

Parameter Domain of the Effectiveness of Coherence in Excitation Transfer Efficiency.

E-mail:

Abstract

To find the effect the of coherence in excitation transfer efficiency in pigment protein complexes, in the wide range of parameter domain, we have compared the results of hierarchical equation of motion approach with the Forster resonance energy transfer. We have used 2-level system and a 3 level V-type system and the conclusions of these simple systems have been confirmed by studying the excitation transfer dynamics in realistic model of FMO-RCC complex with one monomer connected to RCC (i.e. 9-site system) and all three monomers connected to RCC (25-site system). Moreover, in the case of FMO-RCC we have used realistic initial pure state and mixed state in the presence of inhomogeneous protein environment. We find that for the low values of re-organization energy with the low peak position of spectral density and with small width, the coherent and incoherent theory shows almost similar dynamics while for the high value of reorganization energy with wide profile of spectral density, coherence enhances the excitation transfer efficiency as compared to incoherent dynamics.

Photosynthesis starts with the absorption of light by optically active organic molecules. Subsequently, the absorbed energy is transferred to the reaction center (where charge separation occurs) with high quantum efficiency ($\sim 100\%$).¹ It indicates that the implementation of the mechanism of such a high quantum efficiency to the man made light-harvesting devices will lead to the highly efficient light-harvesting devices, which can be used to meet our future renewable energy needs.²⁻⁷

Earlier, the excitation transfer between optically active molecules had been explained with Forster resonance energy transfer (FRET). In the FRET, it had been assumed that the excitation transfer between donor and acceptor is an incoherent process. With the use 2-dimensional electronic spectroscopy (2DES), it has been observed that the excitation energy transiently oscillates between optically active molecules of a pigment-protein complex (PPC) isolated from a photosynthetic bacteria.⁸⁻¹⁰ These transient oscillations were explained as signature of coherence. Following this, it was speculated that this transient oscillatory coherence may play the active role in the high quantum efficiency of excitation transfer in photosynthesis.¹¹⁻¹⁴ Later on these transient oscillations were termed as reminiscent of dynamical coherence, while the non-oscillatory coherence which stays till steady state is termed as stationary coherence.[?] Transient oscillations of excitation energy have also been observed in other different PPC.

However, the comparison of incoherent FRET theory with the coherent hierarchical equation of motion (HEOM) approach illustrate that at room temperature the both the theories provide same dynamical behavior in the case of an isolated PPC known as Fenna-Matthews-Olson (FMO) complex.¹⁵ Recently, in the 2DES experiments at room temperature, it has been observed that the dynamical coherence has almost negligible effect on the excitation energy transfer within isolated FMO complex.¹⁶ FMO complex is a trimer and each monomer contains 8 bacteriochlorophyll-a (BChla) optically active molecules. In a monomer, the BChla molecules are surrounded by in-homogeneous distribution of protein molecules. FMO complex works as a energy transmitting wire between chlorosome antenna and reaction center of photosynthetic bacteria *Chlorobium Tepidum*. Under *in-situ* conditions, chlorosome antenna absorbs the solar light.¹⁷

The PPC's can be divided into three major categories on the basis of the ratio of pigment-pigment coupling to the pigment-phonon coupling. If the pigment-pigment coupling is large as compared to pigment-phonon coupling, then the energy can oscillates between pigments for long time without environmental de-phasing. On the other hand, if the pigment-pigment

coupling is small as compared to pigment-phonon coupling, then the energy cannot oscillates between pigments rather it is transferred from one pigment to the other in a non-oscillatory fashion. In the intermediate range, when the pigment-pigment coupling and pigment-phonon coupling are of the same order, the energy can oscillates coherently on a transient time scale. The FMO complex lies in the third category. It implies that the studies on an isolated FMO complex cannot be generalized on the whole domain of parameters. However, the study of the dynamics of excitation energy transfer on a wide range of parameters by comparing a coherent and incoherent theory is still illusive. In this paper, we have studied the dynamics of excitation transfer between donor and acceptor molecules on wide range of parameters by comparing the FRET approach with HEOM approach.

