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Signature of Quantum Coherence in the Exciton Energy Pathways of the LH2 Photosynthetic Complex

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Cite This: *ACS Omega* 2023, 8, 38871−38878

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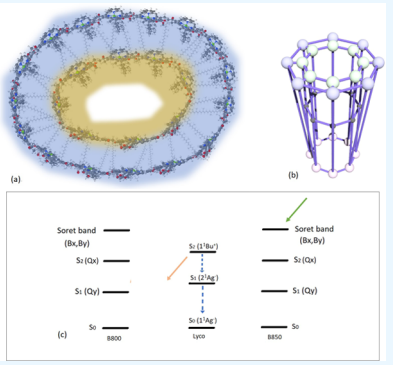
ABSTRACT: Unraveling the energy transfer pathways in photosynthetic complexes is an important step toward understanding their structure−function interplay. Here, we use an open quantum systems approach to investigate energy transfer within the LH2 photosynthetic apparatus and its dependence on environmental conditions. We find that energy transfer pathways strongly depend on the environment-induced dephasing time. A comparison between the computational results and experiments performed on similar systems demonstrates that quantum coherences are present in these systems under physiological conditions and have an important role in shaping the energy transfer pathways. Moreover, our calculations indicate that relatively simple spectroscopy experiments can be used to detect traces of quantum coherence. Finally, our results suggest that quantum coherence may play a role in photosynthesis, but not in enhancing the efficiency as was previously suggested.



INTRODUCTION

Photosynthetic energy transfer complexes (ETCs) are responsible for capturing light and transferring its energy, in the form of excitons, to the reaction center, where it is converted into chemical energy. The pathways in which the energy travels within the ETCs generally depend on the ETC composition and geometrical structure, as well as on parameters such as the position at which the light energy is absorbed, and the external environment of the protein. Understanding the energy pathways in light-harvesting complexes is an essential step toward a general understanding of photosynthetic systems and their operation and to clarify the relation between the geometry of the photosynthetic apparatus and its functionality.[1−5] This relation, which is extensively studied in biology, may also shed light on the interplay of environment and quantum coherence (or quantum correlations) in photosynthetic systems.

The importance of quantum coherence to energy transfer in photosynthetic systems was postulated following 2D spectroscopic measurements that demonstrated long-lived coherent time oscillations (beatings) of the off-diagonal signal.[3,6−12] The question of whether these beatings indeed point to the presence of quantum coherence and whether quantum coherence in any way enhances efficiency is still debated.[13−24]

Interaction of the photosynthetic complex with its environment provides a link between the question of quantum coherence and energy pathways; via a zeno-type interaction,[25] the environment induces dephasing, which reduces quantum coherence, and simultaneously affects the energy transfer pathways.[26] Thus, knowledge on the energy transfer pathways (which can be measured experimentally to some extent[27−29]) can provide information on the presence of quantum coherence in photosynthetic systems. Establishing such a relation is all the more important since while quantum coherence was detected in various forms in photosynthetic complexes by various spectroscopic means,[24,30] the possible relation between quantum coherence and efficiency was raised in the last decade mainly following 2D spectroscopy[31−34] (which is, indeed, nontrivial to interpret.[35,36]) Here, we address this relation, via the study of the energy pathways within the LH2 photosynthetic apparatus of the purple photosynthetic bacterium, *Rhodopseudomonas acidophila*, and specifically their dependence on environment-induced dephasing.

Before proceeding, it is important to explain what we mean here by "quantum coherence", a term that suffers some ambiguity. Typically (especially in the optics community), it refers to finite non-diagonal elements of the density matrix (DM), when written in the eigenstate basis. However, we discuss here exciton transport in photosynthetic complexes out of equilibrium (because exciton current is flowing), and therefore, there are *always* finite off-diagonal elements in the DM (i.e., there is always some "quantum coherence"[37]). Therefore, the importance of quantum coherence should be defined not by the presence of off-diagonal DM elements but

