Exciton dynamics in ring-like photosynthetic light-harvesting complexes: a hopping model

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Excitation localization and dynamics in circular molecular aggregates is considered. It is shown that the Anderson localization of the excitons is taking place even in the finite size of the ring-type systems containing tens of pigments in the case of comparable values of the spectral homogeneity and of the intermolecular resonance interaction. The second type of localization comes from the dynamical disorder caused by exciton interactions with environment fluctuations. Because of these two reasons the hopping type migration of the small-size excitons is postulated to be responsible for the excitation dynamics in this kind of systems. This process is considered for the ensemble of independent rings and for the array of the interacting rings by means of Monte Carlo simulations. The intra-ring and inter-ring energy disorder with possible correlations is accepted in simulations performed for the cases of high and low temperatures. It is shown that for the typical parameters of the peripheral light-harvesting pigment-protein complexes LH2 of photosynthetic bacteria the excitation population reaches equilibrium within 1 ps in the case of the disconnected rings at nonselective excitation conditions, while equilibration on longer time scale is taking place in the system of connected rings. This nonexponential relaxation kinetics is observed at room temperature and is more pronounced by lowering the temperature. In the case of selective excitation the equilibration process is wavelength dependent for the disconnected rings at room temperature and becomes more pronounced by lowering the temperature. The wavelength dependence is resulted from the interplay between exciton population redistribution among pigments and the population, which sticks in the most red pigments.

1. Introduction

In natural photosynthesis two ultra-fast processes are at the basis of the high quantum efficiency: excitation energy transfer among the pigments of the light-harvesting antenna and energy transfer to a reaction center, where a charge separation is initiated. In the membrane of photosynthetic bacteria a complex system of pigment-proteins is responsible for this process to occur. Typically, a reaction center is surrounded by a core antenna, LH1, which in turn is associated to a more peripheral antenna, LH2.1

From the high resolution structures of LH2 of Rhodopseudomonas (Rps.) acidophila and Rhodopseudomonas (Rps.) molischianum2 it follows that the bacteriochlorophyll (Bchl) molecules in peripheral light-harvesting complexes of photosynthetic bacteria (LH2 or B800-850 complexes) are arranged in a symmetric ring-like structure consisting of two concentric rings of polypeptides (α,β) and two rings of pigments.2,3 The first ring consists of 18, in the case of Rhodopseudomonas (Rps.) acidophila (16 in the case of Rhodopseudomonas (Rps.) molischianum), monomeric Bchl has its major absorption band at 800 nm (B800). In the second ring of monomeric Bchl is absent. Due to their C2 symmetry these ring-like structures seem to be very attractive molecular aggregates for studies of the collective excited states (excitons) by analysing the steady-state and transient spectra.

The optical transitions into the exciton states reflect the symmetry of the structural arrangement of the aggregate. For instance, a ring-like aggregate of identical molecules will obey different selection rules in comparison with those of linear aggregates. For a ring with the optical transition dipole moments of the molecules in plane of the ring (almost the actual arrangement of the B850 in LH2), the lowest exciton state (enumerated in the k-space as k = 0) is optically forbidden and a pair of degenerate states just above it contains almost all the dipole strength.1,5,6 A difference in the orientation of the transition dipole moments, a probable difference in the transition frequencies of two molecules in a dimer, as well as slight alternating differences in the intermolecular distances between the adjacent molecules allow to transform the B850 ring of 18 (or 16) monomers into a ring of dimers. In this case the excitation energy band, due to the presence of two molecules per unit cell, splits into two Davydov subbands separated by the energy gap between them.1,6 The optical transitions into both Davydov subbands obey the same selection rule already mentioned, i.e., with the transition dipole moments in the plane of the ring, the states describing the edges of both Davydov components (corresponding to k = 0) are optically forbidden, while almost all dipole strength is concentrated in the transition to pairs of aggregate exciton states next to them. The distribution of the dipole strength between Davydov components is determined...
by the orientations and energies of the two Bchl within the unit cell.

Multiple experiments have been carried out in order to understand the origin of the spectrum of LH2 and to define the exciton localization radius, and various approaches were used for the description of the exciton dynamics (see ref. 1.8 for review).

Since the interpigment interaction in the B800 ring is weak (less than the site inhomogeneity and the exciton–photon coupling), coherence effects play only a minor role in the description of spectroscopic properties and exciton dynamics. The hopping time between pigment molecules is of the order of 1 ps within the B800 ring. 1 The excitation energy transfer time from B800 to B850 is also estimated to be of the order of 1 ps and this process can be understood in terms of the incoherent energy transfer based on modified Förster theory, because of the spatial size of the coherently coupled pigments in B850. 1,9–11 Carotenoid molecules can play an additional role in this type of the energy transfer by modulating the interpigment interaction. 11

