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# Excitation Energy Transfer and Quenching in a Heterodimer: Applications to the Carotenoid-Phthalocyanine Dyads

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## Abstract

Dynamics of a molecular hetero-dimer composed of a long-lived excitation donor and a short-lived acceptor (quencher) is examined. In order to consider various dynamical regimes without any restrictions on the system parameters, the energy transfer is modeled employing the Hierarchical equations of motion, while the relaxation to the ground state is treated by assuming a phenomenological spontaneous non-radiative decay rate. Time scales of the resulting two-exponential evolution are investigated as functions of the energy gap and the resonance coupling between the monomeric constituents of the dimer. Relevance of the present analysis to the recent experimental findings on artificial carotenoid-phthalocyanine dyads is discussed. By examining the first two time scales of the reported time-resolved spectra it is shown that upon the increase of carotenoid conjugation length its first excited state approaches the first excited state of phthalocyanine from above, thereby inducing a remarkable quenching. The proposed model also provides a unified treatment of quenching in the regimes previously distinguished as energy transfer and excitonic state formation.

Keywords: hetero-dimer, energy transfer, relaxation, non-photochemical quenching

## 1 Introduction

Electronic excitation dynamics in molecular aggregates, natural and synthetic, have been extensively studied for several decades (see for instance, (1–4)). The interest to this problem notably increased during the last years due to detailed knowledge of the naturally-occurring molecular structures, e.g. photosynthetic aggregates,<sup>5</sup> and the capability of synthesizing molecular assemblies of predefined architecture.<sup>6–8</sup> Moreover new experimental techniques (e.g. single-molecule pump-probe spectroscopy<sup>9</sup> or non-linear multi-dimensional optical spectroscopy<sup>10,11</sup>) have recently opened possibilities for detailed studies of the role of the coherence (both electronic<sup>12–17</sup> and vibrational<sup>18–21</sup>) in the exciton dynamics within the photosynthetic pigment-protein complexes. The photosynthetic light-harvesting complexes are responsible for collection of solar energy and its subsequent delivery to the reaction center, where this energy is stabilized in the form of a

trans-membrane electrochemical potential.<sup>2,5</sup> Chlorophylls (Chls) and carotenoids (Cars) are the most abundant pigment molecules assembled in these complexes, which are responsible for all the light-induced processes in plants. In addition to the principle role of delivering the absorbed light energy to the reaction center, the light-harvesting complexes from plant photosynthesis, namely from photosystem II (PSII), are also involved in self-protection and regulation of the excitation density depending on the excitation conditions (see ( 22) for a recent review). The Car molecules play the self-protection role against the triplet state formation on Chl molecules. Population of the triplet states on Chl molecules is possible as a result of intersystem crossing from the singlet excited states, which play the major role in the light-harvesting processes. Being in the triplet state Chl molecules contain sufficient energy to convert ground state triplet molecular oxygen to an excited singlet state, known to be destructive to the surrounding medium. Formation of singlet oxygen is inhibited by Car molecules as they accept Chl triplets through triplet energy transfer and the resulting Car triplet excitation is energetically too low to excite singlet oxygen.<sup>23</sup> In addition to such self-protection mechanism caused by the triplet state transfer from Chl to Car molecules, a further mechanism responsible for the excitation density control in oxygen generating PSII is invoked. This regulatory mechanism termed as non-photochemical quenching (NPQ), ensures a high efficiency and robustness of plant photosynthesis under fluctuating light, even at very high intensities.

Though the significance of NPQ in green plants is well identified, the exact nature of the underlying mechanism still remains a matter of debate.<sup>22</sup> Of the many proposed NPQ mechanisms several involve Car molecules - xanthophylls. One proposed mechanism is based on the assumption that a radical<sup>24</sup> or a charge-transfer state of a Chl-Car pair<sup>25,26</sup> may be responsible for NPQ. According to later spectroscopic observations Lutein 1 in LHCII has been identified as a strong candidate to be responsible for the feedback de-excitation, which is the main component of NPQ.<sup>27</sup> More recently<sup>28</sup> a complex charge transfer state involving Lutein 1 and two Chls as an intermediate state in quenching by Lutein 1 has been identified. The notion of lutein (or another Car) as a quencher is attractive in part due to the fact that it possesses a very short ( $\sim 10$ ps) excited state

lifetime. Interestingly, according to recent model simulations, the excitation quenching mechanism at the heart of NPQ should be very fast, possessing a characteristic time of a few ps or even less.<sup>29</sup> Alternatively, the modulation possibility of interactions between Cars and Chls<sup>30</sup> or the energy position of the Car molecule interacting with Chls<sup>31</sup> might be attributed to the quenching ability of Chl dimers due to changes in their mutual interaction driven by an anisotropic polar environment.

Since the possible role of the Car molecule in the NPQ process remains unsettled, additional studies of the excitation dynamics in the artificial dyads composed of covalently linked Car and zinc phthalocyanine (Pc) molecules have been performed.<sup>32–35</sup> The experimental data provide means to observe the energy transfer pathways in a structure similar to the Car-Chl dimer without the complementary effects of the surrounding pigments and the protein scaffold. The conclusions drawn from the energy gap dependence of various relaxation time scales serve as an inspiration to perform a rigorous modeling based on the quantum relaxation theory. To describe the excitation evolution of the dyads composed of covalently linked Car and Pc molecules, the evolution of a molecular hetero-dimer has to be considered by assuming that one monomer (Car molecule in this case) is responsible for excitation quenching. Such quality arises when the spontaneous decay time  $\tau_Q$  of the chosen monomer is comparable to the excitation energy transfer/relaxation time. Indeed, the evolution of the excitation in such systems reveals two characteristic time scales.<sup>36</sup> The first one arises from the thermal relaxation (TR) while the second one - from the relaxation to the ground state (RGS). In this paper we examine the two processes and their interplay as a function of the resonance coupling, the interaction with the thermal bath and most importantly the energy gap between the monomeric excited states in the weak resonance coupling regime, which seems to be appropriate judging by the results obtained for the dyads (especially, ( 32)). To cover a broad scope of dynamical regimes of the model system under consideration we use the hierarchical equations of motion (HEOM) method.<sup>37,38</sup> Since the properties of the constituent monomers can be matched to those of Car  $S_1$  and Chl/Pc  $Q_y$  electronic states, we are able to give a comprehensive interpretation of excitation dynamics in the dyads and make the conclusions about the possible sensitivity to characteristic parameters of the system and, thus, about the mechanism of energy dis-

sipation. In the weak coupling regime the Förster resonance energy transfer (FRET) theory<sup>2,39–41</sup> should be appropriate, hence, we compare the thermalization rates obtained by HEOM and FRET approaches.

The paper is organized in the following way. In Section 2.1 we describe an excitonically coupled dimer and general principles of the evolution of such a system. In Section 2.2 equations of motion are given in detail, while Section 2.3 provides the background for the interpretation of the relaxation time scales. We demonstrate our results in Section 3 paying attention to some peculiar aspects of TR alone and the subsequent net effect of both relaxation processes. Finally, we discuss our findings and their relevance to the experiments performed on the Car-Pc dyads in Section 4, and conclusions are presented in Section 5.

## 2 Model system

### 2.1 Excitation dynamics in a hetero-dimer

Two electronically interacting pigment molecules can be well described by means of the Heitler-London approximation.<sup>2,42</sup> In this case the single ground state and the two singly-excited states of the dimer are given as the product of the ground states of the monomers (sites)  $a, b$ ,  $|g\rangle = |g_a\rangle|g_b\rangle$ , and the product of the  $i$ th monomer in the excited state  $|e_i\rangle$  and  $j$ th monomer in ground states, i.e.  $|i\rangle = |e_i\rangle|g_j\rangle$ , respectively. In this case the Hamiltonian determining the Frenkel exciton states for the dimer can be given by:

$$H_S = \sum_{i=a,b} (\epsilon_i^0 + \lambda_i) Q_i + J(|a\rangle\langle b| + |b\rangle\langle a|), \quad (1)$$

where  $\epsilon_i^0$  denotes the  $i$ th site excitation energy,  $Q_i = |i\rangle\langle i|$  ( $i = a, b$ ) is the projector onto the  $i$ th site, and  $J$  is the resonance coupling between the monomers. The reorganization energy  $\lambda_i$  arises from the interaction of the system with the vibrational degrees of freedom of the monomers and/or with their environment. The latter might be the surrounding protein or the solvent, in either case

it is generalized as the thermal bath. The Hamiltonians of the bath and the system-bath interaction are given respectively by:<sup>4</sup>

$$H_B = T(p) + V_g(q), \quad (2)$$

$$H_{SB} = \sum_{i=a,b} \Delta V_i(q) Q_i. \quad (3)$$

Operators  $T(p)$  and  $V_i(q)$  denote the kinetic energy of the nuclei and the nuclear potential energy surface of the  $i$ th site, accordingly,  $p$  and  $q$  are the generalized momenta and coordinates of the bath. In this notation the reorganization energy is defined as

$$\lambda_i = \langle V_i(q) - V_g(q) \rangle_q, \quad (4)$$

where the angular brackets  $\langle \dots \rangle_q$  denote the averaging over the equilibrium bath. The energy gap operator  $\Delta V_i(q) = V_i(q) - V_g(q) - \lambda_i$  describes the thermal fluctuations of the energy gap between the potential energy surfaces. The time scale of fluctuations,  $\gamma_i^{-1}$ , describes the dissipation time of the reorganization energy. All characteristics of the monomers within the dimer discussed above are depicted in Fig. 1.

