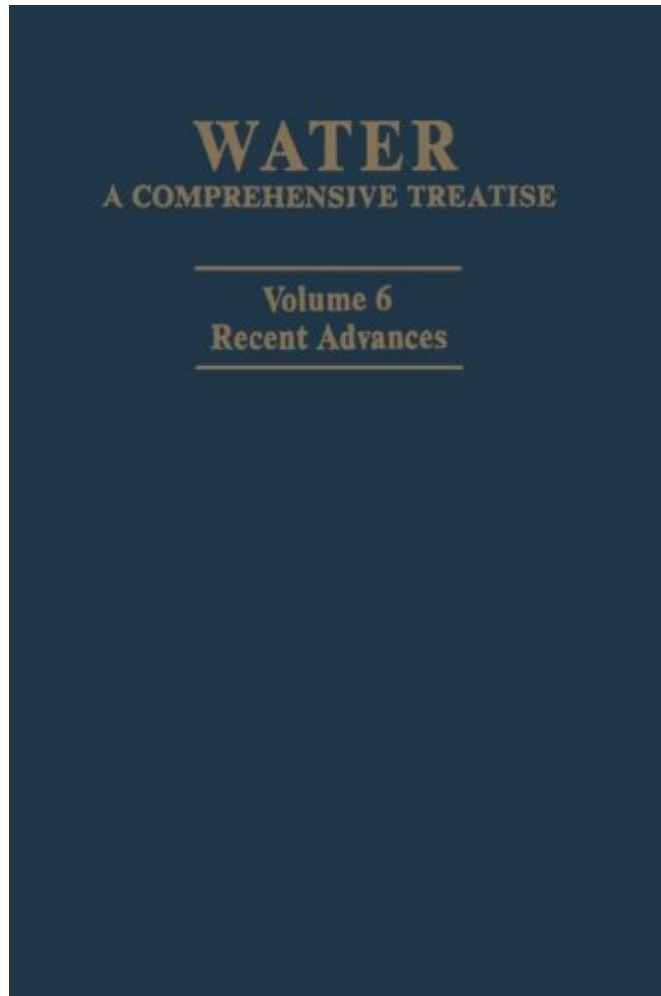




Low-temperature isomers of the water hexamer

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University of California, San Diego,
La Jolla, CA 92093-0314



