H$_5^+$ cluster: Realistic DFT potential surface and dynamics

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Results of recent studies on the H$_5^+$ cluster will be presented. Nowadays high accurate \textit{ab initio} electronic structure calculations can be carried out, however a reliable global representation of the H$_5^+$ PES is still an open and challenging problem \cite{1}. Thus, here we are present an alternative approach following the idea of \textit{ab initio} molecular dynamics simulations, that combines nuclear dynamics methods with first-principles electronic structure calculations within the DFT framework. Such DFT approach using the B3(H) hybrid functional, specially designed for hydrogen-only systems, allows to carry out reliable dynamics calculations, classical or quantum mechanical ones, by computing the potential value at a given configuration “on the fly” with both reasonable accuracy and at low computational cost without any posterior parametrization procedure of the surface \cite{2}. It was found that the DFT/B3(H) approach provides a reliable global description of the potential surface of H$_5^+$ cluster. In the panel (a) of the figure we compare the optimal total energies at MP2, CCSD(T) and DFT/B3(H) levels of theory, and as one can see the DFT/B3(H) calculations clearly describe the aspects of the potential in an excellent agreement with the CCSD(T) ones.

Based on the B3(H) surface both path integral Monte Carlo (PIMC), at low temperature, and multiconfiguration time-dependent Hartree (MCTDH) calculations are carried out to investigate quantum effects on the internal proton transfer (see pair HH radial distribution functions in the panel (b) of the figure), and thermal structural fluctuations on the vibrational zero-point structure of H$_5^+$ cluster \cite{3,4}. Theoretical simulations of the IR spectra of H$_5^+$/D$_5^+$ and their comparison with the experimental ones will also be discussed \cite{5}. Such findings are of particular interest for studying larger species of the H$_n^+$ clusters, as well as gas-phase solvation effects, cluster fragmentation, and collision processes in astrophysical applications.

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