Computer Simulation of the Anisotropy of Fluorescence in Ring Molecular Systems

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Abstract. The time dependence of the anisotropy of fluorescence after an impulsive excitation in the molecular ring (resembling the B850 ring of the purple bacterium *Rhodospseudomonas acidophila*) is calculated. Fast fluctuations of the environment are simulated by dynamic disorder and slow fluctuations by static disorder. Without dynamic disorder modest degrees of static disorder are sufficient to cause the experimentally found initial drop of the anisotropy on a sub-100 fs time scale. In the present investigation we are comparing results for the time-dependent optical anisotropy of the molecular ring for four models of the static disorder: Gaussian disorder in the local energies (Model A), Gaussian disorder in the transfer integrals (Model B), Gaussian disorder in radial positions of molecules (Model C) and Gaussian disorder in angular positions of molecules (Model D). Both types of disorder - static and dynamic - are taken into account simultaneously.

1 Introduction

We are dealing with the ring-shaped units resembling those from antenna complex LH2 of the purple bacterium *Rhodospseudomonas acidophila* in which a highly efficient light collection and excitation transfer towards the reaction center takes place. Due to a strong coupling limit (large interaction J between bacteriochlorophylls) our theoretical approach considers an extended Frenkel exciton states model.

Despite intensive study, the precise role of the protein moiety in governing the dynamics of the excited states is still under debate [1]. At room temperature the solvent and protein environment fluctuate with characteristic time scales ranging from femtoseconds to nanoseconds. The dynamical aspects of the system are reflected in the line shapes of electronic transitions. To fully characterize the line shape of a transition and thereby the dynamics of the system, one needs to know not only the fluctuation amplitude (coupling strength) but also the time scale of each process involved. The observed linewidths reflect the combined influence of static disorder and exciton coupling to intermolecular, intramolecular, and

solvent nuclear motions. The simplest approach is to decompose the line profile into homogeneous and inhomogeneous contributions of the dynamic and static disorder. Yet, a satisfactory understanding of the nature of the static disorder in light-harvesting systems has not been reached [1]. In the site excitation basis, there can be present static disorder in both diagonal and off-diagonal elements. Silbey pointed out several questions: It is not clear whether only the consideration of the former is enough or the latter should be included as well. If both are considered, then there remains a question about whether they are independent or correlated.

Time-dependent experiments of the femtosecond dynamics of the energy transfer and relaxation [2, 3] led for the B850 ring in LH2 complexes to conclusion that the elementary dynamics occurs on a time scale of about 100 fs [4, 5, 6]. For example, depolarization of fluorescence was studied already quite some time ago for a model of electronically coupled molecules [7, 8]. Rahman *et al.* [7] were the first who recognize the importance of the off-diagonal density matrix elements (coherences) [9] which can lead to an initial anisotropy larger than the incoherent theoretical limit of 0.4. Already some time ago substantial relaxation on the time scale of 10-100 fs and an anomalously large initial anisotropy of 0.7 was observed by Nagarjan *et al.* [4]. The high initial anisotropy was ascribed to a coherent excitation of a degenerate pair of states with allowed optical transitions and then relaxation to states at lower energies which have forbidden transitions. Nagarjan *et al.* [5] concluded, that the main features of the spectral relaxation and the decay of anisotropy are reproduced well by a model considering decay processes of electronic coherences within the manifold of the excitonic states and thermal equilibration among the excitonic states. In that contribution the exciton dynamics was not calculated explicitly.

In several steps [10, 11, 12, 13] we have recently extended the former investigations by Kumble and Hochstrasser [14] and Nagarjan *et al.* [5]. For a Gaussian distribution of local energies in the ring units we added the effect of dynamical disorder by using a quantum master equation in the Markovian and non-Markovian limits. We also investigated influence of static disorder in transfer integrals [15, 16].

In our present investigation we are comparing results for the time-dependent optical anisotropy of the molecular ring for four models of the static disorder: Gaussian disorder in the local energies, Gaussian disorder in the transfer integrals, Gaussian disorder in radial positions of molecules and Gaussian disorder in angular positions of molecules.

2 Model

In the following we assume that only one excitation is present on the ring after an impulsive excitation [14]. The Hamiltonian of an exciton in the ideal ring coupled to a bath of harmonic oscillators reads

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

H_{ex}^0 represents the single exciton, i.e. the system. The operator $a_m^\dagger$ (a_m) creates (annihilates) an exciton at site m . J_{mn} (for $m \neq n$) is the so-called transfer integral between sites m and n . H_{ph} describes the bath of phonons in the harmonic approximation. 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 exciton–bath interaction which is assumed to be site–diagonal and linear in the bath coordinates. The term G_q^m denotes the exciton–phonon coupling constant.