Received: April 19, 2023
Accepted: June 15, 2023
Published: October 11, 2023

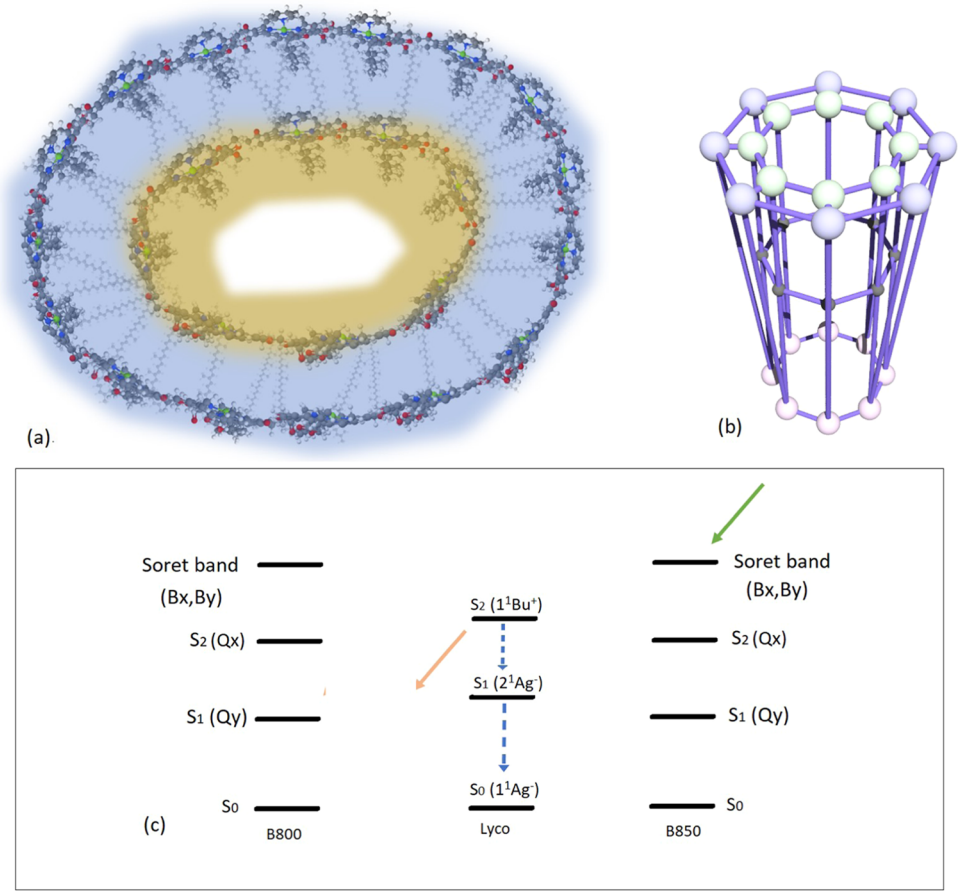


Figure 1. Schematic presentation of the LH2 photosynthetic complex. (a) Top view, including the molecular moieties. (b) Side view of a "balls and sticks" representation of the LH2 complex (see text for detailed explanation). Purple lines represent coupling between neighboring sites (long-range coupling is included in the Hamiltonian but doesn't appear here.) (c) Simplified schematic description of the LH2 electronic structure. Dashed blue arrows show nonradiative decay processes, arrows were added to indicate the excitation site (green) and extraction site (orange) of the BtL pathway (see text).

by their effect on exciton transport. From a rigorous mathematical perspective, current should always be calculated from the off-diagonal elements of the DM. However, if quantum coherence is unimportant (for instance, if there is strong dephasing in the system, leading to diffusive behavior[38]), then one can equally evaluate the current from the diagonal elements of the DM. The deviation between such "classical" currents and currents evaluated from a fully quantum formulation can serve as a measure of the degree of "quantumness" of the system.[13,23,37] We can thus define a signature of quantum coherence as a qualitative change in the currents as the system departs from the diffusive regime (i.e., as the dephasing rate changes). As we discuss below, exciton currents are directly related to exciton densities and to photon emission (i.e., spectroscopic signal) and are used interchangeably hereafter.

