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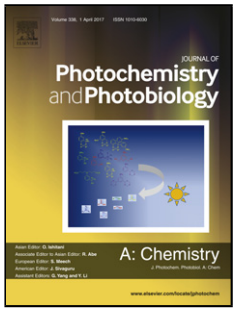


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# Effect of Charge Separation Free Energy Gap on the Rate Constant of Ultrafast Charge Recombination in Ion Pairs Formed by Intramolecular Photoinduced Electron Transfer

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**Abstract**

Regularities of ultrafast charge recombination kinetics in photoinduced intramolecular electron transfer in polar solvent are investigated. The multichannel stochastic model is used to simulate kinetics of charge separation and ensuing ultrafast charge recombination. The rate constant of ultrafast charge recombination occurring in non-equilibrium mode is shown to depend on the free energy gap of the preceding charge separation stage. This is a clear demonstration of violation of one of the fundamental principles of formal chemical kinetics, namely, the postulate of independence of elementary chemical reactions. The simulations revealed two main trends: (i) the charge recombination rate constant typically increases with decreasing the charge separation free energy gap, (ii) the maximum of the charge recombination rate constant, as a function of the charge recombination free energy gap, $|\Delta G_{\mathrm{CR}}|$, shifts toward smaller values of $|\Delta G_{\mathrm{CR}}|$ with decreasing the free energy gap at the previous, charge separation, stage of the reaction. The prediction of ultrafast charge recombination in donor-acceptor dyads with small charge recombination free energy gap is shown to be supported by the experimental data on the kinetics of charge recombination into the first excited state followed the charge separation from the second excited state.

*Keywords:* non-equilibrium electron transfer, solvent relaxation, free energy gap law

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