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A Review of Quantum Coherence and its Effect on Photosynthetic Efficiency in PSII and FMO Complexes

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A Review of Quantum Coherence and its Effect on Photosynthetic Efficiency in PSII and FMO Complexes

An Honors Thesis submitted in partial fulfillment of the requirements for Honors Studies in Chemistry

By

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Table of Contents

Abstract

Photosynthesis in living organisms is one of the most efficient, natural energy harvesting processes on Earth. The absorption of light energy as photons directly energizes electrons in metabolite molecules. These molecules transfer their high energy electrons through a chain system to provide the energy needed for carbon dioxide metabolism. Recently, it has been a subject of debate how this energy transfer via electron transport achieved such high efficiency. One hypothesis is that this transfer system displays fundamentally quantum mechanical behaviors, such as coherence. Here, I will briefly define this concept in quantum mechanics, and explain the role it might play in excited electron energy transfer. I will also discuss alternative hypotheses proposed that claim photosynthetic energy transfer efficiency may not be explained entirely or at all by quantum coherence, as well as what all possibilities could mean for the future of quantum biology.

Introduction

Quantum mechanics arose in the beginning of the twentieth century as an answer to problems that could not be explained by classical physics. While the classical paradigm could accurately describe macroscopic physical systems, it failed to describe particles on an atomic or subatomic basis.[1] Max Planck became one of the first physicists to propose a solution when he postulated in 1900 that matter and electromagnetic radiation interactions were quantized, with energy being exchanged only in integer multiples of $h\nu$, where h represents Planck's constant, approximately 6.626×10^{-34} joule-seconds (J·s) or 4.135×10^{-15} electronvolt-seconds (eV·s), and ν represents the frequency of the electromagnetic wave in Hertz (Hz or s^{-1}).[2,3] This would become one of the earliest hypotheses in quantum theory. Albert Einstein in 1905 further expanded upon Planck's theory with his concept of the photon, a massless quantum of light energy.[2,3] In 1923,

Louis de Broglie added to quantum theory by stating that matter itself had wave-like properties, with a wavelength related to momentum through Planck's constant.[2,3] Quantum mechanics was more formally developed by Erwin Schrödinger with his equation[1].

$$i\hbar\frac{d}{dt}|\psi\rangle = H(t)|\psi\rangle, \quad (1)$$

Where *i* represents the mathematical imaginary unit, $\sqrt{-1}$, $|\psi\rangle$ represents the wave function of the physical system in an isolated state, $\hbar$ represents the reduced Planck constant equal to 1.054 x 10^{-34} joule-seconds or 6.582 x 10^{-16} electronvolt-seconds, and *H(t)* represents the Hamiltonian operator. Through this equation, the ideas of quantum coherence from the superposition of quantum states were developed, as well as quantum entanglement, a form of correlation between specific quantum states, and quantum tunneling, which is the probability of particles to pass through an energy barrier.[2,3] It has been suggested in recent years that all of these non-classical effects are relevant to the operation of biological systems, and, in particular, to the process of photosynthesis.

Photosynthesis is the process of converting light energy (that can be quantized in the form of photons) to carbon-based nutrients in chloroplasts (plants only). This complex metabolic process involves two different processes. The first is known as the dark reaction or Calvin cycle (named after biochemist Melvin Calvin), which is the breakdown of adenosine triphosphate (ATP) to cycle through biosynthetic intermediates to produce organic compounds for survival. The second are the light-dependent reactions, which use the light energy from the Sun to enable the transfer of electrons from water through photosystems to form new ATP through photophosphorylation. The resultant reaction for photosynthesis is shown below.

$$h\nu + 6\,H_2O + 6\,CO_2 \rightarrow C_6H_{12}O_6 + 6\,O_2, \quad (2)$$

Here, $h\nu$ represents the energy from sunlight that reacts with six moles of water and carbon dioxide to produce one mole of glucose and six moles of molecular diatomic oxygen.[7] While these organisms have been sustaining life this way for more than three billion years, the efficiency at which this process takes place is still quite low (relatively).[8,9] The exception to this is the efficiency of primary light-harvesting complexes to release an excited electron for every photon of light absorbed. This is what allows photosynthesis to work viably – not all photons are absorbed but the ones that are absorbed excite electrons with incredible consistency under optimal conditions (low light intensity and minimal stress from the plant's environment).[1] Delocalization of charge, a purely quantum phenomenon, is fundamental to explain the speed, accuracy, and efficiency of this process. In addition to delocalization, superradiance, a phenomenon related to the stimulated emission responsible for laser action, has also been argued to be evidence that a quantum mechanical approach is crucial to understanding photosynthesis at an atomic level.[1,10]

The recent hypothesis that the concepts of quantum mechanics such as coherence, delocalization, and superradiance contribute to the efficiency of the excitation energy transfer process of photosynthesis provide what will be the basis of this honors thesis (quantum coherence, in particular). Coherence is the concept in wave mechanics that two waves with matching amplitudes that are completely in or out of phase will experience constructive or destructive interference, which appears as an increased or decreased amplitude, respectively, creating a superposition of the two waves. The best evidence for this phenomenon is shown by the Young double-slit experiment, shown below in Fig. 1.

