# Photochemical & Photobiological Sciences



View Article Online

## PAPER

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**Cite this:** *Photochem. Photobiol. Sci.*, 2018, **17**, 607

# The effect of solvent relaxation time constants on free energy gap law for ultrafast charge recombination following photoinduced charge separation

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To elucidate the regularities inherent in the kinetics of ultrafast charge recombination following photoinduced charge separation in donor–acceptor dyads in solutions, the simulations of the kinetics have been performed within the stochastic multichannel point-transition model. Increasing the solvent relaxation time scales has been shown to strongly vary the dependence of the charge recombination rate constant on the free energy gap. In slow relaxing solvents the non-equilibrium charge recombination occurring in parallel with solvent relaxation is very effective so that the charge recombination terminates at the non-equilibrium stage. This results in a crucial difference between the free energy gap laws for the ultrafast charge recombination and the thermal charge transfer. For the thermal reactions the well-known Marcus bell-shaped dependence of the rate constant on the free energy gap is realized while for the ultrafast charge recombination only a descending branch is predicted in the whole area of the free energy gap exceeding 0.2 eV. From the available experimental data on the population kinetics of the second and first excited states for a series of Zn–porphyrin–imide dyads in toluene and tetrahydrofuran solutions, an effective rate constant of the charge recombination into the first excited state has been calculated. The obtained rate constant being very high is nearly invariable in the area of the charge recombination free energy gap from 0.2 to 0.6 eV that supports the theoretical prediction.

Received 27th December 2017, Accepted 3rd April 2018 DOI: 10.1039/c7pp00464h

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#### 1. Introduction

The kinetic regularities of thermal chemical reactions have been successfully studied for a long time.<sup>1-7</sup> A distinctive feature of thermal reactions is the equilibrium state of the nuclear subsystem of reactants and the surrounding medium. The equilibrium state is typically unique and has universal properties. The very fact of existence of such regularities is tightly connected with the universal properties of the equilibrium states. Contrary to that, the kinetics of non-equilibrium reactions depends on the nature and the degree of the nonequilibrium of the nuclear subsystem that can strongly vary. So, in the general case, it is difficult to expect universal regularities for them. However, there are classes of reactions with a specific non-equilibrium in which a similar non-equilibrium is created by the previous reaction or a short light pulse. The recombination of charges accompanying their photoinduced separation is one of the examples of such reactions.<sup>8</sup> For the

recombination reactions the nuclear non-equilibrium is formed in the previous, charge separation, stage.

Charge recombination (CR) plays an important role in natural and artificial systems since it accompanies photoinduced charge separation.<sup>5,7,9-14</sup> Ultrafast CR is usually an undesirable process, which often suppresses the quantum yield of the products. In particular, ultrafast CR heavily constrains the effectiveness of modern photovoltaic devices.<sup>14</sup> To date, there exists a problem of controlling the rate of ultrafast CR. A direct method to solve the problem is to establish regularities controlling the kinetics of ultrafast CR. Nevertheless, information on the regularities inherent in the ultrafast CR kinetics is rather scarce. One of the reasons of limited information is connected with the non-equilibrium nature of ultrafast CR. The ultrafast non-equilibrium CR occurs in parallel with the relaxation of the nuclear subsystem and CR kinetics depends on the degree of non-equilibrium that can vary in a series of similar reactions. An uncontrolled variation of the degree of the non-equilibrium, in turn, can prevent establishing the kinetic regularities.

The dependence of the electron transfer rate constant on the free energy gap (FEG),  $-\Delta G$  (the Marcus FEG law), is the most known regularity inherent in the thermal reactions. The

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law predicts the rate constant to have a bell-shaped form with the maximum at  $-\Delta G = E_{\rm rm}$ , where  $E_{\rm rm}$  is the reorganization energy.<sup>15</sup> Such a dependence was experimentally observed for intramolecular charge shift<sup>16,17</sup> and other types of charge transfer.<sup>18–26</sup> On the other hand, the rate constant of geminate CR in excited donor–acceptor complexes demonstrates a monotonic decrease with increasing FEG.<sup>27–29</sup> In such reactions the Marcus normal region was not observed so far. The most probable reason for such a behavior is connected with a non-equilibrium initial vibrational state of donor–acceptor complexes excited by a short laser pulse.<sup>30–32</sup> The models explicitly accounting for the non-equilibrium initial state of the solvent and reorganization of intramolecular vibrations are able to quantitatively reproduce the experimental data on the FEG dependence of the CR rate constant in excited DACs.<sup>31</sup>

Simulations of the CR kinetics in photoexcited donoracceptor complexes have shown that some regularities inherent to the thermal and non-equilibrium charge transfer can strongly differ and even be opposite.<sup>8,32</sup> Such dependencies can serve as an indicator of the charge transfer mechanism. In particular, the dynamic solvent effect on the nonequilibrium charge transfer is predicted to be strong in the area of strong exergonicity and to be weaker in the area of weaker exergonicity while for the thermal reactions the trend to be opposite. For slow, hence thermal, reactions the dynamic solvent effect is observed only in the Marcus normal region in accord with the theory while for ultrafast CR in excited donoracceptor complexes it is observed in the region of strong exergonicity that should be considered as decisive evidence of the non-equilibrium mechanism.<sup>32</sup>

To simulate non-equilibrium ultrafast CR kinetics following intramolecular photoinduced charge separation, the multichannel stochastic point-transition (MCSPT) model is exploited. The MCSPT model is a combination of the Zusman,<sup>33</sup> Sumi-Marcus,<sup>1</sup> Bixon-Jortner,<sup>34</sup> and Barbara hybrid<sup>35,36</sup> models. The model includes the reorganization of the solvent with several relaxation times and the reorganization of several intramolecular high-frequency vibrational modes. It was earlier used and appeared to be able to quantitatively describe a series of kinetic regularities observed in ultrafast charge transfer from the first and second excited states as well as ensuing ultrafast charge recombination either into the first excited or the ground states.<sup>8,31,32,37-43</sup>

The influence of the solvent relaxation characteristics on charge transfer kinetics has been only fragmentarily investigated. The complexity of the problem issues from complex relaxation dynamics of real solvents which are characterized by a few relaxation time scales. Typically the solvent dynamics describes in terms of single relaxation time.<sup>30,33</sup> There are investigations of the influence of the slow solvent relaxation component, which correlates with the solvent viscosity, on the charge transfer kinetics.<sup>32,37,38,41</sup> At the same time, the role of the fast solvent relaxation component in charge transfer kinetics was still not investigated. Here we show an important role of this component in CR kinetics in the region of small CR FEG. This sheds light on the still unanswered question *i.e.*  whether there is a Marcus normal region in ultrafast CR in both excited donor-acceptor complexes and dyads.