We switch to the eigenstates of the electronic system, i.e. to the exciton representation, by a unitary transformation that diagonalizes the system Hamiltonian defined by Eq. 1. The obtained excitonic basis is related to the molecular representation accordingly:

$$\begin{cases} |1\rangle = \cos \theta |a\rangle + \sin \theta |b\rangle; \\ |2\rangle = -\sin \theta |a\rangle + \cos \theta |b\rangle. \end{cases} \quad (5)$$

The mixing angle  $\theta = \frac{1}{2} \arctan(2J/\Delta\epsilon)$  ( $\theta \in [-\pi/4; \pi/4]$ ) depends on the resonance interaction and the energy gap  $\Delta\epsilon = (\epsilon_a^0 + \lambda_a) - (\epsilon_b^0 + \lambda_b)$  between the transition energies of the monomers. This angle describes the degree of delocalization of excitation over the monomeric states. Evi-

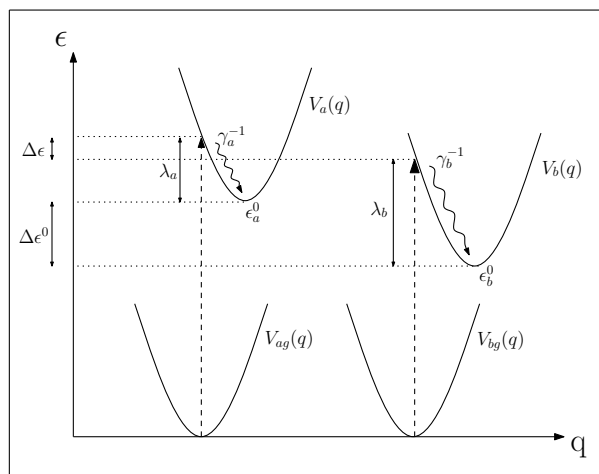


Figure 1: Parameters of the model heterodimer. The constituent monomers are depicted as pairs of mutually shifted nuclear potential energy surfaces  $V(q)$ . The dashed arrows indicate the Franck-Condon transitions. In the case of isolated monomers an optical excitation is followed by the nuclear reorganization on the excited state potential energy surface  $V_i(q)$ , which leads to the dissipation of the reorganization energy  $\lambda_i$  on the time scale of  $\gamma_i^{-1}$  (wiggly arrows). We denote the energies of the relaxed excited states by  $\varepsilon^0$  to distinguish them from the transition energies,  $\varepsilon = \varepsilon^0 + \lambda$ .

dently, in the case of small coupling and/or large energy gap the sites do not share the excitation and the excitation energy transfer can be formulated in the intuitively clear donor-acceptor picture of FRET (see the Appendix for details). However, to formulate a general scheme we invoke the density operator formalism.

The dynamics of an open quantum system is given by a reduced density operator (RDO)  $\rho(t) = \text{Tr}_q W(t)$ , where  $W(t)$  is the total density operator of the system and the bath, and  $\text{Tr}_q$  denotes the trace operation over the nuclear degrees of freedom.<sup>4,43–45</sup> The evolution of the RDO is governed by the Liouville equation:<sup>4,43,44</sup>

$$\frac{d}{dt}\rho(t) = -i\mathcal{L}\rho(t) + \mathcal{D}\rho(t) + \mathcal{K}\rho(t). \quad (6)$$

The three superoperators on the r.h.s. represent the unitary evolution, the dissipative dynamics and the RGS, respectively. The Liouvillian defined as  $\mathcal{L}\bullet \equiv \frac{1}{\hbar}[H_S, \bullet]$ , where the square brackets denote the commutator (we set  $\hbar = 1$ ), generates the quantum coherent evolution. The second term  $\mathcal{D}\rho(t)$  describes the dissipation and pure dephasing within the excited states. The description of



dissipation and the associated excitation redistribution is given in detail in the next Section. The last term is defined as  $\mathcal{K} \bullet \equiv -\sum_i \frac{\kappa_i}{2} \{Q_i, \bullet\}$ , where the curly brackets denote the anticommutator, and  $\kappa_i$  is the decay rate of the  $i$ th excited state. Parameters  $\kappa_i$  can be phenomenologically defined in the site basis.<sup>36</sup> The form of the RGS superoperator guarantees that the diagonal elements of the RDO (the populations)  $\rho_{ii}(t)$  decay with the rates  $\kappa_i$ , while the corresponding off-diagonal elements (the coherences)  $\rho_{ij}(t)$  decay with rates  $\frac{1}{2}(\kappa_i + \kappa_j)$ .

Let us assume now that initially the full density operator is of the factorized form:  $W(0) = \rho(0) \otimes W_{\text{eq}}$ , where  $W_{\text{eq}} = e^{-\beta H_B} / \text{Tr}_q e^{-\beta H_B}$  is the equilibrium density operator of the bath ( $\beta = 1/k_B T$ ). This is an important assumption since it disregards the initial correlations between the system and the bath, however, it is justified in the description of electronic excitations due to the Franck-Condon principle. To be more specific, we further consider the excitation of the system by an ultrashort pulse, which despite its spectral broadness, excites only the monomer  $a$  while the monomer  $b$  is assumed to be optically dark (conf. the Car  $S_1$  state). This results in the initial condition in the site basis as  $\langle i | \rho(0) | j \rangle = \delta_{ij} \delta_{ia}$ .

## 2.2 Hierarchical equations of motion

To describe the dynamics, which follow from the system-bath interaction, we use the recently developed HEOM scheme, which is a non-perturbative approach based on the assumption of Gaussian bath fluctuations.<sup>37,38</sup> It attracts a lot of attention after demonstrating its benefits in the description of electronic excitation dynamics in pigment-protein complexes.<sup>46</sup> While computationally expensive, HEOM has been applied to systems as large as  $\sim 50$  chromophores<sup>47</sup> - this is possible due to extensive parallelization and time-adaptive integration. Other methods to optimize HEOM include on-the-fly filtering<sup>48</sup> and utilization of graphical processing units for calculations.<sup>49</sup>

The explicit form of the hierarchical equations depends on the energy gap correlation function:

$$C_{ij}(t) = \langle \Delta V_i(t) \Delta V_j(0) \rangle_q, \quad (7)$$

were,  $\Delta V_i(t)$  is the energy gap operator in the interaction picture:  $\Delta V_i(t) = e^{iH_B t} \Delta V_i(q) e^{-iH_B t}$ . The correlation function fully determines the effect of the bath on the system. Interestingly, the functional form of Eq. 7 is crucial for the computational demands of HEOM. In practice the correlation functions are obtained from the spectral densities of the bath  $C''_{mn}(\omega)$  via the fluctuation-dissipation relation:

$$C_{ij}(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{1}{1 - e^{-\beta\omega}} e^{-i\omega t} C''_{ij}(\omega) d\omega. \quad (8)$$

The advantage of the spectral density is that it can be determined directly from fluorescence line-narrowing measurements<sup>50,51</sup> or molecular dynamics simulations,<sup>52</sup> and it does not depend on temperature and therefore encompasses the spectral content of the bath alone. In this work we assume that the bath modes at different sites are not correlated,  $C''_{ij}(\omega) = \delta_{ij} C''_i(\omega)$ , and employ the overdamped Brownian oscillator spectral density:<sup>20,43</sup>

$$C''_i(\omega) = 2\lambda_i \frac{\omega\gamma_i}{\omega^2 + \gamma_i^2}. \quad (9)$$

The parameter  $\gamma_i^{-1}$ , as previously discussed, corresponds to the correlation time of the  $i$ th monomer site energy fluctuation, and the reorganization energy now determines the system-bath coupling strength.

