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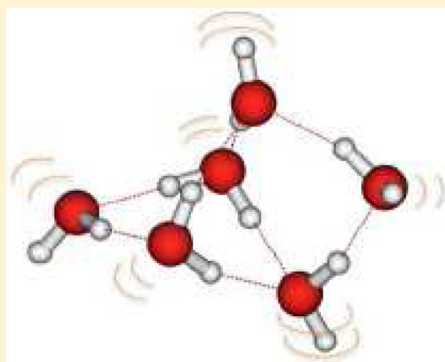
# Cage versus Prism: Electronic Energies of the Water Hexamer

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**ABSTRACT:** Recent experiments show that the cage isomer of the water hexamer is lower in energy than the prism isomer near 0 K, and yet state-of-the-art electronic structure calculations predict the prism to be lower in energy than the cage at 0 K. Here, we study the relative energies of the water hexamers from the parametric two-electron reduced density matrix (2-RDM) method in which the 2-RDM rather than the wave function is the basic variable of the calculations. In agreement with experiment and in contrast with traditional wave function methods, the 2-RDM calculations predict the cage to be more stable than the prism after vibrational zero-point correction. Multiple configurations from the hydrogen bonding are captured by the method. More generally, the results are consistent with our previous 2-RDM applications in that they reveal how multireference correlation in molecular systems is important for resolving small energy differences from hydrogen bonding as well as other types of intermolecular forces, even in systems that are not conventionally considered strongly correlated.



## 1. INTRODUCTION

Isomers of the water hexamer are the smallest stable water clusters whose water molecules are interwoven by three-dimensional networks of hydrogen bonds. Understanding these interactions at the relatively simple level of the hexamers is critical for understanding the behavior of bulk phases of water. The structure and energies of the hexamers, particularly the low-lying prism and cage isomers, have been an important testing ground for both empirical and *ab initio* force fields employed in large-scale simulations of water.<sup>1,2</sup> The water hexamers are also fundamentally interesting from a quantum chemical perspective because of their hydrogen bonding networks.

The energies and intermolecular forces of the water hexamer clusters depend on a subtle balance of electronic correlation and nuclear quantum effects, which presents a considerable challenge for quantum chemical theories. The electronic correlation has been addressed in previous studies,<sup>3–9</sup> including those that have applied coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] in augmented polarized triple- $\zeta$  basis sets<sup>7</sup> and extrapolated complete basis sets.<sup>8,9</sup> The accurate inclusion of nuclear quantum effects has been recently addressed by impressive quantum Monte Carlo (QMC) simulations of the prism and cage on full-dimensional potential energy surfaces (PESs) from CCSD(T).<sup>10</sup> Despite the sophistication of these calculations, there remains a small but important discrepancy with recent experiments,<sup>11</sup> which reveal that the cage structure is the global energy minimum at sufficiently low temperatures. Building upon earlier experiments on water clusters,<sup>12–18</sup> these experiments employed a chirped pulse Fourier microwave spectroscopy with supersonic expansions.<sup>11</sup> The CBS/CCSD(T) calculations, treating the vibrational motion in the harmonic approximation, find the

prism to be more stable than the cage by 0.09 kcal/mol.<sup>8,9,19</sup> The results of QMC simulations that include anharmonic contributions to the vibrational motion find the prism and cage to be isoenergetic, leading to the inference that the two isomers will be found in 1:1 ratios near 0 K.<sup>10</sup>

In this paper, we take a different approach to treating the critical electronic correlation in the prism and cage using the two-particle reduced density matrix (2-RDM) method,<sup>20–25</sup> in which the 2-RDM is parametrized to be *N*-representable with size-extensive energies. The method has been shown to include some multireference correlation effects that are not captured by traditional single-reference correlation methods.<sup>26–30</sup> We present results using parametric 2-RDM (p2-RDM) calculations in an augmented correlation-consistent polarized triple- $\zeta$  (aug-cc-pVTZ) basis set and in the complete basis set (CBS) limit, which, when corrected for vibrational motion, find the cage to be the global minimum energy structure, in agreement with the most accurate experimental measurements. In addition to supporting experimental findings, these results highlight the importance of subtle shades of single- and multireference correlation in describing chemical phenomena like hydrogen bonding.