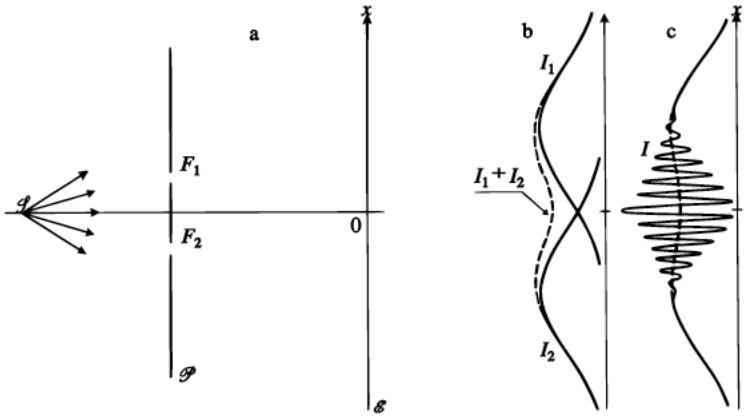

Figure 1: Illustration of Young's double slit experiment. Light originates from the source on the left before traveling through slits F_1 and F_2. Light then passed through a barrier before waves are observed on the right. The middle wave in *c* is a constructive superposition of waves I_1 and I_2 (constructive at the bright fringes, destructive at the dark fringes).[48]

In the last 30 years, scientific methods have been developed that allow measurement of a Frenkel exciton (described in the 1938 study by James Franck and Edward Teller) in various vibrational and quantum states, a coherent superposition of the excitations of individual photosynthetic pigments such as chlorophyll or carotenoids.[1,7,11] One such method is two-dimensional electronic spectroscopy (2DES), capable of analyzing decay of superpositions of vibrating quantum states and excitonic-vibrating states in light harvesting complexes and revealing the presence of cross peaks that oscillate in time.[12,13] Femtosecond (one quadrillionth of a second or 10^{-15} seconds) transient absorption spectroscopy was also developed and had the ability to detect long-lived vibrational coherences in the light reactions of photosynthesis.[14-19] The goal of my research will be to review current literature in support and in opposition of these hypotheses presented in the primary source, "The future of quantum biology," by Adriana Marais, B. Adams, A.K. Ringsmuth et al to determine if in fact coherence plays an integral role in photosynthesis.

This could have a wide variety of far-reaching implications across biochemistry, physics, biology, thermodynamics, and engineering.

A challenge for proving coherence in biological systems before has been the temperature; coherence in these systems is best observed at cryogenic temperatures – temperatures below approximately 150 degrees Celsius (°C) or 123 Kelvin (K) –due to the lack of noise at this temperature. Noise inevitably increases with temperature which leads to shorter decoherence times. Photosynthesis takes place under normal environmental conditions, vastly warmer and noisier, yet excitation energy transfer proceeds with the efficiency and speed of a system exhibiting quantum coherence.[1] Confirmation of quantum coherence in photosynthesis could mean that quantum coherence takes place in other metabolic processes, such as cellular respiration. Furthermore, efficiency of these biological systems at normal environmental conditions could lead to the creation of a biological model of light energy collection that might be useful in the future development of solar energy collectors using materials capable of exploiting quantum coherence, a cost-efficient way of capturing renewable energy.

Results

Experiments completed on the subject of quantum coherence in photosynthesis were analyzed for (1) reliability of results, (2) recency of publication, and (3) replicability. The four experiments that follow offer strong results based on these criteria, as well as offering answers to proposed hypotheses discussed in the Introduction.

SOURCE 1: E. Romero et al, "Quantum coherence in photosynthesis for efficient solar-energy conversion" (2014)

The aim of this study was to determine if electronic coherence was present in the photosystem II reaction center (PSII RC), and if so, to what degree does coherence promote charge separation efficiency.[11] Because charge separation has a direct impact on energy transfer in photosynthesis, results from this experiment could offer insight into whether this same coherence is present in energy transfer, which currently is unknown.[1,11]. A molecular dynamics (MD) model of PSII RC showing essential cofactors to PSII is shown below in Fig. 2.

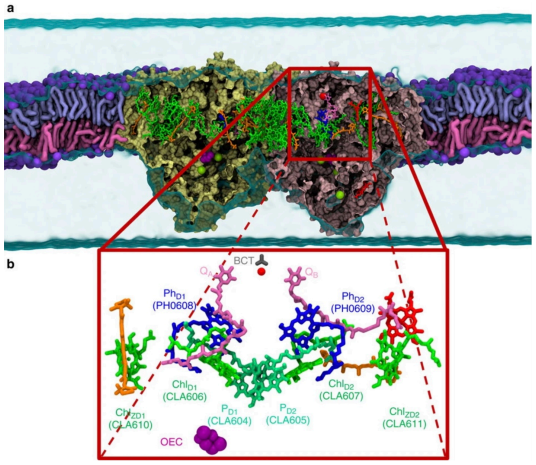

Figure 2: Model of PSII RC showing (a) position in lateral view of phospholipid membrane and (b) MD view of specific cofactors.[13]

When electrons are excited by sunlight, energy is delocalized among cofactors, which leads to a group of excited states also known as excitons.[11,14] How these excitons behave is a key focus of the experiment; whether the absorbed energy is simply delocalized throughout the photosystem, or whether coherent superpositions of energy can be found in the photosystem.

To perform this experiment, a combination of experimental and theoretical procedures was carried out. The experimental procedure utilized two-dimensional electronic spectroscopy (2DES), a high-speed laser pulse spectroscopic method that allows for study of short-lived phenomena in condensed systems, of PSII RC at room temperature (277 K, which is still colder than most rooms to facilitate less environmental noise for analysis) and at cryogenic temperature (80 K). PSII RC complexes were isolated from spinach. For the cryogenic experiment, the sample was diluted with a buffer containing 60% (v/v) glycerol, 20 mM BisTris pH 6.5, 0.06% β-DM. For room temperature experiments, dilution took place with a solution of 10% (v/v) glycerol, 20 mM BisTris pH 6.5 and 0.03% β-DM. The optical densities (the quantifiable property of atoms in a medium to retain absorbed light energy before remitting this energy) were 0.2 in 200 and 500 μm at 675 nm, respectively.[11]

2DES spectra were measured with a diffractive optic-based phase-stabilized four-wave mixing set-up using double modulation lock-in detection for additional noise reduction and sensitivity enhancement.[11,15-17] The laser system used was a PHAROS Femtosecond Light Conversion laser, with a repetition rate of 500 Hz and 2 kHz for cryogenic and room temperature experiments.[11] The results of the subsequent rephasing after stimulation via laser are shown below in Fig. 3.

