

Kinetics of charge separated state population produced by intramolecular electron transfer quenching of second excited state



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ABSTRACT

Ultrafast photoinduced intramolecular charge separation from the second excited singlet state of Zn-porphyrin-amino naphthalene diimide dyad in toluene solution is theoretically studied in the framework of a multichannel stochastic model. The model incorporates four electronic states (the first and the second singlet excited, the charge separated, and the ground states) as well as their vibrational sublevels corresponding to the excitation of intramolecular high frequency vibrational modes. Electron transfer from the second excited state results in creation of the charge separated state with strongly non-equilibrium surrounding solvent and the intramolecular vibrations. The solvent motion to its equilibrium is described in the terms of three relaxation modes. The model explicitly describes the hot transitions from the charge separated state into the first excited state occurring in the course of the nuclear relaxation. Upon termination of the ultrafast decay of the second excited state as well as the relaxation of the solvent and intramolecular vibrations, the populations of the first excited, the ground, and the charge separated states can be far from the thermal equilibrium. Further, the populations approach their equilibrium values in the thermal regime. Simulations of the kinetics of the charge separated state population allow quantitative reproducing the two-humped kinetic curve observed in the experiment. The results of the fitting indicate that the reorganization energy of intramolecular low frequency modes for the intramolecular charge separation from the second excited state is extremely large in the porphyrin-diimide dyad.

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1. Introduction

The photoinduced charge transfer has been intensively studied for a few decades and was reviewed from different standpoints [1–7]. Recently, investigations of the charge transfer from higher (S_2) excited electronic states have been launched [8–20]. The explorations of ultrafast charge separation kinetics show two regularities that are universally observed in the S_2 fluorescence quenching by either intermolecular [14] or intramolecular electron transfer [13,15,16,19–21]: (i) the S_1 state population increases practically simultaneously with the S_2 state decay and (ii) the charge separated (CS) state population is considerably smaller than the initial population of the S_2 state. These regularities directly evidence the charge recombination (CR) into the first excited state, S_1 , to be so fast and efficient that a larger part of the ionic products decays at the stage of the medium relaxation. In other words, the recombination is expected to proceed in the hot regime [22,23].

The scheme of the electronic transitions starting from the second excited state, S_2 , is shown in Fig. 1. The S_2 state excited by a short laser pulse decays to initially produce either S_1 state (due to internal conversion) or the charge separated (CS) state. At first, the intramolecular degrees of freedom of a molecule in the CS state and the surrounding medium are highly nonequilibrium. Further the relaxation of the nuclear subsystem and the CR into the S_1 state proceed in parallel. The charge separation from the S_1 state after its equilibration can proceed in the thermal regime to produce again the CS state. The last can also decay to finally form the ground state, S_0 . The described chain of charge transfers results in the two-humped kinetic curve of the CS state population observed in the experiments [19,20].

Such a sequence of the charge transfers including the hot transitions can be quantitatively described [22] in terms of the multichannel stochastic model [24–28]. This model allowed reproducing the kinetics of the population of the S_2 and S_1 states for a series of directly linked Zn-porphyrin-imide dyads in tetrahydrofuran solution reported in Ref. [13]. Later, the model was applied for simulation of the CS state population kinetics [23,29]. The results of such simulations [29] quantitatively reproduce the

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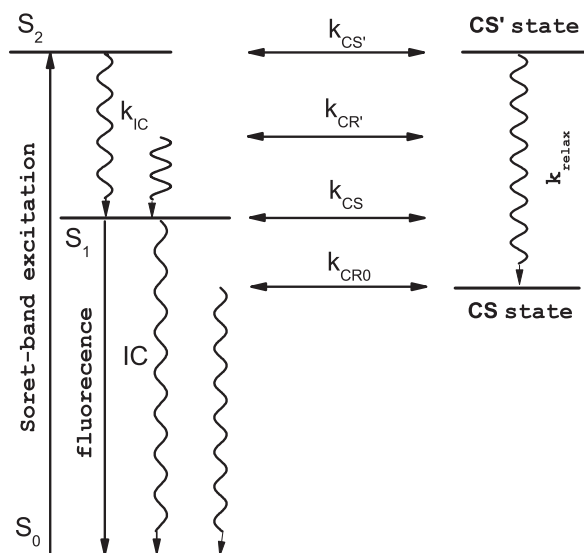


Fig. 1. The scheme of the electronic states involved in photoinduced electron transfer from the second excited state of the porphyrin–amino naphthalene diimide dyad and the transitions between them. The horizontal arrows indicate the electronic transitions (since all transitions are reversible, they are depicted by two-sided arrows) and the vertical wavy lines visualize the medium and intramolecular vibrational relaxation. The designations of the rate constants are also presented.

distinctive features of the experimental two-humped kinetic curve of the CS state population for Zn(II)–porphyrin covalently linked to naphthalene imide in dimethylformamide solution reported in ref [19]. Namely, three timescales: the S_2 state decay, τ_{CS2} , the charge separation from the first excited state, τ_{CS1} , and the CR to the ground state, τ_{CR0} , the magnitudes of the maxima and the minimum between them as well as their positions on the time axis are in a good accord with the experimental data. These studies leave open the questions whether it is possible to use a stochastic model for the non-polar environment, and whether it is possible to reproduce the “whole” curve and not just its “key points”.