The aims of this article are (i) to investigate the kinetics of ultrafast CR following photoinduced intramolecular charge separation, (ii) to investigate the effect of solvent relaxation time scales on the dependence of the CR rate constant on the CR FEG (free energy gap law), (iii) to find out how the parameters controlling the kinetics of charge transfer affect the free energy gap law in the region of small values of the CR FEG, and (iv) to compare the obtained dependencies with the available experimental data on ultrafast CR kinetics.

#### Theory and computational details

The kinetics of photoinduced charge separation (CS) and ensuing ultrafast CR in donor-acceptor pairs can be described in the framework of the stochastic approach<sup>33</sup> generalized to account for the reorganization of a number of intramolecular high-frequency vibrational modes and multi-exponential relaxation of a polar solvent.<sup>31,37,43–50</sup> The model used here includes three electronic states: two states without charge separation, S<sub>h</sub> and S<sub>l</sub> (S<sub>h</sub> stands for the second or first locally excited state while S<sub>l</sub> stands for the first locally excited state or the ground state), and the charge separated state (CSS). A set of coupled differential equations for the probability distribution functions for all electronic states including their excited vibrational sublevels involved in a photoinduced CS and ensuing CR  $\rho_{S_h}^{(\vec{n})}(\mathbf{Q},t), \rho_{S_i}^{(\vec{n})}(\mathbf{Q},t)$ , and  $\rho_{CSS}^{(\vec{n})}(\mathbf{Q},t)$ ,

$$\begin{aligned} \frac{\partial \rho_{J}^{(\vec{n})}}{\partial t} &= \hat{L}_{J} \rho_{J}^{(\vec{n})} - \sum_{\vec{m}} k_{\vec{n}\vec{m}}^{(J)} \left( \rho_{J}^{(\vec{n})} - \rho_{\text{CSS}}^{(\vec{m})} \right) \\ &+ \sum_{\alpha} \frac{\rho_{J}^{(\vec{n}'\alpha)}}{\tau_{\text{V}}^{(n_{\alpha}+1)}} - \sum_{\alpha} \frac{\rho_{J}^{(\vec{n})}}{\tau_{\text{V}}^{(n_{\alpha})}}, \end{aligned} \tag{1} \\ \frac{\partial \rho_{\text{CSS}}^{(\vec{m})}}{\partial t} &= \hat{L}_{\text{CSS}} \rho_{\text{CSS}}^{(\vec{m})} + \sum_{\vec{n}} k_{\vec{n}\vec{m}}^{(S_{\text{h}})} \left( \rho_{\text{Sh}}^{(\vec{n})} - \rho_{\text{CSS}}^{(\vec{m})} \right) \\ &+ \sum_{\vec{n}} k_{\vec{m}\vec{n}}^{(S_{\text{l}})} \left( \rho_{\text{Sl}}^{(\vec{n})} - \rho_{\text{CSS}}^{(\vec{m})} \right) \\ &+ \sum_{\alpha} \frac{\rho_{\text{CSS}}^{(\vec{m}'\alpha)}}{\tau_{\text{V}}^{(m_{\alpha}+1)}} - \sum_{\alpha} \frac{\rho_{\text{CSS}}^{(\vec{m})}}{\tau_{\text{V}}^{(m_{\alpha})}} \end{aligned} \tag{2}$$

is used to describe the temporal evolution of the donor-acceptor system placed in a polar solvent. Here the following designations are used:  $J = S_I$ ,  $S_h$ , the vector  $\mathbf{Q}$  has the components  $Q_1, Q_2, ..., Q_N$ , the vector index  $\vec{n}$  (or  $\vec{m}$ ) in the probability distribution functions stands for the set of quantum numbers,  $\vec{n} = \{n_1, n_2, ..., n_\alpha, ..., n_M\}$ , where  $n_\alpha = 0, 1, 2, ...$  is the quantum number for an  $\alpha$ th intramolecular vibrational mode with a frequency  $\Omega_\alpha, \alpha = 1, ..., M$ , M is the number of the intramolecular vibrational modes. All the frequencies are assumed to satisfy the condition,  $\hbar\Omega_\alpha \gg k_{\rm B}T$  ( $\hbar$  is the Planck constant,  $k_{\rm B}$  is the Boltzmann constant, and T is the temperature). In eqn (1) and (2) the vector index  $\vec{n'}_\alpha$  (or  $\vec{m'}_\alpha$ ) is determined as  $\vec{n'}_\alpha = \{n_1, n_2, ..., n_\alpha + 1, ..., n_M\}$ .

