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NON-EQUILIBRIUM DYNAMICS OF PHOTOINDUCED PROTON-COUPLED ELECTRON TRANSFER

Alexander V. SOUDACKOV and Sharon HAMMES-SCHIFFER
Dept. of Chemistry, The Pennsylvania State University
University Park, PA 16802, U.S.A.

ABSTRACT 1I:

Photoinduced proton-coupled electron transfer (PCET) processes play an important role in a broad range of energy related materials. Recent advances in time-resolved spectroscopic techniques open unique possibilities for direct probing of nonequilibrium relaxation processes in PCET systems following photoexcitation. This talk will present a theoretical formulation for modeling ultrafast dynamics of photoinduced PCET reactions in solution. In this formulation, the PCET system is described in terms of electron-proton vibronic free energy surfaces that depend on multiple collective solvent coordinates. The ultrafast nonadiabatic dynamics following photoexcitation is simulated using a surface hopping method in conjunction with coupled Langevin equations of motion describing the evolution of solvent coordinates. The proposed methodology enables the description of concerted as well as sequential mechanisms of photoinduced PCET. It also explicitly includes effects of proton vibrational relaxation, intramolecular vibrational modes, and nonequilibrium solvent dynamics. Analysis of simulation results for a series of representative model systems, inspired by recent time-resolved spectroscopic experiments on PCET systems, provides insight into the fundamental mechanism of photoinduced PCET and reveals a complex interplay among solvent dynamics, proton vibrational relaxation, and electron and proton transfer.