The excitation transfer dynamics has been studied by considering each pigment as two-level system. In the photosynthesis, the blockade of higher excitons implies that only singly excited subspace needs to be considered.¹⁸ In this sub-space the total Hamiltonian can be written as

$$H = H_S + H_B + H_{SB} . \quad (1)$$

Here H_S denotes the system Hamiltonian^{15,19}

$$H_S = \sum_{j=1}^N \hbar \epsilon_j |j\rangle \langle j| + \sum_{i < j} \Delta_{ji} (|j\rangle \langle i| + |i\rangle \langle j|) , \quad (2)$$

where $|j\rangle$ represents the excited state of j th site and ϵ_j is the difference of transition frequency of j th BChla site with respect to the BChla site with the lowest transition frequency. The Coulomb coupling between j th and i th BChla sites is denoted by Δ_{ji} .

The bath Hamiltonian H_B can be written as

$$H_B = \sum_{j=1}^N \sum_{k=1}^{\infty} \left(\frac{\hat{p}_{jl}^2}{2m_{jk}} + \frac{1}{2} m_{jk} \omega_{jk}^2 \hat{q}_{jk}^2 \right) , \quad (3)$$

where, \hat{p}_{jk} is the momentum, m_{jk} is the mass, ω_{jk} is the angular frequency and \hat{q}_{jk} is the co-ordinate of k th phonon mode associated with j th pigment.

Finally, the system-bath interaction can be described as

$$H_{SB} = - \sum_{j=1}^N \sum_{k=1}^{\infty} g_{jk} |j\rangle \langle j| \hat{q}_{jk} , \quad (4)$$

where g_{jk} is the pigment-phonon coupling of environmental phonons local to j th pigment.

With the use of Hamiltonian Eq.(1), we have studied the excitation transfer dynamics using HEOM approach.^{15,19} Density matrix has been used to study the time evolution excitation energy between donor and acceptor. In the density matrix formalism, the diagonal elements of density matrix represents the population, while off-diagonal elements describe the coherence. The bath has infinite number of degrees of freedom and the study of the evolution of bath degrees of freedom is not required. Hence the bath degrees of freedom has been averaged out and we have used reduced density matrix to study the excitation transfer dynamics. The HEOM approach can be used almost on the whole range of parameter domain of PPC's.⁷ Besides the description of the evolution of diagonal elements of the reduced density matrix, the HEOM approach also shows the time evolution of the off-diagonal (coherent) elements of the reduced density matrix. Next, we have compared the results of HEOM approach with FRET theory. The FRET theory describes the time evolution of diagonal elements of reduced density matrix only and assume that the off-diagonal elements remains zero throughout the evolution. In both the theoretical models, the phonon bath coupled to j th pigment is described by spectral density as follows

$$J_{jk}(\omega) = \sum_{k=1}^{\infty} \frac{g_{jk}^2}{2m_{jk}\omega_{jk}} \delta(\omega - \omega_{jk}) . \quad (5)$$

We have used Lorentz-Drude spectral density

$$J_j(\omega) = \frac{2}{\pi} \left(\frac{\lambda_j \gamma_j \omega}{\gamma_j^2 + \omega^2} \right) , \quad (6)$$

here λ_j represents the re-organization energy (parameter dependent on pigment-phonon coupling) and it illustrate the amplitude of the phonon wing while γ_j describe the width and peak position of the phonon wing [see Fig.5]. Note that, in the FRET theory it is assumed that the distance between dipoles (i.e. the distance between donor and acceptor) should always greater than the size of dipole. It implies that the FRET theory can illustrate good results when $\frac{\lambda_j}{\Delta_{jk}} > 1$.

First, we have studied the excitation transfer dynamics from a donor to acceptor (as two level system) assuming homogeneous environment for both the sites using system Hamiltonian 9. From Fig.1 it is evident that, the with the very small values of γ the HEOM approach and FRET theory gave almost same result. However as we increase the value of γ the coherent (i.e. HEOM) and incoherent (i.e. FRET) theory shows different results. Moreover, at 77 K, the difference between coherent and incoherent theory is about 30% [see Fig.1a] while at 277 K the gap is about 10% at higher values of γ . It implies that for the broader phonon wings with the peak position at high frequency, the presence of coherence enhances the excitation transfer efficiency (ETE). Moreover, the decrease in the trapping of excitation with the increase in temperature indicate towards the active role of coherence.

