DIFFUSION MONTE CARLO STUDIES OF THE ISOTOPIC SUBSTITUTION IN WATER HEXAMER

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Water clusters provide an opportunity to explore the effects of hydrogen bonding on short and long-range structures. Clusters also provide the opportunity to make detailed comparisons between experiment and calculation due to the small number of atoms involved. An area of long-standing interest is the relative energies of the different structures of water clusters. While identifying the minimum energy structure of a particular sized cluster is straight forward, once zero-point energy (ZPE) and thermal effects are accounted for, the relative energies of various structures change. In this talk, we will focus on $(H_2O)_6$ for which the lowest energy structure is the prism. When the ZPE is taken into account for $(H_2O)_6$, the cage becomes lower in energy than the prism. However, when the hexamer is fully deuterated, the ground state structure has been assigned as the prism by Pate and coworkers. Previous Diffusion Monte Carlo (DMC) calculations of the ZPE of the cage and prism structures showed that $(H_2O)_6$ is localized in the cage, while the cage and prism structures of $(D_2O)_6$ have nearly identical ground state energies. These calculations also indicated that there is a high computational cost to obtain reliable results, which is due to the large ensemble sizes needed for the convergence of the ZPE. [a] The expense of these calculations is traced to the nature of the couplings between the high and low frequency vibrations of these clusters.

In this talk, we will present a modified DMC approach in which we introduce a guiding function that provides a good description of the intramolecular vibrations of the water clusters.[b] Specifically, the local energy, $E_L = \hat{H}\Psi_T/\Psi_T$, is used in place of the potential energy surface for the purpose of sampling. Using this method allows us to reduce the computational cost in the evaluation of the ZPE and the ground state wave function by roughly an order of magnitude. Based on these studies, we confirm that the ground state for $(H_2O)_6$ is a cage, but we find that for $(D_2O)_6$, the ZPEs calculated for the cage and prism structures are nearly identical, and the identification of the lowest energy structure is highly sensitive to the subtle details of the potential energy surface that is used for these calculations.

[a]Mallory, J. D. and Mandelshtam, V. A., *J. Phys. Chem. A* (2015), **119**, 6504-6515.

[b]Lee, V. G. M. and McCoy, A. B., *J. Phys. Chem. A* (2019), **123**, 37, 8063-8070.