

Memory Effects in the Fluorescence Depolarization Dynamics Studied within the B850 Ring of Purple Bacteria

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The time dependence of the anisotropy of fluorescence in the B850 ring of the purple bacterium *Rhodospseudomonas acidophila* is calculated using the reduced density matrix formalism. The influence of static and dynamic disorder is taken into account simultaneously. Extending earlier calculations within the Markovian Redfield theory (*Chem. Phys.* **2002**, 275, 1), which were based on a perturbative treatment of the exciton–phonon coupling, the focus of the present work is on memory effects within the exciton dynamics. For this purpose two different ways of treating non-Markovian effects are discussed and compared in a simplified model of the B850 ring with equal intercenter couplings. In addition, the influence of possible elliptical deformations of the ring on the anisotropy of fluorescence is discussed.

I. Introduction

The energy conversion in photosynthesis is initiated by highly efficient light collection and excitation transfer toward the reaction center.^{1–3} These processes take place in the so-called light-harvesting systems (LHs). The LHs of purple bacteria, which are ring-shaped aggregates of proteins that contain two types of pigments, bacteriochlorophylls (BChls) and carotenoids,^{4,5} are especially well studied. In the focus of the present contribution is the antenna complex LH2 from the bacterium *Rhodospseudomonas acidophila*. The first high-resolution three-dimensional X-ray structure of this complex was published by McDermott et al.⁶ in 1995. The complex LH2 consists of nine identical subunits of which each is formed by two proteins with bound BChls. Because this LH2 complex was at the focus of many experimental and theoretical studies already, quite some knowledge has been accumulated about its properties.^{3,7} At the same time, many questions still remain open. There is at present a general understanding that the electronic excitations in the B850 LH2 ring are at least to some extent delocalized, even at room temperature. The resulting excitonic states are properties of a molecular group, not of a single molecule. The possibility of a (partially) coherent exciton transfer in the ring bacteria antenna subunits has been theoretically discussed and applied in several papers.^{8–15}

In a ring without static and dynamic disorder, in which the Q_y transition dipole moments of the B850 BChls all lie approximately in the plane of the ring, all the dipole strength of the B850 band comes from a degenerate pair of orthogonally polarized transitions at an energy slightly higher than the transition energy of the lowest exciton state. The absorption and circular dichroism spectra⁷ as well as hole burning spectra¹⁶

of the LH2 complex are reproduced reasonably well by theoretical treatments that consider extended Frenkel exciton states but invoke moderate static disorder in the excitation energies of the individual BChls. These studies are based on model systems as applied in the present contribution, too. How the parameters of such models of the B850 ring can be deduced from atomistic calculations has been shown in ref 17.

Time-dependent experiments (absorption, fluorescence, photon echo, etc.), which used (sub)picosecond light pulses of low energy with high repetition rate tunable through the infrared absorption bands of the various BChl pigments in a variety of bacterial antenna systems, made it possible to study the long-time as well as the femtosecond dynamics of the energy transfer and relaxation.^{2,18,19} The nature of the rapid relaxation is of interest because it depends on how photosynthetic antenna complexes absorb and transfer energy and because it may provide an experimental window to protein dynamics on very short time scales.²⁰ Depolarization of fluorescence as a result of energy transfer has been studied already quite some time ago for a model of electronically coupled molecules.^{21,22} Rahman et al.²¹ were the first to recognize the importance of the off-diagonal density matrix elements (coherences) for describing the fluorescence anisotropy of molecular systems.²³ Off-diagonal density matrix elements are missing in the well-known Förster theory of exciton transfer²⁴ and can lead to an initial anisotropy larger than the incoherent theoretical limit of 0.4. For the B850 ring in LH2 complexes, it has been shown that the elementary dynamics occurs on a time scale of about 100 fs.^{20,25–28} Part of these experiments were done with spectrally narrow excitation pulses^{20,26–28} and others with spectrally broad pulses.²⁵ Here we will concentrate on the interpretation of experiments with spectrally broad pulses. Already some time ago Nagarajan et al.²⁵ measured the changes in absorption and stimulated emission. Substantial relaxation on the time scale of 10–100 fs and an anomalously large initial anisotropy of 0.7 has been observed. For experiments with spectrally narrow excitation pulses one gets an initial anisotropy close to but not exceeding 0.4.^{20,27,28}

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The experimental results with broad pulses have been interpreted in a simple model of a homogeneous system in which excitations are delocalized over the whole ring. The high initial anisotropy was ascribed to coherent excitation of a degenerate pair of states that allows optical transitions and then relaxation to states at lower energies having forbidden transitions. Nagarajan et al.²⁰ concluded that the main features of the spectral relaxation and the decay of anisotropy are reproduced well by a model that considers decay processes of electronic coherences within the manifold of the exciton states and thermal equilibration among the excitonic states. In that contribution the exciton dynamics has not been calculated explicitly.

In several steps we have recently extended^{29–31} the former investigations by Kumble and Hochstrasser³² and Nagarajan et al.²⁰ of the time-dependent optical anisotropy. Kumble and Hochstrasser³² calculated the time evolution of the quantum states, prepared by impulsive excitation of a statically disordered circular ring, exactly for varying degrees of inhomogeneity (static disorder), without taking into account the interaction with a heat bath (dynamic disorder). For a Gaussian distribution of local energies it has been found that modest degrees of disorder Δ/J (≈ 0.4 – 0.8), where J is the nearest neighbor transfer integral, are sufficient to cause scattering on a sub-100 fs time scale. In our investigations we added the effect of dynamical disorder to this calculation by using a quantum master equation instead of a time-dependent Schrödinger equation.^{29–31} Because those calculations involve the propagation of density matrices instead of wave packets, as in the case of Kumble and Hochstrasser together with orientational averaging, calculating the mean over the static disorder leads to numerically quite demanding computations. Therefore we restricted ourselves to the Markovian limit, i.e., the neglect of memory effects, in the earlier studies. For this purpose we used Redfield theory.^{24,33,34} In the present investigation we are now generalizing this treatment by the inclusion of memory effects because these might be of some importance for the studied ultrafast processes.