The goal in deriving an optimal form of HEOM is to perform a suitable approximation of the integral in Eq. 8 in the form of exponential series

$$C_i(t) = \sum_{k=0}^K c_{ik} e^{-\gamma_{ik} t} + \delta C_{iK}(t), \quad (10)$$

which is based on a certain sum-over-poles scheme and the residue theorem of contour integration. Term  $\delta C_{iK}(t)$  takes into account the difference between the exact correlation function and the approximation. Index  $k = 0$  corresponds to the pole of the spectral density defined by Eq. 9, while the remaining indices  $k = 1, \dots, K$  correspond to the poles from the Bose-Einstein distribution

function. The conventional form of the expansion given by Eq. 10 is the summation over the terms with  $\gamma_{k \geq 1} = 2\pi k/\beta$ , the well known Matsubara frequencies,<sup>44</sup> however, this scheme suffers from slow convergence. Another option is the recently proposed Padé spectrum decomposition of the Bose-Einstein function.<sup>53</sup> We employ here the scheme that uses the  $[K/K]$  Padé approximant, which was shown to provide the optimal expansion in the case of the Brownian oscillator spectral density.<sup>54</sup> For the sake of completeness, the coefficients  $c_{ik}$  and  $\gamma_{ik}$  are given in terms of system characteristics in the Appendix B. We split coefficients  $c_{ik}$  into the real and imaginary parts as  $c_{ik} = c_{ik}^{\Re} + ic_{ik}^{\Im}$  for later convenience. Term  $\delta C_{iK}(t)$  is approximated by a Markovian-white-noise residue ansatz:<sup>55</sup>

$$\delta C_{iK}(t) \approx 4R_K \lambda_i \gamma_i \beta \delta(t) \equiv \Delta_{iK} \delta(t), \quad (11)$$

where  $\delta(t)$  is the Dirac delta function and

$$R_K = \frac{1}{4(K+1)(2K+3)}. \quad (12)$$

The general form of the equations is obtained after replacing the RDO in Eq. 6 by a set of auxiliary density operators (ADOs)  $\rho(t) \rightarrow \rho_{\mathbf{n}}(t)$ , where we define a matrix  $\mathbf{n} = \{n_{10}, \dots, n_{1K}; \dots; n_{N0}, \dots, n_{NK}\}$  of non-negative integers  $n_{ik}$  for an aggregate of  $N$  chromophores. The ADO with index  $\mathbf{0} = \{0, \dots, 0; \dots; 0, \dots, 0\}$  is the RDO itself, while the remaining ones take into account the development of the system-bath correlations. The second term on the r.h.s. of Eq. 6 then reads:

$$\mathcal{D}\rho_{\mathbf{n}}(t) = - \sum_{i=1}^N \left( \sum_{k=0}^K \gamma_{ik} n_{ik} + \delta \mathcal{R}_{iK} \right) \rho_{\mathbf{n}}(t) + \sum_{i=1}^N \sum_{k=0}^K \left( \mathcal{B}_{ik} n_{ik} \rho_{\mathbf{n}_{ik}^-} + \mathcal{A}_{ik} \rho_{\mathbf{n}_{ik}^+} \right), \quad (13)$$

where  $\mathbf{n}_{ik}^{\pm} = \{n_{10}, \dots, n_{1K}; \dots; n_{i0}, \dots, n_{ik} \pm 1, \dots, n_{iK}; \dots; n_{N0}, \dots, n_{NK}\}$ . The auxiliary superoperators are:

$$\delta \mathcal{R}_{iK} \bullet \equiv \frac{\Delta_{iK}}{2} [Q_i, [Q_i, \bullet]], \quad (14)$$

$$\mathcal{B}_{ik\bullet} \equiv i \left( c_{ik}^{\Re}[Q_i, \bullet] - i c_{ik}^{\Im}\{Q_i, \bullet\} \right), \quad (15)$$

$$\mathcal{A}_{i\bullet} \equiv i[Q_i, \bullet]. \quad (16)$$

The sum of indices  $L = \sum_i \sum_k n_{ik}$  defines a *tier* of ADOs, and as can be seen, the superoperators  $\mathcal{A}$  and  $\mathcal{B}$  connect ADOs from the tier  $L$  to those from the tiers  $L \pm 1$ . Thus, formally the hierarchy continues to infinity. Of course, in practical calculations the hierarchy must be truncated at some finite length. Various truncation schemes are possible,<sup>56</sup> but the choice of the scheme is of no consequence if the converged results have been reached. In this work, we adopt the most simple truncation scheme, where all the ADOs with the tier  $L > L_{trunc}$  are simply discarded.  $L_{trunc}$  is chosen to guarantee converged results. Note that HEOM propagate the ADOs in the site basis, yet the results can be presented in any other basis, e.g. the excitonic one. As far as the measurable quantities are concerned, such as the absorption spectra, they are basis-independent, and HEOM intrinsically ensure that the delocalization effects are properly taken into account. Here, we present the results in the site basis so that they are comparable with the results obtained by FRET, and the model parameters are such that the site basis is an approximate eigenbasis.

### 2.3 Interplay of relaxation time scales

In the following we consider the time scales of relaxation in the dimer, which are defined as  $\tau_{TR}$  for the thermal relaxation and as  $\tau_{rgs}$  for the relaxation to the ground state. As for the monomers, we assume that state  $|a\rangle$  is a long-living excited state, and hence  $\kappa_a = 0$ . The short-living state  $|b\rangle$  (lifetime  $\tau_Q$ ) decays with the rate  $\kappa_b = \tau_Q^{-1} \equiv \kappa$  and, thus, plays the role of the quencher. Disregarding the coherent aspect of the initial evolution, we can describe the processes of relaxation within the dimer by the following *effective* Master equation in the excitonic basis:

$$\begin{cases} \dot{\rho}_{11} = - (k_{12} + \kappa \cos^2 \theta) \rho_{11} + k_{21} \rho_{22}; \\ \dot{\rho}_{22} = k_{12} \rho_{11} - (k_{21} + \kappa \sin^2 \theta) \rho_{22}. \end{cases} \quad (17)$$

Here,  $k_{12}$ ,  $k_{21}$  are the thermal rates that satisfy the detailed balance condition  $k_{12}/k_{21} = \exp(-\beta\Delta_e\epsilon^0)$ , where  $\Delta_e\epsilon^0$  denotes the energy gap between the relaxed excitonic states. If the reorganization energies are identical,  $\Delta_e\epsilon^0$  coincides with the excitonic splitting  $\Delta_e\epsilon = \sqrt{\Delta\epsilon^2 + (2J)^2}$ . We call Eq. 17 *effective* in the sense that the full quantum dissipative dynamics are parametrized by the thermal rates, which can be extracted from some general equation of motion for the RDO (in the absence of RGS) by numerical fitting.