The Smoluchowski operators in eqn (1) and (2),

$$\hat{L}_{J} = \sum_{i=1}^{N} \frac{1}{\tau_{i}} \left[ 1 + \left( Q_{i} - Q_{i\min}^{(J)} \right) \frac{\partial}{\partial Q_{i}} + k_{\mathrm{B}} T \frac{\partial^{2}}{\partial Q_{i}^{2}} \right], \tag{3}$$

describe diffusion on the diabatic free energy surfaces with their vibrationally excited sublevels  $U_{\rm S_h}^{(\vec{n})}$ ,  $U_{\rm S_l}^{(\vec{n})}$ , and  $U_{\rm CSS}^{(\vec{n})}$ :

$$U_{J}^{(\vec{n})} = \frac{1}{2} \sum_{i=1}^{N} \left( Q_{i} - Q_{i\min}^{(J)} \right)^{2} + \sum_{\alpha=1}^{M} n_{\alpha} \hbar \Omega_{\alpha} + \Delta G_{J}, \tag{4}$$

where (as shown in Fig. 1)  $\Delta G_{\rm S_h} = 0$ ,  $\Delta G_{\rm S_l} = \Delta G_{\rm CR} + \Delta G_{\rm CS}$ ,  $\Delta G_{\rm CSS} = \Delta G_{\rm CS}$ ,  $\Delta G_{\rm CS}$  and  $\Delta G_{\rm CR}$  are the free energy changes for CS and CR stages, respectively;  $Q_{i\min}^{\rm (S_h)} = 0$ ,  $Q_{i\min}^{\rm (S_l)} = -\sqrt{2E_{ri}^{\rm (ex)}}$ ,  $Q_{i\min}^{\rm (CSS)} = \sqrt{2E_{ri}^{\rm (CS)}}$  ( $i = 1, \dots, N$ ) correspondingly,  $J = S_{\rm h}$ ,  $S_{\rm l}$ , CSS. Here  $E_{ri}^{\rm (ex)}$  and  $E_{ri}^{\rm (CS)}$  are the reorganization energies of the *i*th mode of the solvent ( $i = 1, \dots, N$ ) at the stages of excitation and charge separation, respectively. It is supposed that a non-exponential solvent relaxation describes in terms of N relaxation modes. Each mode of the solvent is associated with a separate collective solvent coordinate,  $Q_i$ , with relaxation time constant  $\tau_i$  ( $i = 1, \dots, N$ ).

Transitions between electronic states and their vibrational sublevels are described by the Zusman parameters<sup>33,45,48</sup>

$$k_{\vec{n}\vec{m}}^{(J)} = \frac{2\pi V_J^2 F_{\vec{n}\vec{m}}}{\hbar} \delta \Big( U_J^{(\vec{n})} - U_{\rm CSS}^{(\vec{m})} \Big), \tag{5}$$



Reaction coordinate Q

**Fig. 1** Free energy curves of the S<sub>I</sub>, S<sub>h</sub>, and the charge separated states. The gray bell visualizes the initial distribution of the particles in the S<sub>h</sub> locally excited electronic state. The regions of localization of electron transitions after photoexcitation and subsequent non-equilibrium charge recombination are represented by ovals of the red and blue colors, respectively. The vertical black and blue arrows stand for the vibrational relaxation/redistribution.

$$F_{\vec{n}\vec{m}} = \prod_{\alpha} \exp \{-S_{\alpha}\} n_{\alpha}! m_{\alpha}! \\ \times \left[ \sum_{r_{\alpha}=0}^{\min(n_{\alpha},m_{\alpha})} \frac{(-1)^{m_{\alpha}-r_{\alpha}} (\sqrt{S_{\alpha}})^{n_{\alpha}+m_{\alpha}-2r_{\alpha}}}{r_{\alpha}! (n_{\alpha}-r_{\alpha})! (m_{\alpha}-r_{\alpha})!} \right]^{2}$$
(6)

Here,  $J = S_{I}$ ,  $S_{h}$ , and  $\delta(U)$  is the Dirac delta function,  $V_{J}$  is the electronic coupling for transitions between the *J*th electronic state and CSS (in what follows we use notations  $V_{CS}$  and  $V_{CR}$  for CS and CR stages, respectively),  $F_{\vec{n}\vec{m}}$  is the Franck–Condon factor for the transition between the vibrational sublevels  $\vec{n}$  of the *J*th electronic state and  $\vec{m}$  of CSS, and  $S_{\alpha} = E_{rv}/\hbar\Omega_{\alpha}$  are the Huang–Rhys factors for charge separation and CR stages which are supposed to be the same.  $E_{rv}$  is the reorganization energy of the intramolecular high-frequency modes. In eqn (1) and (2) the vibrational relaxation is described as a single-quantum irreversible transition  $n_{\alpha} \rightarrow n_{\alpha} - 1$  with the rate constant  $1/\tau_{v\alpha}^{(n\alpha)}$ , where  $\tau_{v\alpha}^{(n\alpha)} = \tau_{v\alpha}^{(1)}/n_{\alpha}$ .

The set of eqn 1 and 2 is solved under the initial conditions

$$\rho_{S_{h}}^{(\vec{n})}(\mathbf{Q},t=0) = A \prod_{\alpha} \frac{S_{\alpha}^{n_{\alpha}} e^{-S_{\alpha}}}{n_{\alpha}!} \exp \left\{ -\frac{1}{2k_{B}T} \sum_{i=1}^{N} \left( Q_{i} + \sqrt{2E_{\mathrm{r}i}^{(\mathrm{ex})}} \right)^{2} \right\} \times \exp \left\{ -\frac{\left[ \hbar \delta \omega_{e}^{(\vec{n})} - \sum_{i=1}^{N} \left( Q_{i} + \sqrt{2E_{\mathrm{r}i}^{(\mathrm{ex})}} \right) \sqrt{2E_{\mathrm{r}i}^{(\mathrm{ex})}} \right]^{2} \tau_{e}^{2}}{2\hbar^{2}} \right\}$$
(7)

$$\rho_{S_{l}}^{(\vec{n})}(\mathbf{Q}, t=0) = \rho_{CSS}^{(\vec{m})}(\mathbf{Q}, t=0) = 0$$
(8)

Here *A* is the normalization factor,  $\hbar \delta \omega_e^{(\vec{n})} = \hbar \omega_e - E_{\rm rm}^{(\rm ex)} + \Delta G_{\rm GS} - \sum n_a \hbar \Omega_a$ ,  $E_{\rm rm}^{(\rm ex)} = \sum E_{\rm ri}^{(\rm ex)}$ ,  $\Delta G_{\rm GS}$ is the free energy change for "electronic transition from the higher locally excited, S<sub>h</sub>, to the lower electronic state, S<sub>l</sub>, and parameters  $\omega_e$  and  $\tau_e$  are the carrier frequency and duration of the pump pulse of the Gaussian form. It is assumed that the pump pulse duration is short so that the solvent is considered to be frozen during excitation and all the high-frequency vibrational modes before photoexcitation are in the ground states.