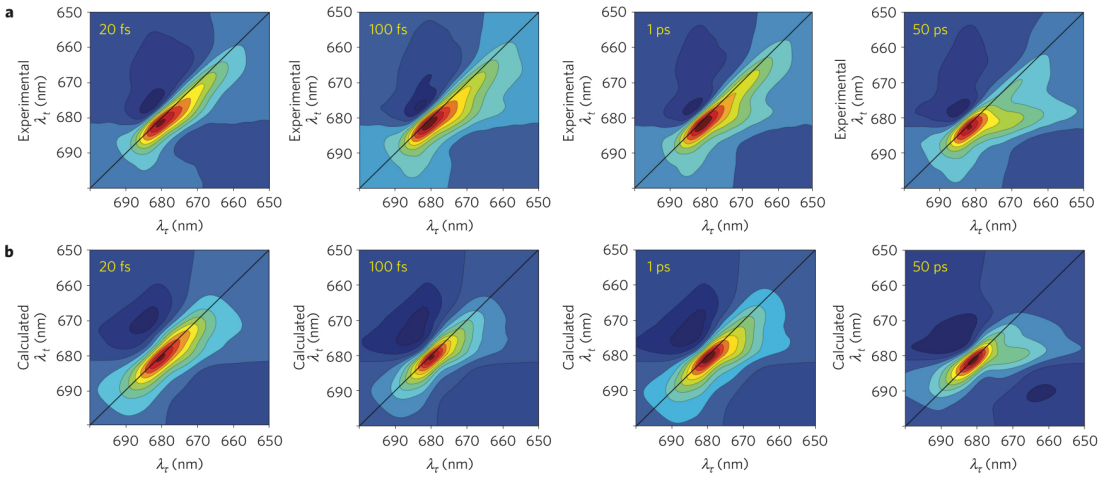

Figure 3: (a) PSII RC rephasing 2D electronic spectra at population times *T* = 20 fs, 100 fs, 1 ps, and 50 ps. (b) Calculated PSII RC rephasing using Redfield theory at the same times according to parameters of entropic exciton-charge transfer (CT) model.[11]

In addition to experimental methodology, computational models were also assembled according to Redfield theory (time evolution of density in a coupled quantum system related to its environment) and a disordered-CT model. In this model, excited states are of all chlorines (Chl and Phe) and four CT states.[11,18.19] Site energies of cofactors were determined via simultaneous and qualitative fit of eight steady state spectra using a modified Redfield approach.[11,18]

The primary results of this study indicated that there was a link between both experimental and theoretical evidence in showing that quantum coherence plays a functional role in the PSII RC. 2DES spectra show similar rephasing between experimental and calculated values, which they claim shows that coherences can survive the aggressive background noise and play an essential role in charge separation (and, by extension, energy transfer) dynamics.[11]

SOURCE 2: A. Shabani et al, "Numerical evidence for robustness of environment-assisted quantum transport." (2014)

As pointed out above, at room temperature interactions with the environment may have a destructive effect on quantum coherence. However, it has been suggested that this decoherence may have a constructive role in quantum transport. This paper explores this hypothesis, called environment-assisted quantum transport (ENAQT). According to ENAQT theory, optimal quantum transport would be achieved by an optimal interplay of the system coherence and decoherence dynamics. To investigate this issue, this computational paper is primarily concerned with studying how variations in the system or its environment can affect the efficiency of ENAQT.[20] Instead of focusing on PSII however, they focus more on the Fenna-Matthews-Olson (FMO) complex, a pigment-protein complex responsible for transporting absorbed solar energy to photosystems for electron transfer. An illustration of the FMO complex is shown below in Fig. 4. In non-coherent energy transfer, energy can be transferred unidirectionally, from one Bacteriochlorophyll (BChl) site to the next. However, in coherent energy transfer, energy can be transferred bidirectionally and energy can occupy potentially more than one BChl site so that energy states must be described as superpositions.

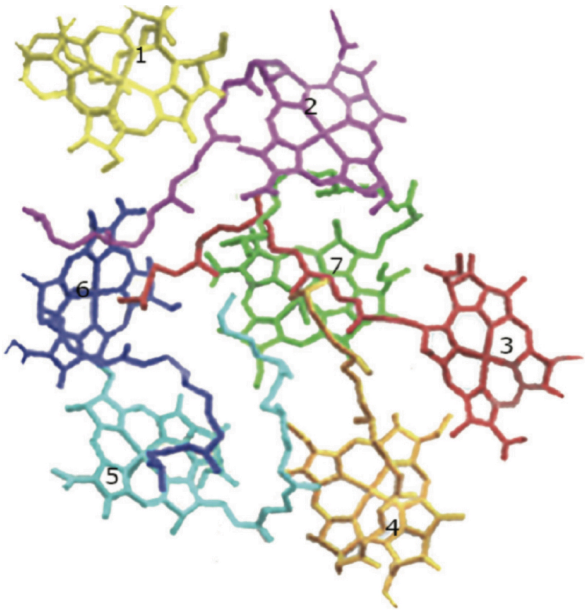

Figure 4: Color illustration of FMO complex, with different BChls represented by different colors and numbers.[20]

