

CCSD(T) Complete Basis Set Limit Relative Energies for Low-Lying Water Hexamer Structures

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MP2 and CCSD(T) complete basis set (CBS) limit relative electronic energies (ΔE_e) have been determined for eight low-lying structures of the water hexamer by combining explicitly correlated MP2-R12 computations with higher-order correlation corrections from CCSD(T) calculations. Higher-order correlation effects are quite substantial and increase ΔE_e by at least $+0.19$ kcal mol⁻¹ and as much as $+0.59$ kcal mol⁻¹. The effects from zero-point vibrational energy (ZPVE) have been assessed from unscaled harmonic vibrational frequencies computed at the MP2 level with a correlation consistent triple- ζ basis set (cc-pVTZ for H and aug-cc-pVTZ for O). ZPVE effects are even more significant than higher-order correlation effects and are uniformly negative, decreasing the relative energies by -0.16 kcal mol⁻¹ to -1.61 kcal mol⁻¹. Although it has been widely accepted that the cage becomes the lowest-energy structure after ZPVE effects are included [*Nature* **1996**, 381, 501–503], the prism is consistently the most stable structure in this work, lying 0.06 kcal mol⁻¹ below the nearly isoenergetic cage isomer at the electronic MP2 CBS limit, 0.25 kcal mol⁻¹ below at the electronic CCSD(T) CBS limit, and 0.09 kcal mol⁻¹ below at the harmonic ZPVE corrected CCSD(T) CBS limit. Moreover, application of any uniform scaling factor less than unity to correct for anharmonicity further stabilizes the prism and increases the relative energies of the other structures.

1. Introduction

The water hexamer is an important and widely studied water cluster because it represents the crossover point from two-dimensional to three-dimensional hydrogen-bonding networks.^{1–8} Even with only six water molecules, there is a staggering number of possible hydrogen-bonding patterns for (H₂O)₆.⁹ Fortunately, only few fundamental motifs give rise to the most stable structures, and they are labeled with descriptive monikers such as “bag”, “book”, “cage”, “cyclic”, and “prism”. Some examples of these structures are shown in Figure 1. Note that different isomers can be obtained through subtle changes in the relative orientations of the H atoms not involved in hydrogen bonding. This distinction is particularly important for the book (Figure 1e and f) and cyclic-boat structures (Figure 1g and h), where the same name is sometimes used to describe different (H₂O)₆ structures. In this work, book-1 and cyclic-boat-1 are used to denote the conformation of these isomers with the lower electronic energy, while the number 2 is appended to the higher-energy structure.

Electronic structure computations indicate that most of the low-lying (H₂O)₆ isomers depicted in Figure 1 have very similar electronic energies,^{1,6} and several forms of the water hexamer have been observed experimentally under various conditions.^{2,7,10–16} In some cases, however, definitive assignment of the observed spectra to a particular structure was not possible, potentially due to the presences of multiple isomers.

In recent years, rather sophisticated and demanding electronic structure computations have been performed on these water hexamer isomers to help resolve their relative electronic energies. For example, in 2002, MP2 complete basis set (CBS) limit relative electronic energies were reported for the book, cage, prism, and cyclic-chair isomers of (H₂O)₆.¹⁷ Electronically,

the prism and cage structures (Figure 1a and b) were found to be isoenergetic with the cage only 0.07 kcal mol⁻¹ above the prism. The book and cyclic structures were only slightly higher in energy at the MP2 CBS limit, 0.25 and 1.00 kcal mol⁻¹, respectively, above the prism isomer. More recently, two groups have examined higher-order correlation effects in this system by computing CCSD(T) relative electronic energies for water hexamer isomers^{18,19} with correlation consistent triple- ζ basis sets augmented with diffuse functions. The CCSD(T) results are in qualitative agreement with the MP2 CBS data, but there are slight quantitative differences in the relative electronic energies on the order of a few tenths of a kcal mol⁻¹, which is not unexpected given the differences in optimized structures and basis sets. (See the Computational Details for more detail about the structures examined in refs 17, 18, and 19.)

The effects of zero-point vibrational energy (ZPVE)^{19–22} and temperature (thermal energy)²³ on the relative energies of the water hexamer isomers have also been examined. The ZPVE represents a large fraction of the total binding energy and significantly changes the relative energies of the isomers. Temperature can also have a significant effect on the energetics of the (H₂O)₆ system. For example, in a study of small water clusters that included the prism, cage, and cyclic-chair water hexamers, a variety of popular model chemistries (e.g., G2, G3, CBS-APNO) revealed that, while the cage and prism forms of the hexamer are the lowest energy structures at very low temperatures, the cyclic-chair structure becomes more favored at higher temperatures.

