Photosynthetic Light Harvesting and Electronic Quantum Coherence Effects

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Summer Lectures on QIS:
Quantum Transport in Chaotic and Disordered Systems,
National Center for Theoretical Sciences (South), Tainan, Taiwan
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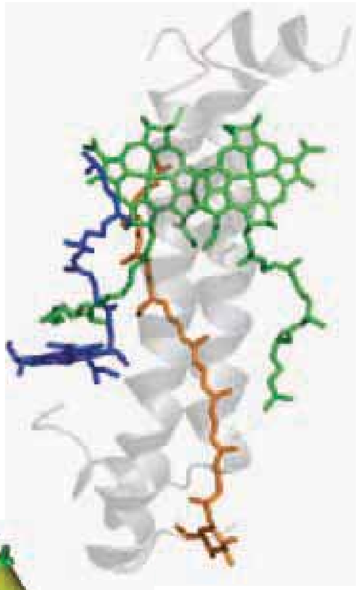
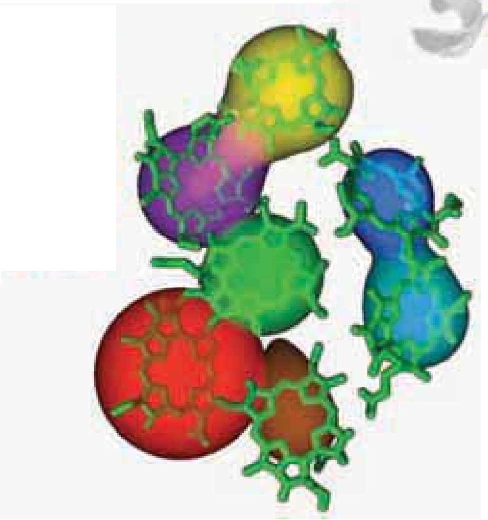
Outline

- Part I: Introduction to photosynthetic light harvesting & theoretical backgrounds
- Part II: Quantum coherence in LH2 from purple bacteria – optimization of light harvesting through delocalization of excitons
- Part III: Excitonic quantum coherence in light harvesting – coherence assistant excitation energy transfer





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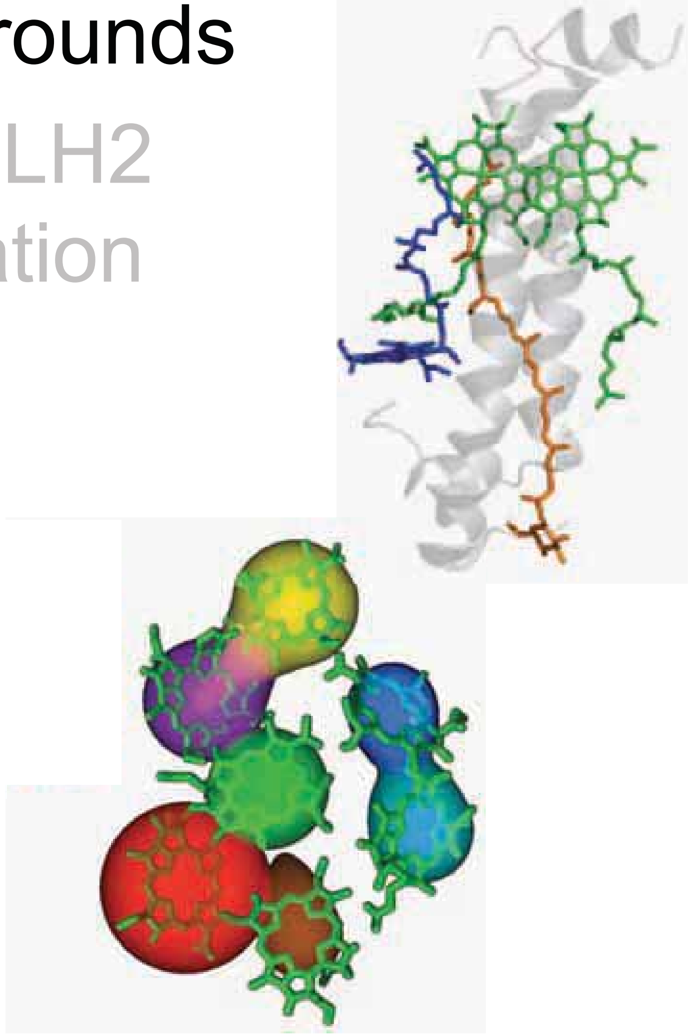
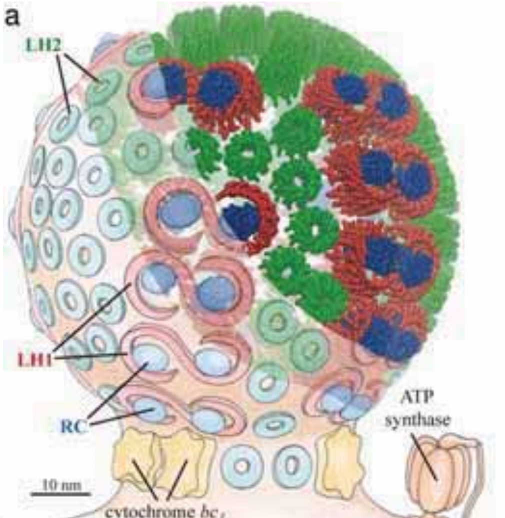
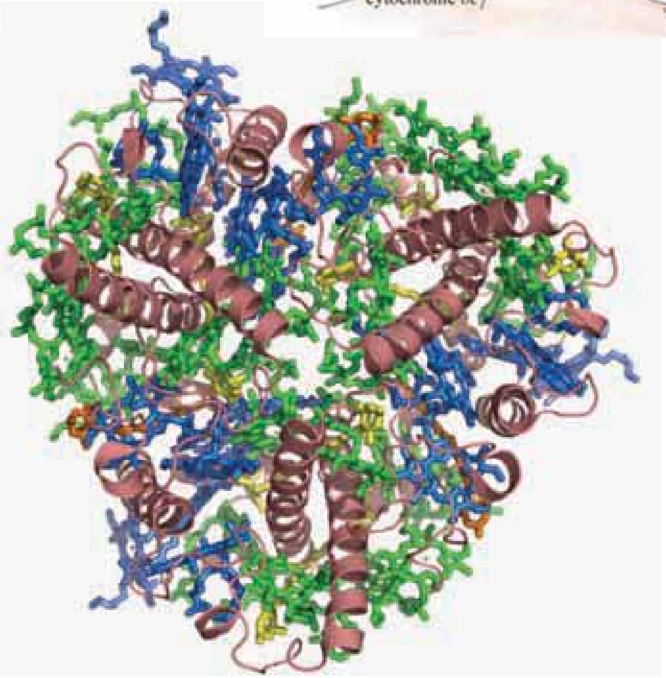