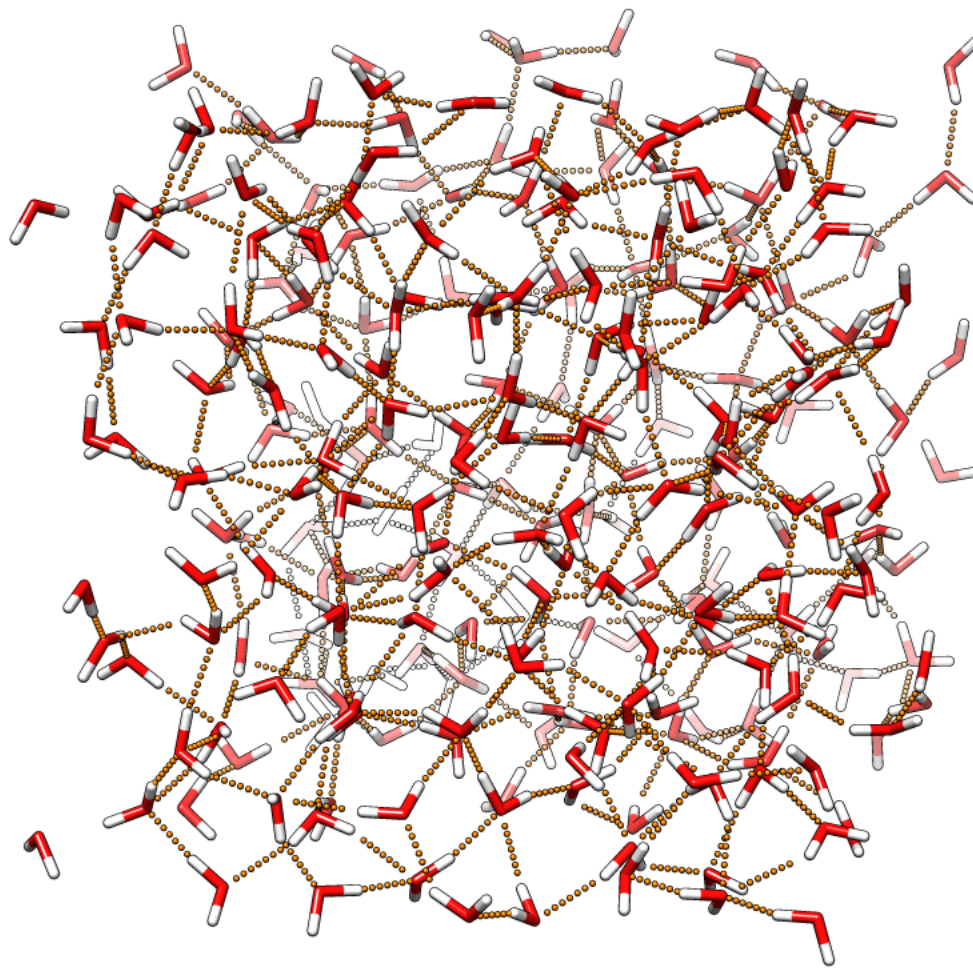
Hundreds of years
Thousands of pages

<http://www.lsbu.ac.uk/water/anmlies.html>

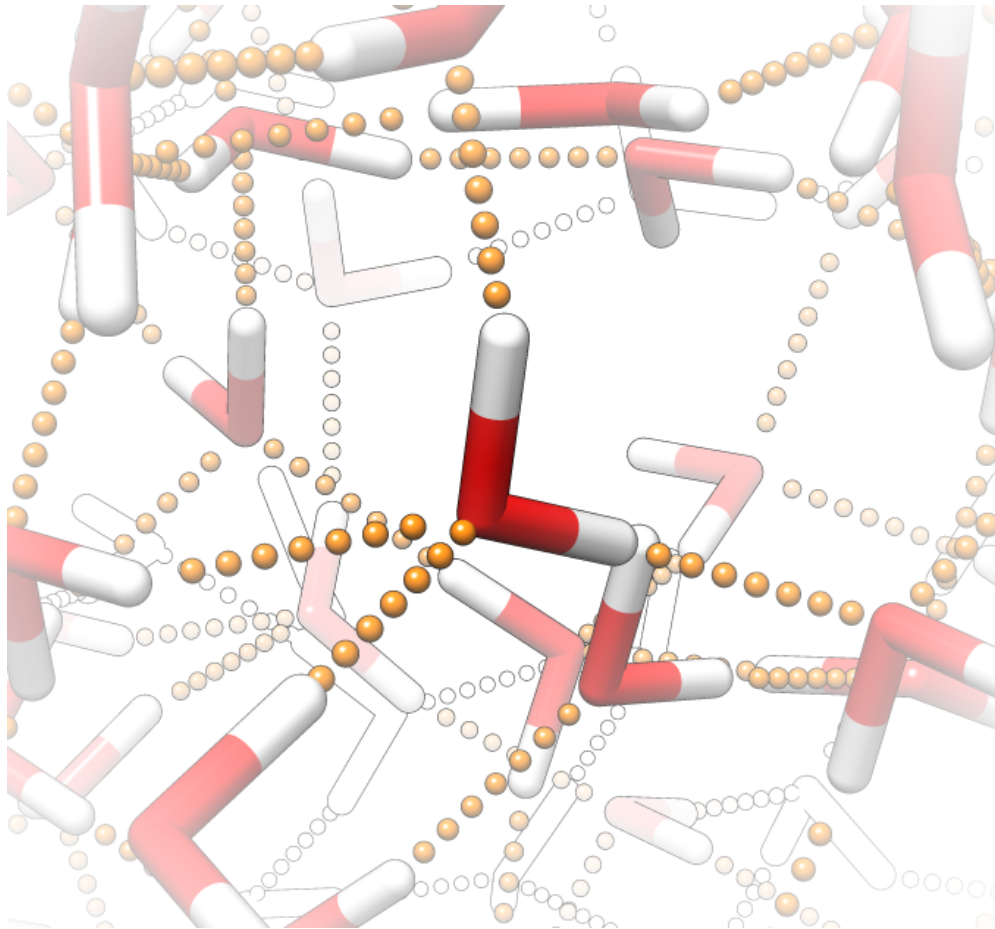
Unanswered Questions

- Does supercooled water has two phases and a second critical point?
- Does normal liquid water consists of smaller clusters of two different states of water?

Liquid Water



Hydrogen Bond Network



J.A. MORRONE, V. SRINIVASAN, D. SEBASTIANI, AND R. CAR, *Proton momentum distribution in water: an open path integral molecular dynamics study*, J. Chem. Phys. **126**, (2007), pp. 234504.

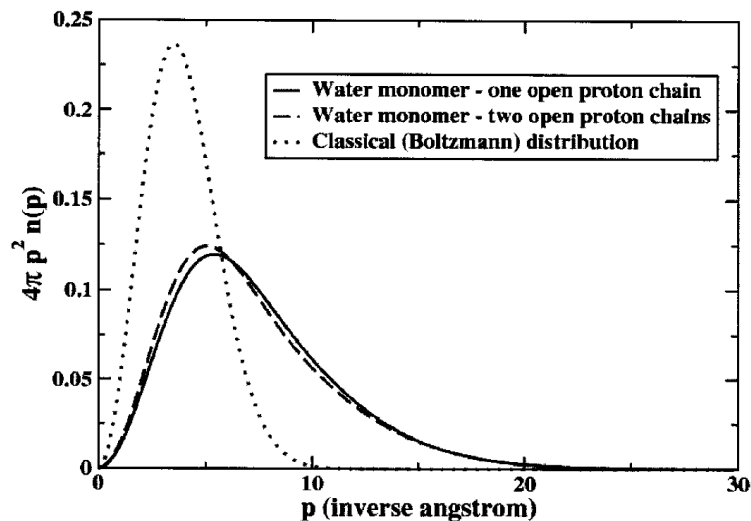
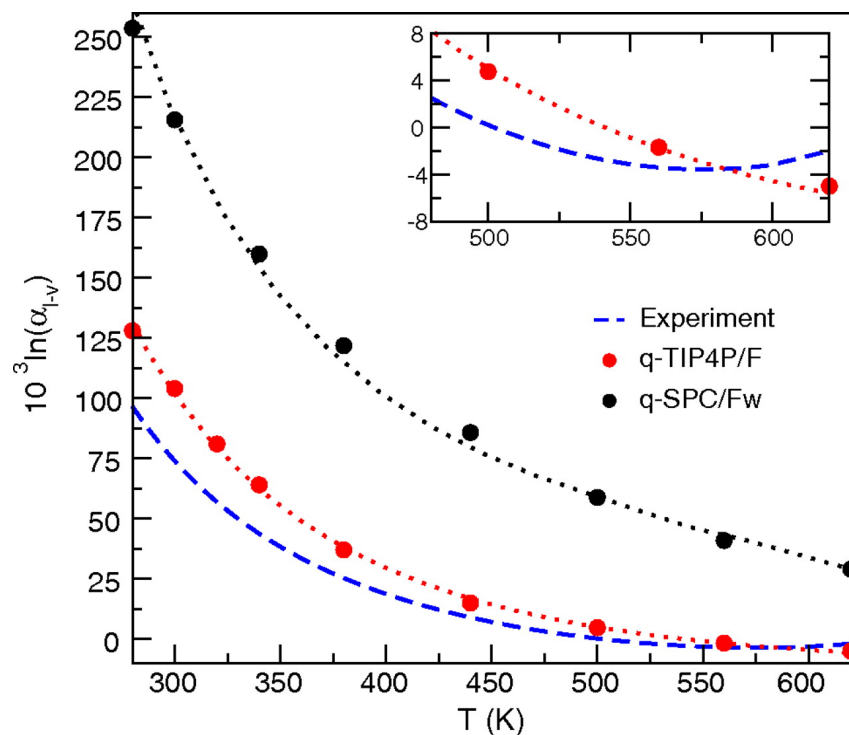