We now go back to our specific system. LH2 is the antenna complex of the purple bacteria,[27,39] responsible for absorbing solar energy, that later travels through the system, until it reaches the reaction center. As schematically described in Figure 1a, it contains two rings of bacteriochlorophylls (BChl), B850 (blue ring) and B800 (orange ring), named after the energy (wavelength) at which they can absorb. Each ring has four BChl energy bands (c) that participate in the energy transfer[28,40,41] (dubbed Qy, Qx, Bx, and By). The last two energy states are sometimes considered as one, namely, the Soret band.[42] B850 contains LH2 $\alpha\beta$ heterodimers, represented by pale green (α) and blue spheres (β) in the side view shown in Figure 1b (although common LH2 is composed of 27 BChls, we choose to study the 24 BChls due to its resolved Hamiltonian.[40,41] We stress, however, that the absolute number of BChls will have no effect on our results). The pale red spheres are the B800 molecules and the gray spheres are the lycopenes (carotenoids in *Rhodospirillum molischianum*[40]) that connect the B850 and B800 rings and create a circular symmetric morphology (shown in Figure 1a as gray longitude molecules).

It is widely accepted that the role of lycopenes is to stabilize the structure of the antenna[43,44] and to participate in the photoprotection mechanism.[41,43−46] An additional possible role is improving the performances of energy transfer in LH2, by enlarging the range of absorbent frequencies in the system, due to the ability of lycopenes to absorb energy in the visible spectrum of the sun (unlike B850 and B800).[28,43,44] When an exciton is generated at the lycopenes, it can travel to one of the rings (i.e., B800 and B850) and then leave the complex toward the reaction center (through a series of complexes LH2 and LHI). While this pathway defines the contribution of lycopene to general energy transfer, the opposite direction (BChls toward lycopenes) results in the dissipation of energy at the lycopenes.[28,43,47]

https://doi.org/10.1021/acsomega.3c02676
ACS Omega 2023, 8, 38871−38878

A recent experiment examining these pathways in LH2 from the purple bacterium *Ectothiorhodospira haloalkaliphila*[28,48] showed a surprising asymmetry. These authors measured the emission spectra after excitation, exciting their system from either the Soret level of B850 rings or s2 of carotenoids (which play an equivalent role as the lycopenes in the system studied here). They found that a strong asymmetry exists (between the two different excitations types), with only ∼5% signal from lycopenes measured when the Soret band was excited, compared to ∼50% in the other direction. This asymmetry was attributed to the blocking of exciton flow from BCHls to lycopenes, but no explanation was given as to the source of this asymmetry, which seems to be disadvantageous for the bacterium.[28]

Here, we suggest a simple explanation to this observed effect. For this aim, we use the steady-state Lindblad equation, taking into account natural physiological conditions. We show that there is a strong dependence of the energy transfer pathways on the environment-induced dephasing rate, and that at physiological conditions, excitations tend to spread out uniformly throughout the system. By considering the specific energetic structure and optical nature of the lycopenes (i.e., that some are dark states which do not emit photons) and the difference in the number of BChl and lycopene units, we provide a simple and physically transparent solution to the puzzle. Comparing our results to recent experiments provides further evidence for the presence of quantum coherence in these systems and sheds new light on the experimental results.

MODEL AND METHOD

We consider here a detailed model of the LH2 system, including the BChls energy bands of Qx and Qy, Soret bands of B850 and B800, and the S_1 and S_2 bands of the lycopenes (described in Figure 1c). We start with the standard tight binding Hamiltonian, $H = \sum_i \epsilon_i e_i^\dagger e_i - \sum_{i,j} t_{i,j} e_i^\dagger e_j$, where i is the site index and $e_i^\dagger(e_i)$ creates an exciton in site i. ϵ_i are the on-site energies, and $t_{i,j}$ is the coupling element between positions i and j. The energies and coupling elements are extracted from measurements,[40,41] and the full Hamiltonian appears in the Supporting Information. We consider the Hamiltonian describing the LH2 system of *R. molischianum* (in which lycopenes play the role of carotenes in *E. haloalkaliphila*). However, as our goal is understanding the general behavior of energy transfer pathways, the differences between the two systems are only quantitative. Furthermore, as we will demonstrate as follows, the general steady-state behavior of the system is rather insensitive to internal details (such as specific Hamiltonian structure), as was verified in ref 23

