

Ultrafast dynamics of hydrated excess protons in CH₃CN:H₂O mixtures

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Abstract. In a combined experimental and theoretical 2D-IR and pump-probe study we determine how ultrafast solvent motions govern the vibrational dynamics of the hydrated proton and the key role played by the underlying proton potential.

Aqueous proton transfer is ubiquitous in chemistry and biology, playing a key role in acid-base neutralization, energy transport and signal transduction, with which for instance hydrogen fuel cells, or light harvesting systems are functioning. Even though the basic idea of the von Grothuss mechanism describes aqueous proton transfer as a consecutive proton transport mechanism through arrays of water molecules, the understanding of the underlying microscopic mechanisms, the role of particular hydrated proton species and associated dynamics at the molecular level have only witnessed recent progress, with ab initio molecular dynamics calculations [1-3], species-specific cluster IR spectroscopy [4-5], and ultrafast IR spectroscopy on acid solutions. In particular femtosecond IR pump-probe and 2D-IR measurements allow for a direct local probing of hydrated proton species through the dynamics of vibrational marker modes [6-8].

Ultrafast 2D-IR experiments with aqueous solutions of hydrochloric acid have shown, upon excitation of O-H stretching modes associated with hydrated proton species, a marked response throughout the IR spectral range, that has been ascribed to strong coupling effects between stretching and bending modes of the hydrated proton species [6]. To distinguish contributions from different hydrated proton species in aqueous acid solutions, we first investigated the Zundel cation H₅O₂⁺ prepared in acetonitrile (CH₃CN) solution [7]. Ultrafast IR pump-probe measurements show O-H stretching and O-H bending lifetimes of 50-60 fs. Both O-H stretching and O-H bending modes, however, only are indirect spectator modes of the proton transfer coordinate. In contrast, the proton transfer mode of H₅O₂⁺ located at 1140 cm⁻¹ in acetonitrile (Figure 1) probes the proton dynamics much more directly [8]. Here we compare vibrational dynamics of H₅O₂⁺ in CH₃CN with protons solvated in aqueous acid solutions by femtosecond 2D-IR and pump-probe measurements

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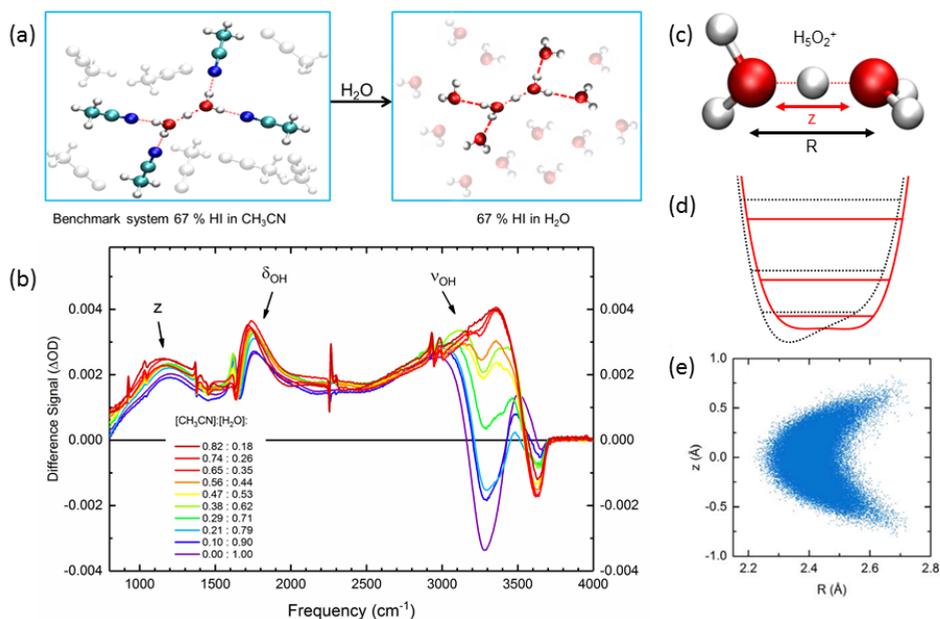


Fig. 1. (a) Hydrogen bonding partners of $H_5O_2^+$ successively changed from CH_3CN to H_2O . (b) ATR-IR spectra of 1 M HI in $CH_3CN:H_2O$ mixtures, displaying the IR-active transitions of the ν_{OH} , δ_{OH} and z vibrational modes. (c) The proton transfer coordinate z and O-O distance coordinate R of $H_5O_2^+$. (d) z has a low-barrier double well potential. (e) $H_5O_2^+$ has a proton distribution function in solution peaking in the centre of the z coordinate.

in the range of the proton transfer mode. A major result is the observation of a $v=1 \rightarrow v=2$ excited-state absorption blue-shifted to higher frequencies compared to the fundamental $v=0 \rightarrow v=1$ transition, confirming the double-well character of the Zundel cation proton transfer mode potential, as opposed to the more typical red-shifted excited state absorption for single-well anharmonic oscillators. Interestingly we observed similar features of $H_5O_2^+$ in acetonitrile and of protons in aqueous solution, strongly suggesting a dominant role of the Zundel cation in aqueous acid solutions that cannot be characterized as a fleeting transition state. Ab initio molecular dynamics calculations support the notion that the double-well potential of the low-barrier strong hydrogen bond of the Zundel cation is modulated at ultrafast time scales, making the inner proton highly fluctuating between the two flanking water molecules, at time scales much shorter than the von Grothuss proton transfer hopping time of about 1 ps.