This work builds on recent high-accuracy electronic structure studies.^{17–19} Explicitly correlated MP2-R12 energies are combined with higher-order correlation corrections from CCSD(T) calculations to estimate the CBS limit CCSD(T) relative electronic energies (ΔE_e) for the eight water hexamer structures shown in Figure 1. Harmonic vibrational frequencies are computed with the MP2 method and a correlation consistent

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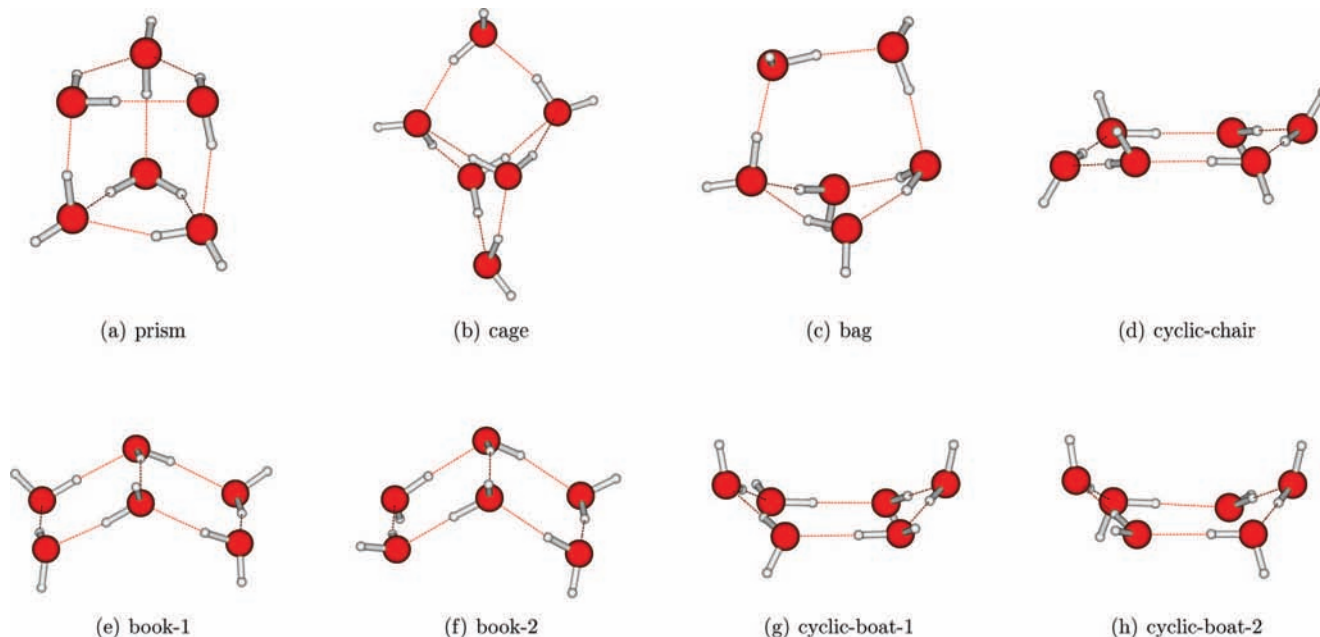


Figure 1. Structures of eight low-lying $(\text{H}_2\text{O})_6$ isomers.

triple- ζ basis set (with diffuse functions on O atoms) and used to examine ZPVE effects on the relative energies (ΔE_0).

2. Computational Details

The authors of refs 17, 18, and 19 graciously provided the Cartesian coordinates for their $(\text{H}_2\text{O})_6$ structures, which enabled us to correlate them with those shown in Figure 1. The book and ring hexamers of ref 17 correspond to book-1 and cyclic-chair in this work. The book and boat structures of ref 19 are identical to the book-1 and cyclic-boat-1 isomers in Figure 1, while the book and boat structures of ref 18 correspond to book-2 and cyclic-boat-2 here. The prism, cage, and cyclic-chair structures were consistent throughout the studies. This work examines these seven unique structures as well as the bag isomer from ref 19.

