Coherent Energy Transfer under Incoherent Light Conditions
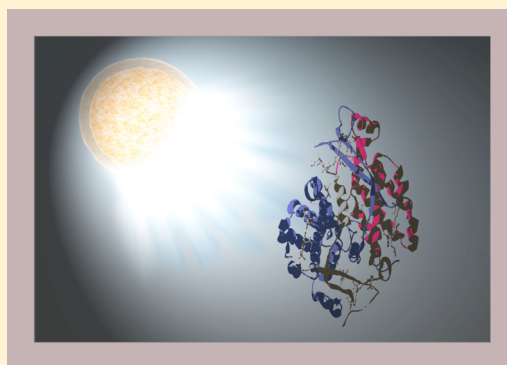
Francesca Fassioli,*[†,§] Alexandra Olaya-Castro,[‡] and Gregory D. Scholes[†]

[†]Lash Miller Chemical Laboratories, Institute for Optical Sciences and Centre for Quantum Information and Quantum Control, University of Toronto, 80 St. George St., Toronto, Ontario, M5S 3H6, Canada

[‡]Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

Ⓢ *Supporting Information*

ABSTRACT: Recent two-dimensional electronic spectroscopy (2DES) experiments have reported evidence of coherent dynamics of electronic excitations in several light-harvesting antennae. However, 2DES uses ultrafast coherent laser pulses as an excitation source; therefore, there is a current debate on whether coherent excitation dynamics is present under natural sunlight — incoherent — illumination conditions. In this letter, we show that even if incoherent light excites an electronic state with no initial quantum superpositions among excitonic states, energy transfer can proceed quantum coherently if nonequilibrium dynamics of the phonon environment takes place. Such nonequilibrium behavior manifests itself in non-Markovian evolution of electronic excitations and is typical of many photosynthetic systems. We therefore argue that light-harvesting antennae have mechanisms that could support coherent evolution under incoherent illumination.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Recent two-dimensional electronic spectroscopy (2DES) experiments reporting exciton coherence beating in several light-harvesting photosynthetic complexes[1–5] have led to the speculation that coherent energy transfer may be relevant for photosynthesis in vivo. The experimental findings and subsequent theoretical studies point toward an exciton–phonon interaction regime that allows for energy to flow in a wave-like manner in the biological environment.[6–12] However, 2DES uses coherent laser pulses to excite the molecular aggregate in a superposition of excitonic states and therefore, there is a current debate on whether these effects are present under natural sunlight — *incoherent* — conditions of illumination.[13–15] For example, it has been claimed that in an isolated molecule an incoherent continuous radiation source excites eigenstates of the molecular Hamiltonian; therefore, because the molecule is in a stationary state, incoherent light does not induce subsequent dynamics. In contrast, coherent light creates a superposition of eigenstates, and hence the state of the system evolves in time.[14,16] Because processes such as internal conversion and intravibrational relaxation take place in molecules[17] even when excitation light is incoherent, the validity of the conclusions of refs 14 and 16 is questionable for real molecules.

A further objection for coherent dynamics under sunlight illumination is that because under continuous pumping it is not possible to assign a known time for photon arrival, different realizations of the absorption process could possibly interfere destructively washing out any quantum effect.[14,15] In the first steps of photosynthesis, however, there is a very distinct separation of time scales among the different physical processes involved that can justify a nonequilibrium picture of these primary events, as we argue in what follows.

In nature, photosynthesis starts with the absorption of a photon by a light-harvesting antenna composed of electronically coupled light-absorbing molecules or chromophores embedded in a protein scaffold and solvent environment. The associated electronic excitation is then transferred within and between antennae and eventually to reaction centers where charge separation takes place.[18] These processes happen on an ultrafast picosecond time scale, in contrast with the nanosecond time scale associated with fluorescence decay. Moreover, under natural illumination conditions, antenna proteins are photo-excited at a rate that is low enough to guarantee that at most there is a single excitation in an antenna at a given time.[19] With these considerations in mind, a plausible picture of energy transfer in photosynthetic light-harvesting under continuous illumination is that of an antenna exhibiting periods of no excitation, followed by *periods of transient excited-state dynamics* upon photon absorption.

Energy transfer is possible due to the fact that unlike the case of an isolated molecule photon absorption excites the molecular aggregate into a state that is no longer an eigenstate of the relevant *system + environment* degrees of freedom. The specific coherent or incoherent nature of this transient process can depend on the initial photoexcited state[20] but is mostly

determined by the interaction between the system of interest and its environment.[7,21] By coherent we mean that excitation transfer is accompanied by coherent evolutions of excitonic superpositions.

It has been argued that in a light-absorbing complex under thermal light, coherences between eigenstates are present for a very short time scale and arise only because the system feels the "turning-on" of the field at time $t = 0$ and consequently are not relevant.[22] This study assumes, however, very weak system–environment coupling such that the system follows a fully Markovian dynamics. In this case, it is known that eigenstate populations and coherences are decoupled and the effect of the environment is simply to damp coherences present in the initial photoexcited state. Under these conditions, coherent dynamics takes place if and only if coherences are initially present.[23] Light-harvesting antennae, however, do not necessarily operate in such regime. Often the relevant energy and time scales of excitonic Hamiltonian evolution, phonon equilibration, and exciton–phonon interaction are comparable.[6,7,9,10,21] In consequence, excitation dynamics has much richer features.

In this letter we show that the transient dynamics of excitations in a light-harvesting system can proceed coherently under conditions relevant for incoherent illumination. In particular, we focus on the typical situation where excited electronic states interact with a slowly relaxing phonon environment at room temperature and show that indeed coherent dynamics arises even if incoherent light excites a state with no excitonic superpositions. The key mechanism supporting such coherent evolution is the nonequilibrium phonon environment that generates non-Markovian evolution of excitations.