Inside one ring the pure exciton Hamiltonian H_{ex}^0 (Eq. (1)) can be diagonalized using the wave vector representation with corresponding delocalized "Bloch" states and energies. Considering homogeneous case with only nearest neighbor transfer matrix elements $J_{mn} = J_{12}(\delta_{m,n+1} + \delta_{m,n-1})$ and using Fourier transformed excitonic operators (Bloch representation)

$$a_k = \sum_n a_n e^{ikn}, \quad k = \frac{2\pi}{N} l, \quad l = 0, \pm 1, \dots, \pm N/2, \tag{2}$$

the simplest exciton Hamiltonian in $\mathbf{k}$ representation reads

$$H_{\text{ex}}^0 = \sum_k E_k a_k^\dagger a_k, \quad \text{with} \quad E_k = -2 J_{12} \cos k. \tag{3}$$

Influence of static disorder is modelled by a Gaussian distribution

A) for the uncorrelated local energy fluctuations ϵ_n (with a standard deviation Δ)

$$H_s^A = \sum_m \epsilon_n a_m^\dagger a_n$$

B) for the uncorrelated transfer integral fluctuations δJ_{nm} with a standard deviation Δ_J

$$H_s^B = \sum_{m,n(m \neq n)} \delta J_{mn} a_m^\dagger a_n.$$

We are using nearest neighbor approximation.

C) for the uncorrelated fluctuations of radial positions of molecules (with standard deviation Δ_r and $\langle r_n \rangle = r_0$)

$$r_n = r_0(1 + \delta r_n)$$

leading to H_s^C .

D) for the uncorrelated fluctuations of positions of molecules on the ring without the changing of orientations of transition dipole moments (with standard deviation Δ_φ)

$$\varphi_n = \varphi_n^0 + \delta\varphi_n$$

leading to H_s^D .

Hamiltonian of the static disorder adds to the Hamiltonian of the ideal ring

$$H = H^0 + H_s^X. \quad (4)$$

All of the Q_y transition dipole moments of the chromophores (bacteriochlorophylls (BChls) B850) in a ring without static and dynamic disorder lie approximately in the plane of the ring and the entire 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 dipole strength $\boldsymbol{\mu}_a$ of eigenstate $|a\rangle$ of the ring with static disorder and the dipole strength $\boldsymbol{\mu}_\alpha$ of eigenstate $|\alpha\rangle$ of the ring without static disorder read

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

where c_n^α and c_n^a are the expansion coefficients of the eigenstates of the unperturbed ring and the disordered one in site representation, respectively. In the case of impulsive excitation the dipole strength is simply redistributed among the exciton levels due to disorder [14]. Thus the impulsive excitation with a pulse of sufficiently wide spectral bandwidth will always prepare the same initial state, irrespective of the actual eigenstates of the real ring. After impulsive excitation with polarization $\mathbf{e}_x$ the excitonic density matrix ρ [11] is given by [5]

$$\begin{aligned} \rho_{\alpha\beta}(t=0; \mathbf{e}_x) &= \frac{1}{A} (\mathbf{e}_x \cdot \boldsymbol{\mu}_\alpha) (\boldsymbol{\mu}_\beta \cdot \mathbf{e}_x), \\ A &= \sum_{\alpha} (\mathbf{e}_x \cdot \boldsymbol{\mu}_\alpha) (\boldsymbol{\mu}_\alpha \cdot \mathbf{e}_x). \end{aligned} \quad (6)$$

The usual time-dependent anisotropy of fluorescence

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

$$S_{xy}(t) = \int P_{xy}(\omega, t) d\omega$$

is determined from

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

The brackets $\langle \rangle$ denote the ensemble average and the orientational average over the sample.

The crucial quantity entering the time dependence of the anisotropy in Eq. (7) is the exciton density matrix ρ . The dynamical equations for the exciton density matrix obtained by Čápek[17] read

$$\frac{d}{dt}\rho_{mn}(t) = \sum_{pq} i(\Omega_{mn,pq} + \delta\Omega_{mn,pq}(t))\rho_{pq}(t). \quad (9)$$

In long time approximation coefficient $\delta\Omega(t \rightarrow \infty)$ becomes time independent.

All details of calculations leading to the time-convolutionless dynamical equations for the exciton density matrix are given elsewhere [13] and we shall not repeat them here. The full time dependence of $\delta\Omega(t)$ is given through time dependent parameters [17]

$$\begin{aligned} \mathcal{A}_{mn}^p(t) = \int_0^t \frac{i\hbar}{N} \sum_k \omega_k^2 (G_{-k}^m - G_{-k}^n) \sum_r G_k^r \sum_{\alpha,\beta} \langle \beta|r \rangle \langle r|\alpha \rangle \langle \alpha|m \rangle \langle p|\beta \rangle \times \\ e^{-\frac{i}{\hbar}(E_\alpha - E_\beta)\tau} \{ [1 + n_B(\hbar\omega_k)] e^{i\omega_k\tau} + n_B(\hbar\omega_k) e^{-i\omega_k\tau} \} d\tau. \end{aligned} \quad (10)$$

Obtaining of the full time dependence of $\delta\Omega(t)$ is not a simple task. We have succeeded to calculate microscopically full time dependence of $\delta\Omega(t)$ only for the simplest molecular model namely dimer [18]. In case of molecular ring we should resort to some simplification [13].

