

Abstract Submitted
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Why does hydronium diffuse much faster than hydroxide in liquid water?¹ MOHAN CHEN, LIXIN ZHENG, Department of Physics, Temple University, BISWAJIT SANTRA, HSIN-YU HO, Department of Chemistry, Princeton University, ROBERT DISTASIO JR., Department of Chemistry and Chemical Biology, Cornell University, MICHAEL KLEIN, Institute for Computational Molecular Science, Temple University, ROBERTO CAR, Department of Chemistry, Princeton University, XIFAN WU, Department of Physics, Temple University — Proton transfer, by solvated hydronium and hydroxide in water, is a fundamental process behind numerous acid-base chemical reactions. Over centuries, Grotthuss mechanism has successfully drawn our attention to the molecular structural changes during proton transfer. Yet, the faster diffusion of hydronium than that of hydroxide has not been fully clarified. We show that an accurate prediction of hydrogen-bond network in liquid water, which includes van der Waals interaction and hybrid functional, is essential to address this issue. Our ab initio molecular dynamics presents that proton transfer by hydronium is consistent with the recently proposed picture of concerted proton transfer. Furthermore, the hypercoordinated structure of hydroxide is significantly favored in the simulation with van der Waals interaction and hybrid functional. The difference in the correlated motions between these two ions naturally ensures the faster migration of hydronium than hydroxide in water.

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