
Photosynthetic Light Harvesting and Electronic Quantum Coherence Effects

Yuan-Chung Cheng

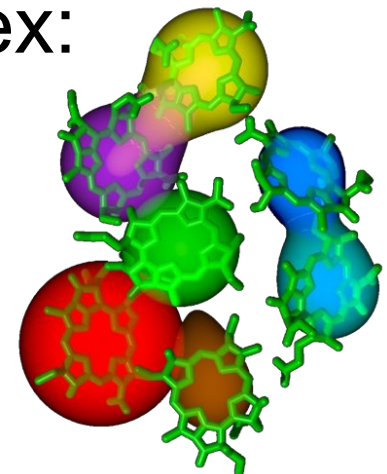
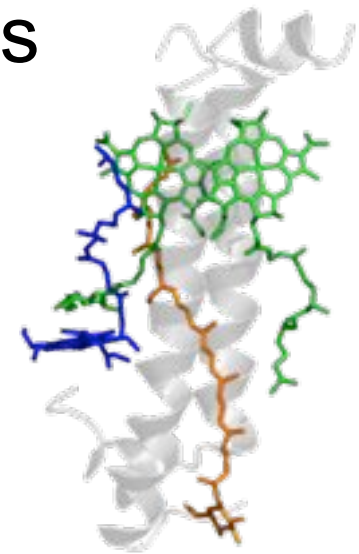
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NTHU Physics, December 5, 2010

Outline

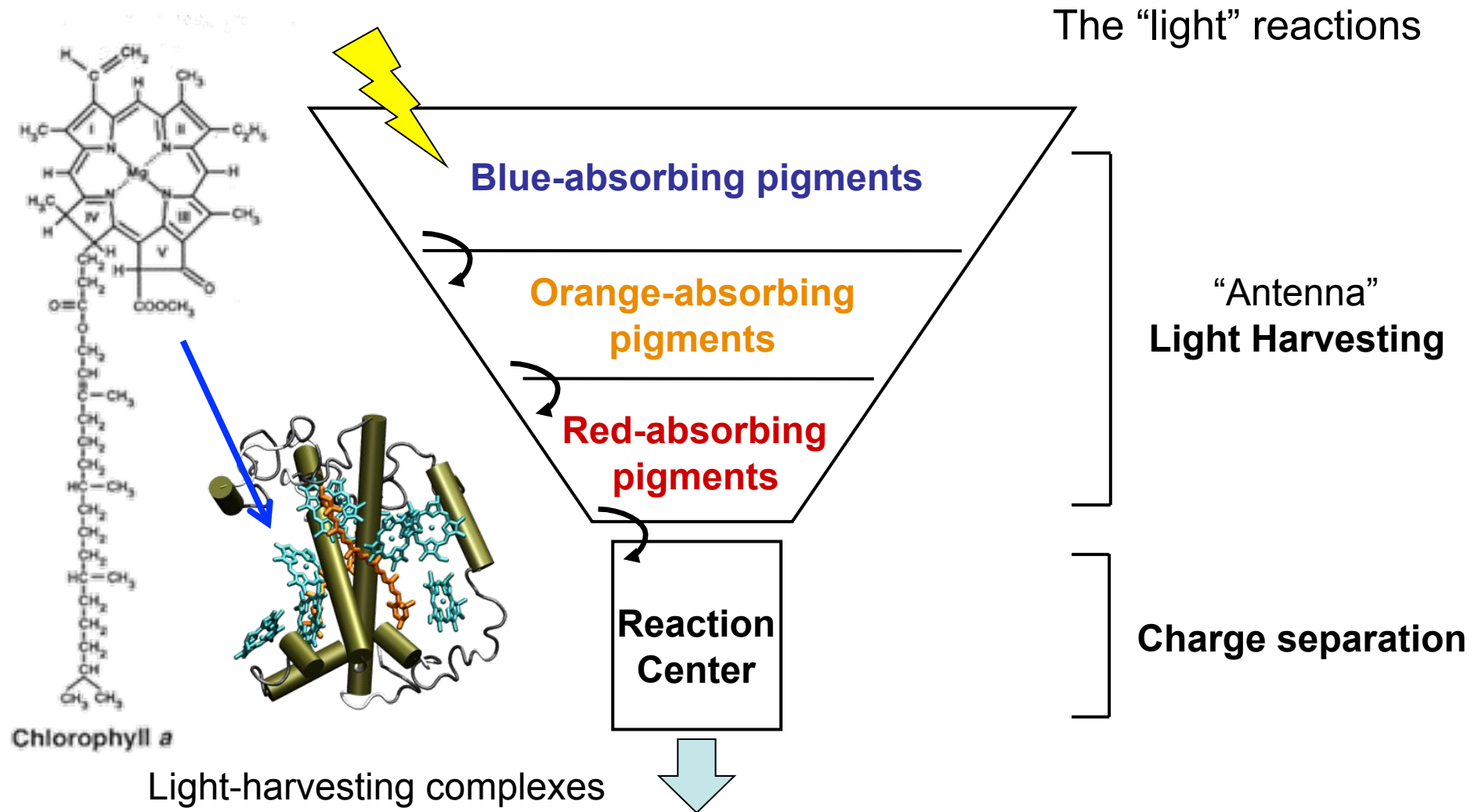
- Photosynthetic light harvesting systems
- Experimental evidences for quantum coherence effects in photosynthesis
- Theoretical modeling of quantum dynamics & nonlinear spectroscopy of light harvesting complexes
- Coherent dynamics in the FMO complex: coherence assisted excitation energy transfer mechanism
- Concluding remarks



Photosynthesis

- Might be the most important photochemical process on earth
- Still, there is much unknown and much to be learned & modeled after
$$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{h\nu} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$
- Collecting sun-light energy with high efficiency is not trivial

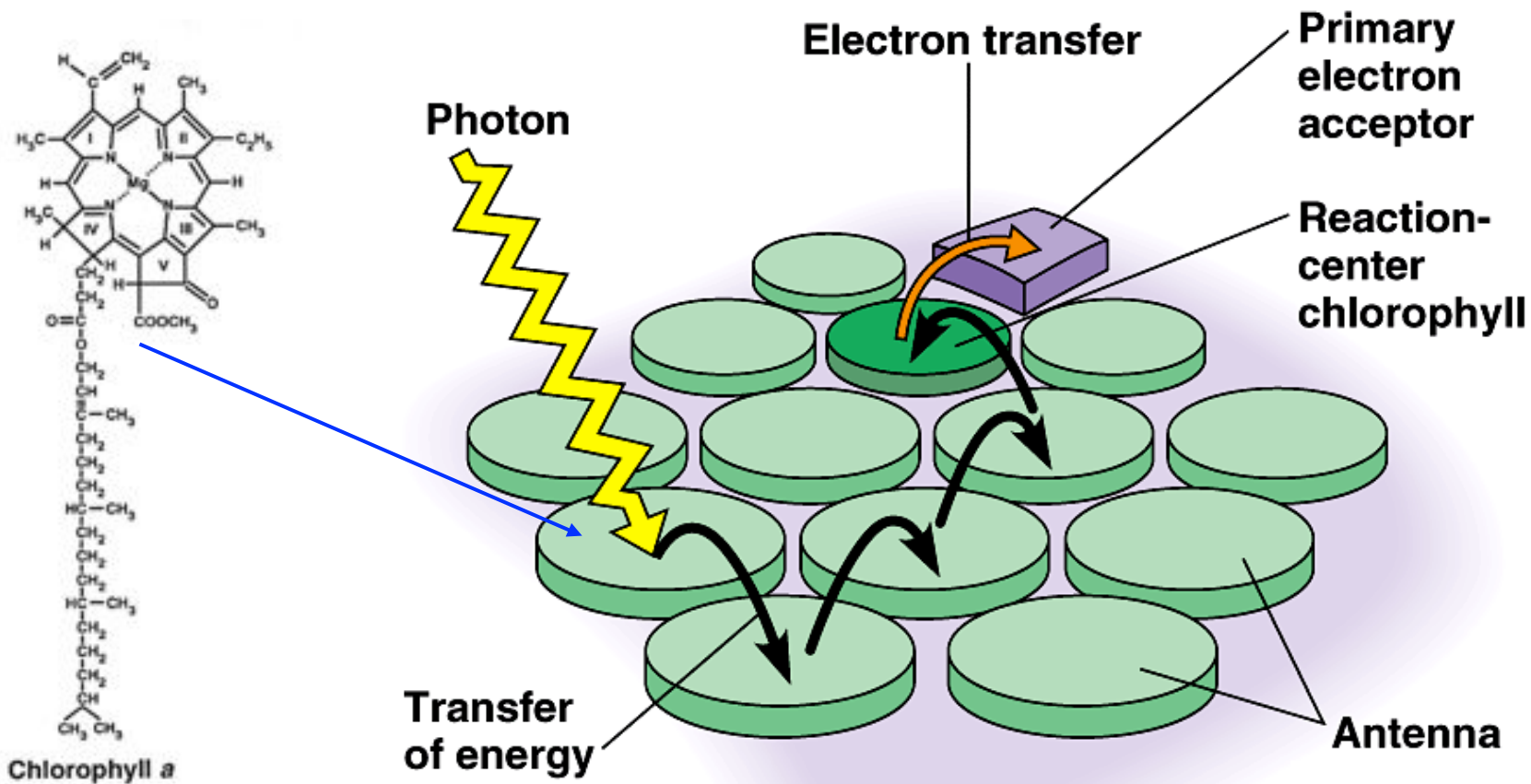
Light Harvesting in Photosynthesis



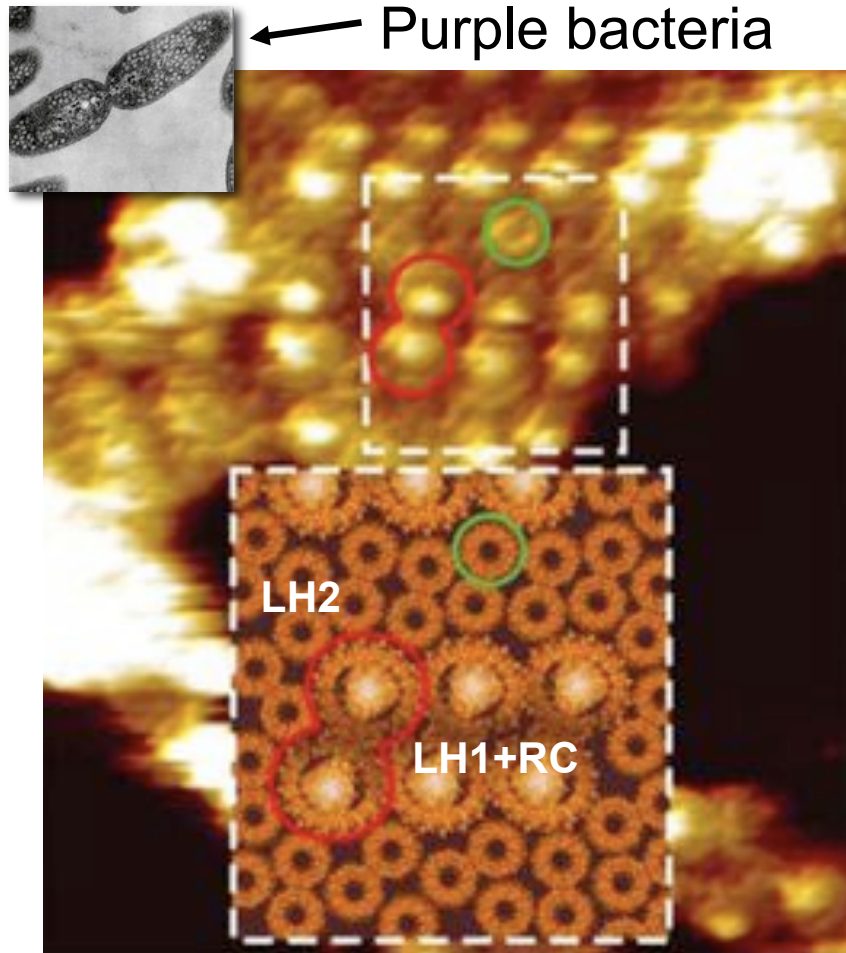
...Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of NADP^+ , ATP synthesis...

Primary Processes of Photosynthesis

Light harvesting in the antenna & charge separation in the reaction center → remarkable, near unity quantum yield

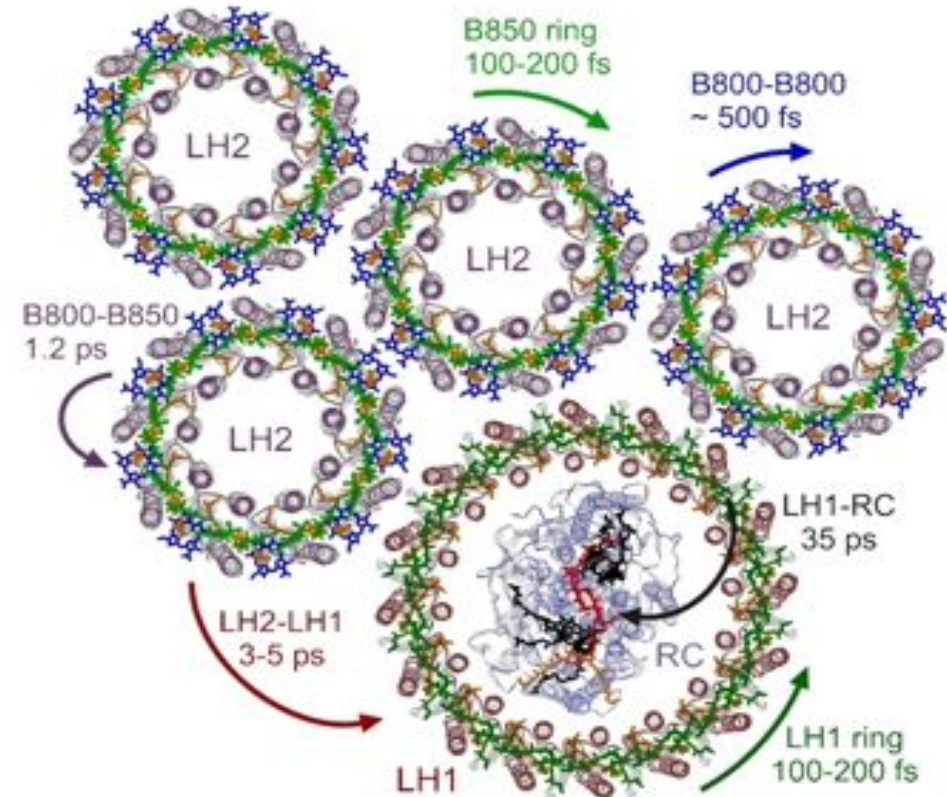


Light-harvesting Apparatus of Purple Bacteria



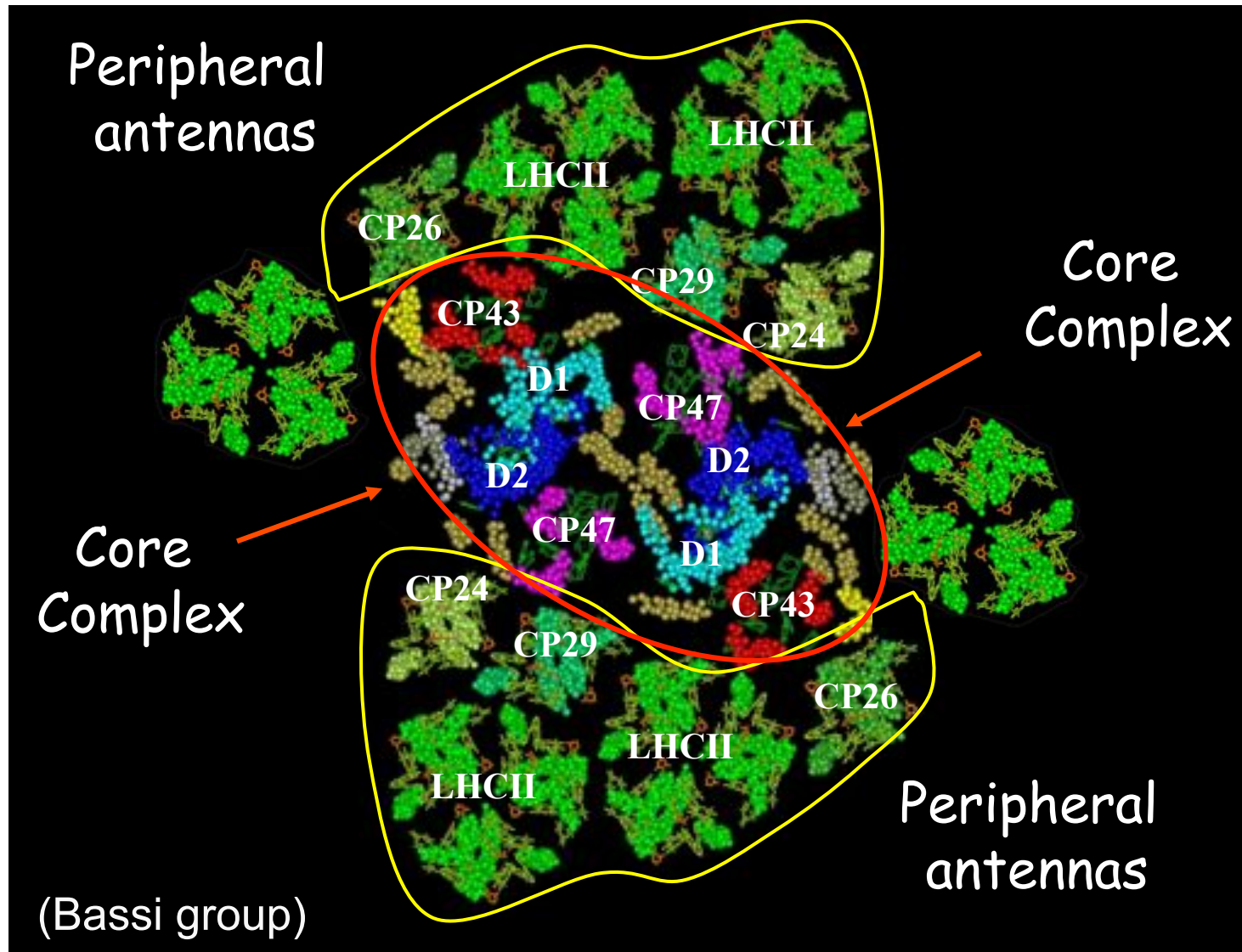
AFM of native photosynthetic membranes of a purple bacterium

Bahatyrova et al., *Nature* **430**, 1058 (2004)

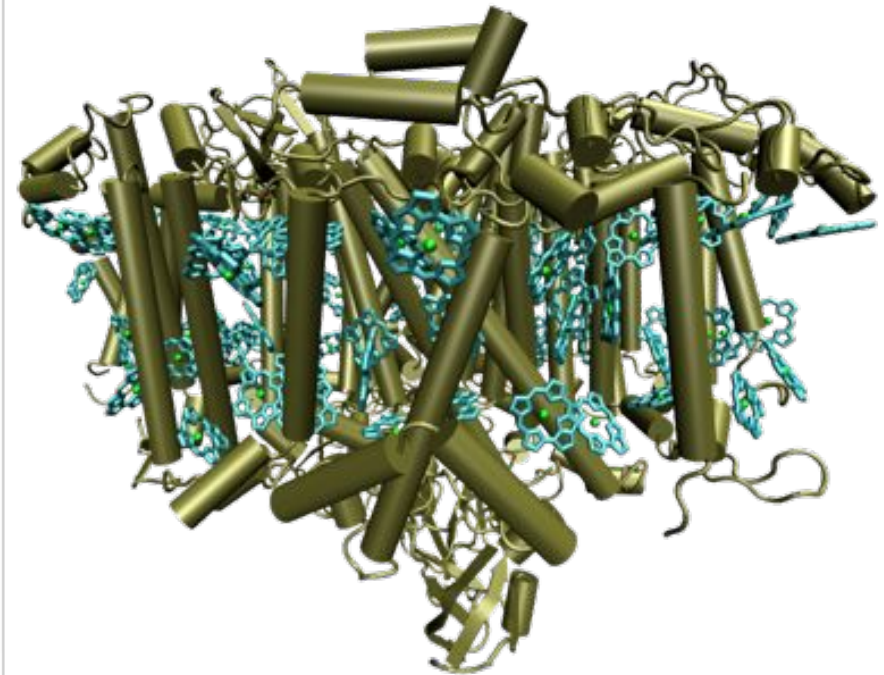
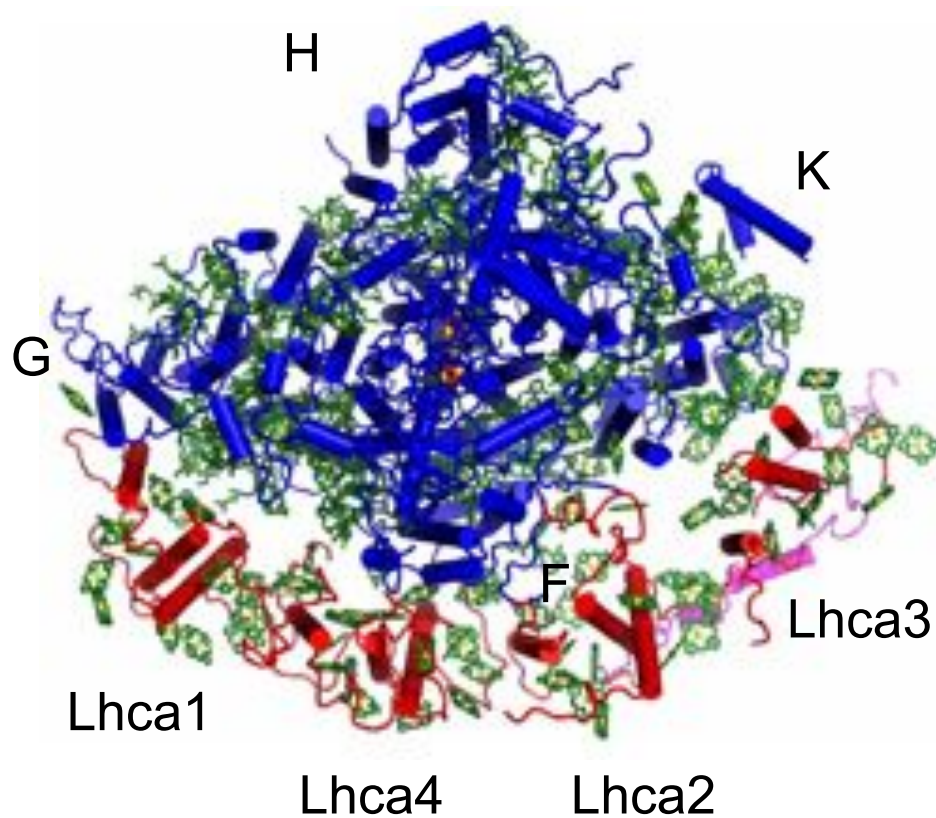


