Finite temperature properties of clusters by replica exchange metadynamics: the water nonamer

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Abstract

We introduce and demonstrate a procedure leading to the computationally convenient and conceptually correct extraction of the free energy of the relevant states of a cluster at finite temperature, including all configurational entropy sources contributions. In the simple case considered for our demonstration, a small water cluster, the entropy is found to change drastically between one relevant state and another, and we show explicitly that the neglect of configurational contributions lead to large errors, totally unacceptable practically no less than conceptually.

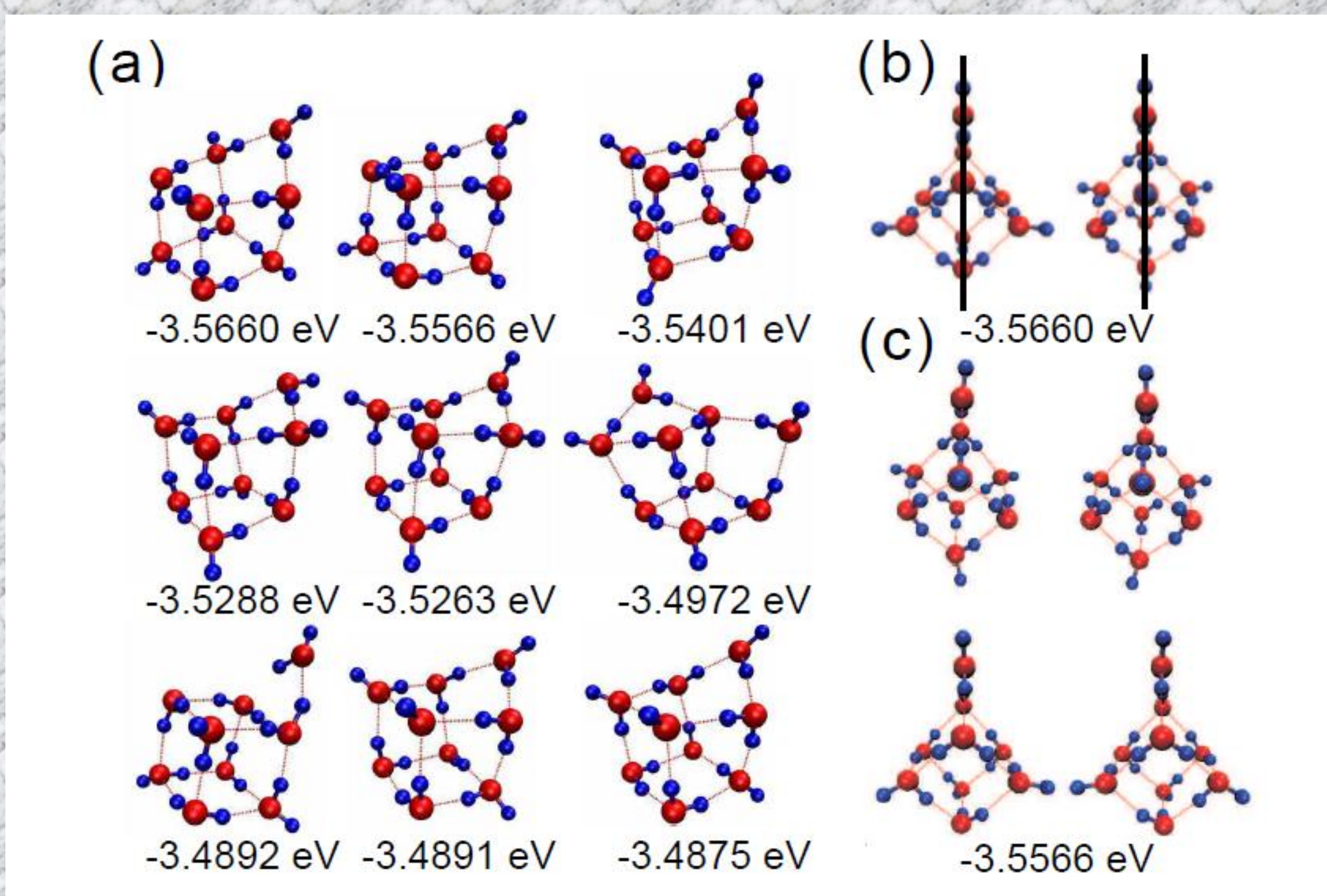
1. Background

•The properties of the cluster at finite temperature are still problematic.

