

Abstract Submitted  
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**Why does hydronium diffuse faster than hydroxide in liquid water?**<sup>1</sup> LIXIN ZHENG, Temple University, BISWAJIT SANTRA, Princeton University, ROBERT DISTASIO, Cornell University, MICHAEL KLEIN, Temple University, ROBERTO CAR, Princeton University, XIFAN WU, Temple University — Experiments show that the hydronium ion ( $\text{H}_3\text{O}^+$ ) diffuses much faster than the hydroxide ion ( $\text{OH}^-$ ) in liquid water. *ab initio* molecular dynamics (AIMD) simulations correctly associated the diffusion mechanism to proton transfer (PT) but have been unable so far to clearly identify the reason for the faster diffusion of hydronium compared to hydroxide, as the diffusion rate was found to depend sensitively on the adopted functional approximation. We carried out AIMD simulations of the solvated water ions using a van der Waals (vdW) inclusive PBE0 hybrid density functional. It is found that not only hydronium diffuses faster than hydroxide but also the absolute rates agree with experiment. The fast diffusion of  $\text{H}_3\text{O}^+$  occurs via concerted PT that enables the ion to jump across several H-bonded molecules in successful transfer events; in contrast, such concerted motion is significantly hindered in  $\text{OH}^-$  where the ion is easily trapped in a hyper-coordination configuration (a local solvation structure that forbids PT). As a result multiple PT events are rare and the diffusion of  $\text{OH}^-$  is significantly slowed down. Such a clear difference between the two ions results from the combined effect of vdW interactions and self-interaction correction.

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