The solution of Eq. 17 is of the form  $\rho_{ii}(t) = a_{i1}e^{\xi_1 t} + a_{i2}e^{\xi_2 t}$ , where  $a_{i1}$ ,  $a_{i2}$  are the amplitudes, and  $\xi_{1;2}$  are the eigenvalues of Eq. 17:

$$-|\xi_{1;2}| = -\frac{k_{12} + k_{21}}{2} - \frac{\kappa}{2} \pm \frac{1}{2}S, \quad (18)$$

where

$$S = \sqrt{(k_{12} + k_{21})^2 - \frac{2\kappa(k_{12} + k_{21})}{\sqrt{(2J/\Delta\epsilon)^2 + 1}} \tanh \frac{\beta\Delta_e\epsilon}{2} + \frac{\kappa^2}{(2J/\Delta\epsilon)^2 + 1}}. \quad (19)$$

The eigenvalues correspond to the time scales of interest as  $\tau_{rgs} = |\xi_1|^{-1}$  and  $\tau_{TR} = |\xi_2|^{-1}$ . Such attribution might look dubious as the origin of the net decay, described by  $\xi_{1;2}$ , is a mixture of both the exciton thermalization due to the interaction between the monomers and the presence of the quencher within the system. However, a closer inspection of the limiting case  $\kappa \rightarrow 0$  reveals, that  $|\xi_1| \rightarrow 0$  and  $|\xi_2| \rightarrow k_{12} + k_{21}$ , which is the classical result for the relaxation to the thermal equilibrium. More generally, when  $k_{12} + k_{21} \gg \kappa$  (usually, thermalization is much faster than the spontaneous decay) we can simplify  $S$  as follows:

$$S \approx k_{12} + k_{21} - \kappa\Phi(J, \Delta\epsilon), \quad (20)$$

where the auxiliary function  $\Phi$  is defined as

$$\Phi(J, \Delta\epsilon) = \tanh\left(\frac{\beta\Delta\epsilon}{2}\sqrt{(2J/\Delta\epsilon)^2 + 1}\right) / \sqrt{(2J/\Delta\epsilon)^2 + 1}. \quad (21)$$

The eigenvalues now read:

$$|\xi_1| \approx \frac{\kappa}{2} (1 + \Phi(J, \Delta\epsilon)), \quad (22)$$

$$|\xi_2| \approx k_{12} + k_{21}. \quad (23)$$

This shows how the effect of the quencher emerges in the dynamics: the first eigenvalue corresponds purely to the RGS, while the second one still gives the rate of thermalization as if the spontaneous decay were absent. We can estimate the time scale for the RGS as:

$$\tau_{rgs} = \frac{2\tau_Q}{1 + \Phi(J, \Delta\epsilon)}. \quad (24)$$

Since  $\Phi(J, \Delta\epsilon) \in [-1; 1]$ , RGS takes place on the time scale within the range  $[\tau_Q; 2\tau_Q]$  if the quenching state is below the donor state ( $\Phi > 0$ ), and on the time scale  $[2\tau_Q; \infty)$  otherwise ( $\Phi < 0$ ). Of course, this relation becomes less accurate when  $\Delta\epsilon \gg k_B T$  or the resonance and system-bath couplings are very small, because the condition  $k_{12} + k_{21} \gg \kappa$  breaks, yet we can use Eq. 24 as a lower bound for  $\tau_{rgs}$ . We will use this analytical result later in the analysis of the results obtained by the numerical simulations.

### 3 Results

In order to understand the time scale of the TR we first analyze the dynamics neglecting the RGS (by setting  $\kappa = 0$ ). The time scale  $\tau_{TR} = (k_{12} + k_{21})^{-1}$  is obtained by solving Eq. 6 using the HEOM approach and subsequently performing numerical fitting by means of the least square routine. We examine the cases of parameters relevant for the FRET regime,  $\lambda \gg J$ . Taking

$\lambda_a = \lambda_b = 400 \text{ cm}^{-1}$  let us consider the cases of  $\lambda/J = 20$  ( $J = 20 \text{ cm}^{-1}$ ), which is fully consistent with the FRET regime, and  $\lambda/J = 5$  ( $J = 80 \text{ cm}^{-1}$ ), which reflects the breaking of the validity of FRET. The calculated dependence of  $\tau_{TR}$  on the energy gap between the monomers is shown in Fig. 2. Calculations at temperature 300 K ( $\beta^{-1} \approx 208 \text{ cm}^{-1}$ ) are performed for two different values of  $\gamma^{-1} = \gamma_a^{-1} = \gamma_b^{-1}$ : 10 fs and 100 fs. We omit the case when the energy gap  $\Delta\epsilon = 0 \text{ cm}^{-1}$ , because the dynamics in that case are not given by the FRET scheme due to the degeneracy of monomer energies, which is out of the scope of this study.

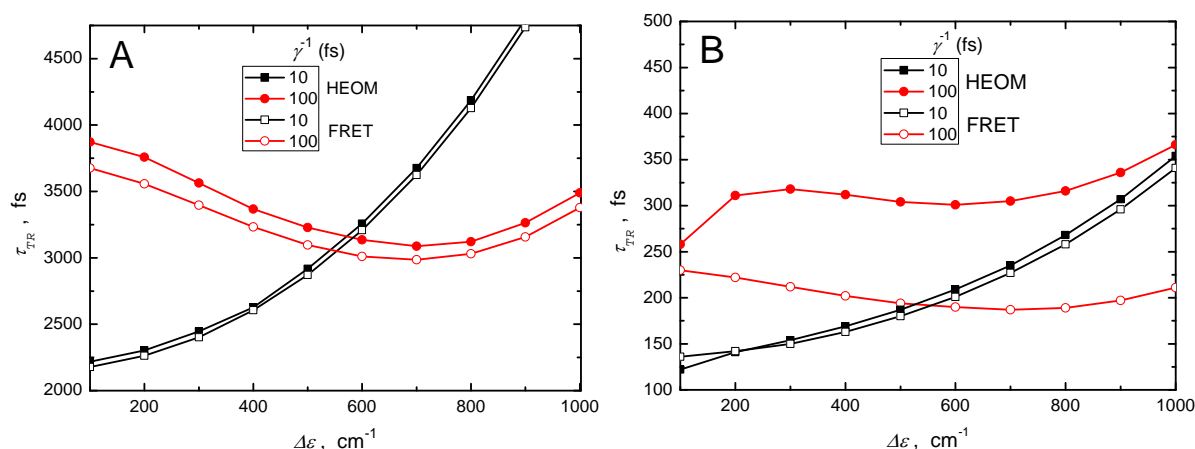


Figure 2: Comparison of TR times given by HEOM and FRET schemes for different energy gaps. For the sake of consistency, all the rates were extracted from the evolution of RDO by numerical fitting. Two cases of resonance coupling correspond to: a)  $J = 20 \text{ cm}^{-1}$ ; b)  $J = 80 \text{ cm}^{-1}$ .

In the case of small resonance coupling and fast correlation decay of the bath (black squares, Fig. 2a) the monotonic rise in the TR time is obtained upon the increase of the energy gap. This is an intuitively clear picture of thermalization and corresponds to a Markovian regime of the bath relaxation. In this case the transfer rates predicted by HEOM and FRET almost match each other. When we switch to the slow correlation decay of the bath (red dots), the dependence changes. Now an optimal system configuration for the excitation transfer around  $\Delta\epsilon \approx 700 \text{ cm}^{-1}$  is well distinguished. This is a non-Markovian regime of the bath dynamics, and the HEOM and FRET predictions are *qualitatively* identical. The FRET approach thus properly describes the parameter regime  $\Delta\epsilon \gg J$  and  $\lambda \gg J$ . We note that the dependence  $\tau_{TR}(\Delta\epsilon)$  is symmetric around  $\Delta\epsilon = 0$  because the TR rate, being the sum of the upward and downward rates  $\xi_2 = k_{12} + k_{21}$ , is invariant

under the change of the sign of  $\Delta\epsilon$ .

In the case of larger resonance coupling, Fig. 2b, the relaxation is substantially faster as should be expected. Another difference is visible in the HEOM results when energy gaps are  $\Delta\epsilon \leq 300\text{cm}^{-1}$ . The decrease of  $\tau_{TR}$  for smaller energy gaps is the manifestation of the excitonic delocalization effects. For larger gaps both HEOM and FRET have an optimal energy gap configuration in the non-Markovian regime. While the absolute difference in  $\tau_{TR}$  values calculated by HEOM and FRET is similar as in Fig. 2a, the relative difference between them in the non-Markovian regime now becomes significant. However, the FRET approach still gives a reasonable prediction.

There are two more points to mention which are not shown here explicitly. The first one is that the rate  $k_{12} + k_{21}$  does not depend on individual reorganization energies, but rather on their sum  $\lambda_a + \lambda_b$ . The second one is that the speed-up seen in the non-Markovian regime diminishes upon decreasing  $\lambda_a + \lambda_b$ .

