Cage versus Prism: Electronic Energies of the Water Hexamer.

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · JULY 2013
Impact Factor: 2.78 · DOI: 10.1021/jp405739d · Source: PubMed

CITATIONS
4

2 AUTHORS, INCLUDING:

Jonathan J Foley
Argonne National Laboratory

17 PUBLICATIONS  75 CITATIONS

SEE PROFILE
Cage versus Prism: Electronic Energies of the Water Hexamer

Jonathan J. Foley, IV †,‡,* and David A. Mazziotti*,†

†Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, United States
‡Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States

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. 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, including those that have applied coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] in augmented polarized triple-ζ basis sets and extrapolated complete basis sets. 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). Despite the sophistication of these calculations, there remains a small but important discrepancy with recent experiments, which reveal that the cage structure is the global energy minimum at sufficiently low temperatures. Building upon earlier experiments on water clusters, these experiments employed a chirped pulse Fourier microwave spectroscopy with supersonic expansions. 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. 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. 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 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. We present results using parametric 2-RDM (p2-RDM) calculations in an augmented correlation-consistent polarized triple-ζ (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. "Relative isomer populations," they wrote, "at different
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. 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. The expression for the energy is minimized as a functional of the 2-RDM to generate the ground-state energy without additional reference treatment of single- and multireference correlation effects, in calculating the energy barrier stabilizing oxywater and the relative populations of the cis and trans isomers of carbonic acid at 210 K.

**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:

\[2D \approx 2D[2T;T] = 2T + 2R[2T;1T]\]  
\[1D \approx D[2T;1T] = 1T + R[2T;1T]\]

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:

\[(2D_{ij})^2 \leq 2D_{ij}^2 D_{ab}\]

\[(2Q_{ij})^2 \leq 2Q_{ij}^2 Q_{ab}\]

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

\[2D_{ij} = 2T_{ij} \approx 1 - \frac{1}{4} \sum_{klcd} f_{ijkl}^{abcd} f_{klcd}^{ijkl} \]

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, labeled in Table 1 as p2-RDM. Unlike CID, 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. Further details of the p2-RDM method can be found elsewhere.

### Table 1. Definitions for the Topological Factors \(f_{ijkl}^{abcd}\) Given by \(f_{n}^{fi}\)

<table>
<thead>
<tr>
<th>Topological Factor, (f_{n}^{fi})</th>
<th>0/0</th>
<th>1/0</th>
<th>2/0</th>
<th>0/1</th>
<th>0/2</th>
<th>1/1</th>
<th>2/1</th>
<th>1/2</th>
<th>2/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CID</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CEPA(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p2-RDM</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(n\) is the number of occupied spin orbitals shared between \(\{ij\}\) and \(\{kl\}\), and \(n\) is the number of virtual spin orbitals shared between \(\{ab\}\) and \(\{cd\}\). The nine possible combinations of \(n/\alpha\) 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.

### 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 Moller–Plesset perturbation theory using Dunning’s triple-ζ basis set plus polarization functions (MP2/TZP) within the electronic structure package GAMESS. 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-pVQZ. The CBS limit of the correlation energy was computed with the two-point formula, with the cc-pVTZ basis sets. The CBS limit of the mean-field energy was computed using a three-point formula, with the cc-pVQZ 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 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

<table>
<thead>
<tr>
<th>Energy of the Cage Relative to the Prism (kcal/mol)</th>
<th>CCSD(T)\textsuperscript{19}</th>
<th>p2-RDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBS</td>
<td>0.25</td>
<td>0.09</td>
</tr>
<tr>
<td>CBS+ZPVE</td>
<td>0.0729</td>
<td>0.0714</td>
</tr>
<tr>
<td>ATZ</td>
<td>−0.0871</td>
<td>−0.0886</td>
</tr>
<tr>
<td>ATZ+ZPVE</td>
<td>−0.821</td>
<td>−0.871</td>
</tr>
<tr>
<td>CBS+ZPVE</td>
<td>−0.599</td>
<td>−0.599</td>
</tr>
</tbody>
</table>

\textsuperscript{1}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.

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.

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 2g natural orbitals corresponding to the hydrogen bonds will generally be the q highest occupied natural orbitals (HONO\textsubscript{s}) and q lowest unoccupied natural orbitals (LUNO\textsubscript{s}). The natural orbitals are the eigenfunctions of the one-electron reduced density matrix (1-RDM).\textsuperscript{31,36} There are eight (q = 8) and nine (q = 9) hydrogen bonds in the cage and prism isomers, respectively. The occupations of the nine LUNO\textsubscript{s} 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\textsubscript{+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.
The energy ordering of the cage and prism isomers of the water hexamer, as determined by recent experiments, 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\(^{8-10}\) 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\(^{27}\) and the various isomers of the five-ring molecule olympicene,\(^{29}\) 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\(^{22}\) and the relative populations of carbonic acid isomers,\(^{26}\) 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.

**REFERENCES**


**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: damazz@uchicago.edu.

*Notes*

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

D.A.M. gratefully acknowledges the NSF under Grant No. CHE-1152425, the ARO under Grant No. W91 INF-11-5-041-0085, the Keck Foundation, and Microsoft Corporation for their support.

![Figure 2](image1.png) 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.

![Figure 3](image2.png) 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.