Hu et al., *Q. Rev. Biophys.* **35**, 1 (2002)

Light-harvesting Apparatus of Higher Plants




Photosystem I Supercomplex of Plants



PS I Core complex
96 Chls

A. Ben Shem, F. Frolow & N. Nelson, Nature, 426, 630-5 (2003).

Chlorophyll Arrangement in the PS I Core



“a paradigmatic scenario of transport phenomena in a nanoscale network”


- electronic couplings & excitons
- complex network
- static & dynamical disorder
- “wet & warm” protein environments
- quantum coherence

distance

 <10 Å

 10-15 Å

Å



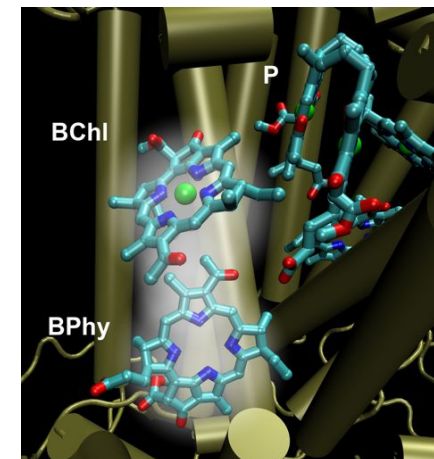
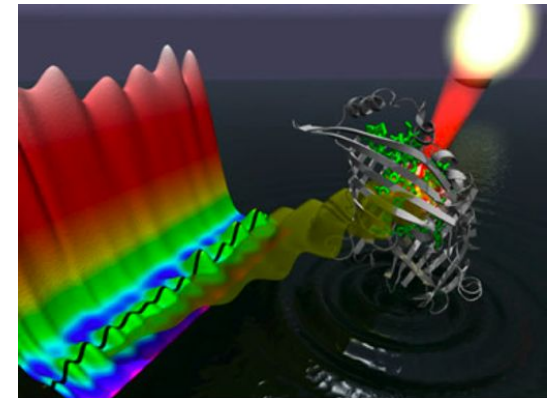
PS I Core complex
96 Chls

Pdb id: 1JB0

A complex chlorophyll network for light harvesting

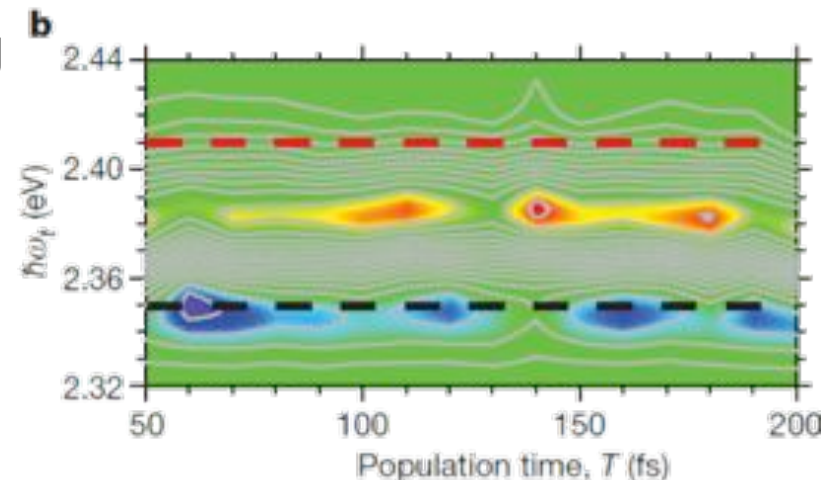
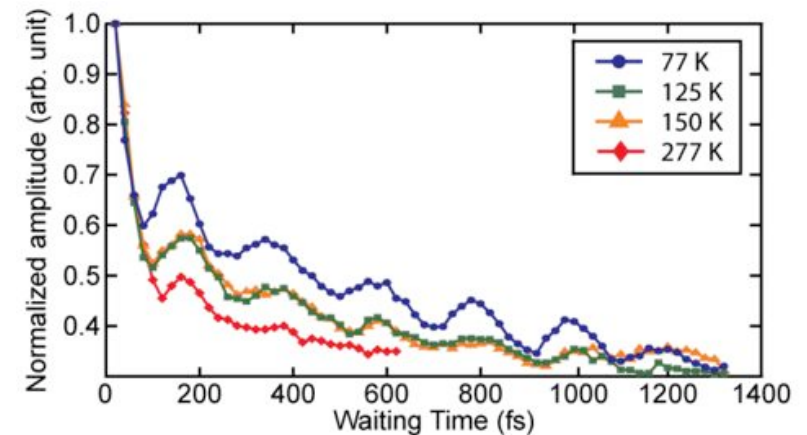
New Insights into Photosynthetic Light Harvesting

- Recent experiments indicate that **quantum coherence** can play a role in light harvesting
- **Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems**, G.S. Engel, T.R. Calhoun, E.L. Read, T. Ahn, T. Mancal, Y.-C. Cheng, R.E. Blankenship & G.R. Fleming, *Nature* **446**, 782 (2007).
- **Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence**, H. Lee, Y.-C. Cheng & G.R. Fleming, *Science* **316**, 1462 (2007).



New Insights into Photosynthetic Light Harvesting

- Recent experiments indicate that quantum coherence can play a role in light harvesting – **even at ambient temperature**
- Long-lived quantum coherence in photosynthetic complexes at physiological temperature**, Gregory S. Engel and coworkers, *arXiv:1001.5108v1* (2010).
- Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature**, G. D. Scholes and coworkers, *Nature*, **463**, 644 (2010).



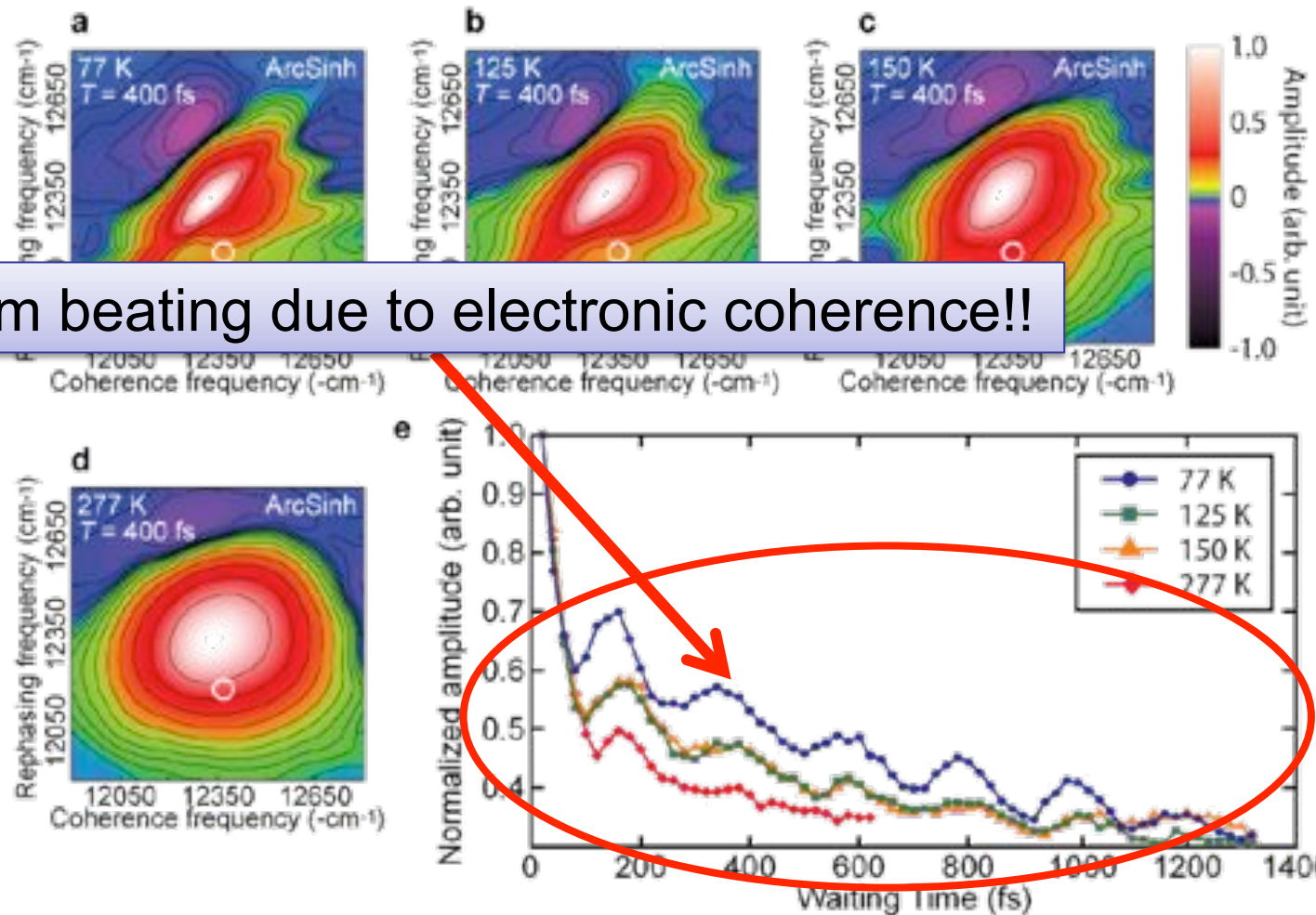
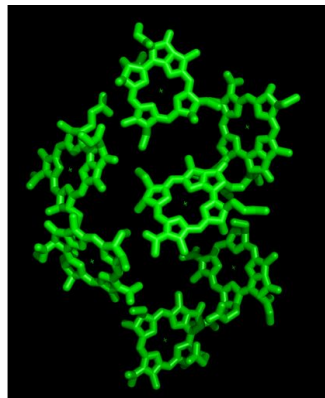
Quantum Coherence in FMO at Physiological Temperature

FMO

2DES

Sp

Quantum beating due to electronic coherence!!



Gregory S. Engel and coworkers, *arXiv:1001.5108v1* (2010)
<http://arxiv.org/abs/1001.5108>

Coherent Evolution of Density Matrix

- Time-evolution of a superposition of

$$|\Psi(t)\rangle = ae^{-i\omega_1 t} |e_1\rangle + be^{-i\omega_2 t} |e_2\rangle$$

- Density matrix with ***excitonic coherence***

$$|\Psi(t)\rangle\langle\Psi(t)| = |a|^2|e_1\rangle\langle e_1| + |b|^2|e_2\rangle\langle e_2|$$

$$+ab^* e^{-i(\omega_1-\omega_2)t} |e_1\rangle\langle e_2| + a^* b e^{i(\omega_1-\omega_2)t} |e_2\rangle\langle e_1|$$

- Coherence oscillation results in energy population moving

phase oscillation

- Coherent phase oscillation: using 2-D photon echo spectroscopy: quantum beats in 2-D signals

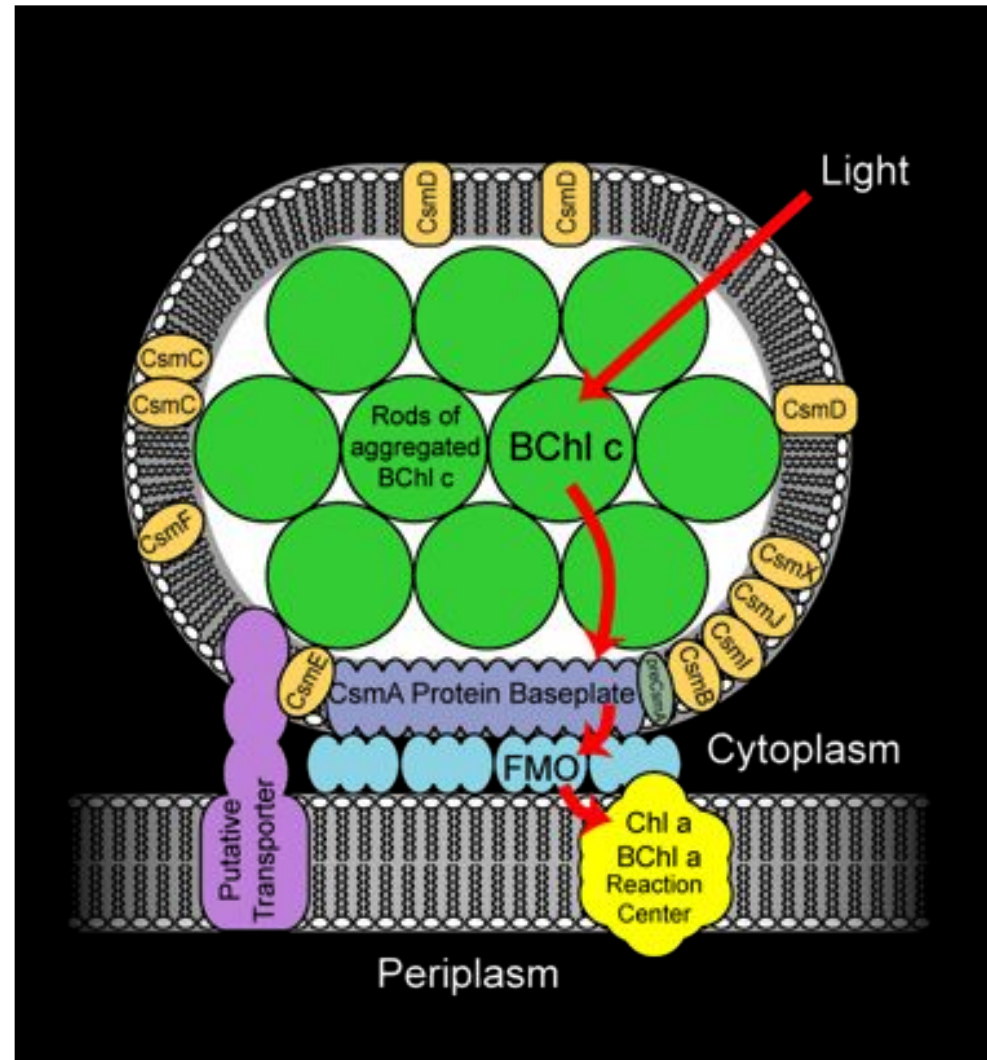
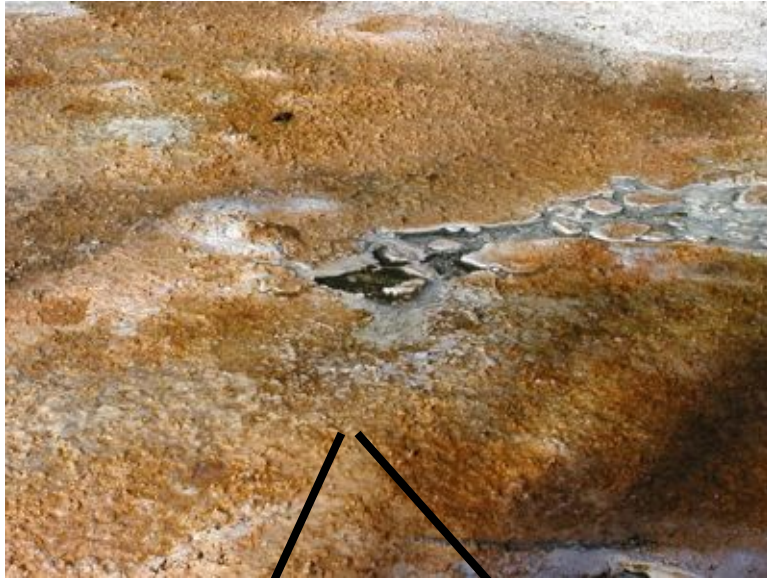
How does such long-lasting electronic coherence affect light harvesting?

Combine experimental results & theoretical modeling to find out!

Strategy for Theoretical Investigations

- In order to elucidate how quantum coherence affects excitation energy transfer in the FMO complex, we
 - Build an effective model for FMO excitations & dynamics of excitation energy transfer
 - Refine the theoretical model by comparing to experimental two-dimensional optical spectra
 - Simulate the dynamics of energy trapping both **with** and **without** quantum coherence
 - Compare the results to determine the role of electronic quantum coherence

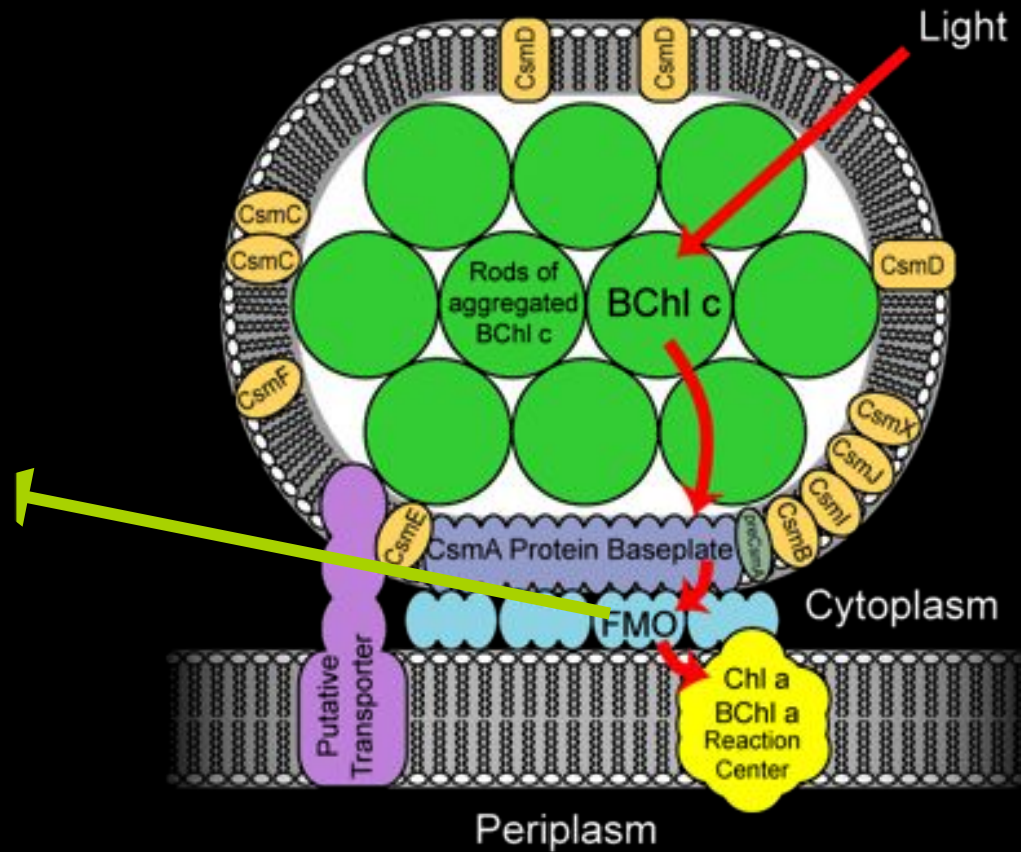
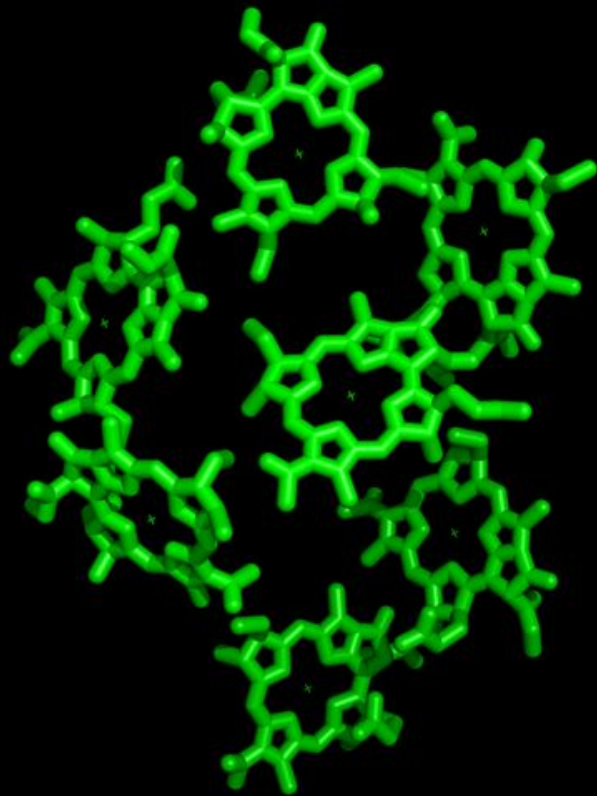
Light-harvesting Apparatus of Green Sulfur Bacteria