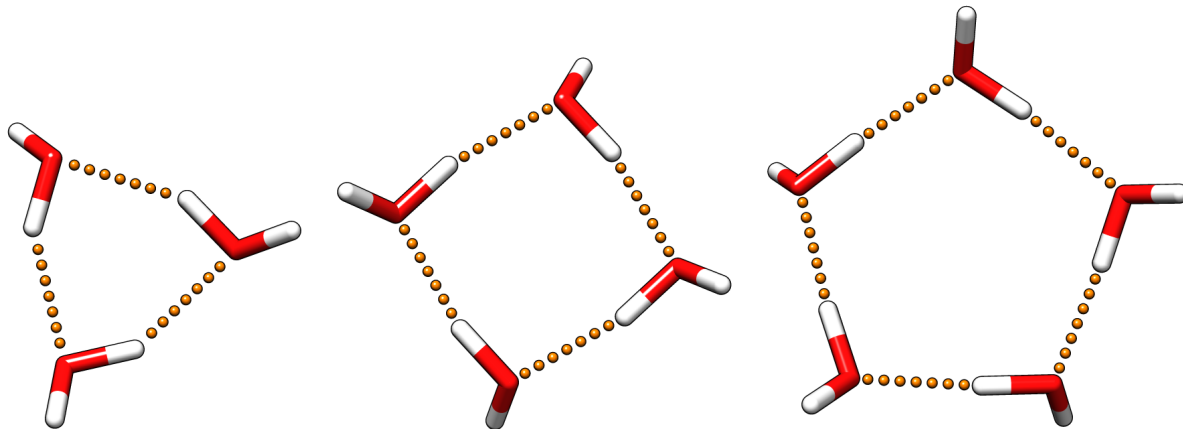
FIG. 1. The radial proton momentum distribution of a single water molecule computed in two different fashions. The solid curve is the result when only one hydrogen path is opened, as is required in the precise methodology. The dashed curve results from a separate simulation that opens two proton paths 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.

T.E. MARKLAND, AND B.J. BERNE, *Unraveling quantum mechanical effects in water using isotopic fractionation*, PNAS **109**, (2012), pp. 79887991.



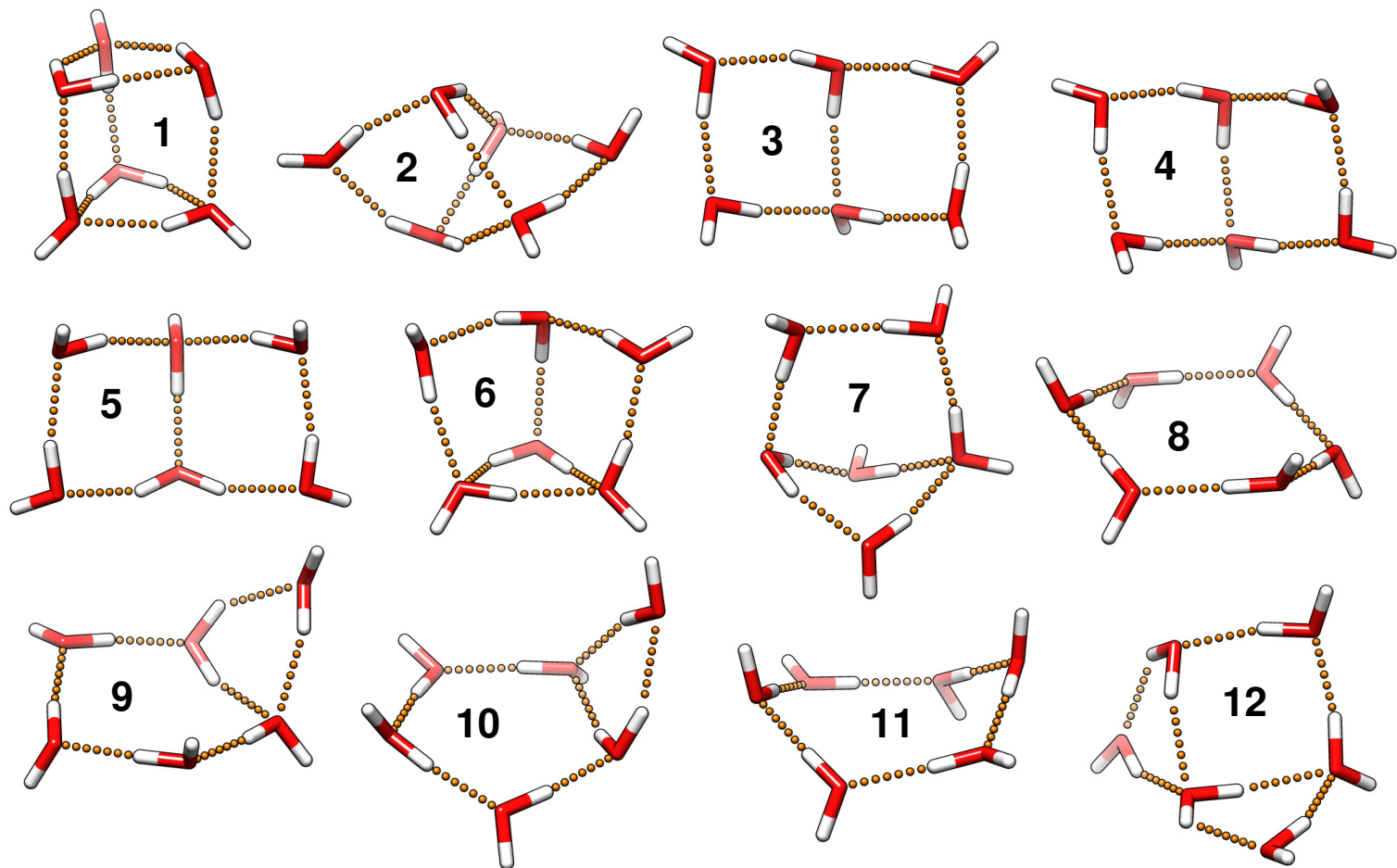
$$\alpha_{l-v} = \frac{(x_{D,l}/x_{H,l})}{x_{D,v}/x_{H,v}}$$