The theoretical model employed in this experiment relies heavily on the Hamiltonian of the FMO complex. The Hamiltonian for excitons in the FMO complex is given in Eq. 2.[20]

$$H_S = \sum_{j,k} \epsilon_j |j\rangle\langle j| + J_{jk}|j\rangle\langle k| \quad , \qquad (2)$$

In this equation, $|j\rangle$ is an excitation state in a chromophore located at site j. Diagonal site energies are represented by ε_js, and the dipole-dipole interactions between chromophores are represented by J_{jk}.[20-24]

Each component of the FMO complex is modeled as interacting with an environment of harmonic oscillators with Gaussian fluctuations, with each BChl coupled to a different bath.[20,25] Using this model, the Drude-Lorentzian correlation function can be applied, which is shown below in Eq. 3.[20,25]

$$C_j(t) = \langle \tilde{B}_j(t)\tilde{B}_j(0)\rangle = \frac{1}{\pi}\int_0^\infty d\omega J(\omega)\frac{\exp(-i\omega t)}{1-\exp(-\hbar\omega/k_B T)}, \quad (3)$$

Here, $J(\omega)$ represents the spectral function, given by Eq. 4

$$J(\omega) = 2\lambda\omega/(\omega^2 + \gamma^2), \quad (4)$$

For FMO, the researchers considered a reorganization energy value of $\lambda = 35$ cm^{-1} and bath cutoff value of $\gamma = 50$ cm^{-1} for each BChl.[20]

The FMO complex was modeled as an open quantum system (BChl and harmonic baths do interact). By doing this, the researchers were able to quantify energy-transfer efficiency (ETE) as defined in the Eq. 5.[20]

$$\eta = 2r_{\text{trap}}\int_0^\infty \langle \text{trap}|\rho(t)|\text{trap}\rangle dt, \quad (5)$$

Here, the |trap⟩ vectors represent states in which an electron has been captured. The quantity ρ is the density matrix of the system, which is used instead of the wavefunction to deal with an open quantum system. The authors assume a trapping rate of $r_{\text{trap}} = (0.5\text{ ps})^{-1}$. The result is the total portion of a traveling exciton captured by the FMO reaction center, η.[20-24]

Using this framework, the authors computed the ETE for many different sets of parameters. The histograms in Figs. 5 and 6 show the distribution of the calculated efficiencies over all the samples.

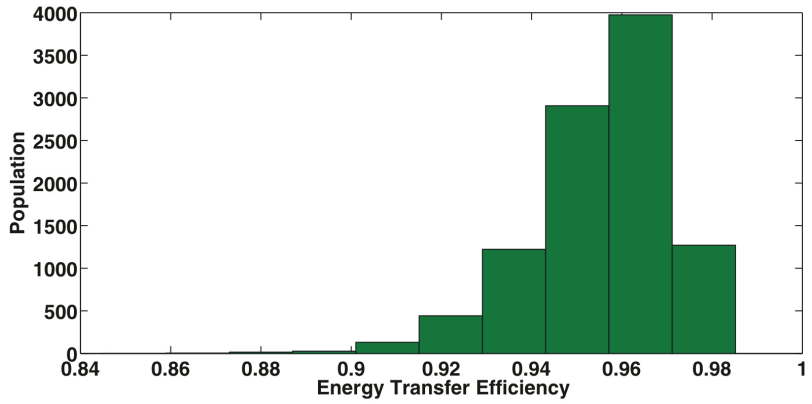

Figure 5: Number of samples yielding ETE values in the ranges indicated, for small variations in BChl locations, site energies, and dipole orientations.[20]

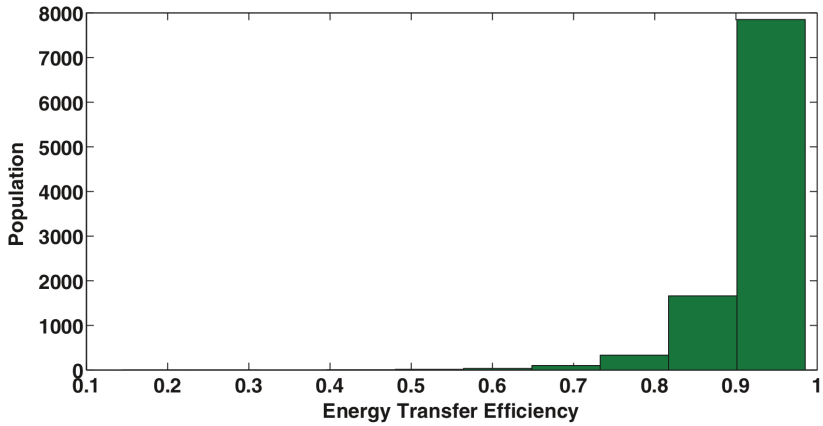

Figure 6: Number of samples yielding ETE values in the ranges indicated, for large variations in BChl locations, site energies, and dipole orientations.[20]

These results indicate that the ETE is quite robust with respect to variations in the system's parameters. Additionally, the authors found some evidence of a strong link between locations of BChl component locations and ETE, suggesting that the compactness of FMO complexes may also influence on ETE.[20] This phenomenon is shown below in Fig. 7.

