

# Mechanisms and kinetic regularities of non-equilibrium ultrafast charge recombination

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The ultrafast charge transfer have attracted considerable interest from the scientific community due to its determining role in photosynthesis, catalysis, dye-sensitized solar cells and various molecular electronic devices. Such reactions typically proceed in non-thermal regime. Non-equilibrium of nuclear intramolecular and solvent degrees of freedom is created by a pump pulse or photoreaction itself at some of its stages. Although there have been many efforts to clarify microscopic mechanisms of non-equilibrium photoreactions by using ultrafast time-resolved spectroscopy techniques, control of the rate and efficiency of photoinduced charge transfer reactions is still an open challenge. One of the most important applications is suppression of ultrafast charge recombination in charge transfer systems. In these systems charge recombination is often regarded as undesirable process, leading to the loss of energy and selectivity of photoreaction. In this report some strategies of ultrafast charge recombination suppression are discussed.

To illustrate the non-equilibrium nature of ultrafast charge transfer, the kinetic regularities of a number of experimentally studied reactions are simulated and analyzed. The analysis includes charge recombination of excited donor-acceptor complexes (DAC), electron transfer (ET) from the second excited state, ultrafast photoinduced ET. The most known manifestations of non-equilibrium character are: the lack of the Marcus normal region in the free energy gap law for charge recombination of the excited donor-acceptor complexes, extremely low quantum yield of the thermalized charge separated states in ultrafast charge transfer from the second excited state. Knowledge of the charge transfer regime is of paramount importance, since the kinetics and yield of products of non-equilibrium reactions demonstrate regularities that significantly differ from those observed in thermal reactions.

Although variation of energetic charge transfer parameters are typically used to control the kinetics, relaxation characteristics of the solvent also can be also effective for the control. The dynamic solvent effect on charge recombination kinetics of photoexcited DACs in polar solvents are discussed. It is appeared that there are strong differences in regularities inherent to charge transfer reactions occurring in the non-equilibrium and thermal regimes. The most important differences are:<sup>[1]</sup> (i) the dynamic solvent effect is strong in the area of weak exergonicity and is weak in the area of strong exergonicity for thermal reactions while for the non-equilibrium reactions the regions of strong and weak dynamic solvent effect are reversed; (ii) increasing the electronic coupling value results in decreasing the dynamic solvent effect magnitude for non-equilibrium ET and in its increase for the thermal reactions; (iii) two-staged regime (fast non-equilibrium and much slower thermal stages) most clearly manifests if the reorganization energy of the relaxation modes noticeably exceeds the charge recombination free energy gap. With the rise of the electronic coupling the kinetics approach to the exponential regime since in the limit of strong electronic coupling the reaction includes only single, non-equilibrium, stage.

These differences are used to clarify the mechanism of charge transfer in real systems. Strong arguments supporting the non-equilibrium mechanism of CR in excited DACs are presented. The decisive argument is the dependence of the dynamic solvent effect on the free energy gap. The experimental data show the dynamic solvent effect to be weak in the area of weak exergonicity and to be stronger in the area of stronger exergonicity<sup>[2]</sup> that is consistent with prediction of non-equilibrium CR mechanism whereas for the thermal reactions an opposite trend is expected.

Non-equilibrium of an intramolecular high frequency vibrational mode can also influence on ultrafast charge transfer. An effect of such a mode excitation by a pumping pulse on ultrafast charge separation and charge recombination kinetics is discussed. It is shown that the effect can be both positive (the vibrational mode excitation increases the charge transfer rate constant) and negative (opposite trend). The effect on charge separation kinetics is predicted to be positive in both regions of low and high exergonicity being negative in between. Physical interpretation of the effects and comparisons with the experimental data are presented.

A very deep analogy between the charge recombination of the excited DACs and the back ET in intramolecular photoinduced ET reactions (compare frames A and B in Fig. 1) that should result in similar regularities inherent to these reactions is discussed.<sup>[3]</sup> In particular, absence of Marcus normal region in the free energy gap law for back ET is predicted.

The non-equilibrium effects are interpreted from a unified point of view in context of the multichannel point-transition stochastic model. The model includes explicit description of the formation and evolution of non-equilibrium state of both the intramolecular vibrations and the surrounding medium.

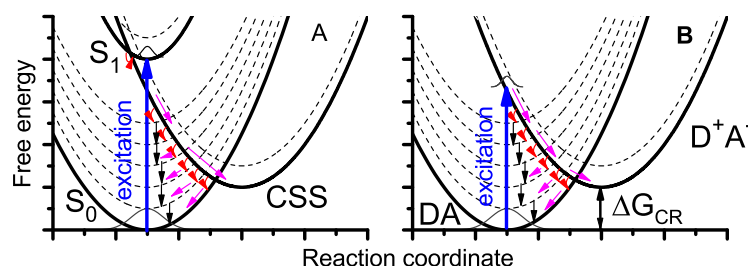


Figure 1: Cuts in the free energy surface of the ground, first excited, and the charge separated state. (A) photoinduced forward ET and ensuing back ET and (B) CR in excited DACs. The dashed lines are the vibrational repetitions of the electronic terms. Electronic transitions occur at the intersections of all sublevels and are shown with red curved arrows. The magenta arrows stand for the solvent relaxation. The relaxation of the high-frequency mode is shown by the black vertical arrows.

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