We use the Lindblad equation,[49]

$$\frac{d\rho}{dt} = -i[H, \rho] + L[\rho]$$

$$L[\rho] = \sum_k \left(V_k \rho V_k^\dagger - \frac{1}{2}\{V_k^\dagger V_k, \rho\} \right) \quad (1)$$

where $\{\cdot,\cdot\}$ is the anti-commutation and V_k are the Lindblad operators, and k = inj, ext, dep, or nr, depicting different environment-system interactions, namely, excitation (or injection), extraction, dephasing, and internal conversions, respectively. The dephasing Lindbladians operate on each site via $V_i = (\gamma_{deph})^{1/2} e_i^\dagger e_i$. Exciton extraction and injection are defined by Lindblad operators $V_{ext} = (\gamma_{ext})^{1/2}\, e_{i_{ext}}$ and $V_{inj} = (\gamma_{inj})^{1/2} e_{\alpha inj}^\dagger$, γ_{deph}, γ_{inj}, and γ_{ext} are the particle dephasing, injection, and extraction rates, respectively. α_{inj} are the indices of the eigenstate where injection takes place. i_{ext} is the extraction that operates on all sites. $V_{nr,s_1\to s_0} = (\gamma_{nr,s_1\to s_0})^{1/2} e_{s_1}^\dagger e_{s_0}$ and $V_{nr,s_2 \to s_1} = (\gamma_{nr,s_2\to s_1})^{1/2} e_{s_2}^\dagger e_{s_1}$ depict the most dominant internal conversions, occur between lycopene states $S_1 \to S_0$ and $S_2 \to S_1$.[50,51] When an exciton is extracted out of the system, the result is an emission of a photon, and thus, the total extraction current is proportional to the total number of photons emitted, e.g., the spectroscopic signal. To simplify the calculation, and in light of the very weak excitation rate experienced by the LH2 complex under natural conditions,[52] we limit the calculation to the single-exciton Fock-space.[53] The rates are given in Table 1.

Table 1. Rate Constants

rate constant	value	references
γ_{inj}	14 s^{-1}	54
γ_{ext}	0.01 ps^{-1}	55−57
$\gamma_{nr,S_2\to S_1}$	0.2 ps^{-1}	1, 58
$\gamma_{nr,S_1\to S_0}$	5 ms^{-1}	50, 59
γ_{dep} (physiological regime)	10 ps^{-1}	6, 17, 60

The Lindblad equation has been widely used in the context of photosynthetic exciton transfer complexes[61−66] and seems particularly adequate to study the steady-state properties of these systems,[23,67,68] as well as other artificial systems showing interplay between dephasing and transport.[69,70] One might criticize the Lindblad equation for not fully capturing the protein vibrational spectrum[64,71−73] and hence being unable to fully capture the detailed exciton transfer dynamics. While such critique would be justified if one wishes to capture the dynamics, we stress that this is not our goal here (which is also why we allow ourselves to draw conclusions on experiments performed on *E. haloalkaliphila* from calculations using the Hamiltonian structure of *R. acidophila*). Rather, our goal is a more general understanding of energy transfer pathways at the steady state (which is where photosynthetic systems operate[68]), which is independent of specific details.

Another possible criticism for the use of the Lindblad equation in its present (dephasing) form is that it does not capture the role of temperature, effectively being a high (infinite) temperature model. As a result, the Lindblad equation in equilibrium does not restore detailed balance. While this is indeed the case, we point that we are not interested in equilibrium properties of the system, and in fact, we consider the case of steady-state non-equilibrium, the properties of which can still be captured (at least qualitatively) with the Lindblad equation.

However, in light of this property of the Lindblad form, we have also carried out calculation of a similar system (taking a simpler Hamiltonian, which only captures the essential features of the system we are interested in, but not the full structure) using the Redfield form of the Markovian approximation,[49] which allows for capturing the detailed balance at equilibrium. These calculations gave qualitatively similar results to the ones presented in the Results section.