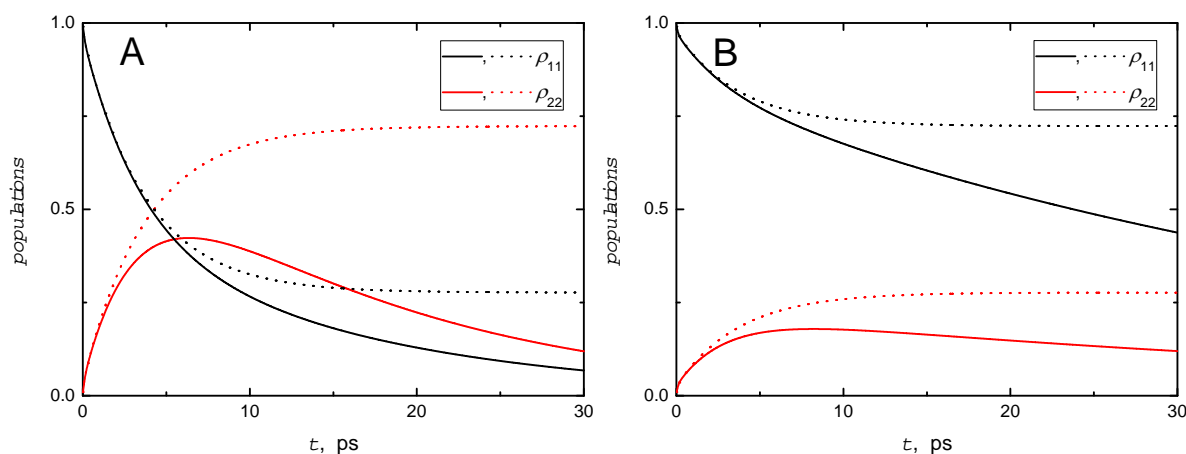


Figure 3: Relaxation in the dimer. The dotted lines correspond to thermal relaxation alone, while the full lines correspond to the combined process. The energy gap is: a)  $\Delta\epsilon = +200\text{cm}^{-1}$ ; b)  $\Delta\epsilon = -200\text{cm}^{-1}$ . Temperature and reorganization energies are the same as in Fig. 2;  $J = 20\text{cm}^{-1}$ ,  $\gamma^{-1} = 100\text{fs}$ .

Let us now take the RGS into account by considering the excitation dynamics in the dimer while assuming  $\tau_Q = 10\text{ps}$ . Fig. 3 shows the excitation evolutions both in the presence (full lines) and in the absence (dotted lines) of the RGS in the cases of  $\Delta\epsilon = \pm 200\text{cm}^{-1}$  ( $J = 20\text{cm}^{-1}$ ). As can



be seen, the energetic position of the quencher has an effect on both the rates and the amplitudes of the process. The amplitude dependence largely comes from the unquenched dynamics. The latter gives us the time scale for TR alone as  $k_{12} + k_{21} = 1/3.8$  ps. By performing a two-exponential fitting we obtain the following time scales for the combined process: a)  $\tau_{TR} = 3.2$  ps,  $\tau_{rgs} = 15.6$  ps; b)  $\tau_{TR} = 2.8$  ps,  $\tau_{rgs} = 46.2$  ps. Although the condition  $k_{12} + k_{21} \gg \kappa$  is not very accurate in this situation, we still can check the time scale  $\tau_{rgs}$  against the theoretical limit given by Eq. 24. For the current parameters it gives: a)  $\tau_{rgs} = 13.8$  ps; b)  $\tau_{rgs} = 36.1$  ps. As we can see, Eq. 24 gives the right tendency although the numerical value is appreciably different for  $\Delta\epsilon = -200$  cm<sup>-1</sup>.

To demonstrate the net effect of the RGS and TR in the non-Markovian regime we calculate evolutions for the energy gaps  $\Delta\epsilon = -200$  cm<sup>-1</sup> and  $\Delta\epsilon = -650$  cm<sup>-1</sup>, as shown in Fig. 4. Other parameters are the same as in Fig. 3, only the reorganization energies are such that  $\lambda_a + \lambda_b = 1000$  cm<sup>-1</sup>. The parameters are chosen to yield a rough fit of the signal decay time scales corresponding to dyads 2 and 3 from Ref. (32). Energy gap  $\Delta\epsilon = -200$  cm<sup>-1</sup> (black line) corresponds to the time scales  $\tau_{TR} = 3.7$  ps,  $\tau_{rgs} = 49.9$  ps, whereas for the gap  $\Delta\epsilon = -650$  cm<sup>-1</sup> (red line) we get  $\tau_{TR} = 2.7$  ps,  $\tau_{rgs} = 311$  ps. Note the decrease of the amplitude associated with the TR.

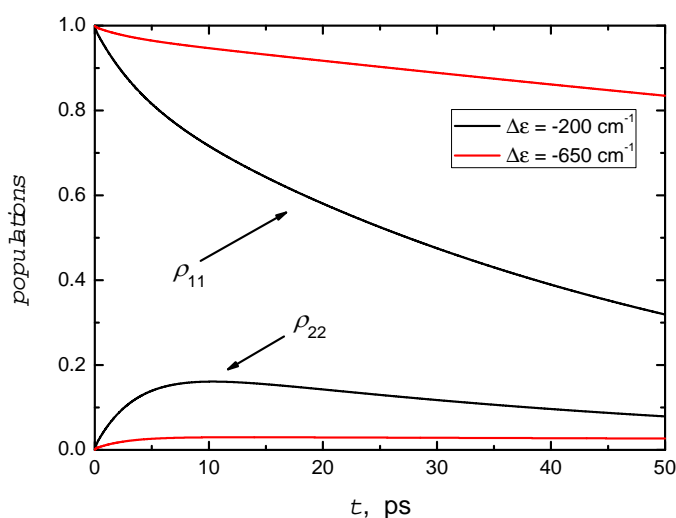


Figure 4: Relaxation in the dimer upon the increase of the energy gap. The black lines correspond to the smaller gap ( $\Delta\epsilon = -200$  cm<sup>-1</sup>), the red ones correspond to the larger gap ( $\Delta\epsilon = -650$  cm<sup>-1</sup>).

## 4 Discussion

### 4.1 Effect of non-Markovian bath dynamics in thermal relaxation

Our calculations of the thermalization dynamics reveals the existence of an optimal energy gap that depends on the system-bath coupling and the relaxation time scale of the bath correlations. Similar results demonstrating the speed-up of the energy transfer upon increasing the value of  $\Delta\epsilon$  in a certain region have also been previously demonstrated.<sup>40,57</sup> For better understanding of its origin, let us start our consideration from the case of the small resonance coupling when the site and the excitonic bases almost coincide and the results of HEOM and FRET are directly comparable. This allows us to follow the details of the energy gap dependence of the excitation transfer in terms of FRET, where the transfer rates have an explicit form. Namely, they are proportional to the overlap of the donor emission and acceptor absorption profiles, Eq. 25. The profile functions of the form of Eq. 26 for the transitions  $|g_i\rangle \rightarrow |e_i\rangle$  define the absorption/emission line-shapes in the various bath regimes separated by values of a corresponding dimensionless modulation parameter  $\chi = 2\lambda/\beta\gamma^2$ .<sup>43</sup> Fig. 5a demonstrates absorption (black line) and emission (gray lines) profiles for different displacements  $\Delta\epsilon$  of the donor in the case of  $\gamma^{-1} = 10$  fs (fast bath). Parameter  $\chi = 0.59$  is close to the fast modulation (homogeneous) limit  $\chi \ll 1$ , which manifests in Lorentzian profiles and the absence of the Stokes shift.<sup>58</sup> In Fig. 5b the same situation is depicted for the case of  $\gamma^{-1} = 100$  fs, which corresponds to  $\chi = 59$ . Condition  $\chi \gg 1$  is known as the slow modulation (inhomogeneous) limit, and it manifests in Gaussian profiles and a clearly developed Stokes shift.<sup>58</sup> The interpretation of relaxation rates in terms of Fig. 5 is the following. In the Markovian bath regime there is little-to-none Stokes shift, and the donor fluorescence yields the best overlap with the acceptor absorption at small  $\Delta\epsilon$ . Whereas in the non-Markovian regime there is a Stokes shift close to its maximum of  $2\lambda$  that needs to be compensated by displacement  $\Delta\epsilon$  to yield the maximum overlap. This is shown in Fig. 2a, where the energy gap for optimal relaxation in the case of slow bath is close to  $\lambda_a + \lambda_b$ .<sup>57</sup>

The case of the relatively large resonance coupling, Fig. 2b, demonstrates similar dependencies