Trimer/Tetramer/Pentamer



Nearly planar

Hexamers



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

Cristóbal Pérez,¹ Matt T. Muckle,¹ Daniel P. Zaleski,¹ Nathan A. Seifert,¹ Berhane Temelso,² George C. Shields,^{2*} Zbigniew Kisiel,^{3*} Brooks H. Pate^{1*}

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 (H_2^{18}O). 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:

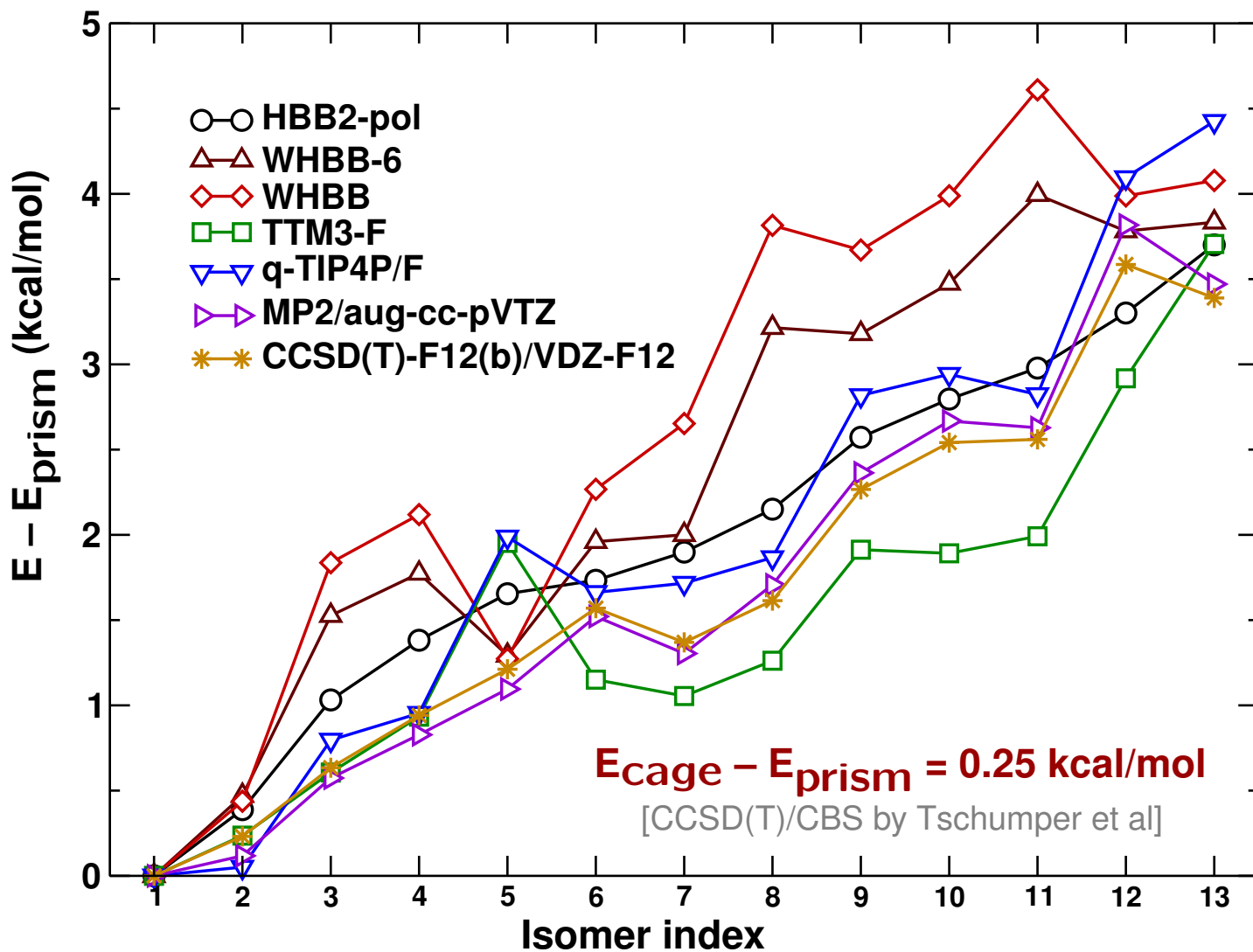
1) Electronic ground state for clamped nuclei.

[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.