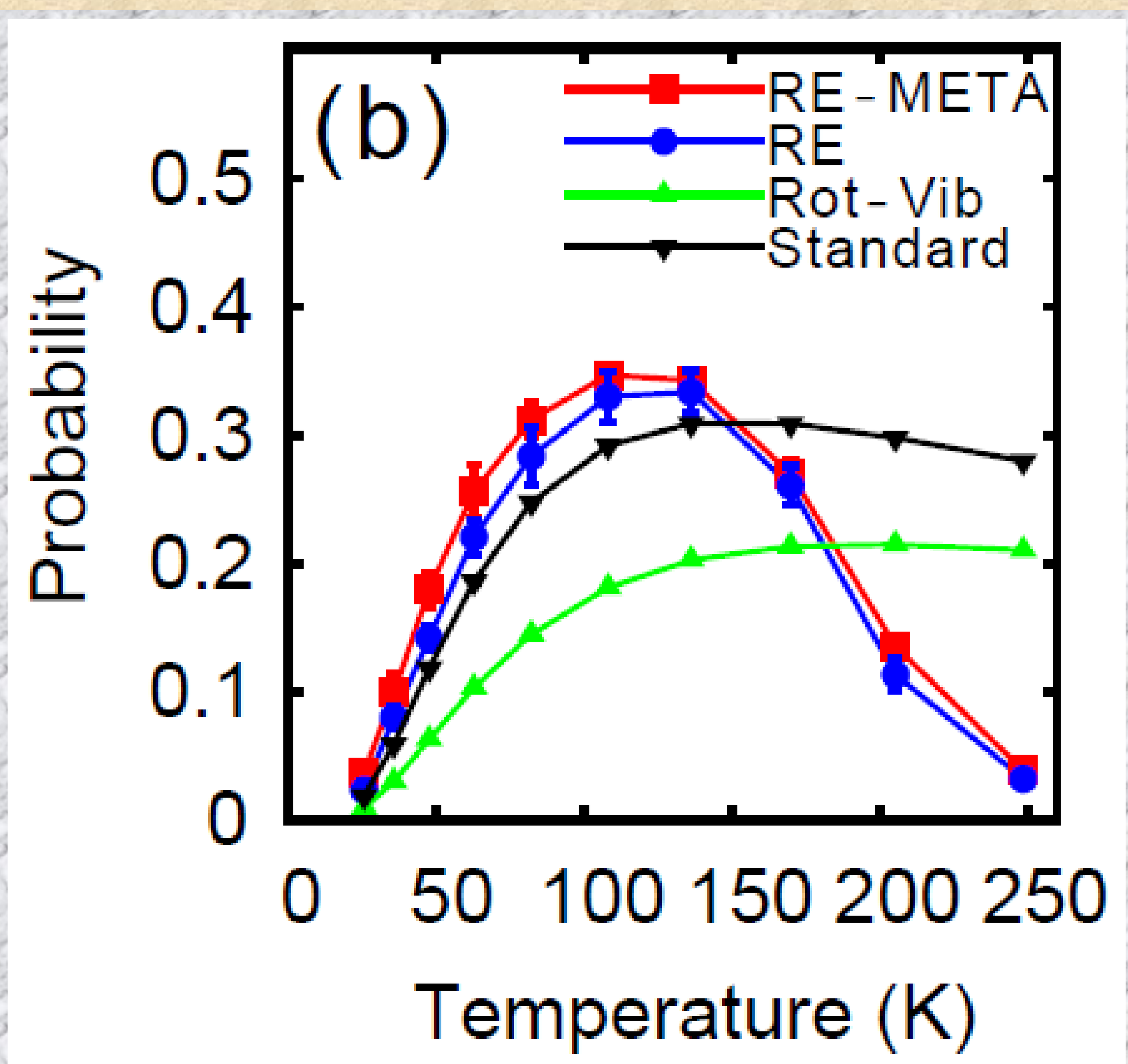
•Clusters are the primary nano-system where matter behaves differently from its usual bulk aggregation.

•Water cluster becomes an important branch of H2O research.

3. The nine lowest energy cluster structures



5. Occupation probabilities versus temperature



Occupation probabilities for the lowest relevant states versus temperature, from RE-META , from normal RE, in rigid-rotor-harmonic approximation. The total simulation is divided in 3 slices to evaluate the statistical error.

2. Simulation method

MD method:

➢TIP4P empirical potential.

➢Reflexed boundary condition

➢Nos éHoover chain thermostat.