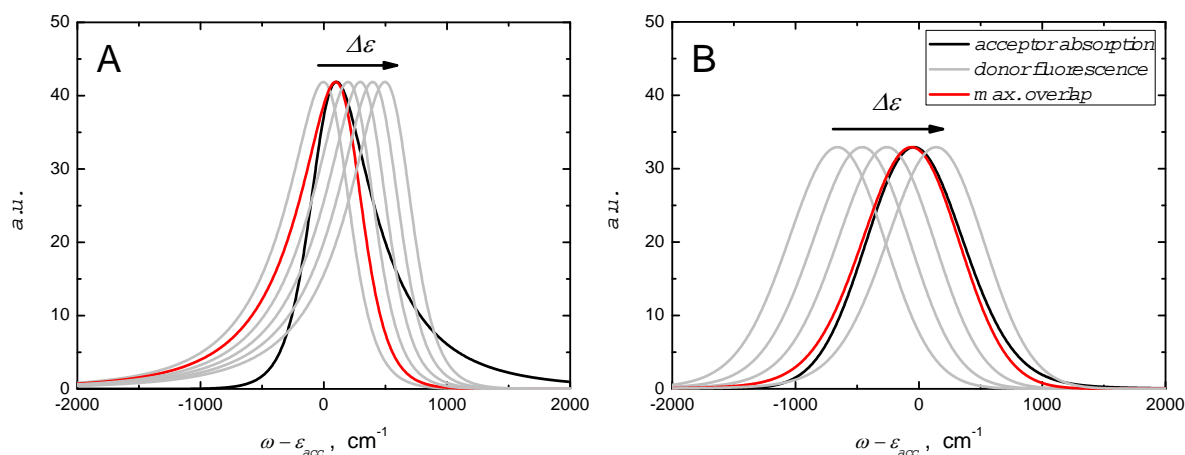


Figure 5: Emission/absorption profiles of the donor and the acceptor in the case of: a) fast bath; b) slow bath. Absorption of the acceptor (black line) is fixed, while the donor emission profiles (gray) are given for different energy gaps. The donor is above the acceptor, and the values of  $\Delta\epsilon$  ( $\text{cm}^{-1}$ ) read (left to right): a) 100, 200, 300, 400, 500, 600; b) 100, 300, 500, 700, 900. The emission profile producing the maximal overlap with the absorption profile is given in red; note that it does not exactly match the optimal  $\Delta\epsilon$  and is given for the purpose of illustration only. Frequency is centered around the maximum of the acceptor absorption.

even though the relative difference between HEOM and FRET is considerable in the case of the slow relaxation of the bath correlation. The main difference other than the globally increased rates, is the speed-up in the region of  $\Delta\epsilon$  where the excitonic mixing is significant. It is interesting to note, that the transfer rates actually depend on the energy gap between the relaxed states  $\Delta\epsilon^0 = \epsilon_a^0 - \epsilon_b^0$  (conf. Fig. 1) as opposed to  $\Delta\epsilon$  defined in Section 2.1. In the case of identical reorganization energies,  $\Delta\lambda = \lambda_a - \lambda_b = 0$ , the gaps  $\Delta\epsilon^0$  and  $\Delta\epsilon$  coincide. Otherwise, the following consequences arise. If the resonance coupling is small, the two energy gaps are simply mutually shifted by  $\Delta\lambda$ . The relaxation time should then be plotted as a function of the gap  $\Delta\epsilon^0$ , and the decrease in  $\tau_{TR}(\Delta\epsilon^0)$  that is now centered at  $\Delta\epsilon^0 = 0$ , would be centered at  $\Delta\epsilon^0 = \Delta\lambda$ . However, if the resonance coupling is large, the relation between  $\Delta\epsilon^0$  and  $\Delta\epsilon$ , or rather  $\Delta_e\epsilon^0$  and  $\Delta_e\epsilon$ , is no longer that simple.<sup>36</sup>

## 4.2 Energy gap dependence of the combined relaxation process

As follows from our analysis presented above, the two time scales of the evolution of the donor-quencher combined dimer have the following origin. One of the rates and the corresponding amplitude is largely determined by details of the relaxation to the thermal equilibrium in the absence of quenching, Fig. 3. While this rate is independent of the sign of  $\Delta\epsilon$ , the amplitude indicates the sign due to thermodynamic reasoning as follows. State  $|1\rangle$  being optically accessible is always initially over-populated with respect to the equilibrium, therefore  $\rho_{11}(t)$  is always decreasing. Yet, the amplitude of the decrease is significantly larger for  $\Delta\epsilon > 0$  (state  $|1\rangle$  is the upper state) than for  $\Delta\epsilon < 0$  (dark state  $|2\rangle$  is the upper state). The second rate is determined by the quencher lifetime and its energy position. Interestingly, if the lifetime and the thermal relaxation time scale are well separated, the RGS time scale does not depend on the system-bath coupling, conf. Eq. 24, yet the asymmetry between the situations of  $\Delta\epsilon > 0$  and  $\Delta\epsilon < 0$  again arises from the thermodynamic groundings, conf. the hyperbolic tangent function in Eq. 21. In this case, the values of  $\tau_{rgs}$  for various resonance couplings and energy gaps are shown in Fig. 6. We can see that when the excited state of the quencher is below the donor excited state ( $\Delta\epsilon > 0$ ), the relaxation time  $\tau_{rgs}$  is less than twice the quencher lifetime and weakly depends on the resonance coupling and the absolute value of the energy gap. In the opposite case,  $\tau_{rgs} > 2\tau_Q$  and the dependence on the energy gap is clearly pronounced.

## 4.3 Excitation evolution in the Car-Pc dyads

The model of excitonically coupled dimer described above can be used for the analysis of the excitation kinetics in Car-Pc dyads, which consist of a zinc Pc covalently linked to a series of Cars with different number of carbon-carbon conjugated double bonds. The evolution of excitation within such systems has been recently traced by means of transient absorption spectroscopy.<sup>32,33</sup> The experiments focused on determining the correlation between the lifetime of the Pc excited state and the number of conjugated double bonds within Car moiety. Berera et al. studied carbonyl-linked dyads<sup>32</sup> (the name comes from the terminal group of Car moiety), while Klotz et al. per-

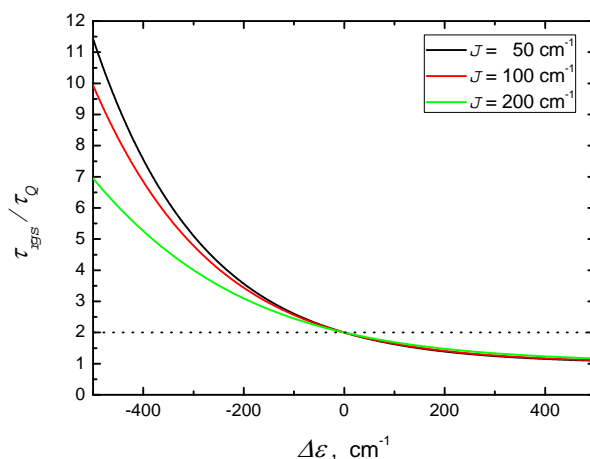


Figure 6: Time scale of the relaxation to the ground state  $\tau_{rgs}$  as a function of the energy gap and the resonance coupling according to Eq. 24. The time scale is normalized to the lifetime of the quencher  $\tau_Q$ .

formed identical measurements on phenylamino-linked dyads.<sup>33</sup> After pumping the system into the  $Q_y$  absorption band of the Pc (670 – 680 nm), the decay of the  $Q_y$  signal (ground state bleach and stimulated emission) was observed both in the kinetic traces at the same wavelength and the evolution-associated decay spectra (EADS) obtained by the global analysis of the time-resolved data.<sup>59</sup> Several time components were needed for an adequate fit, however, we take into consideration only the two fastest ones since we find the rest to be in agreement with the interpretation proposed by the authors. The values of the relevant time scales taken from the figures of the EADS in Refs. ( 32) and ( 33) are summarized accordingly in Table 1 and Table 2.

We map the dyads onto our model assuming that a dimer is formed due to the coupling of the Car first excited state  $S_1$  to the Pc  $Q_y$  state. Car  $S_1$  is an optically dark state, moreover, it is an extremely short-lived state ( $\tau_{S_1} \approx 5 - 10$  ps) due to the ultrafast internal conversion.<sup>23,60</sup> Therefore Car  $S_1$  corresponds to the state  $|b\rangle$  from our generic model, and the long-lived ( $\tau_{Q_y} \sim 3$  ns), bright state  $Q_y$  corresponds to the state  $|a\rangle$ . Upon these definitions the condition  $\Delta\epsilon^0 > 0$  corresponds to  $Q_y$  being above  $S_1$ . We note that  $\epsilon_{S_1}$ , and hence  $\Delta\epsilon^0$ , as of today is still a debated parameter,<sup>60</sup> therefore we use  $\Delta\epsilon^0$  as an adjustable variable in our calculations.