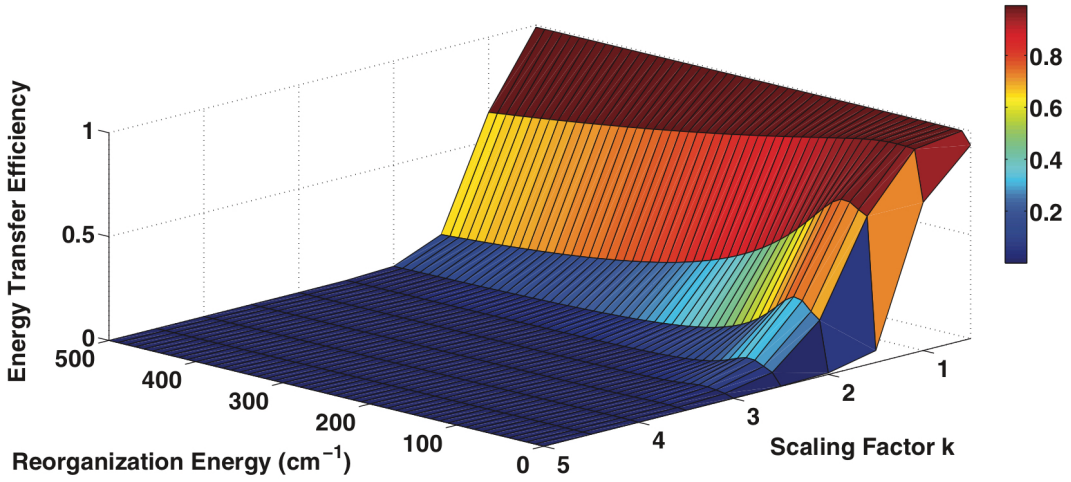

Figure 7: Depiction of ETE as dependent on reorganization energy and scaling factor k (compactness), with more compact configurations yielding a higher ETE.[20]

On this basis, the researchers concluded that ENAQT (a parameter of which is coherence) can greatly assist optimal quantum transport and greatly increase ETE in the FMO complex. Additionally, ENAQT does not disappear when some parameters are outside optimal areas, suggesting quantum efficiency could be maintained at biological conditions. Further experimentation could be done to confirm the calculations given by Shabani et al.

SOURCE 3: Duan et al, "Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer." (2017)

Differing from the last two studies, the research done by Duan et al suggests that while energy transfer likely does proceed with coherent oscillations, there is no evidence to suggest that these coherences are relevant, as they typically decay very quickly (after a few femtoseconds); the oscillations are not long-lived enough to create the superposition of energy states posited by other research. They show this by providing 2D photon echo spectra of the FMO complex at ambient temperatures in aqueous solutions.[27]

This study also employed a two-fold experimental and theoretical approach. Ultrashort coherent light pulses were stimulated from an optical parametric amplifier paired with a PHAROS Light Conversion femtosecond laser. Laser pulses were compressed to a pulse duration of 16 fs full width at half maximum (FWHM). 2D spectra were collected in an all-reflective 2D spectrometer. Excitation energy was kept below 12 nJ per beam to avoid destruction of the excitons. 2D spectra were collected at each fixed waiting time by scanning the delay, $\tau = t_1 - t_2$, in the range of $-128 \leq \tau \leq 128$ fs, with a delay step of 1 fs. 150 spectra were averaged at each delay point.[27] To prepare FMO complex samples, the protein was isolated from the green sulfur bacterium *Chlorobaculum tepidum*. Samples were filtered with a 0.2 μm filter to reduce light scattering. To avoid sample degradation, the cell in the 2D setup was placed on a 2D translator and moved at approximately 20 cm/s. Excitation occurred at about 80 μm.[27]

The theoretical model used was one which employed a standard molecular model of the FMO monomer (with seven BChl units) as described by the appropriate Hamiltonian operator. Electronic coupling elements were kept unchanged to optimize the site energies. A Gaussian distribution was used to model the data graphically with a FWHM of 90 cm^{-1} (except for BChl site 3, which was kept at 54 cm^{-1} to reduce static disorder). 500 spectra were averaged in the calculations. Verification of this theoretical model was performed by comparing calculated results with exact numerical calculations from a study by Nalbach et al.[27,28] The results of both the experimental and theoretical studies done is shown below in Fig. 8.

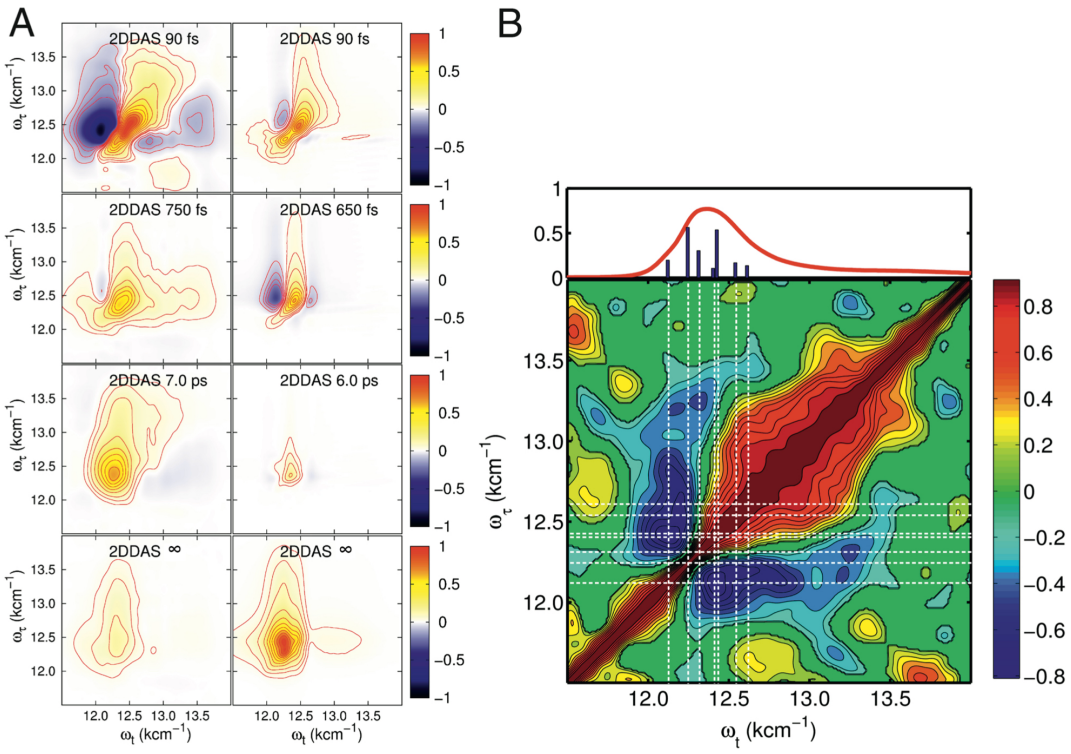

Figure 8: (A) Side-by-side comparison of experimental vs. theoretical spectra for FMO complex. (B) 2D correlation map of residuals.[27]