To model EET in a light-harvesting antenna under sunlight illumination, we focus on the electronic degrees of freedom of the molecular aggregate as our *system* of interest and treat the protein and solvent environment as a phonon *bath*[24] and sunlight as thermal radiation. The total Hamiltonian is given by $H = H_{el} + H_{ph} + H_{rad} + H_{el,ph} + H_{el,rad}$, where

$$H_{el} = \sum_m E_m |m\rangle\langle m| + \sum_n V_{mn}(|m\rangle\langle n| + |n\rangle\langle m|) \tag{1}$$

$$H_{ph} = \sum_k \hbar\omega_k b_k^\dagger b_k \tag{2}$$

$$H_{rad} = \sum_k \hbar\omega_k a_k^\dagger a_k \tag{3}$$

$$H_{el,ph} = \sum_m \sum_k g_k^m (b_k^\dagger + b_k)|m\rangle\langle m| \tag{4}$$

$$H_{el,rad} = -\vec{\mu}\cdot\vec{E} \tag{5}$$

H_{el}, H_{ph}, and H_{rad} represent the electronic, phonon, and radiation field degrees of freedom, respectively, where $|m\rangle$ refers to the site basis with molecule m in the excited state and all other in the ground state and $b_k^\dagger (b_k)$ is the creation (annihilation) operator of a phonon mode of frequency ω_k and similarly with $a_k^\dagger (a_k)$ for the field modes. $H_{el,ph}$ is the coupling between the electronic system and the phonon bath. $H_{el,rad}$ describes the interaction between the electronic system and the radiation field within the dipole approximation, where $\vec{\mu} = \sum_m \vec{\mu}_m (|0\rangle \langle e_m| + |e_m\rangle \langle 0|)$ is an effective dipole moment operator for the molecular aggregate that induces transitions between the ground state and the excitonic states $|e_m\rangle$ that diagonalize

the Hamiltonian H_{el} (eq 1). The field is expressed as $\vec{E} = i\Sigma_k(\hbar\omega_k/(2\varepsilon_0 V))^{1/2}\hat{e}_k(a_k e^{i\mathbf{k}\cdot\mathbf{r}} - a_k^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})$, where $\mathbf{r}$ is the position of the molecular aggregate that we can conveniently set to $\mathbf{r} = 0$. We note that the dipole approximation, which assumes that the electric field is constant in the spatial extent of the molecular aggregate, is typically valid in light-harvesting complexes because the wavelength of light absorption satisfies $\lambda_{abs} \gg l$, where l is the dimension of the aggregate.

The reduced density matrix for the electronic system is obtained in the usual way as the trace over the bath degrees of freedom (phonon and radiation field) of the total density matrix, $\rho(t) = \text{tr}_{ph,rad}\{\rho_{tot}(t)\}$. Because the phonon environment only induces dynamics in the excited electronic state, the total density matrix is separable in electronic, phonon bath, and radiation field degrees of freedom when the light is turned on at $t = 0$; that is, $\rho_{tot}(0) = \rho(0)\otimes\rho_{ph}\otimes\rho_{rad}$. The formal solution for the reduced system's density matrix is given by

$$\tilde{\rho}(t) = \text{tr}_{ph,rad}\left\{ T_+ \exp\left[-\frac{i}{\hbar} \int_0^t (\mathcal{L}_{el,phon}(\tau) + \mathcal{L}_{el,rad}(\tau)) \right. \right.$$
$$\left. \left. d\tau \right]\rho_{ph} \otimes \rho_{rad} \right\}\rho(0) \tag{6}$$

where the tilde indicates the interaction picture representation. Obtaining the time evolution for the reduced density matrix in the above expression is highly nontrivial, first because the interaction between the system and phonon bath cannot be treated perturbatively and also because $[H_{el,ph}, H_{el,rad}] \neq 0$. Our prime aim in this letter is to capture correctly the electronic system's excited-state dynamics due to the coupling to the phonon environment. Therefore, to simplify the treatment, we neglect the effect of the environment in the photoexcitation process in what follows but treat the coupling to the vibrational bath exactly otherwise.

Leaving aside the interaction between the electronic system and the radiation for the moment, we can account for the effect of the phonon bath on the excited-state dynamics (eq 4) through a set of hierarchy of equations of motions (HEOM).[25−27] The HEOM method has already been successfully used to model EET in pigment−protein aggregates.[25,28] In particular, we apply the scaled HEOM developed in ref 27, which has been proven to converge faster than previous formulations.[27,28] We assume independent baths at each chromophore and that the coupling between the electronic degrees of freedom of chromophore m and the phonon bath is characterized by a spectral density of the form $J_m(\omega) = 2\lambda_m\gamma_m\omega/\hbar(\omega^2 + \gamma_m^2)$. λ_m is the reorganization energy and quantifies the energy associated with bath equilibration after electronic excitation. The bath relaxation time is given by γ_m^{-1} and determines the time scale over which nonequilibrium phonon dynamics happens.[17,29] Bath relaxation and bath correlation times are the same.[29] The resulting HEOM for an electronic system in contact with a thermal phonon bath, in the high-temperature limit ($kT > \hbar\gamma$,[21] with $kT \approx 200$ cm^{-1} at room temperature) reads[28]

$$\dot{\rho}_{\mathbf{n}}(t) = \left(-\frac{i}{\hbar}\mathcal{L}_{el} - \sum_{j=1}^{N} n_j \gamma\right)\rho_{\mathbf{n}} - \sum_{j=1}^{N}\sum_{k=1}^{\infty}\frac{c_k}{\nu_k}[V_j, [V_j, \rho_{\mathbf{n}}]]$$

