

The Dynamics of Aqueous Hydroxide Ion Transport from 2D IR Spectroscopy

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Compared to ions of similar size and charge density, the hydroxide ion is able to move through liquid water extremely rapidly. It is believed that this anomalously fast diffusion constant arise from its ability to accept a proton from a neighboring water molecule, leading to translocation of the ion. Despite the seeming simplicity of this reaction, the exact mechanism by which it proceeds remains highly controversial. Central to the debate is how the coordination number about the hydroxide ion and its first solvation shell change over the course of the reaction as well as how strong of a role the remaining solvent plays in guiding the reaction. We have used femtosecond two-dimensional infrared spectroscopy (2D IR) to investigate this process through the vibrational dynamics of the OH stretching vibration in isotopically dilute NaOD/D₂O solutions. Our experiments separate the dynamics of the hydroxide from those of its first solvation shell, characterize the kinetics for proton exchange and show signatures of the intermolecular proton transfer dynamics.