## 2. THEORY

The energy ordering of the hexamers was recently revisited in a beautiful experiment by Pate and co-workers who measured the broad-band rotational spectra of water clusters in low-temperature inert gas expansions using helium, neon, and argon.<sup>11</sup> “Relative isomer populations,” they wrote, “at different

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expansion conditions establish that the cage isomer is the minimum energy structure.” Theoretically resolving such small differences in electronic energy demands sufficient coverage of the one-particle Hilbert space and an accurate and balanced treatment of single- and multireference correlation effects. In this section, we present an overview of the p2-RDM method as well as some additional details.

**A. Overview of the p2-RDM Method.** It has been shown that using the 2-RDM as the fundamental variable, parametrized by  $N$ -representability conditions, captures single-reference correlation as well as some multireference correlation not usually recovered by single-reference theories.<sup>20–22,26–30</sup> In the p2-RDM methods, the 2-RDM is parametrized in terms of single and double excitations to remain very nearly  $N$ -representable. A 2-RDM is  $N$ -representable if it can be derived by integrating an  $N$ -electron density matrix.<sup>31</sup> The expression for the energy is minimized as a functional of the 2-RDM to generate the ground-state energy without additional reference to the many-electron wave function.<sup>20,23,24</sup> This 2-RDM-based method is faster and more accurate than comparable electron-pair-based wave function methods including coupled cluster with single and double excitations (CCSD). The p2-RDM has been used to study systems that require a balanced description of single- and multireference electron correlation effects including the diradical isomers of olympicene<sup>29</sup> and the rotational barrier in diazene.<sup>27</sup> It has also been employed to resolve small energetic differences, which can be sensitive to multireference effects, in calculating the energy barrier stabilizing oxywater<sup>22</sup> and the relative populations of the *cis* and *trans* isomers of carbonic acid at 210 K.<sup>26</sup>

**B. Details of the p2-RDM Method.** The 2-RDM in the p2-RDM method is parametrized using first-order corrections to the Hartree–Fock 1- and 2-RDMs. Higher-order corrections of the 1- and 2-RDMs,  ${}^1R[{}^2T, {}^1T]$  and  ${}^2R[{}^2T, {}^1T]$ , are expressed as functionals of their lowest-order corrections<sup>21</sup>

$${}^2D \approx {}^2D[{}^2T, {}^1T] = {}^2T + {}^2R[{}^2T, {}^1T] \quad (1)$$

$${}^1D \approx {}^1D[{}^2T, {}^1T] = {}^1T + {}^1R[{}^2T, {}^1T] \quad (2)$$

where  ${}^2D$  and  ${}^1D$  are the 2- and 1-RDMs,  ${}^2T$  is the first-order part of  ${}^2D$ , and  ${}^1T$  is the second-order part of  ${}^1D$ . The parametrization must ensure that the 2-RDM remains  $N$ -representable.

$N$ -representability constraints are introduced through the use of the Cauchy–Schwarz inequalities<sup>20,21</sup>

$$({}^2D_{ij}^{ab})^2 \leq {}^2D_{ij}^{ij} {}^2D_{ab}^{ab} \quad (3)$$

$$({}^2Q_{ij}^{ab})^2 \leq {}^2Q_{ij}^{ij} {}^2Q_{ab}^{ab} \quad (4)$$

where  ${}^2Q$  is the two-hole reduced density matrix. Using these inequalities, we can derive a  ${}^2T$  functional for the elements of the 2-RDM  ${}^2D_{ij}^{ab}$  connecting a pair of occupied orbitals,  $i$  and  $j$ , with a pair of unoccupied orbitals,  $a$  and  $b$

$${}^2D_{ij}^{ab} = {}^2T_{ij}^{ab} \sqrt{1 - \frac{1}{4} \sum_{klcd} f_{ijkl}^{abcd} |{}^2T_{kl}^{cd}|^2} \quad (5)$$