$$+ i\sum_{j=1}^{N}\sqrt{(n_j + 1)|c_0|}\,[V_j, \rho_{\mathbf{n}_j^+}]$$

$$+ i\sum_{j=1}^{N}\sqrt{\frac{n_j}{|c_0|}}\,(c_0 V_j\rho_{\mathbf{n}_j^-} - c_0^*\rho_{\mathbf{n}_j^-}V_j) \tag{7}$$

for $\mathbf{n} = (n_1, n_2, \ldots n_N)$ with $0 \leq \sum_i n_i \leq \mathcal{H}$, where $\mathcal{H}$ is the hierarchy at which the equations are truncated and $\mathbf{n}_j^{+(-)}$ differs from $\mathbf{n}$ only by the jth element, $n_j \to n_j + (-)1$. $\nu_{mk} = 2\pi k/\beta\hbar$ ($k \geq 1$) are called Matsubara frequencies, and the coefficients c_i are given by $c_0 = \lambda\gamma(\cot(\beta\hbar\gamma/2) - i)/\hbar$ and $c_k = 4\lambda\gamma\nu_k/((\nu_k^2 - \gamma^2)\beta\hbar^2)$ for $k \geq 1$, where $\beta = 1/(k_B T)$. The reduced density matrix for the electronic system corresponds to $\rho(t) \equiv \rho_{\mathbf{n=0}}(t)$.

Equation 7 assumes that initially the excited electronic state and bath are separable, with the bath in thermal equilibrium. This assumption is appropriate for excitation by photon absorption because: (i) the separation of time scales between different photoexcitation events and exciton lifetime implies that prior to excitation the bath can be assumed in thermal equilibrium and uncorrelated with the ground electronic state and (ii) fast photoexcitation from the ground electronic state occurs according to the Franck–Condon vertical transitions. Therefore, immediately after absorption of a photon the system and bath remain separable.

We now turn to the description of photoexcitation under incoherent light. We treat the interaction between the system and the thermal radiation in the weak-coupling and Born–Markov approximations. It is well known that in this case the excitation/de-excitation process can be described by a Lindblad dissipator of the form[23]

$$\mathcal{L}_{rad}\rho(t) = \sum_m \Gamma_m\left[\sigma_m\rho(t)\sigma_m^\dagger - \frac{1}{2}\{\sigma_m^\dagger\sigma_m, \rho(t)\}\right]$$

$$+ \Gamma_m'\left[\sigma_m^\dagger\rho(t)\sigma_m - \frac{1}{2}\{\sigma_m\sigma_m^\dagger, \rho(t)\}\right] \tag{8}$$

where $\omega_m = \varepsilon_m - \varepsilon_0$ is the energy difference between the excitonic state $|e_m\rangle$ and the ground state and $\sigma_m^\dagger = |e_m\rangle\langle 0|$. The first line on the right-hand side of eq 8 describes relaxation from an exciton $|e_m\rangle$ to the ground state at rate Γ_m, whereas the second line describes excitation from the ground state to exciton $|e_m\rangle$ at rate Γ_m', with $\Gamma_m(\Gamma_m') \propto \mu_m^2$. Similarly as in ref 30, the effect of the radiation can be included by augmenting the electronic Lindblad operator in eq 7 with $\mathcal{L}_{rad}$, that is, $-\frac{i}{\hbar}\mathcal{L}_{el} \to -\frac{i}{\hbar}\mathcal{L}_{el} + \mathcal{L}_{rad}$. This leads to a hybrid HEOM–Born–Markov set of equation of motions.[30]

We can interpret from eq 8 the effect that thermal radiation has on the system: continuous incoherent light will give rise to incoherent transitions from the ground electronic state to an eigenstate $|e_m\rangle$ of the molecular system as well as recombination of the exciton to the ground state. This means that *sunlight will not create any coherence* between the ground and excited states or between excitons. This is to be contrasted with the case of illumination with a coherent pulse of light. In such a case the radiation field creates a superposition of exciton states after the absorption of a single photon, thereby imprinting its correlations on the excited molecular state.[14,16] It was previously suggested that sunlight could be regarded as a series

of random ultrashort spikes and as such sunlight would create a coherent superposition of states.[13] This is not the case because even if one could decompose sunlight as a collection of, for example, femtosecond coherent pulses, the temporal coherence associated with the ensemble is short, on the order of only 1 fs.[31]

The formalism we have presented above allows for a description of the excitation process under continuous illumination with a collection of photoexcitation and de-excitation events, leading to steady-state dynamics. This carries with itself a statistical average of all possible absorptions (and emissions) of a photon at different energies and different instants of time. As previously mentioned in the paper, it has been argued that coherent dynamics will not take place under continuous illumination because in this case it is not possible to assign a known time for photon arrival.[14,15] According to this view, the ground state is being continuously pumped to the excited state, and after a certain time, the system, bath, and radiation field are in an equilibrium state. As such, the system reaches a stationary state in which it is in a statistical mix of ground and excited states and individual absorption events are not meaningful.[14,15] However, as discussed in the Introduction, because of the separation of time scales between energy transfer and photon absorption, it is plausible that short-time (nonstationary) dynamics conditioned on the absorption of a photon take place. If single absorption events are indeed physically meaningful, then to elucidate whether coherent transfer is present under incoherent continuous illumination, we investigate exciton dynamics given an initial state that takes into account the incoherent properties of light. In particular, we will address the following alternative question: Can coherent energy transfer follow from an initial state with no super-positions between excitons?