In what follows we use Markovian version of Eq. (10) with a simple model for correlation functions C_{mn} of the bath assuming that each site (i.e. each chromophore) has its own bath completely uncoupled from the baths of the other sites. Furthermore it is assumed that these baths have identical properties [2, 19]. Then only one correlation function $C(\omega)$ of the bath is needed

$$C_{mn}(\omega) = \delta_{mn}C(\omega) = \delta_{mn}2\pi[1 + n_B(\omega)][J(\omega) - J(-\omega)]. \quad (11)$$

Here $J(\omega)$ is the spectral density of the bath [19] and $n_B(\omega)$ the Bose-Einstein distribution of phonons. The model of the spectral density $J(\omega)$ often used in literature is

$$J(\omega) = \Theta(\omega)j_0 \frac{\omega^2}{2\omega_c^3} e^{-\omega/\omega_c}. \quad (12)$$

Spectral density has its maximum at $2\omega_c$. We shall use (in agreement with [2]) $j_0 = 0.4$ and $\omega_c = 0.2$.

3 Results and Conclusions

The anisotropy of fluorescence (Eq. (7)) has been calculated using dynamical equations for the exciton density matrix ρ to express the time dependence of the optical properties of the ring units in the femtosecond time range. Details are the same as in Ref. [13, 15, 16].

For the numerical time propagation of the density matrix ρ (Eq. 9) the short iterative Arnoldi method [20] as well as the standard Runge-Kutta scheme have

Fig. 1. The time and Δ dependence of the anisotropy depolarization for two models (A) and (B) of the static disorder is given. In the left column the results without the exciton-bath interaction are shown, in the right column the interaction with the bath is taken into account in the Markovian treatment of the dynamic disorder with the $j_0 = 0.4$ and for temperature $T = 0.5$ (in dimensionless units)

been used. An advantage of the short iterative Arnoldi method with respect to the standard Runge-Kutta scheme is the low computational effort for moderate accuracy [21]. 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 adapted. An uniform time grid is important for averaging of various realizations at the same time points without interpolation. The realization averaging and the orientational averaging can easily be parallelized by means of *Message passing interface* (MPI). Some computations were performed on a PC cluster. So instead of running about 10 000 realizations on one node, 312 realizations can be calculated on each of the 32 nodes (or 52 realizations on each of 192 nodes).

In Ref. [14], which does not take the bath into account, 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 $\Delta \approx 0.4 - 0.8$ to reach a decay time below 100 fs.

Results of our simulations are presented graphically in Fig. 1. and Fig. 2. We use dimensionless energies normalized to the transfer integral J_{12} and the renormalized time τ . To convert τ into seconds one has to divide τ by $2\pi c J_{12}$ with c being the speed of light in cm s^{-1} and J_{12} in cm^{-1} . Estimation of the transfer integral J_{12} varies between 250 cm^{-1} and 400 cm^{-1} . For these extreme values of J_{12} our time unit ($\tau = 1$) corresponds to 21.2 fs or 13.3 fs.

In Fig. 1 and 2 the time and static disorder Δ dependence of the anisotropy depolarization for four models of the static disorder is given. In model B) $\Delta = \Delta_J$, in model C) $\Delta = \Delta_r$ and in model D) $\Delta = \Delta_\varphi$. In the left column the results without the exciton-bath interaction are shown, in the right column the interaction with the bath is taken into account in the Markovian treatment of the dynamic disorder with the $j_0 = 0.4$ and for the temperature $T = 0.5$ (in dimensionless units). To convert T into kelvins one has to divide T by k/J_{12} with k being the Boltzmann constant in $\text{cm}^{-1} \text{K}^{-1}$ and J_{12} in cm^{-1} .

Rahman *et al.* [7] were the first who recognized the importance of the off-diagonal density matrix elements (coherences) [9] which can lead to an initial anisotropy $r(0)$ larger than the incoherent theoretical limit of 0.4.

Fig. 2. The same as in Fig. 1 but for the models (C) and (D)

Without dynamic disorder modest degrees of static disorder are sufficient to cause the experimentally found initial drop of the anisotropy on a sub-100 fs time scale. Difference between the Gaussian static disorder in the local energies (Model A) and the Gaussian static disorder in the transfer integrals (Model B) calculations expressed by the time interval in which the anisotropy depolarization reaches $r = 0.4$ (the incoherent theoretical limit) is almost as much as 100 % for the same value of the static disorder $\Delta = \Delta_J$. It means that the same drop of the anisotropy may be caused even by the diagonal static disorder (model A) with Δ or by the static disorder in the transfer integrals with $\Delta_J = 0.5\Delta$. This difference between the Model A and the Model B calculations is still present also in the case, when the exciton interaction with the bath is taken into account. In model C) the strength of the static disorder $\Delta_r = 0.12$ and in model D) the strength of the static disorder $\Delta_\varphi = 0.04$ have practically the same effect as $\Delta = 0.6$ in model A).

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