Going back to the details of the calculation, in order to directly address the experiment, we consider two excitation pathways: (1) the Soret band of B850-to-the lycopenes (BtL, see Figure 1c) where the energy pathway is done by setting i_{inj}

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ACS Omega 2023, 8, 38871−38878

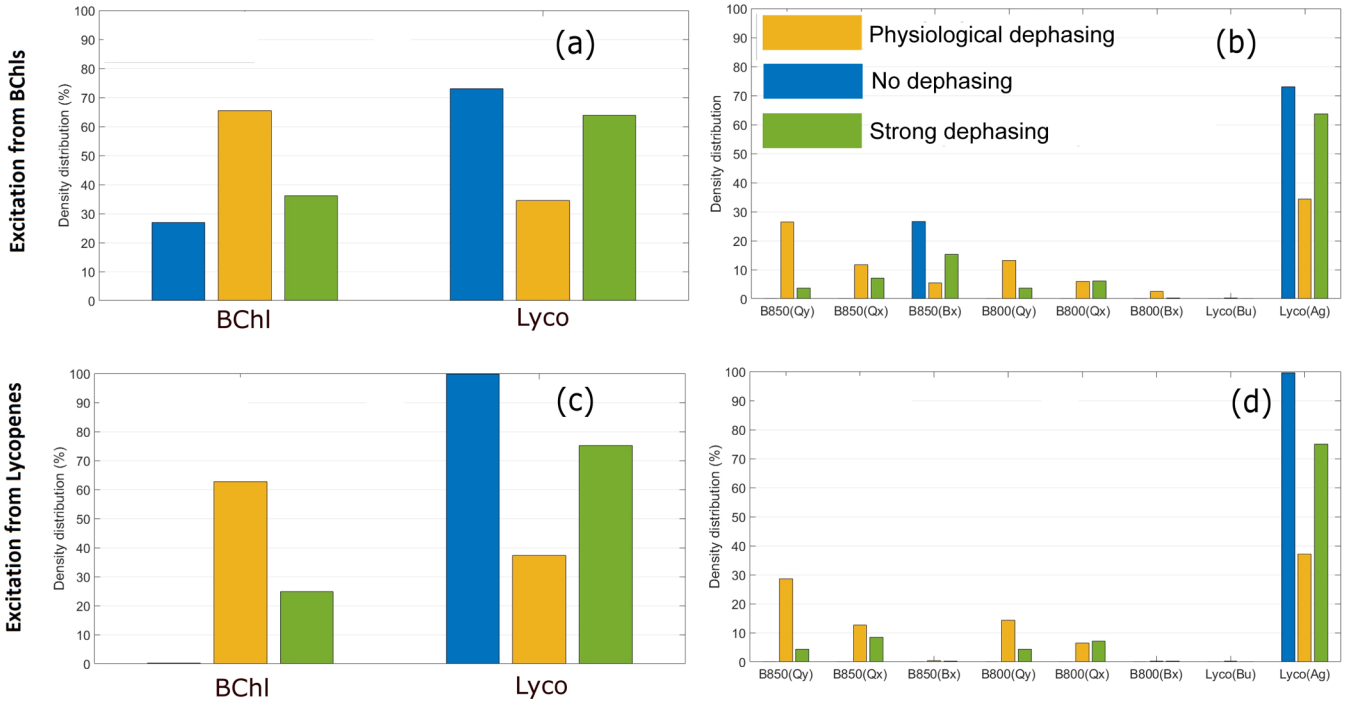

Figure 2. Distribution of density in the LH2 complex corresponding to excitation of lycopenes (a, b) and excitation of soret band of B850 (c, d) for different dephasing conditions: no dephasing (blue bars), intermediate dephasing of $\gamma_{deph} = 10\ ps^{-1}$ (orange bars), and high dephasing rate, $\gamma_{deph} = 10^6\ ps^{-1}$ (green bars). The partial densities are shown for different regimes and energy bands of the complex: Bx and Qy bands of B850 and B800 and Ag (S_0) and Bu (S_2) bands of lycopenes (c, d) and for different types of molecules, lycopenes, and bacteriochlorophylls (a, c), representing a direct sum of panels (b) and (d).

to reside on the B850 sites and evaluating the exciton density in all sites of the complex and (2) the reverse pathway, lycopenes-to- B850 (LtB), evaluated by setting i_{inj} to reside on the lycopene sites. We then find the steady-state DM (ρ), by calculating the kernel of the Lindbladian (right-hand side of eq 1).

