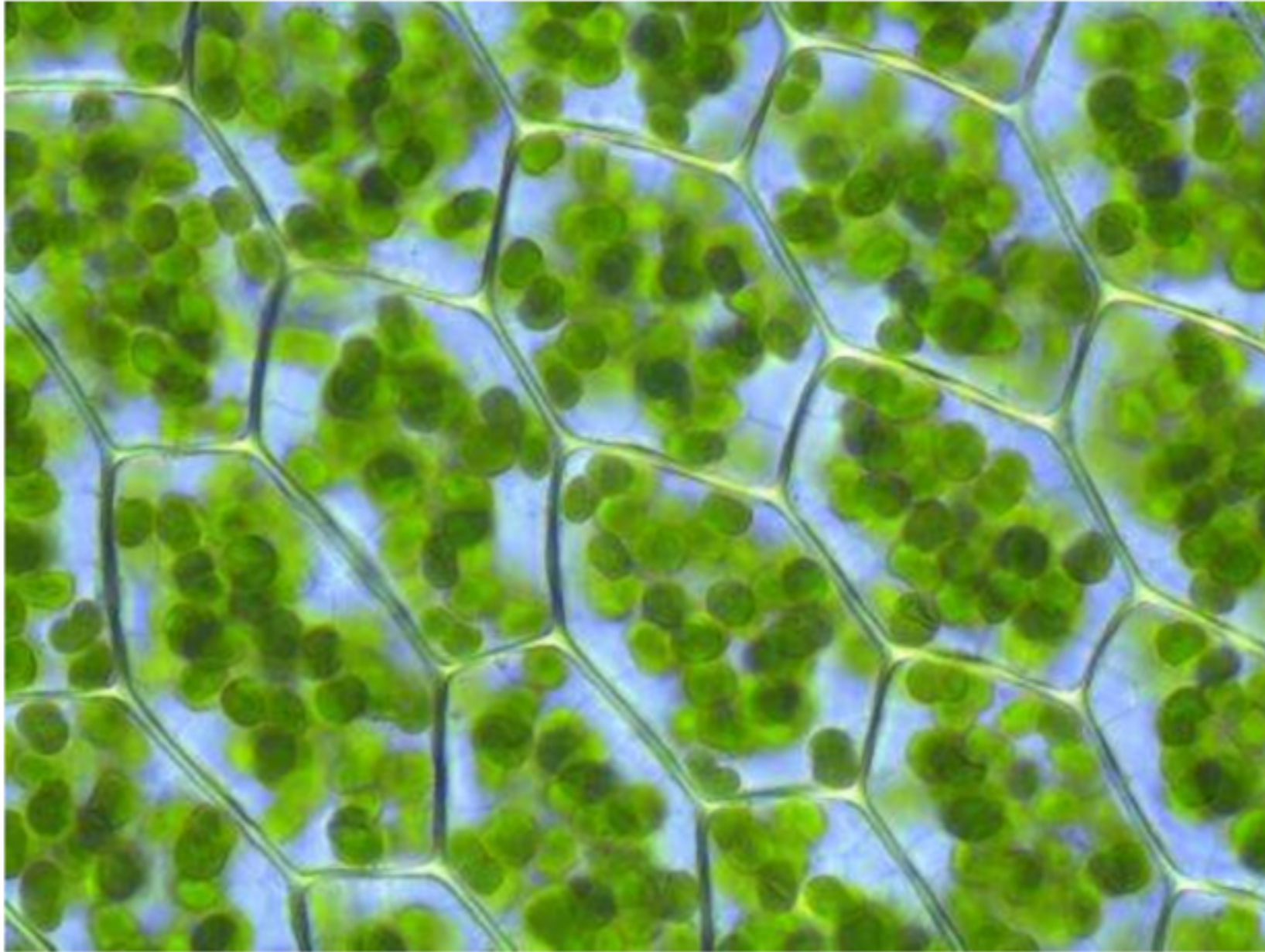


Quantum Mechanics of Photosynthesis



Plant cells with visible chloroplasts (from a moss, *Plagiomnium affine*) Credit: Wikipedia