All structures in this study have been fully optimized at the MP2 level with a correlation consistent triple- ζ basis set (cc-pVTZ basis set for H and aug-cc-pVTZ for O). This basis set will, hereafter, be denoted haTZ. Cartesian coordinates for the MP2/haTZ optimized structures of the prism, cage, bag, cyclic-chair, book-1, and boat-1 were obtained from the Supporting Information for ref 19. The other structures were optimized in this work. It is worth noting that both cyclic-boat structures deviate only slightly from C_2 symmetry. However, if the boat structures are reoptimized at the MP2/haTZ level in C_2 symmetry, the electronic energies increase by approximately $24 \mu E_h$ ($0.015 \text{ kcal mol}^{-1}$). Residual Cartesian gradients of the optimized structures reported here are less than $1 \times 10^{-4} E_h \text{ bohr}^{-1}$.

Previous studies have shown that the correlation energy converges to the CBS limit slowly when using correlation consistent basis sets.²⁴ However, dramatic progress in the field of explicitly correlated R12 methods now allows one to “bypass the slow convergence of the conventional methods, by augmenting the traditional orbital expansions with small number of terms that depend explicitly on the inter-electronic distance r_{12} .”²⁴ In this work, the MP2 CBS limit relative electronic energies ($\Delta E_e^{\text{MP2/CBS}}$) of the eight structures are determined with explicitly correlated MP2-R12 computations²⁵ employing the massive K2—basis set^{26,27} (222 basis functions per monomer, as compared to 74 for the haTZ basis set). This procedure provides

MP2 CBS limit interaction energies comparable to those obtained with extrapolation schemes for correlation consistent basis sets.^{26,28–33} A correction for higher-order correlation effects was calculated from the difference between the MP2 and CCSD(T) relative energies with the haTZ basis set ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$). Reliable estimates of CCSD(T) CBS limit relative energies ($\Delta E_e^{\text{CCSD(T)/CBS}}$) are routinely obtained by combining terms.^{31–40}

$$\Delta E_e^{\text{CCSD(T)/CBS}} = \Delta E_e^{\text{MP2/CBS}} + \delta_{\text{MP2}}^{\text{CCSD(T)}} \quad (1)$$

In all MP2, MP2-R12, and CCSD(T) computations, the 1s-like core orbitals of O were excluded from the correlation procedure (i.e., the frozen core approximation). The geometry optimizations and MP2-R12 calculations were performed with the MPQC software package,^{41,42} and the latter employed the A' resolution of the identity approximation.⁴³ Harmonic vibrational frequencies were obtained with the analytical MP2 Hessians available in Gaussian 03.⁴⁴ Finally, the CCSD(T) computations were performed with the MOLPRO⁴⁵ and PSI3⁴⁶ programs. Electronic energies were converged to at least $1 \times 10^{-7} E_h$ in all single point energy computations. Counterpoise (CP) corrections^{47,48} for basis set superposition error (BSSE)^{49,50} were not applied because (i) the MP2-R12/K2—energies are essentially at the CBS limit where BSSE is zero by definition, and (ii) the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction for higher-order correlation effects in weakly bound noncovalent clusters is rather insensitive to BSSE.^{32,33,51}

3. Results and Discussion

3.1. Relative Electronic Energies. The MP2 CBS limit relative electronic energies ($\Delta E_e^{\text{MP2/CBS}}$) of the eight water hexamer structures are given in the second column of Table 1, and the Cartesian coordinates of the optimized structures can be found in the Supporting Information. The $\Delta E_e^{\text{MP2/CBS}}$ values for the cage, book-1, cyclic-chair, and six isolated monomers (i.e., the electronic dissociation energy, D_e) are virtually identical to the MP2 CBS limits of 0.1, 0.3, 1.1, and $45.9 \text{ kcal mol}^{-1}$, respectively, obtained in an earlier study by Xantheas, Burnham, and Harrison, who applied a customized extrapolation procedure

