Ultrafast proton transport in water-methanol mixtures

Maria Ekimova¹, Felix Hoffmann², Gül Bekçioğlu-Neff², Aidan Rafferty¹, Erik T. J. Nibbering^{1,*}, Daniel Sebastiani^{2,†}

¹ Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, 12489 Berlin, Germany

² Martin-Luther-Universität Halle-Wittenberg, Institut für Chemie, 06120 Halle (Saale), Germany

Abstract. Femtosecond UV/IR pump-probe experiments and ab initio molecular dynamics simulations of 7-hydroxyquinoline in water-methanol mixtures demonstrate an unexpectedly dominant OH⁻/CH₃O⁻ transport pathway but consistent with a solvent-dependent photoacidity free energy-reactivity correlation behaviour.

Photoacids are organic molecules that upon electronic excitation exhibit a large jump in acidity (characterized as $\Delta pK_a = pK_a^*(S_1) - pK_a(S_0) \sim -6$ to -7). Photoacids have been utilized to much effect in time-resolved studies of ultrafast proton transfer dynamics [1-3]. A special class consists of so-called bifunctional photoacids [4-6], where both proton donating and proton accepting groups are part of the same molecule. Bifunctional photoacids allow for a well-defined distance along which proton transport can occur and – thus – defining a highly specific number of solvent molecules that can function as solvent bridge (for protic solvents such as water or methanol often denoted as ‘solvent wire’) through which the proton transport is understood to occur either in concerted or sequential von Grothuss-type fashion.

Hydroxyquinolines have been a favourite choice as bifunctional photoacids [5-6], where the proton donating hydroxyl-group behaves as is known of naphthol photoacid compounds. In addition to that the quinoline nitrogen acts through its lone pair as a photobase, i.e. an increased basicity occurs upon electronic excitation. This fact then propels the basic question how the primary steps of proton transfer occur with hydroxyquinoline (Figure 1a): I) proton donation of the hydroxyl-group to the protic solvent (water or methanol), followed by H⁺ transport with the solvent as proton carrier, and final proton abstraction from a protonated solvent molecule by the quinoline base, or II) proton abstraction by the quinoline base, followed by OH⁻/CH₃O⁻ transport in water or methanol, respectively, and final neutralization by the photoacid hydroxyl group. Alternatively III) a concerted proton transport process through a solvent wire can be envisaged. As the change of acidities (pK_a -values) are differently altered for alcoholic and protonated amine groups upon change of solvent medium, one can envisage that proton transport pathway directionality is affected as well.

* Corresponding author: nibberin@mbi-berlin.de

† Corresponding author: daniel.sebastiani@chemie.uni-halle.de

We present here experimental and theoretical results on ultrafast dynamics of 7-hydroxyquinoline (7HQ) in water/methanol mixtures of various relative composition. Here 7HQ is excited in its neutral form N^* , that then converts to the zwitterionic tautomer Z^* on picosecond time scales. We have reported in a UV/IR pump-probe study the time constants of particular proton transfer steps of differently charged forms of 7HQ in deuterated methanol [6]. Here we expand on our previous results by measuring femtosecond UV/IR pump-spectra of 7HQ in D_2O/CD_3OD mixtures (Figure 1b,c).

Fig. 1. (a) Proton transfer pathways of 7HQ. (b) Transient UV/IR pump-probe spectra of 7HQ in D_2O/CD_3OD solvent mixtures. (c) Transients of vibrational marker modes assigned to the population decay of N^* and the rise of Z^* .