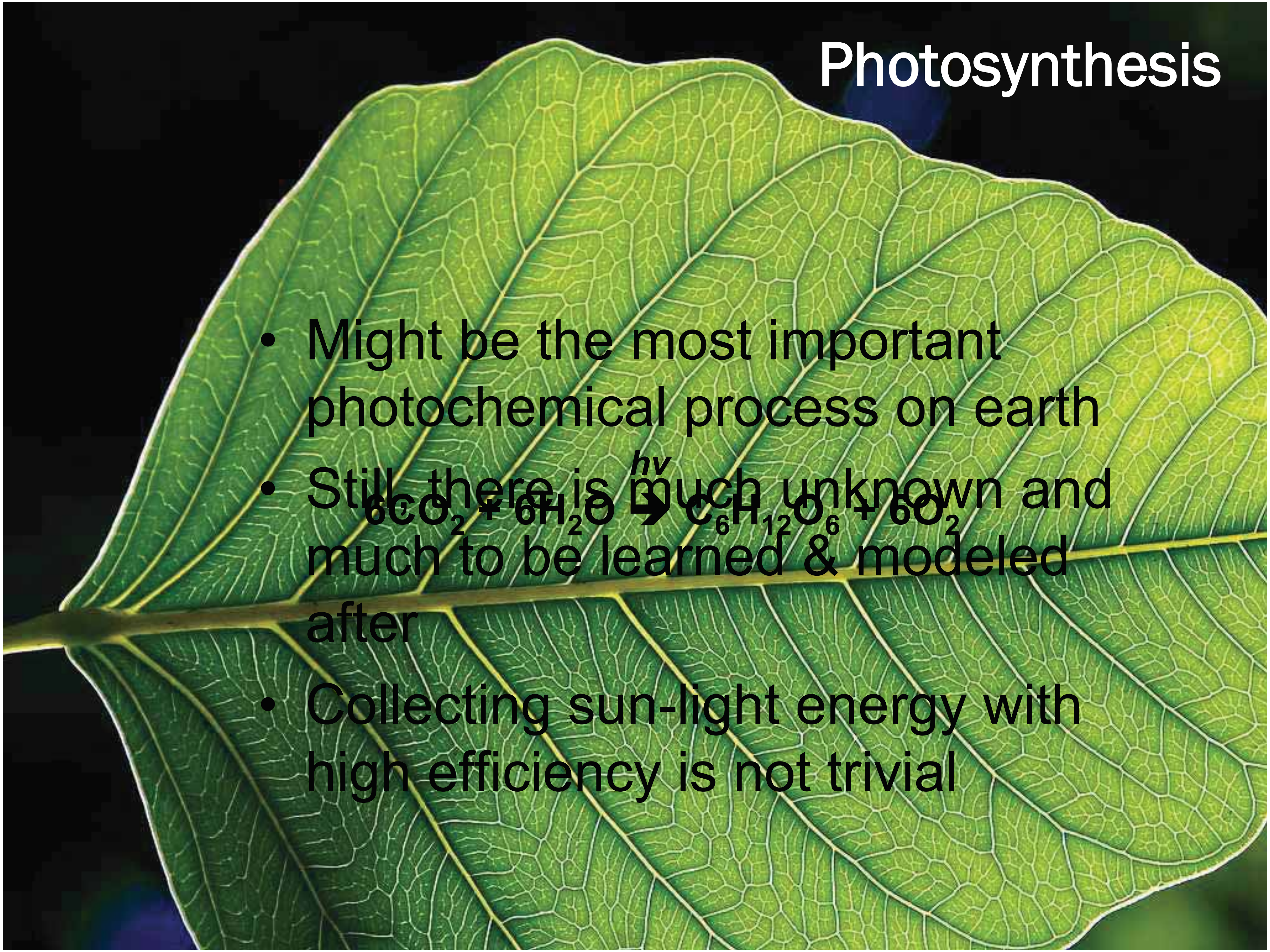
Outline (Part I)

- Brief introduction to photosynthetic light harvesting
- Architectures of photosynthetic light-harvesting apparatus: purple bacteria, green sulfur bacteria, and plants
- Theoretical descriptions for excitation energy transfer in photosynthesis





Photosynthesis

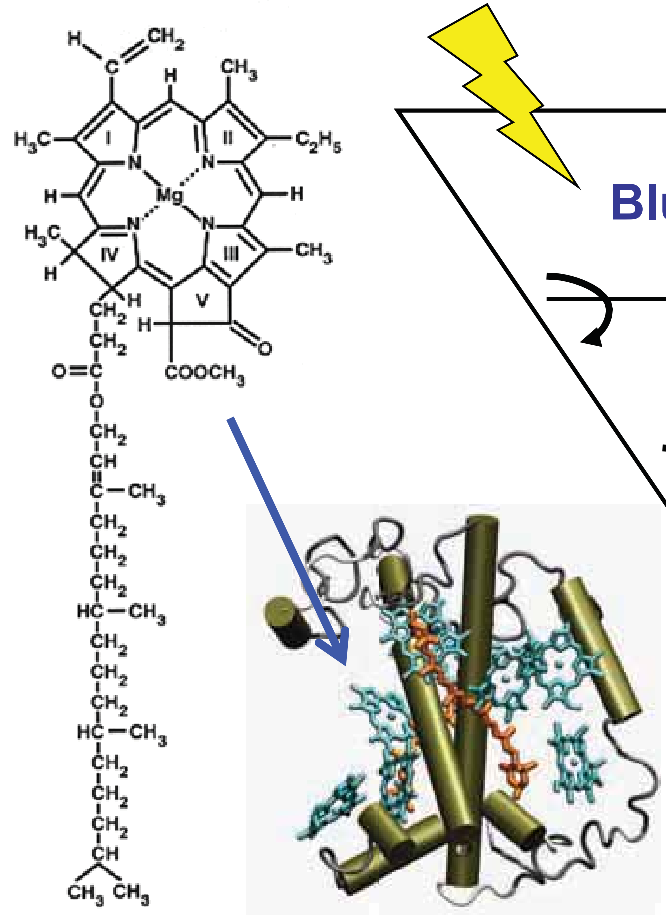


- Might be the most important photochemical process on earth
- Still, there is much unknown and much to be learned & modeled after
- Collecting sun-light energy with high efficiency is not trivial