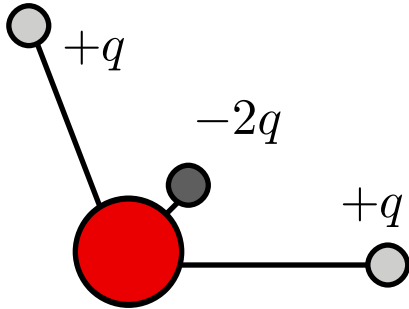
[not necessarily cheap either]



Model Potentials

- q-TIP4P/F S. HABERSHON, T.E. MARKLAND, AND D.E. MANOLOPOULOS, *Competing quantum effects in the dynamics of a flexible water model*, J. Chem. Phys. **131**, (2009), pp. 024501.
- TTM3-F G.S. FANOURGAKIS AND S.S. XANTHEAS, *Development of transferable interaction potentials for water. V. Extension of the flexible, polarizable, Thole-type model potential (TTM3-F, v. 3.0) to describe the vibrational spectra of water clusters and liquid water*, J. Chem. Phys. **128**, (2008), pp. 074506.
- WHBB Y. WANG, X. HUANG, B.C. SHEPLER, B.J. BRAAMS, AND J.M. BOWMAN, *Flexible, ab initio potential, and dipole moment surfaces for water. I. Tests and applications for clusters up to the 22-mer*, J. Chem. Phys. **134**, (2011), pp. 094509.
- HBB2-pol G. R. MEDDERS, V. BABIN, AND F. PAESANI, *A Critical Assessment of Two-Body and Three-Body Interactions in Water*, JCTC **9**(2), (2013), pp. 1103–1114.

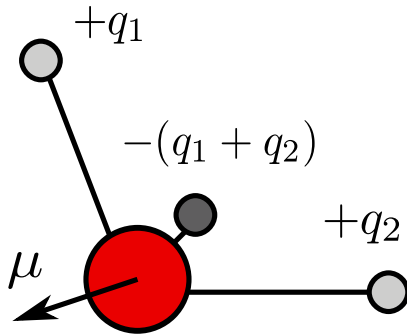
q-TIP4P/F



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

$$E_N = \sum_a E_a + \sum_{a < b} E_{ab}$$

TTM3-F



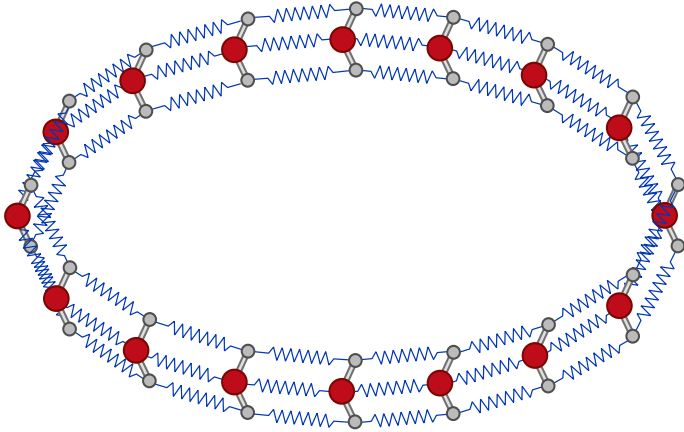
- *Ab initio* intra-molecular sector.
- *Ab initio* geometry-dependent charges.
- Polarizable site.

$$E_N \neq \sum_a E_a + \sum_{a < b} E_{ab}$$

WHBB & HBB2-pol

$$\begin{aligned} E_N = & \sum_a V_1(x_a) & \bullet \text{ } Ab \text{ initio intra-molecular sector.} \\ & + \sum_{a < b} V_2(x_a, x_b) & \bullet \text{ } Ab \text{ initio 2-/3-body terms.} \\ & + \sum_{a < b < c} V_3(x_a, x_b, x_c) & \bullet \text{ Polarizable site(s).} \\ & + V_{ind}(x_1, \dots, x_N) \end{aligned}$$

Partition Function



$$\mathcal{Z} = \text{tr} \exp(-\beta \mathcal{H}) = \lim_{P \rightarrow \infty} \int dq_1 \dots dq_P \exp(-\beta \mathcal{E}_P)$$

$$\text{tr} e^{-\beta \mathcal{H}} = \underbrace{\text{tr} e^{-\beta(\mathcal{K} + \mathcal{V})}}_{\text{Trotter}} = \lim_{P \rightarrow \infty} \text{tr} \left[e^{-\beta \mathcal{K}/P} e^{-\beta \mathcal{V}/P} \right]^P$$

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

$$\mathcal{E}_P = \frac{1}{P} \sum_{a=1}^P V(q_a) + \frac{m \omega_P^2}{2} \sum_{a=1}^P (q_{a+1} - q_a)^2$$

Path Integral Molecular Dynamics

- Linear transformation to “normal modes”.

J. CAO AND B.J. BERNE, *A Born–Oppenheimer approximation for path integrals with an application to electron solvation in polarizable fluids*, J. Chem. Phys. **99**, (1993), pp. 2902–2916.

- Fictitious momenta conjugate to these new variables.
- Nose-Hoover chains at every degree of freedom.

M.E. TUCKERMAN, B.J. BERNE, G.J. MARTYNA, AND M.L. KLEIN, *Efficient molecular dynamics and hybrid Monte Carlo algorithms for path integrals*, J. Chem. Phys. **99**, (1993), pp. 2796–2808.

