EMPLOYING DIFFUSION MONTE CARLO IN THE CALCULATION OF MINIMIZED ENERGY PATHS OF THE $CH_3^+ + H_2 \leftrightarrow CH_5^+ \leftrightarrow CH_3^+ + H_2$ REACTION AND ITS ISOTOPIC VARIANTS

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Protonated methane is presumed by astrochemists to be an important intermediate in the reaction $CH_3^+ + HD \rightarrow CDH_4^+ \rightarrow CH_2D^+ + H_2$ within the interstellar medium. Understanding this reaction can also help shed light on the observed nonstatistical H/D isotopic abundance in the isotopologues of CH_3^+ within the interstellar medium. Interestingly, based on kinetic studies, Gerlich and co-workers showed that all of the reactions in the series $CH_{3-n}D_n^+ + HD \rightarrow CH_{4-n}D_{n+1}^+ \rightarrow CH_{2-n}D_{n+1}^+ + H_2$ have identical net rate constants .[a] This result is independent of the value of n.

In previous studies of CH_5^+, we have employed Diffusion Monte Carlo (DMC)[b] to study ground,[c] and excited states.[d,e,f] By performing the simulation in Jacobi coordinates, we can use Adiabatic DMC[g] to study the properties of the minimized energy paths of CH_5^+ and isotopologues. To determine the minimized energy path, we calculate the quantum zero-point energy and ground state wave function as a function of the distance between the center of mass of the H_2 group and the center of mass of the CH_3^+ group over a range from 0 to 6 Å. Over this range, we find 5 distinct regions of interaction, short range repulsion region, CH_5^+ complexation, short-range fragment interaction, long-range fragment interaction, and a region of no interaction between the two fragments. Interestingly, the range of H_2/CH_3^+ distances spanned by each of the regions is roughly independent of the number or location of the deuterium atoms. Interestingly, the range of H_2/CH_3^+ distances spanned by each of the regions is roughly independent of the number or location of the deuterium atoms.

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