James Allen & coworkers, Photosynth. Res., 75:49 2003

Fenna-Matthews-Olson Complex from Green Sulfur Bacteria

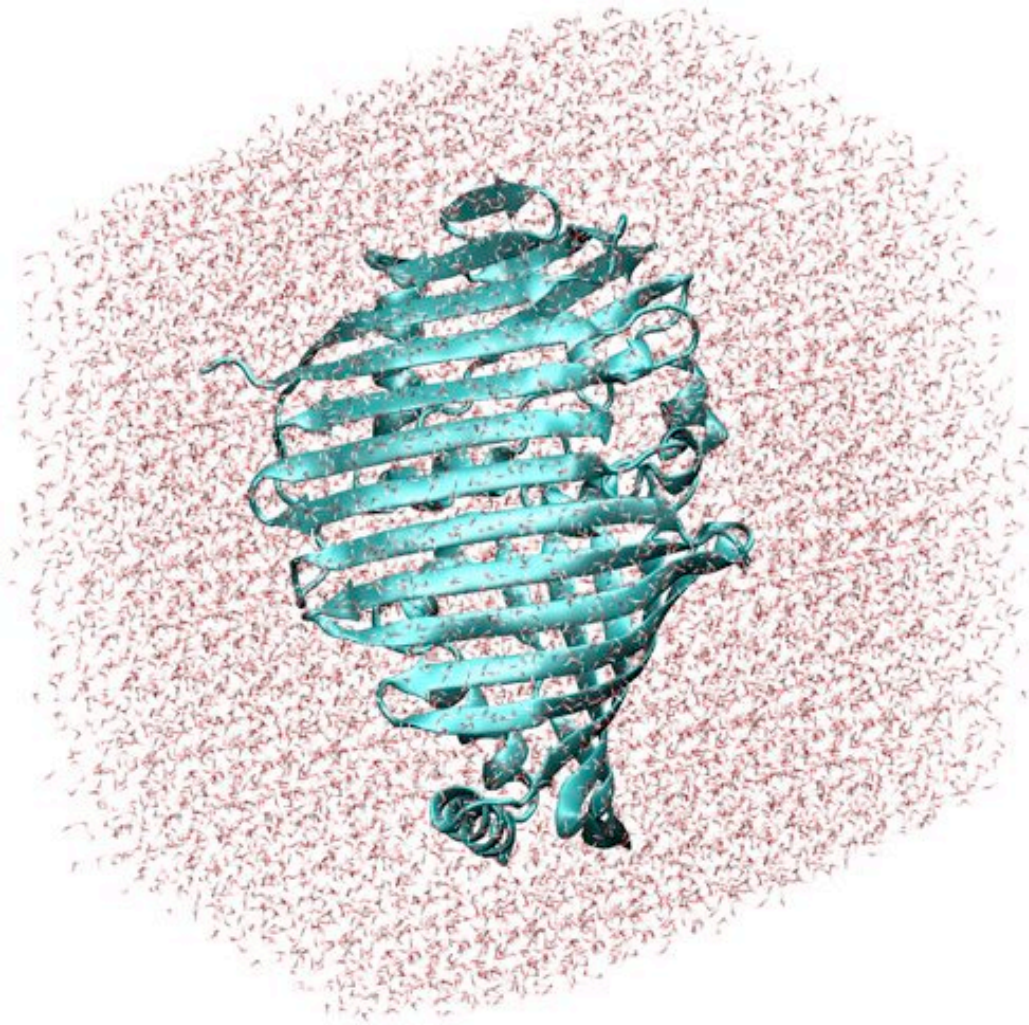
well characterized model



PDB ID: 4bcl, 1m50

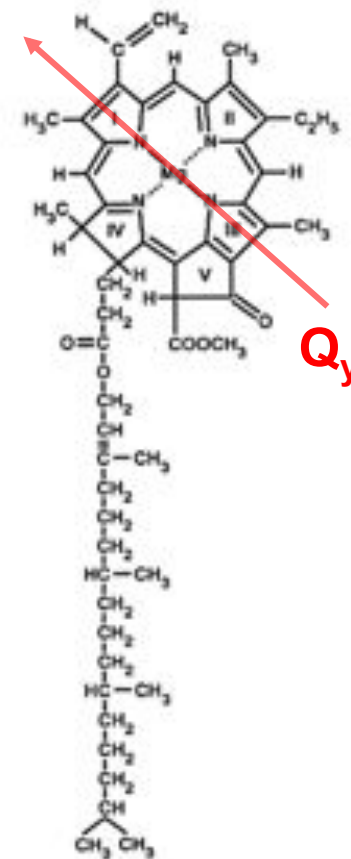
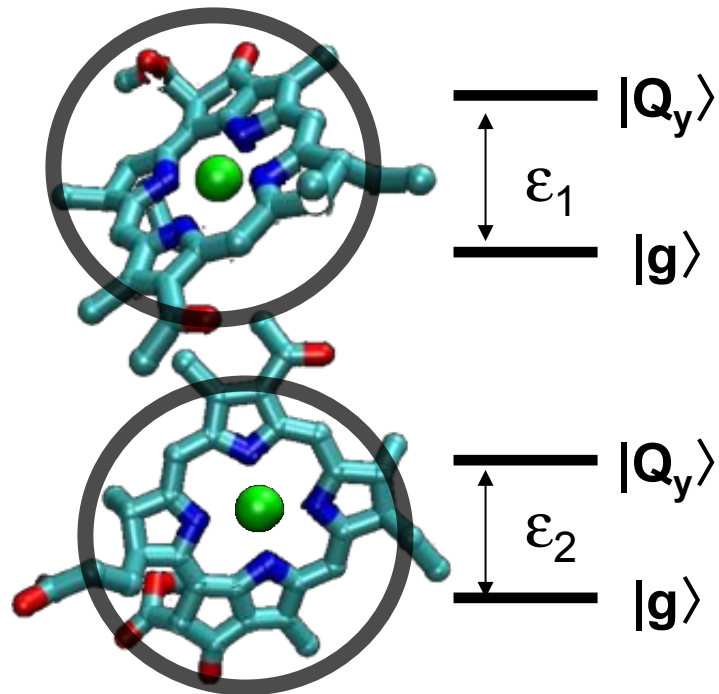
James Allen & coworkers, Photosynth. Res., 75:49 2003

Modeling Excitation Energy Transfer in the FM0?

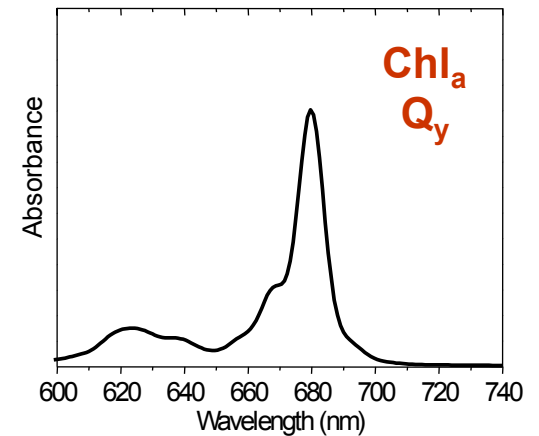


Full quantum dynamics of such a system is infeasible!

Frenkel Exciton Model



Chlorophyll *a*



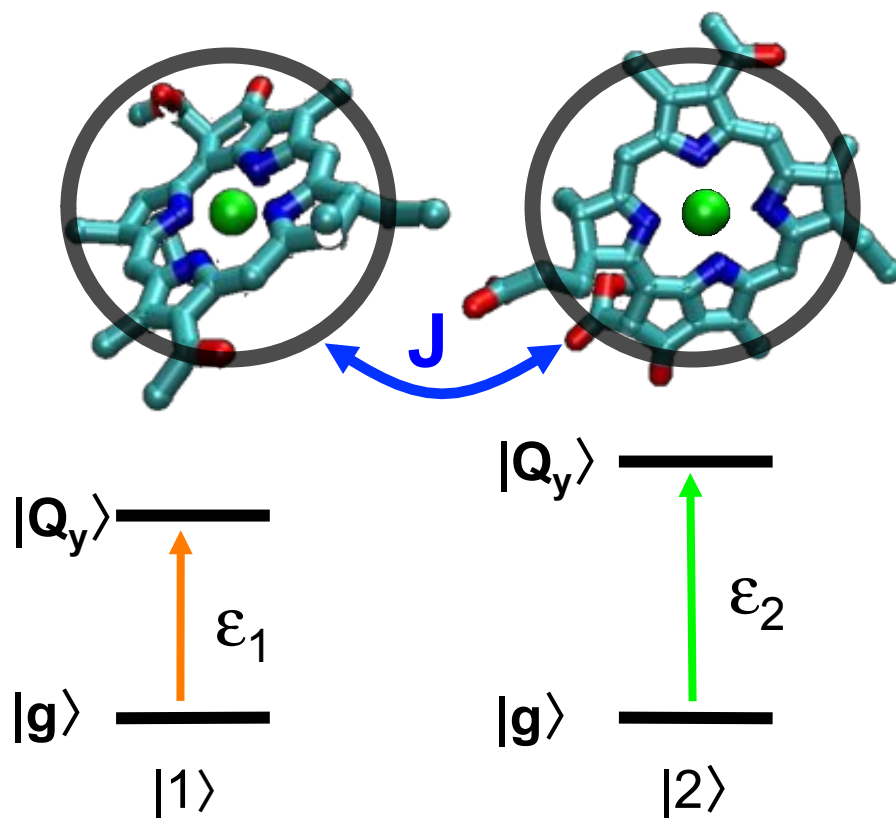
ϵ_1, ϵ_2 : site energy, transition energy modified by proteins

Exciton Hamiltonian and Excitonic Coupling

- Excitations interact with each other through excitonic coupling J
- $H_e \rightarrow$ transition energies and excitonic couplings in multichromophoric systems!!

$$H_e = \begin{bmatrix} \epsilon_1 & J_{12} & \cdots & J_{1N} \\ J_{12} & \epsilon_2 & \cdots & J_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ J_{1N} & J_{2N} & \cdots & \epsilon_N \end{bmatrix}$$

“site basis”



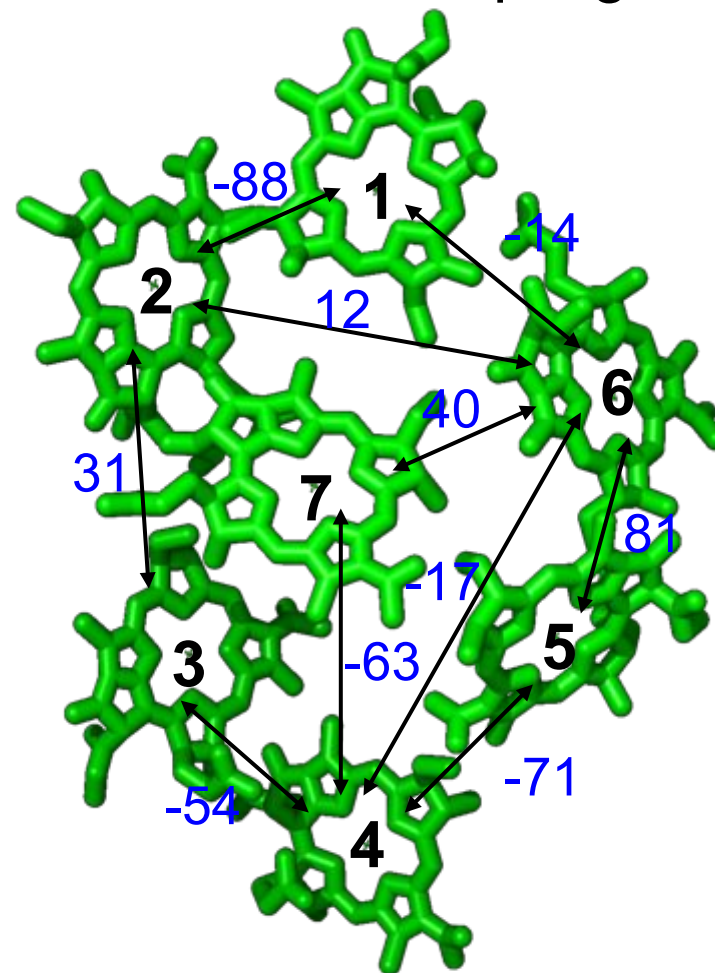
- Excitation energy transfer induced by excitonic coupling J

FMO Complex: Electronic Interactions

- There is a good starting point for the model of FMO Hamiltonian
- Couplings from **quantum chemistry** + transition density cube calculations
- Site energies from fitting to optical spectra

<u>Site energies</u>		
BChl	Monomer	Trimer
1	12,445	12,410
2	12,520	12,530
3	12,205	12,210
4	12,335	12,320
5	12,490	12,480
6	12,640	12,630
7	12,450	12,440

Excitonic couplings



Quantum Dynamics of Excitation Energy Transfer

When system-bath coupling is weak, we can use Redfield equation to describe energy transfer:

$$\partial_t \rho(t) = -i[H_e, \rho(t)] - \mathfrak{R}[\rho(t)]$$

↙ exciton Hamiltonian
↙ dissipation determined by system-bath couplings

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1N} \\ \rho_{12} & \rho_{22} & \cdots & \rho_{2N} \\ \vdots & \vdots & & \vdots \\ \rho_{1N} & \rho_{2N} & \cdots & \rho_{NN} \end{bmatrix}$$

↙ population
↙ coherence

ρ : reduced-system density matrix
 N : number of chromophores

$$\mathfrak{R}[] :$$

$\rho_{nn} \rightarrow \rho_{mm}$: population dynamics (incoherent)
 $\rho_{nm} \rightarrow \rho_{n'm'}$: coherence dynamics

Calculate Nonlinear Spectrum

Also consider light-matter interactions with laser pulses to simulate nonlinear spectrum using dynamical propagation

$$\partial_t \rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \mathfrak{R}[\rho(t)]$$

exciton Hamiltonian dissipation

light-matter interactions

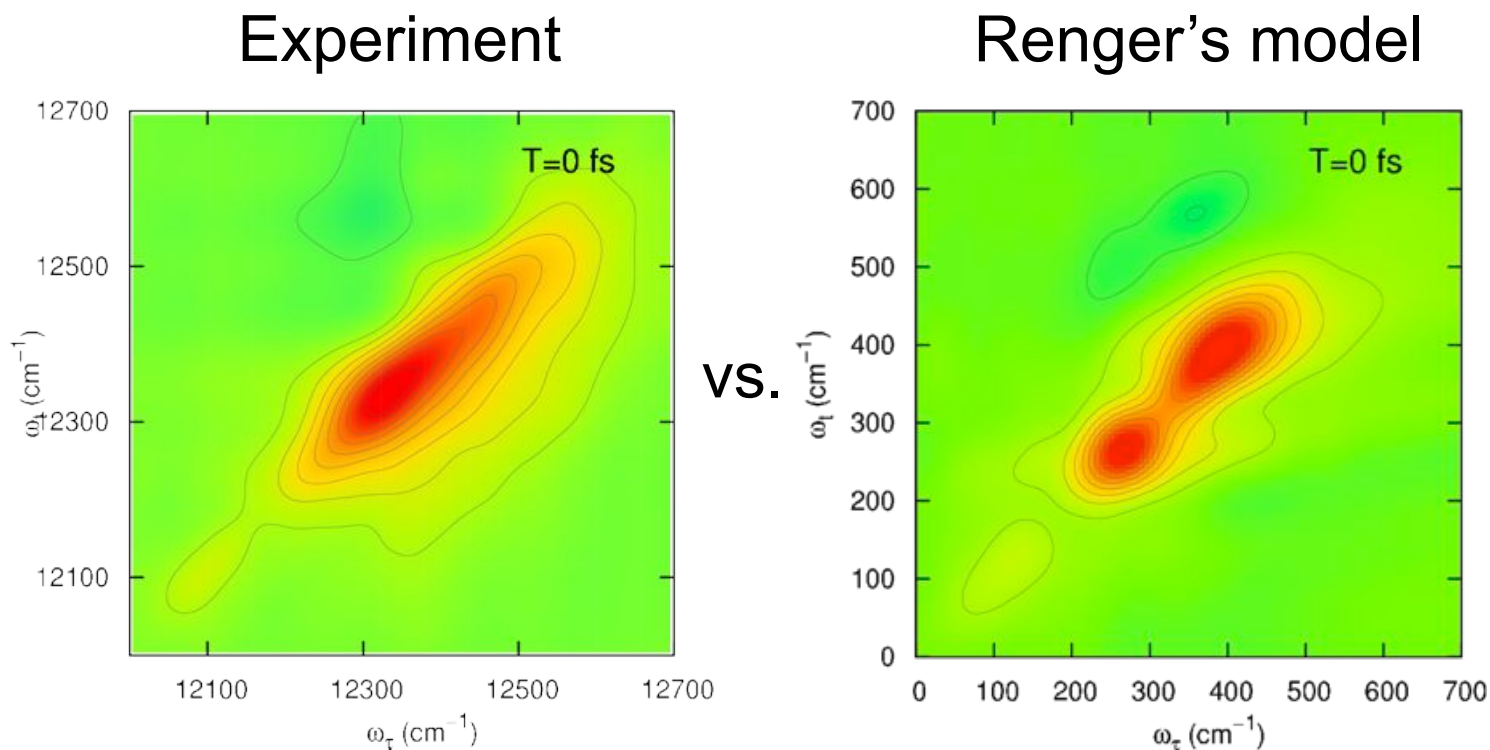
$$H_{\text{int}}(t) = -\hat{V} \cdot \sum_{a=1}^3 \mathbf{E}_a(t)$$

→ Extract photon-echo signal at the phase-matching direction by selective combinations of light-matter interactions in calculations (non-trivial)

QDAS Code

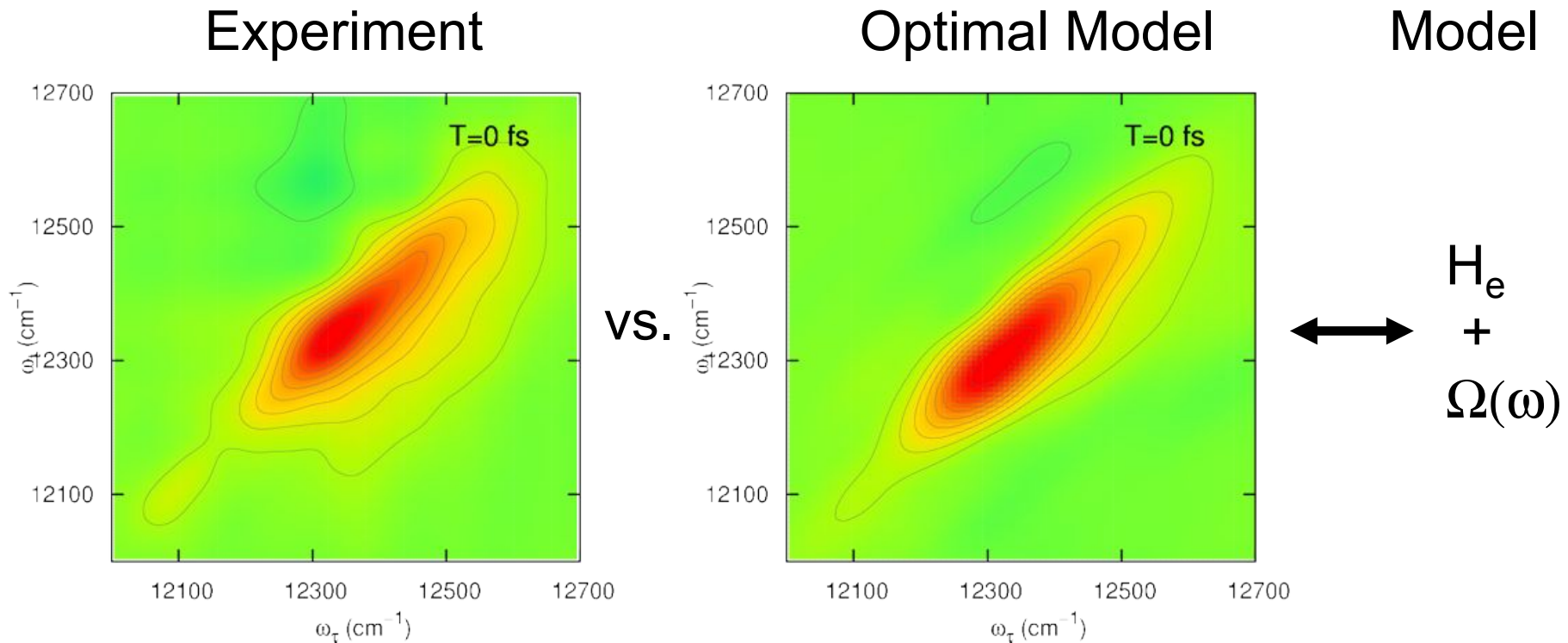
- Quantum Dynamics And Spectroscopy
- Simulates excitation energy transfer dynamics and various linear & nonlinear spectra (Absorption, 2D, 3PEPS...)
- Treats an array of bath spectra densities and bath memory effects
- Includes doubly excited states and average over a Gaussian distribution of disordered energies
- MPI capability for parallel computing

Simulated 2D Spectrum for FMO



- Renger's model does not provide adequate 2D electronic spectra
- Parallel computing is necessary for seeking a better model:
 - each spectrum needs ~ 12 hrs using 128 CPUs on NERSC' Franklin cluster due to extensive Monte-Carlo ensemble averaging procedure
 - > 30 parameters to adjust/optimize