Basic chemical process in photosynthesis:
water + carbon dioxide + light = glucose + oxygen



<http://www.fao.org/docrep/w7241e/w7241e05.htm#1.2.1%20photosynthetic%20efficiency>

Wavelength (400-700) nm utilized by plants (45% of total solar energy). Photosynthetic process is (theoretically) 25% efficient, or combined total solar efficiency of 11%.

compared to Photo-Voltaic ~ 20%

3% for bio-fuel

<http://www.economist.com/blogs/economist-explains/2014/12/economist-explains-1>

Photosynthesis starts within leaves, in sprawling structures aptly called antenna complexes. These are partly made up of molecules of chlorophyll, which give plants their green colour. As sunlight hits the leaf, packets of light called photons bash into the chlorophyll molecules. **In doing so they knock electrons out of their orbits around magnesium atoms.** Electrons have a negative charge, so their loss creates positively charged magnesium ions. **Once separated, each electron-ion pair is known as an exciton;** the photon's energy has, in effect, been poured into it.

Efficiently converting light into electricity requires preserving the exciton's energy as it travels deep within the so-called "reaction centre" of the leaf. The exciton's energy can then be redeployed into reshuffling the constituent atoms within water and carbon-dioxide molecules into simple sugars and oxygen. The key to preserving the exciton's energy lies in way it travels to the "reaction centre".

Researchers discovered to their great surprise in 2007 that plants use a bit of trickery from the realm of quantum physics to help excitons find their way. Rather than bumping randomly through a forest of chlorophyll molecules until they happen to reach their destination, excitons are in what are known as "coherences". In effect, each exciton spreads out over all possible paths simultaneously, and then funnels down through the most efficient route.

The Role of Magnesium in Photosynthesis

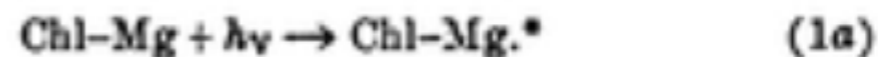
Science 02 Jul 1954:

Vol. 120, Issue 3105, pp. 33-35

DOI: 10.1126/science.120.3105.33



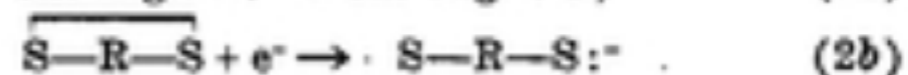
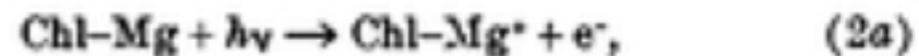
In the ground state the chlorophyll molecule contains Mg covalently linked to any two of the four pyrrole nitrogen atoms. From the standpoint of resonance the Mg atom may be thought of as linked simultaneously by one-half a covalent bond to each of the four N atoms. Extreme forms in which the Mg and N atoms have, respectively, one or more positive and negative formal charges and vice-versa, also contribute, undoubtedly, to the resonance hybrid; but on the whole the Mg atom may be considered neutral. It is here postulated that in photosynthesis it is this essentially neutral Mg atom which absorbs the photon with resultant activation of one of its 3s electrons to a higher energy state:



Subsequent loss of the excited electron to the weak oxidant results in formation of oxidized chlorophyll, characterized by unipositive Mg:



Alternatively, it would appear that absorption of a quantum of sufficiently high energy could result in the immediate ejection of a photoelectron and its direct capture by the oxidant:



In either case (Eqs. 1 and 2), positively ionized chlorophyll should result, and it may be supposed that during active photosynthesis in ordinary sunlight, the

<http://www.nature.com/nature/journal/v446/n7137/abs/nature05678.html>

Experimental “Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems”

Gregory S. et al. (14 February 2007)

“molecular excited states called excitons”

exciton is e^-h^+ pair ($h^+ =$ lattice hole)