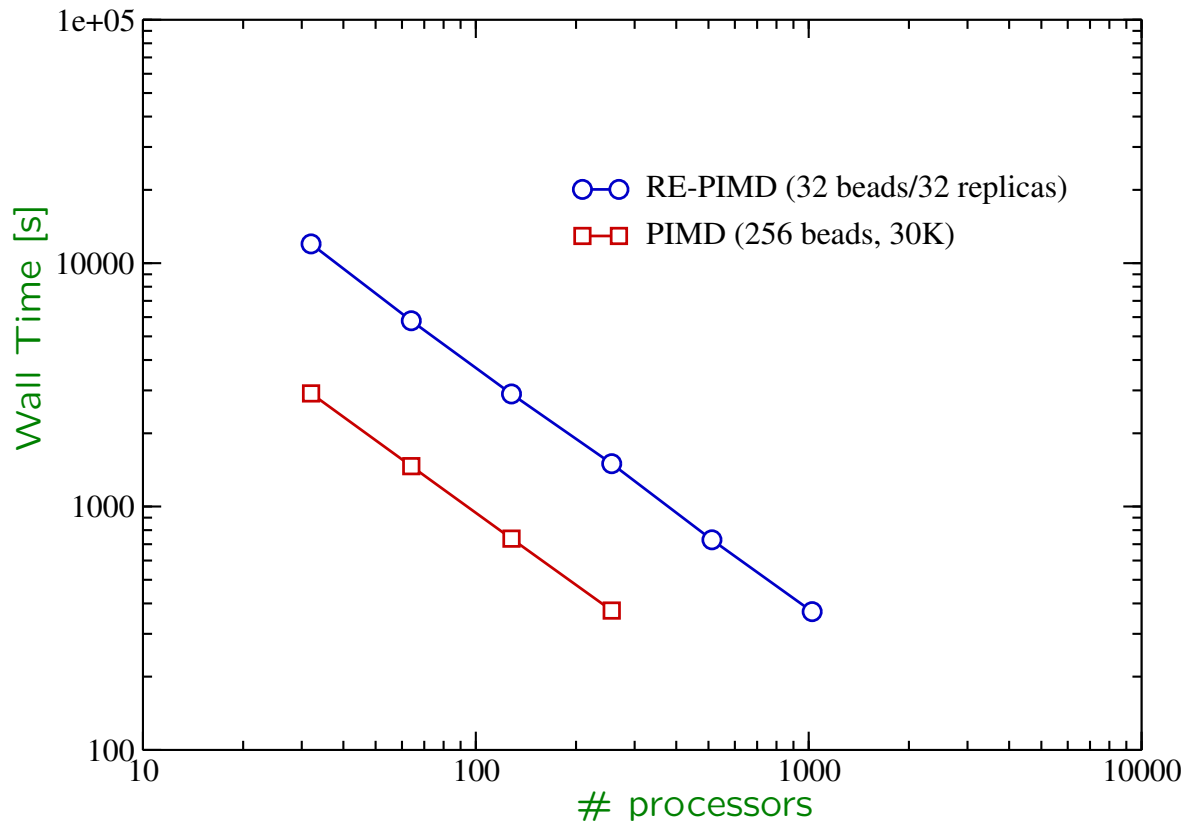
Replica Exchange

- 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

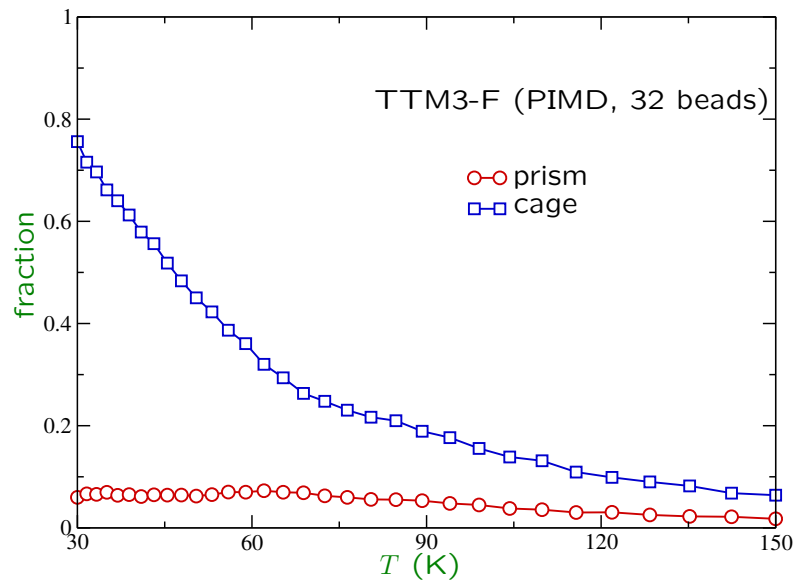
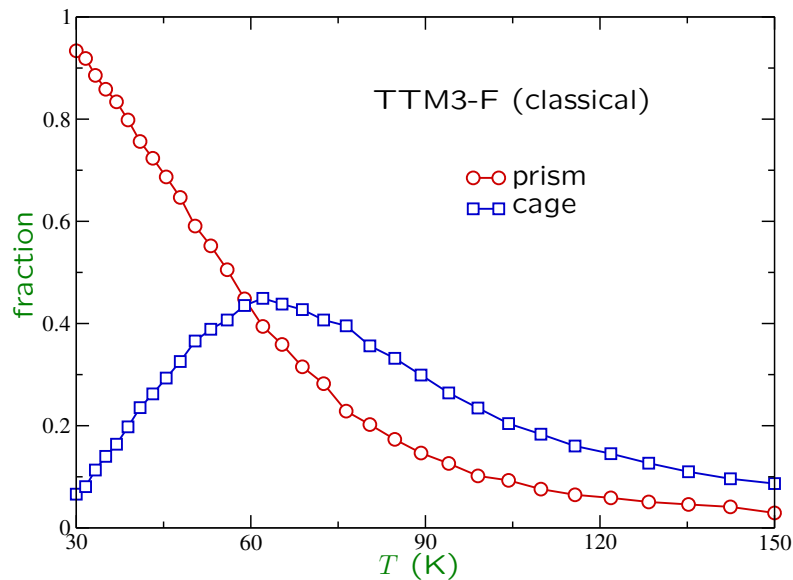
$$\min \left\{ 1, \frac{\pi(q')}{\pi(q)} \right\} = \min \left\{ 1, \frac{\pi_1(y)\pi_2(x)}{\pi_1(x)\pi_2(y)} \right\}$$