When the topological factor  $f_{ijkl}^{abcd}$  is set to 1 in all cases, we have configuration interaction with double excitations (CID); when the topological factor  $f_{ijkl}^{abcd}$  is set to 0 in all cases, we have the coupled electron pair approximation (CEPA-0). When we employ Cauchy–Schwarz inequalities, however, we can obtain

the values of the topological factor, known as the M functional,<sup>20,21</sup> labeled in Table 1 as p2-RDM. Unlike CID,

**Table 1. Definitions for the Topological Factors  $f_{ijkl}^{abcd}$  Given by  $f_{n_o, n_v}^{a,b,c,d}$**

method	Topological Factor, $f_{n_v}^{a,b,c,d}$								
	0/0	1/0	2/0	0/1	0/2	1/1	2/1	1/2	2/2
CID	1	1	1	1	1	1	1	1	1
CEPA(0)	0	0	0	0	0	0	0	0	0
p2-RDM	0	0	1	0	1	1	1	1	1

$a_{n_o}$  is the number of occupied spin orbitals shared between  $\{i,j\}$  and  $\{k,l\}$ , and  $n_v$  is the number of virtual spin orbitals shared between  $\{a,b\}$  and  $\{c,d\}$ . The nine possible combinations of  $n_o/n_v$  and the values of the topological factor for these combinations are listed in the table for the following three methods: CID, CEPA-0, and p2-RDM with the M parameterization.<sup>20,21</sup>

$n_o$  is the number of occupied spin orbitals shared between  $\{i,j\}$  and  $\{k,l\}$ , and  $n_v$  is the number of virtual spin orbitals shared between  $\{a,b\}$  and  $\{c,d\}$ . The nine possible combinations of  $n_o/n_v$  and the values of the topological factor for these combinations are listed in the table for the following three methods: CID, CEPA-0, and p2-RDM with the M parameterization.<sup>20,21</sup>

the p2-RDM method with the M functional is size-extensive, and unlike CEPA-0, it is nearly  $N$ -representable. In practice, we also explicitly include single excitations.<sup>21</sup> Further details of the p2-RDM method can be found elsewhere.<sup>20–22,26–30</sup>

### 3. APPLICATIONS

After providing computational details, we present relative energies and densities of the cage and prism isomers from the p2-RDM method with comparisons to previous calculations.

**A. Computational Details.** Geometries for the cage and prism were taken from ref 8 and optimized by second-order Møller–Plesset perturbation theory using Dunning’s triple- $\zeta$  basis set plus polarization functions<sup>32</sup> (MP2/TZP) within the electronic structure package GAMESS.<sup>33</sup> The nuclear gradients were tightly converged, and the stationary geometries were verified to be local minima through frequency analysis. Using these geometries for the prism and cage, we computed the ground-state energies from the p2-RDM using correlation-consistent basis sets with and without diffuse functions, including cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ.<sup>32</sup> The CBS limit of the correlation energy was computed with the two-point formula,<sup>34</sup>  $E_{\text{corr}}^X = E_{\text{corr}}^{\text{CBS}} + \beta X^{-3}$ , with the cc-pV[DT]Z basis sets. The CBS limit of the mean-field energy was computed using a three-point formula,<sup>35</sup>  $E_{\text{RHF}}^X = E_{\text{RHF}}^{\text{CBS}} + \beta \exp(-\alpha X)$ , with the cc-pV[DTQ]Z basis sets. Although the optimized geometries from MP2 in TZP are not necessarily equal to the optimized geometries from p2-RDM in cc-pVTZ or the CBS limit, previous studies<sup>8</sup> as well as our own calculations show that the PESs of the hexamers are fairly flat, meaning that the energies do not change significantly with geometry. We employed the nuclear zero-point vibrational energy (ZPVE) from ref 19. The largest calculations employed more than 500 one-electron basis functions. Calculations were performed on a cluster of Intel Xeon 2.9 GHz (Sandy Bridge) processors with 380 GB per node.

