

Structure and Dynamics of Solvated Protons in Water Studied with 2D IR spectroscopy

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Using ultrafast 2D IR spectroscopy we investigated the structures adopted by excess protons in water and their dynamics which drive the proton transfer process. Our results give insight into the role of the Zundel complex in the proton transfer mechanism.

The transport of a proton through water certainly belongs to the most common reaction steps in aqueous chemistry. Despite its importance and decades of study there are many remaining questions concerning the structure of the solvated proton and the mechanism of aqueous proton transfer. It is generally accepted that the excess proton can form a large variety of different solvation structures (e.g. Zundel and Eigen complexes) and that their interconversion accompanies the proton transfer process; however, the lifetimes of these structures and their relative populations have not been conclusively determined. In order to gain full insight into the proton transfer mechanism it is necessary to directly probe the temporal evolution of these structures.

We performed ultrafast broadband 2D IR spectroscopy on aqueous solutions of hydrochloric acid. By exciting the O-H stretch vibrations and probing throughout the mid-infrared we investigated the couplings between stretch and bend vibrations of the different water species in the acid which are apparent through stretch-bend cross peaks in the broadband 2D spectra. With this analysis it was possible to isolate the spectral signature of the Zundel complex with its characteristic frequencies at 1760 cm^{-1} and 3200 cm^{-1} . Furthermore, time dependent measurements allowed for the determination of a lower limit on its lifetime of ~ 480 fs. Our results suggest a prominent role of the Zundel complex in the proton transfer mechanism with a larger lifetime and population than previously suggested.

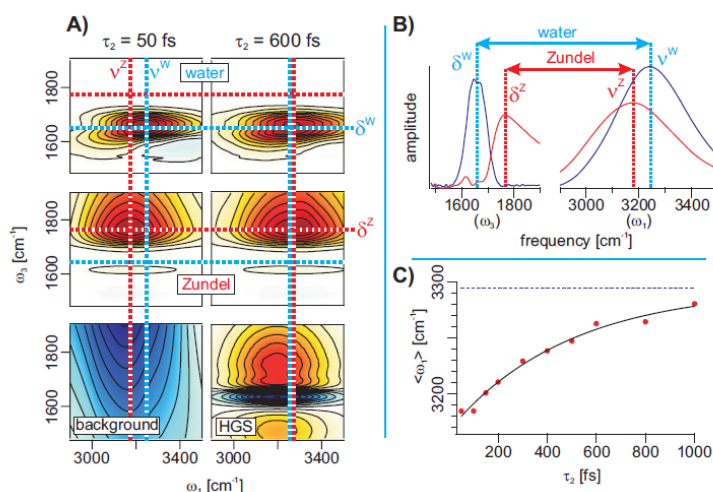


Figure 1

The shape and time evolution of the stretch-bend cross peaks

A) Presentation of the three dominant components for 2DIR spectra of 4M HCl for waiting times of $\tau_2 = 50$ fs and 600 fs. Grid lines illustrate the Zundel (red) and water (blue) peak frequencies.

B) Projections of the stretch-bend cross peaks onto one frequency axis: ω_1 for stretch (v) and ω_3 for bend (δ).

C) Evolution of the peak frequency of the Zundel stretch-bend cross peak in ω_1 with waiting time. The blue dotted line indicates the asymptotic value.