Simulated 2D Spectrum for FMO



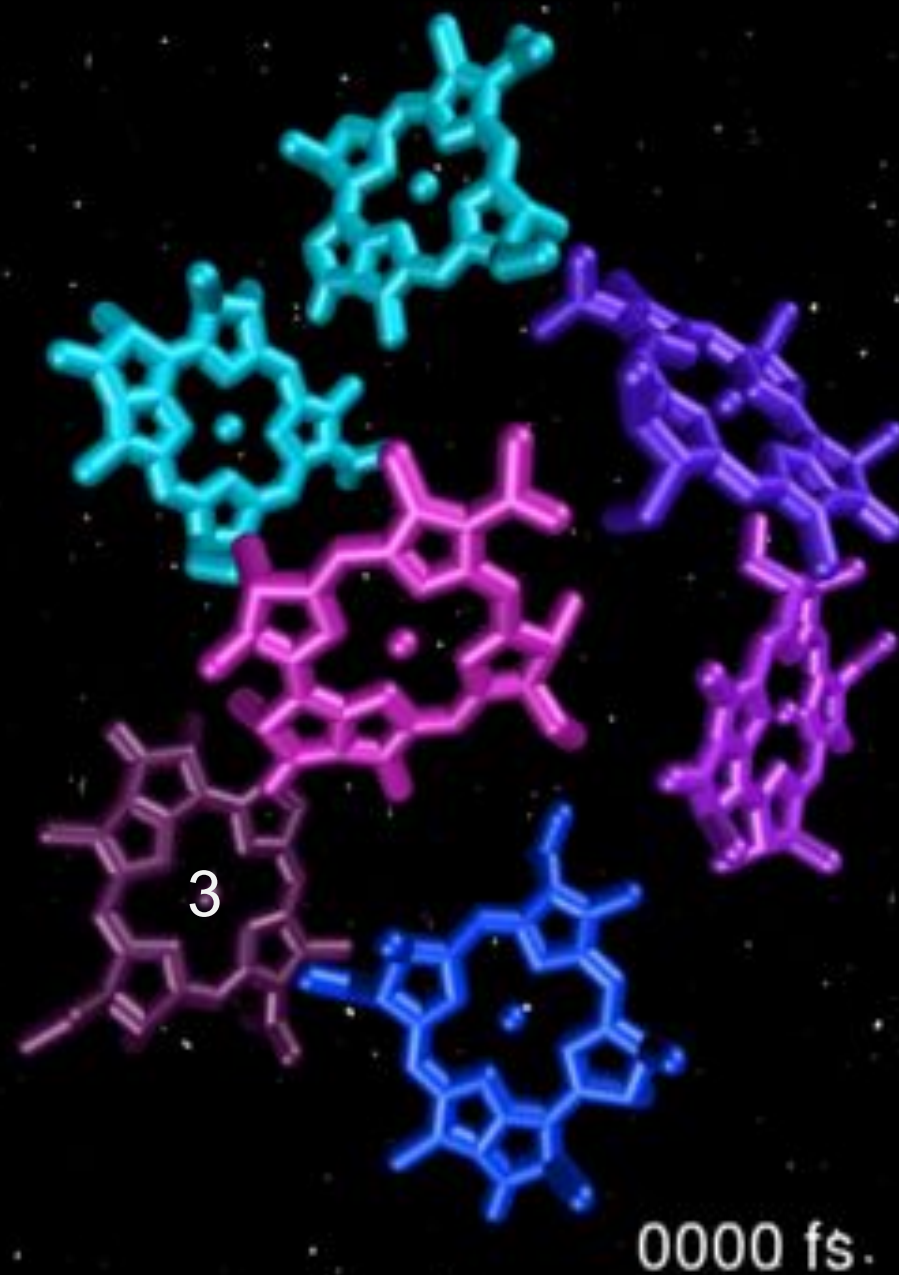
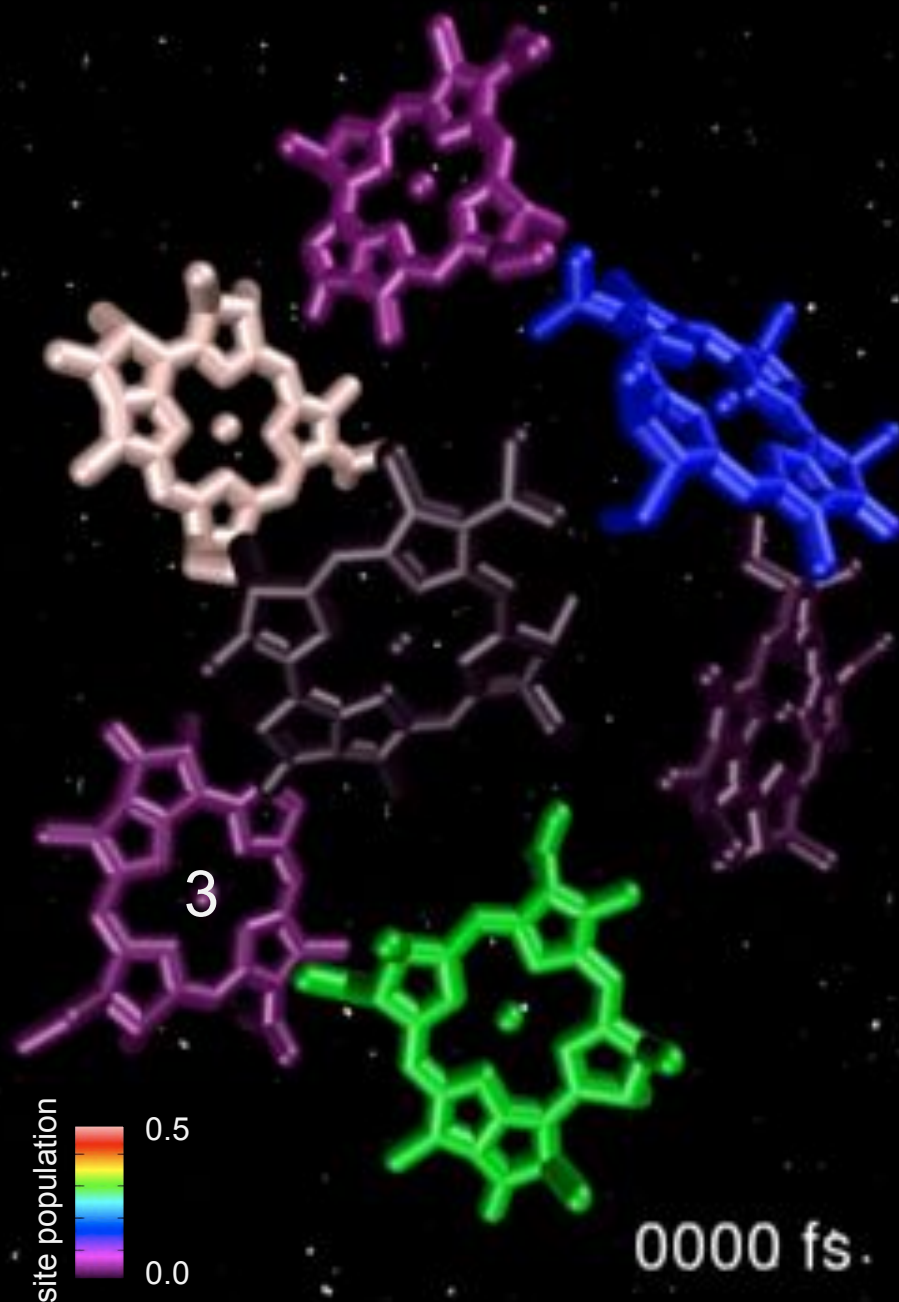
- Iterate to reach good agreement between experiment & theory starting from Renger's model
- Require inclusion of doubly excited states and average over a Gaussian distribution of disordered energies
- Provide refined model → basis for studying coherence effects

Coherent vs. Incoherent Model

- Use the refined theoretical model to investigate the effects of quantum coherence on excitation energy transfer
- Two theories for energy transfer dynamics:
 - Coherent: full quantum master equation
 - Incoherent: population dynamics only
 - ➔ conventional excitation hopping view
- Initial conditions: coherent superposition for the coherent picture, and population-only for the incoherent picture

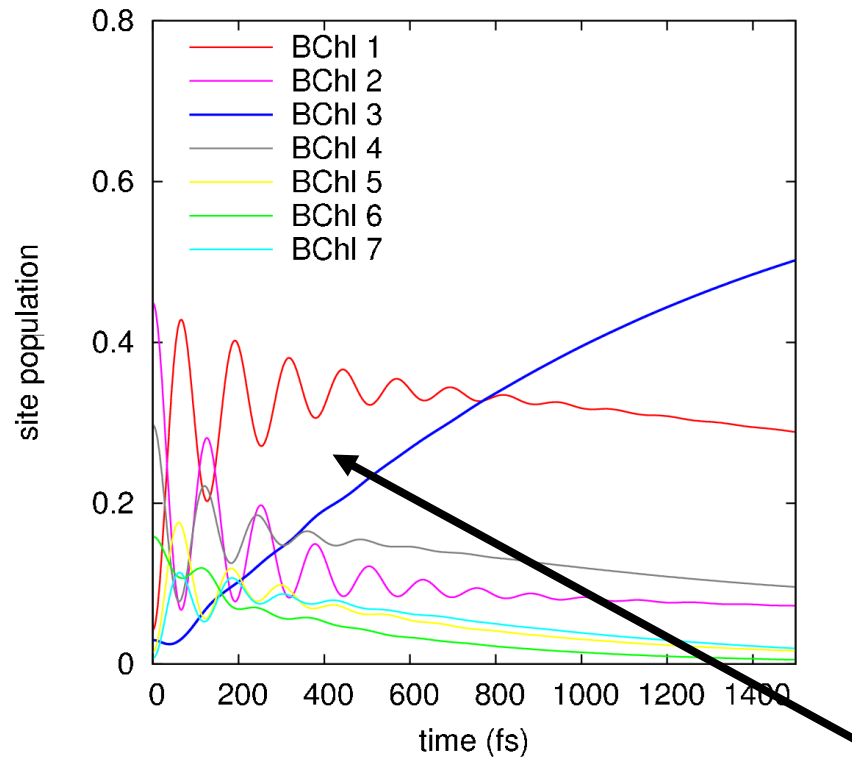
coherent picture

incoherent picture

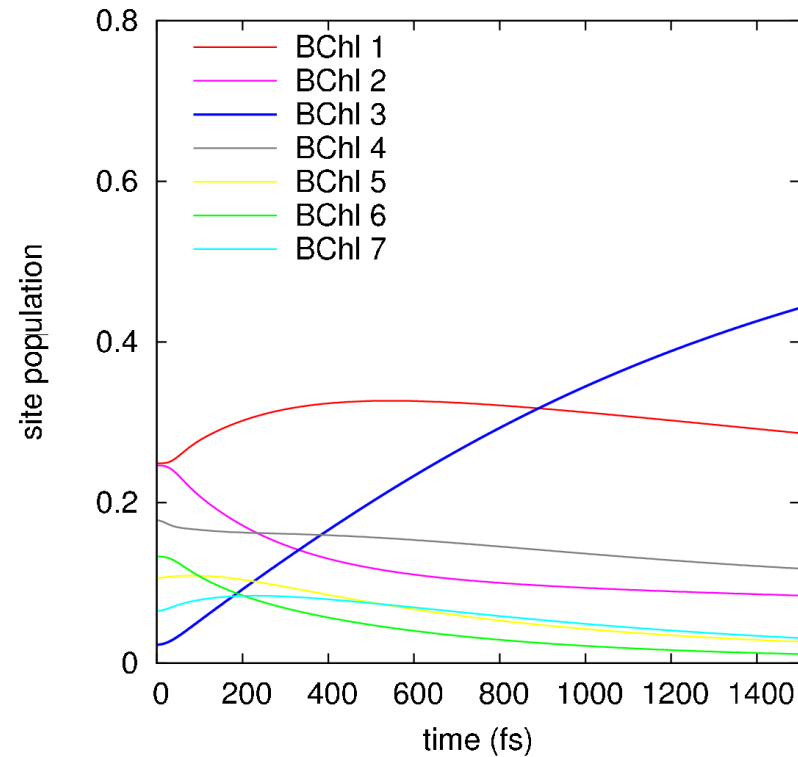


Dynamics in the Site Basis

Coherent Picture



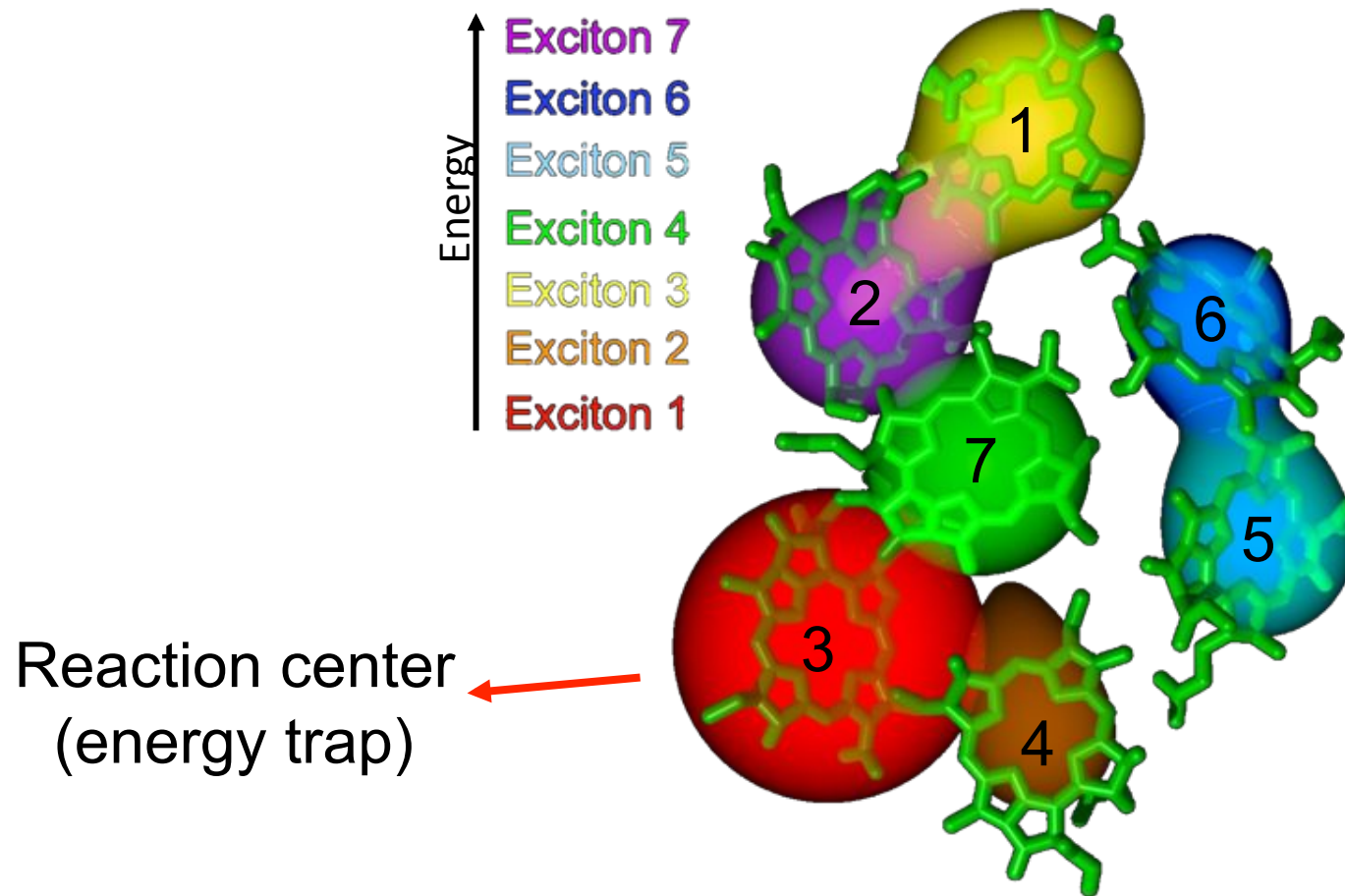
Incoherent Picture



- Reversible population redistribution in space showing interference effects due to quantum coherence
- Efficiencies of reaching BChl 3 only marginally different.

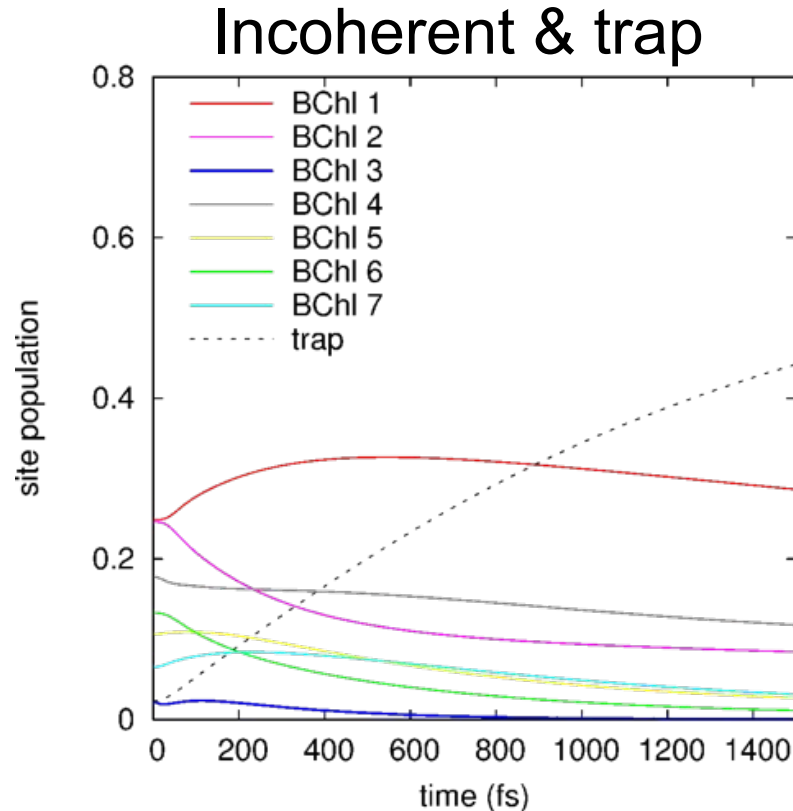
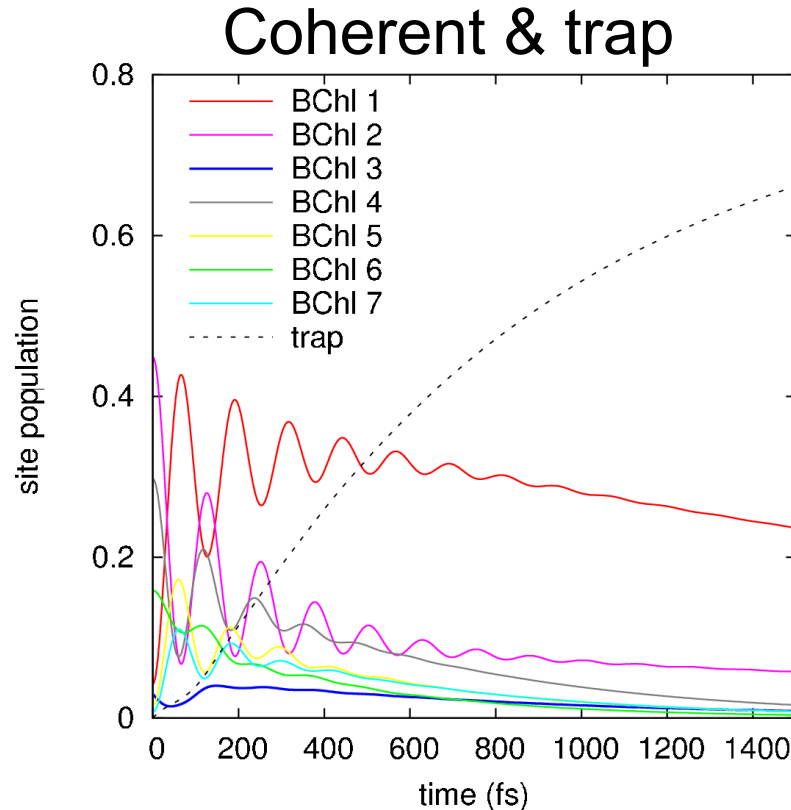
Energy Trapping from BChl 3

FMO complex is a energy wire connected to RC through BChl 3



What if an efficient energy trap is attached to BChl 3?

Coherence Assisted Energy Trapping



- Rapid trapping (50 fs) from BChl 3 enhances efficiency for the coherent case because of the suppression of back transfer
- Quantum coherence may enable excitation to find RC rapidly through reversible sampling in space → *Coherence assisted energy trapping*

Coherence Assisted Energy Trapping

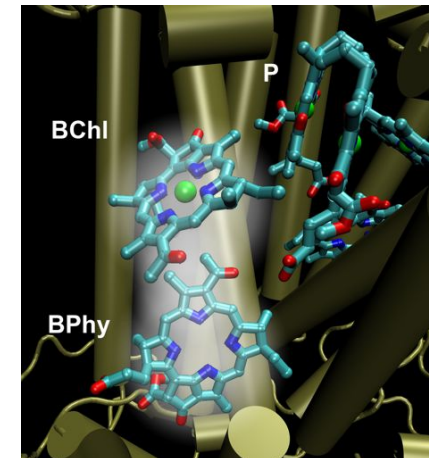
- Long-lived electronic coherence enables the system to perform rapid and reversible sampling in space to search for the trap site
- Efficient trapping process dissipates the energy and localizes the excitation
- The scheme can be more efficient than incoherent hopping and is likely to be more robust on energetically disordered landscape
- This proposal is currently being actively studied by many groups: Aspuru-Guzik (Harvard), Lloyd (MIT), Whaley (Berkeley), Plenio (Imperial College, UK)...

How is the long-lasting quantum coherence achieved?