TABLE 1: Higher-Order Correlation Effects, $\delta_{\text{MP2}}^{\text{CCSD(T)}}$, and Relative Electronic Energies, ΔE_e , at the MP2 and CCSD(T) CBS Limits for the Eight $(\text{H}_2\text{O})_6$ Structures^a

structure	$\Delta E_e^{\text{MP2/CBS}}$	$\delta_{\text{MP2}}^{\text{CCSD(T)}}$	$\Delta E_e^{\text{CCSD(T)/CBS}}$	$\Delta E_e^{\text{CCSD(T)/haTZ } b}$	$\Delta E_e^{\text{CCSD(T)/haTZ } c}$
prism	0.00	+0.00	0.00	0.00	0.00
cage	0.06	+0.19	0.25	0.21	0.28
bag	1.23	+0.39	1.62	1.57	
cyclic-chair	1.21	+0.59	1.80	1.83	1.81
book-1	0.33	+0.39	0.72	0.71	
book-2	0.64	+0.39	1.02		1.06
cyclic-boat-1	2.20	+0.59	2.79	2.84	
cyclic-boat-2	2.28	+0.57	2.85		2.99
six monomers	45.86 ^d	+0.06	45.92 ^d	46.71 ^d	46.6 ^d

^a All values in kcal mol⁻¹. ^b Reference 18. ^c Reference 19. ^d D_e of the prism.

to both CP corrected and uncorrected MP2/aug-cc-pVXZ energies ($X = \text{D,T,Q,5}$).¹⁷ The two sets of results not only suggest that the MP2 CBS results are converged to 0.1 kcal mol⁻¹, but they also confirm that CP corrections need not be applied to the MP2-R12/K2—relative energies.

Corrections for higher-order correlation effects from MP2 and CCSD(T) computations ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) with the haTZ basis set are presented in the third column of Table 1. Note that these corrections significantly increase the energies of the $(\text{H}_2\text{O})_6$ isomers relative to the prism. This stabilization of the prism isomer by the CCSD(T) method with respect to MP2 relative energies is consistent with other studies of the water hexamer at the CCSD(T) level.^{18,19} All of the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ values are positive, increasing ΔE_e in an absolute sense by +0.19 kcal mol⁻¹ to +0.59 kcal mol⁻¹ and in a relative sense by 25% to 316% but having almost no effect on D_e (+0.06 kcal mol⁻¹ or <0.02%). Although other studies of other weakly bound complexes have observed that the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ term is quite insensitive to BSSE,^{32,33,51} the CP corrected D_e of the prism isomer was computed to demonstrate this trend holds true for the water hexamer. When a CP correction is applied, the higher-order correlation correction changes by 0.01 kcal mol⁻¹ from +0.06 to +0.07 kcal mol⁻¹ with the haTZ basis set.

The CCSD(T) CBS limit relative electronic energies were obtained by applying eq 1 to the data in the second and third columns of Table 1, and these results are given in the fourth column. One of the most interesting features of these data is that the near degeneracy of the prism and cage structures at the MP2 CBS limit is lifted at the CCSD(T) CBS limit. Although they are virtually isoenergetic at the former limit, the prism is 0.25 kcal mol⁻¹ more stable than the cage at the CCSD(T) CBS limit.

The $\Delta E_e^{\text{CCSD(T)/CBS}}$ data are in nearly perfect agreement with the CCSD(T)/haTZ relative electronic binding energies reported in refs 18 and 19 (shown in the last two columns of Table 1). Only for the cyclic-boat-2 structure do results differ by more than 0.05 kcal mol⁻¹, and in that case, the deviation still does not exceed 0.14 kcal mol⁻¹. Even the CCSD(T) dissociation energies of the prism reported in the table differ by less than 0.8 kcal mol⁻¹, which corresponds to a relative difference of less than 2%.

3.2. ZPVE Inclusive Relative Energies. As mentioned in the Introduction, the zero-point vibrational energy (ZPVE) can significantly affect the relative energies of these isomers. The first column of data in Table 2 lists the effect of ZPVE (to 2 decimal places for consistency) on the relative energies of the isomers obtained from unscaled MP2/haTZ harmonic vibrational frequencies. These MP2/haTZ δ_{ZPVE} terms are added to the $\Delta E_e^{\text{CCSD(T)/CBS}}$ values from Table 1 to obtain ZPVE corrected relative energies at the CCSD(T) CBS limit (ΔE_0), which are listed in the third column of Table 2.

