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Electron-vibrational coupling decreases trapping by low-energy states in photosynthesis

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ABSTRACT

In photosynthetic light harvesting, states with energy well below that needed for charge separation can be found in abundance. They do not hinder the quantum efficiency of the primary processes; on the contrary, they can be highly functional, extending the absorption towards the red. Although many properties of these states are well described based on spectroscopic and theoretical studies, the physical mechanisms underlying their working are not known. Here we propose a mechanism which utilizes high-frequency vibrations of the photosynthetic pigments and the combined spatio-energetic aspect of the excitation dynamics. We present numerical calculations of the excitation dynamics in explicit electron-vibrational basis, with parameters based on photosynthetic complexes such as the Lhca4 complex of higher plants. The electron-vibrational states have two roles. For the trapped, low-energy excitation they provide a thermally populated ladder out of the trap. And for the high-energy excitation they provide local-bath states, effectively forming a bridge over the trap.

1. Introduction

In photosynthesis, light energy is absorbed by the pigments within the photosystems. The energy is then transferred through the photosystem to its core, where it eventually reaches a reaction center (RC). There the energy is used to drive charge separation for which, depending on the species, a specific amount of energy is needed. The excited state energy landscape of the light-harvesting complexes is built in such a way that it both enables absorption of light across a wide range of the sunlight spectrum and facilitates an efficient energy transport to the core [1]. This is reminiscent of the situation in semiconductor photovoltaics (PV), where all the light energy absorbed above a particular band gap thermalizes to the band edge, and only then it can be extracted as charge. There is a fundamental difference, though. In PV, states below the bandgap act as traps, decreasing the overall efficiency. Accordingly, there has been much effort in trying to get rid of these traps [2,3]. In contrast, in photosynthesis, where the light-harvesting quantum efficiency is very high, excited states with energy lower than that of the reaction center are found frequently. Such states have been observed in the antenna complexes Lhca3 and Lhca4 of photosystem I, in the major light-harvesting complex II (LHCII) in higher plants and algae [4–7], in the fucoxanthin-chlorophyll *a/c* binding protein (FCP) antennas of diatoms [8] and in other complexes [9]. These low-energy excited states may be formed by strong

interaction of a particular pigment with its local (protein) environment, strong excitonic interaction between neighboring pigments (leading to exciton splitting) and by formation of a charge transfer state which mixes with an excitonic state. Because these states are often observed in spectroscopic measurements, they are referred to as red states or red forms.

Not only do these red states not hinder the light harvesting capability of the photosynthetic apparatus, on the contrary, they have been attributed several functional roles. First, in line with their trapping ability, they have been speculated to play a role in the process of non-photochemical quenching (NPQ), a photoprotective dissipation of excess excitation energy [6,10]. For the NPQ-related functionality the red states must be able to recombine quickly to a ground state. However, this is not always the case. Another function of low-lying states is the stabilization of a quasi-final state within one light-harvesting complex. This is typically achieved by strong excitonic interaction, giving rise to a low-energy state, delocalized among a particular group of pigments, with decreased sensitivity to energy disorder [11]. Perhaps both the most straightforward and puzzling function of the red states is the extension of the absorption spectrum to the region energetically below the energy of the reaction center. This is the case of photosystem I and is the main motivation of the current study [12,13]. Finally, there is the possibility of the low-energy states forming without any specific function. Due to the large concentration of pigments within the light-

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harvesting proteins (about 0.5 M [1]), occasional formation of red states by the mechanisms described above, in particular by formation of a mixed exciton-CT state, seems inevitable and was indeed observed [7].

As pointed out recently, explaining the functionality of the low-energy states is one of the big current challenges in photosynthesis. In the paper highlighting the importance of the low-energy states, the authors review the possible origins and spectroscopic signatures of the low-energy states, together with known cases of occurrence [9].

The main conceptual difference between the light harvesting in semiconductors and photosynthetic membrane is the spatial extent of the excitation. In the semiconductor the excited states are highly delocalized: the free electrons can be well described by the well-known Bloch functions, and excitons, when formed, are of the Wannier-Mott type, with large delocalization extent and small binding energy, leading to a fast dissociation [2]. Charge is then extracted from the bulk. In contrast, in photosynthetic membrane the excitation forms Frenkel-type excitons, with the electron closely associated with the hole, and with a relatively small spatial extent of delocalization [14]. This has obvious consequences for the excitation dynamics. Crucially, the influence of the low-energy states is profoundly different. In the photosynthetic case, the excitation can spatially avoid the red state, or escape from it by transfer to a spatially separated state. On the other hand, a low (or high) energy state can represent an obstacle on the way to the reaction center. It is precisely this interplay of the energetic and spatial landscape that makes the photosynthetic light-harvesting dynamics rich and complex and that enables the functional role of the low-energy states.

In this work we address the latter two *modi operandi* of the low-energy states mentioned above. First, we focus on the detrapping from the red state, for instance after absorption of a low-energy photon. In PSI the low-lying states extend the absorption into the red. As shown by fluorescence excitation and transient absorption spectroscopy, at physiological temperature the quantum efficiency of the charge separation after absorbing a red photon approaches unity [13]. This implies efficient detrapping from the red states, necessary for providing enough time to reach the reaction center and separate the charge before recombination happens. But how is this achieved? Interestingly, the efficiency significantly decreases at cryogenic temperatures, freezing the excitation in the low-energy state. This hints at a thermally activated mechanism. Here, we propose a vibronic mechanism of detrapping. It involves the thermal population of a higher intrapigment vibrational state, which is resonant with the excited state of the higher-energy pigment. As a result, once the excitation reaches this state, it is rapidly transported away from the red state. Interestingly, the same mechanism can be used to describe excitation transfer through a high-energy barrier.