Here we follow the assumption that the total system can be split into a relevant system and a thermal bath whose degrees of freedom are not of direct interest for the description of a particular experiment or phenomena. The bath-related relaxation can be described in a variety of ways. Among others these are the path integral methods,^{35,36} the semigroup formalism,^{37–39} and the reduced density matrix (RDM) approaches based on perturbation theory within the system–bath coupling.³³ In the present contribution we concentrate on the latter in which the dynamics is described by quantum master equations. This allows us to calculate the diagonal as well as off-diagonal elements of the RDM and therefore to calculate optical properties of the system. Ab initio calculations¹⁷ indicate that the exciton–phonon coupling is indeed weak but further investigations to study the effects of a perturbative treatment in the exciton–phonon coupling seem to be necessary. Maybe an extension of the modified Redfield equations,^{40,41} which currently cannot handle off-diagonal elements correctly, would be an appropriate alternative. In the present paper second-order perturbation theory within the exciton–phonon coupling is used. The RDM of the relevant system is obtained by tracing out the irrelevant bath modes. In general, this leads to retardation, i.e., to a non-Markovian behavior. Within the quantum master formalism there have been many approaches of treating non-Markovian effects (see, for example, refs 42–50). Because the number of different treatments of non-Markovian effects is too large to be described here in detail, we mention only a few. Under certain conditions and for small systems the time nonlocal problem can

be solved within the frequency domain, i.e., by a Fourier or Laplace transformation.^{44,45,47} The orthogonal set of Laguerre polynomials has also been used to solve the quantum master equation.^{49,50} Other investigations^{46,48,51,52} are based on the time-convolutionless approach,^{53,54} which, in contrast to the more widely used Nakajima–Zwanzig theory,^{55,56} leads to a time-local quantum master equation. The bath correlation function has been rewritten in an approximate fashion⁵⁷ or the spectral density has been decomposed numerically.⁴³ In the present contribution we shall use both the approximate version of the bath correlation function and the numerical decomposition of the spectral density together with the time-convolutionless formalism. No additional approximations such as the so-called secular approximation³⁴ will be made. It has been shown^{23,58} that in contrast to the commonly claimed justification of the secular approximation, the nonsecular terms do not always average out in time.

The rest of the paper is organized as follows. In the next section the model Hamiltonian for the B850 of purple bacteria is introduced and the parameters for the purple bacterium *Rhodospseudomonas acidophila* are given. In section III we describe and compare two different ways of how to treat non-Markovian effects. In the last two sections we show the results obtained for the anisotropy of fluorescence and briefly conclude.

II. Model for the B850 Ring

A. Hamiltonian. In large systems such as LH2, several simultaneously excited states at different BChls are possible in principle. In the following we deal with just one such excitation, which is already present at time $t = 0$. Because the BChls are electronically coupled, the electronic excitations of the ring, the so-called excitons, are delocalized on the ring. For the theory of multi-excitonic states, see, for example, ref 59. Let us first describe the Hamiltonian of an unperturbed ring coupled to a bath of harmonic oscillators

$$\begin{aligned}
 H^0 &= \sum_{m,n} J_{mn} a_m^\dagger a_n + \sum_q \omega_q b_q^\dagger b_q + \\
 &\quad \frac{1}{\sqrt{N}} \sum_m \sum_q G_q^m \omega_q a_m^\dagger a_m (b_q^\dagger + b_{-q}) \\
 &= H_{\text{ex}}^0 + H_{\text{ph}} + H_{\text{ex-ph}}
 \end{aligned} \tag{1}$$

The first term in the Hamiltonian, H_{ex}^0 , represents the single exciton, i.e., the system. The operators a_m^\dagger or a_m create or annihilate an exciton at site m . J_{mn} for $m \neq n$ are the so-called transfer integrals between sites m and n . The diagonal elements J_{nn} are the local energies ϵ_n at site n which may take into account, e.g., a dimerization $\epsilon_{2n} \neq \epsilon_{2n+1}$. The second term in the Hamiltonian, H_{ph} , describes the bath of phonons in the harmonic approximation. It is assumed that each chromophore is connected to a heat bath independent of those from the other chromophores. The phonon creation and annihilation operators are denoted by b_q^\dagger and b_q , respectively. The last term in eq 1, $H_{\text{ex-ph}}$, represents the interaction between the exciton and the bath. The exciton–phonon interaction is assumed to be site-diagonal and linear in the bath coordinates. The term G_q^m denotes the exciton–phonon (system–bath) coupling constant.

In addition to the dynamic disorder given by the coupling to the heat bath, quasi-static disorder is present in the LH2 rings.

This kind of disorder is modeled by the time-dependent part of the Hamiltonian $H = H^0 + H_s(t)$. Here

$$H_s(t) = \sum_n \epsilon_n(t) a_n^\dagger a_n \quad (2)$$

describes fluctuations of the local excitation energies $\epsilon_n(t)$ due to slow motion of the protein environment. These fluctuations have exponentially decaying correlation functions. The mean values and correlation functions are given by

$$\begin{aligned} \langle \epsilon_n(t) \rangle &= 0 \\ \langle \epsilon_n(t) \epsilon_m(\tau) \rangle &= \delta_{nm} \Delta^2 e^{-\lambda|t-\tau|} \end{aligned} \quad (3)$$

For simplification we use only pure static disorder, i.e., the limit $\lambda \rightarrow 0$, and a Gaussian distribution for the uncorrelated local energy fluctuations ϵ_n^s with a standard deviation Δ . So the corresponding part of the Hamiltonian H_s introduces statistic fluctuations of the site energies of the BChls.

At the end of this article an additional elliptical distortion of the ring will be considered. Recent results of LH2 rings bound to mica surfaces⁶⁰ as well as results obtained by single molecule spectroscopy⁶¹ can only be interpreted⁶² by admitting the presence of a C_2 distortion of the ring. It has, up to now, not been concluded whether such C_2 distortion of the LH2 ring is present also in samples in vivo. The elliptical distortion of the ring is described by the part of Hamiltonian H_{ell} ⁶²

$$H_{\text{ell}} = a_J \sum_n \cos \left[\frac{2\pi}{9} \left(n + \frac{1}{2} \right) - \Phi_J \right] (a_n^\dagger a_{n+1} + a_{n+1}^\dagger a_n) \quad (4)$$

where Φ_J is the phase of the modulation imposed by the phase of the underlying deformation along the ring. The modulation amplitude is given by the real parameter a_J .

