Dynamics driven processes in organic photochemistry and photophysics

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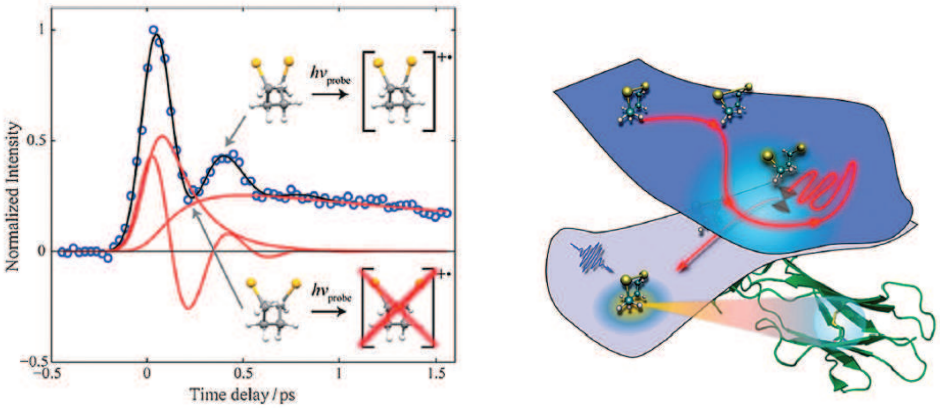
Electronic transitions from high lying excited states are often occurring on the picosecond timescale. This is due to the fact that the initial motion out of the Franck-Condon region directs the wavepacket towards a region of the potential energy landscape where an efficient transition to the lower lying states can take place, e.g., through a conical intersection. If the coupling between the states involves dissociative degrees of freedom not only does the electronic transition take place prior to a statistical distribution of the internal energy so does the associated photochemical reaction. A series of results that highlight the nonstatistical nature of the excited-state deactivation process is presented. The examples are categorized into four groups. 1) Localization of the energy in one degree of freedom in S2->S1 transitions, in which the transition is either determined by the time spent in the S2->S1 coupling region or by the time it takes to reach it. 2) Localization of energy into a single reactive mode, which is dictated by the internal conversion process. 3) Localization of energy into a single mode which distorts the molecular structure and leads to compliance with El-Sayeds rule and thus ultrafast intersystem crossing. 4) Nonstatistical internal conversion as a tool to accomplish biomolecular stability. Herein, the discussion on nonstatistical internal conversion in DNA as a mechanism to eliminate electronic excitation energy is extended to include molecules with an S-S bond as a model of the disulfide bridge in peptides. The talk will present experimental and theoretical results to support the case.



The coherent molecular motion that is initiated via the SS stretch leads to an ultrafast internal conversion and thus a way to get rid of the excitation energy in a thermal manner rather than in a SS rupture..