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Does Coherence Enhance Transport in Photosynthesis?

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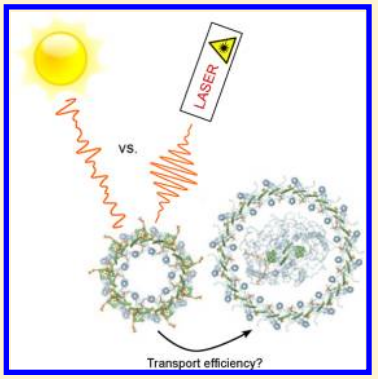
ABSTRACT: Recent observations of coherence in photosynthetic complexes have led to the question of whether quantum effects can occur *in vivo*, not under femtosecond laser pulses but in incoherent sunlight and at steady state, and, if so, whether the coherence explains the high exciton transfer efficiency. We introduce the distinction between state coherence and process coherence and show that although some photosynthetic pathways are partially coherent *processes*, photosynthesis in nature proceeds through stationary *states*. This distinction allows us to rule out several mechanisms of transport enhancement in sunlight. In particular, although they are crucial for understanding exciton transport, neither wavelike motion nor microscopic coherence, on their own, enhance the efficiency. By contrast, two partially coherent mechanisms—ENAQT and supertransfer—can enhance transport even in sunlight and thus constitute motifs for the optimization of artificial sunlight harvesting. Finally, we clarify the importance of ultrafast spectroscopy in understanding incoherent processes.



SECTION: Energy Conversion and Storage; Energy and Charge Transport

Recent observations of oscillatory spectroscopic signals in photosynthetic light-harvesting complexes[1−5] have led to suggestions that dynamical quantum effects may also occur *in vivo*, perhaps having a biological purpose[6−10] and having been favored by natural selection. This question has been difficult to answer because the strong, coherent laser light used in experiments is substantially different from the weak, incoherent sunlight. In particular, because sunlight intensity is constant on excitonic time scales, photosynthetic light harvesting proceeds through steady states and can be described by rate equations.[11] Indeed, the related problem of the photoisomerisation of rhodopsin—the central event of vision—can be adequately described using a completely incoherent model.[12]

In this work, we investigate whether coherence can enhance excitonic transport under incoherent illumination. Several mechanisms by which coherence is known to enhance transport in coherently excited systems do not apply to photosynthesis in sunlight. For example, because sunlight excites the entire complex—and not individual sites—and because transport is through a steady state, there is no "wavelike transport" that might speed up exciton delocalization. Indeed, we argue that, in most cases, coherence may be an evolutionary spandrel—an accidental byproduct of the selection of another property[13]—because it is quite likely that equally efficient incoherent transport mechanisms are possible. However, we also identify mechanisms that *can* enhance transport, even in sunlight. These mechanisms—environment-assisted quantum transport (ENAQT) and supertransfer—constitute viable design principles for the engineering of artificial light-harvesting complexes.

Our findings do not imply that the oscillatory spectroscopic signals seen with coherent light are irrelevant; quite the opposite, coherent optical spectroscopy[14,15] is indispensable for elucidating transfer mechanisms and providing evidence of the strong interchromophoric coupling that can lead to ENAQT and supertransfer in nature.

Photosynthetic complexes consist of a number of (bacterio)-chlorophyll molecules, also called chromophores or sites, held in place by a protein scaffold (see Figure 1).[16] Each chlorophyll can be in the ground or excited states, and the question of coherence in photosynthesis is, roughly speaking, whether a particular excitation can be coherently delocalized over multiple sites. We start by making this question more precise, which requires distinguishing several types of coherence (see Table 1). In particular, we stress the distinction between *state coherence* and *process coherence*, and the fact that one does not imply the other.

A quantum *state*, described by a density matrix ρ, is called "pure" if it can be represented by a wave function, $\rho = |\psi\rangle\langle\psi|$, and "mixed" otherwise. The purity $\mathrm{Tr}(\rho^2)$ is a basis-independent measure of how close a state is to being pure. Off-diagonal elements of ρ are usually called "coherences," but they are basis-dependent: a state diagonal in one orthonormal basis will not be diagonal in any other. Two bases are particularly important in discussing excitonic systems. The site basis is the basis in which each exciton is localized on a particular site, while the energy or exciton basis is the eigenbasis of the system Hamiltonian. Because of the coupling between sites, the two bases usually do not coincide.

