

INVESTIGATING THE NUCLEAR QUANTUM EFFECT ON $\text{H}^+(\text{H}_2\text{O})_6$

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Water clusters provide a set of systems where the influence of nuclear quantum effects on the stability of the hydrogen-bonding network can be studied both experimentally and theoretically. While electronic structures calculations indicate that the lowest energy isomer of $(\text{H}_2\text{O})_6$ is the prism structure, analysis of the spectra of $(\text{H}_2\text{O})_6$ by Johnson and Pate and their co-workers showed that the cage isomer is the lowest energy structure for $(\text{H}_2\text{O})_6$. However, when deuterated, the prism isomer becomes the lowest energy structure again. This was further explored by our group using diffusion Monte Carlo, where we found the introduction of zero-point energy to $(\text{D}_2\text{O})_6$ leads to the cage and prism isomers being nearly degenerate as opposed to $(\text{H}_2\text{O})_6$ where the cage isomer is significantly lower in energy than the prism isomer. Similar effects are seen in protonated water clusters. While smaller protonated water clusters, $\text{H}^+(\text{H}_2\text{O})_{2-5}$, show no observable change in the populations of the isomers observed in the spectra upon deuteration, the spectra of $\text{H}^+(\text{H}_2\text{O})_6$ and $\text{D}^+(\text{D}_2\text{O})_6$ have significant differences due to changes in the populations of isomers that are present.

Through a combination of high-level electronic structure calculations performed by the Jordan and Xantheas groups, vibrational perturbation theory, and diffusion Monte Carlo studies we investigated the effect that deuteration has on the spectrum of $\text{H}^+(\text{H}_2\text{O})_6$. Vibrational perturbation theory provides some insights into how the spectral signatures of each of the isomers of $\text{H}^+(\text{H}_2\text{O})_6$ changes. The challenge of vibrational perturbation theory is that it does not handle large amplitude motions well. Using diffusion Monte Carlo, we obtained an exact anharmonic ground state wave function and relative zero-point energies of several isomers of $\text{H}^+(\text{H}_2\text{O})_6$. The ground state wave functions were found to be localized near the stationary point that each simulation started from. This allows us to use mappings between the structural information, such as OO and OH distances, to the frequencies of hydrogen-bonded OH stretches to explore the contributions of various isomers to the observed spectrum.