

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. Photoacids are organic compounds, such as hydroxy-substituted aromatics, which increase the acidity of the hydroxyl proton upon excitation to a higher electronic state. Dissociation of the proton can be initiated by a short laser pulse and the subsequent cascade of events can be spectroscopically followed in time. Excited-state proton transfer (ESPT) serves as a model system for studying the microscopic reaction mechanism and is therefore of great fundamental interest.^[1]

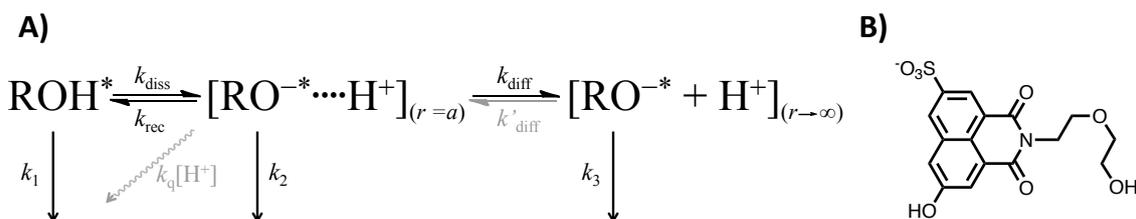


Figure 1: a) Eigen-Weller scheme of the excited-state proton-transfer. All the relevant rate constants are indicated. The rate constants shown in grey need to be considered if proton quenching (k_{q}) or geminate recombination (k'_{diff}) are operative. b) Chemical structure of the 1,8-naphthalimide photoacid.

Despite the wealth of investigations on 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.^[2] Second, ESPT reactions are usually modelled 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 (Fig. 1A).^[3,4] However, the model is often only qualitatively discussed and detailed investigations resolving all microscopic rate constants and relaxation pathways are scarce. Lastly, results 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 (Fig. 1B)^[5] 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 will give 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 modelled using a recently developed global analysis scheme based on time-dependent band-shape functions.^[6] Transient absorption, on the other hand, yields valuable information about the additional decay channels to the ground-state species. The use of a target model based on the reaction scheme enables recovery of all the individual rate constants for the different steps. Lastly, the advantages and disadvantages of the different techniques are discussed.

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