0.91654 -1.34015 0.06658 H 0.99543 -0.40897 0.37722 H 1.85167 -1.60390 -0.11855



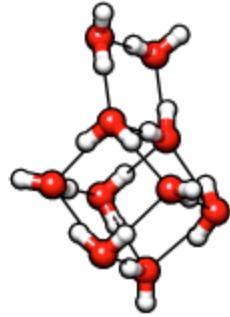
DP7



DP8



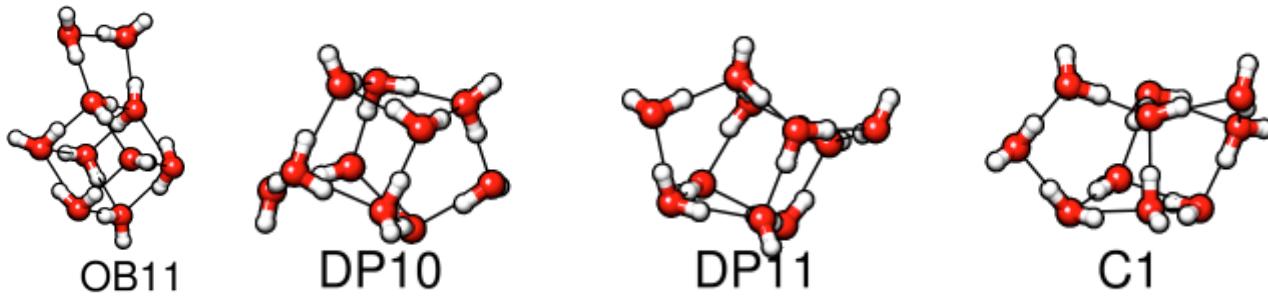
DP9



OB10

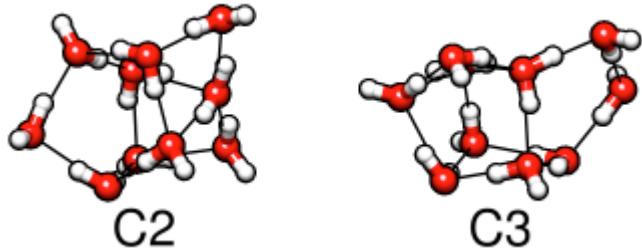
kcal/mol	DP7	DP8	DP9	OB10
$\Delta\Delta E_e$	3.11	3.14	3.21	3.21
$\Delta\Delta G_{298}$	0.66	1.34	0.84	1.46

...-(H ₂ O)10			
OB11 30 (H ₂ O)10 O 3.73533 -1.41001 -0.01843 H 4.18844 -1.61733 0.81271 H 3.80622 -0.43047 -0.10410 O -0.36621 -1.06229 -2.17684 H -1.27500 -1.25697 -1.86406 H -0.34766 -0.08453 -2.22465 O -1.38792 0.93696 2.18393 H -1.40873 -0.06054 2.05272 H -1.66364 1.08528 3.10199 O -1.38191 -1.67718 1.63043 H -0.49096 -1.82864 1.24330 H -1.98408 -1.73575 0.85675 O -0.42791 1.75418 -1.59828 H -0.01622 2.47674 -2.09734 H 0.13074 1.63332 -0.78363 O 0.97972 -1.45411 0.15188 H 0.59849 -1.43161 -0.76802 H 1.94567 -1.64607 0.06377 O 3.57499 1.39135 -0.06124 H 2.67416 1.50018 0.31885 H 4.15137 1.96045 0.46947 O 0.92590 1.18267 0.68825 H 0.25689 1.29892 1.40130 H 0.95794 0.19186 0.54866 O -2.82380 -1.23468 -0.75706 H -3.69261 -1.54958 -1.05077 H -2.93417 -0.25624 -0.57779 O -2.86360 1.40016 -0.20684 H -2.47832 1.41463 0.69559 H -2.13535 1.72005 -0.78118	DP10 30 (H ₂ O)10 O -0.27083 0.03781 2.29411 H 0.22094 0.82657 1.91450 H -0.19679 0.13384 3.25677 O -3.10652 -1.60652 -0.49212 H -3.35509 -2.28346 0.15598 H -3.06480 -0.75972 0.03730 O 3.35935 -1.27152 0.31689 H 2.49137 -1.65192 0.63414 H 3.74009 -1.96520 -0.24260 O -2.74215 0.61191 0.99265 H -1.97409 0.38476 1.55996 H -2.38895 1.31330 0.40437 O 2.57818 1.02853 -0.82320 H 2.91675 0.16919 -0.44016 H 3.36780 1.52417 -1.08997 O 0.91057 -2.18080 0.98291 H 0.49407 -1.48479 1.53733 H 0.40126 -2.15560 0.14507 O 0.89006 2.16271 1.15733 H 0.15661 2.47090 0.58202 H 1.56822 1.84155 0.52354 O 0.14345 0.74741 -2.26710 H 1.05144 0.83256 -1.90591 H -0.12146 -0.17452 -2.05394 O -0.60476 -1.85333 -1.41654 H -0.62316 -2.53270 -2.10892 H -1.55141 -1.78378 -1.09585 O -1.25050 2.37373 -0.65968 H -0.79424 1.77456 -1.32162 H -1.59322 3.12084 -1.17402	DP11 30 (H ₂ O)10 O -2.68008 -0.82836 0.95071 H -1.97316 -0.61105 1.59654 H -2.96162 0.03967 0.57622 O -1.28816 -2.10674 -0.90420 H -1.82200 -2.83732 -1.25341 H -1.87241 -1.64659 -0.22151 O 3.39286 1.17025 0.56583 H 3.86658 1.80180 0.00408 H 3.20476 0.40116 -0.01798 O -0.55247 2.07662 -1.08182 H -0.03853 2.04128 -0.20940 H -0.39882 2.97123 -1.42447 O 2.53229 -0.94294 -1.03825 H 1.73168 -0.67713 -1.58683 H 3.08033 -1.48954 -1.62267 O 0.78717 1.98515 1.18173 H 0.43067 1.24127 1.71610 H 1.73434 1.75873 1.03079 O 0.31129 -0.29228 -2.35103 H -0.34608 -0.92337 -1.98188 H 0.01732 0.58819 -2.02732 O 0.89687 -2.27630 0.86782 H 0.16029 -2.44623 0.24071 H 1.59596 -1.88886 0.29792 O -0.25675 -0.35821 2.34959 H -0.13847 -0.56895 3.28887 H 0.23170 -1.07800 1.85096 O -3.21017 1.58602 -0.34763 H -2.29305 1.82108 -0.62055 H -3.67236 1.39694 -1.17811	C1 30 (H ₂ O)10 O 0.75814 0.12575 -1.98000 H 0.41270 -0.78755 -1.86533 H 1.70896 0.04899 -1.75919 O -0.07522 -2.41677 -1.12261 H -0.88377 -2.24690 -0.54577 H -0.27864 -3.22263 -1.62224 O -2.49643 2.55071 -0.28647 H -2.42595 2.87699 -1.19685 H -1.57225 2.29903 -0.04474 O 2.58136 2.41420 0.60631 H 2.95950 1.57318 0.25629 H 2.87386 3.09417 -0.01986 O -3.78281 0.09795 -0.31470 H -4.54414 0.20634 0.27446 H -3.34724 0.98557 -0.32369 O 0.00649 1.51237 0.22731 H 0.84713 2.00055 0.41490 H 0.20452 1.01592 -0.61759 O -2.06453 -1.90584 0.55437 H -2.69506 -1.22211 0.22171 H -1.56455 -1.46272 1.27028 O -0.15439 -0.46391 2.07669 H -0.17629 -0.07428 2.96455 H -0.11507 0.30553 1.44320 O 1.90752 -1.92838 0.81345 H 1.29883 -2.30472 0.13911 H 1.29574 -1.49549 1.44788 O 3.21162 -0.04285 -0.54125 H 2.76774 -0.74869 0.02237 H 4.09994 -0.38690 -0.72433