Results. As a model system, we choose a subunit of the protein-antenna phycocyanin PC645 of marine cryptophyte algae, where long-lasting coherence in 2DES experiments has been reported.[3,5] In particular, we consider the two dihydrobiliverdin (DBV) chromophores and the two meso-biliverdin (MBV) chromophores. Site energies and electronic couplings are taken from refs 3 and 32. (See the SI for the electronic Hamiltonian H_{el}.) The higher excited states of H_{el} are predominantly delocalized between the two strongly coupled DBVs and are denoted by $|DBV^+\rangle$ and $|DBV^-\rangle$; then, the two lowest excitonic states are mainly localized on the MBVs, and we denote them by $|MBVa\rangle$ and $|MBVb\rangle$.

To examine energy flow within the PC645 subunit under a typical excitation event under incoherent radiation, we choose the bright optically allowed exciton state $|DBV^-\rangle$ as the initial state of the electronic system. Dynamics are simulated according to eq 7. Because we are concerned with the effect of relaxing the Markovian approximation, in particular, by including the finite, nonzero, bath correlation time, we compare dynamics for different bath parameters. We note that although the spectral density for PC645 has not been accurately characterized, based on data on a similar antenna protein from cryptophyte algae, PE545, reorganization energies are expected to lie in the range of $\lambda \approx 100-200$ cm^{-1}, and values for cutoff frequency of the low-frequency vibrational spectra are estimated to be close to $\gamma \approx 30-90$ cm^{-1} (bath correlation time of $\gamma^{-1} \approx 177 - 59$ fs).[33] Furthermore, here we are concerned only with illustrating how coherences can arise due to the bath correlation time associated with the continuum low-frequency spectra. Hence we are not including localized vibrational modes
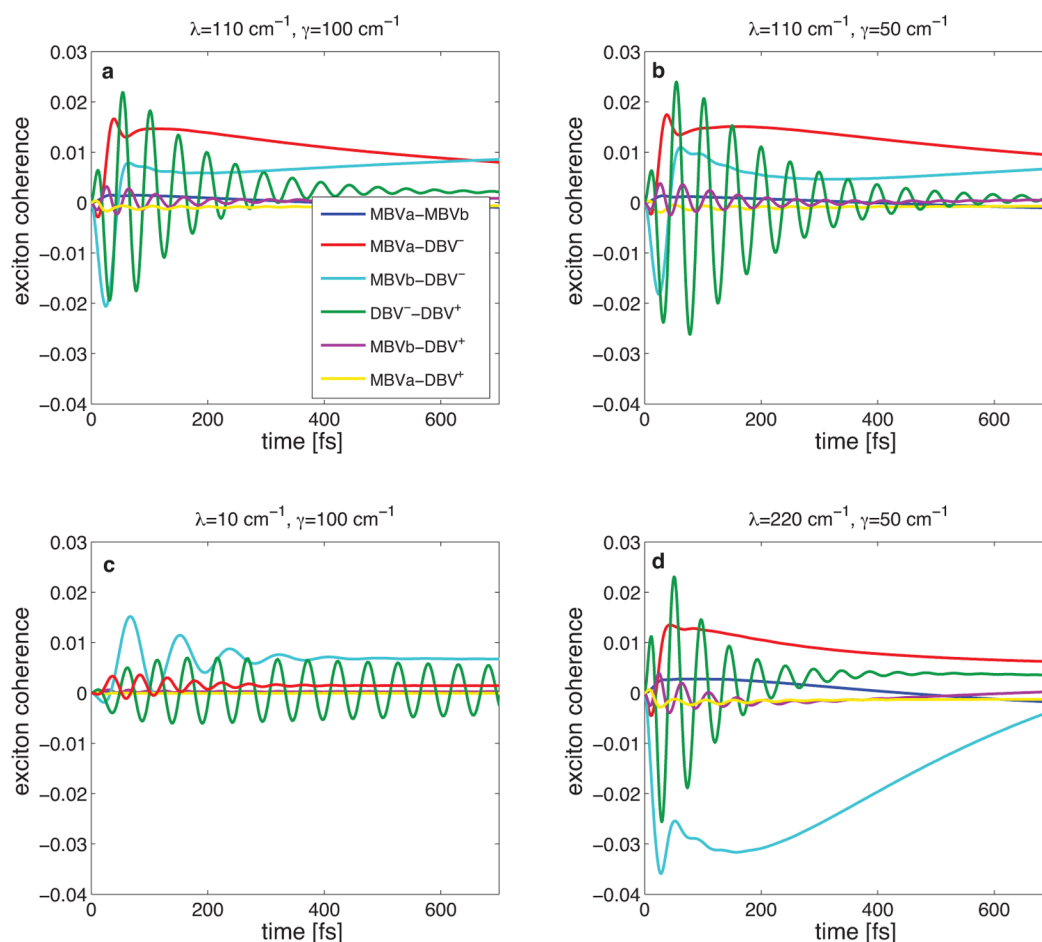
Figure 1. Time evolution of exciton coherence $\mathcal{R}e\{\langle e_i | \rho(t) | e_j \rangle\}$ $(i \neq j)$ for different bath parameters. In all cases the initial state of the electronic system is the exciton state $|DBV^-\rangle$.

that have been shown to support long-lasting coherence and enhance transport to target sites.[11,34] Figure 1 shows the time evolution of coherence between the excitonic states of H_{el}; this is the nondiagonal elements $\langle e_i | \rho(t) | e_j \rangle$ $(i \neq j)$ of the reduced density matrix, for different values of reorganization energy λ and bath correlation time γ^{-1}. Initially there is no excitonic coherence in the system, but in all cases coherence arises during the evolution; furthermore, coherence between $|DBV^+\rangle - |DBV^-\rangle$ and coherences involving $|DBV^{+(-)}\rangle - |MBVa(b)\rangle$ show oscillations for a certain period of time.

