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The Water Hexamer: Cage, Prism, or Both. Full Dimensional Quantum Simulations Say Both

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Supporting Information

ABSTRACT: State-of-the-art quantum simulations on a full-dimensional ab initio potential energy surface are used to characterize the properties of the water hexamer. The relative populations of the different isomers are determined over a wide range of temperatures. While the prism isomer is identified as the global minimum-energy structure, the quantum simulations, which explicitly include zero-point energy and quantum thermal motion, predict that both the cage and prism isomers are present at low temperature down to almost 0 K. This is largely consistent with the available experimental data and, in particular, with very recent measurements of broadband rotational spectra of the water hexamer recorded in supersonic expansions.

The water hexamer holds a special place in the experimental and theoretical studies of water because it is the smallest water cluster in which the monomers form a fully three-dimensional structure. The hexamer has thus been referred to as the "smallest drop of water",[1,2] serving as the prototypical system to understand the molecular structure and dynamics of the water hydrogen-bond network in the bulk phases. Because of the strong directionality of the hydrogen bonds, the hexamer exhibits several low-lying isomeric forms whose structure and energetics have been the subject of extensive investigations over the past decades. Only recently has some consensus begun to emerge.

Various high-resolution spectroscopic techniques have been applied to the study of the hexamer properties. Pioneering measurements of the vibration−rotation tunneling (VRT) spectra in the far-infrared region identified the cage isomer as the dominant structure at ∼6 K.[1] The spectra of different isomers were also measured using helium nanodroplet isolation[2] and molecular tagging ion-dip[3,4] techniques. Vibrational spectra recorded at relatively higher temperatures (T ∼40 K) were originally assigned to the book isomer,[5] but possible alternative assignments have also been proposed based on theoretical calculations.[6] From a recent analysis of broadband rotational spectra recorded in pulsed supersonic expansions in neon and helium, the population ratio for cage/prism/book was estimated to be 1:1:0.25, while only the cage isomer was identified in argon expansions.[7]

On the theoretical side, the modeling of the water hexamer has also evolved, with the development of more accurate interaction potentials and simulation methodologies. At least two factors make the theoretical studies extremely challenging. First, due to the relatively small energy differences between the isomeric structures, the underlying multidimensional potential energy surface (PES) must be known with great accuracy. Second, due to the light mass of the hydrogen atoms and high frequency of the OH vibrations, nuclear quantum effects, such as zero-point motion and tunneling, must be explicitly taken into account. Early studies were limited in both aspects. In the seminal work reported in ref 1. rigid-body diffusion Monte Carlo calculations on a rigid-monomer PES provided support for the assignment of the VRT spectra to the cage isomer, predicting the prism isomer to lie 0.18 kcal/mol (62 cm^{-1}) above it.

Subsequently, using coupled cluster calculations including single, double, and perturbative triple excitations [CCSD(T)] with extrapolation to the complete basis set limit, the prism isomer was identified as the lowest-energy structure, with the cage isomer lying approximately 0.25 kcal/mol (87.5 cm^{-1}) above it.[8,9] Although the explicit inclusion of zero-point energies (ZPEs) calculated within the harmonic approximation led to a significant reduction of the relative energy difference, the prism isomer was still found to be 0.09 kcal/mol (31.5 cm^{-1}) more stable than the cage isomer.[9] By contrast, Møller−Plesset second-order perturbation calculations including harmonic ZPE corrections predicted the chair isomer to be the most stable structure, followed closely by the cage and book isomers, with the prism isomer lying 0.15 kcal/mol (52 cm^{-1}) higher than the chair.[10] Thermochemistry calculations (which are not in agreement with the present work) based on harmonic analyses and moderate electronic structure methods were also reported.[11,12] The number of conflicting theoretical predictions reported for the relative stability of the different hexamer isomers underscores the need for high accuracy in both the potential and the associated dynamics of this centrally important water cluster.