In this paper the multichannel stochastic model simulations are fitted to the experimental two-humped kinetic curve of the CS state population for Zn–porphyrin–amino naphthalene diimide dyad in toluene solution reported in ref [20]. Although the kinetic curve measured in ref [20] is similar to that reported in ref [19] there is an important difference in the systems studied in the works. In this instance the difference in the structure and energetics of the dyads is not expected to be so important as the difference in the polarity of the solvents used. The point is that the two-humped kinetic curve of the CS state population was reproduced with large (about 0.9 eV) magnitude of the medium reorganization energy [29]. Such a large reorganization energy is acceptable for highly polar solvents but for non-polar solvents like toluene it should be considerably smaller [30]. Another aim of this paper is to find a possible solution of this problem.

2. The model of ultrafast charge separation from the second excited state followed by charge recombination

Dynamics of ultrafast charge separation from the second excited state and following CR into the first excited and the ground states can be described in terms of a model including four electronic states: the ground state $|S_0\rangle$, the first and the second singlet excited states, $|S_1\rangle$, $|S_2\rangle$, correspondingly, and the charge separated state, $|CS\rangle$ (see Fig. 2). In the dyad considered the S_1 and S_2 states are associated with the excitation of the Zn–porphyrin and the charge separation with the electron transfer from the excited porphyrin ring to the diimide [20]. The model involving such four electronic

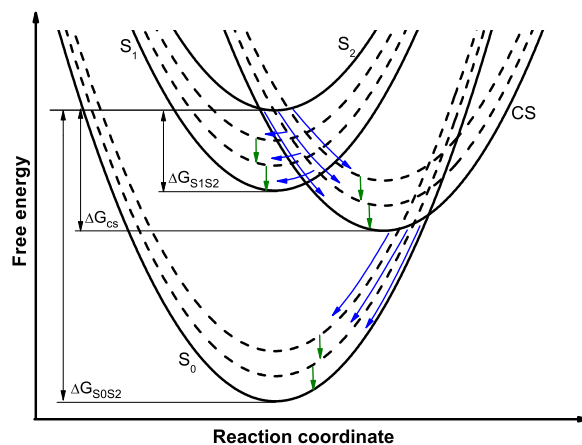


Fig. 2. Cuts in the free energy surface of the ground and the first, second excited states, and the CS state. The dashed lines are the vibrational repetitions of the CS, S_1 , and S_0 electronic states. The repetitions are equidistant in the figure, but for the model with ten vibrational modes the density of the sublevels sharply increases with the free energy rise. Electronic transitions occur at the intersections of all sublevels. The relaxation of the high frequency mode is shown by the green vertical arrows as transitions between the neighbor vibrational sublevels. The medium relaxation is visualized with the blue lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

states and the transitions between them was described in detail in refs [22,23,29]. So, we only briefly outline the designations used hereafter.

The solvent relaxation function, $X(t)$, is written in the form [31–34]

$$X(t) = \sum_{i=1}^N x_i e^{-t/\tau_i} \quad (1)$$

where $x_i = E_{ri}/E_{rm}$, τ_i , and E_{ri} are the weight, the relaxation time constant, and the reorganization energy of the i th medium mode, respectively, $E_{rm} = \sum E_{ri}$, and N is the number of the solvent modes. The relaxation of the toluene solvent is described with three modes, $N=3$.

Diabatic free energy surfaces for the electronic states in the terms of the medium mode coordinates Q_i can be written in the form [24,35]

$$U_{S2} = \sum_{i=1}^N \frac{Q_i^2}{4E_{ri}}, \quad (2)$$

$$U_{CS}^{(\tilde{n})} = \sum_{i=1}^N \frac{(Q_i - 2E_{ri})^2}{4E_{ri}} + \Delta G_{CS} + \sum_{\alpha=1}^M n_{\alpha} \hbar \Omega_{\alpha}, \quad (3)$$

$$U_{S1}^{(\tilde{m})} = \sum_{i=1}^N \frac{Q_i^2}{4E_{ri}} + \Delta G_{S1S2} + \sum_{\alpha=1}^M m_{\alpha} \hbar \Omega_{\alpha}, \quad (4)$$

$$U_{S0}^{(\tilde{l})} = \sum_{i=1}^N \frac{Q_i^2}{4E_{ri}} + \Delta G_{S0S2} + \sum_{\alpha=1}^M l_{\alpha} \hbar \Omega_{\alpha}, \quad (5)$$

where Ω_{α} , n_{α} , m_{α} , l_{α} (n_{α} , m_{α} , and $l_{\alpha}=0, 1, 2, \dots$) are the frequency and the quantum numbers of the α th intramolecular quantum vibrational mode, correspondingly, the indexes \tilde{n} , \tilde{m} , \tilde{l} stand for the sets of quantum numbers $\tilde{n} = \{n_1, n_2, \dots, n_{\alpha}, \dots\}$, $\tilde{m} = \{m_1, n_2, \dots, m_{\alpha}, \dots\}$, and $\tilde{l} = \{l_1, n_2, \dots, l_{\alpha}, \dots\}$, M is the number of the intramolecular quantum vibrational modes, ΔG_{S1S2} and ΔG_{S0S2} are the free energy changes for the transitions $|S_2\rangle \rightarrow |S_1\rangle$ and $|S_2\rangle \rightarrow |S_0\rangle$, correspondingly, ΔG_{CS} is the free energy change for the charge separation $|S_2\rangle \rightarrow |CS\rangle$.

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