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Coherent versus incoherent energy transfer in light harvesting antenna complexes

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Abstract

Equations of motion for one- and two-exciton amplitudes as well as exciton population variables which describe the dynamics of Frenkel excitons in optically excited aggregates are presented. Numerical calculations illustrate the interplay of coherent and incoherent transfer dynamics in a Light-Harvesting Complex II (LHCII) monomer.

Keywords: Coherent and incoherent dynamics; LHCII; Frenkel-excitons; Energy transfer

Energy transfer processes in molecular aggregates such as light-harvesting antenna systems reflect both coherent and incoherent exciton dynamics. Most theoretical studies have focused on either the coherent or the incoherent aspect alone; e.g. some important issues of femtosecond Four-Wave Mixing experiments can be adequately discussed, taking into account only the coherent dynamics [1]. On the other hand, it is well known that an incoherent description based on Förster-type rates reproduces many experimental findings like the multitude of timescales observed in pump test-signals [2]. Obviously, there is a competition between coherent and incoherent mechanisms and the question of the relative importance of these processes arises. To address this question, a theory is needed that treats coherent and incoherent exciton dynamics on equal footing and correctly reproduces the respective known limiting cases. The Haken Strobl model interpolates between the two limits by varying the exciton dephasing rate. This is however an infinite temperature theory that fails to incorporate many of the important energetic and structural informations about the system [3–6]. A new scheme has been developed in a recent paper [7], in which the exciton population at site j, N_j^{tot}, is decomposed as follows

$$N_j^{\mathrm{tot}} \equiv \langle B_j^\dagger \rangle \langle B_j \rangle + N_j, \tag{1}$$

where $B_j^\dagger$ (B_j) creates (annihilates) Frenkel excitons at site j. The first term represents coherent exciton populations, whereas the second term is the incoherent part. This separation is the key element in the new scheme. To calculate the third order optical response of an assembly of coupled three-level-molecules according to this scheme, one has to follow the time-evolution of three dynamic variables: (i) the excitonic transition density $\langle B_j \rangle$, (ii) the density

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of two-exciton transitions $\langle B_iB_j\rangle$ and (iii) the incoherent occupation density N_j. These quantities are dynamically coupled via the equations:

$$\begin{aligned}
i\hbar\partial_t\langle B_j\rangle &= \sum_n \bar{J}_{jn}\langle B_n\rangle - \mu_j E_j\{1 - q_j(|\langle B_j\rangle|^2 + N_j)\} \\
&\quad + \Delta_j\{\langle B_j\rangle^*\langle B_jB_j\rangle + 2N_j\langle B_j\rangle\} \\
&\quad - q_j\sum_n \{J_{jn}(\langle B_j\rangle^*\langle B_jB_n\rangle + N_j\langle B_n\rangle) \\
&\quad + i(\bar{R}_{jn}N_n - \bar{R}^*_{nj}N_j)\langle B_j\rangle\} \\
&\quad + \int_{-\infty}^{t} \hbar\Omega_B(t-t')_j\langle B_j\rangle(t')\,dt', \qquad (2)
\end{aligned}$$

$$\begin{aligned}
i\hbar\partial_t\langle B_iB_j\rangle &= \xi_{ij}\Big\{\sum_n(\bar{J}_{jn}\langle B_iB_n\rangle + \bar{J}_{in}\langle B_nB_j\rangle) \\
&\quad - \mu_i E_i\langle B_j\rangle - \mu_j E_j\langle B_i\rangle\Big\} \\
&\quad + \delta_{ij}\Big\{\kappa_j^2\Big(\sum_n J_{jn}\langle B_jB_n\rangle - \mu_j E_j\langle B_j\rangle\Big) \\
&\quad + (\Delta_j + 2\hbar\Omega_j)\langle B_jB_j\rangle\Big\} \\
&\quad + \int_{-\infty}^{t}\sum_{i'j'}\hbar\Omega_{BB}(t-t')_{ij}^{i'j'}\langle B_{i'}B_{j'}\rangle(t')\,dt', \\
&\qquad (3)
\end{aligned}$$

$$\begin{aligned}
\hbar\partial_t N_j &= \sum_m (R_{jm}N_m - R_{mj}N_j) - 2\Im m\Big[\langle B_j\rangle(t)^* \\
&\quad \times \int_{-\infty}^{t} \hbar\Omega_B(t-t')_j\langle B_j\rangle(t')\,dt'\Big]. \qquad (4)
\end{aligned}$$

The parameters in these equations are discussed in detail in Ref. [7]. Also explicit expressions for the transfer-rates $\bar{R}_{jn}$ and $R_{nj} = 2\mathrm{Re}(\bar{R}_{nj})$ as well as the phonon-induced self-energies $\hbar\Omega_B$ and $\hbar\Omega_{BB}$ have been given there. It is important to note that the approximations implied by the use of Förster-type rates are applied only to the incoherent part of the occupation density N_j; the coherent dynamics is still fully accounted for by the transition densities $\langle B_j\rangle$ and $\langle B_iB_j\rangle$.