Processes can also be described as coherent or incoherent, depending on the degree to which the evolution of an open quantum system is dominated by the unitary part or by the dissipative part.[18] In multichromophoric systems, a process is

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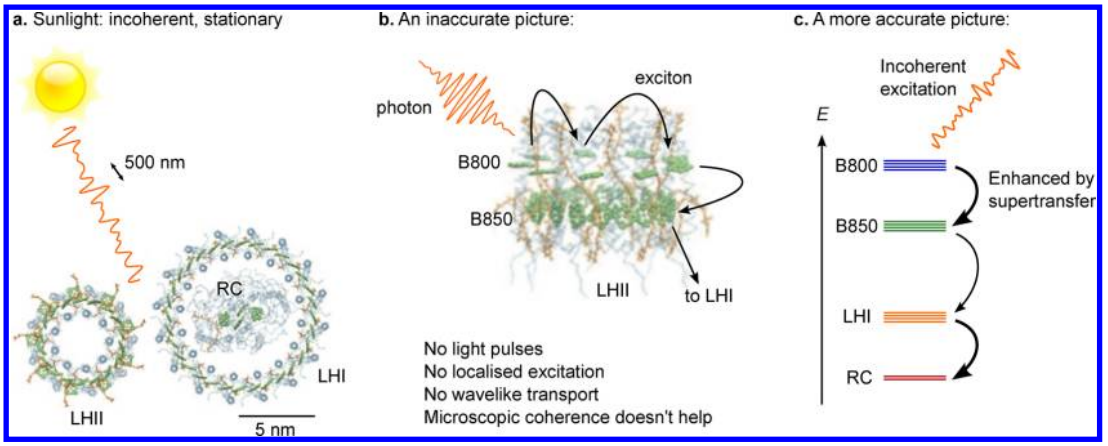

Figure 1. Photosynthesis in incoherent light, illustrated with a simplified model of LHII and LHI complexes from purple bacteria.[16] (a) Sunlight, unlike femtosecond lasers, is incoherent and stationary; therefore, photosynthesis operates at steady state. The wavelength of light is much longer than the complex size. RC: reaction center. (b) A common, but inaccurate view. Because the wavelengths of light are long, it is not the case that a localized state is excited, followed by wavelike transport. Consequently, several coherent mechanisms are not relevant to photosynthesis in vivo. (c) Instead, sunlight only excites stationary states that are diagonal or slightly coherent in the energy basis. Incoherent long-range transfer between different complexes (e.g., B800→B850) can be enhanced by supertransfer, a cooperative effect due to short-range process coherence. Energies not to scale. Renderings of complexes from ref 17 with permission (Copyright 2011 Wiley).

Table 1. Types of Coherence Discussed in This Work

type		definition	remarks
optical coherence		temporal correlation of the light field	The coherence of the incident radiation affects the molecular states that are created.
state coherence	purity	$\mathrm{Tr}(\rho^2)$	Basis-independent.
	in a particular basis	off-diagonal element of density matrix	Basis-dependent. Coherence in energy basis required for isolated system to undergo nontrivial time evolution. Coherence in site basis indicates exciton delocalization.
	static and dynamical coherence	At equilibrium or steady state, the density matrix and the coherences are static (unchanging). They are dynamical otherwise.	In unitary evolution, coherences in the energy basis evolve as $e^{-i\omega_{ij}t}$. Wavelike transport requires dynamical coherence in the energy basis. An open system may have static coherences in any basis.
	microscopic and ensemble coherence	Ensemble coherence is the expectation value of the energy-basis coherences of each realization (whose coherences are microscopic).	Because of averaging, ensemble coherence is less than the average absolute value of microscopic coherences. Expectation values of observables can be calculated either microscopically or using the ensemble average.
process coherence		An open system evolves incoherently if the dissipation dominates the unitary evolution and partially coherently otherwise. In chromophoric systems, this depends on whether a chromophore is more strongly coupled to other chromophores or to the environment.	Basis-independent. Examples: unitary evolution is coherent, Förster transfer is incoherent. Whether a process is coherent does not depend on particular initial states, as discussed in the text. With a coherent initial state, process coherence describes how long the coherence is preserved.

