Short-time frictional solvent effects on conical intersection dynamics for a model photoisomerization

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It is now well appreciated that conical intersections (CIs) often provide an efficient, ultrafast nonadiabatic transition route from an excited electronic state to the ground state for photochemical reactions [1]. Accordingly, much effort---both theoretical and experimental---has been devoted to their study. Our previous efforts in this area [2,3,4] have focused on constructing an approximate model description aimed at elucidating and describing the influence of a solvent (and ultimately a more complex protein environment) on CI structure and dynamics in a photoreaction context. Of particular interest to us are photoreactions in which significant intramolecular charge transfer in the chromophore results in strong coupling to a polar environment. The template for our efforts has been a two valence bond, three coordinate description of the *cis-trans* photoisomerization of a model protonated Schiff base (PSB), itself a model for retinal, of interest in connection with vision. In this talk---after a brief review of salient features of the basic model and prior relevant results such as minimum energy paths and inertial, non-dissipative trajectory results---we will describe our most recent results [5] addressing the inclusion in the model of short-time 'friction', describing energy and momentum transfer effects on the CI and photoisomerization dynamics. These effects are modeled via a generalized Langevin description of dynamical frictions on the PSB intramolecular twist and bond length alteration coordinates and on a nonequilibrium dielectric continuum solvent coordinate. Two model solvents are examined, acetonitrile and water, which are characterized by different solvent time-scales. Nonadiabatic trajectories were generated via Tully's molecular dynamics with quantum transitions, fewest switches algorithm [6]. The important influence of the solvent-dependent generalized friction on the path to the solvent coordinate-induced seam of CIs from the Franck-Condon excitation region, on the location of the nonadiabatic transitions to the ground electronic state, and on the *trans* or *cis* ground state product distribution will be described.

[1] See e.g. B.G. Levine and T. J. Martinez, *Ann. Rev. Phys. Chem.*, **58**, 613 (2007).

[2] I. Burghardt, L.S. Cederbaum and J.T. Hynes, *Faraday Discuss.,* **127,** 395 (2004). For earlier efforts on CI *ground* state reaction effects, see D.Laage, I. Burghardt, T.Sommerfeld and J. T. Hynes, *J. Phys. Chem. A*, **107,** 11271 (2003).

[3] R. Spezia, I. Burghardt and J.T. Hynes, *J. Molec. Phys.*(Robb Issue), **104**, 903 (2006).

[4] I.Burghardt and J.T. Hynes, *J. Phys. Chem. A*, **110**, 11411 (2006).

[5] J. Malhado, Thesis, ENS (2009); J. Malhado, R. Spezia and J.T. Hynes, *J. Phys. Chem. A*, in press, 2010. **DOI:** 10.1021/jp106096m
[6] J. C. Tully, *J. Chem. Phys.,* **93**, 1061 (1990).