In Fig. 8A, the associated decay times, $\tau_{1\text{-}4}$, are shown on the spectra. In Fig. 8B, the red line is the measured absorption spectrum, the blue represents the stick spectrum (observed quantities) of the FMO complex, and the white dashed lines mark exciton energies.[27,29-30] These findings show considerable differences between experimental and theoretical calculations, suggesting that the role coherence plays in the FMO complex absorption of sunlight is not relevant or possibly nonexistent.[27] This claim is further supported by data in Fig. 9.

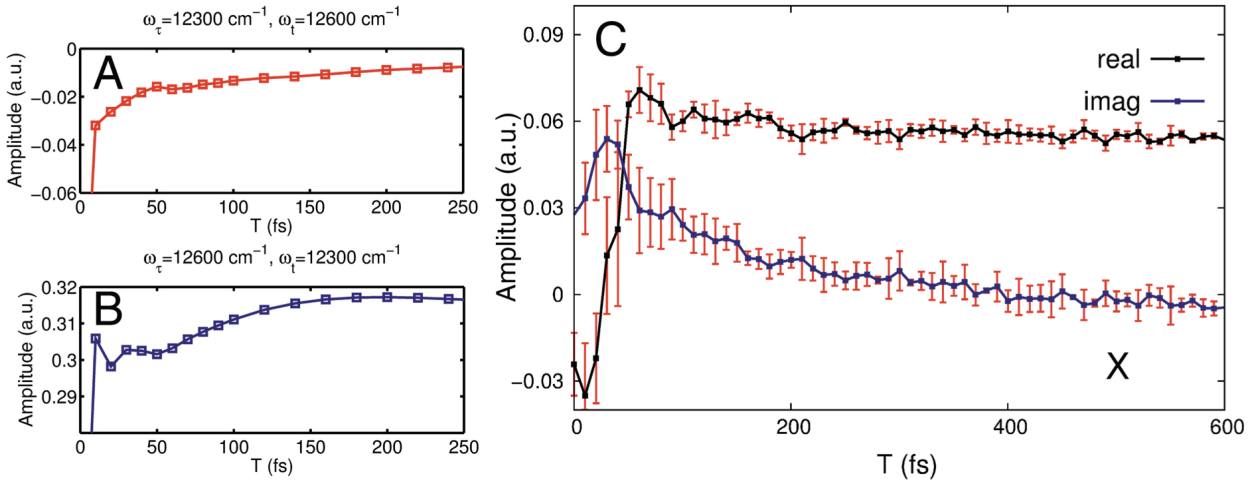

Figure 9: (A and B) Time evolution of calculated 2D photon echo signal at the listed spectral (ω) values, represented by red and blue squares. (C) Real and imaginary (black and blue, respectively) parts of experimentally measured time trace at the spectral positions given in A and B, with error bars showing the variation of four different datasets.[27,31]

Here, the findings indicate that electronic quantum coherence only lasts about 50-60 fs before the amplitudes level off, which is far too short to have a drastic impact on the efficiency of the FMO complex. The researchers conclude that there is lack of long-range coherent energy transport occurring in the FMO complex and, though coherent oscillations are initially present, it is unnecessary in describing the dynamics of FMO energy transport, as well as incredibly unlikely. While this result is very specific to the FMO complex, Duan et al posit the results can most likely be generically applied to all photosynthetic organisms.[27,30]

SOURCE 4: Thyrhaug et al, "Identification and characterization of diverse coherences in the Fenna-Matthews Olson complex" (2018)

Thyrhaug et al posit that long-lived coherences and quantum beats (QBs) are vibronic, a combination of vibrational and excitonic, with all electronic coherences dephasing within 240 fs. Quantum beats are another name for oscillatory phenomena that cannot be explained by classical

physics. In 2007, a study was published suggesting these QBs were long-lived, and were suggested to be coherent superpositions of excitonic states.[32-34] In this study, researchers analyzed QBs in data obtained from two different distinct pulses to characterize the coherences in the FMO complex at 77 K (cryogenic temperature), the same temperature at which QBs were observed in the 2007 study.[32]

To prepare the FMO complex samples, *C. tepidum* was cultured with FMO complexes later isolated. Bacteria were grown under continuous incandescent illumination at 318 K. After isolating the FMO complex (which was done by using a solution of sodium carbonate, Na_2CO_3), the samples underwent dialysis for 72 hours with 20 mM Tris-HCl, pH 8. Samples were purified by using size-exclusion and anion-exchange chromatography. All these separation steps after dialysis were done at 277 K. Finally, before experimentation with 2DES, the sample was dissolved in a 2:1 glycerol:buffer solution and held at 77 K.[32,35-36]

For the 2DES experiment, 100 nm femtosecond pulses were generated by a parametric amplifier using a Yb:KGW laser system (PHAROS, Light Conversion). Pulses were compressed to 14 fs. Output pulses were split using a single beamsplitter, then split once more using a diffractive optic. What resulted was four pulses, which were linearly polarized using a quarter-wave plate and four wire-grid polarizers. Observed spectral resolutions were 36 and 72 cm^{-1}, respectively, with resolutions for detection as 40 cm^{-1} for both. The observed signal:noise ratio was increased by averaging 2DES spectra.[32,37-38]

Modelling of the data was done by fitting the data using the Holstein Hamiltonian to factor in linear coupling of electronic transitions to vibrational modes. Quantum dynamics were simulated through numerical integration of the Schrödinger equation, using an open quantum

system approximation. Resulting data was averaged over 50,000 possible trajectories for absorption data 250,000 trajectories for 2D data.[32, 39-45]

The data, determined experimentally using 2DES and theoretically using the modelling procedure outlined, yielded spectra shown in Fig. 10.