$$6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$$

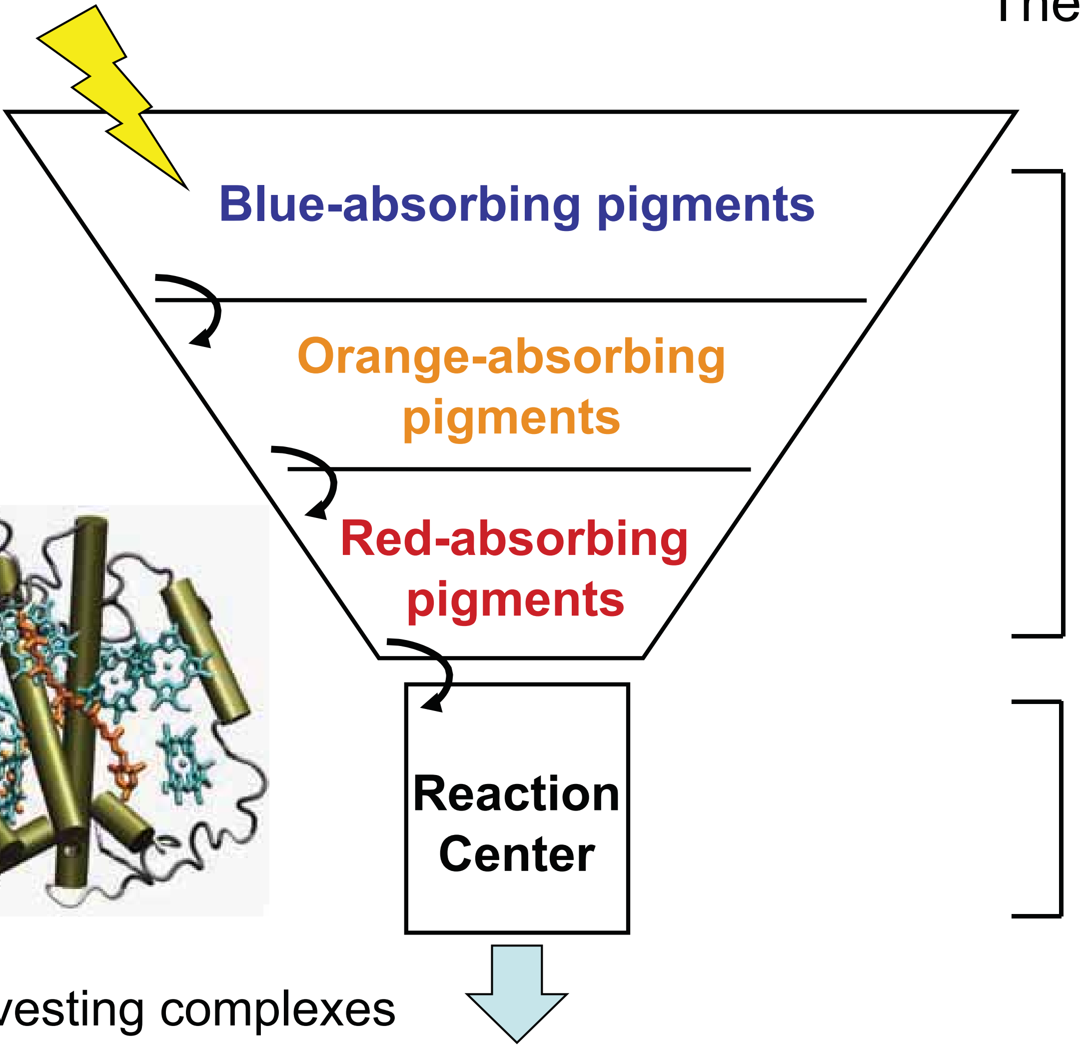
Light Harvesting in Photosynthesis

The “light” reactions



Chlorophyll *a*

Light-harvesting complexes



Blue-absorbing pigments

Orange-absorbing pigments

Red-absorbing pigments

Reaction Center

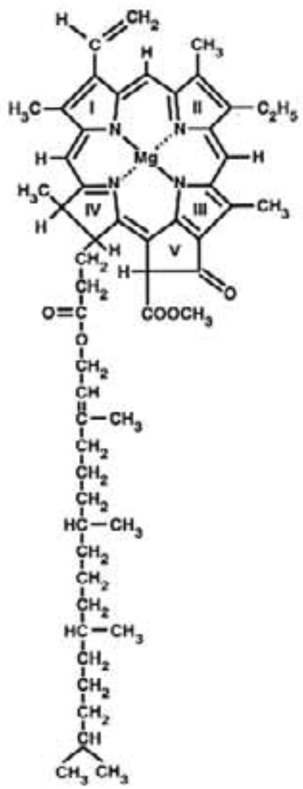
“Antenna”
Light Harvesting

Charge separation

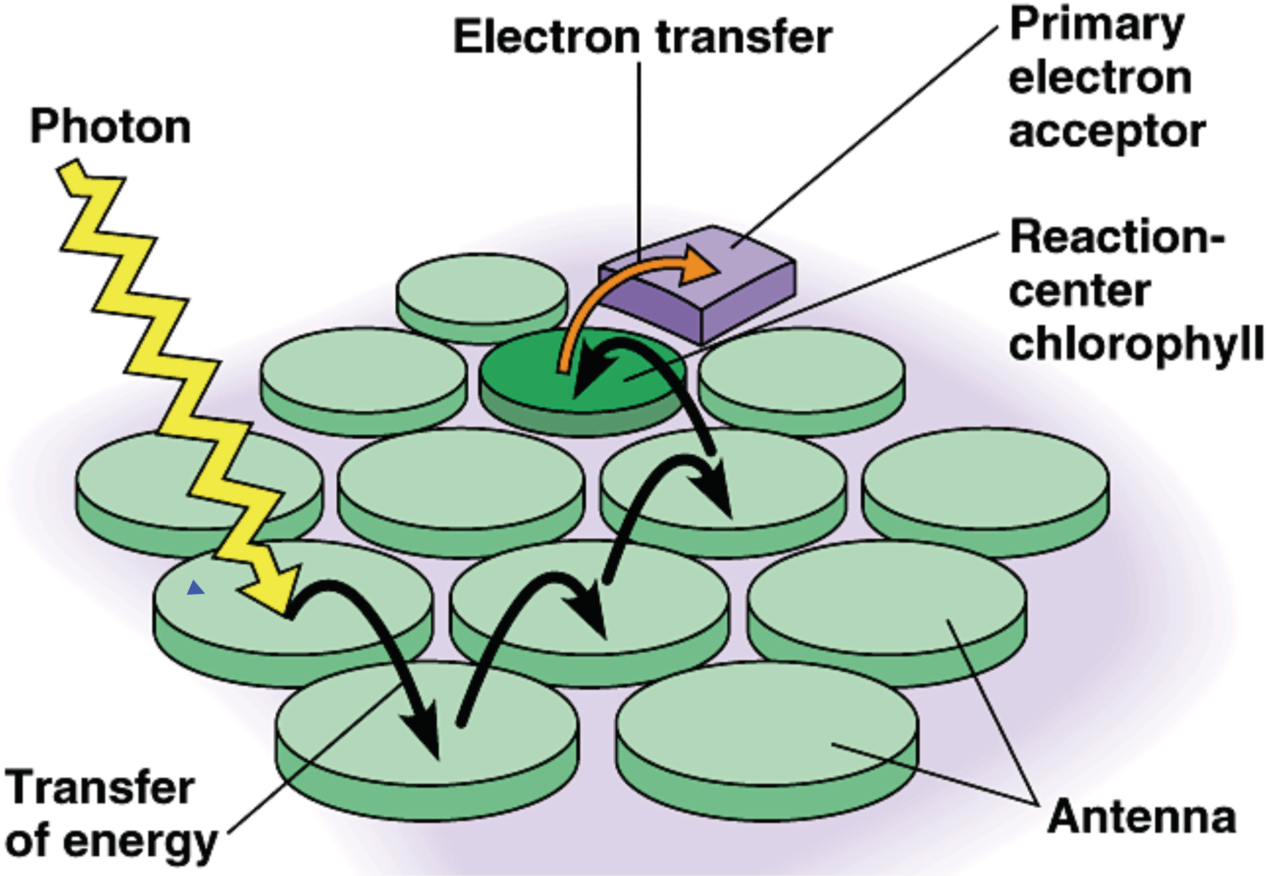
…Secondary electron transfer reactions, Water splitting, Proton transport across thylakoid membrane, Reduction of NADP$^+$, ATP synthesis…

