

PHOTO-INDUCED INTERMOLECULAR CHARGE TRANSFER IN PORPHYRIN COMPLEXES

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Optical excitation of the sequential supermolecule $H_2P - ZnP - Q$ induces an electron transfer from the free-base porphyrin (H_2P) to the quinone (Q) via the zinc porphyrin (ZnP). This process is modeled by equations of motion for the reduced density matrix which are solved numerically and approximately analytically. These two solutions agree very well in a great region of parameter space. It is shown that for the majority of solvents the electron transfer occurs with the superexchange mechanism.

I. INTRODUCTION

The investigation of photoinduced charge transfer is important both for the description of natural photosynthesis [1] and for the creation of artificial photoenergy-converting devices [2]. For experimental realizations of such artificial devices porphyrin complexes are good candidates [3]. Of major interest are those complexes with an additional bridging block between donor and acceptor [4].

Electron transfer reactions can occur through different mechanism [5]: sequential transfer (ST) or superexchange (SE). Changing a building block of the complex [6] or changing the environment [7] can modify which mechanism is most significant. To clarify which mechanism is present one sequentially varies the energetics of the complex [8]. This is done by radical substituting the porphyrin complexes [9] or by changing the polarity of the solvent [10]. Also the geometry and size of a bridging block can be varied and in this way the length of the subsystem through which the electron has to be transferred [11].

SE [12] occurs due to coherent mixing of the levels [13] and plays a role for any detuning of the energy levels [14]. The transfer rate in this channel decreases exponentially with increasing length of the bridge [15]. When incoherent effects such as dissipation and dephasing dominate [16], the transfer is mainly sequential [17], i. e., the levels are occupied mainly in sequential order [18]. An increase in the bridge length induces only a small reduction in the transfer rate [19].

In the case of coherent SE the dynamics is mainly Hamiltonian and can be described on the basis of the Schrödinger equation. The physically important results can be obtained by perturbation theory [20], most successfully by the Marcus theory [21]. In case of ST the environmental influence has to be taken into account. The more natural description of the relaxation process is based on the density matrix (DM) formalism [22]. The master equation that governs the DM evolution as well as the appropriate relaxation coefficients can be derived from such basic information as system-environment coupling strength and spectral density of the environment [23].

The main physics of the system can be described by a DM equation which accounts for relaxation effects phenomenologically [24]. The master equation is analytically solvable only for the simplest models [25]. Most investigations are based on the numerical solution of this equation [26]. However, an estimations can be obtained within the steady-state approximation [27]. Here we perform numerical as well as approximate analytical calculations.

II. MODEL

We investigate the photoinduced electron transfer in supermolecules that consist of sequentially connected molecular blocks, namely donor, bridge, and acceptor. The donor (D) is not able to transfer its charge directly to the acceptor (A) because of

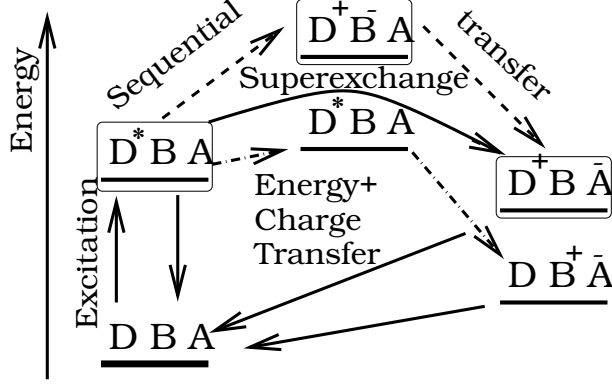


FIG. 1. Schematic view of the energy levels in the $H_2P-ZnP-Q$ complex taken into account in calculation. The three states in the boxes define the charge separation which can happen either by ST or by SE.