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

Performance on Gordon

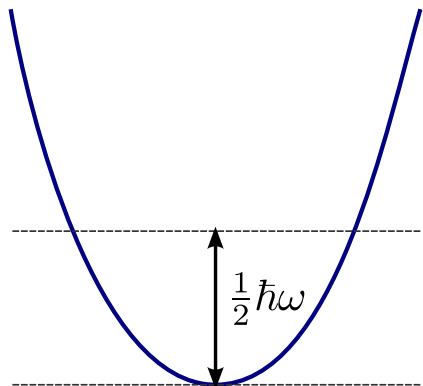
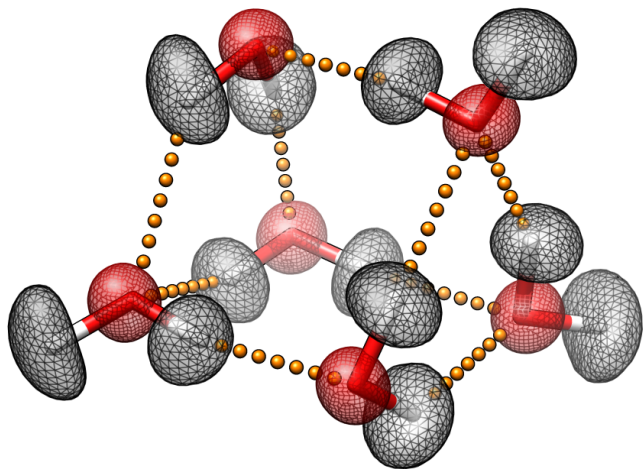


Results (TTM3-F)

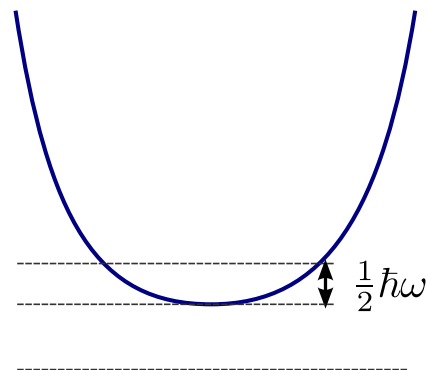
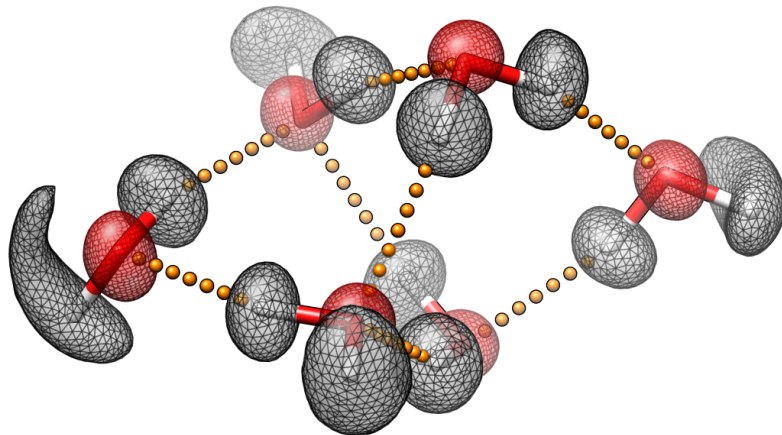


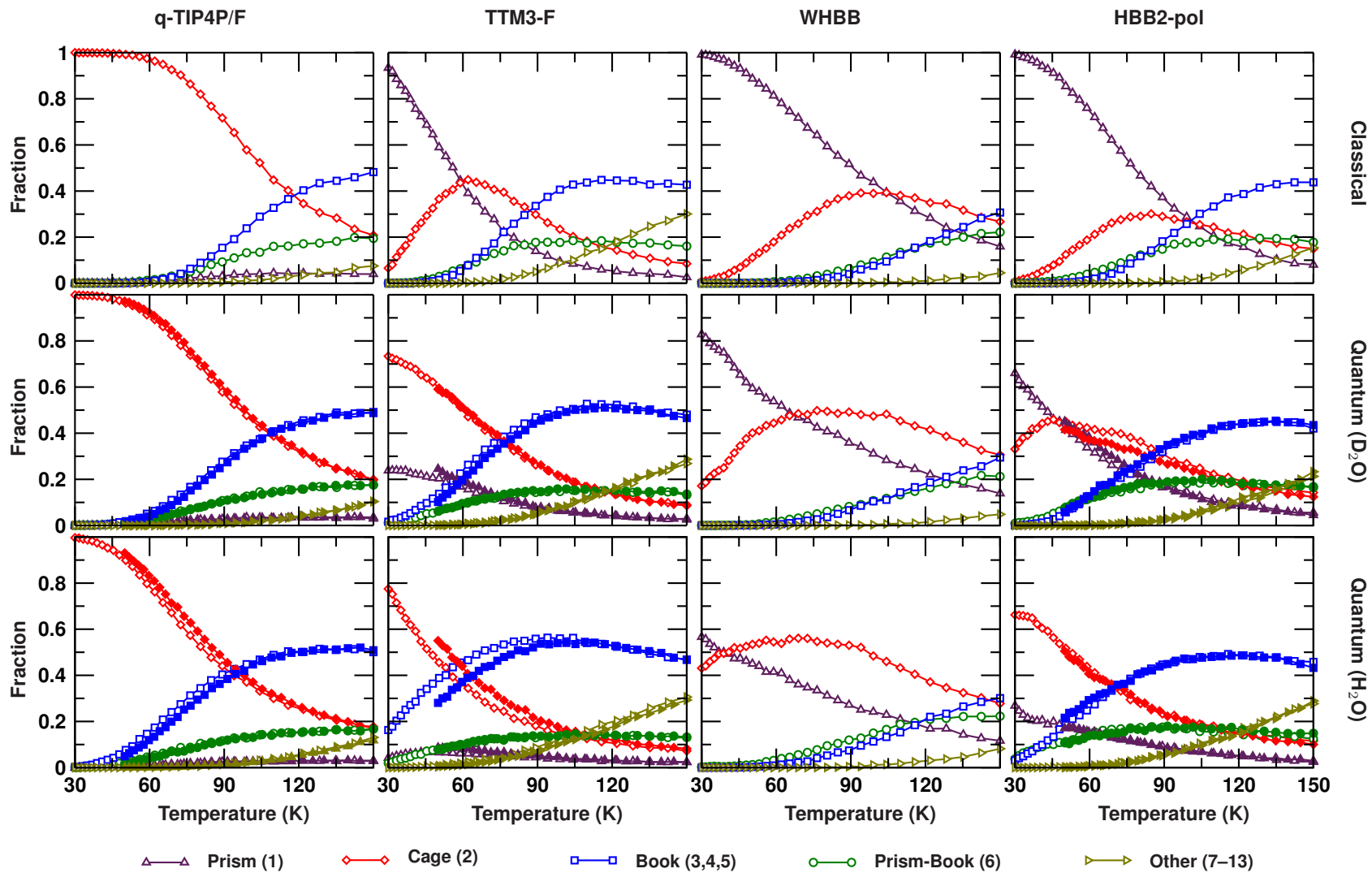
Nuclear quantum effects favor **cage** over **prism**.