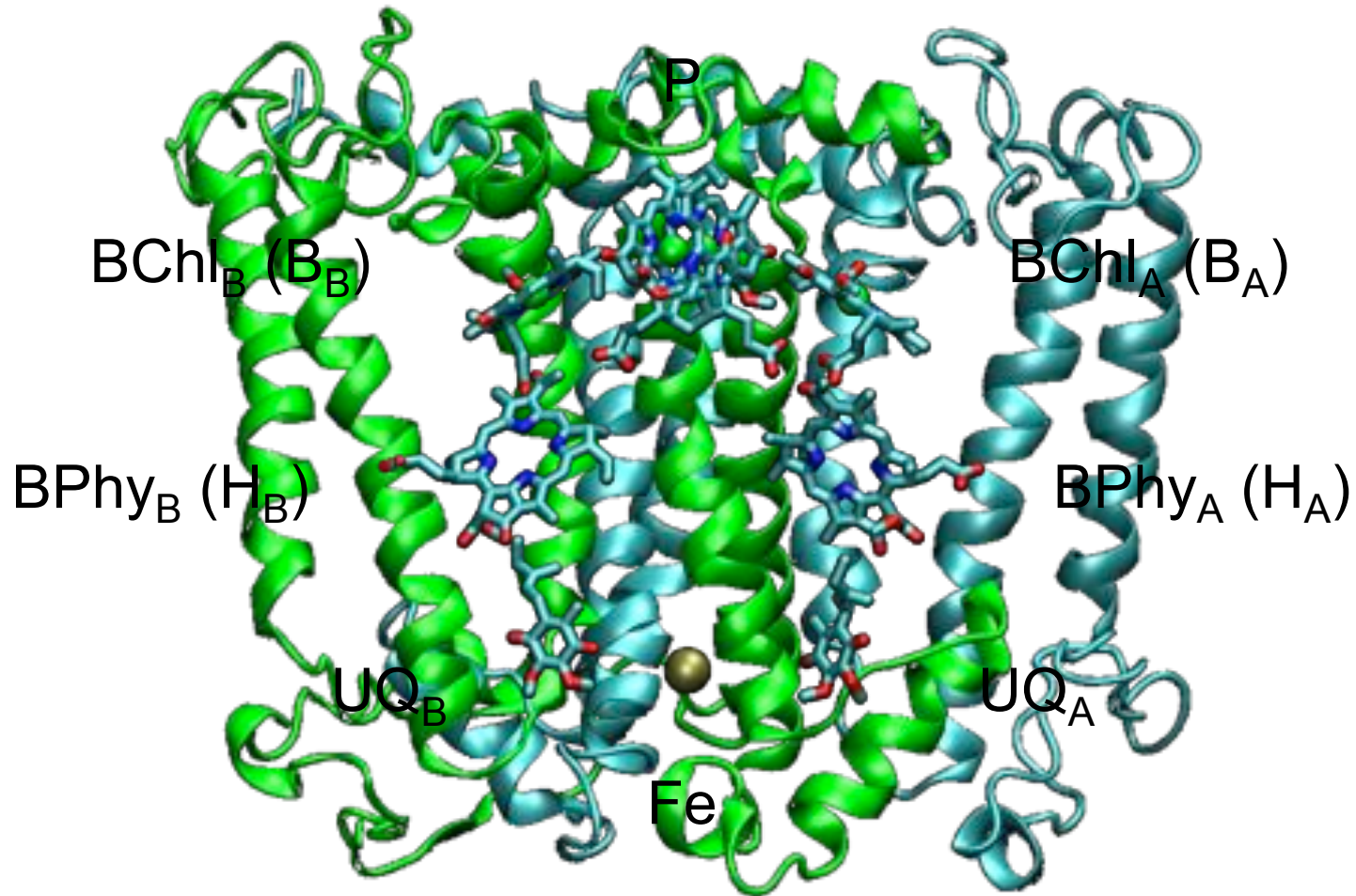
1. Protein environment & correlated motions
2. Non-equilibrium effects in energy transfer

Coherence Photon Echo of Bacterial Reaction Center

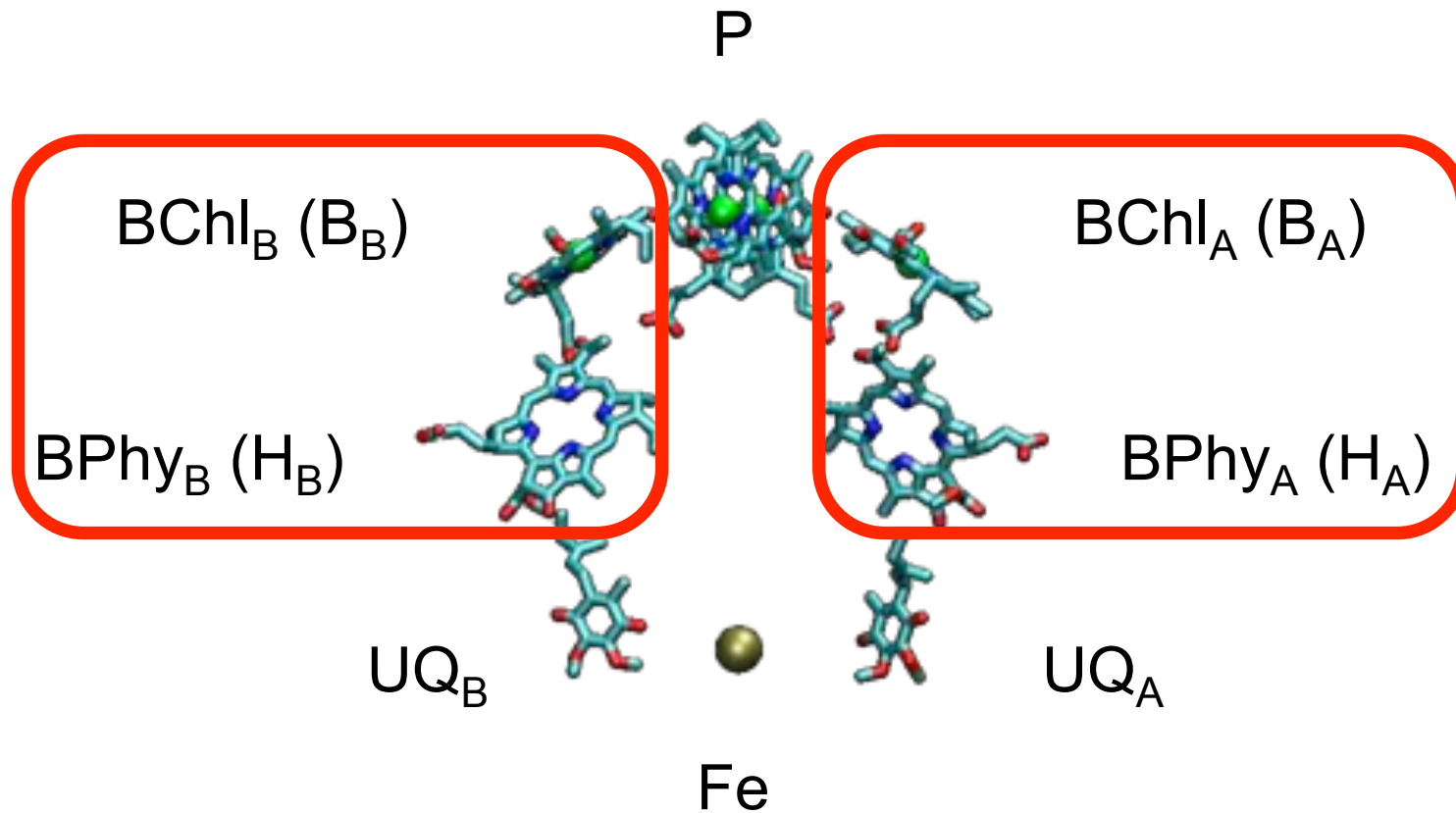
- Protein protection of electronic quantum coherence:
 - H. Lee, Y.-C. Cheng & G.R. Fleming, *Science* **316**, 1462 (2007).



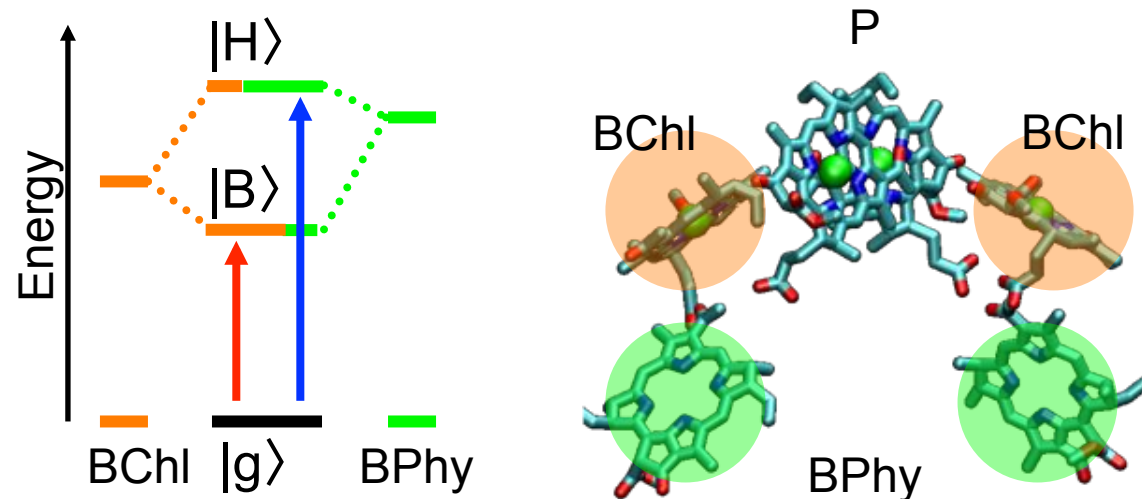
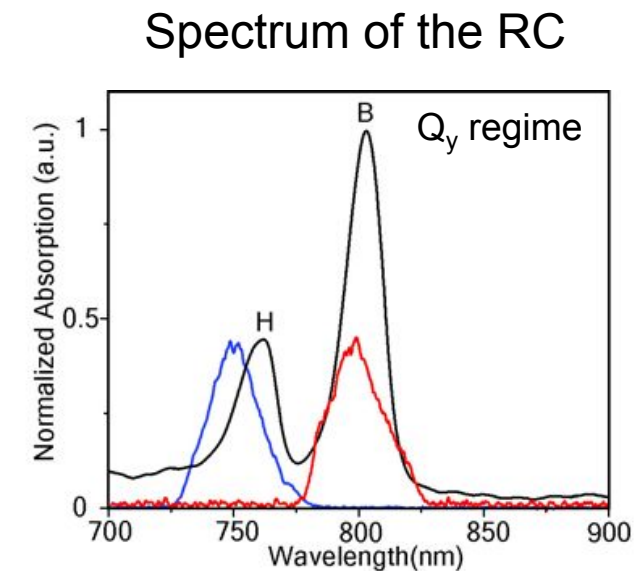
The Reaction Center of Purple Bacteria



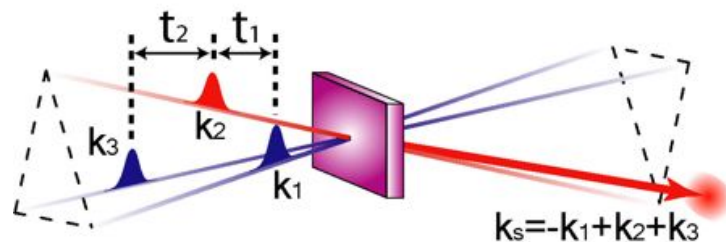
The Reaction Center of Purple Bacteria



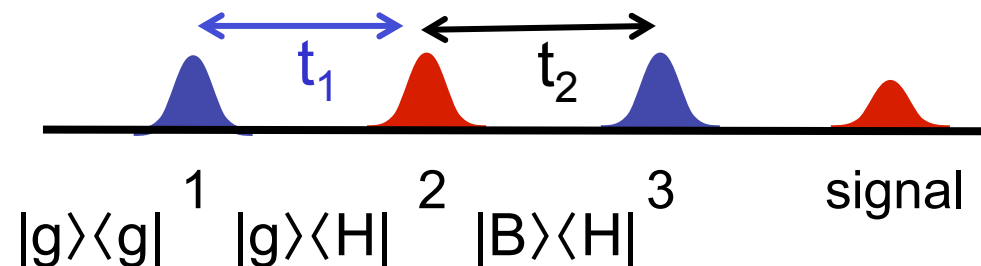
Probing H/B Coherence Dynamics: Two-color Electronic Coherence Photon Echo



- $|H\rangle$ and $|B\rangle$ selectively excited
- Design to probe coherence specifically $|g\rangle\langle H|$ in t_1 , $|B\rangle\langle H|$ in t_2

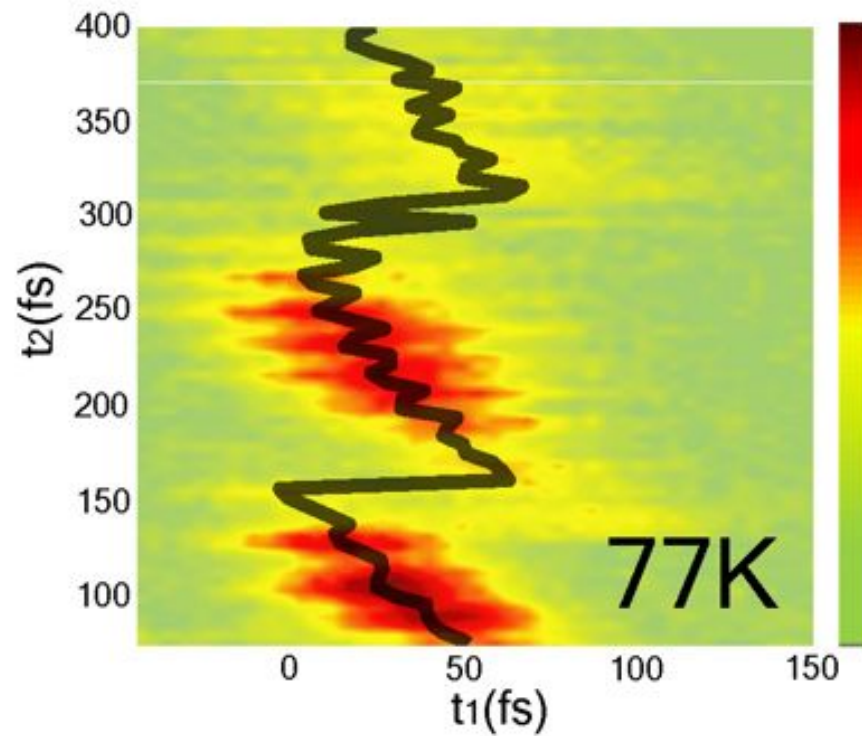


Ordering: 750-800-750 (nm)

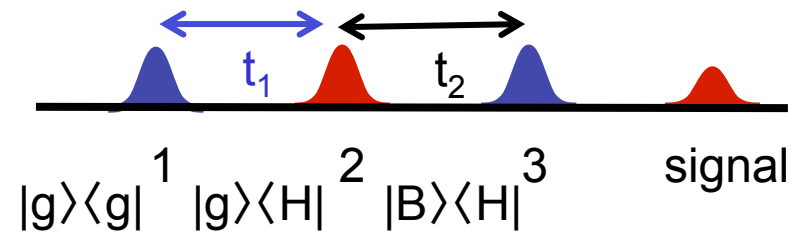
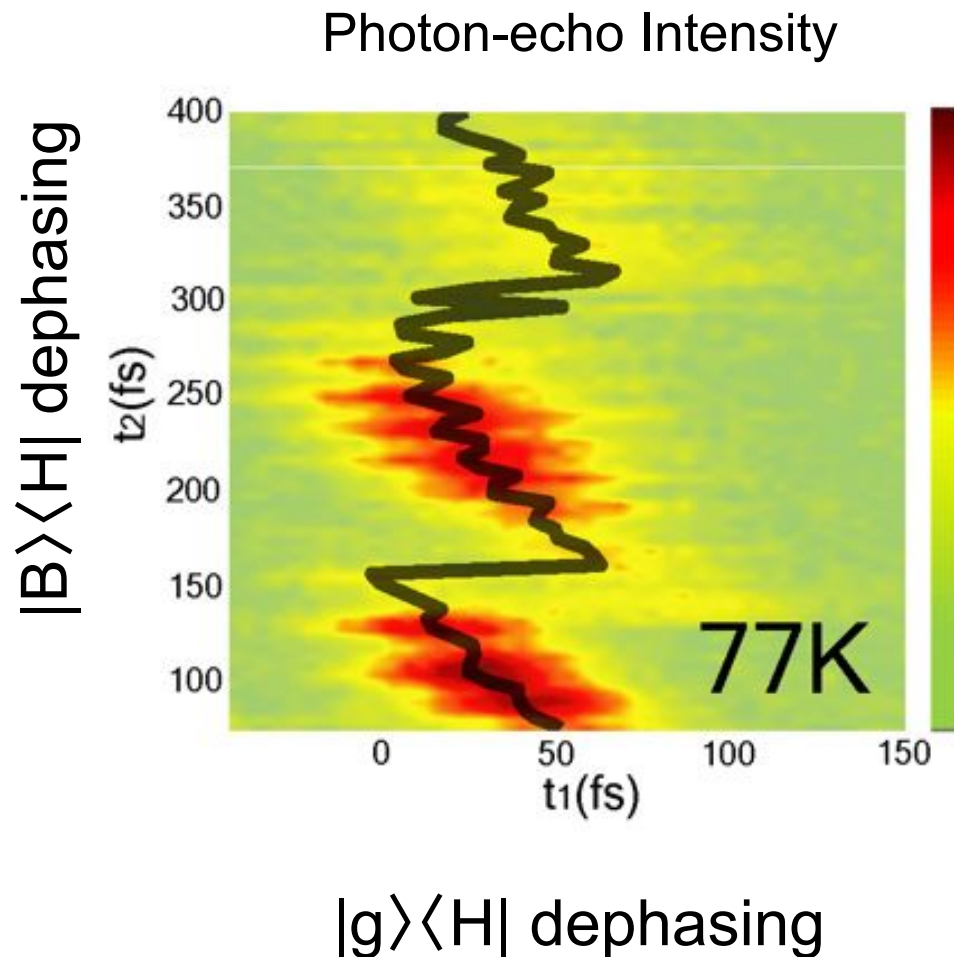


Experimental Data @ 77K

Photon-echo Intensity



Mapping Coherence Dynamics in the RC



- Photon-echo intensity measured in this two-color experiment follows coherence dynamics.
- Along t_1 : $|g\rangle\langle H|$ dephasing
- Along t_2 : $|B\rangle\langle H|$ dephasing

Dephasing of Electronic Coherence

- Phase associated with the time evolution of coherences (off-diagonal density matrix elements):

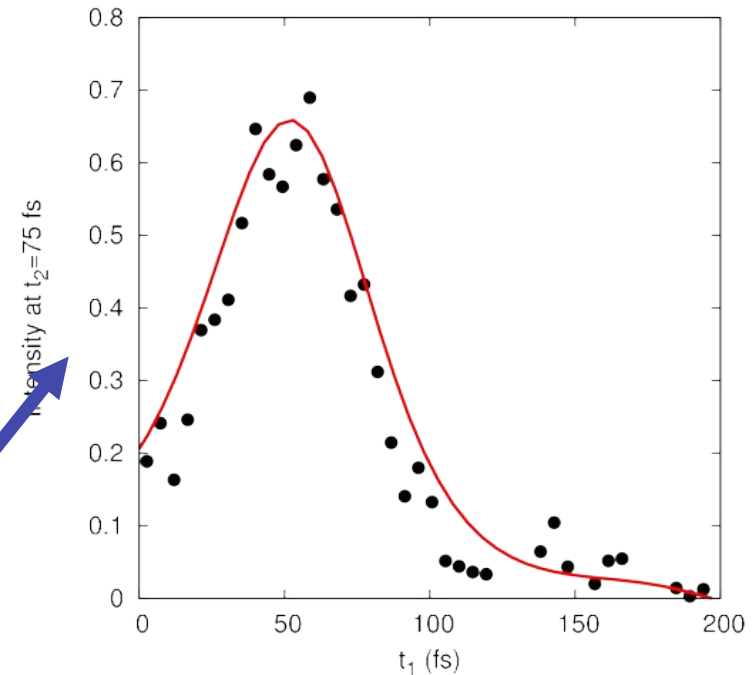
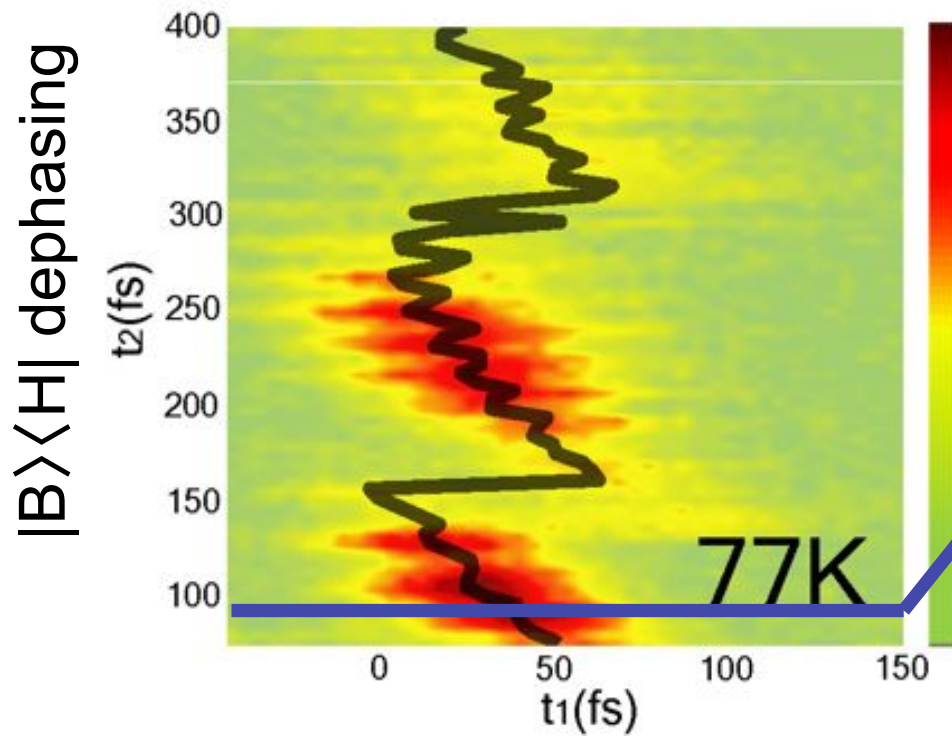
$$\phi_{ij}(t) = e^{-i(w_i - w_j)t}$$

- ➔ Randomness in the energy gap $\delta\omega_{ij}(t)$ results in dephasing
- ➔ Fluctuations of the energy gap are induced by dynamics of the protein environment
- Stronger fluctuation ➔ faster dephasing

Mapping Coherence Dynamics

Photon-echo Intensity

- Rapid $|g\rangle\langle H|$ dephasing (t_1)