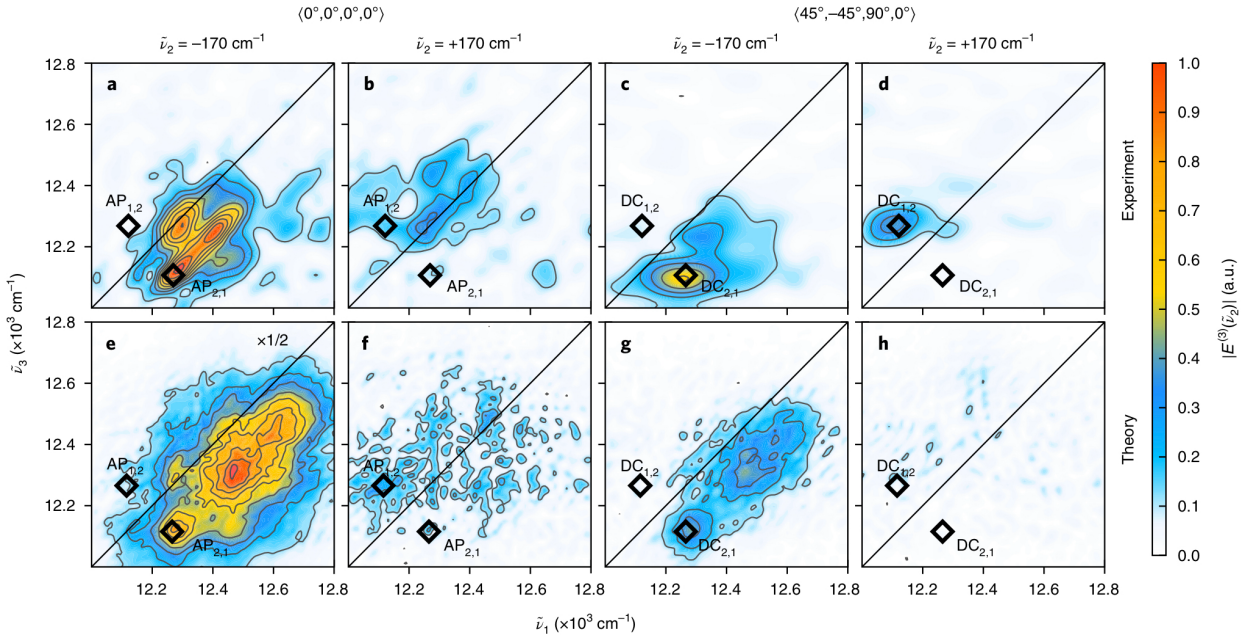

Figure 10: (Top) Fourier amplitude maps at ±170 cm^{-1} obtained by Fourier transformation for experimental data. (Bottom) Fourier amplitude maps at ±170 cm^{-1} obtained by Fourier transformation for theoretical (modeled by dynamics) data.[32]

Here, spectra labeled a, b, e, and f are all-parallel (AP), as denoted by the ⟨ 0, 0, 0, 0 ⟩° above. This is a description of the four pulses resulting from beamsplitting; their pulses are "all-parallel." In contrast, c, d, g, and h have double-crossed (DC) pulse angles, as shown by the ⟨ 45, -45, 90, 0⟩°. The findings here indicate strong QB signals present. This is highly indicative of vibronic coupling, a kind of quantum coherence.

Furthermore, analysis of rephasing suggests that relevant vibronic coherences (not excitonic) are long-lived, as evidenced in Fig. 11.