more coherent the more strongly chromophores are coupled to each other, relative to the strength of their coupling to the environment. For example, Förster transfer is incoherent because the donor and the acceptor are each more strongly coupled to their own dissipative environments then they are to each other, meaning that the slow transport between them will proceed at a simple rate.[18] By contrast, if two sites are strongly coupled, unitary evolution dominates and coherent population oscillations are possible.

The distinction between state and process coherence is important. Although long-lived state coherence implies partial process coherence, the converse need not hold: a process can be coherent even if, in particular cases, it proceeds through mixed states and can be described by rate laws. For example, if an isolated system is prepared in an incoherent mixture of eigenstates, it will evolve unitarily (i.e., coherently) because of its isolation even though it will not display interesting dynamics because it is diagonal in the energy basis. The fact that the system *would* evolve in a wavelike fashion *if* it were excited in the right way shows that the process itself is coherent even if particular realizations are not. That is, the coherent couplings are stronger than the noise even if that cannot be seen with, say, an initially mixed state.

Until recently, most biological processes were thought to occur in an environment so noisy that dissipative terms would dominate the unitary dynamics. The oscillations observed in coherent spectroscopic experiments[1−5] indicate that this need not be so. Femtosecond laser pulses can create nonstationary states—states with coherences in the energy basis—and the fact that these coherences persist for a long time is evidence of partial process coherence. A substantial debate exists about the extent to which these coherences are electronic or vibrational,[19−21] but that distinction is beyond the scope of this work: we will consider them as coherences between the vibronic eigenstates of the complete molecular Hamiltonian.

To understand whether photosynthesis involves coherent states, we must consider optical coherence. Light can be coherent in different ways, with various degrees of temporal, spectral, spatial, and polarizational coherence.[22] Spatial coherence can be assumed because photosynthetic complexes are much smaller than visible wavelengths, while polarization coherence has little influence because of ensemble orientational averaging. The two types of coherence that are more important

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are the (related) temporal and spectral coherences. Classical light is "coherent" if its phase can be predicted at all times, and "partially coherent" otherwise. Sunlight is essentially incoherent because, for blackbody radiation at 5870 K, the coherence time is about 0.6 fs,[23] shorter than other relevant time scales. Light can be described in a fully quantized manner or semiclassically; the latter generally suffices for biological problems.

The coherence of the light absorbed by a molecule affects the resulting molecular state,[11,24,25] even if a single photon is absorbed.[26] The effect is most dramatic for isolated molecules: while coherent light can excite coherences in the energy basis, an ensemble of isolated molecules with nondegenerate levels, excited by incoherent light, will be in a mixture of energy eigenstates.[25,26] Essentially, each nondegenerate transition will be driven by a different frequency component in the light, and these will have uncorrelated phases because the light is incoherent. When the random phases are averaged, the coherences disappear whereas the populations do not. Short pulses *can* excite coherences,[25] but because sunlight intensity is constant on light-harvesting time scales, these "turn-on" effects are negligible.

The behavior is slightly different for open systems. Since the result for isolated systems can be immediately applied to the system and the bath as a whole, coherences between system-bath eigenstates must vanish in the same way. However, upon tracing out the bath, energy-basis coherences of the reduced system may be substantial and may even approach the populations in magnitude.[11] A recent calculation of coherence dynamics in a multichromophoric system embedded in a structured, non-Markovian environment, found the coherences to be small.[27]

