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Structure and dynamics of an excess proton in water: a neural network force-field study

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ABSTRACT

An excess proton in bulk water under normal temperature and pressure appears as a very simple system in physical chemistry. The diffusion of the charge defect is enhanced by Grotthuss shuttling [1], a transfer of H^+ along the hydrogen bond network in water. Six decades ago, two limiting structures for the excess proton in water have been hypothesized: the Eigen [2] and Zundel [3] cations. The relative stability of the two forms is difficult to assess both experimentally and computationally due to a low energy barrier. The mechanism for the proton transfer is thus hard to unravel. The major issue in computer simulations stands in the need of both accurate electronic structure description and long simulations for good statistics. Here we train a machine learning model [4] to reproduce the B3LYP-D3 potential energy surface of an excess proton in liquid water. This precise and accurate model allows the computation of incredibly long path integral molecular dynamics simulations compared with available classical ab initio molecular dynamics simulations using lower levels of DFT. We confirm that the defect lives in low-barrier free energy surface and constantly moves on different hydrogen atoms. We study in detail the contribution of the local environment of the excess proton on its transfer and especially the role of an accepted H-bond on the initial and final host water molecules. We expect these long trajectories generated by neural networks potentials to be a mean to bridge the gap between theory and experiments on acidic water. Although fundamental, this work helps understanding the key mechanism of proton transfer relevant in several domains from biology to energy.

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