These data prove the same quantum beating signals observed at 77 K persist to physiological temperature and show agreement in both phase and frequency, indicating that the experiment is following the same quantum coherence at all temperatures. We observe a 130 fs e-folding lifetime for this excited state coherence at 277 K and observe quantum coherence lasting beyond 300 fs, showing that evolution has had the opportunity to exploit the theorized environmentally assisted quantum transport (EnAQT) mechanism for biological function

<https://www.ucl.ac.uk/news/news-articles/0114/090114-Quantum-mechanics-explains-efficiency-of-photosynthesis>

Theoretical explanation of photosynthesis requires quantum mechanics.

The light collecting macromolecules are composed of chromophores (green) attached to proteins, which first capture sunlight and somehow transfer the energy very efficiently. There was experimental evidence that QM was involved (*ibid*, 2007) but no conclusive theoretical QM understanding.

<https://arxiv.org/pdf/1301.6970.pdf>

ARTICLE

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OPEN

Non-classicality of the molecular vibrations assisting exciton energy transfer at room temperature

Edward J. O'Reilly¹ & Alexandra Olaya-Castro¹

Advancing the debate on quantum effects in light-initiated reactions in biology requires clear identification of non-classical features that these processes can exhibit and utilize. Here we show that in prototype dimers present in a variety of photosynthetic antennae, efficient vibration-assisted energy transfer in the sub-picosecond timescale and at room temperature can manifest and benefit from non-classical fluctuations of collective pigment motions. Non-classicality of initially thermalized vibrations is induced via coherent exciton-vibration interactions and is unambiguously indicated by negativities in the phase-space quasi-probability distribution of the effective collective mode coupled to the electronic dynamics. These quantum effects can be prompted upon incoherent input of excitation. Our results therefore suggest that investigation of the non-classical properties of vibrational motions assisting excitation and charge transport, photoreception and chemical sensing processes could be a touchstone for revealing a role for non-trivial quantum phenomena in biology.

Quoting from the paper

“We therefore put forward the idea that, precisely, investigation of non-classical phenomena associated to such molecular motions can pave the way towards understanding which non-trivial quantum phenomena can have an impact on efficient energy distribution and trapping.”