The Bchl molecules in the B850 ring are strongly coupled, therefore, coherent excitons are expected in this structure. 1 However, due to significant spectral inhomogeneity, which is comparable with the homogeneous absorption bandwidth as well as with the intermolecular resonance interaction, the coherent exciton states must be extensively perturbed. Most of the experimental results, obtained for a wide range of temperatures, can be well understood in terms of small excitons comprising of two to four Bchl (see ref. 12 for the review). This conclusion is also supported by measurements of the super-radiance in LH1 and LH2 complexes of Rhodobacter (Rb.) sphaeroides from 4 K to room temperature 13 leading to the same conclusion of a small radius of the exciton coherence. However, some authors, by using nonlinear absorption data 14 or hole burning experiments 7 for the same LH2 complexes of Rb. sphaeroides, have come to a conclusion that the exciton coherence radius is large, almost covering the whole ring of the pigments. The inhomogeneous distribution among the LH2 complexes as well as within a separate complex is well demonstrated by spectroscopic experiments on single LH2 complexes supporting the conclusion that the absorption spectra of B850 at low temperatures is consistent with the coherent exciton model of a ring-like arrangement of pigments with a disordered distribution of the molecular transition energies. 15–18

The exciton dynamics in the strongly coupled B850 ring at room temperature as measured by transient absorption, 19 polarization decay, 20,21 single–single annihilation 22,23 and three-pulse photon echo, 24 can be well understood by a combination of fast exciton relaxation followed by small exciton hopping between pigments with a mean hopping time of the order of a few hundred femtoseconds. Upon lowering the temperature, a new dynamic feature in the range of 1–100 ps is observed in membrane-bound LH2 complexes. 25–27 At low temperatures the stimulated emission/bleaching band broadens and splits into two bands in about 3 ps. The new red-shifted band continues to move further to the red and broadens in the tens of picoseconds. The results correlate with the low temperature Stokes shift, which was shown to be unusually large in LH2-only mutants of Rb. sphaeroides. 28 These data were interpreted in terms of fast exciton relaxation within a single disordered ring of B850, while the slower phases were assigned to the transfer among the inhomogeneously distributed pigments. 26 Alternatively, a complex relaxation scheme has been proposed, where the initial ultrafast (of the order of 100 fs) exciton relaxation in a separate B850 ring is followed by mixing of the exciton states with charge-transfer (CT) states on a subpicosecond time scale and a subsequent evolution of the population in the charge-transfer state on the picosecond time scale corresponding to self-trapping (analogous to the polaron formation). 27 This possible mixing of the exciton states with the CT states is based on the observation of large Stark effects characterized by a large change in polarizability of LH2 29 and even larger for LH1. 30 However, comparison of the exciton evolution in Rb. sphaeroides membranes and in isolated LH2 complexes demonstrates that most of the effects on the time scale of picoseconds, such as unusually large Stokes-shift and the complex evolution of the emission band, are only observed in the membranes, containing the interacting LH2 complexes. 31 For isolated LH2 changes in absorption spectrum are minor compared to the membrane-bounded form, while the Stokes shift is substantially smaller and the kinetics of the Stokes-shift evolution is much faster, taking place on a subpicosecond time scale. This Stokes shift of separate LH2 complexes recently was attributed to the self-trapped exciton formation, 32 however, the excitation dynamics within this model was not considered.

Here we discuss the problem of the exciton localization and dynamics both in isolated rings of pigments and in an array of connected rings of LH2 complexes. Earlier a qualitatively similar but more simple model was used to describe the excitation dynamics in LH1 complexes and showed good correspondence to the experimental observations at room temperature and at 4 K. 33 Here we develop a sophisticated model based on the hopping of an exciton of small size, which is formed after some ultrafast relaxation of electronic coherences. The model accounts for spectral inhomogeneity in a single ring as well as among the ensemble of rings. It also includes dynamic formation of a Stokes shift in isolated chromophore. Hopping models were successfully applied for molecular polymers as being responsible for charge diffusion in the bulk. The concepts of correlated and uncorrelated distribution of on-site energies were successfully developed and applied. Here we investigate if such a hopping model contains the essential relaxation dynamics observed for isolated LH2 systems and connected aggregates of LH2. The analysis allows to judge the nature of excitations and their extension radius in the LH2 kinds of systems.

