

Nonequilibrium Effects in Photoinduced Ultrafast Charge Transfer Reactions

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Abstract : In the last decade the nonequilibrium charge transfer have attracted considerable interest from the scientific community. Examples of such processes are the charge recombination in excited donor-acceptor complexes and the intramolecular electron transfer from the second excited electronic state. In these reactions the charge transfer proceeds predominantly in the nonequilibrium mode. In the excited donor-acceptor complexes the nuclear nonequilibrium is created by the pump pulse. The intramolecular electron transfer from the second excited electronic state is an example where the nuclear nonequilibrium is created by the forward electron transfer. The kinetics of these nonequilibrium reactions demonstrate a number of peculiar properties. Most important from them are: (i) the absence of the Marcus normal region in the free energy gap law for the charge recombination in excited donor-acceptor complexes, (ii) extremely low quantum yield of thermalized charge separated state in the ultrafast charge transfer from the second excited state, (iii) the nonexponential charge recombination dynamics in excited donor-acceptor complexes, (iv) the dependence of the charge transfer rate constant on the excitation pulse frequency. This report shows that most of these kinetic features can be well reproduced in the framework of stochastic point-transition multichannel model. The model involves an explicit description of the nonequilibrium excited state formation by the pump pulse and accounts for the reorganization of intramolecular high-frequency vibrational modes, for their relaxation as well as for the solvent relaxation. The model is able to quantitatively reproduce complex nonequilibrium charge transfer kinetics observed in modern experiments. The interpretation of the nonequilibrium effects from a unified point of view in the terms of the multichannel point transition stochastic model allows to see similarities and differences of electron transfer mechanism in various molecular donor-acceptor systems and formulates general regularities inherent in these phenomena. The nonequilibrium effects in photoinduced ultrafast charge transfer which have been studied for the last 10 years are analyzed. The methods of suppression of the ultrafast charge recombination, similarities and dissimilarities of electron transfer mechanism in different molecular donor-acceptor systems are discussed. The extremely low quantum yield of the thermalized charge separated state observed in the ultrafast charge transfer from the second excited state in the complex consisting of 1,2,4-trimethoxybenzene and tetracyanoethylene in acetonitrile solution directly demonstrates that its effectiveness can be close to unity. This experimental finding supports the idea that the nonequilibrium charge recombination in the excited donor-acceptor complexes can be also very effective so that the part of thermalized complexes is negligible. It is discussed the regularities inherent to the equilibrium and nonequilibrium reactions. Their fundamental differences are analyzed. Namely the opposite dependencies of the charge transfer rates on the dynamical properties of the solvent. The increase of the solvent viscosity results in decreasing the thermal rate and vice versa increasing the nonequilibrium rate. The dependencies of the rates on the solvent reorganization energy and the free energy gap also can considerably differ. This work was supported by the Russian Science Foundation (Grant No. 16-13-10122).

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