

Modeling charge transfer in a molecular donor-acceptor system

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When describing charge transfer (CT) in molecular donor-acceptor (DA) systems, the preferred metric for their performance is the rate of CT (k_{et}). This rate is often determined with the equation for CT from Marcus theory which entails several variables unique to the DA system of interest. These variables, such as the potential energy offset (ΔG^0) and reorganization energy (λ) can be determined from *ab initio* computations and thus k_{et} can also be determined from simulation over time. One of the drawbacks of using Marcus theory to describe CT in certain systems is its failure to account for quantum effects on its own. In a separate method, Redfield theory is used to find the rate of electronic relaxation which is analogous to k_{et} . This rate can replace the Hamiltonian found in the Marcus equation and may be considered a secondary technique for finding k_{et} . A differentiating attribute between these techniques is how Redfield's rate of electronic relaxation ignores the influence of nuclear reorganization energy on the Hamiltonian, and thus will give a different value for k_{et} even with the same variables. The importance of nuclear reorganization energy varies with different systems, but for a system with significant nuclear motion following CT Redfield theory will give a higher value for k_{et} than Marcus theory. The selection of a Zn^{II}P-H₂P porphyrin DA system is intended to highlight the significance of nuclear reorganization in this context as it is a popular optically active molecular DA system which exhibits a significant change in nuclear coordinates following CT. This project intends to qualitatively compare k_{et} as calculated using both Marcus theory and Redfield theory, as well as to weigh the importance of the nuclear reorganization energy when modeling CT in this porphyrin dimer DA system.

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