Because the bath correlation time determines the time scale of the memory in the bath, we expect that non-Markovian dynamics will be more pronounced as the value of the bath correlation time increases. This is indeed suggested by comparing Figure 1a and Figure 1b, which both correspond to a bath with the same reorganization energy of $\lambda = 110$ cm^{-1} but different bath correlation time. By decreasing γ, and hence increasing the bath correlation time, coherences oscillate for a longer time. We note, however, that we do not expect a monotonic behavior in coherent dynamics as bath correlation time decreases. This is because if γ is decreased well below the value of exciton splitting, then the effective coupling between system and bath becomes weak. As expected, if the bath-correlation time is kept fixed and instead the reorganization energy is varied, coherent oscillations will last longer for lower reorganization energies, as can be seen by comparing Figure 1a and Figure 1c or Figure 1b and Figure 1d. It is also interesting

that for the parameters here considered, the relative values of coherences are larger for a larger reorganization energy.

In our attempt to correlate the emergence of coherence with the degree of non-Markovianity in the system's dynamics, we focus on the trace distance between two quantum states, $D(\rho_1, \rho_2) \equiv (1/2)\text{tr}|\rho_1 - \rho_2|$. The trace distance is a measure of the distinguishability between two states and is always reduced by Markovian evolution, that is, $D(\rho_1(t'), \rho_2(t')) \leq D(\rho_1(t), \rho_2(t))$ $(t' \geq t)$.[35,36] This decrease in distinguishability can be interpreted as information flowing from the system to the bath, whereas increase in the distance between two states can be seen as information flowing back from the bath to the system. In other words, any increase in the trace distance is a signature of non-Markovian evolution and therefore it can be used as a witness for non-Markovianity.

We calculate the time evolution of the trace distance between two different initial states, the eigenstates $|DBV^+\rangle$ and $|DBV^-\rangle$, as a non-Markovianity witness. These states are orthogonal, and hence their distance is maximal at $t = 0$. Figure 2 shows the time evolution of the trace distance for the different parameters of bath reorganization energies and bath correlation times considered in Figure 1. The inset shows the time intervals where the derivative of the trace distance with respect to time is greater than zero, that is, the periods in time when distinguishability between the two states increases. In all cases, we observe periods of non-Markovian dynamics. We see that for larger bath-correlation time (keeping λ fixed) the trace
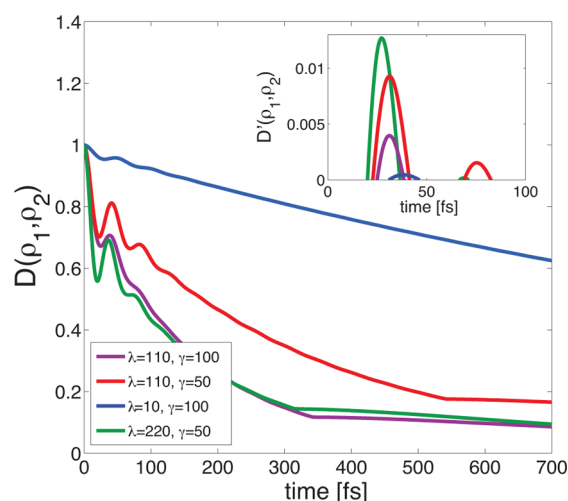
Figure 2. Time evolution of trace distance $D(\rho_1(t),\rho_2(t)) \equiv (1/2)$ $tr|\rho_1(t) - \rho_2(t)|$ for the initial states $\rho_1(0) = |DBV^+\rangle\langle DBV^+|$ and $\rho_2(0) = |DBV^-\rangle\langle DBV^-|$ of the electronic Hamiltonian H_{el} (eq 1). Different curves correspond to the different bath parameters (cm^{-1}) considered in Figure 1. Inset shows the positive values for the rate of change of trace distance $dD(\rho_1(t),\rho_2(t))/dt$.

distance decays slower and that it increases for longer periods of time as evidenced by the witness for non-Markovianity (inset). Qualitatively, this higher degree of non-Markovianity as the bath correlation time increases correlates with longer lasting oscillations in the time evolution of excitonic coherence (Figure 1a,b). By comparing now cases of fixed bath correlation time

but different bath reorganization energy, we see that the trace distance decays faster for larger reorganization energy and that the periods of non-Markovian dynamics (see inset) are comparable. We can conclude that indeed coherent dynamics can emerge after an incoherent excitation when the system is in contact with a slowly relaxing bath supporting non-Markovian evolution of excitons.

The emergence of coherence oscillations between the excitons of H_{el} from an initially incoherent state follows from correlations that form between the system and the slowly relaxing bath.[37] During the bath-correlation time scale, system and bath become correlated, inducing quantum superpositions of excitonic states, which then evolve quantum coherently under an effectively renormalized electronic Hamiltonian. This also explains why, for instance, the maximum amplitude of coherences is larger as reorganization energy increases (compare Figure 1a,c). As the bath equilibrates the dynamics is dominated by decoherence and relaxation between renormalized excitons. In this way, the nonequilibrium bath dynamics creates and supports long-time electronic coherence oscillations. Only for very weak system-bath coupling are the exciton–phonon correlations negligible, and the combined system-bath state can be assumed to be approximately separable throughout the evolution. In this case, the bath induces relaxation only between excitons, leading to vanishing coherence and thermal population of excitonic states in the long-time regime. (See Figure S1 in the SI.)