B. Anisotropy in Fluorescence. Diagonalization of the unperturbed Hamiltonian H_{ex}^0 with $\epsilon_n = 0$ leads to eigenstates $|\tilde{k}\rangle$ and eigenenergies $E_n = -2J \cos \tilde{k}_n$ using $\tilde{k}_n = 2\pi n/N$, $n = 0, \pm 1, \pm 2, \dots, N/2$. For a symmetric coplanar arrangement of site transition moments $\vec{\mu}_n$ dipole-allowed transitions populate only the degenerate $n = \pm 1$ levels of the ideal ring. When static disorder of the site energies is present ($\Delta \neq 0$), the stationary states, i.e., the eigenstates $|a\rangle$ of the Hamiltonian $H_{\text{ex}}^0 + H_s$, correspond to mixtures of $|\tilde{k}\rangle$ states and an excitation will usually prepare a superposition of $|\tilde{k}\rangle$ states.

The dipole strength $\vec{\mu}_a$ of state $|a\rangle$ of the ring with static disorder and the dipole strength $\vec{\mu}_\alpha$ of state $|\alpha\rangle$ of the ring without static disorder read

$$\vec{\mu}_a = \sum_{n=1}^N c_n^a \vec{\mu}_n \quad \vec{\mu}_\alpha = \sum_{n=1}^N c_n^\alpha \vec{\mu}_n \quad (5)$$

where c_n^a and c_n^α are the expansion coefficients of the eigenstates of the unperturbed and the disordered rings in site representation.

In the case of pump-pulse excitation, the dipole strength is simply redistributed among the exciton levels due to disorder.³² So the amplitudes of site excitations and the phase relationships in the initial state are necessarily identical to that of an equal superposition of $n = \pm 1$ excitons of the ideal ring. Thus, generally, the excitation with a pump pulse of sufficiently wide spectral bandwidth will always prepare the same initial state, irrespective of the actual eigenstates of the real ring. This initial state is entirely determined by the selection rules of the ring

without static disorder. After pulse excitation with polarization \vec{e}_x it is given by²⁰

$$\rho_{\alpha\beta}(t=0; \vec{e}_x) = \frac{1}{A} (\vec{e}_x \cdot \vec{\mu}_\alpha) (\vec{\mu}_\beta \cdot \vec{e}_x) \quad A = \sum_\alpha (\vec{e}_x \cdot \vec{\mu}_\alpha) (\vec{\mu}_\alpha \cdot \vec{e}_x) \quad (6)$$

The usual time-dependent anisotropy of fluorescence

$$r(t) = \frac{\langle S_{xx}(t) \rangle - \langle S_{yy}(t) \rangle}{\langle S_{xx}(t) \rangle + 2\langle S_{yy}(t) \rangle} \quad S_{xy}(t) = \int P_{xy}(\omega, t) d\omega \quad (7)$$

uses the excitonic density matrix ρ^{29} in

$$P_{xy}(\omega, t) = A \sum_a \sum_{a'} \rho_{aa'}(t) (\vec{\mu}_a \cdot \vec{e}_y) (\vec{e}_y \cdot \vec{\mu}_{a'}) [\delta(\omega - \omega_{a'0}) + \delta(\omega - \omega_{a0})] \quad (8)$$

The brackets $\langle \rangle$ denote the ensemble average and the orientational average over the sample with fixed relative directions \vec{e}_x and \vec{e}_y of the laser pulses.

C. Parameters. Though the present study mainly aims at the difference between Markovian and non-Markovian calculations of the dynamics in the anisotropy of fluorescence, we nevertheless try to use physically reasonable parameters for our model.²⁹ In reality, the one-exciton band of the ideal ring $E(\tilde{k})$ consists of two groups of 9 transitions arranged asymmetrically relative to the zero local site energy. These Davydov manifolds appear because the 18 BChl molecules in the B850 ring are grouped into heterodimers with different coupling energies within the elementary dimers J_{12} and between them J_{23} as well as different local energies $\epsilon_1 \neq \epsilon_2$. In the presence of static disorder ($\Delta \neq 0$ in H_s) all exciton transitions gain strength at the expense of the low-energy $\tilde{k} = \pm 1$ transitions, which dominate the spectrum of the ideal B850 ring. In what follows we will use the transfer integral J_{12} as the energy unit. For simplicity the homogeneous case $J = J_{12} = J_{23}$, $\epsilon_1 = \epsilon_2 = 0.0$, and Δ between 0.2 and 0.8 was chosen. To convert the time τ in these units into seconds, one has to divide τ by $2\pi c J_{12}$ with c the speed of light. So $\tau = 1$ corresponds to 21.2 fs for $J_{12} = 250 \text{ cm}^{-1}$ and to 13.3 fs for $J_{12} = 400 \text{ cm}^{-1}$. The constant \hbar is set to one.

III. Non-Markovian Theories for the Reduced Density Matrix

The crucial quantity entering the time dependence of the anisotropy in eq 7 is the exciton density matrix. As mentioned in the Introduction we are going to focus on memory effects in the dynamics of the relevant RDM. For this purpose two different non-Markovian treatments are described in this section and the results are compared with each other.

A. Čápek's Theory Using Site Representation. Having defined the Hamiltonian H of the system, i.e., one exciton on a ring and a heat bath, one has to solve the equations of motion for the complete density matrix σ , namely, the Liouville equation

$$i \frac{\partial}{\partial t} \sigma(t) = L \sigma \quad (9)$$

This is not a simple task because one has to find the time development of all matrix elements of the density matrix, diagonal and off-diagonal, in any representation that takes into account the exciton and phonon states. Nevertheless, this treatment is not necessary in many cases. The complete information, which may be obtained from the whole density

matrix, is in many cases not needed in further investigations and can be limited. The transfer problem of, e.g., a Frenkel exciton interacting with a bath, is usually treated by projecting out the bath degrees of freedom. This yields dynamic equations for the single-exciton density matrix ρ complementing the usual single-exciton Liouville equation by terms describing the bath influence. The latter terms must, on the other hand, be properly parametrized.