In this paper we apply these equations to study the dynamics of the coherent and incoherent populations generated by a pulse in resonance with the chlorophyll b (Chlb) band of the LHCII. The relevant equations are the linearized Eq. (2), determining the coherent transition amplitude $\langle B_j\rangle$ and thereby also the coherent population $|\langle B_j\rangle|^2$, and Eq. (4) for the incoherent population N_j. To further simplify the treatment, we replace the integral involving the phonon self-energy by time-local expressions as discussed in Ref. [7]. When the frequency and site dependence of the self-energies is neglected, these expressions reduce to a single dephasing time T_2 and we finally obtain

$$i\hbar(\partial_t + 1/T_2)\langle B_j\rangle = \sum_n \bar{J}_{jn}\langle B_n\rangle - \mu_j E_j, \qquad (5)$$

$$\begin{aligned}
\hbar\partial_t N_j &= \sum_m (R_{jm}N_m - R_{mj}N_j) \\
&\quad + 2\hbar/T_2\langle B_j\rangle(t)^*\langle B_j\rangle(t). \qquad (6)
\end{aligned}$$

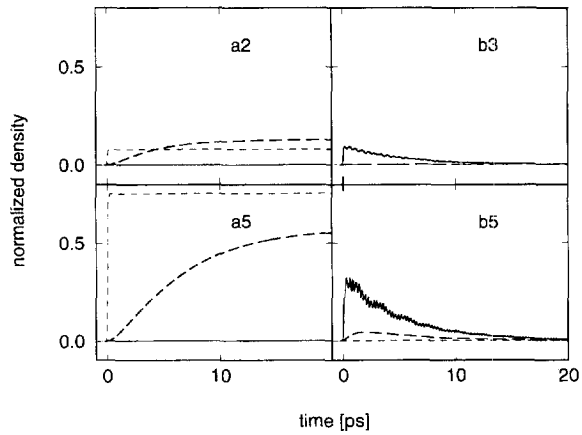

Fig. 1. Time-evolution of the coherent populations $|\langle B_j\rangle|^2$ (solid), incoherent populations N_j (long dashed) and thermalized populations N^{th} (short dashed) at sites *a2*, *a5*, *b3*, *b5* following excitation by a 156 fs Gauss-pulse with central frequency $\hbar\omega = 1.9$ eV. All populations have been normalized to $N_\infty \equiv \bar{N}^{tot}(t\to\infty)$. Exciton parameters and assignment of sites are from Ref. [8], $T_2 = 10$ ps from Ref. [9] and Förster rates R_{ij} for Chlb → Chla transitions taken from Ref. [2] for a temperature $T = 77$ K. The back-transition rates have been determined using detailed balance. For transitions between different Chla or Chlb molecules the values estimated in Ref. [2] have been taken for the mean value $(R_{ij} + R_{ji})/2$ while the ratio R_{ij}/R_{ji} was fixed to fulfill detailed balance.

Fig. 1 shows the coherent and incoherent densities at four representative sites as obtained from a numerical solution of these equations. Also displayed is the thermal distribution $N_j^{\mathrm{th}} \sim \exp[-(\hbar\Omega_j/KT)]$ corresponding to the total density generated until time t (i.e. $\bar{N}^{\mathrm{tot}}(t) \equiv \sum_j N_j^{\mathrm{tot}}(t) = \sum_j N_j^{\mathrm{th}}(t)$). All densities are plotted in units of $N_\infty \equiv N^{\mathrm{tot}}(t \to \infty)$. Due to the resonant excitation in the Chlb-band, a strong coherent amplitude is generated at Chlb-sites, which leads to coherent populations dominating the corresponding incoherent densities. The coherent populations in our calculation show beats reflecting different excitonic energies; these beats are expected to disappear once inhomogeneous broadening is taken into account. Nevertheless, the fact that these contributions result from coherent amplitudes is unaffected by inhomogeneous broadening. The lifetime of all coherent densities is limited by the dephasing time T_2, while the limiting factor for the incoherent densities at Chlb sites is given by the transfer times to Chla molecules. In contrast to Chlb sites, almost no coherent densities build up at Chla sites, because the excitation is off-resonant with respect to the corresponding transitions. The occupation density at these sites is primarily fed by incoherent excitation transfer from other sites. Although, the excitation transfer from Chlb to Chla is obviously completed on a ps timescale, it is evident that the resulting distribution is still far from thermal.

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