2. Formulation of the model

The exciton energy spectrum of a ring of pigment molecules is modulated by the random fluctuations of surrounding proteins, which have a broad range of spectral density. We assume the presence of fast and slow fluctuations of surrounding. The fast ones are responsible for ultrafast dephasing of exciton states. Slow (static) fluctuations introduce static energy disorder. 34,35 In the absence of fast fluctuations (this limit is accessible for instance at low temperatures) for a weak disorder (σphoton < the coupling between the pigments) the spectral shift of all the energy levels is slightly perturbed by the disorder and depends linearly on its value, while for higher values of σphoton this dependence does not persist. 17,35,36 Disorder differs between exciton states and changes the phase relationships between molecular excited states contributing to a particular exciton wavefunction. The resulting redistribution of the dipole strengths between the exciton transitions is used as a possible explanation of the various properties of the LH1 and LH2 absorption spectra 37,38 and of the spectra observed in single molecule spectroscopy. 15–18 This effect of disorder is especially pronounced in extended one-dimensional systems where its infinitesimal value results in Anderson localization of the excitons, while for the two- and three-dimensional systems a critical value of the disorder has to be reached before this type of the localization is realized. 37 For finite one-dimensional systems an additional competition between the exciton localization length and the size of the molecular aggregate is expected. In Fig. 1 we present the wavefunction, ψn, for an arbitrary exciton state, n, in a ring of 18 molecules (n enumerates the molecules) with each pigment characterized by two electronic states corresponding to its lowest electronic transition. The average difference between the transition energies for two adjacent molecules is assumed to be equal to the resonance
interaction, which is typically assumed for LH1 and LH2.\(^1\) Fig. 1 shows an example for a particular realization of the disorder how the exciton may be localized on some molecules in exciton states (as measured by the \(|c_{mk}|^2\) values) constituting the effect of Anderson localization.\(^{39}\) In the case of small disorder (in comparison with the resonance interaction) the Anderson localization is predominantly observed for the states at the edges of the exciton band, while the states in the middle of the band remain delocalized.\(^{39}\)

In addition to the static disorder, the interaction of the exciton with fast intramolecular and protein vibrations must be included. This causes a dephasing of the excited molecules participating in a certain exciton state and results in the homogeneous bandwidth of the corresponding optical transition. This type of interaction, generally called dynamic disorder, operates on the time scale of exciton evolution. The exciton states, localized with respect to the Anderson localization, can undergo a subsequent intramolecular relaxation step resulting in molecular Stokes-shift formation (opposed to the line shift due to exciton relaxation within the exciton band, which we do not identify as the Stokes shift) and/or even exciton self-trapping in the case of large exciton–photon coupling.\(^1\) The time scale of this exciton relaxation can be estimated from the experiments of the single molecular spectroscopy\(^1^{15–18}\) or from the three-pulse photon echo measurements.\(^23\) The observed broad absorption band can be attributed to this dephasing time being of the order of tens of femtoseconds. This conclusion is further supported by modelling the ultrafast spectral evolution in LH1 using a model of coherent excitons with disorder and by analysing the femtosecond time resolved measurements.\(^{30,47}\)

Thus, the exciton dynamics in a ring like LH1 and LH2 with intrinsic diagonal disorder, is complex with various stages of exciton relaxation. The optical absorption most probably can be attributed to the transition into coherent exciton states. Because of the inherent disorder, these exciton states are localized (in the sense of the Anderson localization) on a particular part of the aggregate. The size of the exciton localization depends on the value of the disorder and varies depending on position of the exciton state in the band. A subsequent dephasing and/or self-trapping of the exciton (on the time scale of tens of femtoseconds) takes place because of the exciton–phonon interaction. The rates of the exciton relaxation can be estimated by means of the Redfield theory in terms of the second order perturbation of the exciton–photon and/or vibronic coupling. According to this theoretical approach the corresponding matrix elements of the tensor qualifying the exciton relaxation are proportional to the overlap factor \(S_{k_1,k_2,k_3,k_4}\), where:

\[
S_{k_1,k_2,k_3,k_4} = \sum_m c_{mk_1}^* c_{mk_2} c_{mk_3}^* c_{mk_4}.
\]

Thus, it follows that exciton relaxation is expected to be faster in the center of the exciton band where exciton states are delocalized and overlap of wavefunctions is significant and it slows down at the edges in the case of weak disorder. In the case of strong disorder the overlap of the wavefunctions of different exciton states is small because of the exciton localization (see Fig. 1), and fast exciton relaxation between these states is very unlikely. Thus, exciton localization is expected to be typical in one-dimensional aggregates due to static and dynamic disorder resulting in hopping-type of the exciton dynamics instead of coherent delocalized exciton relaxation.

### 3. Modelling

Based on the previous section, we consider the dynamics of a small exciton localized on a few pigment molecules. We define our system as a circular aggregate of \(N\) identical molecular complexes. Each complex is considered as a two level system with the site dependent transition energy \(E_x^A\) for site \(x\).

We consider the dynamic formation of the intramolecular excitation relaxation resulting in the development of molecular Stokes shift,\(^{43}\) which we take into account by means of the following procedure. Let us define the total Stokes shift of a site \(x\) as \(E_x^\text{Stokes}\). Since the vibrational relaxation is responsible for the Stokes shift formation, the energy interval \(E_x^\text{Stokes}\) is divided into \(M\) equal portions, determining a ladder of energies, \(\xi_m = m\hbar\Omega/M\), where \(m = 0, \ldots, M\) (in accord with the harmonic approximation for the bath). Thus, after the annihilation of the excitation on the site \(x\) the emitted energy is \(E_x^\text{Stokes} = E_x^A - \xi_m\), which is a function of the number \(m\) (the superscripts \(D\) or \(A\) refer to the complex donating the exciton (D) and accepting the exciton (A), respectively). The time evolution of the Stokes shift is determined by rates \(k_\text{shift}\), which are the transition rates from state \(m\) to the subsequent state \(m + 1\). We assume \(k_\text{shift}\) being independent of \(m\). For qualitative consideration the upward transition can be ignored at low temperatures. The number of steps \(M\) is the parameter of a harmonic bath \(\hbar\Omega\) which corresponds to the number of vibrational states involved in the vibrational relaxation. It can be explicitly determined by defining one vibrational mode responsible for the exciton intramolecular relaxation, which can be crucial in the case of high frequency vibrational motion when \(M\) is small. However for a small vibrational frequency a large number of vibrational states is participating the relaxation and the importance of \(M\) becomes negligible. We limit ourselves to this large \(M\) limit.