Čápek^{51,52,63,64} applied several different ways of obtaining the convolution and convolutionless dynamical equations for the exciton density matrix. The equations of motion obtained in site representation read

$$\frac{d}{dt}\rho_{mn}(t) = \sum_{pq} i\omega_{mn,pq}(t) \rho_{pq}(t) \quad (10)$$

where

$$\omega_{mn,pq}(t) = \Omega_{mn,pq} + \delta\Omega_{mn,pq}(t) \quad (11)$$

When the typical system times are much longer than the bath correlation time, i.e., in the Markovian limit, one obtains a system of equations with constant coefficients

$$\begin{aligned} \Omega_{mn,pq} &= \delta_{mp}\delta_{nq}(\epsilon_n - \epsilon_m) + J_{qn}\delta_{mp} - J_{mp}\delta_{nq} \\ i\delta\Omega_{mn,pq} &= -\delta_{mp}\mathcal{A}_{nmq} - \delta_{nq}\mathcal{A}_{mn}^p \\ \mathcal{A}_{mn}^p &= \frac{i}{N} \sum_k \omega_k^2 (G_{-k}^m - G_{-k}^n) \sum_r G_k^r \sum_{\alpha\beta} \langle p|\beta\rangle\langle\beta|r\rangle\langle r|\alpha\rangle\langle\alpha|m\rangle \times \\ &\quad \left\{ \frac{1 + n_B(\omega_k)}{E_\alpha - E_\beta + \omega_k + i\epsilon} + \frac{n_B(\omega_k)}{E_\alpha - E_\beta - \omega_k + i\epsilon} \right\} \quad (12) \end{aligned}$$

Here $n_B(\omega)$ denotes the Bose–Einstein distribution and, as before, $|\alpha\rangle$ and E_α label the corresponding eigenvalues and eigenvectors of $H_{\text{ex}}^0 + H_s$. Čápek suggested the parametrization

$$A_{mn}^p = \text{Re } \mathcal{A}_{mn}^p \quad B_{mn}^p = \text{Im } \mathcal{A}_{mn}^p \quad (13)$$

In the fast carrier regime the coefficients B_{mn}^p become negligible (no renormalization of J_{mn}) and can be omitted. The A_{mn}^m play the same role as the coefficient $\gamma_0 \equiv \gamma_{mm}$ of the Haken–Strobl–Reineker parametrization.⁶⁵ The coefficients A_{mn}^n provide the bath-induced coupling of the off-diagonal to the diagonal elements of $\rho_{mn}(t)$. We have proven²⁹ that this Markov approximation of Čápek's theory (in local site representation) is equivalent to the Redfield theory without secular approximation (in eigenstate representation).

In this paper we do not use the long-time limit of eq 10 but the full time dependence of $\delta\Omega(t)$ ⁶³ given by time dependent parameters

$$\begin{aligned} \mathcal{A}_{mn}^p(t) &= \int_0^t \frac{1}{N} \sum_k \omega_k^2 (G_{-k}^m - G_{-k}^n) \sum_r G_k^r \times \\ &\quad \sum_{\alpha\beta} \langle p|\alpha\rangle\langle\alpha|r\rangle\langle r|\beta\rangle\langle\beta|m\rangle e^{-i(E_\alpha - E_\beta)\tau} \times \\ &\quad \{ [1 + n_B(\omega_k)] e^{i\omega_k\tau} + n_B(\omega_k) e^{-i\omega_k\tau} \} d\tau \quad (14) \end{aligned}$$

To obtain the full time dependence of $\delta\Omega(t)$ is not a simple task. Recently, the full time dependence of $\delta\Omega(t)$ for one of the simplest molecular models, namely the excitonic dimer, was

successfully calculated.⁴² For the present case of a molecular ring we will rewrite eq 14. The Hamiltonian $H_{\text{ex-ph}}$ can be written as

$$H_{\text{ex-ph}} = \sum_m K_m \Phi_m \quad (15)$$

where the system operators K_m and bath operators Φ_m are given by

$$K_m = a_m^\dagger a_m \quad \Phi_m = \frac{1}{\sqrt{N}} \sum_q G_q^m \omega_q (b_q^\dagger + b_q)$$

As usual, we define the bath correlation function

$$C_{mn}(t) = \langle \Phi_m(t) \Phi_n(0) \rangle_B \quad (16)$$

assuming that the expectation values $\langle \Phi_m \rangle_B$ vanish. For most systems the correlations of the fluctuations decay after a certain correlation time τ_c .²⁴ In site representation the operator K_m is given by

$$\langle r|K_m|s\rangle = \delta_{rm}\delta_{sm} \quad (17)$$

Using the simple expression for the time evolution operator $U(\tau)$ in energy representation $\langle \alpha|U(\tau)|\beta\rangle = \delta_{\alpha\beta} e^{-iE_\alpha\tau}$, one gets

$$\langle r|U(\tau)K_m U^\dagger(\tau)|s\rangle = \sum_{\alpha\beta} \langle r|\alpha\rangle\langle\alpha|n\rangle\langle n|\beta\rangle\langle\beta|s\rangle e^{-i(E_\alpha - E_\beta)\tau} \quad (18)$$

After substituting eqs 17 and 18 into eq 14 the final form of the parameters \mathcal{A}_{rs}^m entering the non-Markovian equation of motion for the reduced exciton density matrix in local site representation reads

$$\begin{aligned} \mathcal{A}_{mn}^p(t) &= \sum_{\alpha\beta} \int_0^t d\tau e^{-i(E_\alpha - E_\beta)\tau} \sum_r [C_{nr}^*(\tau) - C_{mr}^*(\tau)] \times \\ &\quad \langle p|\alpha\rangle\langle\alpha|r\rangle\langle r|\beta\rangle\langle\beta|m\rangle \quad (19) \end{aligned}$$

In what follows we use a simple model for C_{mn} . As mentioned in section IIA, each site (chromophore) has its own bath, which is completely uncoupled from the baths of the other sites. Furthermore, it is assumed that these baths have identical properties.^{2,24} Then only one correlation function $C(\omega)$ is needed

$$C_{mn}(\omega) = \delta_{mn} C(\omega) \quad (20)$$

with

$$C_{mn}(\omega) = \int_{-\infty}^{\infty} C_{mn}(\tau) e^{i\omega\tau} d\tau \quad (21)$$

Choosing real eigenvectors $\langle m|\alpha\rangle$ (which is always possible for our system) and omitting the imaginary parts of \mathcal{A}_{rs}^m which cause only a renormalization of the transfer integrals J ,⁶³ and introducing the spectral density $J(\omega)$ ²⁴

$$C(\omega) = 2\pi[1 + n_B(\omega)][J(\omega) - J(-\omega)] \quad (22)$$

we can write

$$\begin{aligned} A_{mn}^p(t) &= \frac{1}{2} \sum_{\alpha\beta} \int_0^t d\tau e^{-i(E_\alpha - E_\beta)\tau} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega 2\pi[1 + n_B(\omega)] \times \\ &\quad [J(\omega) - J(-\omega)] \langle p|\alpha\rangle\langle\alpha|n\rangle\langle n|\beta\rangle - \langle \alpha|m\rangle\langle m|\beta\rangle\langle\beta|m\rangle \quad (23) \end{aligned}$$

In the following we have modeled the spectral density by the form often used dealing with the BCHIs in the LH2 ring

unit^{2,24,66}

$$J(\omega) = \Theta(\omega) j_0 \frac{\omega^2}{2\omega_c^3} e^{-\omega/\omega_c} \quad (24)$$

It has its maximum at $2\omega_c$. In agreement with ref 66 we use $j_0 = 0.2$ or $j_0 = 0.4$ and $\omega_c = 0.2$.

