

Role of vibronic resonances for electron transfer in molecular donor-acceptor complexes

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There is an ongoing interest to model electron transfer in a class of donor-acceptor (D-A) molecular systems. Marcus theory is the tool used to describe electron transfer rates. This project aims to compare the rates predicted by Marcus theory with results obtained by the modeling the time-evolution of a wavefunction in parameterized potential energy surfaces, utilizing a time-evolution operator applied to the initial state vector. The primary result is the rate's dependence on energy offset between donor and acceptor states, using the Marcus model to show a broad peak at the activationless regime for reference. The transitions between vibronic energy levels are maximized at several energy resonance conditions. The rates obtained by wavepacket evolution demonstrate an interesting dependence on energy offset: specifically, the rate is observed to change almost periodically as the energy offset changes. The observed rates generally reflect what Marcus theory predicts in the trends and limits but exhibit additional features originating from vibronic resonances. These additional features are expected to play a role in the interpretation of ultrafast femtosecond probes of D-A complexes. The analysis of the relationship between explored regimes of electron transfer and experimental results for a series of D-A complexes is still being studied.

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