The transition energies of the sites in the ring are assumed to be distributed.\(^{34,43}\) The disorder effect is introduced by taking the site transition energy \(E_x^A\) as a random value from a Gaussian distribution, characterized by the mean value associated with the particular ring, \(E^\text{Stokes}_{\text{ring}}\), and by a dispersion of the distribution \(\sigma_{\text{inter}}\).^2 This kind of disorder is denoted as intra-ring disorder reflecting local inhomogeneities in the system. This kind of definition also allows to introduce the inter-ring disorder reflecting large scale inhomogeneities by defining the ring-dependent energies \(E^\text{Stokes}^{\text{ring}}\) as a Gaussian random numbers characterized by zero mean and the width \(\sigma_{\text{inter}}\).^2 According to these definitions, a ring is constructed in the following way: (1) the mean energy value of the ring, \(E^\text{Stokes}_{\text{ring}}\), is selected randomly in accord with the Gaussian distribution with the dispersion \(\sigma_{\text{inter}}\); (2) the site energies of the ring, \(E_x^A\), are selected in accord with the Gaussian distribution with the dispersion \(\sigma_{\text{inter}}^2\) and the selected mean value \(E^\text{Stokes}_{\text{ring}}\). And this is repeated for each new ring.
We also include the correlations in intra-ring diagonal disorder of each ring using the following procedure. Let $e_{i}^{\text{(0)}}$ denotes the zeroth generation energy of the site $x$ obtained by drawing the independent random numbers as described above. The zeroth generation of the site energies is a set of uncorrelated Gaussian random numbers characterized by width $\sigma_{\text{intra}}$. The first generation of the site energies $e_{i}^{\text{(1)}}$ is created by averaging the zeroth order energy values of neighbouring sites. This procedure introduces nearest-neighbour correlations into the energy picture. By repeating the averaging, higher order correlations of larger extension are introduced, thus, giving the $(n + 1)$-th generation of the site energies accordingly:

$$
e_{i}^{\text{(n+1)}} = \frac{1}{2n+1} \left( e_{i}^{\text{(n)}} + e_{i}^{\text{(n+1)}} \right)$$

(2)

The normalization factor $Z^{\text{(n)}}$ conserves the width of the energy distribution and is calculated from the following relation:

$$(Z^{\text{(n)}})^2 = 2 \left( 1 + \frac{e_{1}^{\text{(0)}}}{e_{1}^{\text{(1)}}} + \frac{e_{2}^{\text{(0)}}}{e_{2}^{\text{(1)}}} + \cdots + \frac{e_{N}^{\text{(0)}}}{e_{N}^{\text{(1)}}} \right),$$

(3)

where $N$ is the number of sites in the lattice. Before making correlations, the mean value of the energies in the 0’th generation is shifted to 0, while after the creation of correlated energies this average value is restored.

The correlated intra-ring and inter-ring disorder reflect the natural biological systems where the surrounding proteins span over large distances exceeding the extension of the aggregate. Thus, intra-ring disorder comes from local differences in nearest surrounding of different pigments (like interactions with the side groups of surrounding protein). The long-range interactions with charges in the protein and distortion of the shape of aggregate due to mechanical tensions build correlations between different pigments inside the ring and lead to inter-ring disorder.

The dynamic parameter of our system is the exciton hopping rate, $k_{x}$, between complexes with the same transition energy. The exciton hopping rates are modulated by energy disorder, i.e. the exciton hopping rate from the $x$th complex onto the $y$th one, $k_{x \rightarrow y}$, is determined as follows:

$$k_{x \rightarrow y} = R(|x-y|) \left( k_{0} \exp \left( -\frac{|E_{x}^{\text{D}} - E_{y}^{\text{D}}|}{k_{B}T} \right) \right) \frac{|E_{x}^{\text{D}} - E_{y}^{\text{D}}|}{k_{0}},$$

(4)

where $R(|x-y|)$ is a distance-dependent factor, $E_{x}^{\text{D}}$ and $E_{y}^{\text{D}}$ are the energies corresponding to complexes $x$ and $y$, respectively, while, $k_{B}$ is the Boltzmann constant and $T$ is the temperature.