Next a simplification suggested by Korolkov, Paramonov, Manz, and Saalfrank in a series of papers^{57,67–69} is applied. Their main idea is to replace one of the sums in eq 14, which mainly represents differences between bath correlation functions

$$\frac{1}{N} \sum_k \omega_k^2 (G_{-k}^m - G_{-k}^n) G_k^r \{ [1 + n_B(\omega_k)] e^{-i\omega_k \tau} + n_B(\omega_k) e^{i\omega_k \tau} \} \quad (25)$$

by another finite sum

$$\sum_{\mu=2}^{18} \sum_{\nu=1}^{\mu-1} K_{\mu\nu} e^{-\gamma_{\mu\nu} \tau} \{ [1 + n_B(\omega_{\mu\nu})] e^{-i\omega_{\mu\nu} \tau} + n_B(\omega_{\mu\nu}) e^{i\omega_{\mu\nu} \tau} \} \quad (26)$$

This replacement is based⁵⁷ on the assumption that the density of the frequencies ω_k in the vicinity of each $\omega_{\mu\nu} = E_\mu - E_\nu$ can be represented by a Lorentzian-type distribution

$$\frac{\gamma_{\mu\nu}}{\gamma_{\mu\nu}^2 + (\omega_{\mu\nu} - \omega)^2}$$

where $\gamma_{\mu\nu} > 0$ determines the width of the distribution that has a maximum at $\omega = \omega_{\mu\nu}$.

Let us denote

$$\mathcal{A}_{m\alpha\beta}^p = \langle p | \alpha \rangle \langle \alpha | m \rangle \langle m | \beta \rangle - \langle \alpha | n \rangle \langle n | \beta \rangle \langle \beta | m \rangle \quad (27)$$

$$K_{\mu\nu}(\omega) = \pi J(\omega) [1 + n_B(\omega_{\mu\nu})] \quad \text{for } \omega > 0$$

$$K_{\mu\nu}(\omega) = \pi J(-\omega) n_B(\omega_{\mu\nu}) \quad \text{for } \omega < 0 \quad (28)$$

$$\Gamma(\omega_{\alpha\beta}, t) = \sum_{\mu=2}^{18} \sum_{\nu=1}^{\mu-1} K_{\mu\nu}(\omega_{\alpha\beta}) (1 - e^{-\gamma_{\mu\nu} t}) \quad (29)$$

Then it is straightforward to show that⁵⁷

$$\mathcal{A}_{mn}^p(t) = \sum_{\alpha\beta} \mathcal{A}_{m\alpha\beta}^p \Gamma(\omega_{\alpha\beta}, t) \quad (30)$$

The normalization of the coefficients $K_{\mu\nu}$ is chosen in such a way that after the Markovian approximation we obtain the correct results for the chosen spectral density $J(\omega)$. As in ref 57 it is assumed that all $\gamma_{\mu\nu}$ are equal, i.e., $\gamma_{\mu\nu} = \gamma$. The main effect of the non-Markovian treatment in the Korolkov–Paramonov model is that the effect of the relaxation operator in dynamical equations for the reduced exciton density matrix is gradually postponed in time. The reduced exciton density matrix has some time to develop with a weaker influence of the bath onto the exciton.

B. Full Decomposition of the Spectral Density. Next we want to combine the time-convolutionless approach with a numerical decomposition of the spectral density (eq 24). A similar idea was used for the first time by Tanimura et al.^{70,71} In their work the decomposition was restricted to a Lorentzian shape of the spectral density. Meier and Tannor⁴³ used a numerical decomposition which is not restricted to any special form of spectral density

$$J(\omega) = \sum_{k=1}^n p_k \frac{\omega}{[(\omega + \Omega_k)^2 + \Gamma_k^2][(\omega - \Omega_k)^2 + \Gamma_k^2]} \quad (31)$$

with arbitrary real parameters p_k , Ω_k , and Γ_k . Using this form it is convenient to calculate the complex bath correlation function

$$C(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} J(\omega) \frac{e^{i\omega t}}{e^{\beta\omega} - 1} \\ = \sum_{k=1}^n \frac{p_k}{4\Omega_k \Gamma_k} \{ e^{i\Omega_k^+ t} n_B(\Omega_k^+) + e^{-i\Omega_k^- t} (n_B(\Omega_k^-) + 1) \} + \\ - \frac{2i}{\beta} \sum_{k=1}^{n'} J(i\nu_k) e^{-\nu_k t} \quad (32)$$

using $\Omega_k^+ = \Omega_k + i\Gamma_k$, $\Omega_k^- = \Omega_k - i\Gamma_k$ and the Matsubara frequencies $\nu_k = 2\pi k/\beta$. In principle, the sum over the Matsubara terms is an infinite one. But for all practical purposes the sum can be truncated at some finite value n' , though for very low temperatures a large number of terms might be needed. We want to emphasize that this expression for the bath correlation function is exact when the decomposition of the spectral density (eq 31) is exact. It is important to note that the time dependence in $C(t)$ is now fully exponential, which enables further analytic treatment. The correlation function for the ohmic spectral density with exponential cutoff can also be integrated directly.^{35,72} But the result is too complicated for further analytic calculations. In a recent analytical study of the spin–boson model⁷² it is shown why $C(t)$ is qualitatively incomplete within the Markov approximation. In the present treatment the only deviations from the correct solution within second-order perturbation theory and with factorized initial conditions may come from deviations in the decomposed spectral density from the original one. But these deviations can be systematically reduced by increasing the order in the decomposition. It is interesting to note that the decay of the terms within the Matsubara sum in eq 32 does not depend on the spectral density but only on temperature. Only the strength of these terms is proportional to the spectral density.