It is important to note that photosynthetic complexes are illuminated by weak sunlight whose intensity is constant at all relevant time scales. Therefore, natural light harvesting, like most dissipative processes driven by a constant force, occurs through a nonequilibrium steady state. The environment ensures that any initial conditions are quickly forgotten, and the constancy of the illumination ensures that all points in time are equivalent; therefore, the density matrix of the system cannot change. The complex is essentially a steady-state heat engine connected to two baths, the radiation at 5870 K and the cooler surroundings, which extracts work while transmitting energy from the radiation to the surroundings. Therefore, after the negligible turn-on transients have decayed, whatever coherences remain in the system after tracing out the bath will also be *stationary*; that is, they will not evolve as $e^{-i\omega_{ij}t}$ as they would if the system were isolated.[11,28] In particular, this means that excitation by sunlight will not be followed by excitonic wavelike motion. Although they will usually be small, large stationary coherences can occur if the detuning between the two levels is small and their relaxation fast, meaning that they are close in energy and broadened enough to make their spectral envelopes indistinguishable.[11] Indeed, tunable systems could be arranged so that the static state coherence between nearly degenerate levels enhances the power from a photovoltaic cell.[29,30]

The steady state that is reached reflects the fact that the wavelength of visible light is much larger than the size of photosynthetic complexes. Because all the chromophores experience the same electric field, the incoming radiation excites collective eigenstates of the whole complex, not individual sites. Therefore, although much can be learned about transport by considering an exciton initially localized on a particular site,[31−38] the picture changes when one incorporates optical excitation.

The Fenna−Matthews−Olson complex (FMO)[16] has been modeled with the excitation starting on sites that are believed to be closest to the chlorosome antenna that actually harvests the light.[31−37] This approach should be adapted for studying light harvesting in sunlight, where the chlorosome excites FMO incoherently, in essentially the same way as incoherent light would (section 4.3 of ref 11). This is because the energy transfer time from chlorosome to FMO (more than 120 ps[39]) is much longer than the coherence times of either the chlorosome or FMO. Consequently, the transfer is by an incoherent Förster mechanism, i.e., populations on the chlorosome are converted into populations on FMO, and not coherences.[18] Even if a particular FMO site were the only site coupled to the chlorosome, the chlorosome would not coherently excite that site, to be followed by wavelike transport; rather, it would excite a mixture of FMO eigenstates in proportion in which they are found on the site.

We now turn to the question in the title, the tantalizing proposal that the partial process coherence of photosynthesis might enhance the efficiency of exciton transport, suggesting it was selected by natural selection. The efficiency can be defined as the proportion of the initially created excitons that reach the reaction center. Several mechanisms have been proposed by which coherence might enhance transport efficiency, and in the following we consider how each of them might operate in the steady-state regime of natural light harvesting. We will first rule out two mechanisms, faster delocalization and microscopic coherence, before describing two mechanisms that may sometimes be said to operate: ENAQT and supertransfer. We will caution, however, that although ENAQT and supertransfer may enhance the efficiency of artificial light-harvesting complexes, the possibility of equally efficient incoherent transport should not be overlooked.

The simplest example of a difference between quantum and classical transport occurs on ordered, infinite lattices. On a one-dimensional lattice, quantum transport is "ballistic" because the variance of the particle's wave function is proportional to time, $\Delta x_{\mathrm{quant}} = c_{\mathrm{quant}}t$. Classical transport, say by random walk, is "diffusive", $\Delta x_{\mathrm{class}} = c_{\mathrm{class}}\sqrt{t}$. Therefore, at sufficiently long times, $\Delta x_{\mathrm{quant}}$ will exceed $\Delta x_{\mathrm{class}}$, even if $c_{\mathrm{class}} > c_{\mathrm{quant}}$.

If an excitation were initially localized, coherent delocalization might well enhance transport to a distant reaction center. However, as we noted above, photosynthetic complexes are much smaller than the wavelength of light, meaning that initial excitations are not localized. Furthermore, in any *finite* system, a classical particle could spread over the entire complex faster than a quantum particle if c_{class} were sufficiently large. Therefore, even if an exciton in a biological complex initially spread ballistically,[35] incoherent transport could cause faster delocalization if the incoherent transfer rates were higher. In other words, the coherent speed-up of delocalization cannot be said to be responsible for the high transport efficiency.