To calculate exciton transfer over large distances, we assume the Förster mechanism of exciton transfer. In this case the distance-dependent function $R(|x-y|)$ is given by:

$$R(|x-y|) = \left( \frac{1}{|x-y|} \right)^{6},$$

(5)

where $|x-y|$ is the distance between complexes $x$ and $y$ and the distance between nearest neighbours is 1. In order to account for the exciton transfer between different rings (for instance, the complex of rings located in the membrane), a triangular two-dimensional lattice of rings is considered as the simplest case. We define the distance between the centers of the nearest-neighbour rings in the lattice as $a_{r}$, while the radius of the ring is defined as $a_{g}$ with $a_{r} - 2a_{g} \geq 1$. In this case the exciton hopping rate between the sites of different rings can be calculated by using eqns. (4) and (5) when $x$ and $y$ are vectors pointing to the sites in different rings.

By taking into account the overall excitation decay rate, $k_{t}$, on each complex, a Monte-Carlo simulations are performed to study the exciton dynamics in this system during the excitation lifetime. Each event in the system is simulated by assuming probabilistic nature of the process with the event probability defined by the ratio of the rate of the corresponding process $k$, with to the total rate of all possible processes, $k_{\text{tot}}$, originating from that particular system state. The total rate $k_{\text{tot}}$ defines the timescale of the event, while the actual time of the event is calculated by drawing random number of exponential distribution with the mean $k_{\text{tot}}^{-1}$. This procedure is repeated after each event and, thus, the random hopping is simulated. We assume the following set of parameters for the simulations. According to the estimates based on various experimental observations the hopping time is of the order of 100 fs at room temperature, thus, we assume, $(k_{0} \exp (\frac{-E_{x}(k_{B}T)}{k_{0}}))^{-1} = 100$ fs, where $T_{0} = 293 K$. From the single molecule spectroscopy data it follows that the excited dephasing time is of the order of $50 – 100$ fs$^{16-18}$ therefore, the total Stokes shift formation time has to be of the same order or slower, thus, we assume $k_{\text{shift}} = (100/M) ~$ fs. A typical value for the resonance interaction between pigments is of the order of 200 – $300 cm^{-1}$,$^{17,27,47}$ The Stokes shift of a separate complex is determined from the low temperature fluorescence spectrum$^{48,49}$ upon excitation to the red side of the absorption band, thus, we can take $E_{x} = 100 cm^{-1}$ at 10 K.$^{49,50}$ The absorption bandwidth at 10 K for the disconnected LH2 complexes is of the order of 270 cm$^{-1}$ (FWHM). As it was already mentioned, the inhomogeneous broadening has two origins, i.e. the intra-ring broadening and the inter-ring broadening. These values can be assumed to be equal to $\sigma_{\text{intra}} = 106 cm^{-1}$ in accord with FWHM$_{\text{intra}} = 300 cm^{-1}$ obtained by adjusting the bandwidths and the shift of the fluorescence spectra for disconnected LH2 complexes, while $\sigma_{\text{inter}} = 54 cm^{-1}$ in accord with the total inhomogeneous bandwidth being equal to 120 cm$^{-1}$. The natural decay of the excitation in an isolated complex is of the order of nanoseconds, and $k_{0}^{-1}$ was set to 1 ns in the calculations.

We start our simulation by mimicking optical excitation conditions. Two kinds of initial conditions are used for the simulations. 1. The nonselective excitation is defined by placing initial excitation randomly at any site without the Stokes-shifted states involved. This case is analogous to broadband optical pulse excitation. Due to the Gaussian diagonal disorder, there will be the Gaussian distribution of energies of initial excited states. 2. The selective excitation is defined by assigning the optical excitation energy dependent probability $P(e_{x};e_{o})$ to each site $x$, which is a probability to place the excitation at particular energy on site $x$, where $e_{o}$ is the optical field frequency. We assume Gaussian spectrum of the optical field. Then the excitation probability is given by $P(e_{x};e_{o}) \propto \exp (-\frac{(e_{x} - e_{o})^2}{2(\sigma_{e})^2})$. The width of the optical excitation is defined by full width at half maximum (FWHM = 2.355$\sigma_{e}$). The overall probability of finding the excitation at particular energy is also weighted by a probability of having a site with this energy coming from the diagonal disorder. This case corresponds to the narrow band optical excitation, which can select particular area in the energy distribution (hole burning regime).

After the initial creation of the excitation we perform Monte Carlo simulations of system dynamics: the hopping motion of the excitation is simulated and its energy dependence on time is recorded until the excitation decays due to its finite lifetime. By repeating the simulations for many independent excitations the statistical distribution of excitation energy as a function of time, $P(E,t)$, is revealed. It is worth noting that this distribution is directly related to the time evolution of the fluorescence spectrum. Assuming the transition dipole magnitude being independent of the transition energy, the relation between $P(E,t)$ and the time-dependent fluorescence spectrum is given by:

$$I_{1}(\omega, t) \propto \int_{0}^{\infty} d\omega' \frac{\rho(\omega', t)}{(\omega - \omega')^2 + \frac{\Gamma^{2}}{4}}$$

(6)
where $\Gamma_h$ is the homogeneous linewidth of a particular exciton transition, which is usually much smaller than the inhomogeneous distribution of transition frequencies, represented by $\rho(E,t)$.

