

DIFFUSION MONTE CARLO STUDY OF VIBRATIONAL EXCITED STATES OF PROTONATED ETHYLENE ( $\text{H}^+(\text{C}_2\text{H}_4)$ )

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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 ( $\text{H}^+(\text{C}_2\text{H}_4)$ ) is one such carbocation, which is formed from the smallest alkene. 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  $\text{H}^+(\text{C}_2\text{H}_4)$  obtained by the Dopfer and Duncan groups.

In this work, we use fixed-node Diffusion Monte Carlo (DMC), based on a potential with CCSD(T)-level accuracy to obtain excited state wave functions and vibration frequencies. The analysis of excited state wave functions confirms that the ion is localized in the non-classical minimum on the potential. It also allows us to explore the couplings among the motions of the hydrogen atoms. The frequencies obtained from the DMC calculations are compared to the experimental frequencies in the IR spectrum. Based on this, one of the weak features between 2500 and 3000  $\text{cm}^{-1}$  in the spectrum is assigned to the combination band of the proton transfer and breathing mode. Lastly, extensions of DMC to calculations of intensity will be discussed