Our calculations assume a separation of system and bath degrees of freedom in the initial state justified by the Franck–Condon principle, which is generally a good approximation in
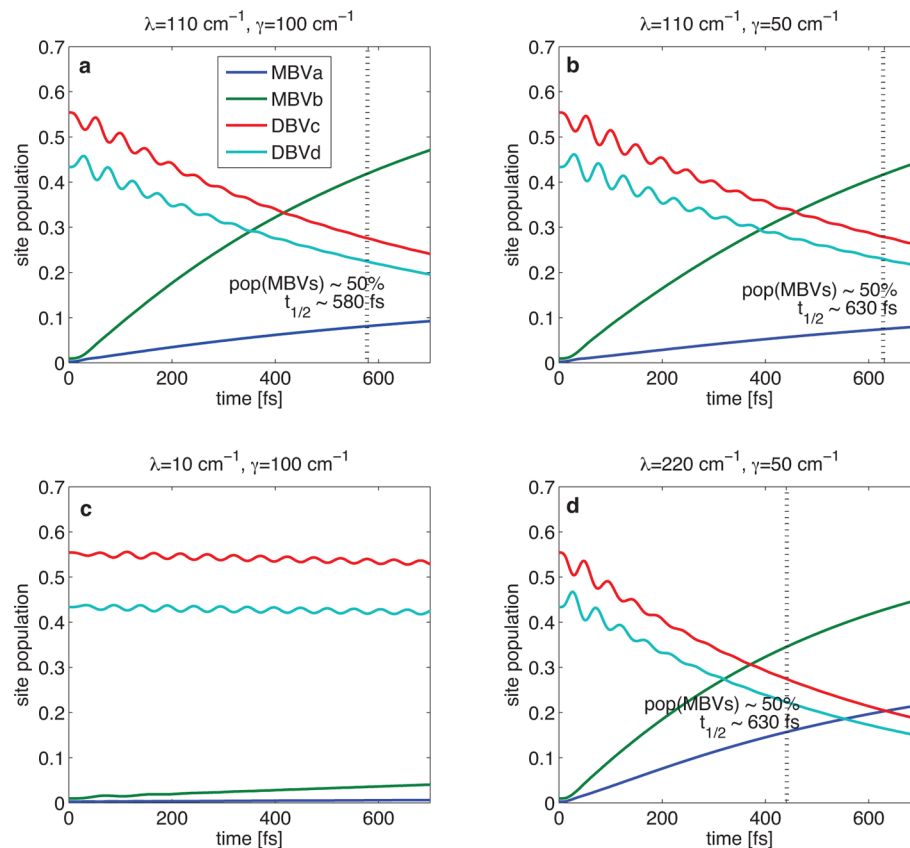

Figure 3. Time evolution of site populations $\langle i|\rho(t)|i\rangle$. Different curves correspond to the different bath parameters considered in Figure 1. Initial electronic state is $|DBV^-\rangle$.

the limit of fast photoexcitation from the ground state. However, we note that if correlations are present in the initial state, then the ensuing system dynamics can be significantly different.[37−39] For instance, it has been shown that Markovian equations are appropriate for long-time dynamics if and only if system-bath correlations are taken into account in the initial state.[37] Nevertheless, it was recently shown that the predicted time scale for coherent dynamics in FMO in 2DES experiments is the same for a separable initial state as for an initial state that accounts for system-bath correlations.[40]

For realistic bath parameters (Figure 1a,b,d), the dephasing time for quantum coherent oscillations is on the order of 200 fs. This time scale appears to be somewhat short; however, only its value relative to the time scale for exciton relaxation is meaningful. To compare these two time scales, we plot in Figure 3 the time evolution of site populations for the bath parameters previously considered. The initially excited exciton transfers the energy toward the lowest energy states, where the final acceptors correspond to the MBVs. As a quantitative measure of transfer time, we take the time $t_{1/2}$ at which the population of the acceptors reaches 50%, which is shown in Figure 3a,d. The transfer time $t_{1/2}$ is a factor of approximately 1.5 to 2 times the time for visible coherent oscillations in the population of chromophores.

The quantum coherent dynamics presented here, following the photoexcitation of a delocalized excitonic state, sheds light onto the process of localization, a phenomenon that is ubiquitous in the condensed phase. In the context of multichromophoric light-harvesting proteins, it is well-known that in extended systems such as the light-harvesting 2 (LH2) antenna complex of purple bacteria, dynamical localization takes place after excitation of a largely delocalized initial state.[41−44] Whereas initially the excitation can be delocalized over the entire B850 ring (18 molecules), the electron−phonon interaction leads to a much shorter steady-state value for exciton coherence length that spans about four chromophores.[42] One way of thinking about the obvious oscillations predicted in coherences and populations is that they accompany, and represent, dynamic exciton localization. Our results suggest that localization may involve oscillatory quantum dynamics and our treatment could be applied to study the time evolution of coherence length after an incoherent excitation in the intermediate electron−phonon coupling regime.

To conclude, in this work, we have addressed the open question of whether coherent energy transfer in light-harvesting antennae is possible under sunlight conditions as opposed to the ultrafast coherent illumination in 2DES experiments. We have considered the situation where the system−bath interaction is described by a smooth continuum spectral density that typically characterizes the interaction of excitons with a low-energy thermal background. The main feature of this phonon bath is its finite relaxation time comparable to the time scale of Hamiltonian evolution of excitons. Using a formalism that is able to capture system-bath correlations arising during this time scale, we have shown that strong enough interaction with the nonequilibrated bath can support the creation and subsequent coherent evolution of excitonic coherences from an initial state with no superpositions at all. The underlying excitonic dynamics is characterized by non-Markovianity here witnessed by an increase in distinguishability of states during the evolution. We therefore argue that mechanisms supporting non-Markovian evolution of excitonic states can, in principle,

support coherent energy transfer starting from states that have no initial superpositions. The quantum coherent EET under an incoherent excitation presented in this letter is expected to be also relevant in situations where the spectral density has more structure, for instance, when excitonic dynamics is directly affected by strong coupling to selected modes of vibration.[11] Our study may also be applicable for light-harvesting complexes that instead of directly absorbing a photon from sunlight receive excitation from another antenna.[45]

Whether the quantum coherent contributions to exciton dynamics predicted in this work have any practical implication for EET requires further investigation. As recently discussed, insight into this question can be gained by analyzing excitation dynamics under coupling both to a slowly relaxing bath and to specific vibrational modes, that is, modes quasi-resonant with excitonic transitions.[11] In general, investigation of the role of coherent evolutions in energy transfer requires development of performance measures that not only account for averages of populations or transfer times but also capture the information embedded in the full density matrix.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Parameters for the electronic Hamiltonian H_{el} and long-time evolution of coherence. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: f.fassioli@ucl.ac.uk.

