Electronic deactivation of keto- and enol-cytosine: A theoretical approach using mixed quantum-classical dynamics

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It is well known that in DNA bases there are several ways to relax after light irradiation. The presence of singlet excited states of different character (basically $\pi\pi^*$ and $n\pi^*$ states) allows for different relaxation pathways to the ground state. Additionally, triplet states can have an important role, being responsible for deactivation events in a much longer time scale. The disentangling of the different relaxation mechanisms is subject of several experimental and theoretical studies, often without clear consensus.

In this contribution, we present dynamical simulations to describe the different relaxation pathways in the canonical form of cytosine (the keto form) and the most stable isomer in gas phase (the enol form). Due to the time scales investigated (fs), pathways involving triplet states can be neglected. In order to account for all the degrees of freedom of the system, we have performed classical trajectories for the nuclei, in combination with *ab initio* quantum calculations for the electrons. This combination is widely applied to describe dynamics in the electronic ground state, but it is still a challenge to employ it to describe non-adiabatic dynamics in the excited state. Here, the quantization of the electronic states in the classical dynamics is considered using the surface hopping method.

Our dynamical studies show different relaxation times for the keto and enol isomers of cytosine and how the presence of two different excited states $n\pi^*$ and $\pi\pi^*$ modifies the deactivation mechanism.