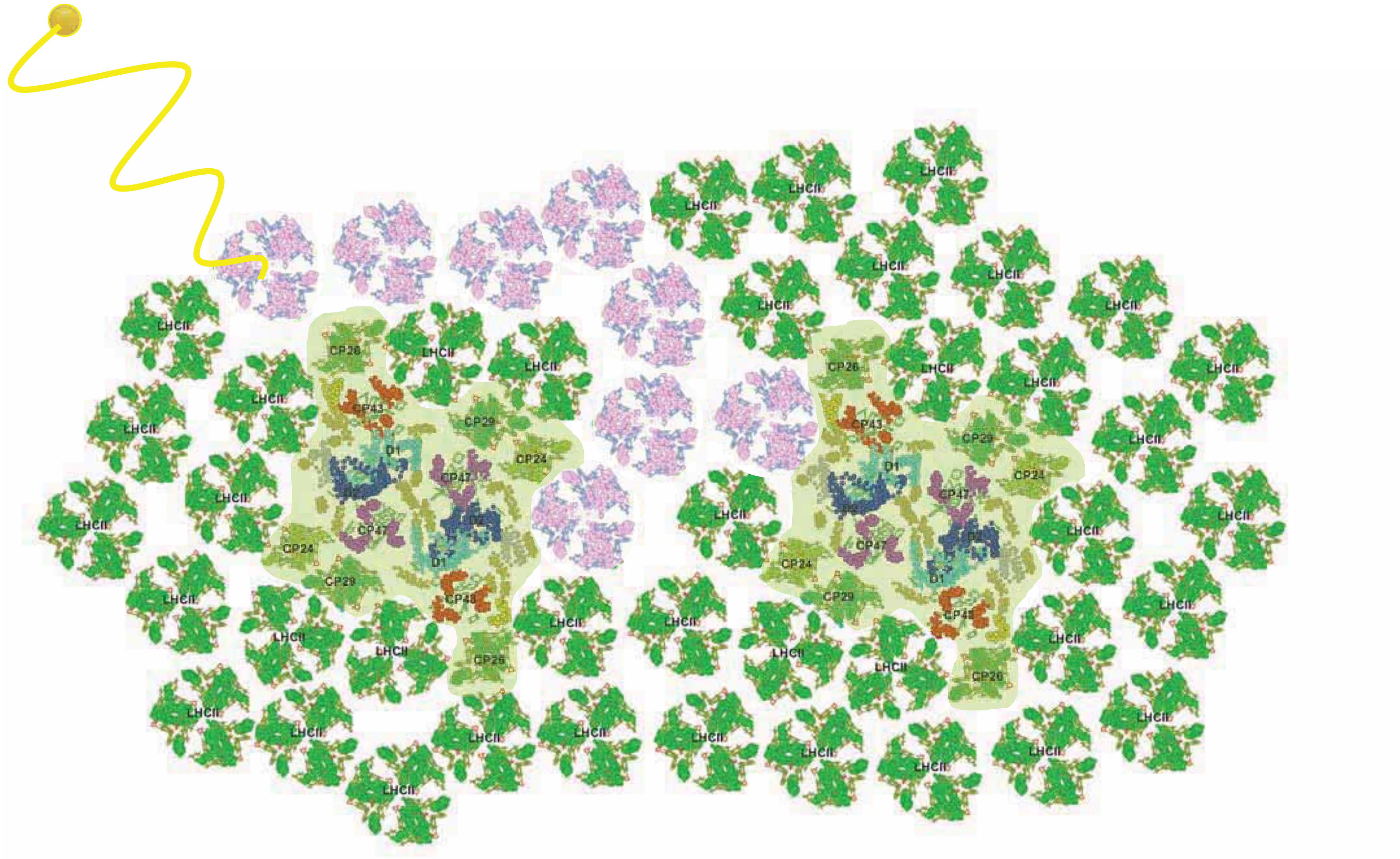
Primary Processes of Photosynthesis

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



Chlorophyll *a*



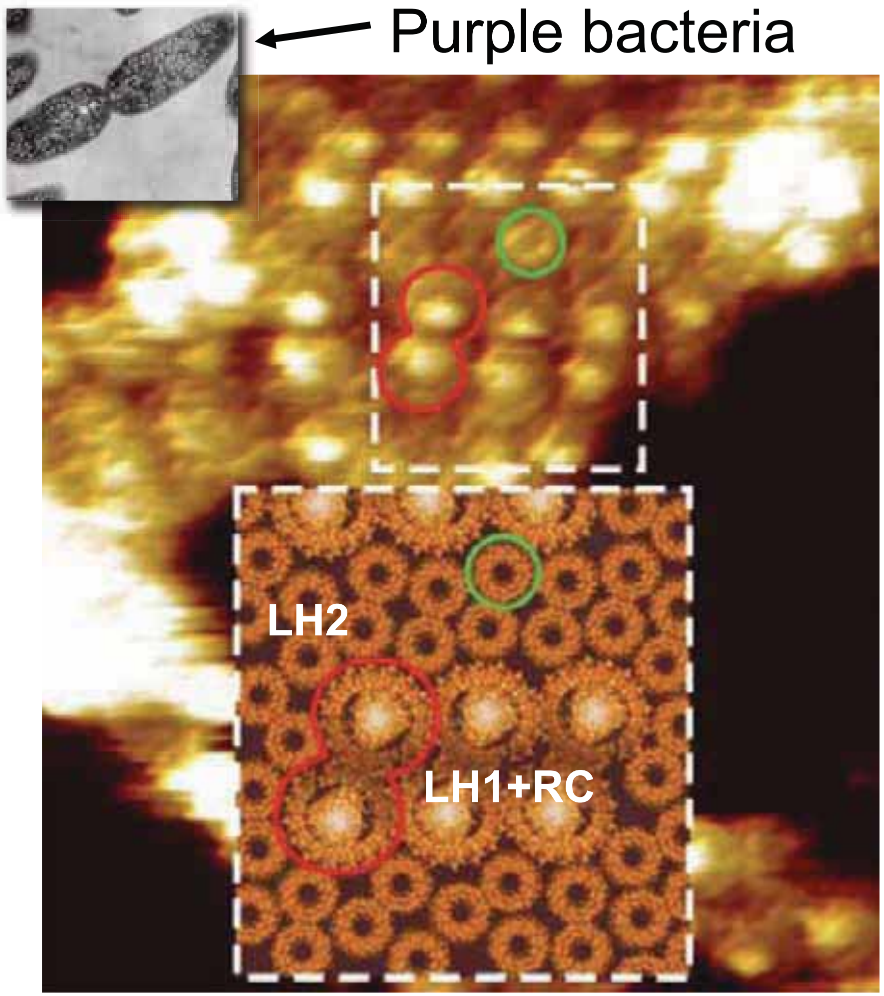


PHOTOSYNTHESIS

Bassi Group

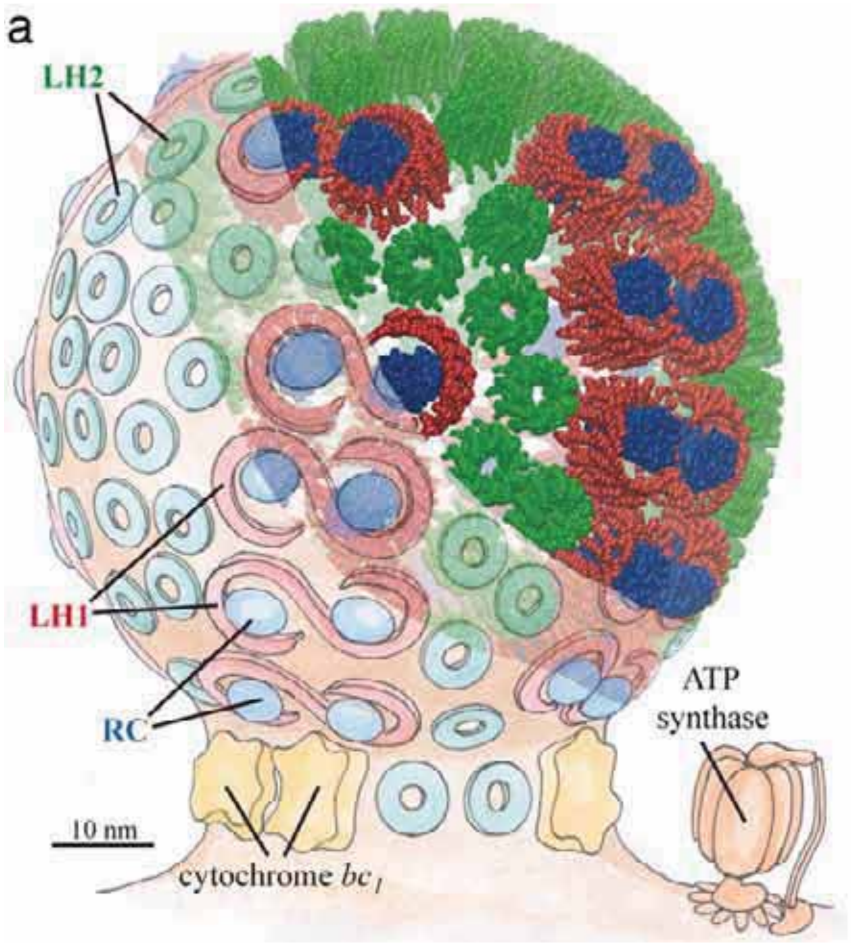
Plant photosystem II

Light-harvesting Apparatus of Purple Bacteria



AFM of native photosynthetic membranes of a purple bacterium