Present Address
§Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Lee, H.; Cheng, Y.-C.; Fleming, G. R. Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence. *Science* **2007**, *316*, 1462−1465.

(2) Engel, G. S.; Calhoun, T. R.; Read, E. L.; Ahn, T.-K.; Mančal, T.; Cheng, Y.-C.; Blankenship, R. E.; Fleming, G. R. Evidence for Wavelike Energy Transfer through Quantum Coherence in Photosynthetic Systems. *Nature* **2007**, *446*, 782−786.

(3) Collini, E.; Wong, C. Y.; Wilk, K. E.; Curmi, P. M. G.; Brumer, P.; Scholes, G. D. Coherently Wired Light-Harvesting in Photosynthetic Marine Algae at Ambient Temperature. *Nature* **2010**, *463*, 644−647.

(4) Panitchayangkoon, G.; Hayes, D.; Fransted, K. A.; Caram, J. R.; Harel, E.; Wen, J.; Blankenship, R. E.; Engel, G. S. Long-lived Quantum Coherence in Photosynthetic Complexes at Physiological Temperature. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 12766−12770.

(5) Turner, D. B.; Dinshaw, R.; Lee, K.-K.; Belsley, M. S.; Wilk, K. E.; Curmi, P. M. G.; Scholes, G. D. Quantitative Investigations of Quantum Coherence for a Light-Harvesting Protein at Conditions Simulating Photosynthesis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4857−4874.

3141

dx.doi.org/10.1021/jz3010317 | *J. Phys. Chem. Lett.* 2012, 3, 3136−3142

(6) Rebentrost, P.; Chakraborty, R.; Aspuru-Guzik, A. Non-Markovian Quantum Jumps in Excitonic Energy Transfer. *J. Chem. Phys.* **2009**, *131*, 184102.

(7) Ishizaki, A; Fleming, G. R. Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 17255−17260.

(8) Huo, P.; Coker, D. F. Iterative Linearized Density Matrix Propagation for Modeling Coherent Excitation Energy Transfer in Photosynthetic Light Harvesting. *J. Chem. Phys.* **2010**, *133*, 184108.

(9) Nalbach, P.; Eckel, J.; Thorwart, M. Quantum Coherent Biomolecular Energy Transfer with Spatially Correlated Fluctuations. *New J. Phys.* **2010**, *12*, 065043.

(10) Huo, P.; Coker, D. F. Theoretical Study of Coherent Excitation Energy Transfer in Cryptophyte Phycocyanin 645 at Physiological Temperature. *J. Phys. Chem. Lett.* **2011**, *2*, 825−833.

(11) Kolli, A.; O' Reilly, E. J.; Scholes, G. D.; Olaya-Castro, A. The Fundamental Role of Localised Vibrations in Excitation Dynamics in Photosynthetic Light-Harvesting Systems. *arXiv.org, e-Print Arch., Biol. Phys.* **2012**, No. arXiv:1203.5056v1[physics.bio-ph].

(12) Scholes, G. D.; Fleming, G. R.; Olaya-Castro, A.; van Grondelle, R. Lessons from Nature About Solar Light Harvesting. *Nature Chem.* **2011**, *3*, 763−774.

(13) Cheng, Y. C.; Fleming, G. R. Dynamics of Light Harvesting in Photosynthesis. *Annu. Rev. Phys. Chem.* **2009**, *60*, 241−262.

(14) Brumer, P.; Shapiro, M. Molecular Response in One Photon Absorption: Coherent Pulsed Laser vs. Thermal Incoherent Source. *arXiv.org, e-Print Arch., Quantum Phys.* **2011**, No. arXiv:1109.0026v2 [quant-ph].

(15) Mancal, T.; Valkunas, L. Exciton Dynamics in Photosynthetic Complexes: Excitation by Coherent and Incoherent Light. *New J. Phys.* **2010**, *12*, 065044.

(16) Jiang, X.-P.; Brumer, P. Creation and Dynamics of Molecular States Prepared with Coherent vs Partially Coherent Pulsed Light. *J. Chem. Phys.* **1991**, *94*, 5833−5843.

(17) May, V.; Kühn, O. *Charge and Energy Transfer Dynamics in Molecular Systems*; Wiley/VHC: Berlin, 2004.

(18) Blankenship, R. E. *Molecular Mechanisms of Photosynthesis*; Blackwell Science: Oxford, U.K., 2002.

(19) Fassioli, F.; Olaya-Castro, A.; Scheuring, S.; Sturgis, J. N.; Johnson, N. F. Energy Transfer in Light-Adapted Photosynthetic Membranes: From Active to Saturated Photosynthesis. *Biophys. J.* **2009**, *97*, 2464−2473.

(20) Fassioli, F.; Nazir, A.; Olaya-Castro, A. Quantum State Tuning of Energy Transfer in a Correlated Environment. *J. Phys. Chem. Lett.* **2010**, *1*, 2139−2143.

(21) Ishizaki, A.; Fleming, G. R. On the Adequacy of the Redfield Equation and Related Approaches to the Study of Quantum Dynamics in Electronic Energy Transfer. *J. Chem. Phys.* **2009**, *130*, 234110.