The Brownian simulation method<sup>43,50,51</sup> is exploited for numerical solution of eqn (1) and (2) with the initial conditions of eqn (7) and (8). The method has been realized in bsmKinetic open-source software<sup>41</sup> which is used for the simulation of the charge separation and recombination kinetics. The CR, at least partially, proceeds in a nonthermal regime and, as a consequence, its kinetics is not exponential. Nevertheless, time-independent effective rate constants are used in the analysis of the experimental data. In order to compare the simulated results with the experimental data, we introduce the effective rate constants for the charge separation and charge recombination stages as follows:

$$k_{\rm CS}^{-1} = \int_0^{t_0} \mathrm{d}t P_{\rm S_h}(t), \quad k_{\rm CR}^{-1} = \int_0^{t_0} \mathrm{d}t P_{\rm CSS}(t) \tag{9}$$

where

$$P_{S_{h}}(t) = \int \rho_{S_{h}}^{(\vec{0})}(\mathbf{Q}, t) \prod_{i=1}^{N} \mathrm{d}Q_{i}$$
(10)

$$P_{\text{CSS}}(t) = \sum_{\vec{n}} \int \rho_{\text{CSS}}^{(\vec{n})}(\mathbf{Q}, t) \prod_{i=1}^{N} \mathrm{d}Q_i$$
(11)

To compare the calculated and experimental CR rate constants, the simulations are terminated at the time moment  $t_0$ when the population of the S<sub>1</sub> state equals 0.99, that is, when the condition is met

$$P_{S_{l}}(t_{0}) = \sum_{\vec{n}} \int \rho_{S_{l}}^{(\vec{n})}(\mathbf{Q}, t_{0}) \prod_{i=1}^{N} dQ_{i} = 0.99$$
(12)

because the value of the population of CSS, equal to 0.01 of the population of the initial excited state, corresponds to the typical sensitivity of experimental setups.

For the considered specific dyads, the spectral density of high-frequency vibrational modes associated with charge transfers is unknown. Fortunately, it was shown that charge transfer rate constants weakly depend on the spectral density provided the total reorganization energy,  $E_{\rm rv} = \sum_{\alpha} E_{\rm rva}$ , is constant and the number of high-frequency vibrational modes, M, exceeds or equals 5 and is fixed.<sup>52</sup> This finding allows exploiting a universal spectral density of high-frequency vibrational modes for the simulation of charge transfer kinetics. To date, only spectral densities for charge transfer in several donor-acceptor complexes are known. In what follows, the spectral density of PhCP/TCNE complexes is used. In the simulations

the magnitude of the total reorganization energy of high-frequency vibrational modes,  $E_{\rm rv}$ , and their number, M = 5, are considered to be the same at the excitation, charge separation, and recombination stages. The frequencies,  $\Omega_{\alpha}$ , and weights,  $E_{\rm rva}/E_{\rm rv}$ , of separate vibrational modes are listed in Table 1.

#### 3. Results and discussion

The kinetics of CR accompanying photoinduced charge separation from the first locally excited state for various donoracceptor systems has been experimentally studied.<sup>2,18,27–29,54–62</sup> In the studies, only the Marcus inverted region was detected. This fact is expected, because for all the

 Table 1
 Frequencies and weights of high-frequency vibrational modes

 for charge transfer in PhCP/TCNE complexes<sup>53</sup>

PhCP/TCNE			
No	$\hbar\Omega_{\alpha},  \mathrm{eV}$	$E_{\rm rv\alpha}/E_{\rm rv}$	
1	0.1272	0.079	
2	0.1469	0.089	
3	0.1823	0.104	
4	0.1935	0.498	
5	0.1993	0.230	

systems the CR FEG is large enough so that the CR has to proceed in the inverted regime according to the Marcus theory of the thermal reactions. At the same time, CR into the first locally excited state after the charge separation from the second locally excited state is typically characterized by a very small CR FEG. However, there are no data in the literature on the dependence of the CR rate constants on the FEG for such reactions. Thus, the question of the existence of the Marcus normal region in CR reactions in dyads is still open.

For thermal electron transfer reactions, the Marcus normal region was detected many times in the area where the FEG is smaller than the total reorganization energy. The reaction is slow in the area of small FEG due to large activation energy. The reason why the Marcus normal region can be absent in ultrafast CR is associated with its non-equilibrium nature. In such reactions the non-equilibrium is created at the charge separation stage (see Fig. 1). In this case, immediately after the charge separation, the particles occupy the region far from their equilibrium position directly in the region of most efficient electronic transitions, so that the activation is not needed and ultrafast CR is expected. On the other hand, slow CR essentially occurs after the thermalization of intramolecular vibrations and solvent and, hence, in the thermal regime. In this limit, one should observe the Marcus normal region. The above speculations show that the dependence of the CR rate constant on the FEG has to be sensitive to parameters such as electronic coupling, solvent relaxation time scale, intramolecular vibrational relaxation rate, and the FEG of the previous stages where the non-equilibrium is formed. In this section, we study how the solvent relaxation time constants (with emphasis on the fast component) affect the FEG law for ultrafast CR.

To evaluate the effect of the solvent relaxation time scales and charge separation FEG,  $-\Delta G_{\rm CS}$ , on ensuing ultrafast CR, we simulate the CR kinetics within the MCSPT model. In the simulations, typical values of invariable parameters are adopted:  $E_{\rm rm}^{(\rm ex)} = 0.01$  eV,  $\tau_{\rm v} = 1.0$  ps. The value of  $\Delta G_{\rm CR}$  is determined by the equation  $\Delta G_{\rm CR} = \Delta G_{\rm S_1} - \Delta G_{\rm CS}$ .