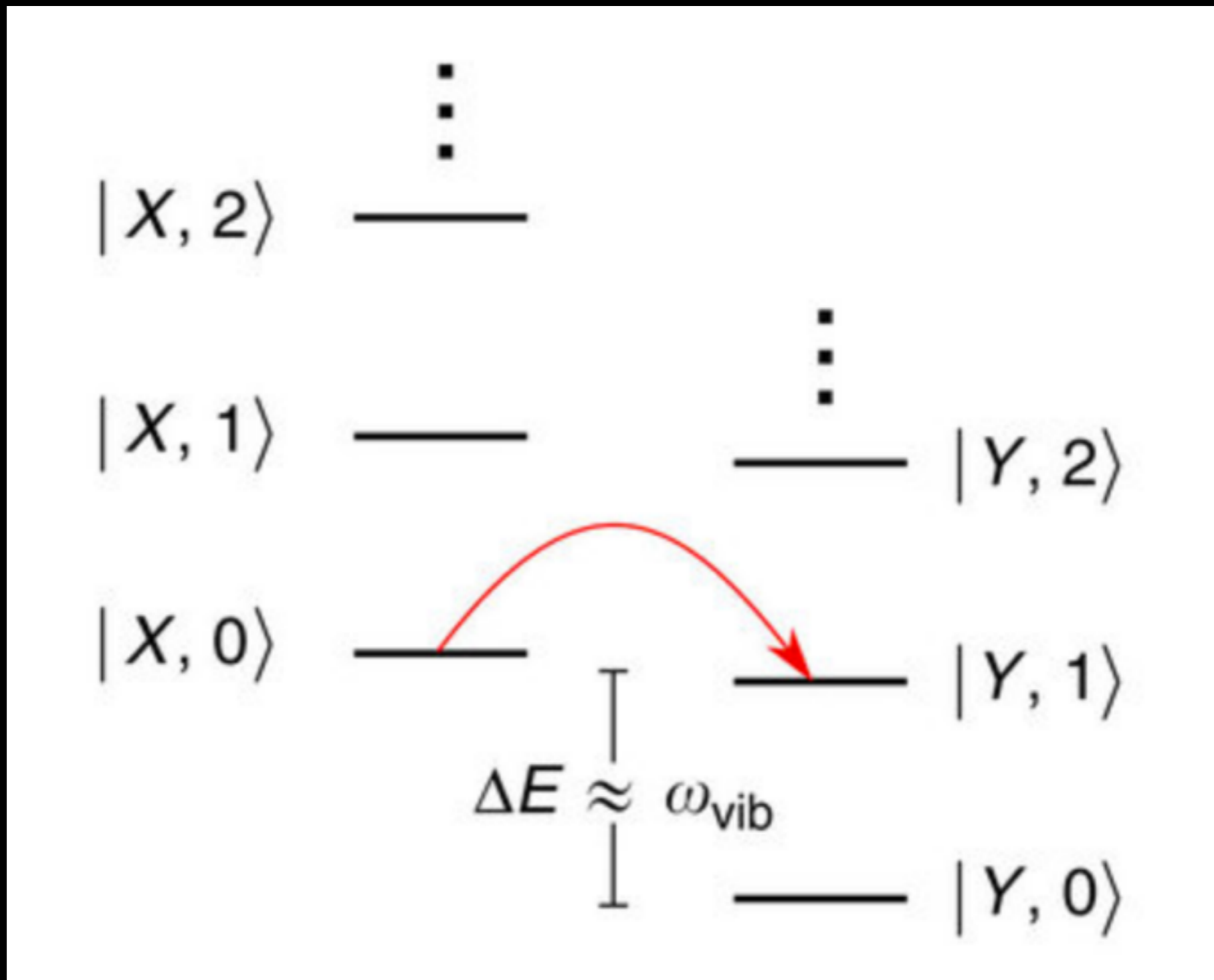
Their model consists of an effective
exciton–vibration (phonon) Hamiltonian

returning to

<https://www.ucl.ac.uk/news/news-articles/0114/090114-Quantum-mechanics-explains-efficiency-of-photosynthesis>

“Molecular vibrations are periodic motions of the atoms in a molecule... When the energy of a collective vibration of two chromophores matches the energy difference between the electronic transitions of these chromophores a **resonance occurs and efficient energy exchange between electronic and vibrational degrees of freedom** takes place. Providing that the energy associated to the vibration is higher than the temperature scale, only a discrete unit or quantum of energy is exchanged. Consequently, as energy is transferred from one chromophore to the other, the collective vibration displays properties that have no classical counterpart.”

schematic coupling of vibrational energies in 2 molecules



$$1000 \text{ cm}^{-1} = 0.124 \text{ eV}$$

$$\Delta E = h\nu_{\text{vib}} , \varepsilon_i = \text{excited electron energy}, V = \text{coupling}$$