Another process which we address is for the excitation to avoid the red states present in the photosystem. As mentioned above, the presence of low-lying, essentially localized states is detrimental in semiconductor PV. Why is this not the case for the photosynthetic apparatus? Low-energy states can often be formed at a place through which the energy is bound to be transferred on its way to the RC [15]. Experiments of Palsson et al. have shown that, even at cryogenic temperatures, half of the excitation quanta makes it to the reaction center, in the presence of deep low-energy traps [13]. Why does the presence of the red states not substantially lower the quantum efficiency of transport? When the excitation falls into the ‘trap’, the excess energy has to be dissipated into some vibrational modes, traditionally thought of as the ‘bath’ for the electronic degrees of freedom (DOF). The most strongly coupled vibrational modes to the electronic DOF are the intrapigment modes, acting as a local bath. Here we argue that ‘dissipating’ the excess energy into such modes results in a ‘transiently hot bath’ either at the donor or the acceptor site. During the lifetime of the vibrational excitation, the energy is not lost and the excitation can use it to escape from the trap. When treating the intramolecular vibrational modes explicitly, as a part of the system, this effect becomes clearly

visible. As a result, the low-energy states do not act as traps during the lifetime of the vibrational energy.

Vibrational-electronic effects in photosynthetic complexes have been explored in detail recently in the context of nonlinear spectroscopy [16–22]. The coupling of the electronic DOF to the local pigment vibrations was shown to facilitate downhill energy transfer across large energy gaps [23], and to influence the first steps in charge separation in PSII-RC [24,25], to give a few photosynthetic examples. Interestingly, strong vibronic coupling can also alter the inner excited state structure of isolated pigments, by mixing of Qx and Qy transitions in pigment molecules [26]. This effect modifies the coupling between the pigments and their spectroscopic response. Concerning the effect on dynamics, the (resonant) vibrations are typically discussed in the context of acceleration of the energy/charge transfer over energy gaps [27]. In that case, the resonance and vibronic mixing are the key parameters. Here, we propose yet another role of these vibronic effects, relying, among other, on the finite lifetime of the vibrations and the spatial aspect of the problem. We show that by utilizing the intramolecular vibrational modes, the low-energy, red, states are easier to escape from and harder to fall into. These results explain how the low-lying excited can be present and functional in the efficient light-harvesting photosynthetic apparatus.

2. Results

2.1. Detrapping: the three-state model

To study the essential features of a trap state in the presence of high-frequency vibrations, we use a simple scheme consisting of two excited states e1, e2 and a low-lying state acting as a red trap (Fig. 1). As the origin of such low-energy states is typically a mixing with a CT state, we denote this state CT. The three electronic states (e1, e2, CT) are each coupled to one vibrational mode. The CT state is supposed to be dynamically localized due to the energy gap and its large displacement with respect to the excited state e1. The displacement of the second excited state e2 (with respect to e1) is small, meaning that the e1-e2 states are excitonically mixed, and the e1 → e2 transfer is determined by exciton relaxation. The excitation dynamics within the whole CT-e1-

Fig. 1. Three-state model, containing a low-energy state with charge-transfer character (CT) and two exciton states e1, e2, all coupled to one vibrational mode with frequency Ω . Here we show a simplified one-dimensional scheme, but in fact each diabatic state (e1, e2, and CT) is coupled to its own effective nuclear coordinate (corresponding to a vibration with frequency Ω). The resulting electron-vibrational dynamics is therefore considered in the 3-dimensional basis of the effective nuclear coordinates Q_1 - Q_3 (not shown). Initially the lowest eigenstate (corresponding to the zero-phonon (ZPL) level of CT) is excited. This is followed by thermal population of the first vibrational sublevel of CT with subsequent transfer (black arrow) to the ZPL of the higher exciton state (predominantly localized at e1). Then, population of the e1-e2 dimer is stabilized by relaxation (black arrow) to the lower exciton state (with predominant contribution of e2).

Fig. 2. Kinetics of the e1, e2 and CT populations in the site representation, calculated at room temperature. Displacements of the {e1 e2 CT} diabatic states along $\{Q_1 Q_2 Q_3\}$ coordinates are $\Delta = \{0.2 \ 0.2 \ 0.9\}$. Parameters of the spectral density: $\gamma = 600 \text{ cm}^{-1}$, $\lambda = 400 \text{ cm}^{-1}$; $\Phi^2 = 0.3$, $\phi^2 = 0.1$. Couplings between diabatic states are $\{M_{CTe1} \ M_{CTe2} \ M_{e1e2}\} = \{25 \ 0 \ 150\} \text{ cm}^{-1}$. Time delays are 0–80 ps. Initial conditions: lowest vibronic level ($b = 1$, corresponding to ZPL of the CT state) is excited. Energies of the zero-phonon levels (ZPL) of the {e1 e2 CT} diabatic states are $\{600 \ 200 \ 40\} \text{ cm}^{-1}$; vibrational frequencies are $\Omega = 470, 570, 610, 675, 775 \text{ cm}^{-1}$.

e2 manifold is described by Redfield theory in the basis of the exciton-vibronic (vibronic) eigenstates in a multi-dimensional configuration space (as in Ref. [28]). Recently, we have verified by comparison with hierarchical equations of motion (HEOM) that Redfield theory in the vibronic basis gives quantitatively correct results over a wide range of parameters, covering the ones used here [29]. The spectral density has the same overdamped Brownian oscillator profile for the electronic and nuclear coordinates, but we use a different scaling of its amplitude for the electronic and vibrational parts (given by dimensionless factors Φ^2 and ϕ^2 , respectively, as described in [28]). As described in Ref. [30], the coupling constants are experimentally accessible in the form of the zero-phonon line (ZPL) linewidth (Φ^2) and vibrational relaxation rate (ϕ^2). The full theoretical description of the model, including the system, bath, their interaction, and the vibronic Redfield theory, can be found in Appendix A1. The concrete values of the parameters used for calculation can be found in the caption of Fig. 2.

