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## Free Energy Gap Law and Nonequilibrium Phenomena in Charge Recombination of Excited Donor-Acceptor Complexes

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### 1. Introduction

One of unanswered question of charge recombination (CR) reaction concerns the free energy dependence of the CR rate constant,  $k_{CR}$ , in the excited donor-acceptor complexes (DAC). The experimental investigations of CR in DACs after their photoexcitation by a short laser pulse at the carrier frequency of the charge transfer band demonstrated unexpected dependence of  $k_{CR}$  on the reaction free energy in the weakly exergonic region. The logarithm of the CR rate constant decreases monotonously, nearly linearly, with increasing the reaction exothermicity,  $-\Delta G_{CR}$ , whereas the standard equilibrium nonadiabatic Marcus theory predicts a bell-shaped dependence.

In this report we present: (1) the hot electron transition mechanism which leads to straightening of the Marcus parabolic dependence, (2) the fit of the available experimental data on the free energy gap law to the generalized stochastic model, (3) the analysis of the extent of the vibrational nonequilibrium in the CR of excited DACs, (4) the estimation of the extent of deviation of CR dynamics from exponential decay.

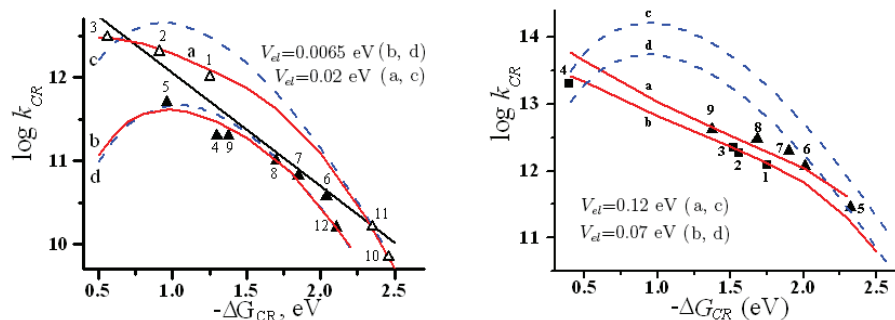
### 2. Multi-channel stochastic model

Ultrafast CR dynamics of excited DACs assisted by intramolecular high-frequency vibrational modes in polar solvents have been investigated within framework of generalized stochastic approach. The model is based on a two-level approach that includes an excited electronic state with charge transfer and the ground neutral state. One takes into account: (1) both the reorganization of the solvent, and the reorganization of the intramolecular quantum high-frequency modes; (2) the relaxation of vibrational excited states; (3) the formation of the electronic excited state with a strongly nonequilibrium nuclear configuration by a short laser pulse. The model allows to simulate the effect of nonequilibrium on CR dynamics in the excited DACs. In the framework of the generalized stochastic approach the CR dynamics are described by a set of Smoluchowski-like equations. In the numerical simulation of the Smoluchowski-like equations the Brownian simulation method in the form proposed before in Ref. [1] was used. The adequacy of this model was tested for a number of DACs and solvents [2, 3].

### 3. Results of CR dynamics simulation

The results of numerical simulation of the CR dynamics for a number of DACs are presented in Fig. 1. Considerable difference between effective,  $k_{CR}$ , and thermal,  $k_{th}$ , CR rates is demonstrated. The experimental data borrowed from Refs. [4-6] are pictured by

symbols. The behavior of CR rate constant  $k_{CR}$  strongly depends from values of electronic coupling,  $V_{el}$ . For smaller values of electronic coupling the Marcus dependence of the effective rate constant on the reaction exothermicity has typical for thermal reactions a bell-shaped form with a small deviation from the thermal rate in the vicinity of the maximum (panel 1, lines b and d, Fig. 1). However the curves with large  $V_{el}$  are characterized by rectification especially in the weakly exothermic. For good approximation be proposed separate the DACs into a few groups with different values of electronic coupling. The nonequilibrium nature of the CR leads to the deviation of the effective CR rate constant from its thermal value. In strongly exothermic region the effective CR rate is close to the thermal one (panels 1 and 2, Fig. 1). In the region of moderate exothermicity  $k_{CR}$  is less than  $k_{th}$  and in the weakly exothermic region the inverse relation,  $k_{CR} > k_{th}$ , is fulfilled. The effective and thermal rate constants at  $-\Delta G_{CR} = 0.56$  eV the complex Per-TCNE in acetonitrile solution have practically the same value (symbol 3, panel 1, Fig. 1), mainly proceeds in nonthermal regime. The exponential decay of the excited complexes is not direct evidence of the equilibrium regime of CR. For example, the CR in the excited Per-TCNE in acetonitrile is known to proceed in exponential regime but CR reaction occurs mainly in nonthermal regime. In this area the thermal rate decreases because of the Marcus activation barrier and the effective rate constant can even rise since the wave packet is initially placed in the area of more powerful sinks so that the inequality  $k_{CR} > k_{th}$  is held. The model provides correct description of the nonexponential CR dynamics in excited DACs.



Panel 1

Panel 2

**Fig. 1:** The free energy dependence of  $k_{CR}$  (in  $s^{-1}$ ) for a number of the DACs (panel 1 [4], panel 2 [5, 6]). Solid straight line is linear approximation to the experimental data. For comparison the thermal rate constant shown as dashed curves (lines c, d).

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**References**

- [1] S.V. Feskov, V.N. Ionkin, A.I. Ivanov, *J. Phys. Chem. A* **110** (2006) 11919.
- [2] S.V. Feskov, V.N. Ionkin, A.I. Ivanov et al, *J. Phys. Chem. A* **112** (2008) 594.
- [3] V.N. Ionkin, A.I. Ivanov, *J. Phys. Chem. A* **113** (2009) 103.
- [4] T. Asahi, N. Mataga, *J. Phys. Chem.* **95** (1991) 1956.
- [5] O. Nicolet, E. Vauthey, *J. Phys. Chem. A* **106** (2002) 5553.
- [6] O. Nicolet, N. Banerji, S. Pages, E. Vauthey, *J. Phys. Chem. A* **109** (2005) 8236.