The DM reflects the probabilities of an exciton to reach each constituent of the LH2 complex and consequently its type, namely, BChls or lycopenes. The absolute majority of excitons in the BChls bands recombine and consequently emit a photon that can excite a neighbored complex in the natural process and can be measured in experiments by spectroscopic tools (as was conducted in, e.g., refs (28 and 48)). Most of the excitons that reach the lycopene bands dissipate and cannot contribute to the inter-complex energy transfer or the measurable photon emission.

RESULTS

In Figure 2, we plot the probability (equivalently the exciton density) of excitons to occupy specific states (and consequently contribute to the photon emission from these states) for both BtL (a, b) and LtB (c, d) pathways in the physiological dephasing condition (orange bars). In order to study the influence of the environment, we compare these results to two limiting cases; no dephasing condition (blue bars) and very strong dephasing (green bars). We point that these cases (especially the strong dephasing limit) are somewhat nonphysical, yet the comparison is useful in order to elucidate the role of dephasing. The obvious differences between the colored bars in Figure 2 indicate that the environment has a significant effect on the way energy is transferred within the complex.

Figure 2a shows that when there is no dephasing (blue bars), the majority of excitation energy (∼72%) occupies the lycopenes in the BtL pathway. Introducing physiological dephasing to the system (orange bars) spreads the excitons among BChls and lycopenes, and only ∼35% reside at the lycopenes. Strong dephasing, similar to the no-dephasing case, allows the majority of excitons (∼62%) to flow from the BChls to the lycopenes. Simply put, in the presence of dephasing (at physiological conditions), the portion of excitons that occupy the BChls when the B850 ring is excited increases by a factor of ∼2 in comparison to a case where there is no dephasing.

The density distribution of the opposite pathway (LtB) is shown in Figure 2c,d, and reflects similar behavior. Figure 2c demonstrates that strong and no dephasing (blue and green bars, respectively) result in localization in the lycopene states, same as in the BtL pathway. On the other hand, physiological conditions (orange bars) spread the density among B800 and B850 rings (Figure 2d) in a way that favors the BChls molecules. As a result, ∼62% out of the total density is in the BChls. The BtL and LtB density distribution indicate that the presence of physiological dephasing is essential for occupying the BChls bands and hence essential for photon emission from these bands.

As seen in Figure 2a,c, the exciton density tends to be strongly localized in the lycopenes in the weak and strong dephasing limit, for both LtB and BtL pathways. The origin of this effect is the differences between the exciton extraction rate and the nonradiative extraction process rate in the lycopenes (see Table 1), a manifestation of the fact that S_1 is a dark state.[1,58,74] For strong dephasing, the difference in populations between BChls and lycopenes is due to the large difference between injection and extraction rates. To see this, we note that the exciton density of the system (through the DM which

https://doi.org/10.1021/acsomega.3c02676
ACS Omega 2023, 8, 38871−38878

solves the Lindblad equation) is such that it tends to minimize the weight of exciton wave functions (and hence the exciton density) localized where the extraction rate is large and maximize it in sites where the extraction rate is small. Put simply, the large difference between the rates makes the lycopenes act as an "exciton sink", which accumulates the majority of the excitons in the complex. This density of lycopenes in the weak dephasing regime is larger (compared to the no dephasing regime) due to the localization effect that resulted from the large differences in the chromophore energies. A moderate dephasing rate (physiological dephasing) tends to spread the exciton density among BChls and lycopenes according to the uniformization population mechanism.[52] This effect competes the tendency of the system to occupy the "exciton sink". Both effects, uniformization and exciton-sink act in the LtB pathway as well as in the BtL pathway, but in the BtL pathway, there is a larger portion of excitons in the BChls (in comparison to the LtB pathway) due to the excitation location.