Studies of photosynthetic complexes have usually considered ensembles, and it is important to consider how individual ensemble realizations contribute to transport. Each photosynthetic organism contains an ensemble of photosynthetic complexes, each of which experiences a slightly different environment (inhomogeneous disorder).[9,10] To properly understand natural light harvesting, it will be important to carry out single-molecule spectroscopic experiments to discern

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the mechanistic details that may be washed out in the ensemble average.[10,40,41]

An intriguing question is whether the state coherences of individual ensemble realizations—the microscopic coherences—play a role. Certainly, the ensemble density matrix, being the average of the microscopic density matrices, will have smaller coherences than the average absolute value of the microscopic coherences. Even if photosynthesis in vivo proceeded through diagonal steady states, the microscopic coherences might be nonzero. It is tempting to think that the potentially large microscopic coherences might increase the efficiency of light harvesting. For example, if each realization used state coherence to enhance the efficiency, one would have to calculate the efficiency for each realization and *then* average over the ensemble.

Having to simulate every realization would be a Herculean task, but is fortunately unnecessary. Changing the order of ensemble averaging and calculating the expectation values of observables—including the efficiency η—makes no difference:

$$\mathrm{Tr}(\eta\langle\rho_S\rangle_{ens}) = \langle\mathrm{Tr}(\eta\rho_S)\rangle_{ens} \tag{1}$$

where $\langle\cdot\rangle_{ens}$ is the average over realizations ρ_S. Although some elements of the ensemble might benefit from state coherence, for others it will be deleterious. For example, if we imagine that the efficiency is proportional to a coherence, $\eta \propto \rho_{12}$, then $\langle\eta\rangle_{ens} \propto \langle\rho_{12}\rangle_{ens} = 0$ if the ensemble is diagonal. Although it is tempting to speculate about the efficiency including terms like $|\rho_{12}|^2$, whose average would not vanish, it should be remembered that $|\rho_{12}|^2$ is not a linear operator on ρ and therefore not a valid observable. Likewise, the purity $\mathrm{Tr}(\rho^2)$ is not an observable, so there is no contradiction if an ensemble of pure states has a purity less than 1. Nonlinear expressions such as these are not observables because they cannot be measured in a single-shot measurement. Determining their expectation values is possible, but it requires the experimental ability to produce multiple copies of the same quantum state, which is not the situation in a genuinely random ensemble. Additionally, we do not claim that quantum systems can only respond linearly to external perturbations, but only that expectation values of observables are linear in ρ, even if the response is nonlinear in the perturbation.

A similar situation occurs if one considers sunlight as a train of femtosecond pulses,[7] in which case there is an ensemble of the phases and arrival times of these pulses. Even if each pulse could excite nonstationary states like a femtosecond laser could, the simpler, incoherent ensemble average will reproduce all the observables.

We do not seek to undermine the usefulness of single-molecule experiments, which are indispensable in elucidating biological *mechanisms*—as patch-clamping was for ion channels. We merely stress that once the mechanism is known, the *outcome* of a process can be calculated either microscopically or using the ensemble average, indicating that microscopic coherences do not play an important role in sunlight harvesting.

This brings us to ENAQT, the first coherent enhancement mechanism that can survive under incoherent illumination. It can occur in systems whose evolution can be modified from coherent to incoherent using an adjustable-strength coupling to a particular bath. ENAQT occurs if the efficiency of transport is highest in the intermediate coupling regime, i.e., higher than it would be in either the unitary or incoherent limits.[32,33,36,42] Although previous work has considered initially localized excitations (i.e., site-to-site transport), the steady state version is easily constructed as well.

In disordered systems, initially localized excitations may be prevented from delocalizing by coherent effects such as Anderson localization. ENAQT occurs if moderate decoherence destroys the coherent localization, allowing the particle to reach its target faster. Similarly, very strong decoherence can prevent transport, meaning that partial coherence can optimize the efficiency. The extent of ENAQT is very dependent on the nature of the particular bath being studied. For certain realistic baths, the transport efficiency in FMO has been found to be optimized in an intermediate coupling regime;[36] therefore, that complex can be said to have enhanced transport over the hypothetical case of weaker or stronger bath coupling. However, as we argue below, this does not show that coherence is necessary for the high efficiency.