their spatial separation. D and A can exchange their charges only through B (Fig. 1). In the present investigation the supermolecule consists of free-base porphyrin(H_2P) as donor, zinc substituted porphyrin(ZnP) as bridge, and benzoquinone as acceptor [1]. In each of those molecular blocks we consider only two molecular orbitals, the LUMO and the HOMO. Each of those orbitals can be occupied by an electron ($|1\rangle$) or not ($|0\rangle$). This model allows us to describe the neutral nonexcited molecule $|1\rangle_{HOMO}|0\rangle_{LUMO}$ and the following three states of the molecule: neutral excited molecule $|0\rangle_{HOMO}|1\rangle_{LUMO}$, positive ion $|0\rangle_{HOMO}|0\rangle_{LUMO}$, and negative ion $|1\rangle_{HOMO}|1\rangle_{LUMO}$. Below Roman indices indicate molecular orbitals ($m = 0$ - HOMO, $m = 1$ - LUMO), while Greek indices indicate molecular blocks ($\mu = 1$ - donor, $\mu = 2$ - bridge, $\mu = 3$ - acceptor). Each of the electronic states has its own vibrational substructure. However the time of vibrational relaxation [2] is two orders of magnitude faster than the characteristic time of the electron transfer [3]. Because of this we assume that only the vibrational ground states play a dominant role in electron transfer.

One can describe the occupation of an orbital by an electron with the appropriate creation operator $c_{\mu m}^+ = |1\rangle_{\mu m}\langle 0|_{\mu m}$ as well as its annihilation $c_{\mu m} = |0\rangle_{\mu m}\langle 1|_{\mu m}$. Then $\hat{n}_{\mu} = \sum_m c_{\mu m}^+ c_{\mu m}$ gives the number of electrons in the molecular block μ .

For the description of charge transfer and other dynamical processes in the system we introduce the Hamiltonian

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} , \quad (1)$$

where H_S characterizes the supermolecule, H_B the dissipative bath, and H_{SB} the interaction between the two. H_S , however, includes the static influence of the environment, namely of the solvent dipoles, which gives rise to a reduction of the energy levels,

$$\hat{H}_S = \sum_{\mu m} E_{\mu m} \hat{n}_{\mu m} + \frac{3}{\epsilon_s + 2} (\hat{E}_{el} + \hat{E}_{ion}) + \hat{V} , \quad (2)$$

The energies $E_{\mu m}$ are calculated in the independent particle approximation [4]. ϵ_s denotes the static dielectric constant of the solvent. $\hat{E}_{el} = \sum_{\mu} (\hat{n}_{\mu} - 1) e^2 / (4\epsilon_0 r_{\mu})$ describes the energy to create an isolated ion. This term depends on the characteristic radius r_{μ} of the molecular blocks. $\hat{E}_{ion} = \sum_{\mu} \sum_{\nu} (\hat{n}_{\mu} - 1)(\hat{n}_{\nu} - 1) e^2 / (4\pi\epsilon_0 r_{\mu\nu})$ includes the interaction between the already created ions. It depends on the distance between the molecular blocks $r_{\mu\nu}$. The last contribution to the system Hamiltonian is the hopping term $\hat{V} = \sum_{\mu\nu} v_{\mu\nu} (\hat{V}_{\mu\nu}^+ + \hat{V}_{\mu\nu}^-) ((\hat{n}_{\mu} - 1)^2 + (\hat{n}_{\nu} - 1)^2)$, which includes the coherent hopping between each pair of LUMO $\hat{V}_{\mu\nu}^- = c_{\nu 1}^+ c_{\mu 1}$, $\hat{V}^+ = (\hat{V}^-)^+$ as well as the corresponding intensities $v_{\mu\nu}$. The matrix elements of this operator give nonzero contribution only if one of the states has a charge separation. Because there is no direct connection between donor and acceptor we assume $v_{13} = 0$.