The results of the simulations are presented in Fig. 2. It is important that in the whole area of the CR FEG shown in Fig. 2, the inequality  $-\Delta G_{\rm CR} < E_{\rm rm} + E_{\rm rv}$  is held, so that for thermal reactions only the Marcus normal region, that is, an increase of the CR rate constant with increasing CR FEG, is expected in accordance with the Marcus theory. In the simulations, the CR free energy change,  $\Delta G_{\rm CR}$ , varies in parallel with  $\Delta G_{\rm CS}$  so that the sum  $\Delta G_{\rm CS} + \Delta G_{\rm CR}$  is kept constant. The latter takes two values, -2.1 and -0.9 eV, that are typical of the CR into the ground and the first locally excited states, respectively.

Fig. 2 uncovers four trends: (i) there are electron transfer parameters such that the Marcus normal region is absent in the area of the CR FEG ( $-\Delta G_{CR} > 0.2 \text{ eV}$ ) (all the solid lines in panel a); (ii) increasing the charge separation FEG,  $-\Delta G_{CS}$ , leads to a decrease of the CR rate constant, and the effect reaches its maximum in the region of small CR FEG (compare the solid and dashed curves in panel b); (iii) decreasing both



**Fig. 2** Free energy gap dependencies of the CR rate constant,  $k_{CR}$ . Parameters used:  $V_{CR} = 0.03 \text{ eV}$ ,  $V_{CS} = 0.05 \text{ eV}$ ,  $E_{rv} = 0.2 \text{ eV}$ ,  $E_{rm}^{(ex)} = 0.01 \text{ eV}$ ,  $E_{rm}^{(CS)} = 0.65 \text{ eV}$ . Panel (a):  $\Delta G_{S_1} = -0.9 \text{ eV}$ ,  $x_1 = 0.686$ ,  $x_2 = 0.314$ ,  $\tau_2 = 5.0 \text{ ps}$  (solid lines) and 0.63 ps (dashed lines),  $\tau_1 = 0.089 \text{ ps}$  (black lines, 1), 0.2 ps (red lines, 2), and 0.5 ps (blue lines, 3). Panel (b):  $\Delta G_{S_1} = -0.9 \text{ eV}$  (solid lines),  $\Delta G_{S_1} = -2.1 \text{ eV}$  (dashed lines),  $x_1 = 0.686$ ,  $x_2 = 0.314$ ,  $\tau_2 = 0.63 \text{ ps}$ ,  $\tau_1 = 0.089 \text{ ps}$  (black lines, 1), and 0.2 ps (red lines, 2). Panel (c): all parameters are the same as in panel a except for  $\Delta G_{S_1} = -2.1 \text{ eV}$  and  $x_1 = x_2 = 0.5$  (solid lines).

solvent relaxation time constants,  $\tau_1$  and  $\tau_2$ , leads to an acceleration of the CR in the area of the CR FEG  $-\Delta G_{\rm CR} > 0.2$  eV (compare curve 3 with curve 1 and the solid curve with the dashed curve for the same series in panels a and c) that reflects the dynamic solvent effect,<sup>33</sup> (iv) increasing both solvent relaxation times,  $\tau_1$  and  $\tau_2$  (compare curve 1 with curve 3 and the dashed curve with the solid curve for the same series

in panel a), results in suppression of the Marcus normal region or makes the Marcus inverted region more pronounced. It should be noted that the first and second trends reflect the non-equilibrium nature of the CR. For the CR occurring in the thermal mode the FEG of the previous stage cannot influence the CR kinetics. The described influence is a demonstration of the violation of the fundamental Ostwald principle of elementary reaction independence.<sup>63</sup>

To explain the uncovered trends we outline the physical processes involved in the charge separation and following CR. The forward photoinduced charge transfer occurring in the region of the locally excited state and CSS term intersections can be imagined as the appearance of a wave packet on the vibrational sublevels of the CSS term in the neighborhood of the intersections. The distance between the wave packet and the corresponding term minimum is a measure of the solvent non-equilibrium created by the charge separation. The solvent relaxation is visualized as the wave packet motion to the term minimum. In parallel with this motion, the wave packet partially transits to the nearest lower vibrational sublevel due to intramolecular vibrational relaxation. In the course of the relaxation the wave packet travels across the CSS and S1 term intersections where non-equilibrium CR occurs. The reason for the decrease in the CR rate constant with increasing charge separation FEG can be clarified by taking into account the dependence of the initial position of the wave packet on the CS FEG. For small values of CS FEG and the values of CR FEG considered here, the wave packet appears in the area of intersections of CSS and GS terms with large Franck-Condon factors where efficient non-equilibrium CR occurs. Increasing CS FEG with fixed CR FEG results in shifting the initial position of the wave packet farther from the CSS term minimum to the area where the Franck-Condon factors are smaller. As a result, the initial CR rate constant becomes smaller which decreases the effective CR rate constant. This is the mechanism of the CR deceleration with increasing CS FEG. Obviously, a considerable effect can be observed only if the CR is ultrafast, that is, occurs at the time scale of the nuclear relaxation.

The solvent relaxation time scale differently affects the thermal and non-equilibrium electron transfer rate. Although increasing the solvent relaxation time scale slows both the thermal and non-equilibrium electron transfer, there is a cardinal difference between the effects in these cases. For the thermal reactions the dependence of the rate constant on the solvent relaxation time is strong when the electronic coupling is strong (solvent controlled regime) and vanishes in the limit of weak electronic coupling,<sup>33</sup> while for the non-equilibrium CR the dependence is strong for weak electronic coupling and weak in the opposite case.<sup>64</sup> Another difference concerns the FEG law. For non-equilibrium CR, the effect of the solvent relaxation time on the FEG law is much more pronounced than those for the thermal reactions.