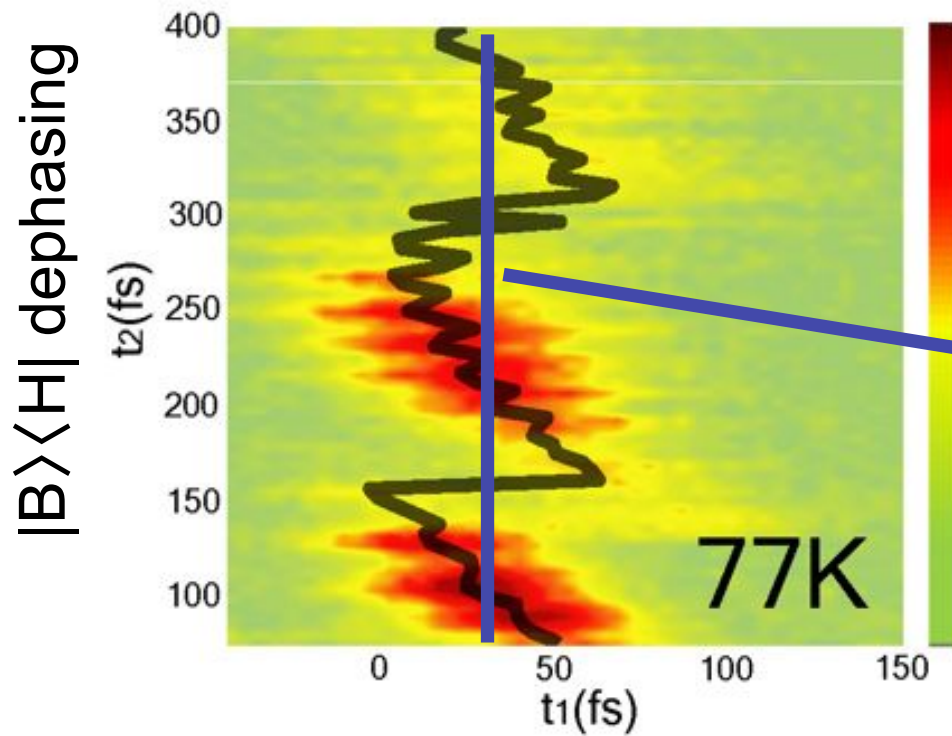


$|g\rangle\langle H|$ dephasing

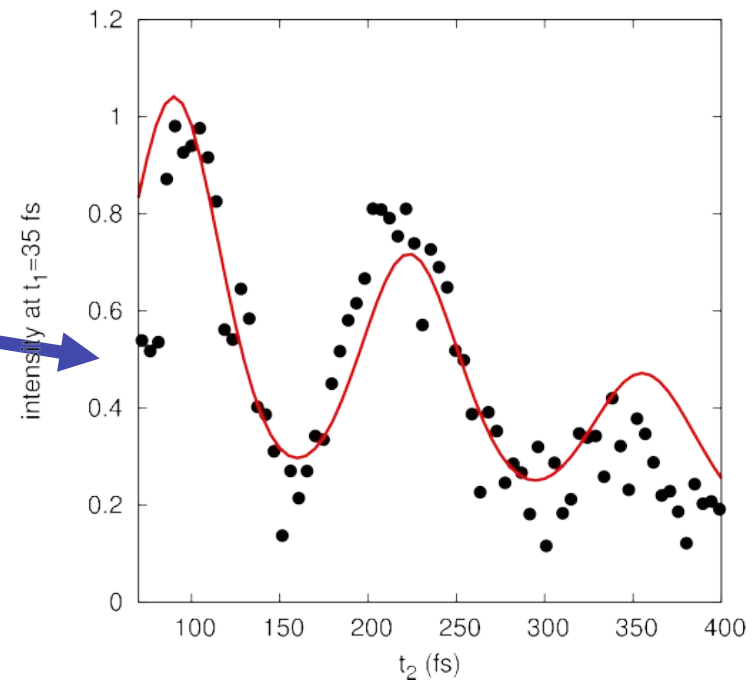
➔ Large E_H fluctuations.

Mapping Coherence Dynamics

Photon-echo Intensity



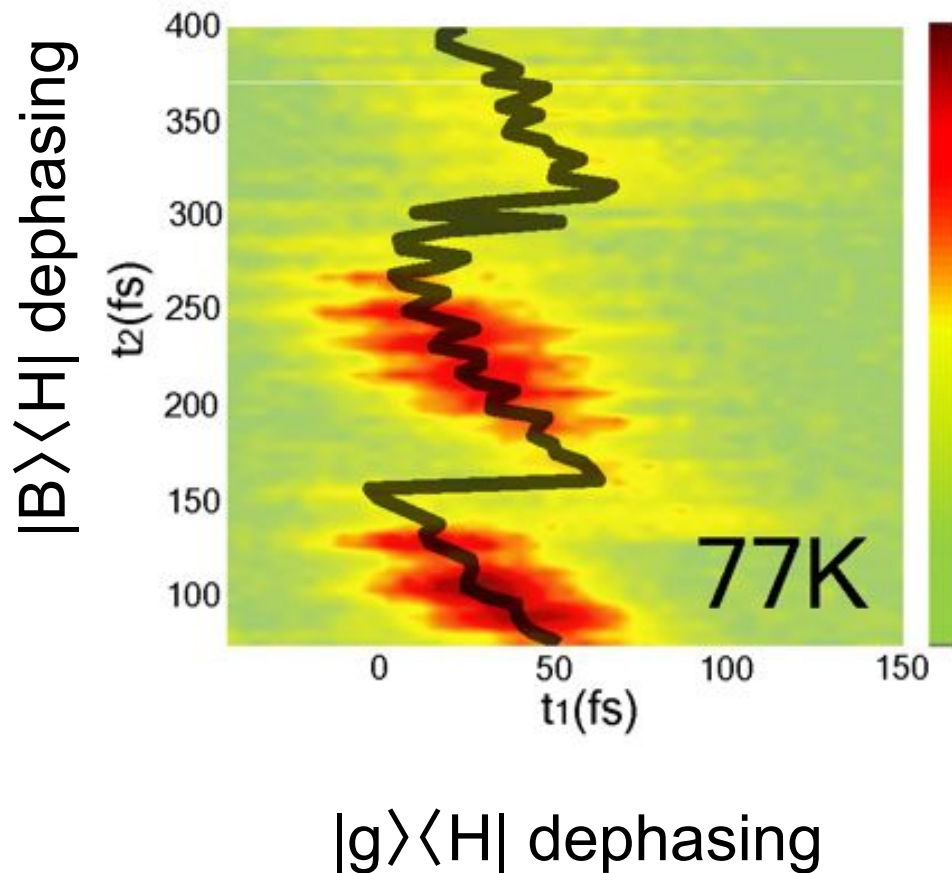
- Slow $|B\rangle\langle H|$ dephasing (t_2)



$|g\rangle\langle H|$ dephasing

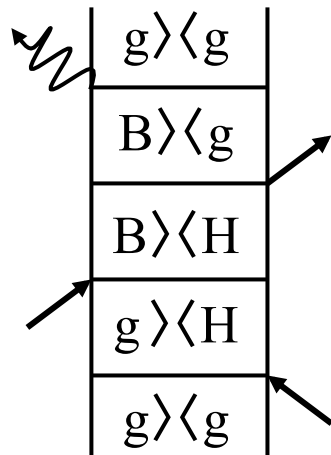
➔ Smaller $E_H - E_B$ energy gap fluctuations.

Mapping Coherence Dynamics



- Rapid $|g\rangle\langle H|$ dephasing (t_1)
→ Large E_H fluctuations.
- Slow $|B\rangle\langle H|$ dephasing (t_2)
→ Smaller $E_H - E_B$ energy gap fluctuations.
- Energy fluctuations on B and H are highly correlated.
- Evidence for correlated protein environments!

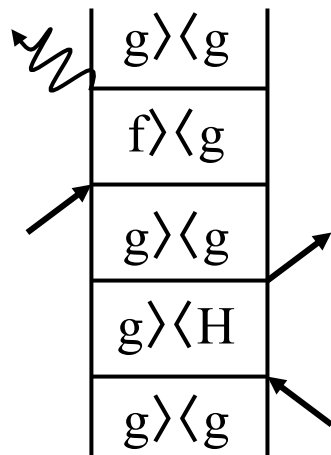
Theoretical Modeling



Impulsive response function formalism.
 BPhy-BChl electronic coupling $\sim 220 \text{ cm}^{-1}$.
 Transition energy fluctuations on Bphy/BChl:

$$C_{BPhy}(t) = \lambda_{BPhy} \exp(-t^2 / \tau_0^2) + \Delta_0^2,$$

$$C_{BChl}(t) = \lambda_{BChl} \exp(-t^2 / \tau_0^2) + \Delta_0^2.$$

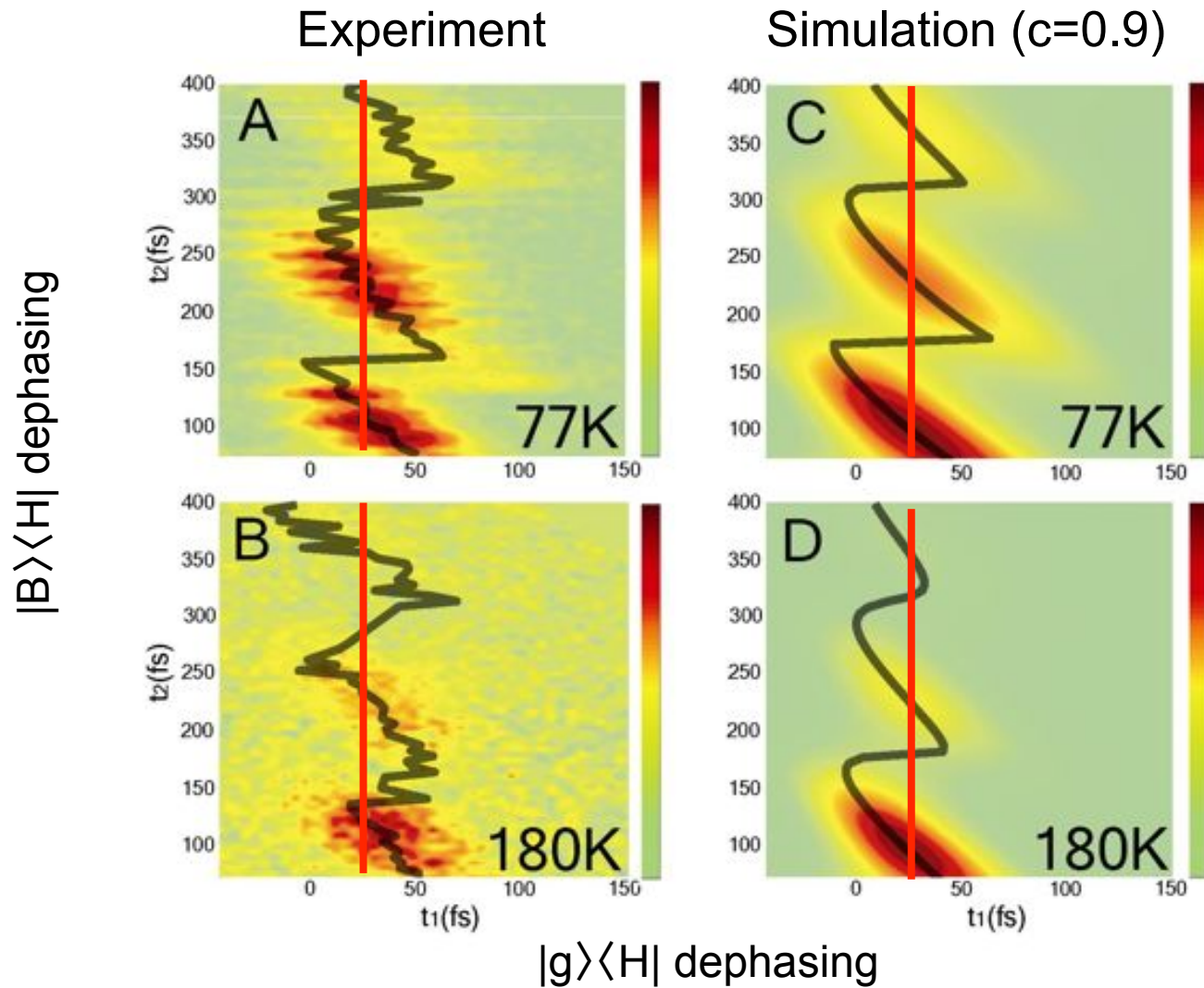


Cross-correlation between BPhy and BChl
 fluctuations (described by c):

$$C_{hb}(t) = \lambda_{hb} \exp(-t^2 / \tau_0^2) + \Delta_0^2; \quad \lambda_{hb} = c \sqrt{\lambda_h \lambda_b}.$$

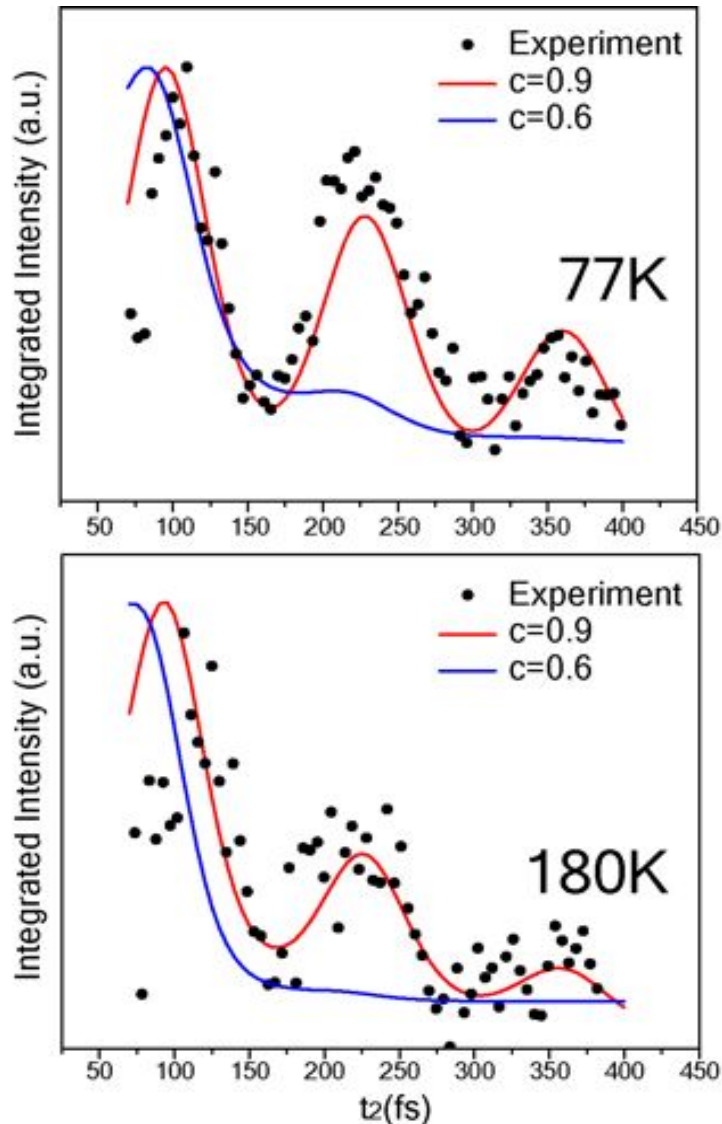
250 cm^{-1} vibrational mode coupled to BPhy
 (sawtooth pattern).

Experiment vs. Theory



H. Lee, Y.-C. Cheng, G.R. Fleming, *Science* **316**, 1462 (2007).

Protein Protection of Electronic Coherence



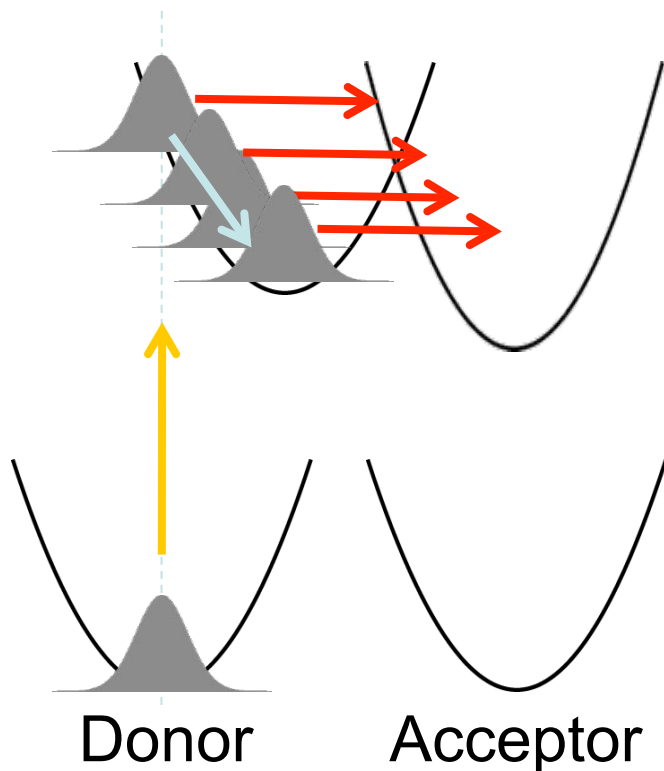
- Electronic coupling alone ($c=0.6$) cannot explain the long dephasing time
- Strong cross-correlations ($c \sim 0.9$) between protein environments responsible for long-lived $|B\rangle\langle H|$ coherence
- ➔ “*Protein protection of excitonic coherence*”

$|B\rangle\langle H|$ dephasing times: $t_{g,77K} = 440\text{fs}$, $t_{g,180K} = 310\text{fs}$

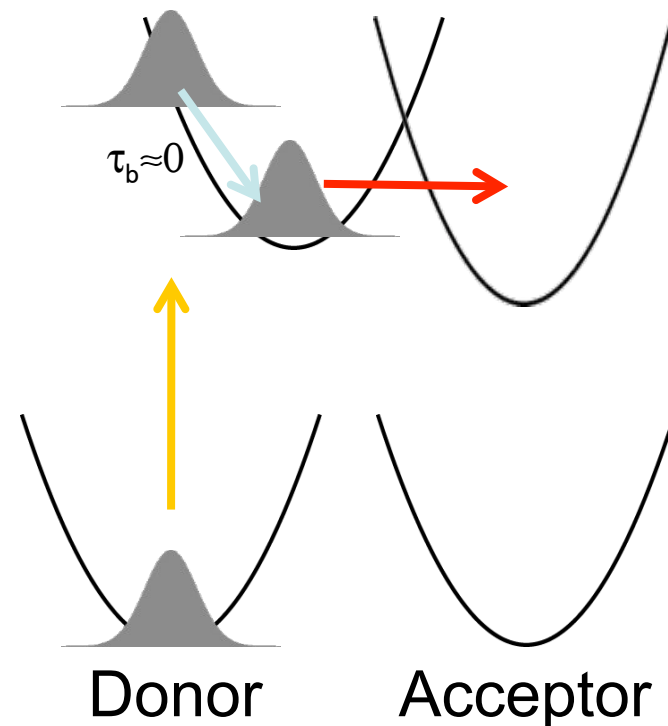
Non-equilibrium Effects in Excitation Energy transfer

- Non-equilibrium effects could be important in ultrafast dynamics
- Conventional theories assume that baths are always in equilibrium \rightarrow over-estimate of coherence dephasing rate!