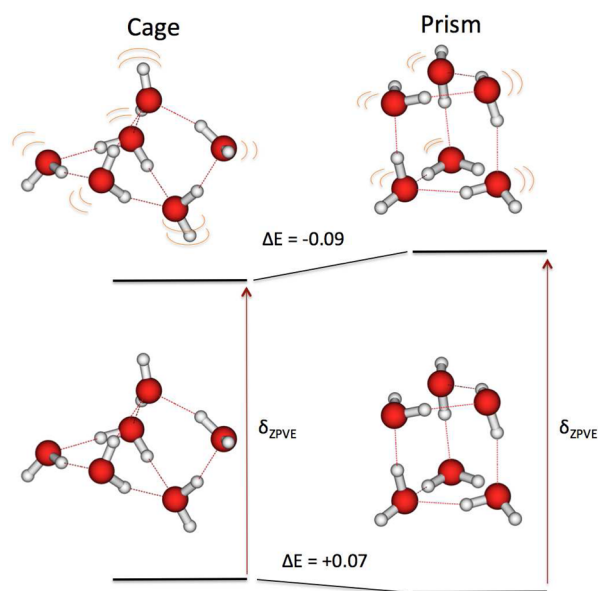
**B. Results.** The electronic energy of the cage relative to the prism is predicted by the p2-RDM calculations to decrease with increasing basis set size, with the cage being less stable than the prism by 1.5 and 0.07 kcal/mol in the cc-pVDZ and aug-cc-pVTZ basis sets, respectively. Calculations extrapolated to the CBS limit also find the cage to be just 0.07 kcal/mol above the prism, so that when ZPVE is considered, the cage is predicted to be more stable than the prism by about 0.09 kcal/mol at both the aug-cc-pVTZ and CBS level (see Table 2 and Figure

**Table 2. Relative Energies (kcal/mol) of the Cage and the Prism from p2-RDM Compared to Previously Reported CCSD(T)/CBS Estimates<sup>a</sup>**

Energy of the Cage Relative to the Prism (kcal/mol)					
CCSD(T) <sup>19</sup>		p2-RDM			
CBS	CBS+ZPVE	ATZ	CBS	ATZ+ZPVE	CBS+ZPVE
0.25	0.09	0.0729	0.0714	−0.0871	−0.0886

<sup>a</sup>Energies with ( $E$ +ZPVE) and without ( $E$ ) the zero-point vibrational energy (ZPVE) are reported. The p2-RDM relative energies were computed in the aug-cc-pVTZ (ATZ) basis set and the CBS limit.

1). This prediction reverses the relative energies predicted by the CBS/CCSD(T) calculations.<sup>19</sup> From the QMC studies, it is



**Figure 1.** Schematic of relative energies of the prism and cage isomers in kcal/mol considering only the electronic energy (bottom) and considering both electronic and ZPVE (top). While the electronic energy of the prism isomer is slightly lower than that of the cage, the nuclear zero-point energy raises the energy of the cage less than the energy of the prism, leading to the prediction that the cage is the global minimum energy structure at 0 K.

clear that more sophisticated treatment of nuclear motion tends to stabilize the cage relative to the prism; however, the PESs used by these simulations were derived from CCSD(T) energies, which likely overstabilize the prism relative to the cage, leading to a 1:1 (cage/prism) isomeric ratio at 0 K. From the electronic energies predicted by the p2-RDM, along with corrections for nuclear motion, one would expect the isomeric ratios to tend toward 1:0 near 0 K.