4. Simulation of the hopping motion: the case of isolated rings

Let us assume that the coherence size of the exciton equals 2, thus, we will consider the incoherent exciton hopping in a ring of nine complexes characterized by uncorrelated diagonal disorder. The Monte-Carlo simulations give fast (of the order of hundred femtoseconds) equilibration of excitons in the ring at room temperature upon selective excitation into the lower edge of the absorption band (see Fig. 2) as might be expected. Similar dynamics is observed when the system is excited into the maximum of the absorption band or to higher energies. The relaxation process is nonexponential due to a distribution of hopping distances, and the leading term originates from the Stokes shift and nearest-neighbour hopping.

In the case of selective excitation into the very blue edge of the absorption band the final shape of the exciton distribution behaves as a one-peak function as a result of the exciton hopping in the aggregate resulting in predominant population of the lower energy sites and the molecular Stokes shift (see Fig. 3a and b). The final width of the exciton distribution is much broader compared to the original excitation spectrum due to the thermally assisted hopping motion. In the case of selective excitation into the very red part of the absorption band the population of the excitations is equilibrated also on the same time scale but the final distribution is characterized by a broad band with the red-shifted maximum with an additional broad wing to higher energies (see Fig. 3c). The first originates from the population of initially excited molecules that are Stokes shifted, while the broad wing corresponds to the distribution of transition energies in the ensemble due to exciton equilibration at room temperature. This complex shape of the distribution is obtained because of the competition of two processes: thermal activation and Stokes shift. These two competing processes cause the dependence of the fluorescence spectrum on the excitation wavelength as shown in Fig. 3. For nonselective excitation the final distribution of the population mainly resembles the Stokes shift, $E_S$ (see Fig. 4). The dependence of the final population distribution on the excitation conditions reflect that the different rings are disconnected and the complete equilibration of population in the ensemble of rings cannot be achieved, while the equilibration inside each ring is very fast.

The effects due to disorder are substantially enhanced at low temperatures, because then the excitation will not be able to escape when it is trapped in some local minimum in the one-dimensional arrangement of the system. Thus, in the case of uncorrelated disorder and with selective excitation even in the vicinity of the maximum of the absorption band the excitation population finally is distributed as a double peaked structure. This is because in some systems in the ensemble the excitations are able to move to other minima thereby generating a broad red-shifted band in the population distribution within several hundreds of femtoseconds, while others, corresponding to excitation in some local minimum, are responsible for the population of the Stokes shifted band, which appears within hundred femtoseconds. This situation can be modified by assuming correlated disorder and/or by increasing the number of coherently coupled pigments in the ring (i.e., decreasing the number of sites per ring). However, in all cases the value of the Stokes shift and the rate of its formation have an important influence on the equilibrated excitation distribution in the ensemble of single rings.

Modelling the low temperature dynamics with $N = 5$ and assuming correlated disorder with a correlation radius corresponding to the ring size results in the spectral evolution shown in Fig. 5. The dynamics of the Stokes shift formation is taken into account as it was described in the previous section by assuming $M = 50$ thereby allowing for energy transfer through “hot” states. The possibility to escape from the initially excited complex is much larger in the case of excitation into the
maximum of the absorption band leading to a much more red-shifted fluorescence band as compared to the initial excitation wavelength (see Fig. 5b). Almost complete escape of the excitation from the initially excited complex is observed when excitation occurs into the blue part of the absorption spectrum (see Fig. 5a), and the fluorescence is strongly red shifted (almost 400 cm$^{-1}$). In the case of the selective excitation into the low energy wings of the absorption, the hopping motion is not possible, and a single Stokes shifted fluorescence band is obtained (see Fig. 5c). Nonselective excitation results in a broad fluorescence band, which is shifted 200 cm$^{-1}$ from the absorption maximum as shown in Fig. 6.

5. Simulation of the hopping motion: the case of connected rings

In photosynthetic membranes the LH2 rings are organized into larger light-harvesting systems and the exciton can be transferred between the rings. However, in trying to understand the resulting exciton dynamics one has to take into account the fact that the exciton interring transfer rate is much slower than the rate of nearest-neighbour exciton transfer inside the ring (as has been experimentally confirmed, for instance, in the case of the LH2-LH1 transfer$^1$). Therefore, the distance between the nearest pigments located on different rings has to be postulated larger than the nearest-neighbour distance $a = 1$ between pigments in the ring. Here we assume the following relation between different distances: $a_r = 2a + 2a$, implying that the distance between neighbouring sites on different rings is at least two times larger than the distance $a$.