In Fig. 2 the kinetics of the $CT \rightarrow e1 \rightarrow e2$ detrapping is shown in the site representation (where we present populations of the sites e1, e2 and CT, obtained as the sum of their contributions to all the vibronic states). The initially populated CT is depopulated due to uphill transfer to the intermediate exciton level (localized mostly at e1), followed by relaxation to the lower level (predominantly localized at e2). At thermal equilibrium (reached within about 80 ps) population of intermediate e1 is very small, whereas steady-state populations of e2 and CT are determined by their relative energies. In our example, e2 is higher than CT, so that its population is less than of CT. In real systems, the excitation is further transferred from e2 to other pigments and, finally, to the reaction center. In this way the energy will be trapped by the charge transfer states of the RC, and if these trap states lie lower in energy than the antenna CT, this CT will be sooner or later completely depopulated. The efficiency (quantum yield) of the whole process is determined by a competition between energy transfer to the RC and nonradiative losses (including deactivation of the red CTs) [31]. The

bottleneck of this process is the detrapping from the CTs, which is very slow. Below we consider the possibility to increase the detrapping rate in the presence of vibrations, coupled to the excited states.

In Fig. 2 we demonstrate that the detrapping rate can be significantly increased if the vibrational mode is in resonance with the energy gap between the electronic states. Tuning of the vibrational frequency around the gap between the CT and neighboring antenna state (which is about 600 cm^{-1} in a real antenna, for example in Lhca4 [32]), a more than two-fold speed up of the CT depopulation can be obtained (Fig. 2). This depopulation is mirrored by a fast population of the primary acceptor state, e2, from where the excitation can be quickly delivered to the RC. In a real antenna, we can have a manifold of strongly coupled excited states instead of just two corresponding to our model. The effect will qualitatively be the same. What is important is the resonance of the gap between the CT and the nearest excited state with some vibrational quantum.

It can be shown that the effect of electron-vibronic resonance is more pronounced when increasing the exciton coupling M_{e1e2} between the e1-e2 states (see Fig. S3 in the Supplementary Information (SI)). Large coupling produces higher degree of e1-e2 delocalization and faster relaxation rate, meaning that stabilization of the mixed CT-e1 population becomes more efficient. The degree of detrapping can also be changed by shifting the diabatic e2 energy (at fixed coupling value) as shown in Fig. S4 in the SI. The detrapping enhancement due to the vibrational resonance (shown in Fig. 2) is more pronounced when the CT state is more localized; the difference between the resonant and off-resonant cases is larger upon decreasing the exciton-CT coupling M_{CTe1} and/or increasing the displacement Δ of the CT state (which is larger due to the possible CT character). The Huang-Rhys factor $S = \Delta^2/2$ for the vibration in the excited states equals 0.02, which corresponds to the typical values found in natural complexes. Increase of S (stronger vibronic effects) produces faster transfer, but the resonant effect becomes less pronounced (see Fig. S5 in the SI). On the other hand, for smaller S the resonance is deeper, but the transfer becomes slower.

Thinking about the eigenstate kinetics, two pictures are equivalent: the probabilistic, rate picture and the stochastic picture. Because of detailed balance, the trapping rate (vibrational relaxation) is by a factor of $\exp(\Delta E/k_B T)$ (about 20 under realistic parameters, at room temperature) faster than its uphill counterpart. The excitation which manages the uphill step (thinking in the stochastic view) has a very limited window of opportunity to escape the trapping region. The detrapping thus works when the escape rate outcompetes the trapping one. This is enabled by our vibronic mechanism.

The working details of the three-level scheme, including the vibronic mixing effects, the sensitivity to its parameters and some spectroscopical signatures can be found in the first section of the SI. These details are to a large extent model-specific and are not crucial for the concept of vibronic detrapping. They, however, provide a deeper insight into the working of this mechanism.

2.2. Detrapping: the four-state model

In a real antenna, the excited state e1 is in fact coupled to a rich manifold of exciton states responsible for the transfer to the reaction center, where the excitation of the primary donor initiates a sequence of charge transfer steps resulting in the formation of the final radical pair (RP). Coupling of e1 to many states produces, in principle, a better stabilization of the energy detrapped from the CT. This is sometimes called an ‘entropic’ effect, when the transfer from a single state to a large number of states is largely unidirectional, with a suppressed back-transfer rate. If, in addition, the final RP is lower in energy than CT (which usually is the case), the population balance will be further shifted towards predominant formation of RP. This can be illustrated by a four-state model (Fig. 3), where the exciton states of the antenna are still described by just two states (e1, e2), but stabilization of the detrapping occurs in the presence of one more low-lying state, i.e. the

Fig. 3. Left: Four-state model, containing a charge-transfer-character (CT) state, exciton states e1, e2, and a final radical pair (RP) coupled to a single vibrational mode with frequency Ω . Initial population of the lowest sublevel (ZPL) of CT is followed by population of the e1-e2 dimer (similar to Fig. 1), that is stabilized by relaxation to the final RP. **Right:** Kinetics of the CT, e1, e2, and RP populations in the site representation calculated at room temperature. Displacements of the {e1 e2 CT RP} diabatic states along $\{Q_1 Q_2 Q_3 Q_4\}$ coordinates are $\Delta = \{0.2 \ 0.2 \ 0.9 \ 0.9\}$. Parameters of the spectral density: $\gamma = 400 \text{ cm}^{-1}$, $\lambda = 200 \text{ cm}^{-1}$; $\Phi^2 = 0.3$, $\phi^2 = 0.1$. Couplings between diabatic states are $\{M_{CTe1} \ M_{e1e2} \ M_{e2RP}\} = \{25 \ 150 \ 100\} \text{ cm}^{-1}$ (other couplings are zero). Time delays are 0–100 ps. Energies of the electronic levels (ZPL) of the {e1 e2 CT RP} diabatic states are $\{600 \ 200 \ 40\text{--}150\} \text{ cm}^{-1}$; vibrational frequencies are $\Omega = 500$ (dashed), 600 (solid), 700 (dotted) cm^{-1} .

final RP. Such a scheme gives faster (compared to the three-state model) depopulation of the initially excited CT. Furthermore, by tuning the vibrational frequency around the CT-e1 gap we find a more pronounced resonance effect.

