

Quantum Dynamical Simulation of Intramolecular Singlet Fission in Covalently Coupled Pentacene Dimers

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Singlet fission is a multiple exciton generation process by which two triplet excitons are generated from a singlet exciton through a spin-allowed mechanism [1]. First invoked in the 1960s to explain the appearance of delayed fluorescence in some organic molecular crystals [2], singlet fission has re-emerged as an active research topic in the context of energy conversion as it has the potential to overcome the Shockley-Queisser limit [3]. Here, we employ a quantum dynamical approach based on a model vibronic Hamiltonian to analyse the dynamics of intramolecular singlet fission in a series of modified pentacene dimers where the pentacene-like moieties are covalently bonded to selected linkers [4-8]. The results show that the population of the multiexcitonic state, corresponding to the first step of the intramolecular singlet fission process, occurs mainly through a superexchange-like mechanism involving doubly excited and charge transfer states that participate in a virtual way. The instrumental roles that conformational flexibility and molecular vibrations play in the process are also discussed.

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