In order to prove the above mechanism, we turn to analyze the local currents and exciton densities within the complex under different conditions. The relation between currents and densities has been established recently,[52] and it can be analytically shown that at the energy extraction sites (i.e., sinks), the exciton current is simply proportional to the exciton density at the extraction site.[52] The local currents between chromophores in the complex are calculated via $J_{i,j} = 2t_{i,j}\mathrm{Im}(\rho_{i,j})$,[13] where i and j are indices of the chromophores in the system and Im stands for the imaginary part of the complex DM element $\rho_{i,j}$ (detailed derivation can be found in ref 26). The exciton occupation at site i is simply the diagonal element ρ_{ii}.

Figure 3 shows the local currents and densities for the three different regimes of dephasing: no dephasing (a, d), intermediate dephasing (physiological conditions) (b, e), and extreme dephasing rate (c, f) for the BtL (a−c) and LtB (d−f) pathways. Lines represent site-to-site currents, and the width and color correspond to the current magnitude. Spheres represent exciton density, with the radius of the sphere proportional to the density in each site.

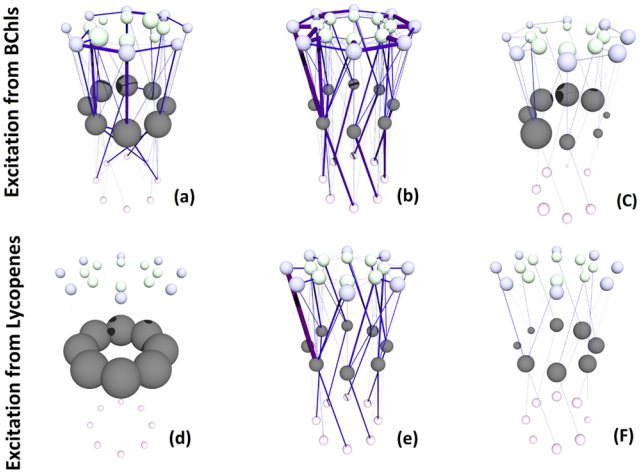

Figure 3. Local currents and normalized exciton populations in LH2 for different excitation conditions: excitation of B850 (a−c) and excitation of lycopenes (d−f). Top ring is the α (blue spheres) and β (green spheres) dimers of B850, lower ring is the B800 ring, and the gray spheres represent the lycopenes. The local currents are shown by lines, and their width and color correspond to the current magnitude. The sizes of the sphere encode the local density of the site. The data are shown for different dephasing conditions: no dephasing (a, c), intermediate dephasing of $\gamma_{\mathrm{deph}} = 10\ \mathrm{ps}^{-1}$ (b,e), and high dephasing rate, $\gamma_{\mathrm{deph}} = 10^{6}\ \mathrm{ps}^{-1}$ (c, f).

What can be seen from Figure 3a is that under low dephasing rate in the LtB pathway, weak local currents flow toward the lycopenes from B850 and B800 to occupy the favorable lycopene ring, and hence, the populations are essentially limited to the ring of lycopenes. For excitation in the lycopenes sites (d), local currents are negligible (hence, their width cannot be represented in the figure) due to the localization of the wave function. In the strong dephasing limit (c,f), the local currents and densities indicate similar behavior, where only densities and local currents that are near the lycopenes are strong enough to be visible in this representation. Local currents show that excitons flow toward the lycopenes, especially in the BtL pathway (c).

When the dephasing rate is intermediate (physiological regime, Figures 3b,e), the currents spread through the entire complex, resulting in emission from both BChls and lycopenes, almost regardless of the injection site (albeit the asymmetry discussed in Figure 2, which we address below).