To demonstrate the difference in kinetics of the thermal and non-equilibrium charge transfer, the FEG dependencies of the CS rate constant,  $k_{CS}$ , for two solvent relaxation time scales



**Fig. 3** Free energy gap dependencies of the CS rate constant,  $k_{\text{CS}}$ . The stochastic simulation results are shown by the solid ( $\tau_2 = 0.63$  ps,  $x_1 = 0.686$ ,  $x_2 = 0.314$ ) and dashed ( $\tau_2 = 5$  ps,  $x_1 = x_2 = 0.5$ ) lines. Parameters used:  $V_{\text{CR}} = 0.03 \text{ eV}$ ,  $V_{\text{CS}} = 0.05 \text{ eV}$ ,  $E_{\text{rv}} = 0.2 \text{ eV}$ ,  $E_{\text{res}}^{(\text{ex})} = 0.01 \text{ eV}$ ,  $E_{\text{rcs}}^{(\text{CS})} = 0.65 \text{ eV}$ , the fast relaxation time constant,  $\tau_1$ , varies from 0.089 ps (black line, 1), 0.2 ps (red lines, 2), 0.5 ps (blue lines, 3), and 1 ps (magenta line, 4).

are pictured in Fig. 3. The fast and slow relaxation times correspond to acetonitrile and valeronitrile, respectively. The reorganization energy at the excitation stage is small, so the excitation of a dyad by a short laser pulse produces a locally excited state with a distribution of nuclear degrees of freedom close to thermal and CS proceeding nearly in the thermal regime. Fig. 3 shows that the CS rate constant in the area of small CS FEG increases with increasing CS exergonicity in full accord with the prediction of the Marcus theory of the thermal reactions. There is a growth of the CS rate constant with decreasing solvent relaxation time which decreases with the CS FEG in contrast to non-equilibrium CR.

As was mentioned earlier, small FEGs are usual for the CR into the first excited state following the CS from the second excited state,<sup>6,24,65–75</sup> however, for such reactions, the dependence of the CR rate constant on CR FEG has never been discussed in the literature. This is because of the absence of direct experimental data on the kinetics of such CR. At the same time, there are indirect data in the literature from which the rate constant CR can be extracted. Indeed, in ref. 6 the rate constant of the population of the first locally excited state, the rate constant of the second locally excited state decay, and the time constant of the internal conversion  $S_h \rightarrow S_l$  were reported for several dyads consisting of the Zn–porphyrin–imides.

It should be noticed that in ref. 6 not only the rate constant but also the population kinetics of the second and first excited states were reported. Both kinetics were later simulated and are reported in ref. 43. A good fitting was obtained that evidences in favor of the nonequilibrium mechanism of ultrafast charge recombination to produce the first excited state. That investigation justified the applicability and effectiveness of the multichannel point transition stochastic model in simulating ultrafast photoinduced charge separation and ensuing charge recombination in dyads. But the fitting itself does not provide ideas how to control charge recombination. This work is aimed to clarify how and why the parameters of donor–acceptor dyads and solvents affect the rate constant of ultrafast charge recombination. The effects are discussed in terms of the rate constants that are typically used in the discussion of experimental results.

Supposing the possibility of describing the reaction kinetics in terms of time-independent effective rate constants, the kinetics of the fast electronic transitions is reduced to eqn (13)– (15)

$$\frac{\mathrm{d}P_2}{\mathrm{d}t} = -(k_{\rm CS} + k_{\rm NR})P_2,\tag{13}$$

$$\frac{\mathrm{d}P_{\mathrm{CSS}}}{\mathrm{d}t} = k_{\mathrm{CS}}P_2 - k_{\mathrm{CR}}P_{\mathrm{CSS}},\tag{14}$$

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = k_{\mathrm{NR}}P_2 + k_{\mathrm{CR}}P_{\mathrm{CSS}} \tag{15}$$

with the initial conditions  $P_2(0) = 1$ ,  $P_1(0) = 0$ , and  $P_{\text{CSS}}(0) = 0$ . Here  $P_2$ ,  $P_1$ , and  $P_{\text{CSS}}$  are the populations of the second, first locally excited and charge separated states, respectively.  $k_{\text{CS}}$  and  $k_{\text{CR}}$  are the effective charge separation and CR rate constants and  $k_{\text{NR}} = 1/\tau_{\text{NR}}$  is the rate constant of the internal conversion  $S_h \rightarrow S_1$  with  $\tau_{\text{NR}} = 2.33$  ps in the fitting. Here it is assumed that CS and CR proceed irreversibly. This is justified by rather large values of the CS and CR FEG.

From eqn (13)–(15) an expression for the first excited state population  $P_1(t)$  can be derived that includes one unknown quantity,  $k_{CR}$ . Finally, from the fitting of the obtained population  $P_1(t)$  to that given by the equation

$$P_1(t) = 1 - \exp[-\lambda_p(t - t_1)]$$
(16)

the CR rate constant can be determined. Here the rate constant of the S<sub>1</sub> state population rise,  $\lambda_p$ , is known<sup>6</sup> and  $t_1$  is variable. The time shift  $t_1$  is introduced because the quality of the fitting with  $t_1 = 0$  is rather bad. Much better fitting is obtained with  $t_1 = 0.07$  ps, the same for all compounds and both solvents. Such a delay is natural from the physical point of view. Indeed, eqn (16) with  $t_1 = 0$  shows a fast increase in the population of the S<sub>1</sub> state at early times while the main channel in the accepted scheme  $S_h \rightarrow CSS \rightarrow S_l$  supposes some delay between the decay of the Sh state and the rise of the Sl state population. The time shift  $t_1$  somehow accounts for the delay. Such a short delay can be missed in experiments with fluorescence up-conversion apparatus when the fwhm of the instrumental response is 110 fs.6 A little bit worse fitting can be obtained with  $t_1 = 0.05$  ps. Such a decrease of  $t_1$  results in an increase of  $k_{\rm CR}$  by 10–20% for charge recombination in toluene and by up to 30% in THF. Accounting for some errors in the determination of  $\lambda_{\rm p}$  and the rate constant of the  $S_{\rm h}$  state decay, we can expect  $k_{\rm CR}$  to be estimated to factor of 2 accuracy or even worse.