As usual the bath is given by harmonic oscillators with creation and annihilation operators a_λ^+ and a_λ . The system bath interaction comprises both irradiative and radiative transitions. For $t \ll 1 - 10$ ns the latter one can be neglected. The irradiative contribution corresponds to energy transfer to the solvent and spreading of energy over vibrational modes of the supermolecule

$$\hat{H}_{SB} = \sum_{\lambda} \sum_{\mu\nu} K_{\lambda,\mu\nu} v_{\mu\nu} (a_\lambda^+ + a_\lambda) (\hat{V}_{\mu\nu}^+ + \hat{V}_{\mu\nu}^-), \quad (3)$$

where $K_{\lambda,\mu\nu}$ reflects the interaction strength between bath mode λ and quantum transition between LUMO levels of molecules μ and ν .

Initially we use the whole density matrix of system and bath for the description of the dynamics. After applying the Markov and rotating wave approximations and tracing out the bath modes [] we obtain the equation of motion for the reduced density matrix (RDM)

$$\begin{aligned} \dot{\sigma} = -i/\hbar [\hat{H}_S, \sigma] &+ \sum_{\mu\nu} \Gamma_{\mu\nu} \{ (n(\omega_{\mu 1 \nu 1}) + 1) ([\hat{V}_{\mu\nu}^- \sigma, \hat{V}_{\mu\nu}^+] + [\hat{V}_{\mu\nu}^-, \sigma \hat{V}_{\mu\nu}^+]) \\ &+ n(\omega_{\mu 1 \nu 1}) ([\hat{V}_{\mu\nu}^+ \sigma, \hat{V}_{\mu\nu}^-] + [\hat{V}_{\mu\nu}^+, \sigma \hat{V}_{\mu\nu}^-]) \}, \end{aligned} \quad (4)$$

where the dissipation intensity $\Gamma_{\mu\nu} = \pi K_{\mu\nu}^2 \rho(\omega_{\mu 1 \nu 1}) v_{\mu\nu}^2$ depends on the coupling $K_{\mu\nu}$ of the transition $\mu 1 \rightsquigarrow \nu 1$ and on the bath mode of the same frequency. $\Gamma_{\mu\nu}$ depends also on the density ρ of bath modes at the transition frequency $\omega_{\mu 1 \nu 1}$ and on the corresponding coherent coupling $v_{\mu\nu}$ between the system states. $n(\omega)$ denotes Bose-Einstein distribution.

For simplicity we introduce a superindex $i = \{\mu m\}$, the intensities of the dissipative transitions $d_{ij} = \Gamma_{ij} n(-\omega_{ij})$ between each pair of states, as well as the corresponding dephasing intensities $\gamma_{ij} = 1/2 \sum_k (d_{ik} + d_{kj})$. Taking these simplifications into account one gets

$$\dot{\sigma}_{ii} = -i/\hbar \sum_j (V_{ij} \sigma_{ji} - \sigma_{ij} V_{ji}) - \sum_i d_{ij} \sigma_{ii} + \sum_j d_{ji} \sigma_{jj}, \quad (5)$$

$$\dot{\sigma}_{ij} = (-i\omega_{ij} - \gamma_{ij}) \sigma_{ij} - i/\hbar V_{ij} (\sigma_{jj} - \sigma_{ii}). \quad (6)$$

The simplification is that we do not calculate the system parameters, rather we extract them from experimental data.

III. EXTRACTION OF SYSTEM PARAMETERS

The porphyrin absorption spectra [] consist of high frequency Soret bands and low frequency Q bands. In case of ZnP the Q band has two subbands, $Q(0,0)$ and $Q(1,0)$. In the free-base porphyrin H_2P the reduction of symmetry induces a splitting of each subband into two, namely $\bar{Q}^x(0,0)$, $\bar{Q}^y(0,0)$ and $\bar{Q}^x(1,0)$, $\bar{Q}^y(1,0)$. So the emission spectra of ZnP and H_2P consist of two and four bands, respectively. Each of the abovementioned spectra can be represented as a sum of Lorentzians with good precision. It is important to note that the spectra of porphyrin complexes contain all bands of the isolated porphyrins without essential changes. We use the lowest band of each spectrum. The corresponding frequencies and widths are shown in table 1.