To confirm the effect of coherence in ETE, we have studied the V-type system shown in Fig.2a. For the incoherent equal initial excitation at both the donors, it is observed that at 77 K, for the high value of γ the difference of the trapped population at acceptor studied by HEOM and FRET is about 40% [see Fig.2b]. While for the two level system this difference is about 30% at $\gamma = 1000 \text{ cm}^{-1}$. It implies that the interference between pathways shown by Fig.2a additionally enhances the trapping of population. It further confirms the enhancement of excitation trapping at acceptor site by the coherence at high values of γ .

Next, we have studied the excitation trapping by varying the values of λ at fixed value of γ in the two level system. From Fig.3a, it is clear that at room temperature for the low values of reorganization energy the difference between coherent and incoherent trapping is constant. For the high values of reorganization energy the excitation trapping by HEOM

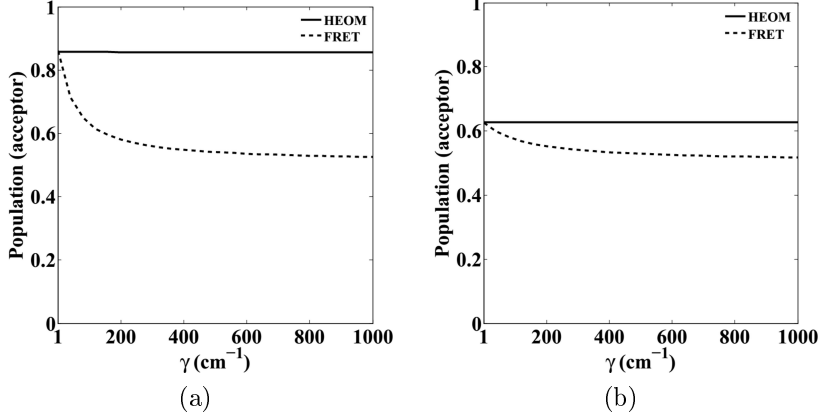


Figure 1: Comparison of the trapping of (steady state) population at the acceptor molecule (a) at cryogenic temperature 77 K and (b) at room temperature 277 K in two level system. Here solid (dashed) line illustrates the dynamics with HEOM approach (FRET approach). We have used $\lambda = 35 \text{ cm}^{-1}$ and assume that donor is initially excited (i.e. $\rho_{donor}(t = 0) = 1$). In HEOM approach, we have used 5 hierarchy levels with 3 bath exponential terms.¹⁵ At 77 K (277 K) the time step is 1 fs (0.5 fs).

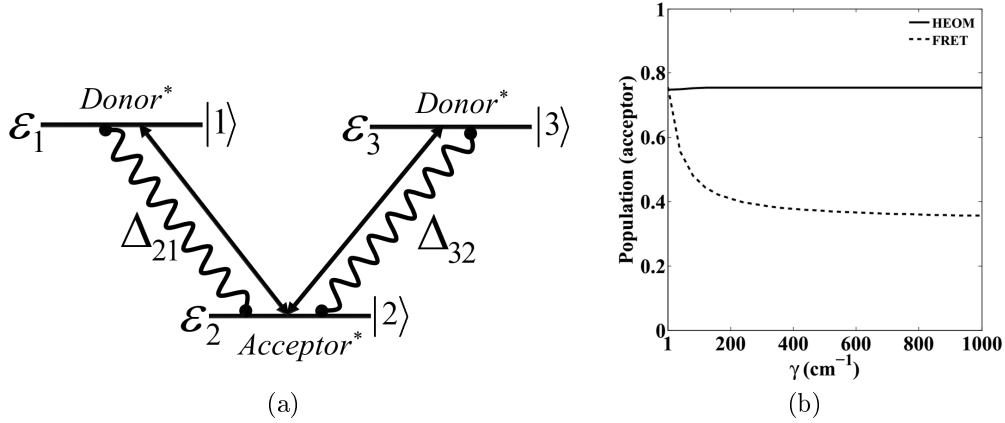


Figure 2: (a) Three level V-type system. (b) Comparison of the trapping of (steady state) population at the acceptor molecule at cryogenic temperature 77 K in V-type system. Here solid (dashed) line illustrates the dynamics with HEOM approach (FRET approach). We have used $\lambda = 35 \text{ cm}^{-1}$ and assume that donors are equally initially excited (i.e. $\rho_{donor1}(t = 0) = \rho_{donor3}(t = 0) = 0.5$). In HEOM approach, we have used $\Delta t = 1 \text{ fs}$, 3 hierarchy levels with 3 bath exponential terms.