TABLE 2: Harmonic ZPVE Corrections, δ_{ZPVE} , and ZPVE Corrected CCSD(T) CBS Limit Relative Energies, ΔE_0 , for the Eight $(\text{H}_2\text{O})_6$ Structures^a

structure	δ_{ZPVE}	$\Delta E_0^{\text{CCSD(T)/CBS}}$	δ_{ZPVE}^b	δ_{ZPVE}^c	δ_{ZPVE}^d
prism	+0.00	0.00	+0.00	+0.00	+0.00
cage	-0.16	0.09	-0.35	-0.20	+1.10
bag	-0.78	0.84			+0.49
cyclic-chair	-1.29	0.51	-1.59	-1.18	+1.25
book-1	-0.51	0.21			+0.76
book-2	-0.54	0.48		-0.58	
cyclic-boat-1	-1.51	1.28	-1.89		-0.23
cyclic-boat-2	-1.61	1.24		-1.49	
six monomers	-13.71	32.21 ^e		-13.85	

^a All values in kcal mol⁻¹. ^b HF/6-311G(d, p) values from ref 20. ^c MP2/aug-cc-pVDZ values from ref 21. ^d MP2/haTZ values from ref 19. ^e D_0 of the prism.

The δ_{ZPVE} corrections are all negative, decreasing the energies of the isomers relative to the prism structure by as little as -0.16 kcal mol⁻¹ for the cage and by as much as -1.61 kcal mol⁻¹ for the cyclic-boat-2 structure. The ZPVE has a much larger absolute effect on the dissociation energy, -13.71 kcal mol⁻¹. Despite these significant negative corrections, the prism remains the lowest energy isomer at the ZPVE corrected CCSD(T) CBS limit. In a sense, the δ_{ZPVE} shifts essentially reverse the effects of the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ corrections. For example, $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ increases the relative energy of the cage by +0.19 kcal mol⁻¹, while δ_{ZPVE} pushes it back down by -0.16 kcal mol⁻¹. As a result, the cage is, once again, virtually isoenergetic with the prism at the harmonic ZPVE corrected CCSD(T) CBS limit ($\Delta E_0 = +0.09$ kcal mol⁻¹). The ZPVE corrections to the relative energies of the other isomers are even more pronounced, which effectively compresses the energetic spectrum of $(\text{H}_2\text{O})_6$ structures. The electronic energies of the eight isomers are separated by 2.85 kcal mol⁻¹ at the CCSD(T) CBS limit but only by 1.28 kcal mol⁻¹ after MP2/haTZ harmonic ZPVE effects are included.

While the large amplitude vibrational motions in weakly bound, noncovalent clusters tend to be highly anharmonic, this anharmonicity will not likely lead to qualitative changes in relative energetics of the $(\text{H}_2\text{O})_6$ structures examined here. Appropriate empirical scaling factors are a popular and straightforward means to estimate the anharmonic ZPVE.^{52,53} In this particular case, all of the harmonic δ_{ZPVE} terms in Table 2 are negative. Consequently, any scaling factor less than unity will stabilize the prism and increase ΔE_0 of the other isomers. Only with frequency scaling factors greater than unity could another isomer end up with a ZPVE inclusive energy lower than that of the prism. In fact, a scaling factor >1.39 is required to produce an isomer with an energy that is lower than that of the prism. (See figure in Supporting Information.) Typical ZPVE scaling factors for MP2 harmonic vibrational frequencies are slightly

less than unity (~ 0.95). Consequently, corrections for anharmonicity are not likely to change the overall conclusions drawn from the ΔE_0 values reported in Table 2. While diffusion quantum Monte Carlo (DQMC) calculations with the VRT(ASP-W)III potential also predict that ZPVE stabilizes the cage isomer,⁵⁴ the effect is an order of magnitude larger (-1.6 kcal mol⁻¹) than the harmonic value reported here. However, the DQMC ZPVE corrections were obtained utilizing a 2-body (with many-body polarization components), rigid monomer potential fit to experimental microwave and far-IR transitions for (D₂O)₂, and direct comparison to our harmonic ZPVE data for fully flexible monomers is not entirely rigorous.

