Nuclear quantum effects in protonated water clusters

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Résumé

Water is a key ingredient for life and plays a central role as solvent in many biochemical reactions. However, the intrinsically quantum nature of the hydrogen nucleus, revealing itself in a large variety of physical manifestations, including proton transport, is still elusive. Here we study, by an unprecedented combination of state-of-the-art quantum Monte Carlo methods and path-integral molecular dynamics, the structure and hydrogen-bond dynamics of the protonated water hexamer, the fundamental unit for the hydrated proton. We show that nuclear quantum effects and thermal ones cooperate to produce an unexpected non-monotonic behavior of the hydrogen-bond length as a function of temperature. This behavior can be explained by an inverse Ubbelohde effect, as it results from quantum delocalization of the hydrated proton across two water molecules upon temperature rise. The corresponding hydrogen bond is the shortest precisely around 250-300 K. As a consequence, room temperature is revealed to be the "sweet spot" for proton transport and diffusion, and thus for many phenomena depending on proton transport, including life.

Mots-Clés: quantum Monte Carlo, nuclear quantum effects, water clusters

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