Firstly, let us discuss the carbonyl-linked dyads in tetrahydrofuran (THF).<sup>32</sup> The experimentally determined decay times for all these dyads are presented in Table 1. Starting with dyad 3

(11 double bonds) the first two time scales (3.8ps and 56ps) are of the order of correspondingly the energy transfer in weakly coupled molecular aggregates and the lifetime of the  $S_1$  state. If we subsequently assume that these time scales correspond to the rates  $\xi_2$  and  $\xi_1$ , Eq. 18, the following estimates are to be proposed. Since the longer time scale is more than twice the Car  $S_1$  lifetime  $\tau_{S_1}$  (which we approximated here and further as  $\tau_{S_1} \equiv \tau_Q = 10$ ps), we can expect that the  $S_1$  state is actually above the  $Q_y$  state. Next, by noting that the sum of the eigenvalues Eq. 18 yields  $k_{12} + k_{21} = |\xi_1| + |\xi_2| - \kappa$ , we can estimate the thermalization time scale to be  $(k_{12} + k_{21})^{-1} \approx 5$ ps. This indicates that the transfer proceeds within the Förster regime, i.e. the resonance coupling is small ( $J \ll \Delta\epsilon$ ) and the reorganization energies are large ( $\lambda \gg J$ ), which is plausible in the dyad, since the Car  $S_1$  state, while being close to the Pc, optically carries no transition dipole. To obtain the set of parameters consistent with both time scales we have performed modeling by using the HEOM scheme with the RGS for certain ranges of  $J$ ,  $\lambda$  and  $\Delta\epsilon$ . The results are given in Fig. 4 (black line), and the determined parameters yield the time scales  $\tau_{TR} = 3.7$ ps,  $\tau_{rgs} = 49.9$ ps when the relaxed Car  $S_1$  is  $200\text{cm}^{-1}$  above the relaxed Pc  $Q_y$ . Such a slow thermalization requires not only a small resonance coupling ( $J = 20\text{cm}^{-1}$ ) but also considerably large reorganization energies:  $\lambda_a + \lambda_b = 1000\text{cm}^{-1}$ . This might look surprising bearing in mind that the FWHM of the  $Q_y$  absorption, which is proportional to  $\lambda_{Q_y}$ , is roughly  $400\text{cm}^{-1}$  at most. However, we cannot assess  $\lambda_{S_1}$  in the same way, and the latter might make a significant contribution.<sup>61</sup> To make sure that the obtained time scales are not just coincidental, but are instead indicative of a consistent physical mechanism, we varied the energy gap while keeping all the other parameters unchanged. We found that shifting the energy gap to  $\Delta\epsilon^0 = -650\text{cm}^{-1}$  yields  $\tau_{TR} = 2.7$ ps,  $\tau_{rgs} = 311$ ps, Fig. 4 (red line). The latter time scales are characteristic for dyad 2 (10 double bonds), although global analysis indicates three time scales: 1ps, 8ps and 300ps. Here, we make an assumption that the actual rate most probably has the value between  $(1\text{ps})^{-1}$  and  $(8\text{ps})^{-1}$ , because both processes have relatively small amplitudes. A further shift in energy,  $\Delta\epsilon^0 = -1100\text{cm}^{-1}$ , yields time scales  $\tau_{TR} = 2.7$ ps,  $\tau_{rgs} = 2.7$ ns, which resemble those of dyad 1 (9 double bonds): 1.25ps, 3ns. The time scale  $\tau_{TR}$  almost coincides with the previous value due to approximate symmetry of the

non-Markovian rate function  $\tau_{TR}(\Delta\epsilon)$ . What is important, the value of  $\tau_{rgs}$  illustrates the highly non-linear dependence  $\tau_{rgs}(\Delta\epsilon)$  in the region of negative energy gaps, Fig. 6. These results are summarized in Table 1.

**Table 1: Comparison of experimentally detected and theoretically obtained time scales for carbonyl-linked dyads in THF. DB denotes the number of conjugated double bonds of Car moiety;  $\tau_{1st}$  denotes the fastest time scale shown in Fig. 2 from Ref. (32) and  $\tau_{2nd}$  is the second fastest time scale. \*these are two individual time scales in Ref. (32); see text for details.**

Experiment			Theory		
DB	$\tau_{1st}$ , ps	$\tau_{2nd}$ , ps	$\Delta\epsilon^0$ , cm <sup>-1</sup>	$\tau_{TR}$ , ps	$\tau_{rgs}$ , ps
9	1.25	3000	-1100	2.7	2700
10	(1 – 8)*	300	-650	2.7	311
11	3.8	56	-200	3.7	49.9

Before formulating the general conclusion from these findings we would like to note that in dyad 3, the rise at > 550nm on the 3.8ps time scale has been previously attributed to the inverted kinetics behavior. However, the rise of the mentioned component could in principle be due to the initial under-population (with respect to the equilibrium) of the optically dark state  $|2\rangle$  as discussed above. In Fig. 4 we can see the initial rise of  $\rho_{22}$  on the time scale  $\tau_{TR}$ , and the amplitude is decreasing upon the increase of  $\Delta\epsilon^0$ , which correlates with the experimental observations. Therefore we can suggest that in the carbonyl-linked dyads in THF, the Car  $S_1$  state approaches Pc  $Q_y$  state from above upon increasing the conjugation length of the carotenoid from 9 double bonds (no significant quenching;  $S_1$  state "too high") to 11 double bonds ( $S_1$  state right above the  $Q_y$  state; significant quenching). The modeling presented here demonstrates how the so-called "molecular gear shift mechanism"<sup>62</sup> could function in the presence of a small resonance coupling and *without* switching of the states due to addition of a single double bond.

Let us now consider the phenylamino-linked dyads in toluene and THF.<sup>33</sup> Since the evolutions have a strikingly different character depending on the solvent, we start with Dyad-10 and Dyad-11 (10 and 11 double bonds, accordingly) in toluene, and the corresponding decay times are presented in Table 2. Again, the first two time scales resemble those of thermalization and

relaxation: 0.4 ps and 67 ps for Dyad-10, 0.5 ps and 29 ps for Dyad-11. The TR on the time scale of several hundreds of femtoseconds points to larger resonance coupling than previously. The RGS time scale suggests that the quenching state is again above the donor state. On the assumption that the dyads are similar to those of Ref. ( 32), we keep all parameters the same only setting the resonance coupling to  $J = 80 \text{ cm}^{-1}$ . Varying the energy gap we find that  $\Delta\epsilon^0 = -150 \text{ cm}^{-1}$  yields  $\tau_{TR} = 530 \text{ fs}$ ,  $\tau_{rgs} = 31 \text{ ps}$ , and  $\Delta\epsilon^0 = -300 \text{ cm}^{-1}$  yields  $\tau_{TR} = 420 \text{ fs}$ ,  $\tau_{rgs} = 52 \text{ ps}$ . The results are summarized in Table 2. Both the time scales and the amplitudes correlate with the observed Pc  $Q_y$  signal, except that experimentally no rising component in the excited state absorption of Car  $S_1$  was detected. It has been suggested<sup>33</sup> that this could be due to excitonic mixing of the states which would instantaneously populate the state  $|2\rangle$  as well as  $|1\rangle$  and therefore only the decay would be observed. In our calculations this is not the case, because despite rather large  $J$ , the difference in reorganization energy  $\Delta\lambda$  makes the energy gap  $\Delta\epsilon$  too broad to yield detectable excitonic mixing. This introduces a discrepancy between our model and the spectroscopic data, unless the Car  $S_1$  contribution to the signal is overwhelmed by the decay of the components from other participating states.

