DIFFUSION MONTE CARLO STUDIES OF THE GROUND-STATE STRUCTURE AND ENERGETICS OF H_5^+ AND ITS ISOTOLOGUES

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H_5^+ is an important intermediate in the proton transfer reaction between H_3^+ and H_2 in interstellar clouds. The highly fluxional nature of this simple molecular ion makes theoretical studies challenging. Diffusion Monte Carlo (DMC) is an excellent method to obtain accurate zero-point energies of such systems, given a potential energy surface (PES). In this work, the zero-point energies of H_5^+ and its deuterated isotopologues are calculated using DMC, with the full-dimensional PES's from the Roncero group[a] and the Bowman group.[b] The results are in good agreement with the previously reported values.[c] Using the descendant weighting method, projections of the probability amplitude onto various internal coordinates are investigated. Based on these projections, the ground-state expectation values of some microscopic properties, including the molecular geometries, rotational constants and dipole moments, are evaluated to aid in future high-resolution spectroscopic studies. Furthermore, the PES contains 120 equivalent minima, and the results of the DMC simulations are used to explore the extent to which the system is able to tunnel among these minima. The results show very low probabilities for exchanges between the center and outer hydrogen atoms at the ground vibrational state, due to the relatively high barriers that seperate these minima. Higher probabilities are predicted for the excited states.

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[b] Z. Xie, B. J. Braams, and J. M. Bowman, J. Chem. Phys. 122, 224307 (2005)
[c] P. H. Acioli, Z. Xie, B. J. Braams, and J. M. Bowman, J. Chem. Phys. 128, 104318 (2008)