approach increases, while it remains constant for the FRET. Hence the difference between excitation trapping increases with the increase in reorganization energy. Moreover, it implies that even at room temperature the coherent trapping can be enhanced by 40% as compared

to the incoherent trapping of excitation energy for high values of reorganization energy. The excitation trapping has also been compared by varying the energy gap (ΔE) between donor and acceptor for two level system with fixed value of λ and γ . As illustrated in Fig.3b, at room temperature, for both the coherent and incoherent approaches the excitation trapping increases with the increase in ΔE . However, for the incoherent FRET theory, the increase in the excitation trapping is little slower as compared to coherent HEOM approach. Which results in the enhancement of excitation trapping by almost 10% with the coherent transfer as compared to incoherent transfer.

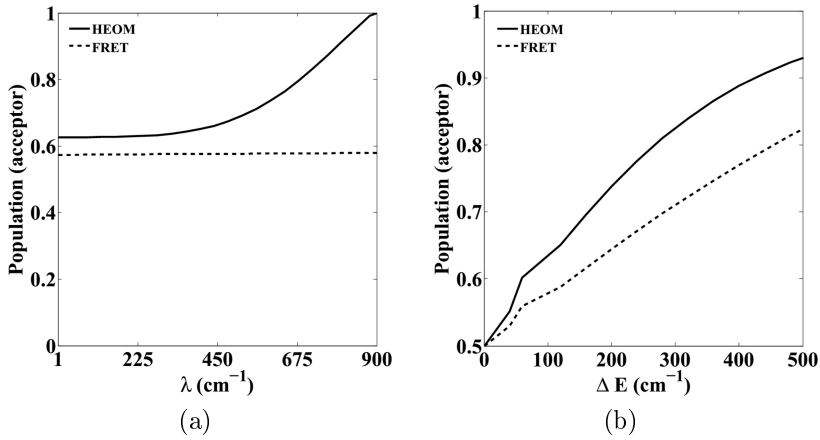


Figure 3: Comparison of the trapping of (steady state) population at the acceptor molecule at room temperature 277 K with (a) the variation of re-organization energy and (b) by changing the energy difference between donor and acceptor. Here solid (dashed) line illustrates the dynamics with HEOM approach (FRET approach). In (a) we have used $\gamma = 100 \text{ cm}^{-1}$ and in (b) we have used $\lambda = 35 \text{ cm}^{-1}$ and $\gamma = 100 \text{ cm}^{-1}$. In HEOM approach, we have used $\Delta t = 0.5 \text{ fs}$ and 5 hierarchy levels with 3 bath exponential terms.

Next, we have confirmed these results on a realistic model e.g. FMO-RCC complex. First, we have studied the excitation trapping using one monomer connected to RCC pigment i.e. a 9-site system. For the FMO complex, we have used inhomogeneous protein environment around the different sites (see Table1) and the values of transition frequency and Coloumb coupling are taken from the paper of Olbrich et .al. Following Wilkins and Dattani,¹⁵ it is considered that within the FMO complex, the coherence plays no role in the excitation transfer [see Fig.6]. With the use of time-resolved absorption and fluorescence spectroscopy in the

FMO-RCC complex, it is observed that for FMO complexes which are energetically coupled to the RCC there is 76% transfer of population. To confirm this experimental observation with the use of HEOM approach, we have used the following initial pure state obtained by the interaction of femto-second laser pulse with FMO complex.²⁰

$$\begin{aligned}
|\psi\rangle &= \sqrt{0.3260} |1\rangle + \sqrt{0.0795} |2\rangle + \sqrt{0.0005} |3\rangle \\
&+ \sqrt{0.2641} |4\rangle + \sqrt{0.0321} |5\rangle + \sqrt{0.0127} |6\rangle \\
&+ \sqrt{0.2826} |7\rangle + \sqrt{0.0025} |8\rangle .
\end{aligned} \tag{7}$$

We have observed the same amount of transfer (i.e. 76%) for the Coulomb couplings and reorganization energies given in the matrix 13 and Table2 respectively, with the site energy of 12000 cm⁻¹ [see Fig.7]. The Hamiltonian used for the 9-site FMO-RCC complex is given in the matrix12. Next, we have compared the dynamics of excitation trapping with the use of following initial mixed state¹ in both the dynamical approaches.