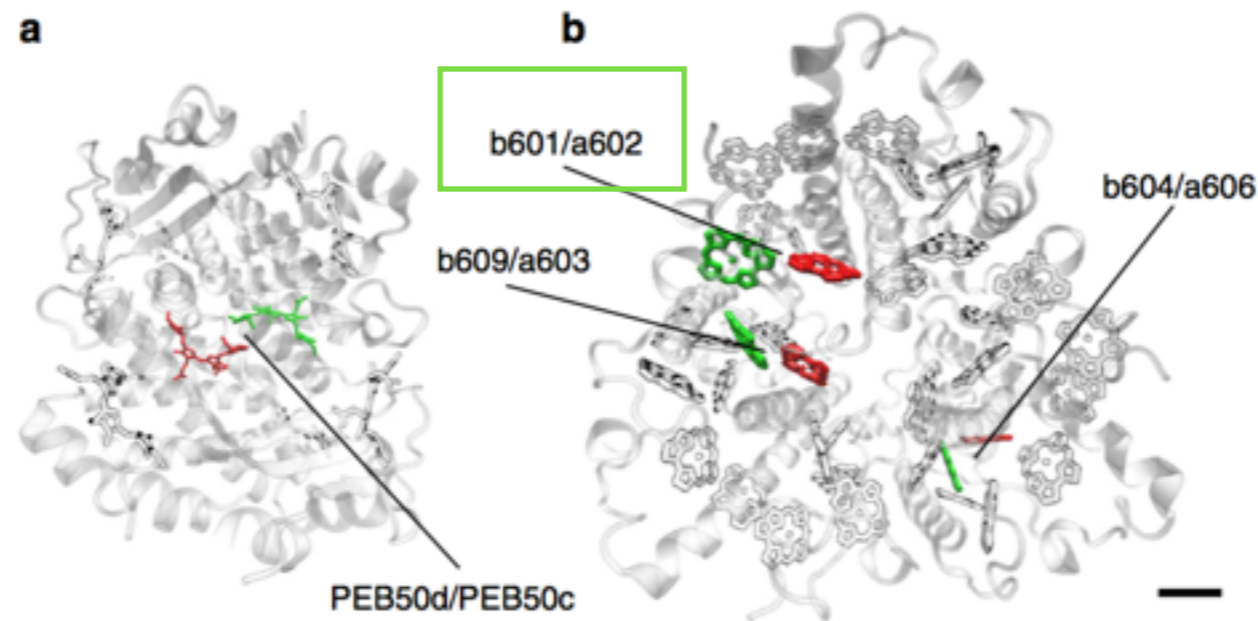
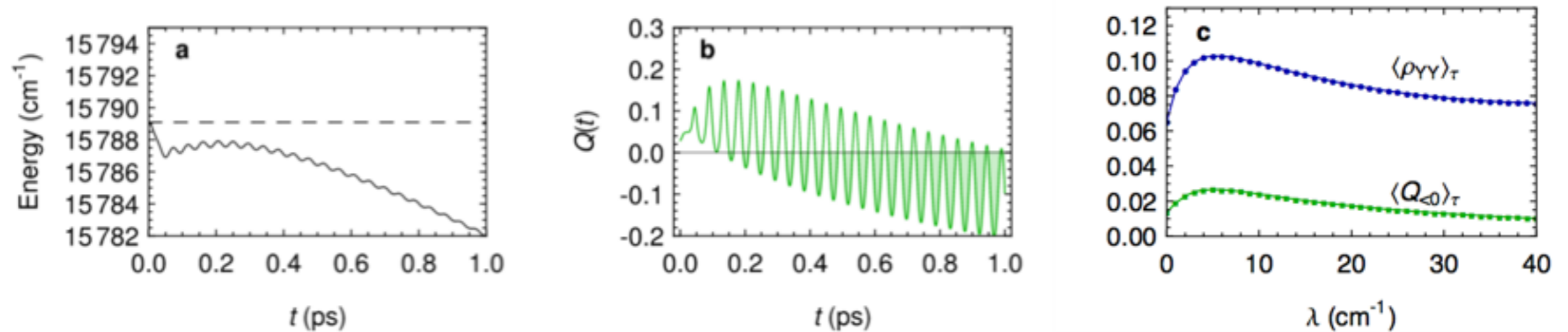