If one compares eq 32 with the approximate ad hoc expression (eq 26) it can be seen that the sum over the Matsubara frequencies is completely missing in the ad hoc expression. So that expression cannot be correct for low temperatures. In addition, the arguments of the Bose–Einstein functions in eq 32 are complex. But the biggest advantage of the numerical decomposition of the spectral density is that the parameters p_k , Ω_k , and Γ_k can be determined according to a given, fixed rule.

One way to proceed would be to use the decomposed spectral density together with Čápek’s non-Markovian theory, which is defined in site representation. Instead, let us proceed with a calculation in energy representation, which results in simpler expressions. The details of this treatment based on the time-convolutionless formalism are given elsewhere.⁷³ Defining

$$\Lambda_m(t) = \int_0^t dt' C(t') e^{-iH_s t'} K_m e^{iH_s t'} \quad (33)$$

allows the non-Hermitian effective Hamiltonian

$$H_{\text{eff}} = H_s - i \sum_m K_m \Lambda_m(t) \quad (34)$$

to be introduced. With these definitions the non-Markovian

TABLE 1: Parameters Used for Approximating the Spectral Density by Eq 31

$(p_k/\eta\omega_c^4)$	(Γ_k/ω_c)	(Ω_k/ω_c)
0.0610	0.1859	0.7722
0.2238	0.2519	1.0265
0.7154	0.3421	1.3324
2.1763	0.4756	1.7134
22.4378	1.0974	2.8675
92.4717	2.0149	3.7483
6.7073	0.6930	2.2062
1.1677	0.1326	0.5514
-101.2753	4.6477	7.7516

quantum master equation is given by

$$\frac{\partial \rho(t)}{\partial t} = -i(H_{\text{eff}}\rho(t) - \rho(t)H_{\text{eff}}^\dagger) + \sum_m (K_m \rho(t) \Lambda_m^\dagger(t) + \Lambda_m(t) \rho(t) K_m) \quad (35)$$

The Markovian limit of these expressions can easily be obtained by moving the upper integration boundary in eq 33 to infinity.²⁴ The advantage of the decomposition of the spectral density comes with the calculation of the matrix elements of the operator $\Lambda(t)$ in energy representation

$$\langle \mu | \Lambda_m(t) | \nu \rangle = \langle \mu | K_m | \nu \rangle \int_0^t dt' C(t') e^{-i\omega_{\mu\nu}t'} = \langle \mu | K_m | \nu \rangle \Theta^+(t, \omega_{\mu\nu}) \quad (36)$$

Here we introduced the function

$$\Theta^+(t, \omega_{\mu\nu}) = \sum_{k=1}^n \frac{p_k}{4\Omega_k \Gamma_k} \left\{ \frac{n_B(\Omega_k^+)}{i(\Omega_k^+ - \omega_{\mu\nu})} [e^{i(\Omega_k^+ - \omega_{\mu\nu})t} - 1] + \frac{[n_B(\Omega_k^-) + 1]}{i(-\Omega_k^- - \omega_{\mu\nu})} [e^{i(-\Omega_k^- - \omega_{\mu\nu})t} - 1] \right\} - \frac{2i}{\beta} \sum_{k=1}^{n'} \frac{J(i\nu_k)}{\nu_k + i\omega_{\mu\nu}} [e^{(-\nu_k - i\omega_{\mu\nu})t} - 1] \quad (37)$$

following the notation of ref 74. For the non-Markovian treatment $\Theta^+(t, \omega_{\mu\nu})$ has to be calculated at every moment in time instead of only once as in the Markovian limit. Fortunately, in the present approach the evaluation of the matrix elements (eq 36) does not contain any numerical integration anymore.

Next the spectral density shall be decomposed using eq 31. The spectral density (eq 24) starts quadratically in ω for small ω whereas all terms of the decomposition grow linearly in ω for small ω . Unfortunately, one cannot increase the power of ω within the decomposition functions because then one cannot use the residuum theorem any longer to determine the bath correlation functions. For an accurate decomposition of an Ohmic spectral density with exponential cutoff three terms ($n = 3$) were needed.⁴³ In the present case nine terms were necessary for an accurate fit. The parameters are given in Table 1 and the spectral density (eq 24) and its decomposition are compared in Figure 1.

After the decomposition is complete, all parameters for the non-Markovian theory are known. In contrast to this, using Čápek's theory together with the Korolkov–Manz–Paramonov approximation at least one parameter is unknown. But we can obtain the same population dynamics within both non-Markovian theories using γ (see eq 29) as a fitting parameter, as

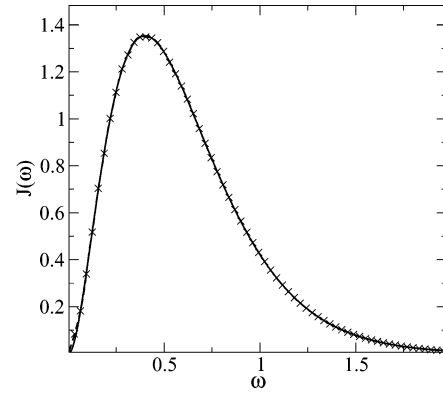


Figure 1. Exact spectral density as given by eq 24 (solid line) and its approximate decomposition using 9 terms in the decomposition (eq 31). The approximation is shown by a dashed line together with crosses.

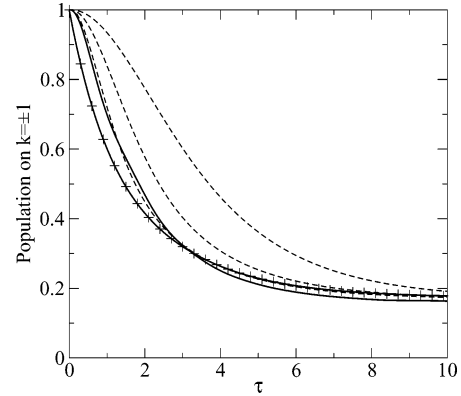


Figure 2. Comparison of different results for the population of the $\tilde{k} = \pm 1$ state as a function of time for $j_0 = 0.2$, $\Delta = 0.0$, $T = 1$. The solid line with crosses shows the Markovian results, and the solid line without crosses, the non-Markovian results using the decomposition of the spectral density. The three dashed curves show the non-Markovian theory of Čápek together with the approximation for the correlation for $\gamma = 0.2, 0.6$, and 1.5 (from top to bottom).

