

Ultrafast excited-state charge transfer at a conical intersection: effects of an environment

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Conical intersections (CIs) are known to play a key role in the ultrafast decay of photoexcited molecular systems. By their particular topology, they provide a “funnel” for efficient and rapid passage from a photochemically accessed excited state to the ground electronic state. CIs, or *seams* of conical intersections in multidimensional systems, have thus been referred to as “transition states” for excited-state dynamical processes.

While CI topologies are expected to be extremely sensitive to environmental effects, few theoretical studies have been undertaken to date to analyze such effects. In this contribution, we focus on excited-state processes at CIs involving charge transfer phenomena, and develop theoretical models to describe the influence of a polar and/or polarizable environment upon such processes. Indeed, a number of recent experiments on photoactive biological chromophores featuring charge transfer type CIs highlight the environment’s pronounced impact upon the excited-state decay (which varies markedly depending on whether the native protein species or the bare chromophore in different solvents is considered). This suggests that the chromophore’s local environment tends to modify the character, topology and even the existence of conical intersections. Against this background, we address a model for the C=C *cis–trans* isomerization in protonated Schiff bases (PSBs) via a S₁–S₀ CI, and describe the charge properties and charge translocation phenomena associated with this CI.^{1,2,3} A diabatic model in a basis of valence bond (VB) type, charge localized states is developed,³ which is particularly adapted to describe the interaction with a polar/polarizable environment. In this first analysis, the electrostatic effects induced by a solution phase environment are accounted for by a dielectric continuum model. This translates to the image of free energy surfaces for the coupled chromophore–environment system represented by molecular coordinates plus a solvent coordinate.³ The latter plays the role of an additional dynamical variable determining the combined chromophore–solvent reactive path. The interplay between the quantum dynamics in the solute’s internal degrees of freedom and the effects of nonequilibrium solvation is examined and contrasted with static vs. equilibrium solvation limits.

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