Figure 1 | Prototype dimers. (a,b) Cryptophyte antennae phycoerythrin 545 (PE545) and LHCII present in higher plants have pairs of pigments whose electronic and vibrational parameters fall in the regime of our vibration-assisted transport model. (a) Representation of the pigments and protein environment of a PE545 complex of *Rhodomonas* CS24 (Protein Data Bank ID code 1XG0, ref. 32). The central PEB dimer pigments PEB_{50c} and PEB_{50d} are highlighted in red and green, respectively. For this PEB₅₀ dimer, there is an uncertainty in the value of the energy gap^{32,33}. We take parameters from refs 32,33 such that $\Delta\varepsilon = 1,042 \text{ cm}^{-1}$ and $V = 92 \text{ cm}^{-1}$, so $\Delta E = 1,058.2 \text{ cm}^{-1}$ being quasi-resonant with an intramolecular mode of frequency $\omega_{\text{vib}} = 1,111 \text{ cm}^{-1}$. The strength of linear coupling to this mode is $g = \omega_{\text{vib}}(0.0578)^{1/2} = 267.1 \text{ cm}^{-1}$. (b) Representation of the LHCII antennae of *Spinacia oleracea* (Protein Data Bank ID code 1RWT, ref. 34). Several pairs of close Chl_b-Chl_a (red-green) chlorophylls satisfy the conditions of our model. In particular, we consider the Chl_{b601}-Chl_{a602} pair for which $\Delta\varepsilon = 661 \text{ cm}^{-1}$ and $V = -47.1 \text{ cm}^{-1}$, resulting in $\Delta E = 667.7 \text{ cm}^{-1}$ (ref. 66). An intramolecular vibrational mode of frequency $\omega_{\text{vib}} = 742.0 \text{ cm}^{-1}$ is close to this energy gap and each chromophore couples to this mode with strength $g = \omega_{\text{vib}}(0.03942)^{1/2} = 147.3 \text{ cm}^{-1}$ as obtained from (ref. 40). Scale bar: 1 nm.

Negative Mandel parameter Q implies QM

Mandel, L. Sub-poissonian photon statistics in resonance fluorescence. Opt. Lett. 4, 205–207 (1979)



Supplementary Figure S1. The LHCII complex of green plants contains weakly electronically coupled dimers whose energy gaps are resonant with vibrational modes. Here we present results from the $\text{Chl}_{(b601)}\text{-Chl}_{(a602)}$ pair with electronic parameters⁴⁹ $\varepsilon_{(b601)} = 15764 \text{ cm}^{-1}$, $\varepsilon_{(a602)} = 15103 \text{ cm}^{-1}$, $V = -47.1 \text{ cm}^{-1}$ and resulting $\Delta E = 667.7 \text{ cm}^{-1}$. A vibrational mode of frequency $\omega_{\text{vib}} = 742.0 \text{ cm}^{-1}$ is close to this energy gap and each chromophore couples to this mode with strength $g = \omega_{\text{vib}}\sqrt{0.03942} = 147.3 \text{ cm}^{-1}$, as obtained from ref. 36. The thermal background is characterized by $\lambda = 37 \text{ cm}^{-1}$, $\Omega_c = 30 \text{ cm}^{-1}$ as in ref. 36. The strength of system-bath interactions $\sqrt{\lambda\Omega_c}$ is smaller than in PE545 and therefore this dimer lies closer to the regime of coherent evolution of the exciton-vibration system, where the dissipation energy into the bath is transiently prevented. Shown here are (a) the energy of the exciton-vibration system and (b) the Mandel Q parameter of the vibrational mode for $\lambda = 37 \text{ cm}^{-1}$ (shaded regions denote times of non-classicality) and (c) averages over timescale $\tau \approx 0.4 \text{ ps}$ as a function of reorganization energy.

ρ = exciton population

“...indicating a direct quantitative relation between efficient energy transfer in the timescale t and the degree of non-classicality.”