Photon-induced dynamics

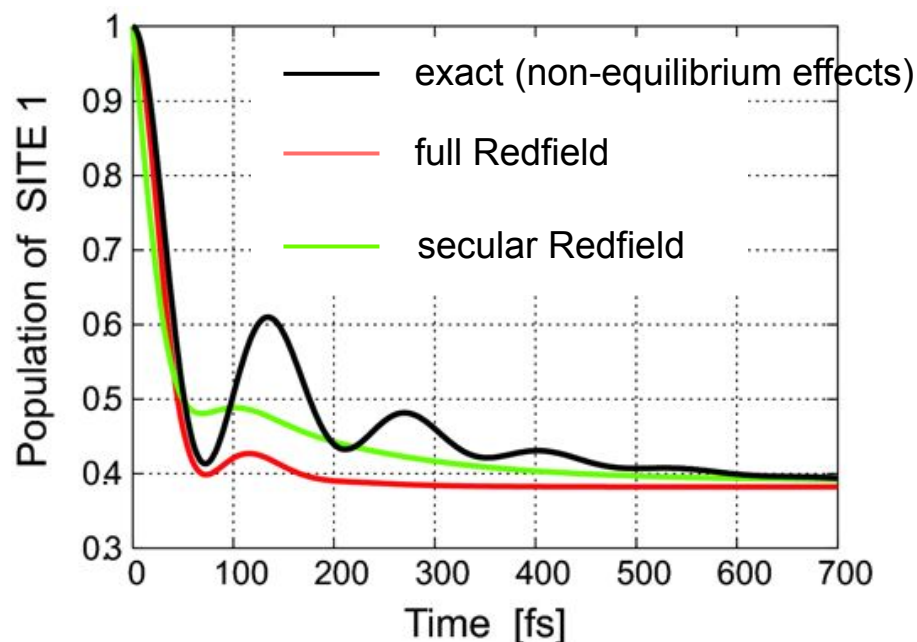


Redfield/Forster picture

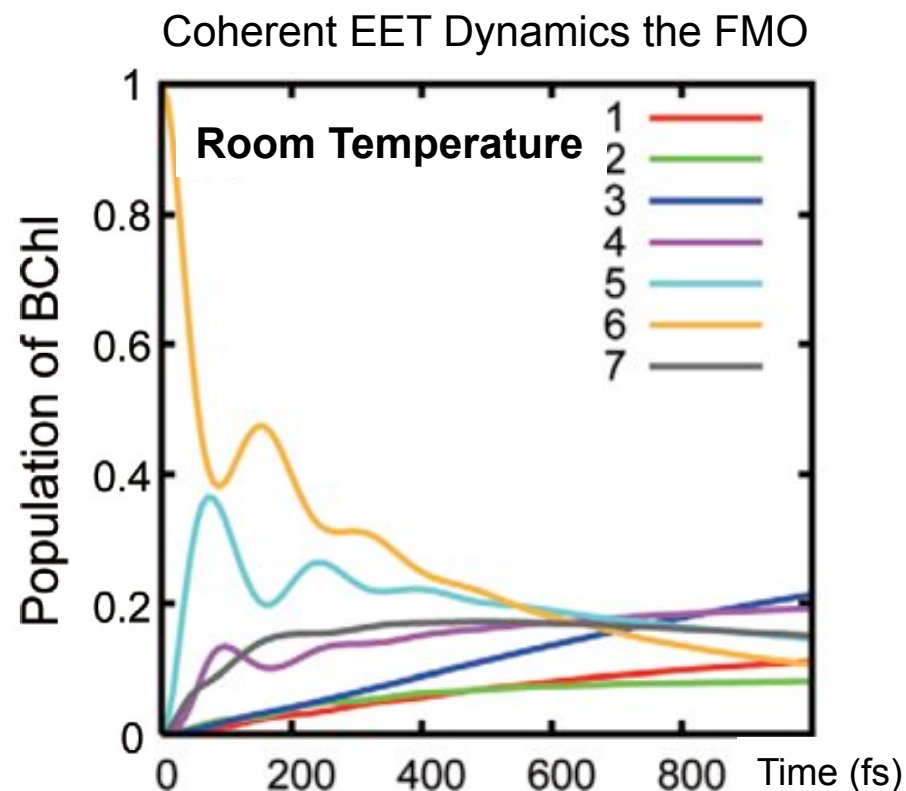


Non-equilibrium Effects Lead to Longer Decoherence Time

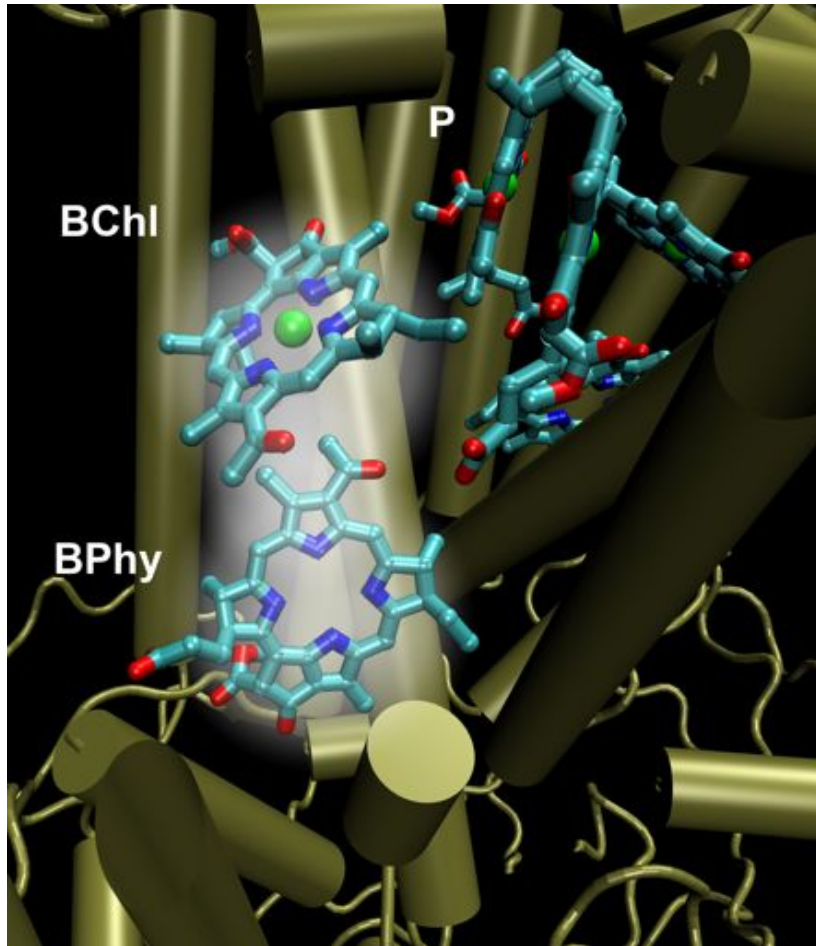
- Calculations based on new theoretical formalism including non-equilibrium bath effects show longer decoherence time
- New theory predicts quantum coherence lasting in the FMO complex at physiological temperature (Ishizaki & Fleming, PNAS 2000)



Benchmark calculations on a spin-boson model.
Ishizaki & Fleming, JCP 2009.



Concluding Remarks



Pigments and proteins in the reaction center of a purple bacteria

- Energy transfer through quantum coherence has been revealed in photosynthesis
- Coherent dynamics may promote energy trapping in light harvesting
- Correlations in protein dynamics & non-equilibrium bath effects contribute to the preservation of coherence
- High-performance computing crucial for studies of quantum dynamics, spectra, molecular quantum chemistry, protein dynamics, complex organization ...etc.

Acknowledgements

- Graham Fleming (UC Berkeley)
- Seogjoo Jang (Queens College, CUNY)
- The Fleming Group (UC Berkeley)

- National Science Council of Taiwan

Thank You!

Propagating Dynamics with Bath Memory

- We use a time-nonlocal approach to retain memory effects:

$$\frac{d}{dt}\rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \int_0^t K(t, \tau) \rho(\tau) d\tau$$

- Important for the description of peak shape
- $K(t, \tau)$ ← memory kernel, can be calculated from $\Omega(\omega)$ using perturbation theory
- Decompose $K(t, \tau)$ into exponentials to facilitate efficient propagation of time-nonlocal dynamics

Propagating Dynamics with Bath Memory

- Redfield theory \rightarrow does not describe full $\langle \delta\omega(t)\delta\omega(0) \rangle$

$$\frac{d}{dt}\rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \Re(t) \cdot \rho(t)$$

- We use a time-nonlocal approach to retain memory effects:

$$\frac{d}{dt}\rho(t) = -i[H_e + H_{\text{int}}(t), \rho(t)] - \int_0^t K(t, \tau) \rho(\tau) d\tau$$

- $K(t, \tau) \leftarrow$ memory kernel, can be calculated from $C(t)$ using perturbation theory

Theoretical Background

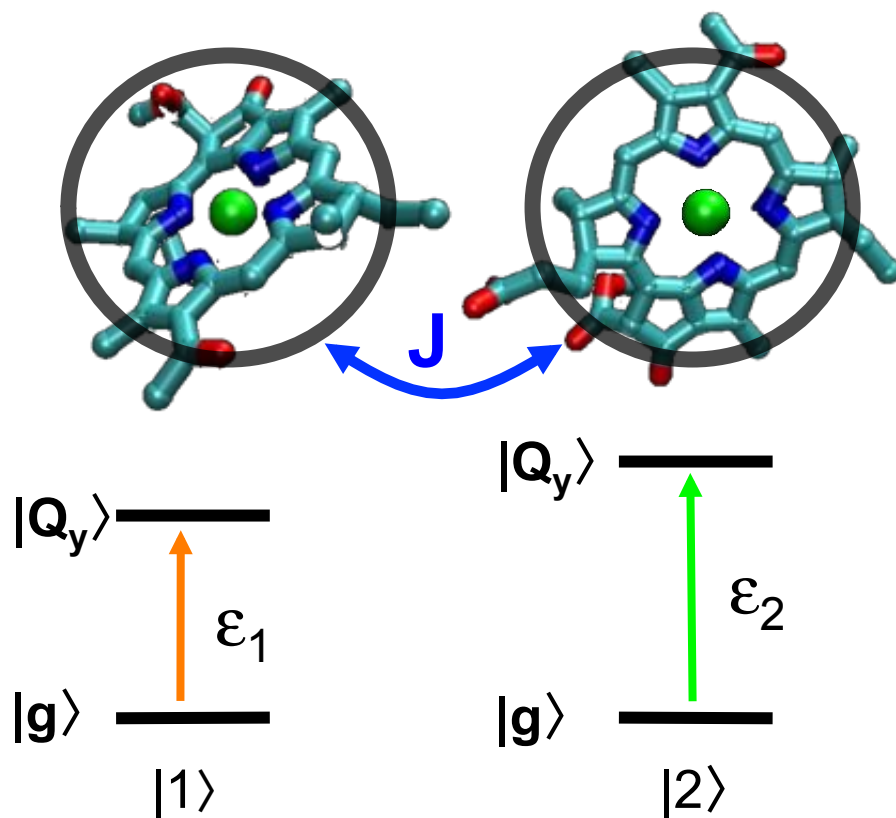
Photosynthetic Excitons & Quantum Dynamics

Exciton Hamiltonian and Excitonic Coupling

- Excitations interact with each other through excitonic coupling J
- $H_e \rightarrow$ transition energies and excitonic couplings in multichromophoric systems!!

$$H_e = \begin{bmatrix} \epsilon_1 & J_{12} & \dots & J_{1N} \\ J_{12} & \epsilon_2 & \dots & J_{2N} \\ \vdots & \vdots & \dots & \vdots \\ J_{1N} & J_{2N} & \dots & \epsilon_N \end{bmatrix}$$

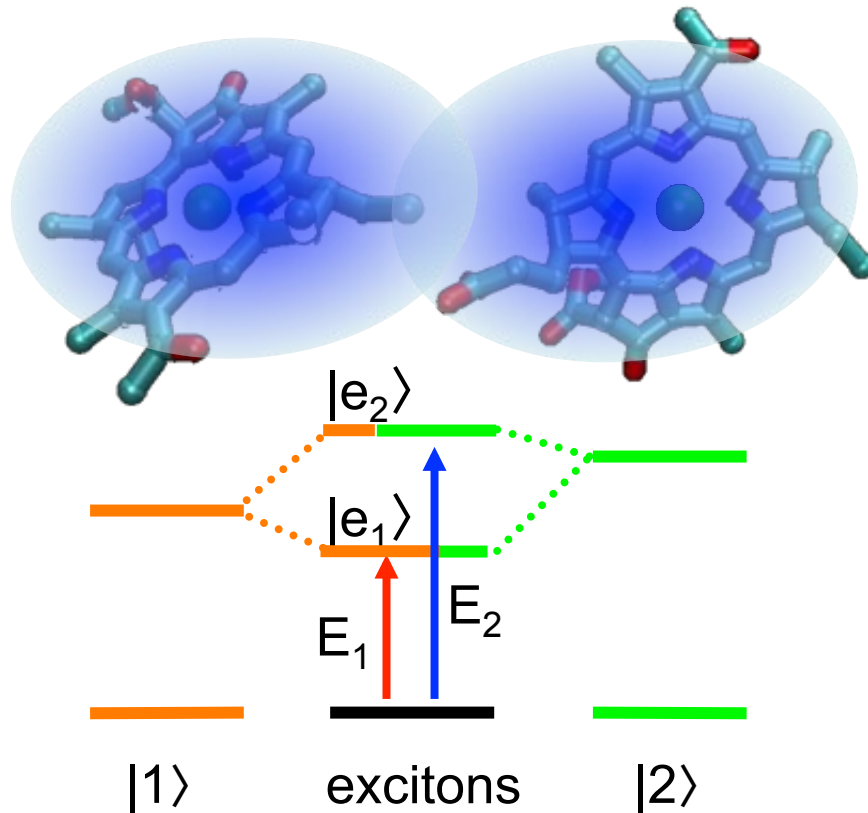
“site basis”



- Excitation energy transfer induced by excitonic coupling J
- When J is significant, the eigenstates of H_e has to be considered \rightarrow excitons

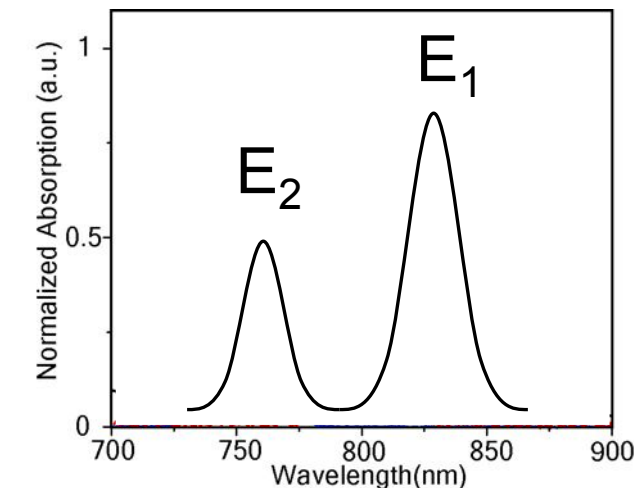
Excitonic Coupling and Photosynthetic Excitons

- Excitonic coupling J can result in delocalized excitations \rightarrow excitons
- Optical transitions correspond to excitonic transitions

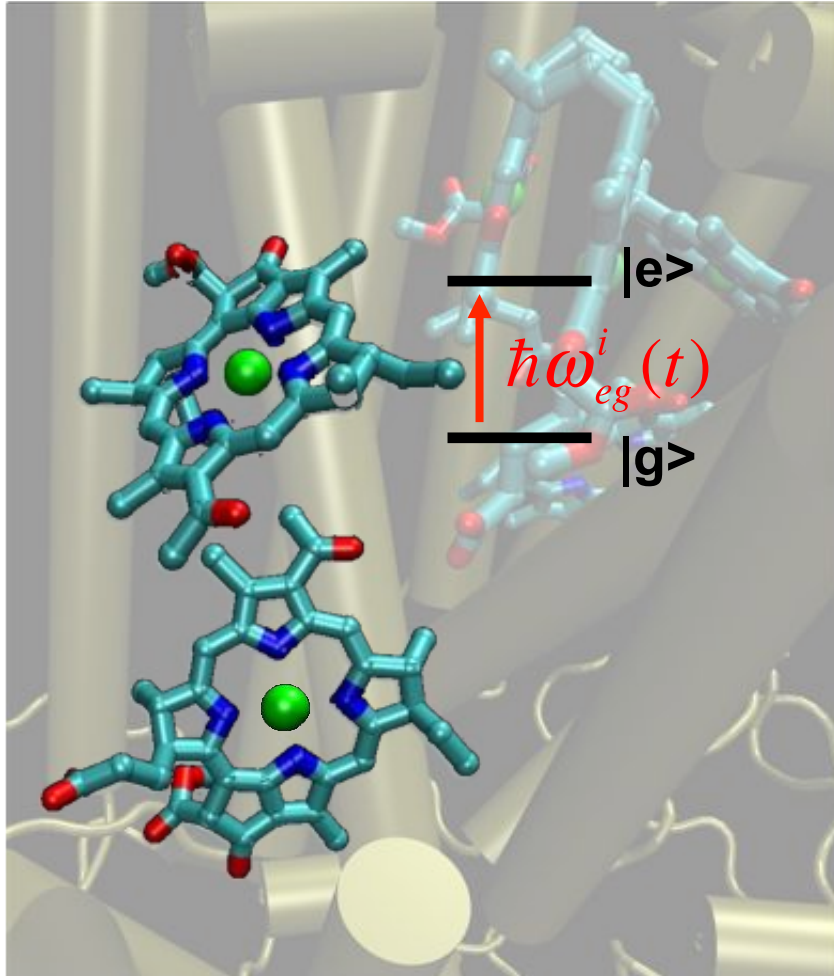


$$H_e = \begin{bmatrix} E_1 & 0 & \dots & 0 \\ 0 & E_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E_N \end{bmatrix}$$

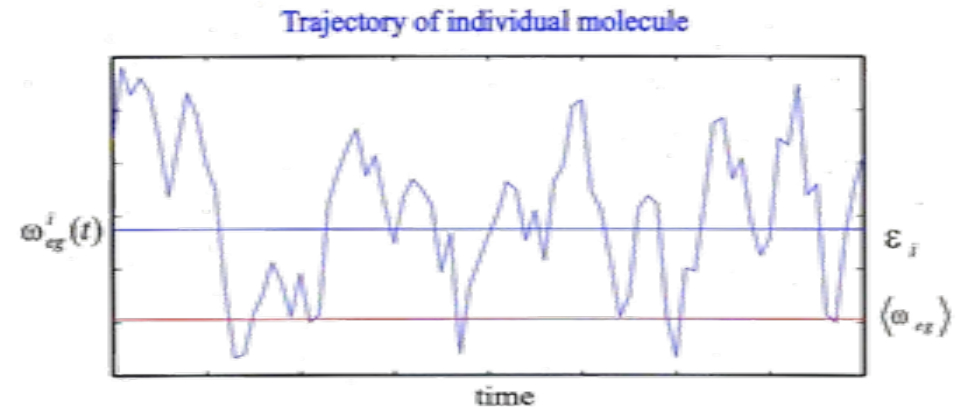
“exciton basis”



Dynamics in the Condensed Phase



Energy of an individual chromophore i modulated by its protein environment:



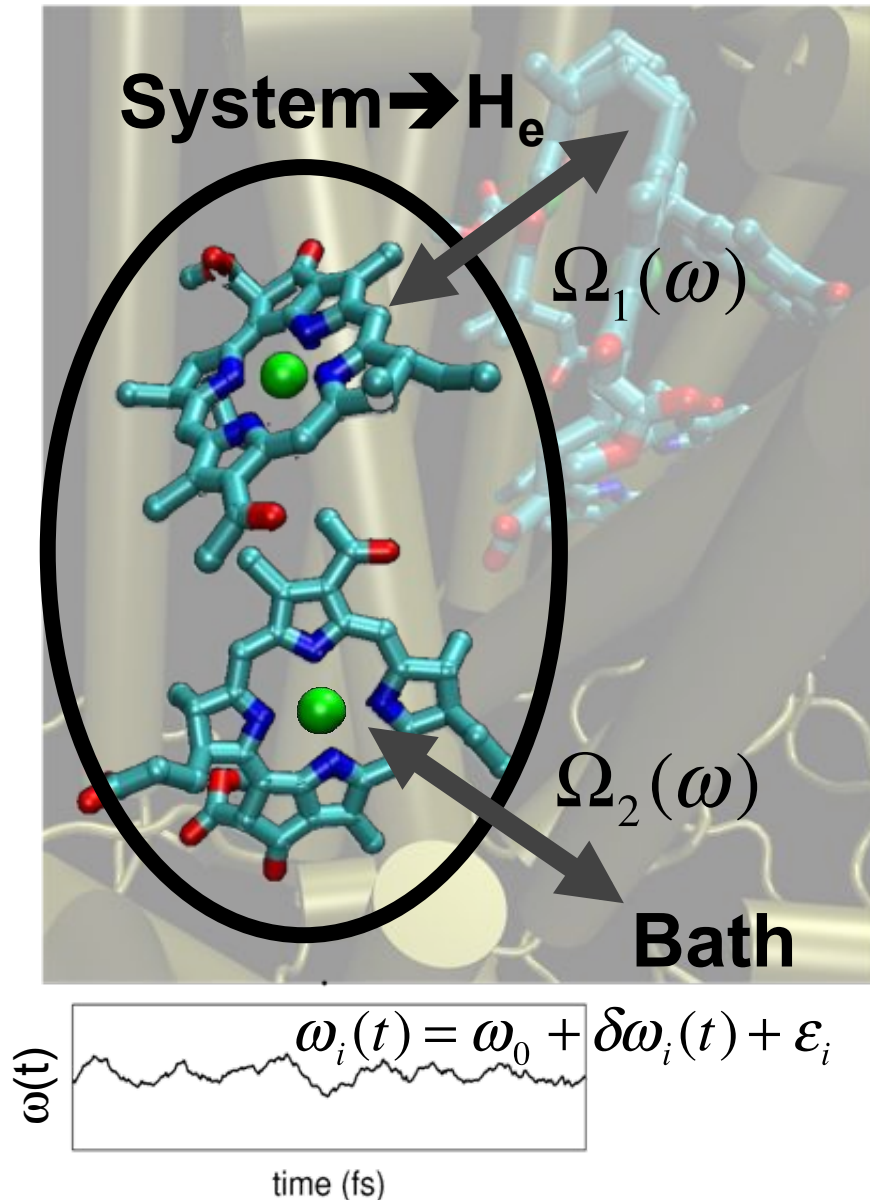
$$\omega_{eg}^i(t) = \langle\omega_{eg}\rangle + \delta\omega_i(t) + \epsilon_i$$

$\delta\omega_i(t) \rightarrow$ fast, dynamical changes

$\epsilon_i \rightarrow$ slow, static changes

$f(\epsilon_i)$: inhomogeneous broadening

Modeling Excitation Energy Transfer: System-Bath Model



- Environments (baths)
 \rightarrow harmonic oscillators
- System-bath couplings
 \rightarrow correlation function:

$$C(t) = \langle \delta\omega(t) \delta\omega(0) \rangle$$

or spectral densities:

$$\Omega(\omega) = \sum_{\alpha} \frac{c_{\alpha}^2}{2m_{\alpha}\omega_{\alpha}} \delta(\omega - \omega_{\alpha})$$

- Reduced density matrix:

$$\rho = \sum_n P_n |\psi_n\rangle \langle \psi_n|$$

$\rightarrow H_e$ and $\Omega(\omega)$ determine the dynamics, $\rho(t)$.