The data on the CR rate constant obtained for Zn-porphyrin-imide dyads in toluene and tetrahydrofuran (THF) solutions are presented in Fig. 4 with circles and triangles, respectively. For these dyads the values of  $\Delta G_{CR}$ ,  $E_{rm}^{(CR)}$  and  $E_{rv}$ were earlier estimated in ref. 6 for both solvents. Here we use those data. The dynamics characteristics,  $x_i$  and  $\tau_i$ , for THF



**Fig. 4** Free energy change dependencies of the CR rate constant,  $k_{CS}$ . The stochastic simulation results are shown by the solid and dashed lines for the toluene (red) and THF (black) solvents. The rate constants calculated from the experimental data reported in ref. 6 are pictured by red circles and black triangles for toluene and THF solvents, respectively. The dyads are numbered as follows: ZP-MePH (1), ZP-PH (2), ZP-ClPH (3), ZP-Cl\_2PH (4), ZP-Cl\_4PH (5). Here ZP stands for Zn-5, 15-bis(3,5-di*tert*-butylphenyl)-porphyrin, PH – for phthalimide. Parameters borrowed from ref. 6:  $V_{CS} = 0.03$  eV,  $E_{rv} = 0.31$  eV,  $E_{rm}^{(CS)} = 0.27$  eV (toluene) and 0.56 eV (THF).  $\Delta G_{S_1} = -0.85$  eV.<sup>67</sup> The values of  $V_{CR}$  in eV are indicated near the corresponding curve.

and toluene solvents are borrowed from ref. 76 and 77, respectively. They are listed in Table 2.

The comparison of the simulated CR rate constant dependence on the CR FEG for Zn-porphyrin-imide dyads in toluene and THF is presented in Fig. 4 with red and black lines, respectively. In the simulations all the parameters of the dyads are considered to be known except for the electronic coupling between the charge separated and  $S_1$  states,  $V_{CR}$ , which was not estimated in earlier studies. In the area  $|\Delta G_{CR}|$ > 0.2 eV, the curves with V<sub>CR</sub> between 0.03 and 0.045 eV satisfactorily fit the data extracted from the experiment for both toluene and THF solvents. Accounting for drastic difference between predictions of equilibrium and nonequilibrium theories (compare the curves for thermal reactions presented in Fig. 3 with those for nonequilibrium reactions in Fig. 4), we can conclude that these experimental data are convincing evidence of the nonequilibrium mechanism of intramolecular ultrafast CR.

In the area of small CR FEG ( $|\Delta G_{CR}| < 0.2$  eV) in slow solvent, THF, the theory predicts a very fast decrease of the CR

**Table 2** The time constants of solvent relaxation modes,  $\tau_i$  in ps, and their weights,  $x_i$ 

Parameter/solvent	THF <sup>76</sup>	Toluene <sup>77</sup>
x <sub>1</sub>	0.447	0.36
$\tau_1$	0.228	0.08
$x_2$	0.553	0.24
$\tau_2$	1.520	0.65
<i>x</i> <sub>3</sub>	_	0.27
$\tau_3$	_	3.00
$x_4$	_	0.13
$ au_4$	—	120.0

rate constant with decreasing  $|\Delta G_{\rm CR}|$ , which seems to be not supported by the experimental data. The things are, there is one more dyad, ZP-C14PH in THF (not shown in Fig. 4), for which the value of  $|\Delta G_{\rm CR}|$  is close to zero and  $k_{\rm CR}$  is about 11 ps<sup>-1</sup>. Although in this dyad the thermal charge recombination is reversible and eqn (13)–(15) do not account for it, we may use the estimation obtained with an irreversible model because charge recombination proceeds faster than the solvent relaxation. The following stage of the thermal charge separation from the S<sub>1</sub> state is expected to be slower than the solvent relaxation due to the high free energy barrier for reactions with nearly zero FEG. So, the occupancy of the S<sub>1</sub> state and its following decay are well separated in time and the analysis within the irreversible model can be used for rough estimation of the charge recombination rate constant in this dyad.

To elucidate the discrepancy let us analyze the kinetics of the CSS population. In Fig. 5 the CR kinetics for a few values of  $|\Delta G_{\rm CR}|$  is pictured with the same parameters as shown in Fig. 4. It clearly demonstrates that the number of particles avoiding the non-equilibrium CR increases and the thermal rate constant decreases with decreasing value of  $|\Delta G_{\rm CR}|$ . For



**Fig. 5** Kinetics of CSS population,  $P_{CSS}$ , for a few values of the FEG,  $-\Delta G_{CR}$ : 0.1 eV (black lines), 0.15 eV (red), and 0.3 eV (blue). Parameters used:  $V_{CR} = 0.03$  eV,  $V_{CS} = 0.03$  eV,  $E_{rv} = 0.31$  eV. The kinetics of the CSS population in two solvents are presented: toluene,  $E_{rm}^{(CS)} = 0.27$  eV (panel a) and THF,  $E_{rm}^{(CS)} = 0.56$  eV (panel b).

 $|\Delta G_{\rm CR}| < 0.2$  eV the number of dyads in the charge separated state survived at the non-equilibrium stage exceeds 1% and the thermal stage is accounted for in the effective CR rate constant calculations. It should be mentioned that at the times when the population of the CSS is approached to 1% the population of the S<sub>h</sub> state is close to zero and the equality  $P_{\text{CSS}} = 1 - 1$  $P_1$  is held. The CR being rather slow at the thermal stage considerably reduces the effective CR rate constant. It appears that in the experimental data analysis, the slow thermal stage can be omitted since in the experimental time window a slow increase in the S<sub>1</sub> state population cannot be seen. Indeed, if we exclude the thermal stage from the CR rate constant calculations, the results of the simulations much better fit the experimental data (see the blue dashed lines). An example of such calculation of the effective rate constant of CR in THF for  $|\Delta G_{\rm CR}| = 0.15$  eV is pictured in panel (b) of Fig. 5. According to eqn (9), the rate is equal to the reciprocal of the area of the red shaded figure. As one can expect, this effect in THF is much greater than that in toluene. The difference is caused by a larger reorganization energy in THF because of its greater polarity. The larger reorganization energy leads to a larger free energy barrier between the term minima of the charge separated and S1 states which results in slower thermal CR.