$$\begin{aligned}
\rho_{11} &= 0.29; \rho_{22} = 0.09; \rho_{33} = 0; \rho_{44} = .01; \\
\rho_{55} &= .026; \rho_{66} = .017; \rho_{77} = .017; \rho_{88} = .55 \\
\rho_{ij} &= 0; \quad i \neq j .
\end{aligned} \tag{8}$$

Our simulation shows that at very small values of γ , the coherent and incoherent approaches shows almost same amount of trapping of excitation at the RCC pigment both at cryogenic temperature 77 K (as shown in Fig.4a) and at the room temperature 277 K (as evident from Fig.4b). With the increase in the values of γ , the coherent dynamics shows the enhancement in the trapping, which will become constant for the large values of γ . On the other hand, with the increase in the values of γ , the incoherent dynamics shows the decline in the trapping of population at RCC pigment. It is clear from Fig.4b that at 77 K, an enhancement of about 50% can be obtained with the coherent dynamics as compared to incoherent dynamics in a realistic model.

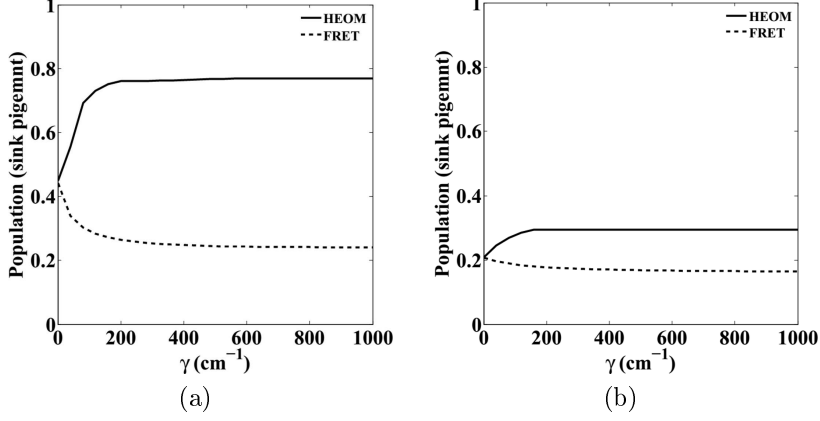


Figure 4: Comparison of the trapping of (steady state) population at the RCC pigment (a) at cryogenic temperature 77 K and (b) at room temperature 277 K in 9 level system. Here solid (dashed) line illustrates the dynamics with HEOM approach (FRET approach). In HEOM approach, we have used 4 hierarchy levels with 3 bath exponential terms and Δt is chosen to be 1 fs.

Next, we have studied the excitation transfer dynamics using 25-site model i.e. when full FMO is considered to be connected to the RCC pigment. Again, we have used the initial pure state (Eq.(7)) in HEOM approach to justify the experimental observations. We find that when full FMO is connected to the RCC pigment, the 76% transfer can be achieved with the RCC pigment of transition energy 11860 cm^{-1} [see Fig.8], while all other parameters of RCC pigment of 9-site system and 25-site system are same.

Supporting Information Available

The Hamiltonian used for 2 level system is

$$\hat{H}_{3\text{-site}} = \begin{pmatrix} 100 & 20 \\ 20 & 100 \end{pmatrix} \quad (9)$$

