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CFEL – Building 99, seminar room I+II (ground floor)

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Ultrafast Nonadiabatic Dynamics in Biological Chromophores in the Gas Phase and in Solution

The way in which the solvent and cluster environment affects the photophysics and photochemistry of isolated organic and biological chromophores has been the focus of many ultrafast pump-probe experiments in solution. In the gas phase, phenol, for example, is known to undergo photo-degradation, via O-H bond fission, following near-UV irradiation. Biological chromophores – like adenine (for example) – are also known to undergo photodegradation via N-H bond fission at elevated photon energies, but their prevailing excited state decay mechanisms ensure photostability – i.e. they undergo ultrafast internal conversion via well-characterised molecular distortions that lead to state degeneracies along the excited state potential energy surface – without detriment to the starting molecule.

In a water cluster or in bulk water solution, the additional complexities of hydrogen-bonds affect the non-radiative decay pathways available to phenol and adenine. Intrinsic excited state solute → solvent or solvent → solute hydrogen transfers provide new channels by which the excited state molecule can decay.

In the first part of my talk, the ‘power’ of hydrogen bonding will be illustrated by static and dynamic theoretical calculations showing how excited state intramolecular hydrogen transfer in biological sunscreens found on the human skin and in the eye can afford natural photostability. I will then extend on this by outlining mechanisms by which excited state deactivations are encouraged via solute-solvent/cluster intermolecular hydrogen transfer reactions. In this part of the talk, I will outline the excited state reactivity of the solute (i.e. phenol, indole and adenine) with water clusters and water ‘wires’ both in the gas phase and in

bulk water solution. Such data successfully explain experimental observations of, for example, the presence of the solvated electron and the ultrafast deactivation of photo-excited phenol, adenine and adenosine in aqueous – the mechanisms of which are expected to be somewhat generic and extendable to other biologically relevant chromophores.