2.3. Transfer over a red trap

To study the transfer over a red CT state (where population of the CT-ZPL with subsequent detrapping can be outcompeted by direct vibration-assisted superexchange between the excited states) we consider the four-state model shown in Fig. 4.

We take the initial excitation localized at the site e0. This can be modeled by supposing an impulsive optical excitation of the whole complex from the ground state, with all the transition dipoles artificially set to zero except one for the e0 diabatic state. The initial wavepacket will be localized near the bottom of e0 even if the e0-ZPL is delocalized due to resonant mixing with the vibrational sublevel of CT.

Fig. 4. Four-state model, containing three excited states e0, e1, e2 and charge-transfer (CT) state coupled to a single vibrational mode with frequency Ω . Vibronic dynamics is considered in the 4-dimensional basis of the effective nuclear coordinates Q_1 – Q_4 (not shown). Initially the e0 site is excited. This is followed by transfers to the CT (with population of its ZPL and vibrational sublevels) with subsequent transfer to higher exciton level of the e1-e2 dimer (predominantly localized at e1) and relaxation to the lower level (with predominant contribution of e2).

Excitation of higher levels of e0 is about $\Delta^2/2$, i.e. only 2% of the ZPL.

Kinetics of the site populations upon excitation of e0 are shown in Fig. 5. For the CT state we show the total population (magenta curves) and a population of CT-ZPL (black curve). The difference corresponds to population of the hot vibronic states of CT, mixed with the e0 and e1 states. Notice that in Fig. 5 we explore the case when both e0-CT and e1-CT gaps are in resonance with the vibrational frequency.

Without vibrational relaxation (coupling to vibrational bath is $\phi^2 = 0$) we observe quick population of the vibronic states of CT with immediate transfer to e1/e2 (see top left frame of Fig. 5). Population of the final e2 state is faster than population of the CT-ZPL. Notice that relaxation to CT-ZPL still exists even at $\phi^2 = 0$ due to some degree of electronic mixing present in all the vibronic states. Although we use small coupling to the electronic bath in this example ($\Phi^2 = 0.03$) relaxation to CT-ZPL is non-negligible. This relaxation becomes faster for non-zero coupling to the vibrational bath (see next two frames with $\phi^2 = 0.0002$ and 0.0006). Notice, however, that in these two cases the vibronic states of the CT are populated faster than the CT-ZPL and the rate of $e0 \rightarrow CT \rightarrow e1/e2$ transfer still competes with the red (CT-ZPL) state population. Further increase of the vibrational relaxation rate (to $\phi^2 = 0.006$) significantly reduces the speed of direct $e0 \rightarrow CT \rightarrow e1/e2$ superexchange (bottom right frame). The total CT population is now dominated by the CT-ZPL contribution (magenta and black curves are now growing synchronously). This is the ‘detrapping’ limit, when the CT-ZPL is populated first, i.e. prior to the e1/e2 population. Larger values of ϕ^2 , i.e. $\phi^2 = 0.06$ and 0.6 do not change the kinetics compared with the $\phi^2 = 0.006$ case (see Fig. S6 in the SI).

Similar switching from the ‘passage over red state’ to the ‘detrapping’ is observed when the e0 state is moved out of resonance (see Figs. S6, S7 in the SI). Kinetics are qualitatively similar to the case of ‘double resonance’ (shown in Figs. 5 and S6), but noticeably slower (as shown in Fig. S7).

3. Conclusions

Photosynthetic chlorophyll pigments have high-frequency, underdamped intramolecular vibrational modes, coupled to the electronic degrees of freedom. We have demonstrated that the presence of such

Fig. 5. Kinetics of the e0, CT, e1 and e2 populations in the site representation calculated for room temperature. Kinetics of the total CT population (magenta) is shown together with the kinetics of the CT-ZPL level only (black). Displacements of the {e0 e1 e2 CT} diabatic states along { Q_1 Q_2 Q_3 Q_4 } coordinates are $\Delta = \{0.2 \ 0.2 \ 0.2 \ 0.8\}$. Couplings between diabatic states are $\{M_{CTe0} \ M_{CTe1} \ M_{e1e2}\} = \{25 \ 25 \ 150\} \text{ cm}^{-1}$ (other couplings are zero). Energies of the electronic levels (ZPL) of the {e0 e1 e2 CT} diabatic states are $\{660 \ 600 \ 200 \ 40\} \text{ cm}^{-1}$; vibrational frequency is $\Omega = 600 \text{ cm}^{-1}$. Time delays are 0–20 ps. Parameters of the spectral density: $\gamma = 400 \text{ cm}^{-1}$, $\lambda = 200 \text{ cm}^{-1}$; $\Phi^2 = 0.03$, $\Phi^2 = 0$ (top left), 0.0002 (top right), 0.0006 (bottom left), and 0.006 (bottom right).

vibrations can contribute decisively to the functionality of low-energy states. For the excitation of the low-energy states (e.g. after absorption of a red photon), the vibrational levels provide transient states through which the energy can escape the trap. For the excitation with higher energy, the vibrational states provide a way over the trap, without falling (i.e. relaxing) into it and getting trapped. The key features of the vibrational modes are their high frequency to bridge the energy gap between the trap and higher-energy pigments, their long (ps) lifetime, providing enough time to escape to the adjacent pigments and avoid trapping, and reasonably large Huang-Rhys factor S (coupling to the excited electrons). In our calculations these requirements are fulfilled. Crucially, the parameters we used are in the range typical for the low-energy photosynthetic pigments [9,33]. For instance, the spectral density measured for LHCII contains a lot of modes with S about 0.02 and some vibrational modes characterized by even stronger coupling, i.e. 388 cm^{-1} and 742 cm^{-1} modes with $S = 0.06$ and $S = 0.04$, respectively [34]. The values describing the interaction with the environment take into account this experimentally obtained spectral density. Natural photosynthetic systems have some degree of energetic disorder. As a result, the resonance between the energy gaps and vibrational frequencies will never be perfect. However, as we also show in the last section of the SI, the vibronic transfer mechanism is relatively forgiving to detuning [30]. Because of the multitude of available

