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Ultrafast Photoacid-Base Reactions in Aqueous Solution

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Microscopic descriptions of solution phase photoacid-base reactions involve the concept of “tight”contact and “loose”solvent separated reaction pairs for the elementary steps of proton transfer. Typically one has to deal with multiple distributions of complexes with possible different configurations, that makes ultrafast experiments rather involved {1]. Even when only the dynamics on the fastest time scales are followed, one has to take this into account. In this contribution we will show to what information is obtained with both ultrafast infrared and sof-x-ray spectroscopies upon electronic excitation of a photoacid [2,3], 2-naphthol-6,8-disulfonate (2N-6,8-diS), and imidazole base (HIm) or azide anion (N_3^-) in aqueous solution.
Ultrafast UV/IR spectroscopy is more sensitive in probing IR-active transitions of 2N-6,8-diS, providing insight into the proton release of the photoacid, the first step in proton transfer of the bimolecular reaction. For molar concentrations of base (HIm/N_3^-) initial components in the transient IR-active transitions reveal not only the fraction of photoacid exhibiting reaction dynamics but also the subpicosecond time scale this occurs. Interestingly the transient spectra reveal a broadband continuum much akin to the Zundel continuum with dynamics that may hinting at a stronger hydrogen bond [2] with a possible double well potential of the proton transfer coordinate of the reactive 2N-6,8-diS –base reactive complex.
Ultrafast nitrogen K-edge spectroscopy on the other hand reveals when the base (HIm/N_3^-) is converted into the conjugate acid (HImH$^+$ -the imidazolium cation-, or HN_3 –hydrazoic acid). This will first and foremost provide information on the time scale of completion of the proton transfer reaction, yet spectral shifts observed for HIm resonances also are indicative of the changes in strength of the hydrogen bonds of imidazole before, during after the proton transfer reaction: a frequency upshift implies a stronger hydrogen bond, whereas the opposite frequency downshift means a weaker hydrogen bond.
We have observed the interplay of contributions by multiple imidazole molecules in the proximity of the photoacid 2N-6,8-diS, that can only be disentangled in a combined experimental and theoretical approach. From classical dynamics simulations we deduce the probability density distributions of HIm around 2N-6,8-diS and conclude that under our sample conditions hydrogen bonding as well pi-pi stacking interactions are important, hence the relative contributions are of similar magnitude. This finding has led us to conclude that IVR in and vibrational energy dissipation from 2N-6,8-diS will lead to a transient local heating in the first hydration shell, leading to changes in the hydrogen bonds of imidazole on a time scale of 1 ps.

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