To investigate further the proton transfer dynamics of 7HQ, we correlate obtained time constants with excited-state pK_a^* -values using reported free-energy-reactivity correlation relationships [2,3] (closely related to Marcus theory for electron transfer) and investigating trends in derived pK_a^* -values as a function of solvent composition. Here we observe that the derived pK_a^* -values for different charged forms of 7HQ in D_2O , CD_3OD and CH_3OH perfectly match with reported pK_a^* -values of 7HQ in H_2O [5]. Moreover, our observations for electronically excited 7HQ follow the general rule when going from water to methanol, that an OH acid (carboxylic acids, aromatic alcohols, phenols, naphthols) will decrease in acidity by 3-5 pK_a -units, whereas cationic acids (protonated amines, protonated pyridines, protonated quinolines) are getting weaker by only about 1 pK_a -unit [7]. As we are in the position of having both a naphthol proton donating group and a quinoline proton accepting unit in 7HQ, we can assess the solvent-dependent acid-base chemical properties of both functional groups. Comparing the derived 7HQ pK_a^* -values for the H_2O , CH_3OH and CD_3OD cases, we see a decrease in acidity of ~ 1.2 - 1.3 pK_a^* units when going from H_2O to CH_3OH , and a further ~ 0.3 - 0.5 pK_a^* unit when going from CH_3OH to CD_3OD . Hence the free-energy reactivity analysis of 7HQ in water and methanol (Figure 2a), and water-methanol mixtures (Figure 2b) strongly support the notion that water/methanol transport pathway II is the dominant reaction channel.

For a further corroboration of the proposed mechanism we performed QM/MM molecular dynamics simulations in the S_1 -state. Starting from either the 7HQ cation C^* or anion A^* , we confirm that the formation of the cation, and correspondingly the hydroxide/methoxide ion, as the initial step is strongly favoured (Figure 2c). Our simulations suggest a sequential transfer as the dominant pathway under

participation of all solvent species, i.e. water, methanol, methoxide, and hydroxide ions. As the main driving force, we identify hydrogen bond fluctuations of the first and second solvation shell of the charge defect. Similarly, to hydroxide ion transport in neat water [8,9], a hydrogen bonding configuration around the hydroxide or methoxide ion resembling that of the neutral molecule facilitates the transfer (Figure 2d,e).

We gratefully acknowledge financial support by the German Science Foundation (Project Number NI 492/13-1+SE 1008/11-1). F.H. thanks the Fonds der Chemischen Industrie for a Kekulé fellowship.

Fig. 2. (a) Free-energy reactivity relationship for different proton transfer steps of 7HQ in H_2O , CH_3OH and CD_3OD . (b) Free-energy reactivity relationship of 7HQ in $\text{D}_2\text{O}:\text{CD}_3\text{OD}$ mixtures. (c) Snapshot of a QM/MM MD simulation of 7HQ showing the first step in the CH_3O^- -transport mechanism along a methanol bridge. (d) Four-fold hydrogen-bonded OH^- before transfer event. (e) Three-fold OH^- in the transfer transition state. Arrows illustrate movement of the water molecule whose hydrogen bond breaks in the course of the transfer and the movement of the transferred proton, respectively.

1. R. Simkovitch, D. Pines, N. Agmon, E. Pines, D. Huppert, J. Phys. Chem. B **120**, 12615 (2016)
2. K. Adamczyk, M. Prémont-Schwarz, D. Pines, E. Pines, E. T. J. Nibbering, Science **326**, 1690 (2009)
3. M. Prémont-Schwarz, T. Barak, D. Pines, E. T. J. Nibbering, E. Pines, J. Phys. Chem. B **117**, 4594 (2013)
4. J. Ditkovich, T. Mukra, D. Pines, D. Huppert, E. Pines, J. Phys. Chem. B **119**, 2690 (2015).
5. E. Bardez, Isr. J. Chem. **39**, 319-332 (1999)
6. F. Hoffmann, M. Ekimova, G. Bekçioğlu-Neff, E. T. J. Nibbering, D. Sebastiani, J. Phys. Chem. B **120**, 9378 (2016)
7. B. G. Cox, *Acids and Bases: Solvent Effects on Acid-Base Strength* (Oxford University Press, Oxford, 2013)
8. D. Marx, M. E. Tuckerman, J. Hutter, M. Parrinello, Nature **397**, 601 (1999)
9. D. Marx, A. Chandra, M.E. Tuckerman, Chem. Rev. **110**, 2174 (2010)