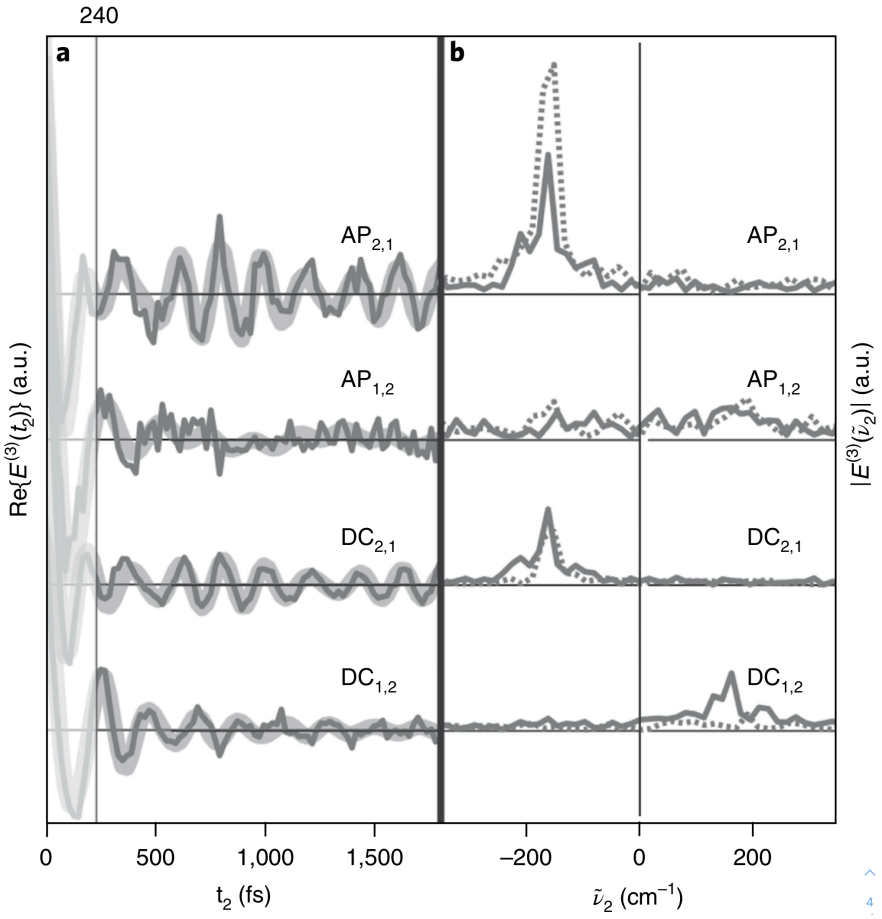

Figure 11: (a) Rephasing traces at cross-peak locations. (b) Fourier transformations of the experimental data in a.[32]

Here, QBs are observed in the order of picoseconds (ps), but coherences are shown to die off by 240 fs. Additionally, the dotted line in Fig. 11b shows the vibronic exciton model employed. The experimental data seems to line up with this theoretical model near perfectly. Thus, Thyrhaug et al conclude that vibronic coupling is what is observed for efficient photosynthetic energy transfer in the FMO complex instead of excitonic coherence.[32,37,39]

Discussion

As a result of this literature review, it is concluded that quantum coherence is a present phenomenon in plants and photosynthesizing bacteria. However, it is less likely to be strictly excitonic in nature, as posited by Sources 1 and 2. The findings in Source 1, written by Romero et al, show a correlation between experimental and theoretical methods employed in their determination that electronic quantum coherence plays a role in charge transfer (which is fundamentally linked to energy transfer) in PSII RC. Shabani et al (Source 2) provide calculations through computer dynamics software that show how compaction and electron trapping affects electron transfer efficiency (ETE). Both sources provided meritable results, however, research done in Sources 3 and 4 present that vibronic coherences, a combination of existing vibrational coherences with excitonic coherences, are the more likely coherent phenomenon taking place. Duan et al (Source 3) found that decay times of excitonic coherences were far too quick to have any real impact on FMO photosynthetic efficiency. Through Fourier analysis, Source 4 (Thyrhaug et al) found that quantum beats persistent with ps lifespans are consistent with vibronic coupling, whereas excitonic coherences decay before 240 fs, having no real impact on photosynthesis. Both studies involved extensive experimental and theoretical work completed and were published more recently.

Additionally, the research done by Shabani et al is quite similar to the work done by Chenu et al (2015) "Coherence in energy transfer and photosynthesis." This research suggests the optimal level of energy transfer occurs when the levels of coherent and incoherent transfer are balanced. This is detailed below in Fig. 12.

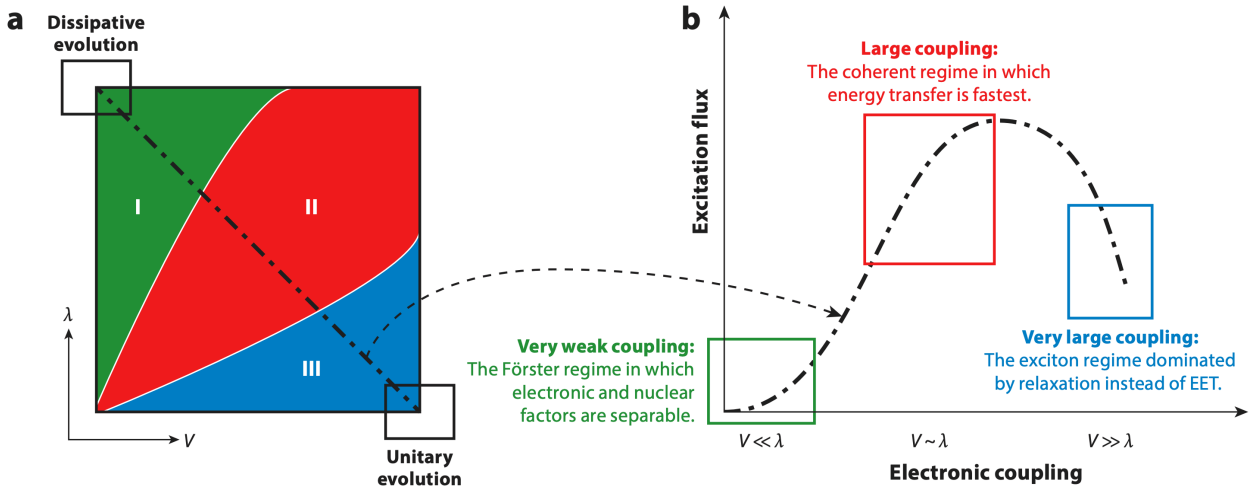

Figure 12: Models depicting optimal excitation flux as a combination of Förster and coupling regimes, as well as the intermediate between dissipative and unitary evolutions.[46]

Here, when the levels of Förster or coupling regimes are dominant, the excitation that is present is very weak. However, when combined, excitation (and subsequent energy transfer) is more favorable. Fig. 12b depicts the combination of incoherent weak coupling and large coherent coupling aiding in a coherent energy transfer process.[46] Additional research into this field could aid in the creation of massively cost-saving quantum harvesting techniques, essential to further development of renewable energy technologies.[47]

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