An Excited-State Proton Transfer Disentangled by fs Broadband Spectroscopies

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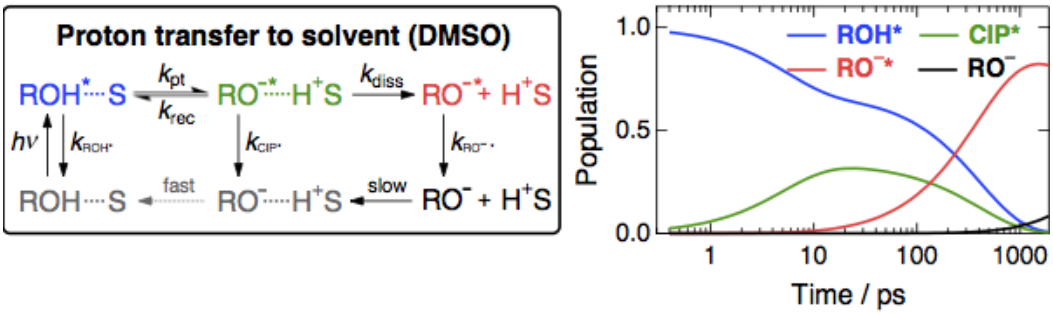
Proton transfer is undoubtedly one of the most significant reactions in chemistry and biology. The discovery of excited-state acids, also known as photoacids, has enabled detailed time-resolved investigations on the mechanism and kinetics of the dissociation process.[1] Despite the wealth of investigations on excited-state proton-transfer (ESPT) reactions, some aspects are still under discussion. For example, the influence of solvent environment on ESPT is recognized both from experimental and theoretical viewpoints but only a few studies have explicitly accounted for the dynamic solvent relaxation in the excited-state. Second, ESPT reactions are usually modeled according to the Eigen-Weller scheme which consists of an initial short-range proton-transfer step producing contact ion pairs followed by a diffusion-controlled separation into free ions (**Figure**). However, the model is often discussed only qualitatively and detailed investigations resolving all microscopic rate constants and relaxation pathways are scarce. Lastly, data obtained using different spectroscopic techniques have sometimes resulted in differing interpretations of the studied processes.



In our communication, we report on the ESPT from a 1,8-naphthalimide-derived "super" photoacid[2] to solvent (DMSO) investigated using three fs broadband techniques: visible and IR transient absorptions, in addition to fluorescence up–conversion. We will demonstrate how a combination of these techniques gives much deeper insight into the overall photocycle including both ground- and excited-state species. Broadband fluorescence up–conversion gives us direct access to the solvent relaxation reported by the dynamic Stokes shift of the fluorescence band which is modeled using a recently developed global analysis scheme based on time-dependent band-shape functions.[3] Transient absorption, on the other hand, yields valuable information about the additional decay channels to the ground-state species. Lastly, the use of a target model based on the reaction scheme (**Figure**) enables recovery of all the individual rate constants and concentrations of the different intermediates.

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[2] T. Kumpulainen, B. H. Bakker, M. Hilbers, A. M. Brouwer, *J. Phys. Chem. B*, **2015**, 119, 2515-2524.
[3] T. Kumpulainen, A. Rosspeintner, E. Vauthey, *Phys. Chem. Chem. Phys.*, **2017**, 19, 8815-8825.