

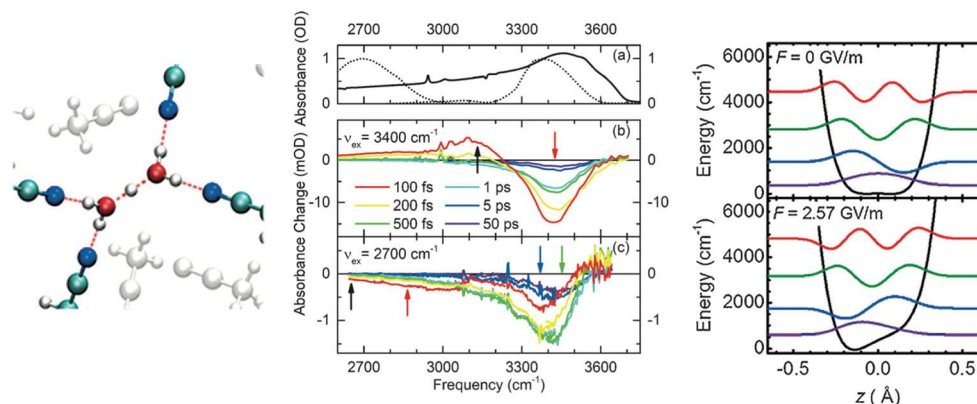
# The Hydrated Excess Proton - Ultrafast Vibrational Dynamics of the Zundel Cation $H_5O_2^+$

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Hydrated excess protons play a crucial role in proton transport through bulk water and acid-base chemistry. Despite substantial effort the prevailing molecular structures that determine the microscopic mechanisms of proton transport under thermal equilibrium conditions have remained elusive. Here, we apply femtosecond infrared (IR) spectroscopy to directly probe the vibrational response of hydrated protons, i.e. Zundel cations  $H_5O_2^+$  selectively prepared in acetonitrile solution [1]. We unravel the distinct character of the broadband absorption continuum from OH stretching and bending vibrations as well as the proton transfer mode  $z$ . Vibrational lifetimes are in the (sub-) 100 fs time range, much shorter than for bulk water. Highest level QM/MM molecular dynamics simulations yield the proton transfer mode IR line shape with excellent accuracy and thus provide a microscopic picture of evolving molecular structures. Our analysis suggests a picture of proton hydration where the IR absorption continuum is a hallmark of ultrafast frequency modulations of the proton transfer vibration  $z$  coupled to combination and overtone bands. Exceptional broad IR line shapes primarily arise from fluctuating electric fields due to the polar solvent. An outlook to the dynamics of hydrated excess protons in water will be given.



Zundel cation  $H_5O_2^+$  in acetonitrile (left), vibrational response of hydrated protons (middle) and schematic of field distorted proton transfer potential  $z$  (right).

## References:

[1] F. Dahms, R. Costard, E. Pines, B. P. Fingerhut, E. T. J. Nibbering, and T. Elsaesser, *Angew. Chem. Int. Ed.* **55**, 10600 (2016).