

Singlet Fission: An Electronic Structure Perspective and A Simple Kinetic Model

Xintian Feng*and Anna I. Krylov†

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

January 28, 2014

Abstract

Electronic structure aspects of singlet fission (SF) process and nonadiabatic coupling between bright singly excitonic state and dark multiexciton state are discussed. Correlated adiabatic wave functions of the bright singlet and dark multiexciton states of tetracene dimers are analyzed in terms of their character (excitonic, charge-resonance, multiexciton). Norm of one-particle transition density matrix is proposed as a proxy for couplings. We found that the couplings between bright singly excitonic and dark multiexciton state depend strongly on the weights of charge-resonance configurations in these states. The effect of fragment orientation and interfragment distance on couplings is analyzed.

A simple three-state model for the dynamics of SF process is developed. The model facilitates the analysis of the relative significance of different factors, such as electronic energies, couplings, and the entropic contributions. The entropic contributions to the rates are important; they drive the SF process in endo-ergic cases (such as tetracene). By considering series of three acenes (tetracene, pentacene, and hexacene), we explained the experimentally observed 3 orders of magnitude difference in the rate of SF in tetracene and pentacene and predicted that the rate in hexacene will be slightly faster than in pentacene. This trend is driven by the increased thermodynamic drive for SF (Gibbs free energy difference of the initial excitonic state and two separated triplets).

*xintianf@usc.edu

†krylov@usc.edu