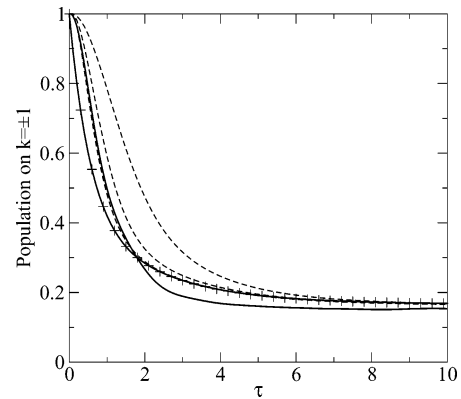


Figure 3. Same as Figure 2, but for $j_0 = 0.4$ and $\gamma = 0.4, 1.2$, and 2.5 .

can be seen in Figures 2 and 3 for two different damping strengths. Such fits are of course temperature dependent. It can also be found from this comparison that the parameter γ seems to be more or less proportional to the damping strength as was argued in ref 69. Because the approach derived in the present subsection contains an explicit procedure to determine the parameters by fitting the spectral density and because it does not contain any high-temperature approximation, this approach will be used below for the exciton dynamics in the B850 ring.

For the numerical time propagation of the density matrix the short iterative Arnoldi method⁷⁴ was used. Recently, this method

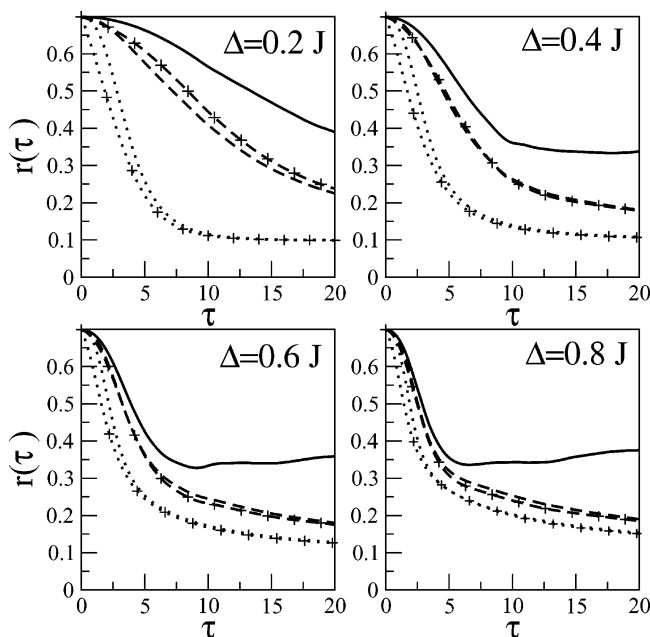


Figure 4. Time dependence of the anisotropy of fluorescence for different static disorder Δ . The results without dissipation are given by the solid line. The dashed lines show the anisotropy for low temperature $T = 0.01J$ and the dotted lines for high temperature $T = J$. Results for which the Markov approximation was invoked are marked by additional crosses.

has been applied to an electron-transfer problem with a stationary relaxation operator Λ ⁷⁵ but it can be applied very successfully in the case of weak time dependence of Λ as well. An advantage of the short iterative Arnoldi method with respect to the standard Runge–Kutta scheme is the low computational effort for moderate accuracy.⁷⁵ Furthermore, the expansion coefficients are adapted at each time to a fixed time step with a prespecified tolerance, in contrast to the Runge–Kutta scheme in which the time step is usually adapted. A uniform time grid is important for the averaging over various disorder and orientation realizations at the same points in time without interpolation. The disorder and orientation averaging can easily be parallelized by means of the *Message passing interface* (MPI). The computations were performed on a PC cluster using 64 CPUs. So instead of running about 10 000 realizations on one node, 156 realizations were calculated on each of the 64 CPUs.

IV. Results for the B850 Ring

The anisotropy of fluorescence has been calculated using eq 7. The Markovian as well as the non-Markovian dynamical equations for the exciton density matrix ρ have been applied to express the time dependence of the optical properties of the model LH2 ring of BChls in the femtosecond time range. All other details are the same as in ref 29. In the wave packet calculations by Kumble and Hochstrasser,³² the anisotropy of fluorescence of the LH2 ring decreases from 0.7 to 0.3–0.35 and subsequently reaches a final value of 0.4. One needs a strength of static disorder of $\Delta \approx 0.4$ – $0.8J$ to reach a decay time below 100 fs.

Figure 4 shows the results for the anisotropy of fluorescence for an undistorted ring for different strengths of static disorder. As can be seen, the initial decay is always faster if dissipation is included. For weak static disorder, $\Delta = 0.2J$, one can see some distinct non-Markovian features. In the case of high temperatures the initial decay in the first femtoseconds is much

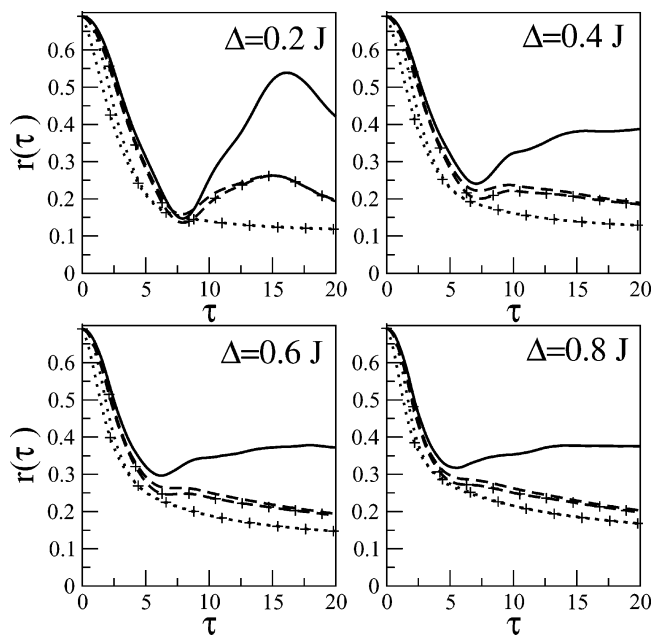


Figure 5. Same as Figure 4 but with elliptical deformation of the ring as described in the text.

faster within the Markov approximation. This can easily be understood by looking at eq 37 for the non-Markovian case. At $t = 0$ the function $\Theta^+(t=0, \omega_{\mu,\nu})$ vanishes and then gradually increases with time. To obtain the Markovian limit, one has to set $t = \infty$, i.e., $\Theta^+(t=\infty, \omega_{\mu,\nu})$, which means full dissipation already at $t = 0$ in the dynamical calculations. For longer times the non-Markovian features disappear in the anisotropy of fluorescence. Looking at the curves for low temperatures one sees that the memory effects are smaller around $t = 0$ but then develop up to some certain stage and stay for longer times than in the high-temperature case.

