

Using Ultrafast Spectroscopy and Computer Simulations to Re-examine Our Picture of Photoinduced Electron Transfer

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Spectroscopic experiments, both time-resolved and steady-state, have provided us exquisite insight into the dynamics of photoinduced charge transfer processes. Interpretation of these experiments has been aided by Marcus theory and its numerous derivatives, a linear-response theory based primarily on a picture of spherical reactants immersed in a continuum solvent. Although this model has found much practical success, it completely ignores the molecular nature of the system, and many of the parameters underlying the theory are not directly accessible by experiment. We must therefore combine detailed computer simulations with insight from experiments in order to answer the fundamental question: how good are the predictions of traditional sphere/continuum models when the molecularity of the system is accounted for? To address this, we will present the results of combined experimental and computation studies of electron donor and acceptor systems and will demonstrate the shortcomings of traditional sphere/continuum models when the molecularity of the system is accounted for directly.

The first system we will examine are electron donor/acceptor complexes (EDACs), donor/acceptor pairs whose electronic structure allows for direct excitation from the neutral to ion pair states. Although the thermodynamics and charge recombination kinetics of EDACs have been the subject of intense study, the structural dynamics of the EDACs and their relation to charge recombination are still poorly understood. Using a unique combination of ultrafast spectroscopy and mixed quantum/classical simulations, we find that neither the ground nor excited state of EDACs can be described using a single, well-defined, structure, and that rearrangement from predominately face-to-face π stacks to edge-to-face T-shaped structures dominate the excited state structural dynamics.[1] Given the sensitivity of charge-transfer processes to donor/acceptor orientation, future theoretical descriptions of EDAC recombination dynamics must take into account the molecularity and structural evolution of the excited state in order to properly model the reaction.

Additionally, we will use classical molecular dynamics simulations to explore electron donor/acceptor systems in ways that are impossible with experimental techniques alone. We are able to demonstrate with umbrella sampling molecular dynamics simulations that the hard-sphere model and continuum electrostatics are poor descriptors of the reactant and product potentials of mean force, functions that describe the spatial distribution of donor/acceptor pairs and factor into predictions for the reaction driving force using the Weller equation. We will also show that simulated solvent reorganization energies deviate strongly from the predictions of continuum electrostatics, and that the linear-response approximation can break down in weakly polar solvents. The results of our experiments and simulations demonstrate that the real dynamics underlying photoinduced electron transfer are significantly more complex than traditional theories would predict.

[1] Rumble, C. A.; Vauthey, E. *Phys. Chem. Chem. Phys.* **21**, 11797–11809