vibrational modes, we expect our mechanism to be robust in the presence of disorder [35]. In our calculations, the small systems reach thermal equilibrium, inevitably with significant population of the low-lying state. In contrast, real photosynthetic systems, such as photosystem I, are much larger and less connected, making the spatial propagation of the excitation important. As a result, the excitation can escape from the trap and the kinetics of the detrapping/trap avoidance are crucial. It is the interplay of the spatial and energetic aspects, which makes the kinetics matter. Our vibronic mechanism enables fast detrapping and transfer over the trap state. We therefore propose that the vibronic mechanism outlined here can contribute to the remarkable functionality of low-energy states in photosynthetic light harvesting.

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Conflicts of Interest

The authors declare no conflict of interest.

Appendix A. Theoretical description

In this Appendix we provide the theoretical description of the problem, including the electron-vibrational Hamiltonian, the interaction with a vibrational bath, and Redfield theory for the system dynamics.

A.1. Electron-vibrational Hamiltonian

The system (excited-state) Hamiltonian in the site (diabatic) representation is [30,36]:

$$H_e = \sum_n |n\rangle \left[\omega_{n0} + \sum_{j,s} \frac{1}{2} \Omega_j (\Delta_n^{js})^2 + \sum_{j,s} \Omega_j (\beta_{js}^+ \beta_{js} + \frac{1}{2}) - \sum_{j,s} \frac{1}{\sqrt{2}} \Omega_j \Delta_n^{js} (\beta_{js} + \beta_{js}^+) \right] \langle n| + \sum_{nm} |n\rangle M_{nm} \langle m| \quad (1)$$

The electron-vibrational states are given by a direct product of the electronic (one-exciton) wavefunctions $|n\rangle$ and vibrational wavefunctions $|a_{js}\rangle$ for j -th mode depending on effective nuclear coordinates (labelled 's'). The basis wavefunctions $|a_{js}\rangle$ are unshifted, i.e. they have zero displacement along the s -coordinates. The creation and annihilation phonon operators β_{js}^+ and β_{js} for the j -th nuclear mode are working in this unshifted basis.

Displacement of the electronic surfaces along the s -coordinates (characterized by dimensionless Δ_n^{js} values) is described by the shifting operators $\Omega_j \Delta_n^{js} (\beta_{js} + \beta_{js}^+)/\sqrt{2}$, where Ω_j is the frequency of j -th mode. As each of the N pigments has its own vibrational mode, the electronic surfaces will be dependent on the nuclear coordinates in the N -dimensional configuration space. The zero-phonon transition energy corresponding to a pure electronic excitation of the n -th state is ω_{n0} . The interaction between the diabatic states is given by the energies M_{nm} that are assumed to be independent on the vibrational coordinates. Diagonalization of the Hamiltonian (1) gives the exciton-vibronic (vibronic) eigenstates:

$$H_e C^e = C^e E^e; \quad |b\rangle = \sum_{n,a} C_{n,a}^e |n, a\rangle; \quad E_{bb'}^e = \delta_{bb'} \omega_b \quad (2)$$

where $|n,a\rangle$ denote a product of the electronic $|n\rangle$ and vibrational wavefunctions $|a\rangle$, where $|a\rangle = |a_{11}, \dots, a_{js}, \dots\rangle$ is the product of wavefunctions corresponding to the s -th coordinate of the j -th vibrational mode. C^e is the transformation matrix, whose elements show participation of the unshifted states $|n,a\rangle$ in the vibronic states of the one-exciton manifold b .

A.2. System-bath interaction Hamiltonian

The system-bath Hamiltonian in the site representation is:

$$V_e = \sum_n |n\rangle \left[\Phi_n + \sum_{j,s} \phi_n^{js} (Q_{js} - \Delta_n^{js}) \right] \langle n| \quad (3)$$

$$Q_{js} = \frac{1}{\sqrt{2}} (\beta_{js} + \beta_{js}^+);$$

where ϕ_n are bath-induced fluctuations responsible for vibrational relaxation of the s -coordinate of the j -th mode (Q_{js}) in the corresponding electronic (diabatic) states. The coupling is linear in the vibrational coordinate Q measured from the minimum of the potential surface [37,38].

The coupling of the n -th site to the bath degrees of freedom (phonons and vibrational modes of the environment) is described by a correlation function, given by $\langle \Phi_n(t) \Phi_n(0) \rangle$. In the frequency domain the system-bath coupling is described by the spectral density $C(\omega)$, which is given by the Fourier transformation of this correlation function $\langle \Phi_n(t) \Phi_n(0) \rangle$ (a more detailed explanation of these features is given in Ref. [30]). Switching from the site representation to the exciton basis, one finds that fluctuations of the site energies produce off-diagonal dynamic disorder, i.e. fluctuations connecting different exciton eigenstates (and inducing relaxation between any pair of the exciton states, containing some participation of the n -th site). The Redfield relaxation tensor, that arises from the perturbative treatment of the system-bath interaction in the exciton basis, is proportional to the spectral density $C(\omega)$ and to the exciton wavefunction amplitudes (giving participation of the n -th site to the exciton states involved). In this manner, the Φ term in Eq. (3) is responsible for electronic relaxation. Similarly, it can be shown that the fluctuation term represented by the product of ϕ and the vibrational coordinate Q (counted from the potential minimum) induces relaxation between the neighboring vibrational sublevels ($a \rightarrow a \pm 1$) of a harmonic oscillator. The combined action of the two terms (acting on the electronic and vibrational system coordinates) describes a relaxation within a mixed exciton-vibronic (vibronic) manifold [30].

