

The Dynamics of Excess Protons in Liquid Water Viewed through 2D IR Spectroscopy

M. Thämer⁺, L. De Marco[#], W. Carpenter, J. A. Fournier, R. Biswas, G.A. Voth, A. Tokmakoff

Department of Chemistry, Institute for Biophysical Dynamics, and James Franck Institute, The University of Chicago, Chicago, IL 60637, USA. E-mail: tokmakoff@uchicago.edu

[#]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139,

⁺ Current Address: Fritz-Haber-Institut, Berlin, Germany

We investigate the dynamics of protons in strong acid solutions using 2D IR spectroscopy of the acid continuum band. We observe a crosspeak between stretching and bending vibrations associated with the excess proton at (3200 cm⁻¹, 1760 cm⁻¹) that is assigned to a persistent Zundel complex.

Studying the structure of the excess proton in liquid water and the manner in which the excess charge is transported through water's dynamic hydrogen bond network remains a daunting experimental challenge. The high mobility of protons in water has long been attributed to a proton transfer mechanism involving a sequential displacement of protons along a chain of hydrogen bonds that displaces the over long distance but not a particular proton. Although the excess charge is often considered to take a hydronium form, molecular dynamics simulations point to a mechanism involving the interchange between two limiting structures: the Eigen (H₃O⁺(H₂O)₃) and Zundel (H⁺(H₂O)₂) complexes. We have investigated the 2D IR spectroscopy of the infrared continuum band observed in strong acid solutions in order to gain insight into the excess proton structures present and the mechanism of their interconversion. By investigating the region between 3600-1300 cm⁻¹, we find two resonances linked by a crosspeak between stretching and bending vibrations associated with the excess proton (ω_1, ω_3) = (3200 cm⁻¹, 1760 cm⁻¹). 2D IR peak shifts with waiting time indicate that this species persists for at least 480 fs. Building on previous theoretical and gas phase assignments, and our spectral modeling with empirical valence bond simulations, we show that these bands are characteristic of the flanking waters of the Zundel complex.