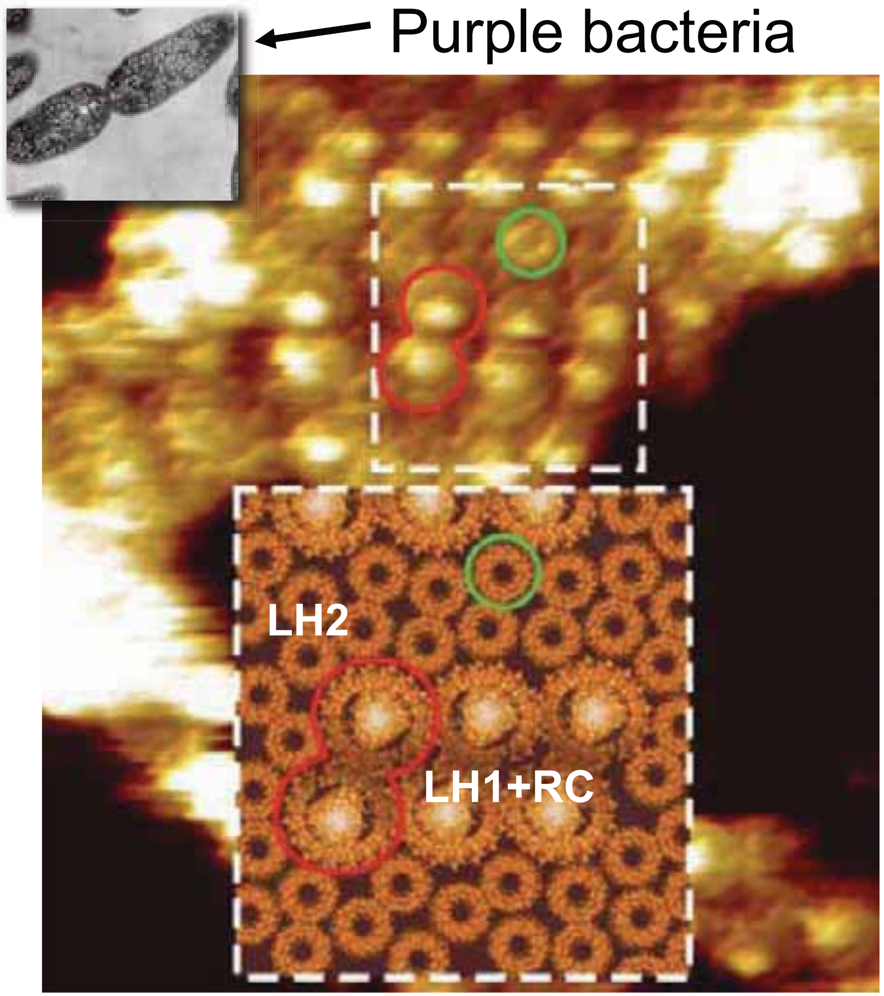
Bahatyrova et al., *Nature* **430**, 1058 (2004)



Architecture of a spherical chromatophore vesicle

Şener M K et al. PNAS 2007;104:15723-15728

Light-harvesting Apparatus of Purple Bacteria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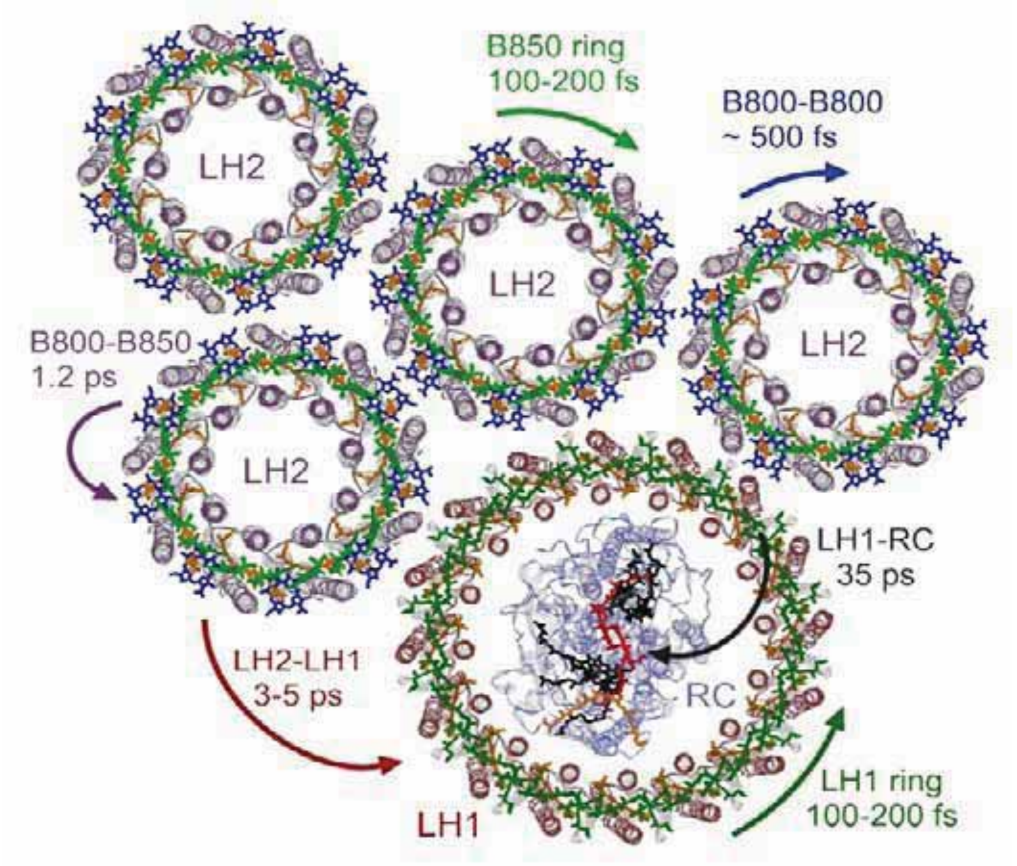
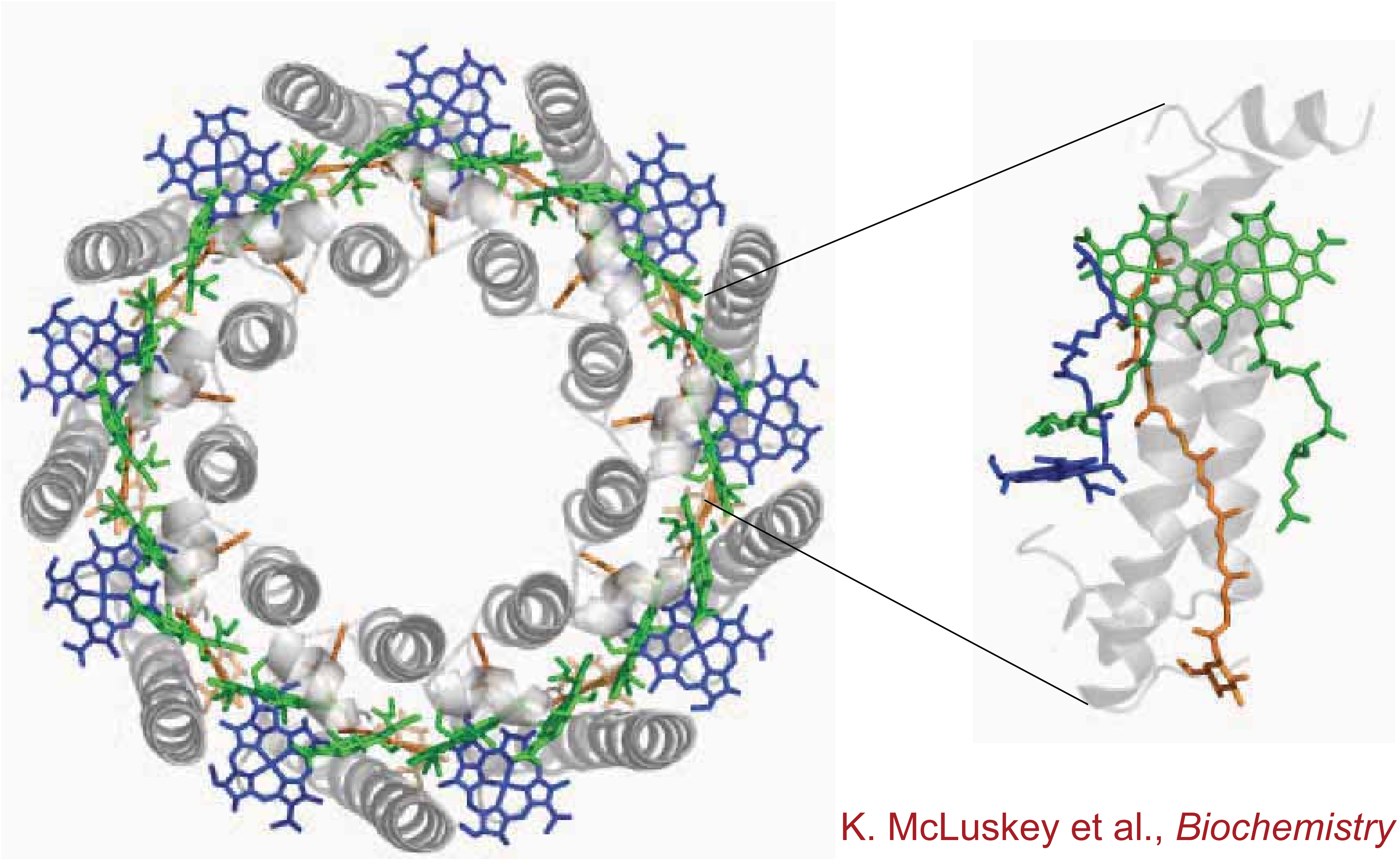