2 Dimensional Electronic Spectroscopy (2DES)

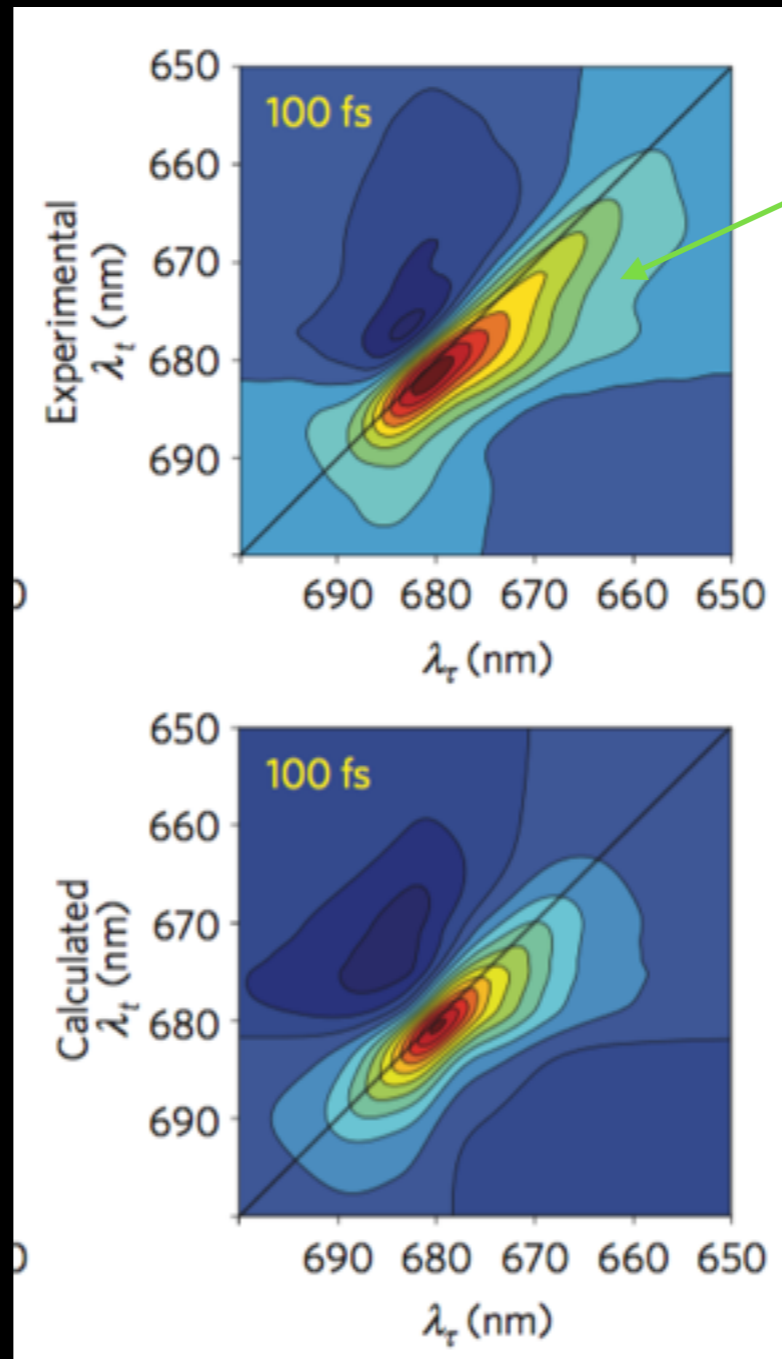
<http://www.nature.com/nphys/journal/v10/n9/full/nphys3017.html>

3 pulse laser excitation of **bacterial molecule** (July 2014)

*Fourier transform
of time data*

re-phasing time t
 $\Delta(3^{\text{rd}}, \text{signal})$

exciton charge
transfer model



coherence

coherence time τ
 $\Delta(1^{\text{st}}, 2^{\text{nd}})$

Quantum Biology?

<http://www.nature.com/news/2011/110615/full/474272a.html>

Or Not!? 100 fs coherence time too short...

<http://lanl.arxiv.org/pdf/1610.08425v1> (Oct 2016, unpublished)

Fenna-Matthew-Olson (FMO) protein

“This constitutes the main result of our work and confirms the orthodox picture of rapidly decaying electronic coherence on a time scale of 60 fs in the exciton dynamics in the FMO protein complex at ambient temperature. In turn, it disproves any contributions of quantum coherence to biological functionality under ambient conditions in natural light-harvesting units...”