To investigate further possible roles of hydration shell water around the Zundel cation we study protons in a series of acetonitrile/water mixtures with different relative concentrations of acetonitrile and water. Figure 2 shows a comparison to the 2D-IR spectra measured for solutions of protons in $[CH_3CN]:[H_2O]$ mixtures for different water fractions going from 0.18 to 1.0. We have investigated a broader spectral range around the proton transfer marker transition as previously published [8]. These measurements show a clear similarity in terms of the fundamental ground-state bleach/stimulated emission and of the blue-shifted excited-state absorption contributions for all water fractions investigated. The $v=0 \rightarrow v=1$ bleach contributions appear to shift to higher values at the detection frequency for increasing fraction of water, in line with the frequency upshift of the location of the crossover to positive signals assigned to the excited-state $v=1 \rightarrow v=2$ transition of the proton transfer mode. Interestingly, a marked positive signal is also observed for higher

excitation/lower detection frequencies (excitation frequency $\nu_1 > 1230 \text{ cm}^{-1}$, detection frequency $\nu_3 < 1050 \text{ cm}^{-1}$) for in particular $[\text{CH}_3\text{CN}]:[\text{H}_2\text{O}]$ mixtures with intermediate values of 0.38:0.62 to 0.21:0.79. This feature marks the emergence of additional contributions of librational motions of the added water. The smooth continuous changes in the spectra when going from neat acetonitrile to neat water suggest that modification in the first and second solvation shell around the solvated excess proton impose only moderate changes in the ultrafast modulation of the proton transfer mode potential.

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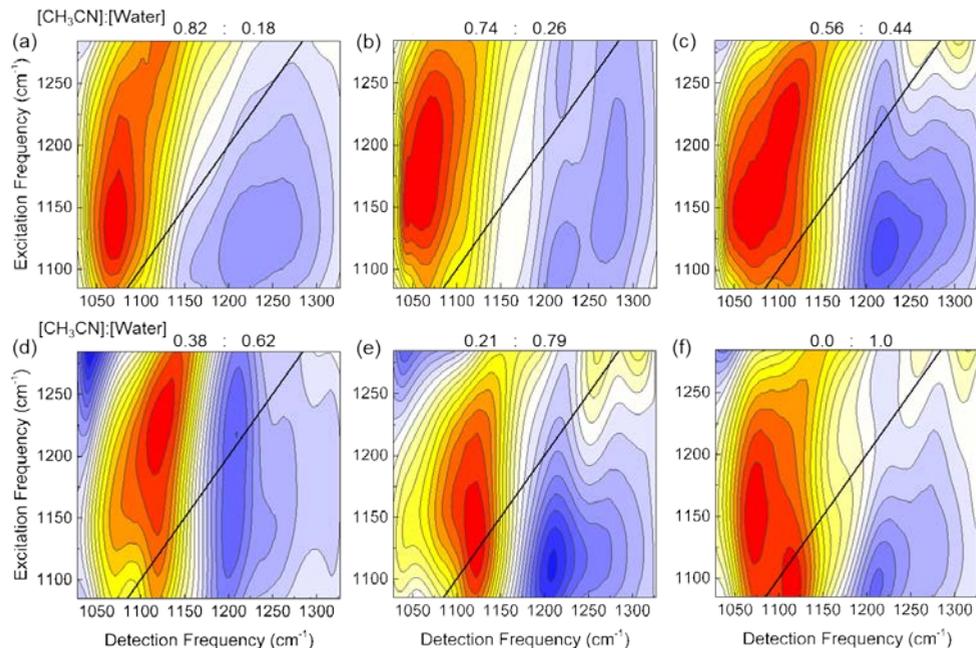


Fig. 2. (a-f) Series of 2D-IR measurements measured at $T = 0$ fs waiting time for HI in $[\text{CH}_3\text{CN}]:[\text{H}_2\text{O}]$ mixtures.

1. D. Marx, M. E. Tuckerman, J. Hutter, M. Parrinello, *Nature* **397**, 601 (1999)
2. J. Xu, Y. Zhang, G. A. Voth, *J. Phys. Chem. Lett.* **2**, 81 (2011)
3. W. Kulig, N. Agmon, *Nature Chem.* **5**, 29 (2013)
4. C. T. Wolke, J. A. Fournier, L. C. Dzugas, M. R. Fagiani, T. T. Odbadrakh, H. Knorke, K. D. Jordan, A. B. McCoy, K. R. Asmis, M. A. Johnson, *Science* **354**, 1131 (2016)
5. Q. Yu, J. M. Bowman, *J. Am. Chem. Soc.* **139**, 10984 (2017)
6. M. Thämer, L. De Marco, K. Ramasesha, A. Mandal, A. Tokmakoff, *Science* **350**, 78 (2015)
7. F. Dahms, R. Costard, E. Pines, B. P. Fingerhut, E. T. J. Nibbering, T. Elsaesser, *Angew. Chem. Int. Ed.* **55**, 10600 (2016)
8. F. Dahms, B. P. Fingerhut, E. T. J. Nibbering, E. Pines, T. Elsaesser, *Science* **55**, 10600 (2017)