Notice that in Eq. (3) we neglect the off-diagonal coupling, i.e. bath-induced modulation of interaction energies M_{nm} . We suppose that fluctuations acting on different sites (n), different vibrational modes (j), and different nuclear coordinates (s) are uncorrelated. In the following it is convenient to treat the ϕ_n and Φ_n quantities as dimensionless. The matrix elements of the system-bath Hamiltonian in the eigenstate (adiabatic) representation are:

$$V_{bb'} = [(C^e)^\dagger V_e C^e]_{bb'}. \quad (4)$$

A.3. Redfield relaxation tensor

The Redfield tensor can be calculated in a standard way [37–41]:

$$R_{b_1 b_2 b_3 b_4} = -V_{b_4 b_2} \bar{V}_{b_3 b_1} (J_{b_2 b_4} + J_{b_1 b_3}) + \delta_{b_2 b_4} \sum_b V_{b_3 b} \bar{V}_{b b_1} J_{b b_3} + \delta_{b_1 b_3} \sum_b V_{b_4 b} \bar{V}_{b b_2} J_{b b_4} \quad (5)$$

$$J_{bb'} = \frac{1}{2} C(\omega_{bb'}) \left[\coth \frac{\omega_{bb'}}{2k_B T} - 1 \right]; \quad \omega_{bb'} = \omega_b - \omega_{b'},$$

where $V_{bb'}$ is the matrix element of the system-bath Hamiltonian in the eigenstate representation. We take the bath spectral density in the form of an overdamped Brownian oscillator (with reorganization energy λ and damping constant γ):

$$C(\omega) = 2\lambda \frac{\omega\gamma}{\omega^2 + \gamma^2}. \quad (6)$$

If $C(\omega)$ is expressed in the units of energy, then the $V_{bb'}$ elements in Eq. (5) should be expressed through the dimensionless ϕ and Φ amplitudes (horizontal bar means an averaging over the bath). In Eq. (4) we suppose that the λ and γ values are the same for all the electronic states, but the differences in system-bath coupling for different sites can be accounted for by a scaling of the ϕ and Φ amplitudes.

The Redfield tensor $R_{b_1 b_2 b_3 b_4}$ determines the dynamics of the one-exciton populations $\rho_{b_1 b_2}(t)$. In the Liouville space the populations are given by vector $\rho_\alpha(t)$, whereas the one-exciton relaxation tensor is $R_{\alpha\beta}$, with $\alpha = b_1 + (b_2 - 1)N_b$ and $\beta = b_3 + (b_4 - 1)N_b$, where N_b is the vibronic cutoff, i.e. the number of one-exciton vibronic states included into the modelling of the dynamics. For computation, the $R_{\alpha\beta}$ tensor can be expressed as a product $B \otimes A$ of the tensors $B_{b_2 b_4}$ and $A_{b_1 b_3}$. In matrix notation:

$$R = -\sum_{n,j,s} (\bar{\phi}_n^{js})^2 (B_n^{js} \otimes A_n^{js} + A_n^{js} \otimes B_n^{js}) - \sum_n (\bar{\Phi}_n)^2 (B_n^e \otimes A_n^e + A_n^e \otimes B_n^e) + \sum_n (B_n \otimes I + I \otimes B_n) \quad (7)$$

$$B_n^e = C_n^\dagger C_n; \quad A_n^e = B_n^e * J; \quad C_n = \sum_{a,b} |a\rangle C_{n,a,b}^e \langle b|$$

$$B_n^{js} = C_n^\dagger Q_n^{js} C_n; \quad A_n^{js} = B_n^{js} * J; \quad Q_n^{js} = Q_{js} - \Delta_n^{js}$$

$$B_n = (\bar{\Phi}_n)^2 C_n^\dagger C_n (C_n^\dagger C_n * J) + \sum_{js} (\bar{\phi}_n^{js})^2 C_n^\dagger Q_n^{js} C_n (C_n^\dagger Q_n^{js} C_n * J).$$

Here I is a unity operator, C_n is a fragment of the C^e corresponding to a fixed electronic site n (the sum of independent contributions from different sites appears since we use an uncorrelated fluctuation model). In terms like $C_n Q_n C_n$ we assume a matrix multiplication, B^*J denotes an array multiply (product of the elements of the matrices), $\otimes$ stand for a Kronecker tensor product. Such a form is useful for numerical evaluation of the Redfield tensor. The dynamics of vibronic populations is then given by:

$$\dot{\rho}_\alpha = -i\omega_\alpha \rho_\alpha - \sum_\beta R_{\alpha\beta} \rho_\beta, \quad (8)$$

where $\omega_\alpha = \omega_{b1b2} = \omega_{b1} - \omega_{b2}$. In the present modeling (restricted to a 4-state model with a single vibration, i.e. $n = 1-4$, $j = 1$, $s = 1-4$) we suppose for simplicity that

$$\overline{(\varphi_g^{js})^2} = \overline{(\varphi_n^{js})^2} = \varphi^2; \quad \overline{(\Phi_n)^2} = \Phi^2; \quad (9)$$

i.e. couplings to electronic and vibrational baths are site-independent (with additional scaling for the CT state in proportion to its displacement value).

Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemphys.2019.02.011>.