Hu et al., *Q. Rev. Biophys.* **35**, 1 (2002)

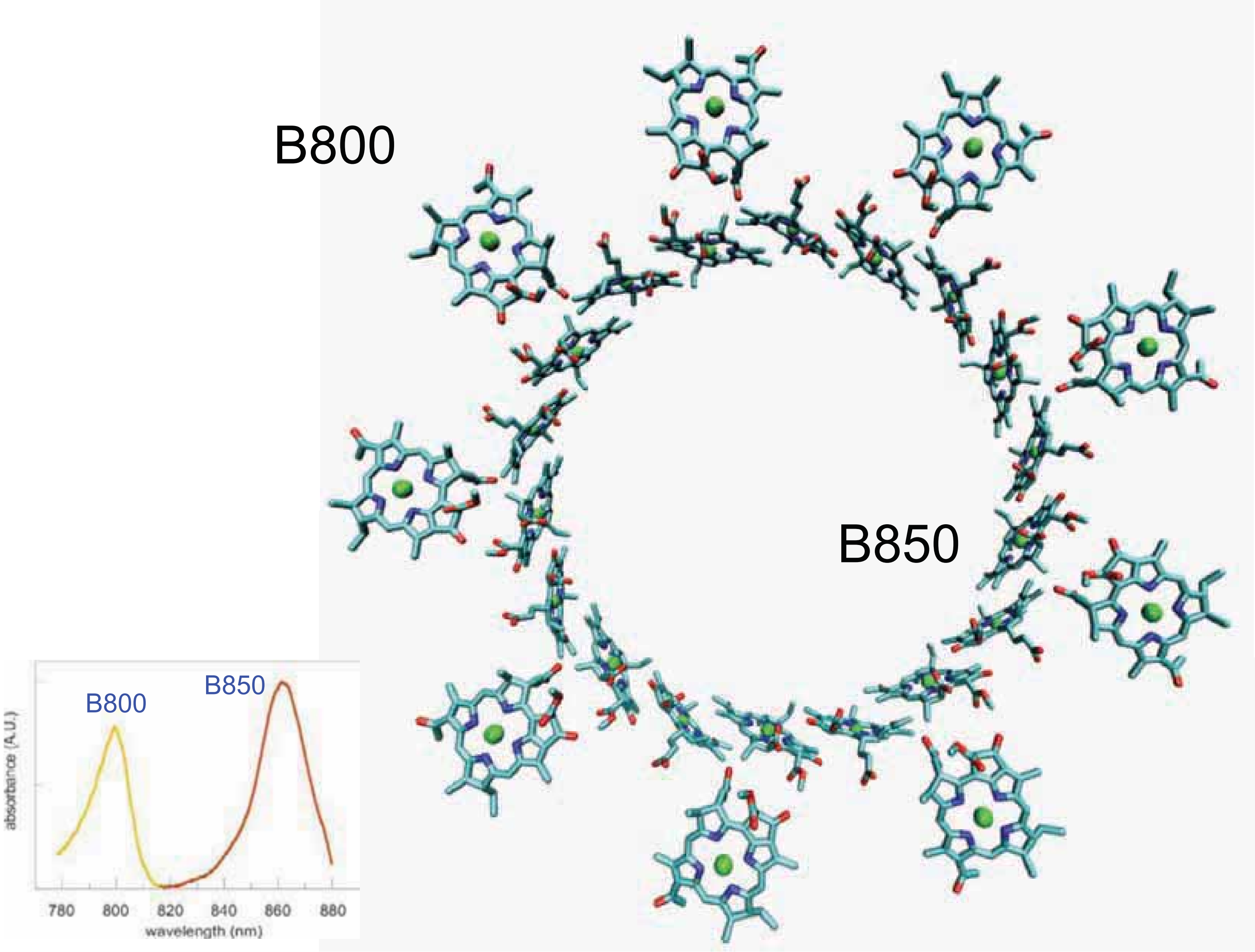
Photosynthetic Pigment-Protein Complexes



LH2 from Rhodopseudomonas acidophila Strain 7050

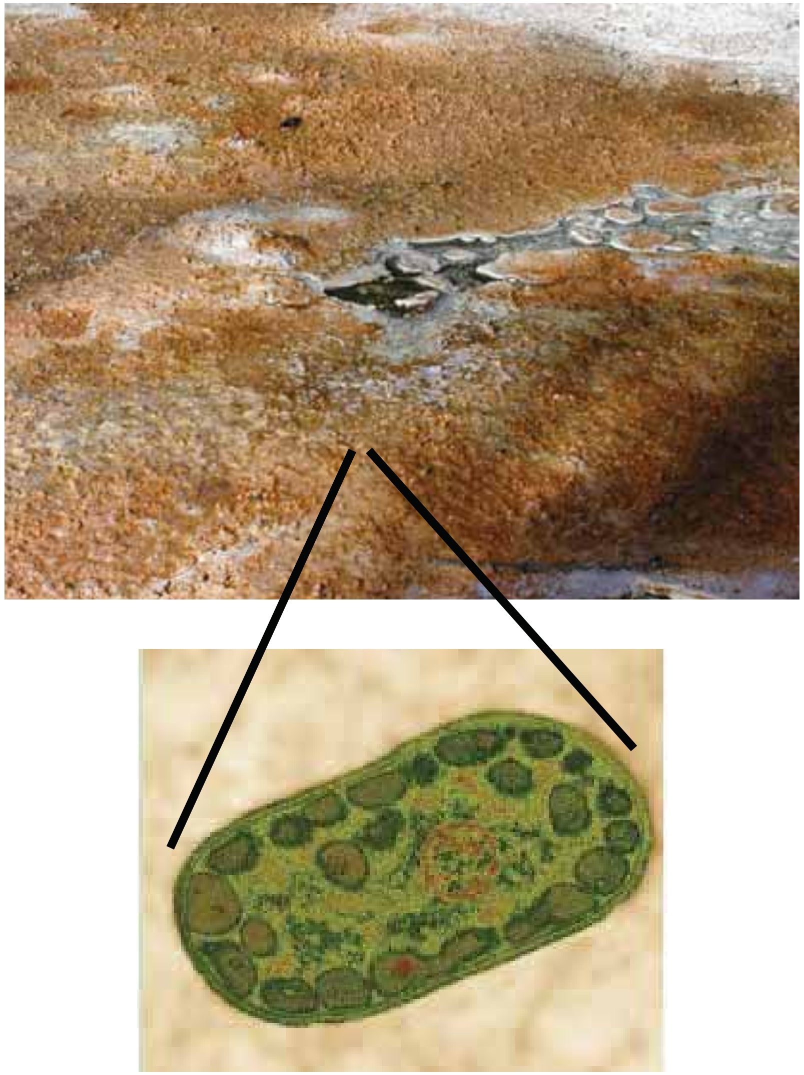
K. McLuskey et al., *Biochemistry* **40**, 8713 (2001).