The present study reports on state-of-the-art quantum simulations of the water hexamer performed on the full-dimensional ab initio WHBB potential energy surface.[13] Within the harmonic approximation for zero-point energy, the WHBB PES predicts the prism isomer to lie below the cage isomer by 28 cm^{-1}, in excellent agreement with the corresponding CCSD(T) value.[9] To go beyond the harmonic ZPE

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corrections, full dimensional diffusion Monte Carlo (DMC) calculations were employed to determine the wave functions and energies of the low-lying isomers. The DMC calculations were performed in the standard fashion with different numbers of walkers (4×10^4, 8×10^4, and 16×10^4).[14−16] In each case, three independent calculations were performed starting at the minimum energy configurations corresponding to the prism, cage, and book isomers, respectively. The computational details of the DMC calculations are given in the Supporting Information (SI). The ZPEs of the book and cage isomers relative to the prism ZPE are shown in Figure 1 (bottom panel). While the DMC results allow the unambiguous identification of the book isomer as a relatively higher-energy structure, lying 330 cm^{-1} above prism, the fully anharmonic ZPEs of the cage and prism isomers are identical within the statistical uncertainty. (As with the cage-prism energy difference, inclusion of harmonic ZPE significantly decreases the energy differences between the cage and book isomers relative to the prism isomer, in agreement with the CCSD(T) calculations.[9]) Inspection of the DMC wave functions shown in the top panel of Figure 1 indicates that a larger degree of floppiness is associated with the cage isomer, and the hydrogen atoms of the four free OH groups are significantly delocalized in space due to zero-point motion effects.

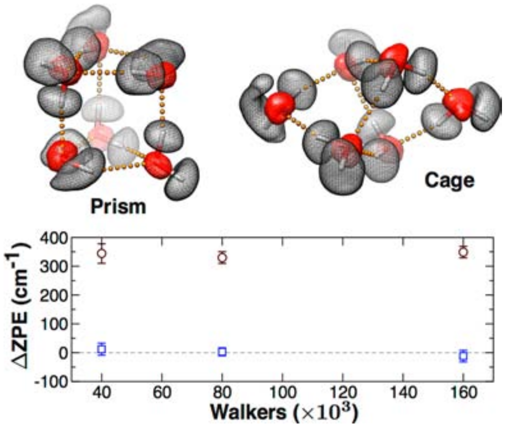

Figure 1. Top panel: Three-dimensional representation of the DMC wave functions for the prism (left) and cage (right) structures (isosurfaces of 2×10^{-4} are shown). Bottom panel: Zero-point energy of the cage (squares) and book (circles) isomers relative to the prism isomer ZPE obtained from the DMC calculations with 4×10^4, 8×10^4, and 16×10^4 walkers.

To characterize the relative stability of the different isomers at non-zero temperatures, the replica-exchange (RE) method[18] was combined with classical (MD) and path-integral (PIMD) molecular dynamics.[19,20] Both RE-MD and RE-PIMD simulations were performed between 30 and 150 K. This temperature range was chosen according to the following conditions, which permit a computationally optimal implementation of the RE method: (1) the upper limit was determined to be high enough to facilitate the rapid interconversion between the different isomers, and (2) the temperature difference between adjacent replicas was made small enough to allow for an efficient random walk in the replica space. The latter constraint implicitly defined the lowest temperature accessible in the simulations. The relative populations of the different isomers were determined using an rmsd-based criterion applied to the path centroids of each trajectory frame, taking into account all 6! × 26 possible permutations of equivalent atoms along with the inversion symmetry. The computational details specific to the RE-MD and RE-PIMD simulations are described in the SI.

The temperature dependence of the isomer populations obtained from both classical (RE- MD) and quantum (RE-PIMD) simulations is shown in Figure 2a. Only the five lowest-energy structures shown in Figure 2b, corresponding to prism, cage, double-tetramer, book, and prism-book, were found with sizeable populations below 150 K.[21] Because of their similarity, the book and double-tetramer isomers could not be uniquely distinguished at these temperatures, and therefore, only the sum of their populations is reported in Figure 2a.

Two sets of RE-PIMD simulations were performed employing different numbers of quasi-particles ("beads") to discretize the Feynman's paths. Simulations with 32 beads were carried out in the temperature range from 30 to 150 K, while, due to the constraints associated with the RE-PIMD method, simulations with 64 beads were limited to temperatures above 50 K. Although the exact quantum properties can only be recovered in the limit of an infinite number of beads,[22] the