On the basis of the experimental spectra we determine $E_{D^*BA} = 1.82eV$ and $E_{DB^*A} = 2.03eV$ (in CH_2Cl_2). The authors of Ref. [1] give the energies of two other levels, $E_{D+B-A} = 2.44eV$ and $E_{D+BA^-} = 1.42eV$. This allows to calculate $E_{DB+A^-} = 1.21eV$. The hopping intensity $v_{23} = v = 2.2meV$ is calculated in Ref. [1]. On the other hand Rempel et al. [2] estimate the electron coupling of the initially excited and charged bridge states $v_{12} = V = 65meV$. We take the intensity of the intermolecular conversions Γ_{21}, Γ_{23} in range $1 - 10 \times 10^{11} s^{-1}$ [3].

Table 1: Low-energy bands of the porphyrin spectra for CH_2Cl_2 as solvent.

	Absorption		Emission	
	Frequency, eV	Width, eV	Frequency, eV	Width, eV
H_2P	$\nu_{00}^x = 1.91$	$\gamma_{00}^x = 0.06$	$\nu_{01}^x = 1.73$	$\gamma_{01}^x = 0.05$
ZnP	$\nu_{00} = 2.13$	$\gamma_{00} = 0.07$	$\nu_{01} = 1.92$	$\gamma_{01} = 0.05$

The main parameter which controls the electron transfer in a triad is the relative energy of the state D^+B^-A . This state has a strong coupling to the solvent that changes the energy of the state. The values of the energy $E_{D^+B^-A}$ calculated in the present model are shown in table 2 for some solvents. In table 2 ϵ_s denotes the static dielectric permittivity, ϵ_∞ the optic dielectric permittivity, MTHF 2-methyl-tetrahydrofuran, and CYCLO denotes cyclohexane. The calculated value $E_{D^+B^-A} = 2.86eV$ deviates 15% from the data of Ref. .

IV. RESULTS

The time evolution of charge transfer within the supermolecule is described by Eqs. (5) and (6). At initial time only the donor state is occupied. The calculations were performed with two methods, direct numerical integration and analytic approximation.

For the numerical simulation the eigenvalues and -vectors of the system are calculated and with these the time evolution of the system is known. The simulation of the system dynamics with the parameters determined in the previous section shows exponential growth of the acceptor population. Such a behavior can be accurately fitted to the formula $P_3(t) = P_3(\infty)[1 - \exp(-k_{ET}t)]$, where $k_{ET} \simeq 5 \times 10^9 s^{-1}$ and $P_3(\infty) \simeq 0.95$ for CH_2Cl_2 as solvent. The population of the bridge state does not exceed 0.005. This shows that the SE mechanism dominates over the ST for the chosen set of parameters. In this case the system dynamics can be described by two values: the acceptor population at infinite time $P_3(\infty)$ and the reaction rate k_{ET} that we deduce from the dynamics via the following formula $k_{ET} = P_3(\infty)/\{\int_0^\infty [1 - P_3(t)]dt\}$.

The analytical approach is valid for the kinetic limit $t \gg 1/\gamma_{ij}$. In Laplace-space we can replace $1/(i\omega_{ij} + \gamma_{ij} + s)$ by $1/(i\omega_{ij} + \gamma_{ij})$, where s denotes the Laplace variable. This allows to simplify Eqs. (5) and (6) and we define a new relaxation operator $(L\sigma)_{ii}^{new} = -\sum_i g_{ij}\sigma_{ii} + \sum_j g_{ji}\sigma_{jj}$. In this expression the transition coefficients g_{ij} contain both, dissipative and coherent contributions

$$g_{ij} = d_{ij} + v_{ij}v_{ji}\gamma_{ij}/[\hbar^2(\omega_{ij}^2 + \gamma_{ij}^2)]. \quad (7)$$