kcal/mol	OB11	DP10	DP11	C1
$\Delta\Delta E_e$	3.23	3.29	3.40	4.42
$\Delta\Delta G_{298}$	1.67	0.93	1.06	1.44

...-(H ₂ O)10			
C2 30 (H ₂ O)10 O -0.66131 2.77378 0.59449 H -0.51236 2.02134 1.20476 H -1.22586 2.38572 -0.10707 O 2.96680 -2.14784 -0.09973 H 3.34000 -2.35223 0.77102 H 2.85353 -1.16627 -0.09867 O -1.34238 -1.77390 1.39147 H -2.16153 -1.51196 0.90729 H -0.81647 -2.29004 0.74554 O 0.38377 -2.85239 -0.59458 H 0.35358 -3.68010 -1.09861 H 1.34328 -2.70044 -0.38077 O 2.09061 0.43066 0.09882 H 1.45894 0.41797 0.85529 H 2.24422 1.39406 -0.08011 O 1.88985 3.10341 -0.34316 H 0.93583 3.09403 -0.06512 H 2.30478 3.77340 0.22048 O 0.15063 -0.28848 -1.81459 H 0.89204 0.04720 -1.25961 H 0.07820 -1.22731 -1.54286 O 0.05520 0.39420 2.00169 H -0.49836 -0.41821 1.77822 H 0.17966 0.35939 2.96284 O -3.52429 -0.78812 -0.03987 H -3.08734 -0.06958 -0.55472 H -4.12794 -0.32596 0.56146 O -2.01701 1.16324 -1.33165 H -2.29314 1.51673 -2.19224 H -1.19595 0.61580 -1.53029	C3 30 (H ₂ O)10 O -0.75262 -0.10860 -1.95067 H -1.70028 -0.02016 -1.71845 H -0.32037 0.53538 -1.34195 O 0.10256 1.60647 0.10876 H 1.00936 1.99517 -0.01407 H 0.17143 0.97899 0.86313 O -3.25100 0.16443 -0.59702 H -4.14172 0.22716 -0.97491 H -3.05209 1.06576 -0.22308 O -0.16181 -2.53145 -1.00924 H -0.32690 -1.64193 -1.44389 H -0.19631 -3.18633 -1.72353 O 0.01987 -0.40556 2.04861 H -0.04453 -0.38695 3.01588 H -0.77113 -0.93593 1.73140 O -2.42734 2.58016 0.31170 H -2.55141 2.77733 1.25255 H -1.45461 2.41471 0.21496 O 3.86078 -0.04414 -0.34927 H 3.22947 -0.72148 0.01242 H 4.09233 -0.36842 -1.23220 O 2.05407 -1.84172 0.63746 H 1.41747 -2.21935 -0.00495 H 1.47235 -1.37376 1.27088 O 2.66630 2.40398 -0.27892 H 3.13461 2.86179 0.43509 H 3.13363 1.53189 -0.36263 O -1.99317 -1.82616 1.00673 H -1.47815 -2.30244 0.31906 H -2.56429 -1.21077 0.49922		



kcal/mol	C2	C3		
$\Delta\Delta E_e$	4.42	4.47		
$\Delta\Delta G_{298}$	1.35	0.62		