To quantify the influence of the reaction monitoring time, the dependencies of the effective CR rate constant,  $k_{CR}$ , on the final population of the ground state are pictured in Fig. 6. Here  $P_{S_1}^f = P_{S_1}(t_0)$  (see Fig. 5, panel (a)) is the population of the  $S_1$  state at the moment of the simulation termination. Fig. 6 shows that the effective CR rate constant relatively weakly depends on  $P_{S_1}^f$  if this value is achieved at the nonequilibrium stage of CR that is the case when CR FEG exceeds 0.2 eV. In contrast, in the area of small CR FEG, the effective CR rate constant strongly depends on  $P_{S_1}^f$  and, hence, on the time moment of the termination of the  $S_1$  population monitoring. In this case the CR includes the nonequilibrium and thermal stages with strongly different rates. As a result, the effective rate constant can be strongly overestimated if the  $S_1$  decay is not moni-



**Fig. 6** Dependencies of the effective CR rate constant,  $k_{CS}$ , on the degree of the reactant transformation to the products (population of the S<sub>1</sub> state,  $P_{S_1}$ ). The simulation results are shown by the red (toluene,  $E_{rm}^{(CS)} = 0.27 \text{ eV}$ ) and black (THF,  $E_{rm}^{(CS)} = 0.56 \text{ eV}$ ) lines. Parameters used:  $\Delta G_{S_1} = -0.85 \text{ eV}$ ,  $V_{CR} = 0.03 \text{ eV}$ ,  $V_{CS} = 0.03 \text{ eV}$ ,  $E_{rv} = 0.31 \text{ eV}$ . The values of the free energy gap,  $|\Delta G_{CR}|$  in eV, are shown near the lines.

tored up to a given value of the  $S_l$  population. These uncertainties are created by the non-equilibrium nature of the ultrafast CR leading to the non-exponential decay of the CSS population. In this case, the effective rate constant is poorly defined and, therefore, is not a suitable characteristic of the kinetics of CR.

Formally, the data on CR in toluene extracted from the experiment show the Marcus normal region in the area 0.2 <  $|\Delta G_{\rm CR}| < 0.6$  eV, however, one should account for the small magnitude of the variation of the CR rate constant that is, undoubtedly, smaller than the error of its determination. An additional error is created by a relatively low precision of the determination of the CR FEG. These facts do not allow one to make an unambiguous conclusion about the presence of the Marcus normal region in this area of FEG. Nevertheless, the experimental data clearly evidence that the CR is ultrafast even at small values of the CR FEG and the CR rate constant is nearly invariable in the interval of the CR FEG between 0.2 and 0.6 eV. This means that the overwhelming majority of the CR proceeds at the stage of the solvent relaxation, that is, occurs in the non-equilibrium mode. As the simulations show, in this case the normal Marcus region is either absent or strongly suppressed. In other words, the slope of the curve  $\ln k_{\rm CR}(|\Delta G_{\rm CR}|)$  in the area of small CR FEG 0.2 <  $|\Delta G_{\rm CR}|$  < 0.6 eV is either negative or weakly positive.

#### 4. Conclusions

The simulations of ultrafast CR following photoinduced charge transfer have shown that the free energy gap law for CR strongly depends on the solvent relaxation time scales. The decrease of the slow and fast relaxation time constants results in an increase of the CR rate constant and suppression of the Marcus normal region. In slow solvents and for small free energy gaps between S<sub>h</sub> and S<sub>l</sub> states, only the inverted dependence of the rate constant of ultrafast non-equilibrium CR on the CR FEG (an increase in the CR rate constant with a decrease in the value of CR FEG to 0.2 eV) is predicted. This is possible when electronic coupling is not weak and the CR completely proceeds in the non-equilibrium mode, that is, in parallel with the solvent relaxation. In the opposite limit of weak electronic coupling, the probability of CR in the nonequilibrium mode is small, and CR proceeds in the thermal regime after thermalization. In this limit, a bell-shaped dependence of the CR rate constant on CR FEG, predicted by the Marcus's theory of thermal reactions,<sup>15</sup> is expected.

The comparison of the simulations with the experimental data for Zn-porphyrin-imide dyads in toluene has shown that the rate constant of the CR into the first excited state of Zn-porphyrin slowly increases with increasing CR FEG in the interval from 0.2 to 0.6 eV. For the dyads in the slower solvent, THF, the effective CR rate constant, in accord with the simulation results, is expected to slowly decrease with increasing CR FEG in the same interval. However, the available experimental data on CR kinetics are still scarce and additional

experimental investigations are needed to finally clarify the behavior of the CR rate constant in the region of small CR FEG.

Real solvents are characterized by a few relaxation time scales. The solvent relaxation is described in terms of the solvent relaxation function X(t)

$$X(t) = x_1 e^{-(t/\tau_1)^2} + \sum_{i=2}^N x_i e^{-t/\tau_i}$$
(17)

that can be determined from the data on transient fluorescence spectra.<sup>78-80</sup> Here N is the number of solvent relaxation modes and  $x_i$  and  $\tau_i$  are their weights and time constants. So far only charge transfer rate constant dependence on a long solvent relaxation time which correlates with the solvent viscosity has been investigated. In this paper the effect of the shortest relaxation time, which is associated with the inertial motion of solvent molecules,78-80 on the CR rate constant has been explored. The effect is especially strong in the region of small CR FEG. It is shown that increasing the fastest relaxation time can fully suppress the Marcus normal region in ultrafast CR occurring in the non-equilibrium mode. Here the inertial mode of the solvent relaxation is approximated by the diffusional motion. The possibility of the approximation of the inertial relaxation by diffusion motion and how large is the error in calculating the probability of an electronic transition due to such a substitution are discussed in ref. 81.

The simulations have shown that ultrafast CR kinetics is sensitive not only to the slow, but also to the fast solvent relaxation dynamics. To quantitatively fit the simulated kinetics to the experimental data, knowledge of the solvent relaxation characteristics is required. However, the precision of experimentally measuring the shortest time constant of the solvent relaxation function, which typically does not exceed 100 fs, is still rather low since the duration of widely used laser pumping and probing pulses is comparable to the shortest solvent relaxation time. At the same time, the parameters of slower components of the solvent relaxation are determined with high precision.

### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 16-13-10122).

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