

Theoretical investigation of the excited state proton transfer in 3-cyano-6-hydroxycoumarin

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Photoacids are molecules that allow for local control of environmental acidity by applying a laser pulse or light source. The various applications for these molecules range across many fields, from photolithography to localized drug delivery and investigations on protein folding. 3-cyano-6-hydroxycoumarin (CHCM) has been proposed as a potential super-photoacid with the ability to de-protonate on a picosecond time scale.[1] However, results from the transient absorption spectroscopy indicate that after undergoing excited state proton transfer, the molecule rapidly de-excites into the ground state of the anion becoming a conjugate base. Here we present theoretical interpretation of the experimentally observed photodynamics of CHCM. Gas-phase TD-DFT simulations of a hydrogen-bonded CHCM-water complex indicate that the bright S_1 state undergoes a conical intersection with the dark S_2 state along the proton transfer coordinate (Fig. 1). This conical intersection is a plausible mechanism of radiationless decay of the excited state population. Solvent effects are accounted for via the polarizable continuum model (PCM) and the effective fragment potential (EFP)[2] methods. The hybrid TD-DFT/EFP approach provides realistic representation of the polarizable solvent at a cost comparable to the gas phase TD-DFT computations.

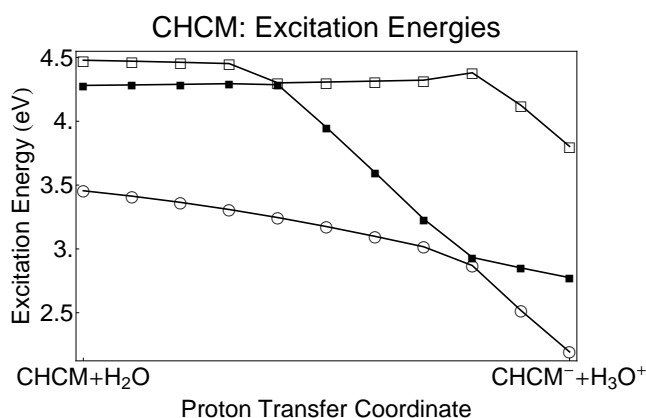


Figure 1: Three lowest electronic excited states of CHCM along the proton transfer coordinate.

[1] Solntzev, K.; private communications

[2] M. S. Gordon; L. Slipchenko; H. Li; J. H. Jensen in *Annual Reports in Computational Chemistry*; Spellmeyer, D. C., Wheeler, R., Eds.; Elsevier: 2007; Vol. III, p 177.