

DIFFUSION MONTE CARLO STUDY OF $C_2H_5^+$ USING AN AB INITIO POTENTIAL ENERGY SURFACE

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Carbocations are a class of important organic intermediates, which exist in hydrocarbon plasmas and are believed to play a role in the chemistry in the interstellar medium. Protonated ethylene ($C_2H_5^+$) is one such carbocation, which is formed from the smallest alkene family. It is also important in mass spectrometry as it appears in the mass spectra of many organic molecules and it is used as the protonating agent in chemical-ionization mass spectrometry. High-level electronic structure calculations predict that the minimum energy structure is the non-classical one in which the excess proton is equidistant from the two carbon atoms. This was confirmed by the IR spectrum of $C_2H_5^+$ obtained by the Dopfer and Duncan groups.

In this work, the ground state wavefunction and structure of $C_2H_5^+$ is obtained from Diffusion Monte Carlo (DMC) based on a potential with CCSD(T)-level accuracy, evaluated using several machine learning approaches. The effect of the shared proton motion on the IR spectrum as well as the coupling between the vibration of the shared proton and other higher frequency motion will be discussed. The impact of deuteration on these couplings also will be described. Lastly, the excited state for the shared proton motion can be obtained by fixed-node DMC, allowing us to explore the excited state wave functions, and particularly the possibility of accessing the classical carbocation structure through vibrational excitation.