(22) Hoki, K.; Brumer, P. Excitation of Biomolecules by Coherent vs. Incoherent Light: Model Rhodopsin Photoisomerization. *Procedia Chem.* **2011**, *3*, 122−131.

(23) Breuer, H.-P.; Petruccione, F. *The Theory of Open Quantum Systems*; Oxford University Press: New York, 2002.

(24) Gilmore, J.; McKenzie, R. H. Spin Boson Models for Quantum Decoherence of Electronic Excitations of Biomolecules and Quantum Dots in a Solvent. *J. Phys.: Condens. Matter* **2005**, *17*, 1735−1746.

(25) Ishizaki, A.; Fleming, G. R. Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach. *J. Chem. Phys.* **2009**, *130*, 234111.

(26) Tanimura, Y.; Kubo, R. Time Evolution of a Quantum System in Contact with a Nearly Gaussian-Markoffian Noise Bath. *J. Phys. Soc. Jpn.* **1989**, *58*, 101−114.

(27) Shi, Q.; Chen, L.; Nan, G.; Xu, R.-X.; Yan, Y. Efficient Hierarchical Liouville Space Propagator to Quantum Dissipative Dynamics. *J. Chem. Phys.* **2009**, *130*, 084105.

(28) Zhu, J.; Kais, S.; Rebentrost, P.; Aspuru-Guzik, A. Modified Scaled Hierarchical Equation of Motion Approach for the Study of Quantum Coherence in Photosynthetic Complexes. *J. Phys. Chem. B* **2011**, *115*, 1531−1537.

(29) Ishizaki, A.; Calhoun, T. R.; Schlau-Cohen, G. S.; Fleming, G. R. Quantum Coherence and its Interplay with Protein Environments in Photosynthetic Electronic Energy Transfer. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7319−7337.

(30) Kreisbeck, C.; Kramer, T.; Rodríguez, M.; Hein, B. High-Performance Solution of Hierarchical Equations of Motion for Studying Energy Transfer in Light-Harvesting Complexes. *J. Chem. Theory Comput.* **2011**, *7*, 2166−2174.

(31) Roberts, G. Interference Effects in Femtosecond Spectroscopy. *Philos. Trans. R. Soc., A* **2002**, *360*, 987−1021.

(32) Mirkovic, T.; Doust, A. B.; Kim, J.; Wilk, K. E.; Curutchet, C.; Mennucci, B.; Cammi, R.; Curmib, P. M. G.; Scholes, G. D. Ultrafast Light Harvesting Dynamics in the Cryptophyte Phycocyanin 645. *Photochem. Photobiol. Sci.* **2007**, *6*, 964−975.

(33) Novoderezhkin, V. I.; Doust, A. B.; Curutchet, C.; Scholes, G. D.; van Grondelle, R. Excitation Dynamics in Phycoerythrin 545: Modeling of Steady-State Spectra and Transient Absorption with Modified Redfield Theory. *Biophys. J.* **2010**, *99*, 344−352.

(34) Womick, J. M.; Moran, A. M. Vibronic Enhancement of Exciton Sizes and Energy Transport in Photosynthetic Complexes. *J. Phys. Chem. B* **2011**, *115*, 1347−1356.

(35) Breuer, H.-P.; Laine, E.-M.; Piilo, J. Measure for the Degree of Non-Markovian Behavior of Quantum Processes in Open Systems. *Phys. Rev. Lett.* **2009**, *103*, 210401.

(36) Ruskai, M. B. Beyond Strong Subadditivity? Improved Bounds on the Contraction of Generalized Relative Entropy. *Rev. Math. Phys.* **1994**, *6*, 1147−1161.

(37) Suárez, A.; Silbey, R.; Oppenheim, I. Memory Effects in the Relaxation of Quantum Open Systems. *J. Chem. Phys.* **1992**, *97*, 5101−5107.

(38) Dijkstra, A. G.; Tanimura, Y. Non-Markovianity: Initial Correlations and Nonlinear Optical Measurements. *Proc. R. Soc. A* **2012**, *370*, 3658−3671.

(39) Meier, C.; Tannor, D. J. Non-Markovian evolution of the density operator in the presence of strong laser fields. *J. Chem. Phys.* **1999**, *111*, 3365−3376.

(40) Dijkstra, A. G.; Tanimura, Y. The role of the environment time scale in light-harvesting efficiency and coherent oscillations. *New J. Phys.* **2012**, *14*, 073027.

(41) Pullerits, T.; Chachisvilis, M.; Sundström, V. Exciton Delocalization Length in the B850 Antenna of Rhodobacter sphaeroides. *J. Phys. Chem.* **1996**, *100*, 10787−10792.

(42) Khün, O.; Sundström, V. Pump-Probe Spectroscopy of Dissipative Energy Transfer Dynamics in Photosynthetic Antenna Complexes: A Density Matrix Approach. *J. Chem. Phys.* **1997**, *107*, 4154−4164.

(43) Meier, T.; Chernyak, V.; Mukamel, S. Multiple Exciton Coherence Sizes in Photosynthetic Antenna Complexes Viewed by Pump-Probe Spectroscopy. *J. Phys. Chem. B* **1997**, *101*, 7332−7342.

(44) Novoderezhkin, V.; Monshouwer, R.; van Grondelle, R. Exciton (De)Localization in the LH2 Antenna of Rhodobacter sphaeroides as Revealed by Relative Difference Absorption Measurements of the LH2 Antenna and the B820 Subunit. *J. Phys. Chem. B* **1999**, *103*, 10540−10548.

(45) Schmidt am Busch, M.; Müh, F.; El-Amine Madjet, M.; Renger, T. The Eighth Bacteriochlorophyll Completes the Excitation Energy Funnel in the FMO Protein. *J. Phys. Chem. Lett.* **2011**, *2*, 93−98.