TRACKING THE PHOTOIONIZATION OF ANILINE IN WATER: THE ROLE OF $\pi\sigma^*$ STATES

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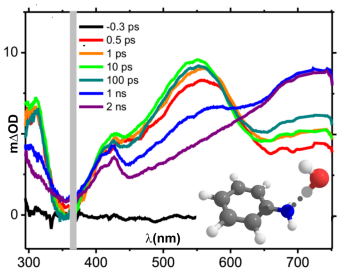
The dynamics of aniline in water, after excitation along its lowest energy absorption (267 nm), has been investigated, from the femto (fs) to the nanoseconds (ns) scale, by pump-probe broadband transient absorption (TA) methods. The complex prompt TA spectrum, which evolves over the fs to ns scales, is analyzed by using a pump-repump-probe scheme that permits to interrogate the nature of the contributing species. The results permit us to identify, in addition to the long-living $\pi\pi^*$ state responsible of the fluorescence, the formation of a charge transfer to solvent state (CTTS) that will autoionize to form the fully solvated cation and electron. The nature of this CTTS state is discussed in terms of the 3s/$\pi\sigma^*$ state characterized in the gas phase[a] and the specific water-solute interactions established.



[a] J. O. F. Thompson *et al. J. Chem. Phys.* **142**, 114309 (2015); doi:10.1063/1.4914330