Redfield Picture of Excitation Energy Transfer

When system-bath coupling is weak, we can use Redfield equation to describe energy transfer:

$$\partial_t \rho(t) = -i[H_e, \rho(t)] - \mathfrak{R}[\rho(t)]$$

↙ exciton Hamiltonian
↙ dissipation determined by $\Omega(\omega)$

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1N} \\ \rho_{12} & \rho_{22} & \cdots & \rho_{2N} \\ \vdots & \vdots & & \vdots \\ \rho_{1N} & \rho_{2N} & \cdots & \rho_{NN} \end{bmatrix}$$

↙ population
↙ coherence

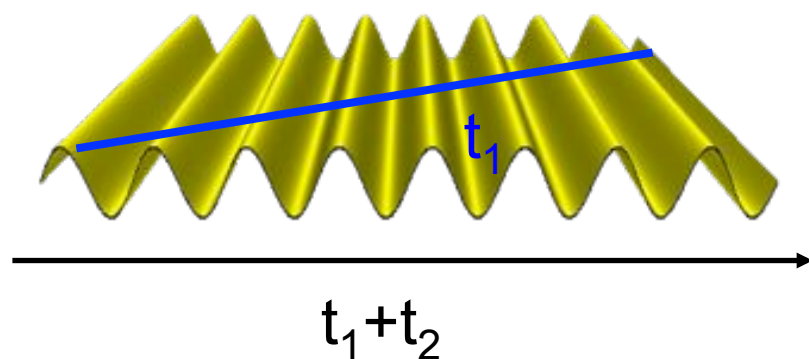
ρ : reduced-system density matrix
 N : number of chromophores

$$\mathfrak{R}[\rho] :$$

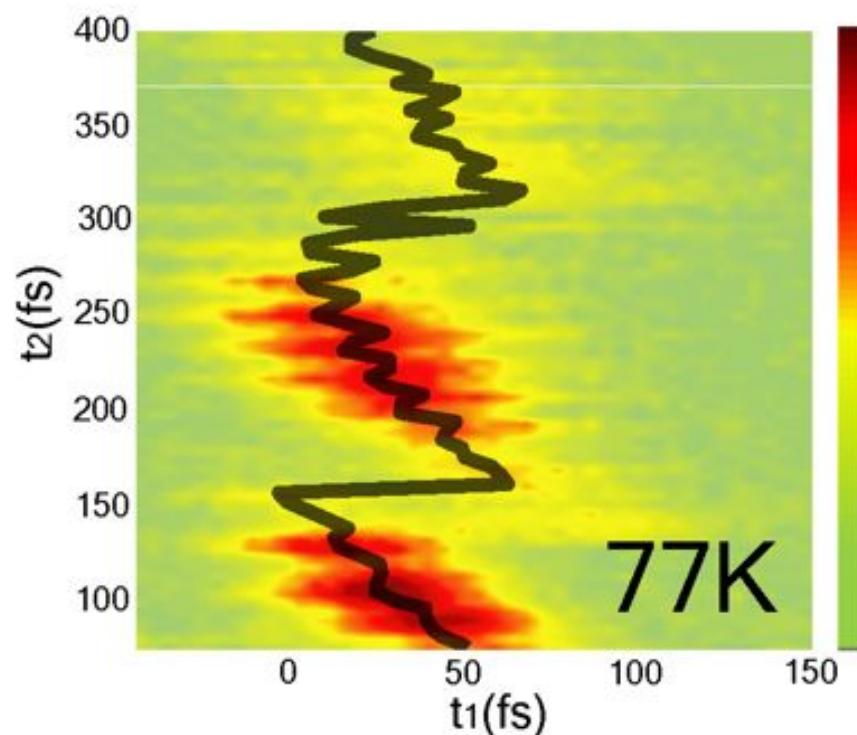
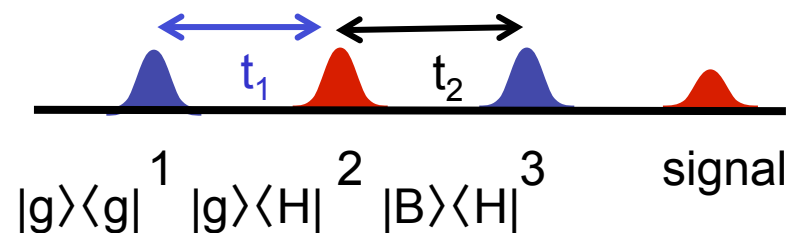
$\rho_{nn} \rightarrow \rho_{mm}$: population dynamics (incoherent)
 $\rho_{nm} \rightarrow \rho_{n'm'}$: coherence dynamics

Sawtooth Pattern from Vibrational Coherence

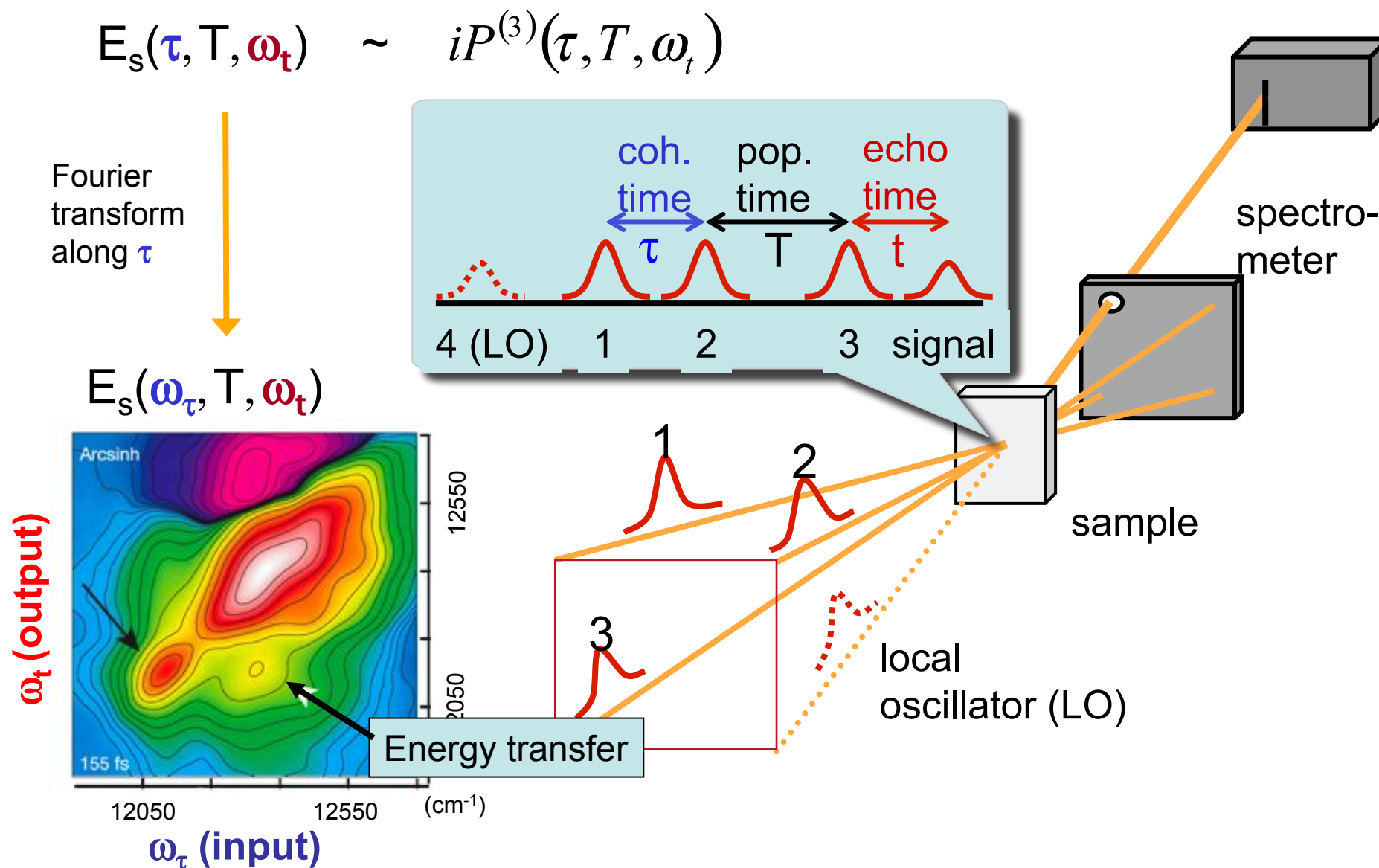
Vibrational coherence induced by pulse 1 explains the sawtooth pattern:



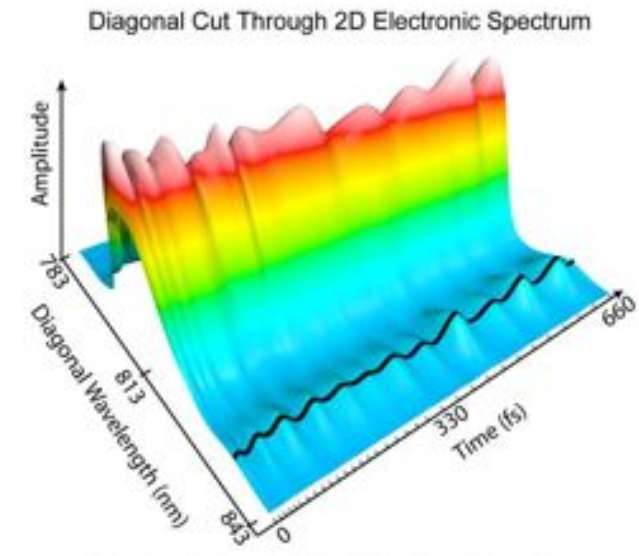
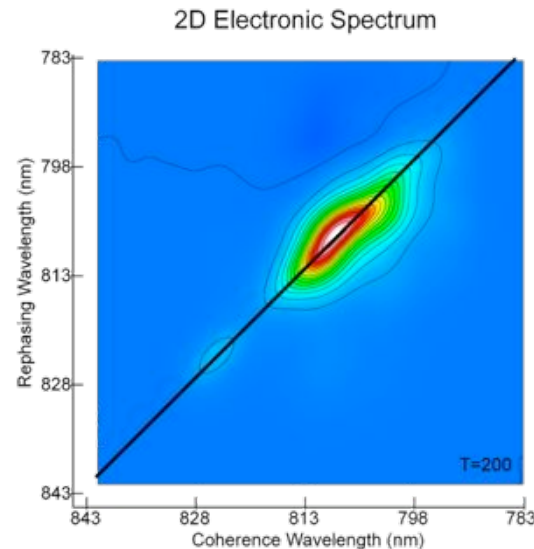
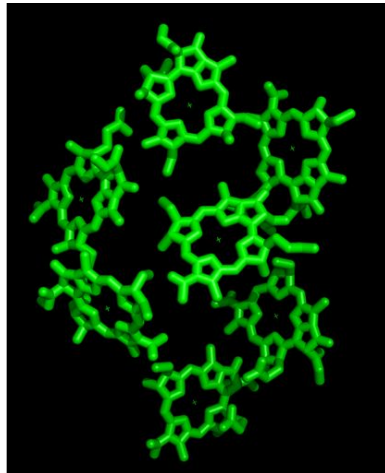
A non-orthogonal cut (t_1) leads to the sawtooth pattern



Two-dimensional Electronic Spectroscopy



Electronic Coherence in FMO (77K)

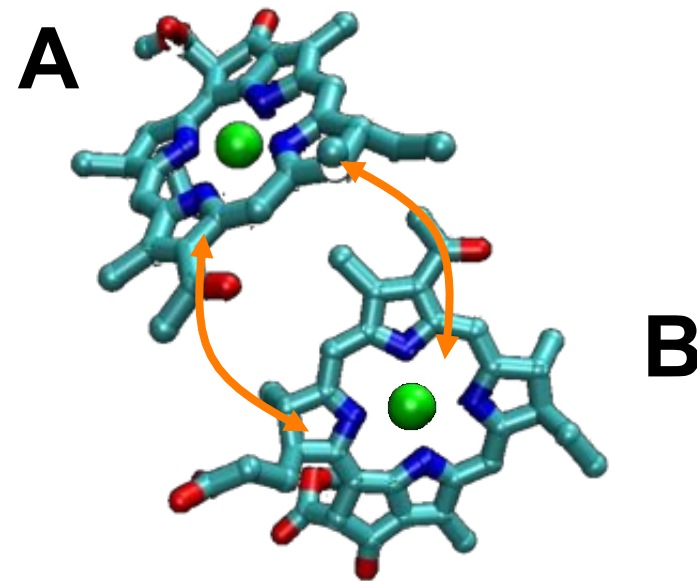
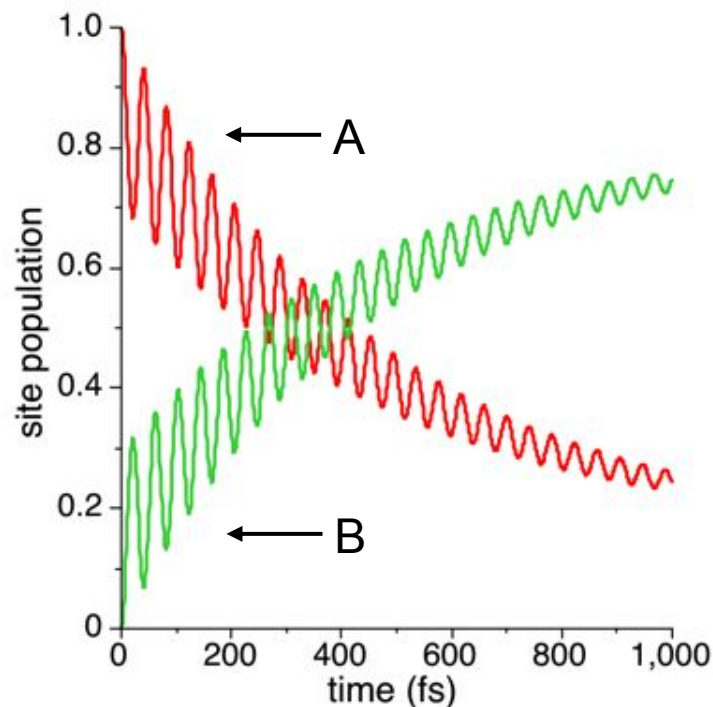


- 2D electronic spectra show quantum beats on the diagonal cuts
- Strong evidence for long-lasting excitonic coherence (> 600 fs) in the Fenna-Matthews-Olson Complex
→ coherent wavelike energy transfer
- True electronic quantum effect may play a role in energy transfer

G.S. Engel, T.R. Calhoun, E.L. Read, T. Ahn, T. Mancal, **Y.-C. Cheng**, R.E. Blankenship & G.R. Fleming, *Nature* **446**, 782 (2007)

Simple Model for Coherence Assisted Energy Trapping

Consider energy transfer within a dimer of two coherently coupled sites:

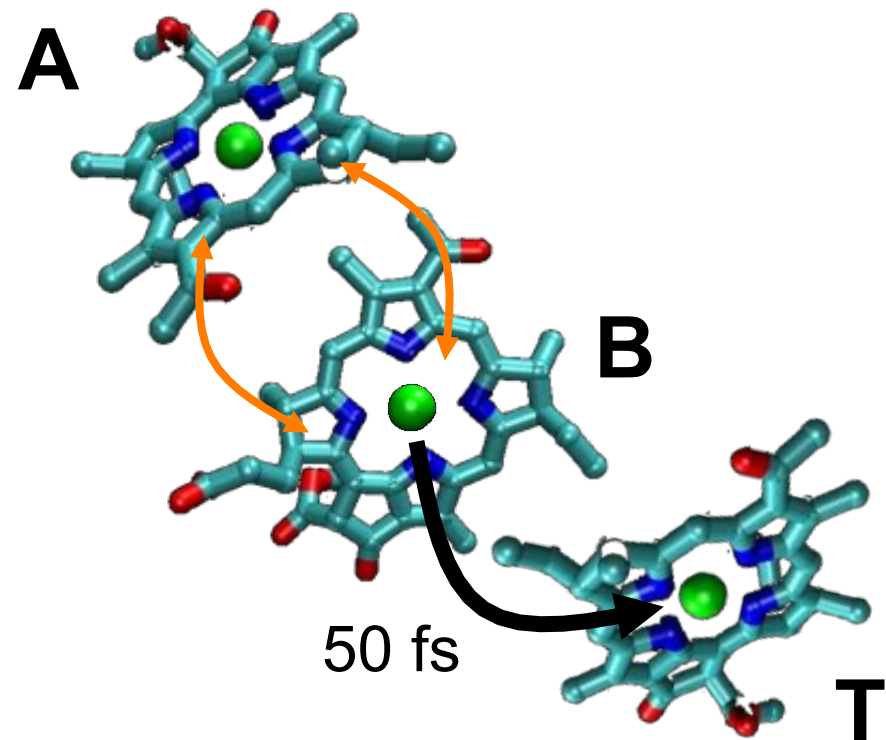
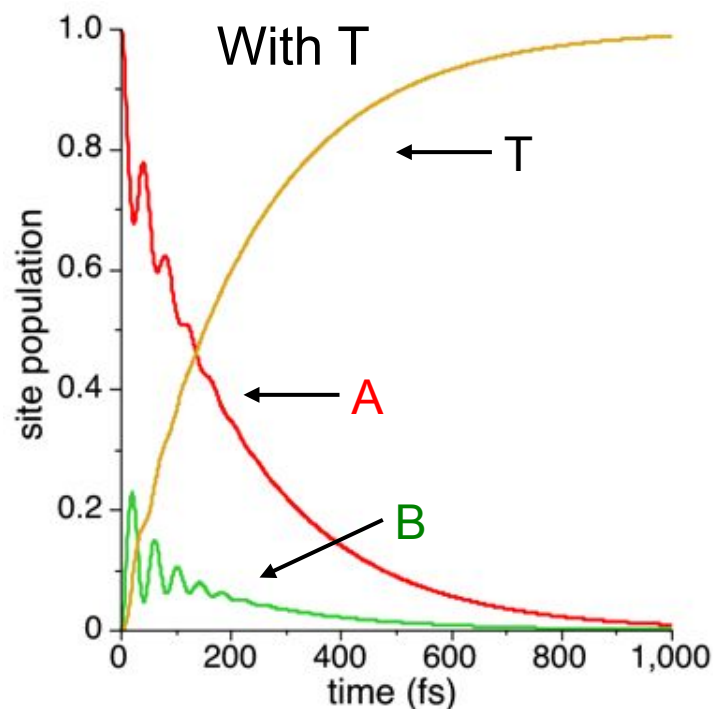


Effective $A \rightarrow B$ time: 500 fs

Bloch dynamics using 450 fs A/B dephasing time, 500 fs intrinsic $A \rightarrow B$ transfer time; actually modeled based on parameters suitable for a photosynthetic reaction center

Simple Model for Coherence Assisted Energy Trapping

Adding rapid trapping by T results in rapid A population decay
➔ only possible because of coherent oscillation

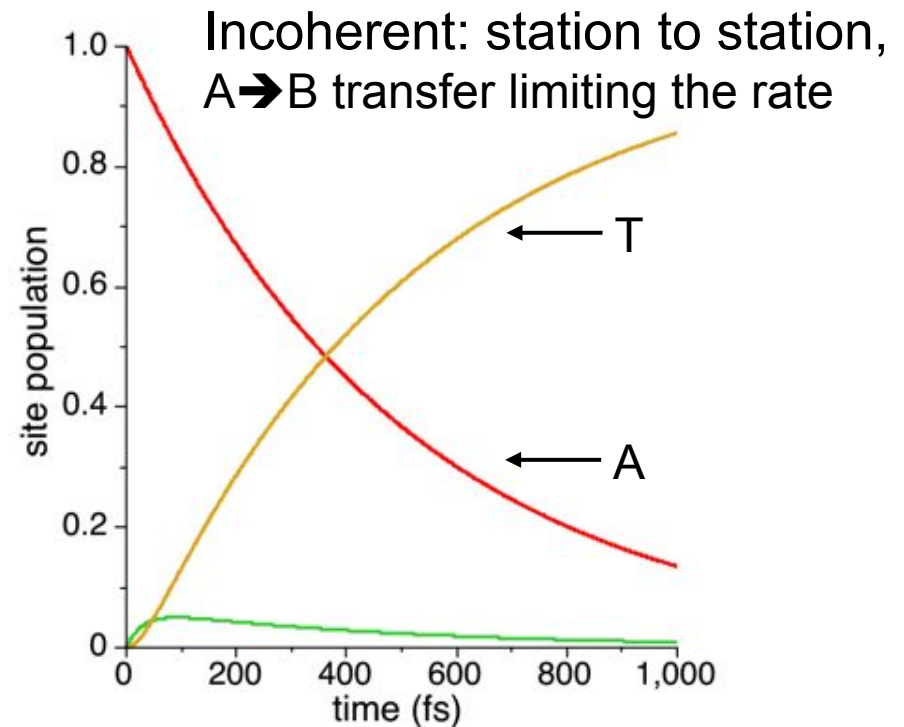
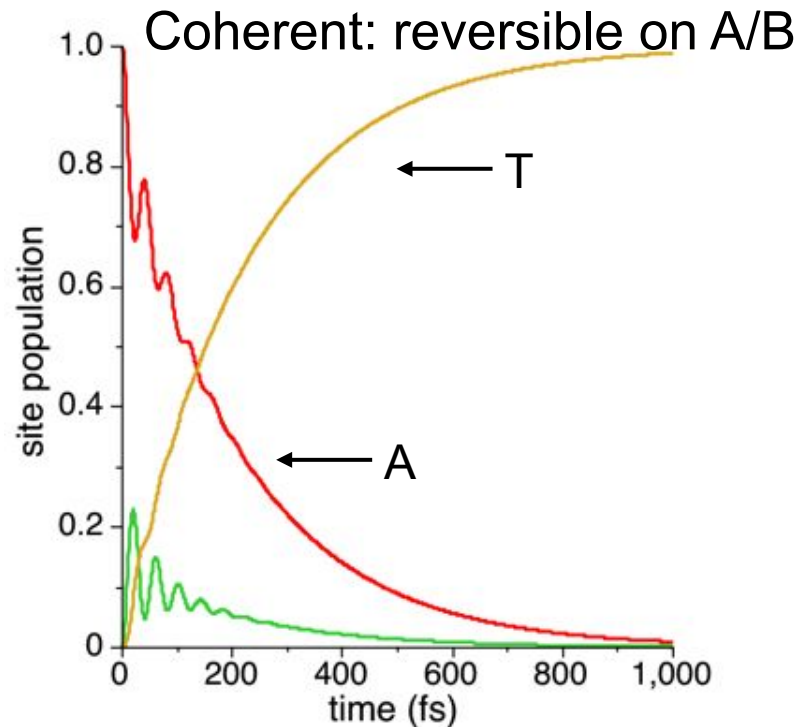


T efficiently captures energy on B at the maxima!!

450 fs A/B dephasing time, 500 fs A→B transfer time, 50 fs B→T time.

Simple Model for Coherence Assisted Energy Trapping

Quantum coherence promotes the efficiency of light capture



This model explains efficient excitation energy trapping in the photosynthetic reaction center of purple bacteria