Low-temperature isomers of the water hexamer

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Hundreds of years
Thousands of pages

http://www.lsbu.ac.uk/water/anmlies.html
Unanswered Questions

- Does supercooled water have two phases and a second critical point?

- Does normal liquid water consist of smaller clusters of two different states of water?
Liquid Water
Hydrogen Bond Network
FIG. 1. The radial proton momentum distribution of a single water molecule computed in two different fashions. The solid curve is the result when only one hydrogen path is opened, as is required in the precise methodology. The dashed curve results from a separate simulation that opens two proton paths and tabulates both end-to-end distances. Although this procedure facilitates more rapid sampling, it yields a result that is somewhat redshifted and narrowed. Also plotted is the classical momentum distribution of the system (dotted line) in order to underline the difference between the classical and quantum results.

\[ \alpha_{l-v} = \left( \frac{x_{D,l}}{x_{H,l}} \right) \left( \frac{x_{D,v}}{x_{H,v}} \right) \]
Trimer/Tetramer/Pentamer

Nearly planar
Hexamers
Structures of Cage, Prism, and Book Isomers of Water Hexamer from Broadband Rotational Spectroscopy

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Theory predicts the water hexamer to be the smallest water cluster with a three-dimensional hydrogen-bonding network as its minimum energy structure. There are several possible low-energy isomers, and calculations with different methods and basis sets assign them different relative stabilities. Previous experimental work has provided evidence for the cage, book, and cyclic isomers, but no experiment has identified multiple coexisting structures. Here, we report that broadband rotational spectroscopy in a pulsed supersonic expansion unambiguously identifies all three isomers; we determined their oxygen framework structures by means of oxygen-18–substituted water (H218O). Relative isomer populations at different expansion conditions establish that the cage isomer is the minimum energy structure. Rotational spectra consistent with predicted heptamer and nonamer structures have also been identified.

The intermolecular hydrogen-bonding interactions of water are responsible for many remarkable physical properties of the liquid and solid phases of the compound and furthermore play a pivotal role in solution chemistry and biochemistry. As a result, the accurate description of the water intermolecular potential is one of the most important problems in chemistry (1). One key method for quantitative analysis of water interactions is the size-selective study of the structures of water clusters (2–5). This problem has been attacked using several state-of-the-art techniques, including far-infrared (FIR) spectroscopy (6–9), helium nanodroplet isolation (HENDI) spectroscopy (10), infrared spectroscopy of size-selected molecular beams (11), molecular tagging ion-dip infrared spectroscopy (12, 13), and argon-mediated, population-modulated attachment spectroscopy (14). Here, we report chirped-pulse Fourier transform microwave
Born-Oppenheimer approximation:

1) Electronic ground state for clamped nuclei.
   
   [CCSD(T) is very demanding: memory $\propto O(N_{\text{atom}}^4)$,
   time $\propto O(N_{\text{atom}}^8)$]

2) QM treatment of the nuclei.
   [not necessarily cheap either]
$E_{cage} - E_{prism} = 0.25 \text{ kcal/mol}$

[CCSD(T)/CBS by Tschumper et al]
# Model Potentials

- **q-TIP4P/F**
  

- **TTM3-F**
  

- **WHBB**
  

- **HBB2-pol**
  
q-TIP4P/F

- Very crude intra-molecular terms.
- Geometry-independent point charges.
- No polarization.

\[ E_N = \sum_a E_a + \sum_{a<b} E_{ab} \]
Ab initio intra-molecular sector.

Ab initio geometry-dependent charges.

Polarizable site.

\[ E_N \neq \sum_a E_a + \sum_{a<b} E_{ab} \]
WHBB & HBB2-pol

\[ E_N = \sum_a V_1(x_a) + \sum_{a<b} V_2(x_a, x_b) + \sum_{a<b<c} V_3(x_a, x_b, x_c) + V_{\text{ind}}(x_1, \ldots, x_N) \]

- *Ab initio* intra-molecular sector.
- *Ab initio* 2-/3-body terms.
- Polarizable site(s).
\[ \mathcal{Z} = \text{tr} \exp(-\beta \mathcal{H}) = \lim_{P \to \infty} \int dq_1 \ldots dq_P \exp(-\beta \mathcal{E}_P) \]

\[ \text{tr} e^{-\beta \mathcal{H}} = \text{tr} e^{-\beta (\mathcal{H} + \mathcal{V})} = \lim_{P \to \infty} \text{tr} \left[ e^{-\beta \mathcal{H}/P} e^{-\beta \mathcal{V}/P} \right]^P \]

\[ \langle q_1 | e^{-\beta \mathcal{H}/P} e^{-\beta \mathcal{V}/P} | q_2 \rangle \propto \exp \left[ -\beta m \omega_P^2 (q_1 - q_2)^2 / 2 - \beta V(q_2) / P \right], \quad \omega_P^2 = \frac{P}{\hbar^2 \beta^2} \]

\[ \mathcal{E}_P = \frac{1}{P} \sum_{a=1}^{P} V(q_a) + \frac{m \omega_P^2}{2} \sum_{a=1}^{P} (q_{a+1} - q_a)^2 \]
Path Integral Molecular Dynamics

- Linear transformation to “normal modes”.


- Fictitious momenta conjugate to these new variables.


- Nose-Hoover chains at every degree of freedom.
Replica Exchange

- Two chains sampling different (but related) densities $\pi_1(x)$ and $\pi_2(x)$ can be joined into a chain that samples $q = (x, y) \sim \pi(q) = \pi_1(x)\pi_2(y)$.

- The $q = (x, y) \rightarrow q' = (y, x)$ move with Metropolis acceptance probability

$$\min\left\{1, \frac{\pi(q')}{\pi(q)}\right\} = \min\left\{1, \frac{\pi_1(y)\pi_2(x)}{\pi_1(x)\pi_2(y)}\right\}$$

preserves $\pi(q) = \pi_1(x)\pi_2(y)$. 
Performance on Gordon

![Graph showing performance comparison between RE-PIMD (32 beads/32 replicas) and PIMD (256 beads, 30K).]
Results (TTM3-F)

Nuclear quantum effects favor cage over prism.
Free Energies

\[ F_{\text{Cage}} - F_{\text{Prism}} = -k_B T \ln \frac{\#\text{Cage}}{\#\text{Prism}} \]

\[ F_{\text{Cage}} - F_{\text{Prism}} \approx \Delta E + k_B T \sum_n \ln \frac{1 - e^{-\hbar \omega_n^{\text{Cage}} / k_B T}}{1 - e^{-\hbar \omega_n^{\text{Prism}} / k_B T}} \]
Summary

- There is several nearly iso-energetic non-planar isomers of water hexamer.
- Their thermal equilibrium is due a subtle balance between energetic, entropic, and nuclear quantum effects.
- The relative stability of the prism isomer increases upon substitution of $\text{H}_2\text{O}$ with $\text{D}_2\text{O}$. 