The purpose of the present paper is to demonstrate the role of a small but significant amount of multireference correlation in stabilizing the energy of the cage relative to the energy of the prism. We show that the addition of a harmonic ZPVE to the electronic energy is sufficient in the case of the p2-RDM method to stabilize the cage relative to the prism. Such stabilization is not achieved by standard single-reference wave function methods. Using ZPVEs from our MP2 calculations in the cc-pVTZ basis set rather than those from the literature<sup>19</sup> does not significantly change the results. Furthermore, as shown in the QMC studies,<sup>10</sup> a more detailed study of

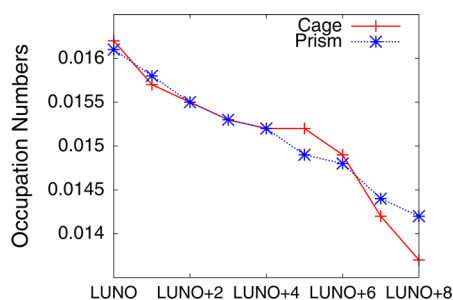
anharmonic vibrational corrections, beyond the scope of the present study, only further stabilizes the cage relative to the prism.

Both the size of the basis set and the recovery of electron correlation are critical to capturing the relative energies of the water hexamer clusters. In addition to the large basis set of Table 2, we also employed a smaller polarized double- $\zeta$  basis set in which we could compare CCSD, CCSD(T), and p2-RDM directly. The CCSD, CCSD(T), and p2-RDM methods give the following energies for the cage relative to the prism: −0.821, −0.871, and −0.599 kcal/mol. While the addition of triple excitations raises the relative energy of the cage from CCSD by 0.05 kcal/mol, the p2-RDM method lowers the relative energy from CCSD by more than 0.2 kcal/mol. Previous p2-RDM studies of oxywater,<sup>22</sup> carbonic acid,<sup>26</sup> and the HOOO radical<sup>28</sup> have shown that the p2-RDM method can capture small but important energy changes, attributable to multireference effects, that are missed by traditional methods like CCSD and CCSD(T). Although neither coupled cluster nor p2-RDM methods predict the cage to be the most stable structure in the polarized double- $\zeta$  basis set, in the larger aug-cc-pVTZ basis set and CBS limit, the additional electronic stability of the cage from p2-RDM translates into the cage being the global energy minimum of the PES (after the addition of the ZPVE).

For all methods, although the total electronic energy of the cage relative to the prism decreases significantly as the size of the basis set increases, the correlation energy of the cage relative to the prism actually increases with basis set size. Opposite trends in the total and correlation energies are achieved because the correlation energy's increase is more than offset by a corresponding decrease in the mean-field (Hartree–Fock) energy with basis set size. At the CBS limit, the Hartree–Fock energies of the cage and prism differ by less than 0.01 kcal per mole, with the cage isomer being slightly favored. For all methods in either large basis sets or the CBS limit, the addition of the correlation energy destabilizes the cage relative to the prism. However, this destabilization is greater for the coupled cluster methods than that for the p2-RDM method. In the case of the p2-RDM method, the destabilization of the cage is sufficiently small for it to be reversed by the addition of the ZPVE, as shown in Figure 1.

The hydrogen bonds in the water hexamers are not as strong as the covalent bonds connecting the oxygen and hydrogen in the water molecule. Consequently, the  $2q$  natural orbitals corresponding to the hydrogen bonds will generally be the  $q$  highest occupied natural orbitals (HONOs) and  $q$  lowest unoccupied natural orbitals (LUNOs). The natural orbitals are the eigenfunctions of the one-electron reduced density matrix (1-RDM).<sup>31,36</sup> There are eight ( $q = 8$ ) and nine ( $q = 9$ ) hydrogen bonds in the cage and prism isomers, respectively. The occupations of the nine LUNOs are shown in Figure 2 for both the cage and prism isomers. Importantly, the cage's occupation of its ninth orbital is significantly less than the prism's occupation of its ninth orbital, which reflects the additional hydrogen bond of the prism. This decrease in the occupation of the cage's ninth orbital (relative to the prism) seems to coincide with an increase in the occupation of the cage's sixth orbital (LUNO+5). The greater density filling of the cage's sixth orbital may compensate in energetic stability for the cage's lack of an additional ninth hydrogen bond. Such tradeoffs indicate the subtlety of electron correlation present in the hydrogen bonding of the water hexamer clusters.





