Effect of the Excitation Pulse Carrier Frequency on the Ultrafast Electron Transfer Dynamics

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The influence of the excitation pulse carrier frequency on the ultrafast charge recombination dynamics in excited donor-acceptor complexes has been explored. The theoretical description involves the explicit treatment of both the optical formation of the nuclear wave-packet on the excited free energy surface and its ensuing dynamics.

For nonadiabatic reactions in non-Markovian solvents, theory predicts a positive spectral effect (increasing of the charge recombination rate with the excitation pulse frequency) in the Marcus normal region and a negative spectral effect (decreasing of the charge recombination rate with the excitation pulse frequency) in the Marcus inverted region.

For charge recombination from an excited adiabatic state of a donor-acceptor complex induced by the nonadiabatic interaction operator, the negative spectral effect is invariably predicted. The magnitude of this spectral effect decreases strongly within increasing electronic coupling.

The mechanism of this phenomenon is analyzed and a semiquantitative interpretation is suggested. The role of the vibrational coherence in the recombination dynamics is discussed.

The variation of the excitation pulse carrier frequency within the charge transfer absorption band of the complex can alter the effective charge recombination rate by up to a factor 2.

An experimental investigation of the ultrafast charge recombination dynamics of donor-acceptor complexes in valeronitrile has shown the spectral effect to be rather small but reliably detectable. For one complex, the charge recombination dynamics was found to slow down upon increasing the excitation frequency, while the opposite behaviour was observed with the other complex. These experimental observations follow qualitatively the predictions of the theory.