Assuming the bridge population to be zero allows us to find the dynamics of the acceptor state in the form $P_3(t) = P_3(\infty)[1 - \exp(-k_{ET}t)]$, where the final population $P_3(\infty)$ and the reaction rate k_{ET} are expressed in terms of the coefficients g_{ij}

$$k_{ET} = g_{23} + \frac{g_{23}(g_{12} - g_{32})}{g_{21} + g_{23}}, \quad P_3(\infty) = \frac{g_{12}g_{23}}{g_{21} + g_{23}}(k_{ET})^{-1}. \quad (8)$$

Table 2: Energy of the charged bridge state and transfer rates in different solvents.

Solvent	75% CH_2Cl_2 +25% CH_3CN	CH_2Cl_2	MTHF	CYCLO
ϵ_s	15.75	9.08	6.24	2.02
ϵ_∞	2.00	2.01	2.03	2.03
$E_{D^+B^-A}$, eV	1.89	2.86	3.18	5.30
k_{ET} , s^{-1}	3.98×10^{11}	5.01×10^9	7.94×10^8	3.80×10^8

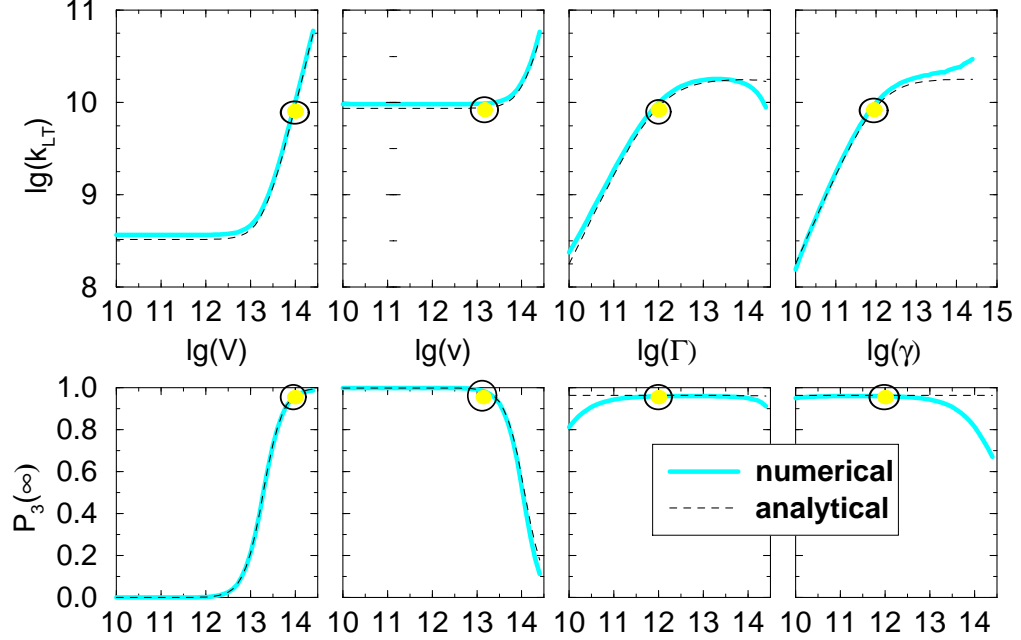


FIG. 2. The dependence of the reaction rate (upper row) and final population of the acceptor state (lower row) on the parameters $V = v_{12}$, $v = v_{23}$, $\Gamma = \Gamma_{21}$, $\gamma = \Gamma_{23}$. Solid lines correspond to the numerical solution and dashed lines to the analytical solution. The circles show the realistic parameter values for CH_2Cl_2 as solvent.