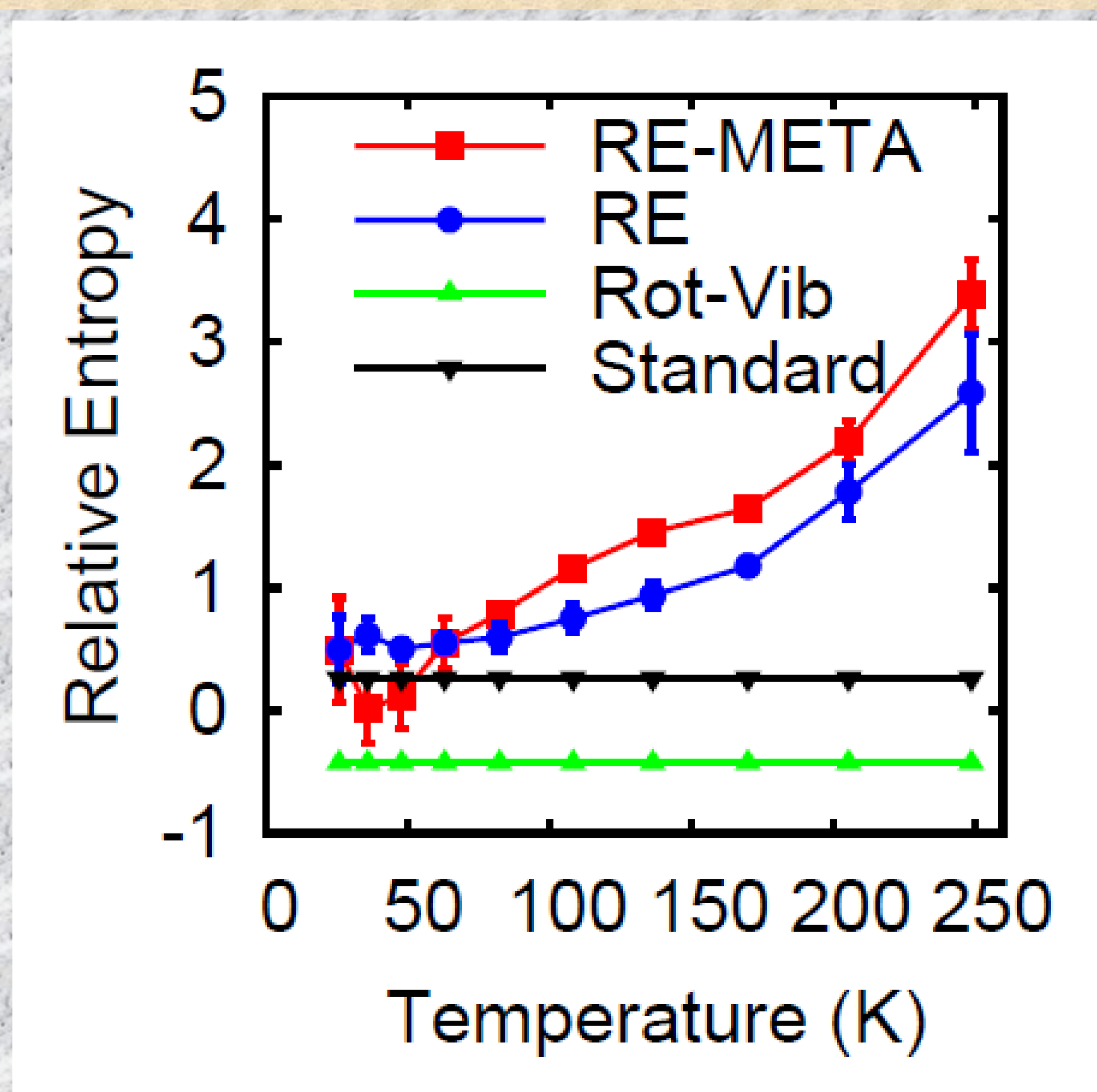
➢Time step: 0.2 fs. Total simulation time:50 ns

Sampling Method:

➢Metadynamics

➢Replica exchange

4.Relative entropy of the first excited state



At low temperature the entropy difference between simulation results and rigid-rotor-harmonic approximation is approximately a constant value which is approximately equal to ln 2. It is the configurational entropy.

6. Summary

We have shown how the full configurational complexity of a small cluster can be directly, realistically and economically accessed by a suitable sampling, combining replica exchange with metadynamics techniques (RE-META). This proves extremely effective in searching the cluster's relevant states, and in measuring their thermal population for increasing temperature. In the water nonamer, these populations are shown to differ largely from those routinely predicted by rigid-rotor-harmonic approximation. The entropy of relevant cluster states is measured, and surprising differences between one and another are understood in terms of configurational multiplicities, also related to symmetry.

Thank you!

J. Am. Chem. Soc., 2011, 133 (8), pp 2535–2540