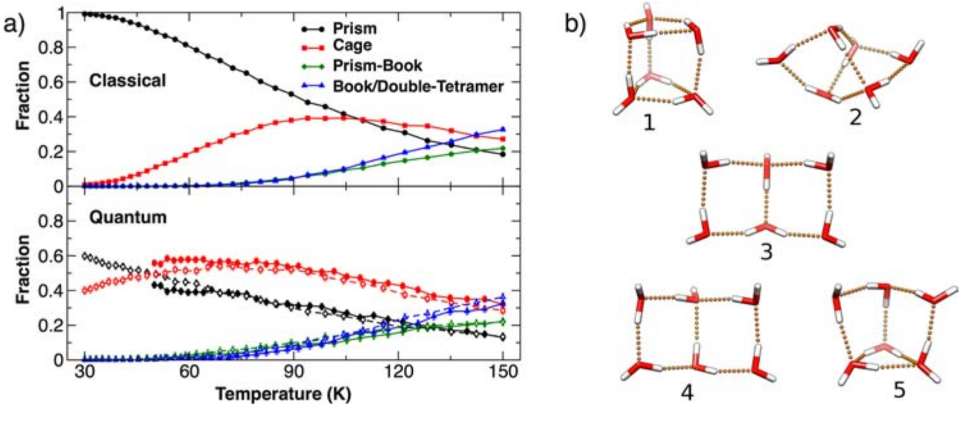

Figure 2. (a) Populations of the water hexamer isomers at different temperatures obtained from classical (top panel) and quantum (bottom panel) replica-exchange simulations. Black, prism; red, cage; green, prism-book; blue, book/double tetramer. In the bottom panel, the open symbols correspond to the RE-PIMD results with 32 beads, while the filled symbols correspond to the RE-PIMD results with 64 beads. (b) Low-energy structures of the $(H_2O)_6$ cluster calculated on the WHBB water potential energy surface. 1, prism (−46.021 kcal/mol); 2, cage (−45.626 kcal/mol); 3, double-tetramer (−44.883 kcal/mol); 4, book (−44.210 kcal/mol); and 5, prism-book (−43.792 kcal/mol).

quantum populations reported in Figure 2a display a weak dependence on the number of beads. This suggests that the RE-PIMD simulations effectively capture the essential nuclear quantum effects associated with the water hexamer in the temperature range examined. Several conclusions can be made from the analysis of the data shown in Figure 2a. First, the comparison between the RE-MD and RE-PIMD results demonstrates the quantum nature of the water hexamer, with a significant departure from the classical behavior being observed for $T \leq 100$ K. Second, unlike the classical case in which the prism isomer dominates below ∼50 K, the populations of the cage and prism isomers calculated quantum-mechanically remain comparable over a wide range of temperatures down to ∼30 K. Importantly, while the crossing between the cage and prism populations occurs at ∼50 K in simulations with 32 beads, the RE-PIMD results with 64 beads display weaker curvatures as a function of temperature. This implies that the (more accurate) RE-PIMD simulations with 64 beads predict that the crossing would occur at lower temperatures. The temperature dependence of the cage and prism populations obtained from the RE-PIMD simulations is, thus, consistent with the (0 K) DMC results. Third, both the RE-MD and RE-PIMD results predict that the population of the cage increases with temperature and then at temperatures above 100 K, the book isomer population increases rapidly. These effect are due the intrinsic entropies of the isomers, with book > cage > prism.[10]

The cage and prism entropy difference can be seen clearly from the free energy differences, which is obtained from the relative populations of the cage and prism isomers as follows:

$$\Delta F = F^{(\mathrm{cage})} - F^{(\mathrm{prism})} = -k_{\mathrm{B}}T \ln \frac{\text{cage population}}{\text{prism population}}$$

where k_{B} is the Boltzmann constant. ΔF is shown for the classical and quantum cases in Figure 3 , where, not surprisingly, large differences are seen. In both cases, the temperature dependence of ΔF can be effectively analyzed within the harmonic approximation, in which the energy of each isomer is approximated as a sum of uncoupled vibrations with frequencies calculated at the corresponding WHBB PES minima. Doing this analysis enables an extrapolation of ΔF to 0 K thereby making direct contact with the DMC results. Within this approximation, the classical free energy difference between the two isomers is expected to be linear in temperature, which is in perfect agreement with the ΔF values derived from the RE-MD simulations (pink filled circles). By contrast, due to the discrete nature of the quantum excitation spectra of the two isomers, the quantum free energy difference is a nonlinear function of temperature (solid blue line). Importantly, the slope of the quantum ΔF "builds up" progressively with temperature as an increasing number of vibrational modes becomes thermally accessible.

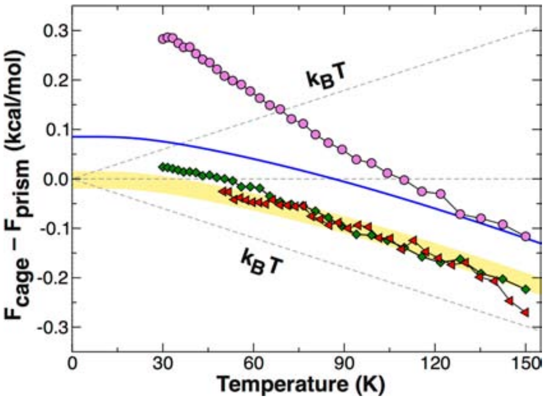

Figure 3. Free-energy difference between the cage and prism isomers as obtained from classical RE-MD (circles) and quantum RE-PIMD (32 beads, diamonds; and 64 beads, triangles) simulations. The blue line corresponds to the free-energy difference calculated within the harmonic approximation. The shaded area represents the fit of the harmonic free energy difference to the 64 beads RE-PIMD results. The dashed lines delimit the $|\Delta F| \leq k_{\mathrm{B}}T$ regions in which both isomers have sizeable populations.