The origin of the behavior described above can be traced to the effect of dephasing on the distribution of exciton populations. In a recent set of papers,[52,53] it was demonstrated that what dephasing does (in the context of exciton transport) is to distribute the exciton population evenly (or at least to reduce the variations in population) within the system, an effect dubbed "population uniformization". When there are specific exciton injection and extraction sites, this effect leads to an enhancement of efficiency at intermediate dephasing rates, the so-called environment-assisted quantum transport (ENAQT) effect.[52]

For the LH2 pathways, we consider here, where all sites are extraction sites (similar to the situation in spectroscopy experiments), the effect of dephasing is still similar and the population uniformization mechanism is still effective. However, it results not in an increase in efficiency, but rather in a change in the spectra itself. For weak and strong dephasing, where currents and populations are localized in the lycopenes sites the complex will emit from the lycopenes. However, at intermediate (physiological) dephasing, all sites are excited equally. Therefore, there is little difference if BChls or lycopenes were the source of excitation, emission (which is, again, proportional to exciton population) will occur from all (bright) sites. This observation also explains the slight asymmetry between the BtL and LtS pathways seen in Figure 2 (orange bars). The reason is rather simple; there are more BChls sites than lycopene sites, and so a uniform spread of populations will naturally lead to more BChl sites occupied and hence more emission from these bands.

DISCUSSION AND CONCLUSION

In order to compare our results to the experimental results from refs 28, 48, we take another step in the calculation and convert the density shown in Figure 2 to current, i.e., to the signal that can be detected in an experiment. The relation between density and currents is easily obtained by simply multiplying the density of a state by the rate of extraction from that state. When this is done, it is found that the signal from the lycopene S2 state when excited from the BChls is ∼3% (Figure 2), close to the experimental results.[28,48]

https://doi.org/10.1021/acsomega.3c02676
ACS Omega 2023, 8, 38871−38878

The authors of ref 28 argue that the low signal from the lycopenes is due to the blocking of exciton flow from BChls to the lycopenes, which maybe due to the weak coupling between the BChl and lycopene states.[48] However, this argument is inconsistent because if the current is blocked because of weak coupling, then it would have been blocked also when exciting in the opposite pathway, in contradiction to the experimental observations (which show substantial signal in the reverse pathway). What we showed here is that the flow is not "blocked" (see Figure 3). Rather, the dephasing-induced uniform distribution of excitons pushes excitons in the lycopenes to dark states (because all lycopene states are equally populated), which do not contribute to the signal. Our results thus not only reproduce the experimental findings but shed new light on their origin.

The lycopenes can absorb photons that could not be absorbed by other molecules in the antenna. With no dephasing, this energy is bound to the lycopenes, as described above. On the other hand, an extreme dephasing rate leads to the same result. This means that under extreme dephasing conditions (very strong or no dephasing), there is almost no photon emission from lycopenes since most of the excitons in the lycopenes occupy the Lyco(Ag) state (see Figure 3b,d), which is a dark state. Therefore, both quantum coherence and dephasing must coexist in order for the LH2 system to extract the energy absorbed by the lycopenes and transferred to the BChls. The optimal balance between them occurs exactly at the physiological regime, which may indicate that the physiological conditions enable the improved transfer between different complexes in an organism.

However, we stress that this increased ability to extract harvested solar energy, which increases the overall efficiency of the system, is different from the exciton transfer efficiency, which was widely discussed in the literature.[13−22] The latter refers to the ability of an exciton, once absorbed, to reach the reaction center and was very recently shown to be essentially independent of dephasing.[23] The former, on the other hand, refers to the total ability of the system to absorb photons (rather than its ability to transfer the photon energy once it was absorbed). Thus, our calculations support the conclusion of ref 23, leading to the intriguing idea that the interplay between quantum coherence and dephasing increases the overall efficiency by opening new channels for photon absorption. Put simply, when dephasing is present, the light, which is absorbed in the lycopenes (and which would otherwise stay localized on the lycopenes), finds its way to the BChls and then more easily to the reaction center. Thus, we conclude that being in a mixed quantum-classical regime (i.e., finite dephasing but still appreciable quantum coherence) may benefit photosynthesis, but not through the enhancement of exciton transfer efficiency, but through better exploitation of absorbed light.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02676.

Detailed structure if the LH2 Hamiltonian used in our calculations (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

E.Z.H. acknowledges support from the Ilse Katz Institute for Nanoscale Science and Technology. The authors are grateful to M.Zwolak for valuable discussions. This work was supported by the Israel Science Fund grant no. 1360/17.

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