STRUCTURE AND DYNAMICS OF HHe_3^+: THE EMERGENCE OF LARGE-SCALE NUCLEAR DELOCALIZATION

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The HHe_3^+ cation is a model system for solvated triatomic molecules, which consists of a (quasi)linear HHe_2^+ core (chromophore) and a weakly-bound solvating He.[b] The equilibrium structure is T-shaped, but the "quantum" structure is very different, showing large-scale nuclear delocalization. In order to study the structure and dynamics of HHe_3^+ we performed path-integral molecular dynamics and variational nuclear-motion computations,[c] based on a new, highly accurate, neural-network potential-energy surface.[d] We tested the new potential on the HHe_2^+ cation. The computed rovibrational transitions have excellent agreement with experimental data, showing the high quality of the potential. As to the HHe_3^+, we determined the vibrational states below and above the dissociation limit, corresponding to the solvating He and the chromophore, respectively. The computed chromophore vibrational frequencies have good agreement with the experimental results. Note that, the frequencies of the chromophore vibrations are significantly shifted compared to that of the HHe_2^+, because the intermolecular bond is relatively strong. In order to investigate the "quantum" structure, we computed and plotted the nuclear density, which shows the spatial distribution of solvating He with respect to the chromophore. The nuclear density was obtained from path integral molecular dynamics computations and the vibrational wave functions from the nuclear-motion computation. The plots reveal that the true shape of the complex is completely different from the equilibrium structure: the solvating He is fully delocalized, forming a torus around the central proton even in the vibrational ground state. Delocalization is observed for each state, and its exact pattern reflects the type of vibrational excitation.

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