As seen, the temperature dependence of ΔF calculated within the harmonic approximation closely resembles the behavior of the actual quantum free-energy differences derived from the RE-PIMD simulations with 32 and 64 beads. However, the ZPE difference $\Delta E_0 = F^{(\mathrm{cage})}_{T=0\mathrm{K}} - F^{(\mathrm{prism})}_{T=0\mathrm{K}}$ predicted within the harmonic approximation appears to be significantly overestimated relative to the RE-PIMD results. The analysis of the quantum free energy, thus, indicates that the explicit inclusion of the anharmonic nuclear quantum effects is critical for the correct description of the zero-point motion although it appears not to affect significantly the corresponding excitation spectra. On the basis of this observation, it is possible to fit the quantum free energy curves obtained from the RE-PIMD simulations using the zero-point energy difference (ΔE_0) between the cage and prism isomers as the only unknown parameter. Least-squares fits to ΔF calculated from RE-PIMD simulations with 32 and 64 beads lead to $\Delta E_0 = 0.015$ kcal/mol (5.2 cm^{-1}) and $\Delta E_0 = -0.001$ kcal/mol (-0.35 cm^{-1}), respectively. The statistical uncertainty associated with ΔE_0 was assessed heuristically by considering all possible fits derived from the RE-PIMD results with 64 beads using different data points between 50 and 130 K (shaded area in Figure 3). On the basis of the RE-PIMD results, the quantum free energy curve is expected to reside within the region defined by $|\Delta F| \leq k_{\mathrm{B}}T$ (delimited by the two dashed lines in Figure 3) down to very low temperatures, indicating that both cage and prism isomers have sizeable populations at $T \sim 0$ K. This analysis of the quantum ΔF allows to develop a direct connection between the finite-temperature RE-PIMD 0 K DMC results. In particular, the prediction of a nearly zero energy difference between the cage and prism isomers derived from the fit of the quantum ΔF down to 0 K is in complete accord with the ZPE values obtained from the DMC calculations. Importantly, the RE-PIMD results clearly show that, as the temperature increases, the cage free energy drops below that of the prism isomer due to the relatively higher entropy of the former.

Direct insights into possible cage/prism interconversion pathways were gained from the analysis of both DMC and PIMD simulations. In this regard, DMC calculations with 4×10^4 walkers were particularly revealing, indicating that both cage/prism and prism/cage transitions proceed through book-like structures reminiscent of the isomers 3 and 4 in Figure 2.[17] In DMC calculations with larger numbers of walkers, fewer interconversion events were observed due to the significantly slower relaxation. Similar pathways were found in PIMD simulations carried out at temperatures high enough ($T \sim 100$ K) to induce frequent cage/prism transitions.

In summary, DMC and RE-PIMD simulations of the water hexamer on the WHBB potential energy surface indicate that: (a) The energies of the cage and prism isomers at 0 K are essentially identical within the statistical uncertainty. (b) The population of the cage isomer increases relative to the prism population as the temperature increases, with the population of the book isomer remaining very small up to ~60 K. At higher temperatures the book population raises and eventually becomes dominant above 150 K. The temperature dependence of the isomer populations is mainly determined by the competition between energetic and entropic effects, with the latter favoring the book structure over the cage structure, and the cage structure over the prism structure. (c) Large nuclear quantum effects are found at temperatures below 100 K, which are responsible for significant differences in the isomer populations. (d) The transition between the cage and prism isomers proceeds through book-like structures.

The present results suggest that noticeable variations in the isomer populations are to be expected in response to small perturbations caused by slightly different experimental setups. This is largely consistent with recent measurements of the hexamer rotational spectra in supersonic expansions with rare-gas atoms.[7] A direct comparison with the experimental data thus requires an accurate assessment of the rare-gas perturbations of the different isomers and efforts along these lines are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, including tables with the normal mode frequencies of the cage and prism isomers calculated on the WHBB PES as well as a figure illustrating the cage/prism interconversion mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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