The Hamiltonian used for V-type system is

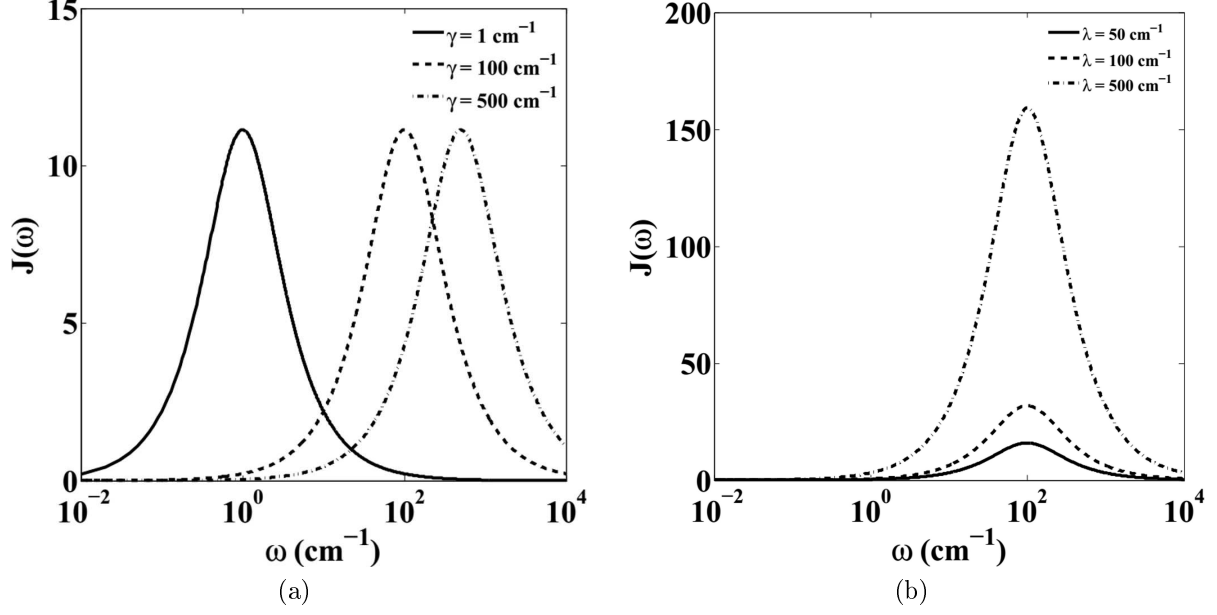


Figure 5: Profile of the Lorentz-Drude spectral density at different values of (a) γ and (b) λ .

$$\hat{H}_{3-site} = \begin{pmatrix} 100 & 20 & 0 \\ 20 & 0 & 20 \\ 0 & 20 & 100 \end{pmatrix} \quad (10)$$

The Hamiltonian used for 8-site system is given below

$$\hat{H}_{8-site} = \begin{pmatrix} 218.8 & -80.3 & 3.5 & -4.0 & 4.5 & -10.2 & -4.9 & 21.0 \\ -80.3 & 114.0 & 23.5 & 6.7 & 0.5 & 7.5 & 1.5 & 3.3 \\ 3.5 & 23.5 & 33.4 & -49.8 & -1.5 & -6.5 & 1.2 & 0.7 \\ -4.0 & 6.7 & -49.8 & 146.3 & -63.4 & -13.3 & -42.2 & -1.2 \\ 4.5 & 0.5 & -1.5 & -63.4 & 97.9 & 55.8 & 4.7 & 2.8 \\ -10.2 & 7.5 & -6.5 & -13.3 & 55.8 & 122.1 & 33.0 & -7.3 \\ -4.9 & 1.5 & 1.2 & -42.2 & 4.7 & 33.0 & 525.1 & -8.7 \\ 21.0 & 3.3 & 0.7 & -1.2 & 2.8 & -7.3 & -8.7 & 251.1 \end{pmatrix} \quad (11)$$

Table 1: Values of λ and γ for the 8-site system.

Site numbers	λ (in cm^{-1})	γ (in cm^{-1})
1	15	15.0
2	31	22.6
3	17	15.8
4	13	13.2
5	11	11.8
6	14	14.2
7	20	16.2
8	38	25.8

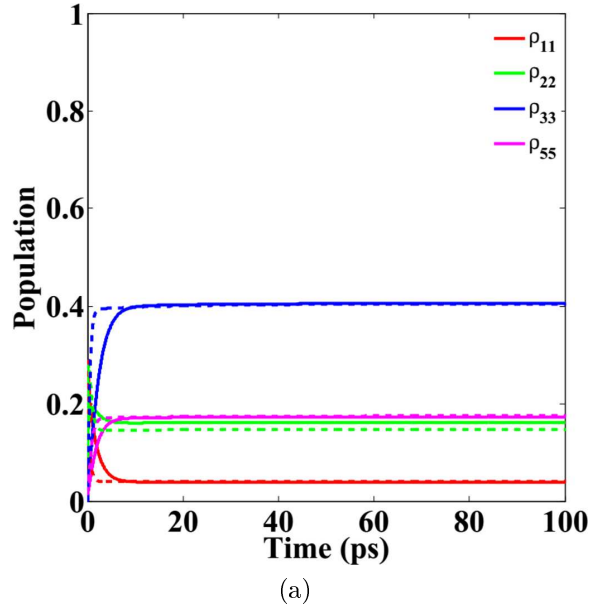


Figure 6: Comparison of the dynamics of excitation transfer studied by HEOM (solid lines) for monomer of FMO complex (i.e. 8 site system) with the dynamics studied by FRET (dotted lines).

