USING DIFFUSION MONTE CARLO TO PROBE THE ROTATIONALLY EXCITED STATES OF H_3^+ AND ITS ISOTOPOLOGUES

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$H_{3-n}D_n^+$ are among the most abundant polyatomic ions in the universe.[a] Moreover, the deuterated isotopologues are thought to play a key role in the astrochemical reactions governing the H/D fractionation of "metallic" species in the interstellar medium.[b] An accurate quantum mechanical treatment of these species, as well as any reactions involving them, requires a methodology capable of capturing their large fluxionality as well as the constraints, due to particle exchange symmetries, on their physically allowed rovibrational states. Diffusion Monte Carlo (DMC) has been shown to be a highly successful technique for treating quantum zero-point effects of very floppy molecules and clusters and our group has recently developed a fixed-node DMC methodology capable of including the effects of rotational excitation.[c] Here, we report the results of DMC calculations of the rotationally excited states of H_3^+ and its isotopologues. In particular, comparison with converged variational calculations involving states with $J \leq 20$ provides the most thorough test yet of the range of quantum states over which the assumptions underlying our rotationally excited state DMC methodology can be reliably applied. Finally, the implications of this work on our overall goal of using DMC based methodologies to map out the energetics of the reaction of $H_{3-n}D_n^+$ with HD will be discussed.

[a] T. R. Geballe and T. Oka, Science 312, 1610 (2006)
[b] E. Hugo, O. Asvany, and S. Schlemmer, J. Chem. Phys. 130, 164302 (2009)
[c] A. S. Petit and A. B. McCoy, J. Phys. Chem. A 113, 12706 (2009)