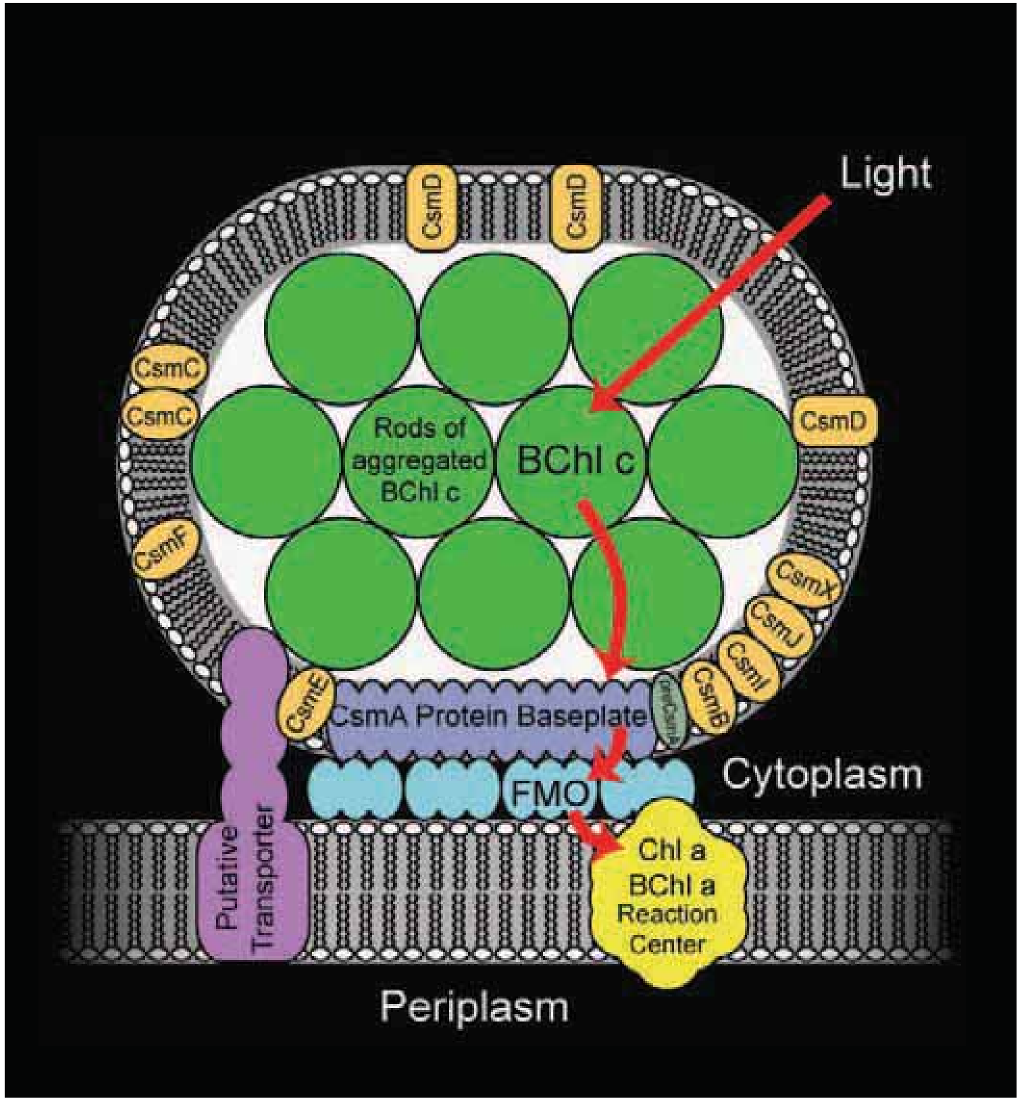
Bacterial Chlorophyll Arrangement in LH2



Ensemble abs. spectrum of LH2 (J. Kohler)

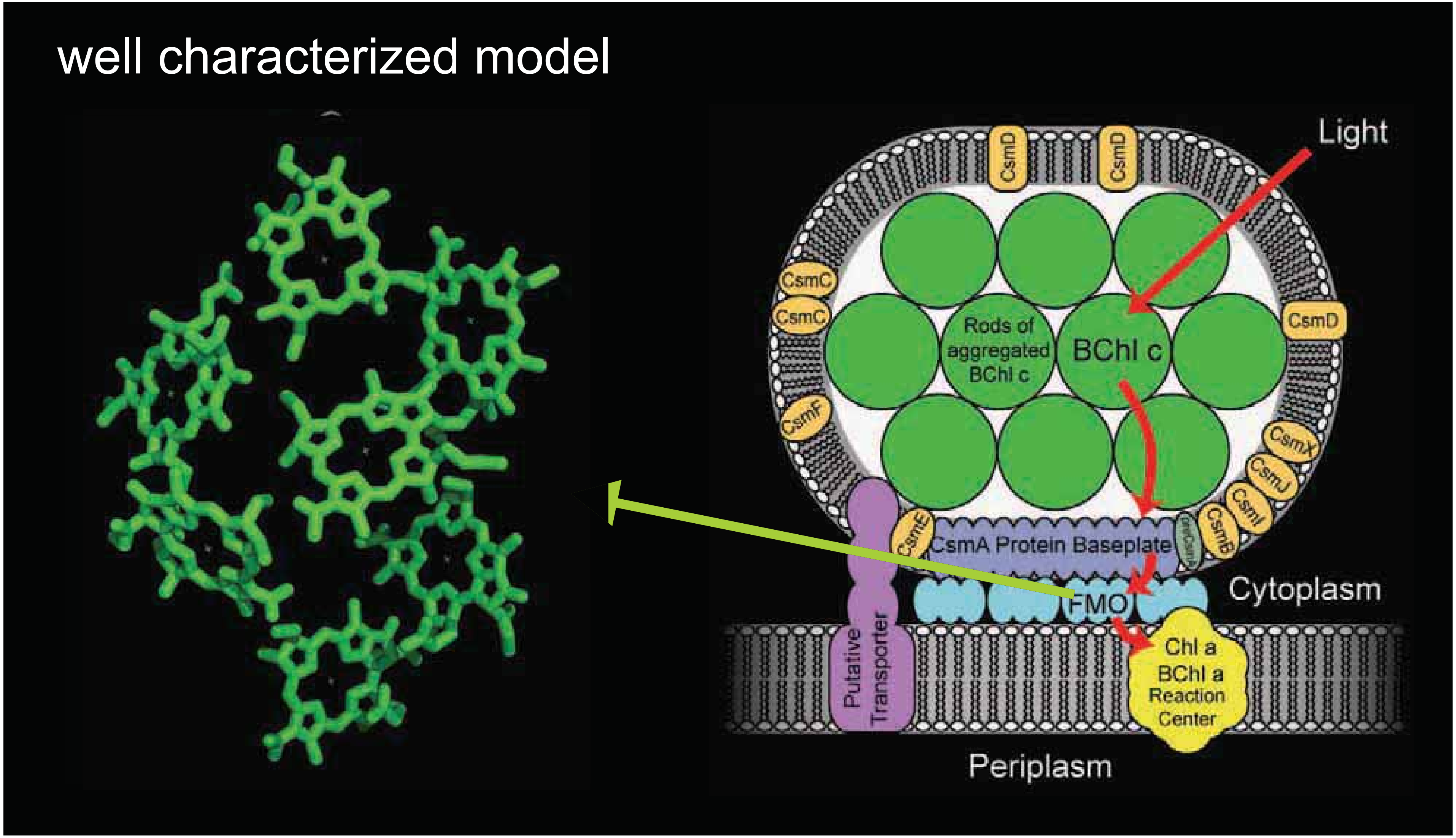
Light-harvesting Apparatus of Green Sulfur Bacteria