References

- [1] R.E. Blankenship, *Molecular Mechanisms of Photosynthesis*, 2nd ed., Wiley-Blackwell, 2014.
- [2] P. Würfel, *Physics of Solar Cells: From Principles to New Concepts*, Wiley-VCH, Weinheim, 2005.
- [3] J.-L. Bredas, E.H. Sargent, G.D. Scholes, Photovoltaic concepts inspired by coherence effects in photosynthetic systems, *Nat. Mater.* 16 (2017) 35–44, <https://doi.org/10.1038/nmat4767>.
- [4] E. Wientjes, G. Roest, R. Croce, From red to blue to far-red in Lhc4: how does the protein modulate the spectral properties of the pigments? *Biochim. Biophys. Acta – Bioenergy* 2012 (1817) 711–717, <https://doi.org/10.1016/j.bbabi.2012.02.030>.
- [5] F. Passarini, E. Wientjes, H. van Amerongen, R. Croce, Photosystem I light-harvesting complex Lhc4 adopts multiple conformations: red forms and excited-state quenching are mutually exclusive, *Biochim. Biophys. Acta – Bioenergy* 1797 (2010) 501–508, <https://doi.org/10.1016/j.bbabi.2010.01.015>.
- [6] Y. Miloslavina, A. Wehner, P.H. Lambrev, E. Wientjes, M. Reus, G. Garab, R. Croce, A.R. Holzwarth, Far-red fluorescence: a direct spectroscopic marker for LHCII oligomer formation in non-photochemical quenching, *FEBS Lett.* 582 (2008) 3625–3631.
- [7] T.P.J. Krüger, V.I. Novoderezhkin, C. Iliaia, R. van Grondelle, Fluorescence spectral dynamics of single LHCII trimers, *Biophys. J.* 98 (2010) 3093–3101, <https://doi.org/10.1016/j.bpj.2010.03.028>.
- [8] T.P.J. Krüger, P. Malý, M.T.A. Alexandre, T. Mančal, C. Büchel, R. van Grondelle, How reduced excitonic coupling enhances light harvesting in the main photosynthetic antennae of diatoms, *Proc. Natl. Acad. Sci. U.S.A.* 114 (2017) E11063–E11071, <https://doi.org/10.1073/pnas.1714656115>.
- [9] J.R. Reimers, M. Biczysko, D. Bruce, D.F. Coker, T.J. Frankcombe, H. Hashimoto, J. Hauer, R. Jankowiak, T. Kramer, J. Linnanto, F. Mamedov, F. Müh, M. Rätsep, T. Renger, S. Styring, J. Wan, Z. Wang, Z.Y. Wang-Otomo, Y.X. Weng, C. Yang, J.P. Zhang, A. Freiberg, E. Krausz, Challenges facing an understanding of the nature of low-energy excited states in photosynthesis, *Biochim. Biophys. Acta – Bioenergy* 2016 (1857) 1627–1640, <https://doi.org/10.1016/j.bbabi.2016.06.010>.
- [10] M.G. Müller, P. Lambrev, M. Reus, E. Wientjes, R. Croce, A.R. Holzwarth, Singlet energy dissipation in the photosystem II light-harvesting complex does not involve energy transfer to carotenoids, *Chemphyschem.* 11 (2010) 1289–1296, <https://doi.org/10.1002/cphc.200900852>.
- [11] C. Ramanan, J.M. Gruber, P. Malý, M. Negretti, V.I. Novoderezhkin, T.P.J. Krüger, T. Mančal, R. Croce, R. van Grondelle, The role of exciton delocalization in the major photosynthetic light-harvesting antenna of plants, *Biophys. J.* 108 (2015) 1047–1056, <https://doi.org/10.1016/j.bpj.2015.01.019>.
- [12] L.-O. Palsson, J.P. Dekker, E. Schlödder, R. Monshouwer, R. van Grondelle, Polarized site-selective fluorescence spectroscopy of the long-wavelength emitting chlorophylls in isolated Photosystem I particles of *Synechococcus elongatus*, *Photosynth. Res.* 48 (1996) 239–246.
- [13] L.-O. Palsson, C. Flemming, B. Gobets, R. van Grondelle, J.P. Dekker, E. Schlödder, Energy transfer and charge separation in photosystem I-P700 oxidation upon selective excitation of the long-wavelength antenna chlorophylls of *Synechococcus elongatus*, *Biophys. J.* 74 (1998) 2611–2622.
- [14] H. van Amerongen, L. Valkunas, R. van Grondelle, *Photosynthetic Excitons*, World Scientific, Singapore, 2000.
- [15] S. Yin, M.G. Dahlbom, P.J. Canfield, N.S. Hush, R. Kobayashi, J.R. Reimers, Assignment of the Qy, absorption spectrum of photosystem-I from thermodynamic calculations based on CAM-B3LYP calculations at the PW91-optimized protein structure, *J. Phys. Chem. B* 111 (2007) 9923–9930, <https://doi.org/10.1021/jp070030p>.
- [16] N. Christensson, H.F. Kauffmann, T. Pullerits, T. Mančal, Origin of long-lived coherences in light-harvesting complexes, *J. Phys. Chem. B* 116 (2012) 7449–7454, <https://doi.org/10.1021/jp304649c>.
- [17] A. Kolli, E.J. O'Reilly, G.D. Scholes, A. Olaya-Castro, The fundamental role of quantized vibrations in coherent light harvesting by cryptophyte algae, *J. Chem. Phys.* 137 (2012) 174109, <https://doi.org/10.1063/1.4764100>.
- [18] B. Hein, C. Kreisbeck, T. Kramer, M. Rodríguez, Modelling of oscillations in two-dimensional echo-spectra of the Fenna Matthews Olson complex, *New J. Phys.* 14 (2012) 023018, <https://doi.org/10.1088/1367-2630/14/2/023018>.
- [19] A.W. Chin, S.F. Huelga, M.B. Plenio, Coherence and decoherence in biological systems: principles of noise-assisted transport and the origin of long-lived coherences, *Philos. Trans. R. Soc. A* 370 (2012) 3638–3657, <https://doi.org/10.1098/rsta.2011.0224>.
- [20] A. Chenu, N. Christensson, H.F. Kauffmann, T. Mančal, Enhancement of vibronic and ground-state vibrational coherences in 2D spectra of photosynthetic complexes, *Sci. Rep.* 3 (2013) 2029, <https://doi.org/10.1038/srep02029>.
- [21] V. Butkus, D. Zigmantas, D. Abramavicius, L. Valkunas, Distinctive character of electronic and vibrational coherences in disordered molecular aggregates, *Chem. Phys. Lett.* 587 (2013) 93–98, <https://doi.org/10.1016/j.cplett.2013.09.043>.
- [22] V. Tiwari, W.K. Peters, D.M. Jonas, Electronic resonance with anticorrelated pigment vibrations drives photosynthetic energy transfer outside the adiabatic framework, *Proc. Natl. Acad. Sci. U.S.A.* 110 (2013) 1203–1208, <https://doi.org/10.1073/pnas.1211157110>.
- [23] S.M. Blau, D.I.G. Bennett, C. Kreisbeck, G.D. Scholes, A. Aspuru-Guzik, Local protein solvation drives direct down-conversion in phycobiliprotein PC645 via incoherent vibronic transport, *Proc. Natl. Acad. Sci. U.S.A.* (2018) 1–24, <https://doi.org/10.1073/pnas.1800370115>.
- [24] F.D. Fuller, J. Pan, A. Gelzinis, V. Butkus, S.S. Senlik, D.E. Wilcox, C.F. Yocum, L. Valkunas, D. Abramavicius, J.P. Ogilvie, Vibronic coherence in oxygenic photosynthesis, *Nat. Chem.* 6 (2014) 706–711, <https://doi.org/10.1038/nchem.2005>.
- [25] E. Romero, R. Augulis, V.I. Novoderezhkin, M. Ferretti, J. Thieme, D. Zigmantas, R. van Grondelle, Quantum coherence in photosynthesis for efficient solar-energy conversion, *Nat. Phys.* 10 (2014) 676–682, <https://doi.org/10.1038/nphys3017>.
- [26] J.R. Reimers, Z.L. Cai, R. Kobayashi, M. Rätsep, A. Freiberg, E. Krausz, Assignment of the Q-bands of the chlorophylls: coherence loss via Q x Q y mixing, *Sci. Rep.* 3 (2013) 2761, <https://doi.org/10.1038/srep02761>.
- [27] D. Abramavicius, L. Valkunas, Role of coherent vibrations in energy transfer and conversion in photosynthetic pigment – protein complexes, *Photosynth. Res.* 127 (2015) 33–47, <https://doi.org/10.1007/s1120-015-0080-6>.
- [28] V.I. Novoderezhkin, E. Romero, J. Prior, R. van Grondelle, Exciton-vibronic resonance and dynamics of charge separation in the photosystem II reaction center, *Phys. Chem. Chem. Phys.* 19 (2017) 5195–5208, <https://doi.org/10.1039/C6CP07308E>.
- [29] D.I.G. Bennett, P. Maly, C. Kreisbeck, R. Van Grondelle, Mechanistic regimes of vibronic transport in a heterodimer and the design principle of incoherent vibronic transport in phycobiliproteins, *J. Phys. Chem. Lett.* 9 (2018) 2665, <https://doi.org/10.1021/acs.jpclett.8b00844>.
- [30] P. Malý, O.J.G. Somsen, V.I. Novoderezhkin, T. Mančal, R. Van Grondelle, The role of resonant vibrations in electronic energy transfer, *ChemPhysChem.* 17 (2016) 1356–1368, <https://doi.org/10.1002/cphc.201500965>.
- [31] R. van Grondelle, Excitation energy transfer, trapping and annihilation in photosynthetic systems, *Biochim. Biophys. Acta* 811 (1985) 147–195, [https://doi.org/10.1016/0304-4173\(85\)90017-5](https://doi.org/10.1016/0304-4173(85)90017-5).
- [32] V.I. Novoderezhkin, R. Croce, M. Wahadoszamen, I. Polukhina, E. Romero, R. van Grondelle, Mixing of exciton and charge-transfer states in light-harvesting complex Lhc4a, *Phys. Chem. Chem. Phys.* 18 (2016) 19368–19377, <https://doi.org/10.1039/C6CP02225A>.
- [33] V.I. Novoderezhkin, R. Croce, R. Van Grondelle, Dynamics of the mixed exciton and charge-transfer states in light-harvesting complex Lhc4: hierarchical equation approach, *BBA – Bioenergy* 2018 (1859) 655–665, <https://doi.org/10.1016/j.bbabi.2018.06.016>.
- [34] V.I. Novoderezhkin, M.A. Palacios, H. van Amerongen, R. Van Grondelle, Energy-transfer dynamics in the LHCII complex of higher plants: modified redfield approach, *J. Phys. Chem. B* 108 (2004) 10363–10375, <https://doi.org/10.1021/jp0496001>.