The Hamiltonian used for 9-site system is given below

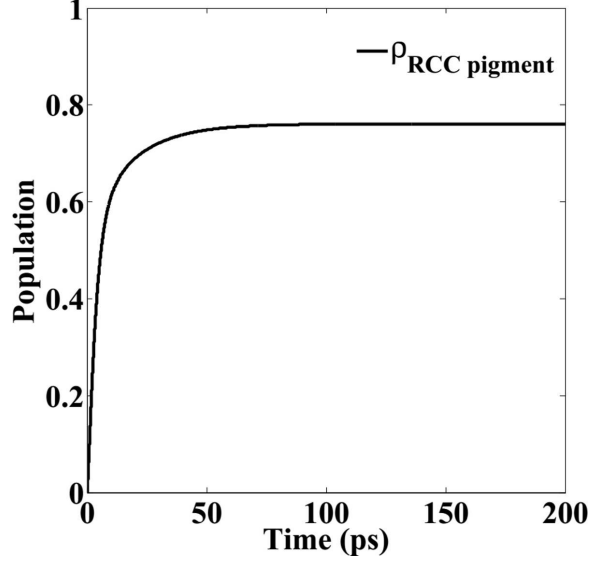


Figure 7: Dynamics of excitation trapping at RCC pigment in 9-site model with $\gamma = 200$ cm^{-1} . Here we have used time step of 1 fs and 4 hierarchy levels with 3 exponential bath terms.

$$\hat{H} = \begin{pmatrix} \hat{H}_{8\text{-site}} & \hat{H}_{RCC}^\dagger \\ \hat{H}_{RCC} & 0.0 \end{pmatrix} \quad (12)$$

$$\hat{H}_{RCC} = \begin{pmatrix} 2.0 & 4.5 & 13.0 & 9.0 & 5.5 & 2.0 & 3.5 & 0.5 \end{pmatrix} \quad (13)$$

Table 2: Values of λ and γ for the RCC pigment.

Site name	λ (in cm^{-1})	γ (in cm^{-1})
RCC pigment	113	1-1000

The Hamiltonian used for 25-site system is given below

$$\hat{H} = \begin{pmatrix} \hat{H}_{8\text{-site}} & \hat{H}_{\text{inter-monomer}} & \text{coupling} & \hat{H}_{\text{inter-monomer}}^\dagger & \text{coupling} & \hat{H}_{RCC}^\dagger \\ \hat{H}_{\text{inter-monomer}}^\dagger & \text{coupling} & \hat{H}_{8\text{-site}} & \hat{H}_{\text{inter-monomer}} & \text{coupling} & \hat{H}_{RCC}^\dagger \\ \hat{H}_{\text{inter-monomer}} & \text{coupling} & \hat{H}_{\text{inter-monomer}}^\dagger & \text{coupling} & \hat{H}_{8\text{-site}} & \hat{H}_{RCC}^\dagger \\ \hat{H}_{RCC} & & \hat{H}_{RCC} & & \hat{H}_{RCC} & -140.0 \end{pmatrix} \quad (14)$$