Prism



Cage



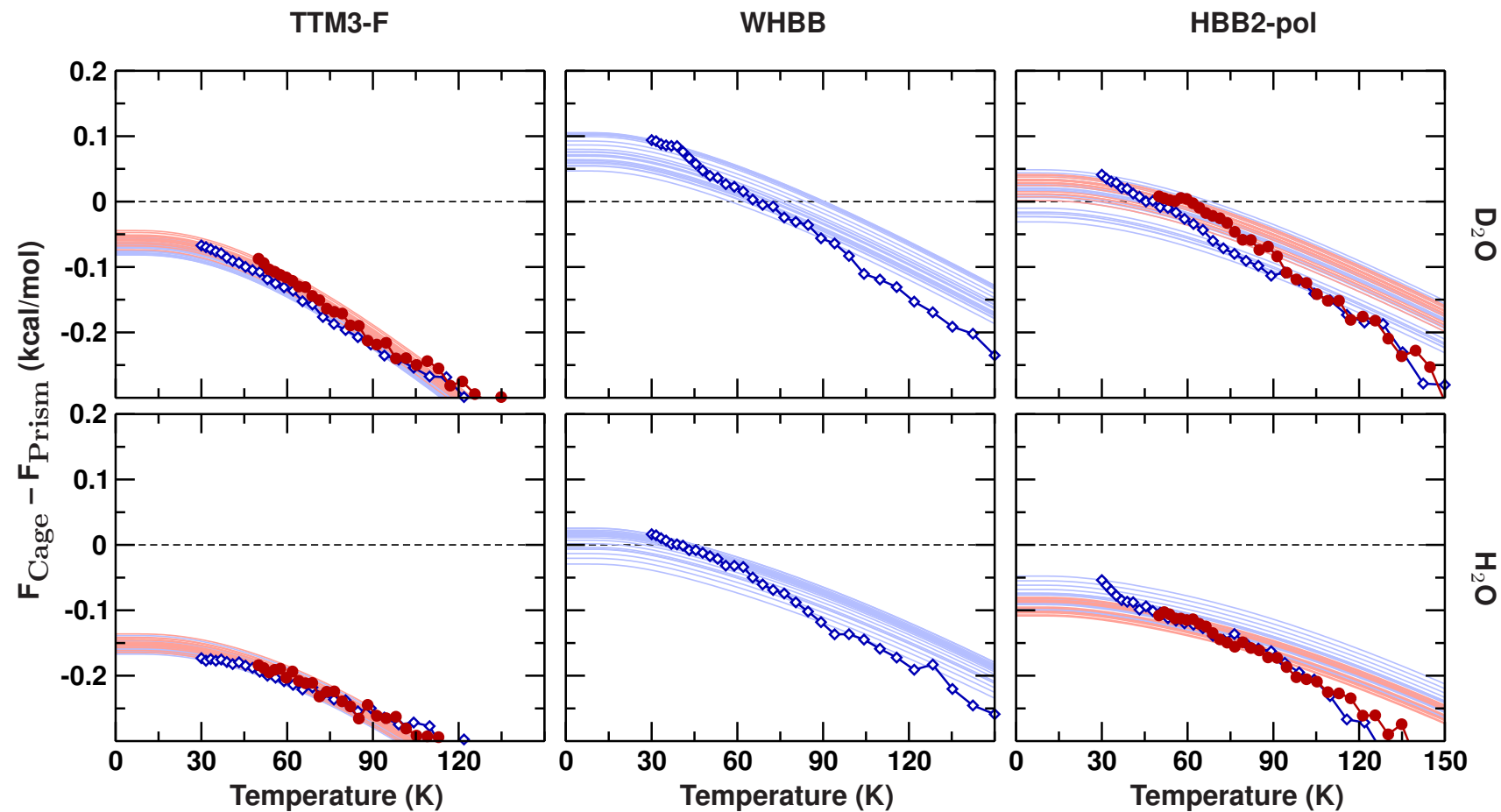


Free Energies

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

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

Free Energies



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 H_2O with D_2O .