- [35] Y. Fujihashi, M. Higashi, A. Ishizaki, Intramolecular vibrations complement the robustness of primary charge separation in the Photosystem II reaction center, *J. Phys. Chem. Lett.* 9 (2018) 4921–4929, <https://doi.org/10.1021/acs.jpclett.8b02119>.
- [36] V.I. Novoderezhkin, A.G. Yakovlev, R. Van Grondelle, V.A. Shuvalov, Coherent nuclear and electronic dynamics in primary charge separation in photosynthetic reaction centers: a Redfield theory approach, *J. Phys. Chem. B* 108 (2004) 7445–7457, <https://doi.org/10.1021/jp0373346>.
- [37] J.M. Jean, R.A. Friesner, G.R. Fleming, Application of a multilevel Redfield theory to electron transfer in condensed phases, *J. Chem. Phys.* 96 (1992) 5827, <https://doi.org/10.1063/1.462858>.
- [38] J.M.M. Jean, Time- and frequency-resolved spontaneous emission as a probe of coherence effects in ultrafast electron transfer reactions, *J. Chem. Phys.* 101 (1994) 10464, <https://doi.org/10.1063/1.467864>.
- [39] A.G. Redfield, The theory of relaxation processes, *Adv. Magn. Opt. Reson.* 1 (1965) 1–32.
- [40] W.T. Pollard, R.A. Friesner, Solution of the Redfield equation for the dissipative quantum dynamics of multilevel systems, *J. Chem. Phys.* 100 (1994) 5054–5065.
- [41] W.T. Pollard, A.K. Felts, R.A. Friesner, The Redfield equation in condensed phase quantum dynamics, *Adv. Chem. Phys.* 93 (1996).