A second possible design motif is supertransfer, an enhancement of long-range incoherent transport by short-range process coherence.[43−45] Named after superradiance, it involves a donor complex and an acceptor complex, each composed of several chromophores. The two complexes are far apart and the weak transfer between them is incoherent (Förster), but the total incoherent rate depends on the process coherence *within* the donor. In the complete absence of process coherence, each chromophore in the donor is independently incoherently coupled to each chromophore in the acceptor by the dipole−dipole interaction. In the alternative case, the excitons within the donor are delocalized across multiple sites, allowing for cooperative transfer and an enhanced overall incoherent rate. In excitonic systems, this effect is also known as multichromophoric Förster resonant energy transfer.[46,47]

In the extreme case, incoherent transfer of excitons symmetrically delocalized across M chromophores on the donor can be up to M times faster than if the chromophores only communicated individually[44] (see also the renormalization scheme in ref 48). For example, we consider a donor and an acceptor, each composed of two chromophores, all of whose dipole moments are parallel and with magnitude μ. In the incoherent case, each chromophore in the donor has a 1/2 chance of being occupied and transmits to each acceptor chromophore with a Fermi-golden-rule rate $\gamma \sim |\mu_D\mu_A|^2 = \mu^4$. This gives a total incoherent rate of $\Gamma_{incoh} = 2\gamma$. If local coherence is present and the donor is in the symmetric ground state with the dipole $(\mu_1 + \mu_2)/\sqrt{2}$ that communicates with the corresponding state on the acceptor, the total incoherent rate is doubled:

$$\Gamma_{coh} \sim \left|\left(\frac{\mu_1+\mu_2}{\sqrt{2}}\right)_D\left(\frac{\mu_1+\mu_2}{\sqrt{2}}\right)_A\right|^2 = 4\mu^4 = 2\Gamma_{incoh} \tag{2}$$

Supertransfer persists in incoherent light and at steady state, meaning that biomolecular networks in which supertransfer occurs, such as the LHI and LHII complexes[47] in Figure 1, may be said to have enhanced efficiency compared to the situation where all the chromophores were individually coupled.[45]

ENAQT and supertransfer are both robust effects that may be used to explain the high transport efficiency in some complexes and that may be used in the design of artificial complexes. However, we must caution against the conclusions that process coherence always assists transport or that it is necessary for high transport efficiencies. Indeed, for any particularly efficient coherent process, one could increase the efficiency by adding additional incoherent rates directly to the

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reaction center. Therefore, in engineering artificial light-harvesting systems, one should not consider process coherence necessarily advantageous. This is not to say that there are no design motifs to be learned from photosynthesis: in certain artificial systems, ENAQT and supertransfer may be of great use.

The same caution should be applied to hypotheses that coherence is responsible for the high efficiency of photosynthetic exciton transport or that it was favored by natural selection. Even if, for a particular bath, ENAQT calculations show that moderate coherence helps, we should recognize that evolution was not constrained to any particular bath (i.e., protein cage) and that a different bath could have yielded a more efficient, albeit incoherent, process. For this reason, the observed process coherence may be an evolutionary spandrel:[13] it could well be that in trying to increase incoherent couplings and create an energy funnel to the reaction center, evolution brought the chromophores closer, making strong interchromophoric couplings—and thus partial process coherence—unavoidable.

To summarize, although natural light harvesting proceeds through stationary states, long-lived dynamical coherences in ultrafast experiments remain remarkable because they show that the couplings between the chromophores are stronger than their couplings to their respective baths, which can indicate ENAQT or supertransfer even under incoherent illumination. Therefore, this artificial phenomenon is relevant not because it occurs in the same way in vivo, but because it may indicate energy transport mechanisms that are qualitatively different from the previously assumed incoherent site-to-site hopping. Because this is the case if the observed dynamical coherences are of electronic and not vibrational nature, additional studies should address the origin of the oscillations.[20,21]

A remaining challenge is to construct models of energy transfer under incoherent light based on spectroscopic data acquired with coherent light sources. Quantum process tomography helps achieve this goal by systematically correlating the prepared input and measured output states in the excitonic system.[49,50] A complete characterization may permit the control of energy flow using coherent light in the spirit of quantum control,[51,52] in which case dynamical coherences would be essential to achieving the desired goal.

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Notes

The authors declare no competing financial interest.

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