The internal structure of each of the rings is assumed to be the same as in the case of the disconnected rings. Thus, for the calculation of the exciton dynamics at room temperature each ring consists of nine sites and the disorder is not correlated. In this case two distinct components can be distinguished in the exciton equilibration dynamics. A fast one, taking less than 1 ps, which corresponds to the exciton equilibration within the ring resulting in an exciton distribution that is similar to that observed for the disconnected rings (see Fig. 7). However on a longer time scale, much slower inter-ring equilibration manifests itself leading to complete exciton equilibration in the ensemble of rings on this time scale (see Fig. 8). Thus, for connected rings at room temperature a total equilibration is reached within tens of picoseconds and the final distribution is independent of the excitation wavelength. The final width of the exciton distribution is much broader compared to the excitation spectrum due to thermally assisted hopping motion. In the case of nonselective excitation, the evolution of exciton distribution is similar to the case of the disconnected rings as shown in Fig. 9.

Fig. 5 Initial (i), intermediate at 100 fs (m) and final (at 1 ps) (f) distributions of the exciton population in the system of the disconnected rings at $T = 10$ K in the case of the selective excitation into the blue wing of the absorption band (a), to the maximum of the absorption band (b) and into the red wing of the absorption band (c) (excitation energy is ±300 cm$^{-1}$ from the absorption maximum, FWHM of the excitation pulse is 100 cm$^{-1}$). A dashed line indicates the excitation spectrum.

Fig. 6 Initial (i), intermediate at 100 fs (m) and final (at 1 ps) (f) distributions of the exciton population in the system of the disconnected rings at $T = 10$ K in the case of the nonselective excitation.

Fig. 7 Dynamics of the exciton population in the system of 100 rings arranged in the triangular lattice at room temperature in the case of the red-shifted selective short pulse excitation (excitation energy is ~300 cm$^{-1}$ from the absorption maximum, FWHM of the excitation pulse is 100 cm$^{-1}$). Dark (bright) area represents low (high) amplitude of the distribution $P(E,t)$.

Fig. 8 Initial (i), after 100 fs (fine dots), intermediate at 1 ps (m) and final (at 10 ps) (f) distributions of the exciton population at room temperature in the case of the selective excitation into the blue wing of the absorption band (a), to the maximum of the band (b) and into the red wing of the absorption band (c) (excitation energy is ±300 cm$^{-1}$ from the absorption maximum, FWHM of the excitation pulse is 100 cm$^{-1}$). A dashed line indicates the excitation spectrum.

Fig. 9

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mum, FWHM of the excitation pulse is 100 cm
indicates the excitation spectrum.

A shift of the exciton distribution is observed as compared to red-
along with the blue side of the absorption band, a much larger
the case of excitation in the maximum of the absorption band,
shifted exciton distribution is rapidly reached (see Fig. 10). In
the low energy wing of the absorption band a single Stokes
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N
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1 from the absorption maxi-
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For selective excitation in

33 Qualitatively the fluorescence band forma-
considered as using such a localized picture.

The interaction of the exciton with local vibrational modes
gives rise to an additional localization. For substantial values
of the disorder when the Anderson-type of localization is
significant for all the exciton states, the interaction with local
vibrations would result in a small additional shrinking of the
exciton localization radius. In the opposite case for small
values of the disorder the exciton interaction with local vibra-
tions may cause substantial exciton localization.32 In conclu-
sion, after excitation generation by light it evolves according to
the delocalized (coherent) exciton representation30 losing the
cohesive phase matching because of the exciton interaction
with local vibrations and resulting in the
localization of the exciton on this time scale of the exciton
relaxation. The subsequent exciton migration can then be
considered as using such a localized picture.

Fast exciton equilibration in ring-type structures in the case of
nonselective excitation can be well described by means of the
hopping model as demonstrated by modelling of the exciton
dynamics in LH1.32 Qualitatively the fluorescence band forma-
tion based on such a model can be understood as follows. At
infinite high temperatures it would be Stokes shifted only. By
lowering temperature additional red shift of the fluorescence
band is expected because of the Boltzmann factor weighting
distributions of site energies. However, some differences are
expected in the evolution of the exciton population upon
selective excitation. Our application of the hopping model to
LH2 aggregates show that the exciton equilibration in discon-
ected rings depends on the excitation conditions even at room
temperature as shown in Fig. 3. This dependence is most
pronounced for excitation to the red of the absorption band
resulting in a bimodal distribution of the excitation population.
One mode originates from rings in which the red most complex
is excited. The second mode of the distribution of the population
is related to the inhomogeneous distribution of transition
energies of the ensemble of the systems. This effect is even more
pronounced at low temperatures (see Fig. 5). In the case of the
disconnected rings a substantial amount of the exciton popula-
tion remains in the initially excited complex, while only the

To study the exciton dynamics in the system of connected
circles at low temperatures the same parameters of the rings as
used in the previous section for isolated rings were applied, i.e.,
N = 5 and with correlated disorder. For selective excitation in
the low energy wing of the absorption band a single Stokes
shifted exciton distribution is rapidly reached (see Fig. 10). In
the case of excitation in the maximum of the absorption band,
as well as in the blue side of the absorption band, a much larger
shift of the exciton distribution is observed as compared to red-
side excitation. This feature is very similar to the case obtained
for disconnected rings, however because of the hopping motion
of excitons over larger distances a larger shift of the exciton
distribution compared to the case of the disconnected rings is
reached. Nonselective excitation yields a broad fluorescence
band, which is very similar to the case of the disconnected rings
as shown in Fig. 11.

