

**Why Does Hydronium Diffuse Faster Than Hydroxide in Liquid Water**

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**Abstract:**

Proton transfer via hydronium and hydroxide ions in water is ubiquitous. It underlies acid-base chemistry, certain enzyme reactions, and even infection by the flu. Despite two-centuries of investigation, the mechanism underlying why hydronium diffuses faster than hydroxide in water is still not understood. Herein, we employ state of the art Density Functional Theory based molecular dynamics, with corrections for nonlocal van der Waals interactions, and self-interaction in the electronic ground state, to model water and the hydrated water ions. At this level of theory, structural diffusion of hydronium preserves the previously recognized concerted behavior. However, by contrast, proton transfer via hydroxide is dominated by stepwise events, arising from a stabilized hyper-coordination solvation structure that discourages proton transfer. Specifically, the latter exhibits non-planar geometry, which agrees with neutron scattering results. Asymmetry in the temporal correlation of proton transfer enables hydronium to diffuse faster than hydroxide and may underlie observed isotope anomalies.