The MP2/haTZ ZPVE corrections reported in the second column of Table 2 are very similar to those in the fourth and fifth columns from HF/6-311G (d, p) and MP2/aug-cc-pVDZ computations, respectively.^{20,21} All three sets of δ_{ZPVE} data are uniformly negative, which indicates the same overall effects from ZPVE and leads to consistent conclusions (i.e., $\Delta E_0 < \Delta E_c$). These results are in stark contrast to a recent study of the (H₂O)₆ system where the corresponding ΔE_0 values were almost always larger than ΔE_c when computed with a variety of density functional theory (DFT) techniques methods as well as the MP2 method with the haTZ basis set.¹⁹ In an attempt to resolve this discrepancy, we have also computed ZPVE corrections to the relative energies of the (H₂O)₆ isomers using five of the same DFT method/basis set combinations. These DFT δ_{ZPVE} results are reported in the Supporting Information and are consistent with the MP2 data from this work as well as the δ_{ZPVE} values from refs 20 and 21. Although scaling factors were used¹⁹ to determine the ZPVE corrected relative binding energies, they cannot account for discrepancies in the sign of δ_{ZPVE} in situations where the same method and basis set have been used to compute the harmonic vibrational frequencies (vide supra). While we can readily reproduce the electronic energies reported in ref 19, we have, as yet, not been able to reproduce their ZPVE corrected data. Therefore, raw electronic and ZPVE inclusive energies are provided in the Supporting Information to support the data reported here.

4. Conclusions

The MP2 and CCSD(T) CBS limit relative energies for eight low-lying structures of the water hexamer have been presented. Although the prism is the lowest-energy structure at both limits, the energies of the other structures relative to the prism (ΔE_c) increase significantly when higher-order correlation effects are included. The $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction increases ΔE_c by at least +0.19 kcal mol⁻¹ for the cage isomer and by as much as +0.59 kcal mol⁻¹ for the cyclic-chair and cyclic-boat-1 structures. Only when computing D_e of the prism do higher-order correlation corrections have a negligible effect. The CCSD(T) electronic dissociation energy of the prism differs from the MP2 value by only +0.06 kcal mol⁻¹.

Corrections for ZPVE (δ_{ZPVE}) from MP2/haTZ harmonic vibrational frequencies have the opposite sign of those for higher-order correlation effects ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) and tend to be somewhat larger. The δ_{ZPVE} terms decrease ΔE_c by at least -0.16 kcal mol⁻¹ for the cage structure and as much as -1.61 kcal mol⁻¹ for the cyclic-boat-2 isomer. Thus, the ZPVE effectively compresses the energetic separation between the eight isomers. At the CCSD(T) CBS limit, the largest $\Delta E_c = +2.85$ kcal mol⁻¹ while the maximum $\Delta E_0 = +1.28$ kcal mol⁻¹.

Despite the significant corrections from higher-order correlation effects and ZPVE, the relative energetics of these (H₂O)₆ isomers are qualitatively similar at the electronic and ZPVE

corrected CCSD(T) CBS limits. The prism is consistently the lowest energy structure, and the cage is nearly isoenergetic with the prism ($\Delta E_c = +0.25$ kcal mol⁻¹ and $\Delta E_0 = +0.09$ kcal mol⁻¹). The book isomers are slightly higher in energy. The bag and cyclic-chair structures are a bit further up the energetic spectrum, while the cyclic-boats are consistently the highest-energy structures examined in this work.

Since the 1996 *Nature* paper by Liu et al., it has been widely accepted that the cage becomes the most stable structure after ZPVE effects are included.³ In contrast, this work indicates that ZPVE corrections do not change the energetic ordering of the minima as long as sufficiently sophisticated electronic structure techniques are employed to capture higher-order correlation effects. In light of the data presented here, it is certainly reasonable to expect that the prism and cage structures (and even the book-1 isomer) would be observed in very low temperature experiments. However, one must hesitate from concluding that the prism, for example, is the most "stable" structure given the fleeting nature of these (H₂O)₆ species.⁵⁵

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Note Added in Proof. During the review process, a closely related work⁵⁶ was published that reports benchmark electronic energies from diffusion Monte Carlo (DMC) computations. The DMC relative energies of +0.84, +1.43, and +3.88 kcal mol⁻¹ for the cage, book-1, and cyclic-chair structures, respectively, are approximately 2 times larger than the corresponding $\Delta E_c^{\text{CCSD(T)/CBS}}$ values reported in Table 1. Yet, both sets of relative energies are consistent to within the statistical errors of the DMC computations. Combining the DMC electronic energies with our harmonic ZPVE corrections from Table 2 leads to the prism being significantly more stable than the cage (0.68 kcal mol⁻¹ versus our $\Delta E_0^{\text{CCSD(T)/CBS}}$ value of 0.09 kcal mol⁻¹).

Supporting Information Available: Tables of Cartesian coordinates for the MP2/haTZ-optimized structures from this work, ZPVE corrections from MP2 and DFT computations, and the corresponding raw electronic and zero-point vibrational energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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