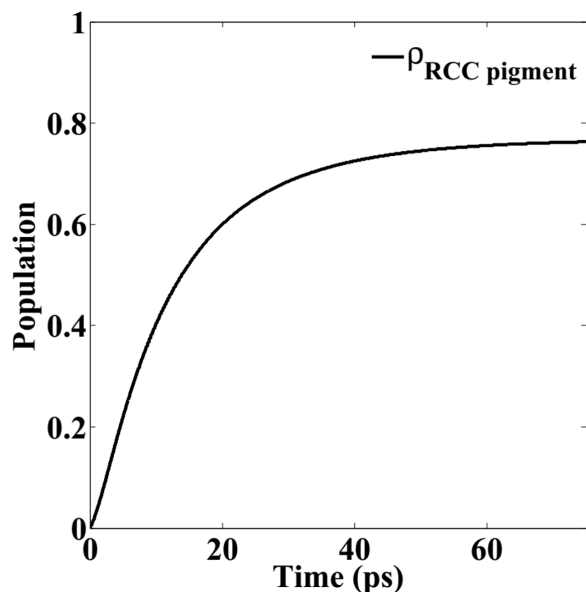


Figure 8: Dynamics of excitation trapping at RCC pigment in 25-site model with $\gamma = 200 \text{ cm}^{-1}$. Here we have used time step of 1 fs and 3 hierarchy levels with 2 exponential bath terms.

References

- (1) Schmidt am Busch, M.; Muh, 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.
- (2) Meyer, G. J. Chemist’s Quest for Inexpensive, Efficient, and Stable Photovoltaics. *J. Phys. Chem. Lett.* **2011**, *2*, 1965–1966.
- (3) Gust, D.; Moore, T. A.; Moore, A. L. Solar Fuels via Artificial Photosynthesis. *Acc. Chem. Res.* **2009**, *42*, 1890–1898.
- (4) Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.
- (5) Mallouk, T. E. The Emerging Technology of Solar Fuels. *J. Phys. Chem. Lett.* **2010**, *1*, 2738–2739.

- (6) Vullev, V. I. From Biomimesis to Bioinspiration: What's the Benefit for Solar Energy Conversion Applications? *J.Phys. Chem. Lett.* **2011**, *2*, 503–508.
- (7) Gust, D.; Moore, T. A.; Moore, A. L. Mimicking Photosynthetic Solar Energy Transduction. *Acc. Chem. Res.* **2001**, *34*, 40–48.
- (8) Engel, G. S.; Calhoun, T. R.; Read, E. L.; Ahn, T.-K.; Mancal, 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.
- (9) 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. *PNAS* **2010**, *107*, 12766–12770.
- (10) Panitchayangkoon, G.; Voronine, D. V.; Abramavicius, D.; Caram, J. R.; Lewis, N. H. C.; Mukamel, S.; Engel, G. S. Direct Evidence of Quantum Transport in Photosynthetic Light-Harvesting Complexes. *PNAS* **2011**, *108*, 20908–20912.
- (11) Lambert, N.; Chen, Y.-N.; Cheng, Y.-C.; Li, C.-M.; Chen, G.-Y.; Nori, F. Quantum Biology. *Nat Phys* **2013**, *9*, 10–18.
- (12) Scholes, G. D.; Fleming, G. R.; Olaya-Castro, A.; van Grondelle, R. Lessons from Nature about Solar Light Harvesting. *Nat Chem* **2011**, *3*, 763–774.
- (13) 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.
- (14) Scholes, G. D. Quantum-Coherent Electronic Energy Transfer: Did Nature Think of It First? *J. Phys. Chem. Lett.* **2010**, *1*, 2–8.
- (15) Wilkins, D. M.; Dattani, N. S. Why Quantum Coherence Is Not Important in the Fenna-Matthews-Olsen Complex. *J. Chem. Theory Comput.* **2015**, *11*, 3411–3419.

- (16) Duan, H.-G.; Prokhorenko, V. I.; Cogdell, R. J.; Ashraf, K.; Stevens, A. L.; Thorwart, M.; Miller, R. J. D. Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer. *PNAS* **2017**, *114*, 8493–8498.
- (17) Milder, M. T. W.; Bruggemann, B.; Grondelle, R. v.; Herek, J. L. Revisiting the Optical Properties of the FMO Protein. *Photosynth Res* **2010**, *104*, 257–274.
- (18) Dong, H.; Li, S.-W.; Yi, Z.; Agarwal, G. S.; Scully, M. O. Photon-blockade induced photon anti-bunching in photosynthetic antenas with cyclic structures. *arXiv:1608.04364v2* **2017**,
- (19) Ishizaki, A.; Fleming, G. R. Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature. *PNAS* **2009**, *106*, 17255–17260.
- (20) Singh, D.; Dasgupta, S. Effect of 8th Chromophore: A Comprehensive Study of Excitation Energy Transfer in FMO complex. *arXiv:1711.05054* **2017**,

Graphical TOC Entry