**Table 2: Comparison of experimentally detected and theoretically obtained time scales for phenylamino-linked dyads in toluene. Notation is the same as in Table 1; the experimental data is taken from Fig. 2 from Ref. ( 33)**

DB	Experiment		$\Delta\epsilon^0, \text{ cm}^{-1}$	Theory	
	$\tau_{1st}, \text{ ps}$	$\tau_{2nd}, \text{ ps}$		$\tau_{TR}, \text{ ps}$	$\tau_{rgs}, \text{ ps}$
10	0.4	67	-300	0.42	52
11	0.5	29	-150	0.53	31

The same dyads evolve on entirely different time scales in THF. The thermalization time scale  $(k_{12} + k_{21})^{-1}$  varies from 8.7 ps to 5.6 ps (Dyads -8 to -11), which is again indicative of the Förster regime. Such a drastic drop in the transfer rates suggests that some other state than  $S_1$  should be responsible for the quenching. Yet if we consider the lifetime of this quencher to be similar to the one of the Car  $S_1$ , we can notice, that  $\tau_{rgs} < 2\tau_Q$ , which means that the excitation energy of the quencher is now below the one of the donor. There are two more arguments that would support



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3 this hypothesis. Firstly, the decrease of the signal at 700nm proceeds in two steps of comparable  
4 amplitudes (conf., Fig. 3a). Secondly, there is no significant energy gap dependence on  $\tau_{rgs}$  (conf.,  
5 Fig. 6). What weakens the hypothesis is the absence of a rising counterpart component in the  
6 spectra.  
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11 Our treatment thus leads to a unified picture of processes within a range of different dyads. As  
12 an important result we have demonstrated that a significant decrease in the quenching time for Pc  
13 in the dyads for longer Cars does not necessarily indicates that the Car  $S_1$  state is below the Pc  
14  $Q_y$ , although such an argument is sometimes given. At this point it is interesting to note that if  
15 our assignment of the rates  $\xi_1$  and  $\xi_2$  to the observed time scales is correct, the experiments on the  
16 dyads provide a direct proof of an energy gap dependent speed-up of the TR due to non-Markovian  
17 bath. We would like to note that by the modeling discussed above we did not intend to actually  
18 pinpoint the parameters yielding the experimentally detected time scales. For instance, we did  
19 not include the variation of  $\tau_Q$  with the length of the Car backbone. At this stage we also do not  
20 consider whether the quenching state is actually the  $S_1$  or  $S^*$ , or a charge transfer state. Instead, our  
21 goal was to provide insights into the evolution of the donor-quencher system, especially focusing  
22 on the role of the system-bath interaction which is usually neglected.  
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36 Calculations with different resonance couplings show that there is no significant difference in  
37 the quenching mechanism while changing from the incoherent energy transfer (Förster) regime to  
38 the coherent one. Although the excitations are localized in our current scheme due to large energy  
39 gap  $\Delta\epsilon$ , in our previous work<sup>36</sup> we have taken into consideration a finite delocalization (as due  
40 to  $\Delta\epsilon = J$ ,  $J \approx \lambda$ ). We have demonstrated therein that the excitation decays with a single rate  
41 because the joint system of excitonically mixed states is kept in a dynamical equilibrium. The time  
42 scale of the decay is governed by the same law, Eq. 24. This discloses a common misconception  
43 associated with the role of excitonic mixing in the quenching of excitation energy. Namely, it has  
44 been implied that the efficient quenching might arise as a consequence of the excitonic mixing of  
45 lifetimes.<sup>63</sup> As can be seen, when the excitation decay is rigorously included into the quantum  
46 dissipative dynamics, Eq. 6, the rates  $\kappa \cos^2 \theta$  and  $\kappa \sin^2 \theta$  are *not* the true rates of the global  
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energy dissipation. Instead, the exciton-phonon interaction leads to the Master equation of the type given by Eq. 17, thus the actual rate of the RGS is  $\xi_1$ , and  $\xi_1 > \kappa \sin^2 \theta$  for all  $\Delta\epsilon \neq 0$ . Hence, from our unified perspective it does not seem that the quenching mechanisms termed as "energy transfer" and "excitonic coupling"<sup>33,35</sup> would really be distinct from one another.

## 5 Conclusions

In this work we have modeled artificial Car-Pc dyads as heterodimers consisting of resonantly coupled excitation donor and quencher, namely, an acceptor of an extremely short lifetime. We have demonstrated that the given method provides a unified picture of different (viz., carbonyl- or phenylamino- linked) dyads, and that it is capable of consistently explaining the first two time components of the transient absorption spectra. We have come to the conclusion that the first time scale is associated with the energy transfer from the Pc  $Q_y$  state to the Car  $S_1$  state, contrary to the interpretation in terms of the inverse kinetics scheme. The energy transfer proceeds within the FRET regime, and certain indications of non-Markovian bath correlations can be distinguished. The second time scale is related to the quenching rate, for which we obtained an analytical approximation in terms of the Car  $S_1$  lifetime, energy gap and resonance coupling. The latter expression, together with the numerical results, shows that a significant quenching can be achieved even if the relaxed  $S_1$  state is energetically above the  $Q_y$  state, which contradicts the common expectations that the two states must be swapped under quenched conditions. Moreover, the unified treatment of coherent and incoherent energy transfer regimes allowed us to demonstrate that, except for the speed-up in thermal relaxation, no qualitatively new features in the overall dynamics arise because of excitonic mixing. Although the formation of excitonic states is sometimes distinguished as a separate regime of quenching, we show that due to the exciton-phonon coupling the evolution of the excitation is in principle equivalent to that within an incoherent donor-quencher system.

## Acknowledgment

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## A Transfer rates within FRET theory

According to FRET, the excitation from the donor chromophore to the acceptor chromophore is transferred with the rate:

$$k_{ab} \propto |J_{ab}|^2 \int_{-\infty}^{\infty} d\omega \tilde{F}_a(\omega) \tilde{A}_b(\omega), \quad (25)$$

where  $\tilde{F}_a(\omega)$  and  $\tilde{A}_b(\omega)$  are the fluorescence and absorption profiles of the donor ( $|a\rangle$ ) and acceptor ( $|b\rangle$ ) accordingly. Tilde denotes the Fourier transform, and the profile functions in the time domain read:

$$\begin{cases} F_a(t) = \exp(-i(\epsilon_a^0 - \lambda_a)t - g_a^*(t)), \\ A_b(t) = \exp(-i(\epsilon_b^0 + \lambda_b)t - g_b(t)); \end{cases} \quad (26)$$

here,  $g(t)$  is the line shape function<sup>43</sup> defined as

$$g_i(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 C_i(t_2), \quad (27)$$

and  $C_i(t)$  is the energy gap correlation function, Eq. 7.

## B HEOM coefficients

The coefficients  $c_{ik}^{\mathfrak{R}}$ ,  $c_{ik}^{\mathfrak{S}}$  and  $\gamma_{ik}$  introduced in Section 2.2 are given as:<sup>54</sup>

$$c_{ik}^{\mathfrak{R}} = \begin{cases} \frac{2\lambda_i}{\beta} + \sum_{k'=1}^K \frac{4\eta_{k'}\lambda_i\gamma_i^2}{\beta(\gamma_i^2 - \varphi_{k'}^2)} - 2R_K\beta\lambda_i\gamma_i^2, & k = 0; \\ \frac{4\eta_k\lambda_i\varphi_k\gamma_i}{\beta(\varphi_k^2 - \gamma_i^2)}, & k > 0; \end{cases} \quad (28)$$

$$c_{ik}^{\mathfrak{S}} = \begin{cases} -\lambda_i\gamma_i, & k = 0; \\ 0, & k > 0; \end{cases} \quad (29)$$

$$\gamma_{ik} = \begin{cases} \gamma_i, & k = 0; \\ \varphi_k, & k > 0. \end{cases} \quad (30)$$

The Padé coefficients  $\eta_k$  and poles  $\varphi_k$  are calculated by defining the following matrices:

$$\Lambda_{mn} = \frac{\delta_{m,n\pm 1}}{\sqrt{(2m+1)(2n+1)}}, \quad (31)$$

where  $m, n = 1, 2, \dots, 2K+1$ , and

$$\tilde{\Lambda}_{mn} = \frac{\delta_{m,n\pm 1}}{\sqrt{(2m+3)(2n+3)}}, \quad (32)$$

where  $m, n = 1, 2, \dots, 2K$ . The matrices  $\Lambda_{mn}$  and  $\tilde{\Lambda}_{mn}$  have the eigenvalues  $\pm \frac{2}{\psi_k}$  and  $\pm \frac{2}{\tilde{\psi}_k}$ , accordingly. The Padé poles are then  $\varphi_k = \frac{\psi_k}{\beta}$ , and the coefficients are

$$\eta_k = \frac{1}{2}R_K \prod_{j=1}^K (\tilde{\psi}_j^2 - \psi_k^2) / \prod_{j \neq k}^K (\psi_j^2 - \psi_k^2). \quad (33)$$

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Graphical TOC Entry