6. Discussion

It is well known that in extended one-dimensional systems in
the presence of any small value of the disorder the exciton
states are localized.39 However, the radius of the localized
exciton is dependent on the ratio between the dispersion of
the disorder and the exciton bandwidth.1 For a finite size of the
molecular aggregate, as is the case in a ring-type molecular
arrangements discussed here, the value of the localization
radius relative to the size of the aggregate provides an addi-
tional parameter that determines the transition between delo-
calized-to-localized exciton states for different values of the
disorder. As is shown in Fig. 1 the exciton wavefunctions
display a clear localized behaviour for all the exciton states
in the system of 18 molecules characterized by typical para-
meters of the B850 ring of Bchl of \textit{Rps. acidophila}. It is
noteworthy that the value of the disorder is assumed to be of
the same order of magnitude as the value of the resonance
interaction. Smaller values of the disorder would lead to a
variation in the localization radius for the different exciton
states, with the states at the edge of the exciton band charac-
terized by a smaller radius of localization and with an
increase of the radius of localization towards the center of
the exciton band becoming commensurable with the size of the
aggregate for smaller values of the disorder.

The interaction of the exciton with local vibrational modes
gives rise to an additional localization. For substantial values
of the disorder when the Anderson-type of localization is
significant for all the exciton states, the interaction with local
vibrations would result in a small additional shrinking of the
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values of the disorder the exciton interaction with local vibra-
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Fig. 9 Initial (i), intermediate at 1 ps (m) and final (at 10 ps) (f) distributions of the exciton population in the system of 100 rings arranged in the triangular lattice at room temperature in the case of the nonselective excitation.

Fig. 10 Initial (i), after 100 fs (fine dots), intermediate at 1 ps (m) and final (at 10 ps) (f) distributions of the exciton population in the system of 100 rings arranged in the triangular lattice at T = 10 K in the case of the selective excitation into the blue wing of the absorption band (a), to the maximum of the band (b) and into the red wing of the absorption band (c) (excitation energy is ±300 cm\(^{-1}\) from the absorption maximum, FWHM of the excitation pulse is 100 cm\(^{-1}\)). A dashed line indicates the excitation spectrum.

Fig. 11 Initial (i), intermediate at 1 ps (m) and final (at 10 ps) (f) distributions of the exciton population in the system of 100 rings arranged in the triangular lattice at T = 10 K in the case of the nonselective excitation.

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remaining part gives rise to a broad distribution due to down hill energy transfer to even lower energy sites in the ensemble.

When exciton migration between rings in a system of connected rings is induced in the model the final exciton distribution becomes independent of the excitation wavelength at room temperature as shown in Fig. 8. However, at low temperature equilibration of the excitation distribution is restricted because of the large Stokes shift and the fast rate of its formation, and equilibrated state is not reached in the case of selective red-side excitation on the time scale under consideration (Fig. 10). Equilibration can be reached on a much slower time scale as a result of long distance excitation hopping between the suitable molecular complexes.15

In the case of correlated disorder the amount of excitons remaining in the initially excited state decreases due to an increased probability of down hill energy transfer and the formation of the broad red-shifted distribution. The amount of excitons remaining in the initial excited state is also sensitive to the size of the localized exciton with more down hill energy transfer for the larger number of the coherently coupled pigments (smaller values of sites per ring N). The spectral distribution of the final population displays itself in the fluorescence spectra with the homogeneous bandwidths as modulating factors.

Aggregation of the separate rings into clusters increases the number of accessible sites for the exciton hopping, leading to the two time scales of the exciton dynamics. A fast one (subpicosecond time scale) represents the exciton migration in the ring resembling the case of the isolated rings, while a slow phase is related to the exciton equilibration in the whole system reached even at low temperatures. This kind of organization of the rings explains the observation of a bimodal spectral evolution on the basis of single molecular spectra of LH2. 15–17

Finally, the approach presented here qualitatively reproduces recent experimental observations of the fluorescence properties of interconnected ring-like complexes using selective excitation, 35,49 which are qualitatively similar to those of LH1.50 Indeed, at low temperatures position of the fluorescence is independent (or very weakly dependent) of the excitation wavelength when exciting to the blue side of the absorption band, while the fluorescence follows the excitation wavelength at the red-side of the absorption band. In addition, the fluorescence bandwidth is independent of the excitation wavelength except upon excitation in the very red edge. The same conclusions also follow from our model calculations as presented in Fig. 5.

Correlation of the disorder suggests some global distortion of the ring-type aggregate, possibly similar to that suggested on the basis of single molecular spectra of LH2.15–17 Most probably the exact exciton dynamics is determined by a model, which is in between the stochastic exciton hopping and the coherent exciton relaxation. It might be expected that the correlation of the disorder results in the relaxation between some coherent exciton states at the very initial moment after the excitation of the system. Additional effect could be obtained from the exciton interaction with long-wavelength phonons, which have also to be taken into consideration.

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