Increasing the static disorder Δ the difference between the Markovian and the non-Markovian calculations is similar at high temperatures. The Markovian decay is always somewhat faster or equal to the non-Markovian one. This is different for the low-temperature case. Here the non-Markovian decay is faster for $\Delta = 0.2$. For $\Delta = 0.4$ the Markovian and non-Markovian results are almost indistinguishable. For $\Delta = 0.6$ and $\Delta = 0.8$ the Markovian decay is faster. So there is no clear trend of the memory effects on the anisotropy of fluorescence.

So far the ring symmetry has been used to describe the polarization properties of the Frenkel exciton states. We have made calculations that take into account a possible C_2 distortion of the ring using the model C by Matsushita et al.⁶¹ in which the transfer integral J is cosine modulated. Local transition dipole moments lie tangentially to the ellipse. The results for the anisotropy of fluorescence are shown in Figure 5 for the elliptical deformation $a_J = 0.2$ (see eq 4). There are profound changes in the dynamics of the anisotropy for small static disorder whereas for larger static disorder the changes seem to disappear more or less. For $\Delta = 0.2$ all curves show a very similar initial decay. At larger times, the results without dissipation show strong oscillatory features that are more and more damped for higher temperatures. The non-Markovian effects in all the calculations with elliptical distortion are similar or smaller than in the case without deformation of the ring. It is interesting to note that with distortion the Markovian decay is always faster than the non-Markovian one also for low temperatures. In total, the memory effects play an even smaller role if elliptical distortion is present.

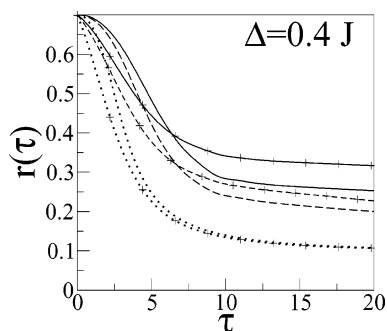


Figure 6. Dependence of the anisotropy of fluorescence on the cutoff frequencies ω_c . The results shown are for high temperature $T = J$ and static disorder $\Delta = 0.4J$. The dotted lines show the same results as those in Figure 4, upper right panel, i.e., $\omega_c = 0.2$. The dashed lines have been calculated using $\omega_c = 0.05$, and the solid ones, using $\omega_c = 0.025$. Results for which the Markov approximation was invoked are marked by additional crosses.

In addition, the dependence of the anisotropy of fluorescence on the cutoff frequencies ω_c has been studied. The non-Markovian behavior should be enhanced for smaller cutoff frequencies. Using the spectral density as given by eq 24, the maximum value of the spectral density changes inversely proportional to the cutoff frequency. So with decreasing ω_c the maximum value of the spectral density increases. But at the same time the maximum position of the spectral density $2\omega_c$ becomes smaller and the main transition frequencies of the system are then in the tail region of the spectral density. So, effectively, the damping becomes smaller. In Figure 6 Markovian and non-Markovian results are compared for three different cutoff frequencies ω_c . As expected, the non-Markovian effect becomes much more visible for small ω_c . But for the realistic value $\omega_c = 0.2$ the non-Markovian effect is still rather small.

V. Conclusion

The LH2 ring structure of antenna subunits of purple bacteria photosynthetic systems has been taken as a motivation for our investigation of time-dependent optical spectra, in particular the dynamics of the anisotropy of fluorescence. Although calculations with static disorder only³² or with static and dynamic disorder within the Markov approximation²⁹ had been performed already, here we focused on the effects of memory in the quantum master equation and on possible elliptical distortions of the ring symmetry. On one hand, the non-Markovian effects in the anisotropy are rather moderate and seem to be reduced or hidden by large static disorder. On the other hand, the effects of an elliptical deformation of the ring on the dynamics of the anisotropy for small static disorder are rather severe. In this case the memory effects are even smaller. It was concluded in ref 32 based on measurements by Chachisvilis et al.⁷⁶ that the time decay of the anisotropy during the first tens of femtoseconds is temperature independent in the case of LH2 subunits. In the experiments by Chachisvilis et al.⁷⁶ the transient anisotropy is measured with 40–50 fs excitation pulses with a wavelength around 882 nm. So in these experiments at least a subset of optically allowed exciton transitions is excited which leads to interference. If no elliptical distortion was present in those experiments, our results show that Δ should be around 0.8 or even larger. But because the time resolution of the experiments in ref 76 was not so high, this very restrictive statement about the strength of the static disorder can only be made with caution. We expect that some temperature dependence can be seen using experiments with shorter laser pulses.

The conclusions would be drastically different if elliptical deformation was present in the experiment. Then the initial decay is almost temperature-independent for all values of static disorder, as can be seen in Figure 5. In that case we could not draw any conclusion about the strength of Δ .

One of the findings of the present contribution is that memory effects play only a minor role for the comparison of calculated and measured initial decay. All the calculations discussed above were obtained with the non-Markovian theory based on the decomposition of the spectral density and a time-convolutionless approach. Using Čápek's theory together with the approximation for the bath correlation function has the drawback that at least one parameter is to some extent unknown. Taking a wrong value for this parameter can easily lead to an overestimation of the non-Markovian effects by a factor of 2 or 3, as can be seen in Figures 2 and 3.

In the present paper we adopted the viewpoint that the exciton is already present at $t = 0$ and that the system and bath are initially uncorrelated. For a consistent theory initial correlations need to be taken into account as well. They can be viewed as the memory from the past.⁴³ This could probably be done best in an approach where the exciton creation by a light pulse is also taken into account.⁷⁷ This would ask for a non-Markovian theory with a proper handling of time-dependent fields.⁴³ Work in this direction is in progress.

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