**Figure 2.** Plot of the nine LUNOs (LUNO through LUNO+8) for the cage and prism. For the cage, with eight hydrogen bonds, the HONO–7 through LUNO+7 have strong correspondence to orbitals active in hydrogen bonding. For the prism, with nine hydrogen bonds, the HONO–8 through LUNO+8 have strong correspondence to orbitals active in hydrogen bonding.

We can also approximately view the electron density of the hydrogen bonds by examining the electron density of the appropriate natural orbitals. Figure 3 shows the electron densities for the six “highest” occupied natural orbitals and the six lowest “unoccupied” natural orbitals of the cage isomer. The HONOs show that density is localized around the oxygen atoms, which serve as hydrogen-bonding donors; the LUNOs show that density is localized around the hydrogen atoms, which serve as hydrogen-bonding acceptors. While the densities of the LUNOs may be relatively low, the electron configurations associated with these orbitals are likely of great importance in capturing the subtle energy differences between isomers. The electron densities of the HONOs and LUNOs associated with hydrogen bonding are nearly identical between the cage and prism (not shown) structures. However, noticeable differences are observed between the cage and prism in their ninth HONOs (HONO–8) and their ninth LUNOs (LUNO+8). These differences likely reflect the lack of a ninth hydrogen bond in the cage isomer. Overall, these pictures of the orbital electron densities are consistent with our findings.

#### 4. CONCLUSIONS

The energy ordering of the cage and prism isomers of the water hexamer, as determined by recent experiments,<sup>11</sup> can be recovered by reduced-density-matrix-based electronic structure calculations in large basis sets with corrections for the zero-point nuclear motion. In contrast, previous electronic structure

calculations with CCSD(T) in the CBS limit<sup>8–10</sup> have predicted the prism to be lower in energy than the cage. The difference in these results likely arises from the important but subtle role played by multireference correlation effects. In recent applications to studying the rotational barrier in diazene<sup>27</sup> and the various isomers of the five-ring molecule olympicene,<sup>29</sup> the p2-RDM method has been shown to recover as much as 10 kcal/mol of multireference correlation that is not described by traditional single-reference methods. Perhaps more importantly, in applications to the stability of oxywater<sup>22</sup> and the relative populations of carbonic acid isomers,<sup>26</sup> the p2-RDM has been shown to recover small but potentially critical amounts of multireference correlation (0.5–2 kcal/mol) not well described by traditional single-reference methods. Although the water hexamers are not typically considered to possess significant multireference correlation, in the calculation of small energy differences, as in the cases of oxywater and carbonic acid, minor multireference effects can become quite significant. These computational results have important implications for future constructions of ab initio force fields and PESs used in classical or quantum mechanical simulations of water’s structure and dynamics. More generally, they provide new insight into the importance of multireference electron correlation in the accurate quantitative description of hydrogen bonding and other intermolecular forces.

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##### Notes

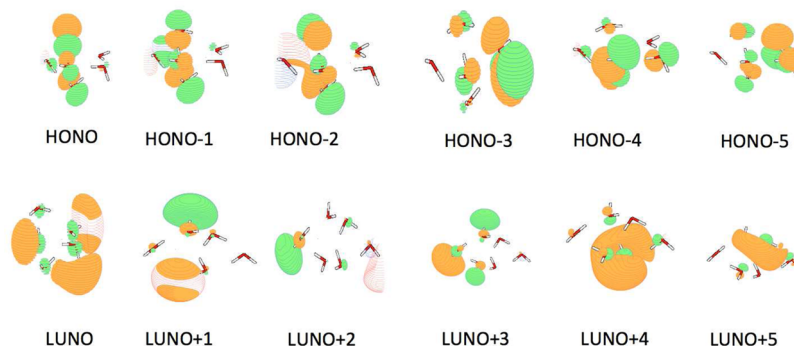
The authors declare no competing financial interest.

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**Figure 3.** The electron densities of the six HONOs and six LUNOs of the cage isomer are shown. The HONOs show that density is localized about one or more oxygen atoms, which serve as hydrogen-bonding donors, and the LUNOs show that density is localized about hydrogen atoms, which serve as hydrogen-bonding acceptors.

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