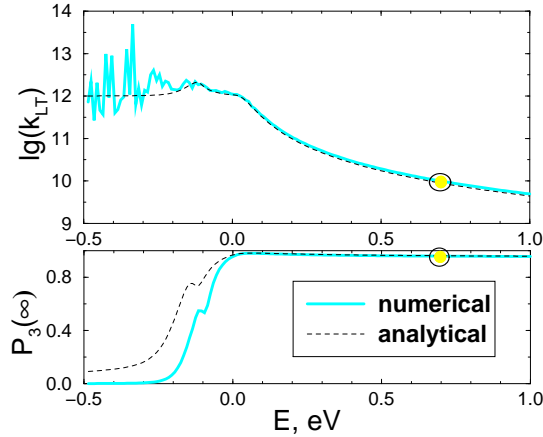


FIG. 3. Dependence of reaction rate (upper picture) and final acceptor population (lower picture) on the energy of the bridge state $E = E_{D+B-A}$. Solid lines correspond to the numerical solution and dashed lines to the analytical solution.

V. DISCUSSION

The following question will now be discussed: How does the mechanism and speed of the reaction depend on a deviation of the parameters from the determined values? Namely which parameters have to be changed in order to change not only the reaction rate quantitatively, but the dominant mechanism of reaction and the qualitative behavior of dynamics at all. To answer these questions we calculate the system dynamics while varying one parameter at a time and keeping the other parameters unchanged. The dependencies of transfer rate k_{ET} and final population $P_3(\infty)$ on coherent couplings $V = v_{12}$, $v = v_{23}$ and dissipation intensities $\Gamma = \Gamma_{21}$, $\gamma = \Gamma_{23}$ are shown in Fig. 2.

In particular, the decrease of the coherent coupling V induces a quadratic decrease of the reaction rate k_{ET} until saturation $V \sim 10^{10} ps^{-1}$. Then k_{ET} reaches its lower bound and does not depend on V anymore. This corresponds to the crossover of the reaction mechanism from SE mechanism to ST. But, due to the big energy difference

between donor and bridge state the efficiency of this ST is extremely low, i. e., $P_3 \sim 0$. The considered variation of the coherent coupling can be experimentally performed by exchanging building blocks in the supermolecule.

The most crucial change in the reaction dynamics can be induced by changing the energies of the system levels. As discussed above this can be done by altering the solvent. Most important is the relative energy of the bridge state $|D^+B^-A\rangle$. The results of the corresponding calculations are presented in Fig. 3. For high energies of the bridge state $E_{D+B-A} \gg E_{D^*BA}$ the numerical and analytical results do not differ from each other. The reaction occurs with the SE mechanism that coincides with the conclusion of Ref. . This is the case for the most of solvents (see table 2). The smooth decrease of energy induces an increase of the reaction rate up to the maximal value near 1ps^{-1} .

While the bridge energy approaches the energy of the donor state the ST mechanism starts to contribute to the process. As can be seen in table 2 this regime can be reached by the use strong polar solvents. The analytical solution does not coincide with the numerical one anymore because the used approximations are no more valid in this region. In the case $E_{D+B-A} < E_{D^*BA}$ one cannot approximate the dynamics of the acceptor population in the form $P_3 \sim [1 - \exp(-k_{ET}t)]$. A high value of the bridge energy ensures the transition of the whole population to the acceptor state $|D^+BA^- \rangle$. In the intermediate case, when the bridge state has the same energy as the acceptor state, the final population spreads itself over these two states $P_3(\infty) = 0.5$. At even lower bridge energies the population gets trapped at the bridge state.

We performed calculations for the electron transfer in the supermolecular complex $H_2P - ZnP - Q$ within the RDM formalism. The resulting analytical and numerical reaction rates are in good agreement with each other and in qualitative correspondence with experimental data []. The SE mechanism of electron transfer dominates over the sequential one. The qualitative character of the transfer reaction is stable with respect to a small variation of the system parameter. The crossover between the reaction mechanisms can be forced by lowering the bridge state energy to the energy of the donor state.

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