

Practical Proxies of Couplings and Quantum Interferences among Pathways for Dexter Energy Transfer

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When global spin of a molecular assembly during energy transfer is conserved, but the spin of donor and acceptor is changed, the Förster mechanism is forbidden and the Dexter mechanism through exchange of electrons is dominant. Dexter energy transfer reaction includes singlet fission, triplet fusion and triplet energy transfer (TT), which are essential for light harvesting, energy conversion and other wide-ranging photoinduced phenomena. However, the molecular level understanding and calculation of Dexter energy transfer are still quite challenging.

We started with the study of the triplet fusion reaction during singlet oxygen photosensitization reaction, and built a kinetic model to calculate the reaction rates based on a divide-to-conquer principle.[1] Taking 6-aza-2-thiothymine as PS, the spatial factor of the reaction was investigated by calculating the rate along different directions and intermolecular distance.[2] Then we proposed proxies for estimating the coupling strength in both diabatic and adiabatic pictures for general Dexter energy transfer, and verified them with the reaction in Eq (1). The result explains the curiously small coupling to the $1\Sigma_g$ state along specific incidence directions, and provides a comprehensive understanding of the reaction mechanism of Dexter energy transfer problems.[3]

Then we investigated the Dexter energy transfer in non-covalent assemblies with the pathway analysis based on quantum chemical calculation. We calculated the coupling strength of triplet energy transfer (TT) in various architectures: D–A, D–B–A, D–multi(B)–A and D-B-multi(A), using constrained DFT methods. The effective couplings of different pathways from 1-particle, 2-particle and through-space interactions were evaluated using configuration interaction with the constrained density functional theory (CDFT-CI) method, and quantum interference among them are interpreted. We found that 1-particle, 2-particle and through-space interactions all contribute significantly, generating many more pathways than for electron transfer.[4] The quantum interferences among them change dramatically with geometries, providing the possibility of control by molecular design.

References:

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