USING DIFFUSION MONTE CARLO TO GENERATE VIBRATIONAL NORMAL MODES AND SPECTRA: PROTONATED WATER CLUSTERS

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Diffusion Monte Carlo (DMC) is a stochastic method used to generate the ground state vibrational wave function of a molecular system. Using DMC, one can understand the effects of vibrational zero-point energy on the structure of interest. Due to the informative physics in the ground state wave function, our group has previously implemented a technique to generate excited state energies and wave functions from DMC in order to understand the vibrational spectroscopy of small water-ion complexes.[a] [b] In this work, we extend this approach and apply it to larger protonated water clusters. Specifically, we are investigating the zero-order molecular vibrations and strong vibrational couplings that lead to spectral broadening. To begin, we use DMC to generate the ground state vibrational wave functions of $H^+(H_2O)_{n=3,4}$ and $D^+(D_2O)_{n=3,4}$. We discover tunneling in a few modes: the umbrella mode of the central hydronium, as well as the rotational coordinate of the outer water molecules. From these observations, we conclude that there are planar, high-symmetry, vibrationally-averaged structures sampled by these ions in their ground states. Using the saddle-point structures to define vibrational coordinates, we build our excited state approximation to investigate which vibrational states contribute intensity to the complicated infrared spectra. In the method's extension, we refine our approximation of higher order excited states, and we accommodate for strong vibrational coupling through a reduced-dimensional Hamiltonian. The Hamiltonian couples states that are energetically near the fundamental excitation of the hydrogen-bonded OH stretches. The method, in general, allows us to go beyond harmonic approximations by including the anharmonicity of the ground state wave function, yet it also allows us to calculate excited state energies using simple approximations akin to the harmonic oscillator. We find the results of our calculation reinforce the previously held idea that there exist strong couplings between the hydrogen-bonded OH stretch fundamentals and a series of dark modes, which lead to intensity borrowing in both size clusters.

[a] McCoy, A.B; Diken, E. G; Johnson, M.A. JPCA. 2009 113 (26), 7346-7352

[b] Timothy L. Guasco, T.L.; Johnson,M.A.; McCoy, A.B. JPCA. 2011 115 (23), 5847-5858