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

Fenna-Matthews-Olson Complex from Green Sulfur Bacteria

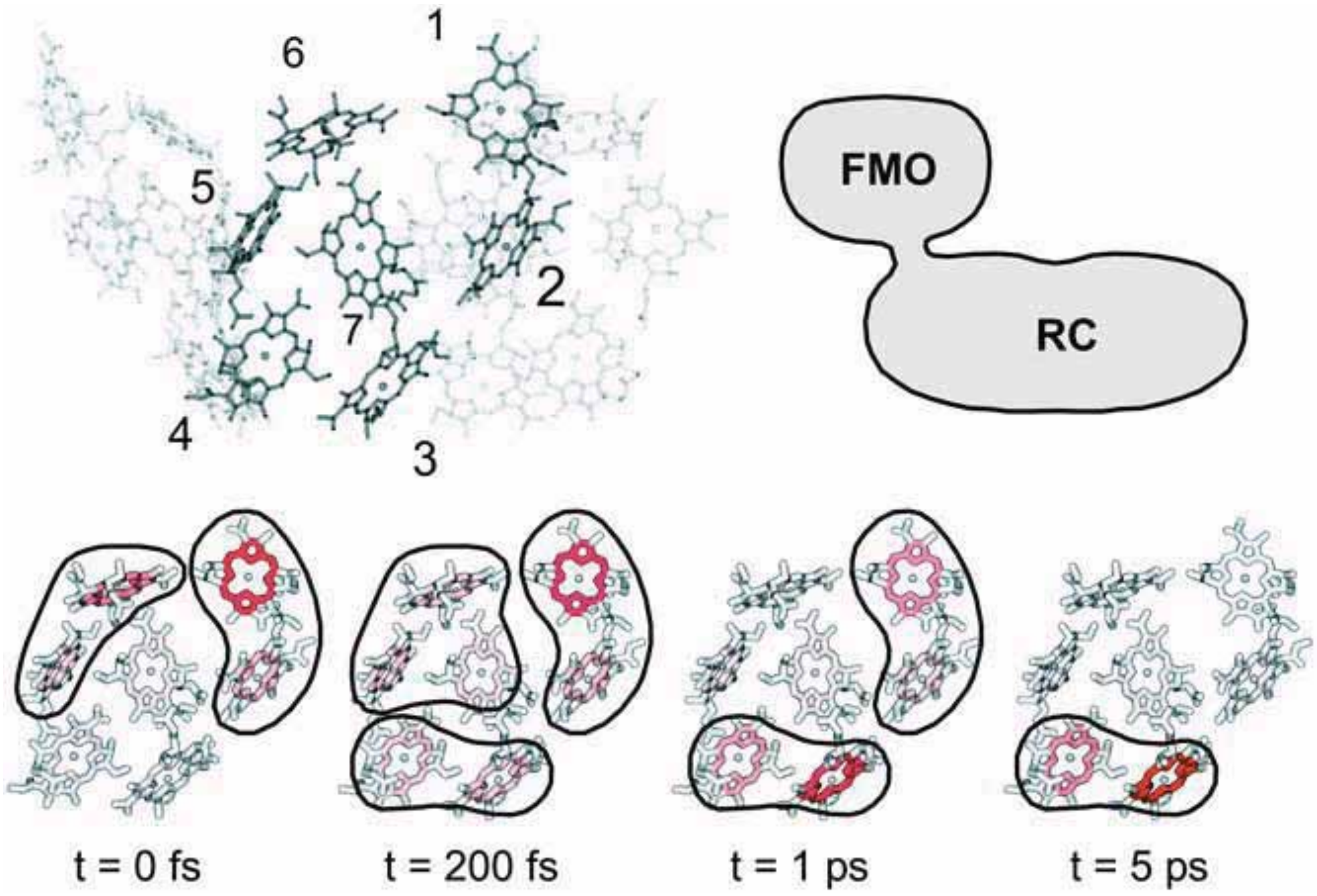


well characterized model

PDB ID: 4bcl, 1m50

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

Energy Transfer Time Scales in FMO

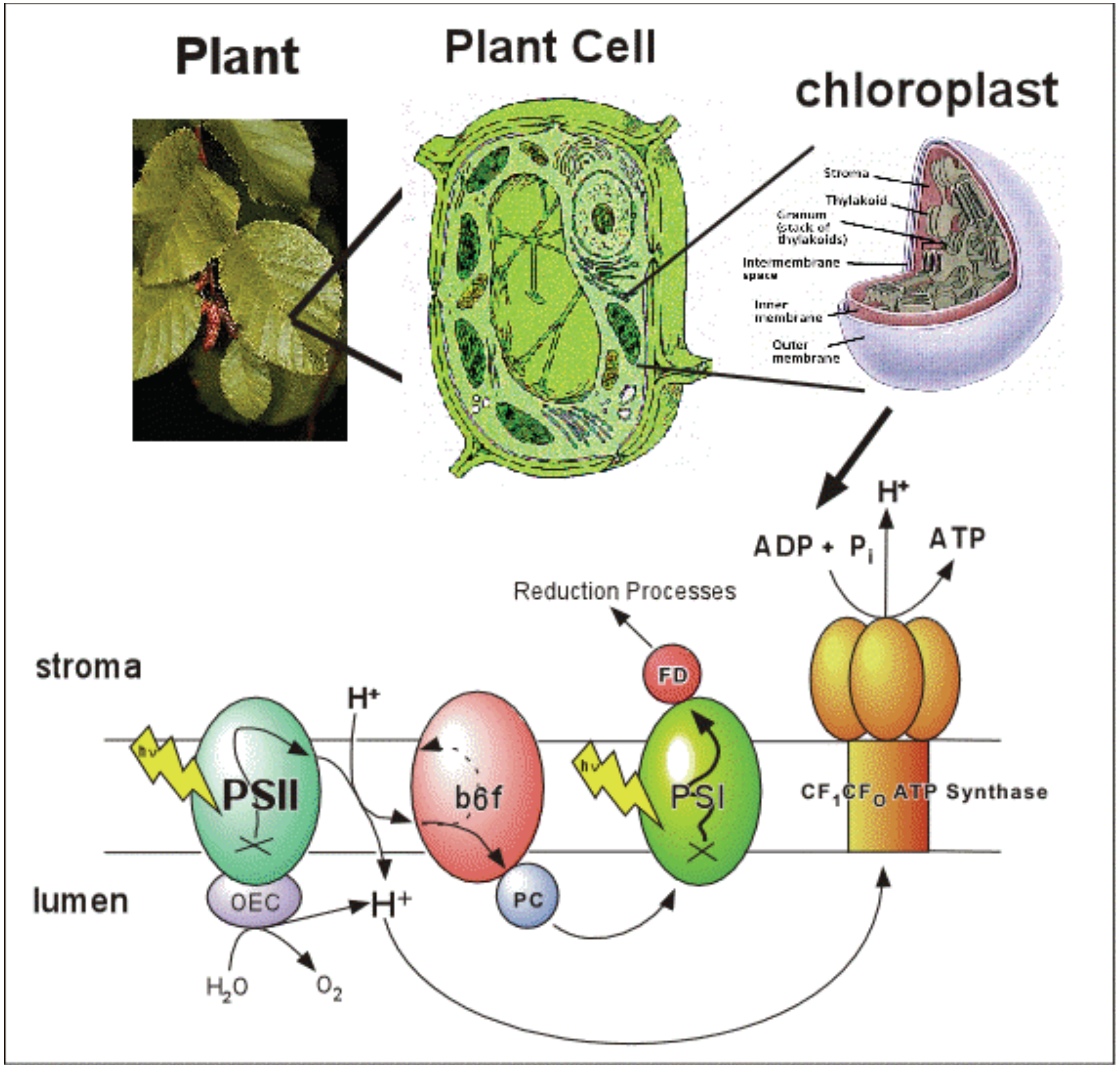


t = 0 fs
t = 200 fs
t = 1 ps
t = 5 ps

Energy transfer from one end to the other in a few ps

J. Adolphs & T. Renger, Biophys. J. 91, 2778 (2006).

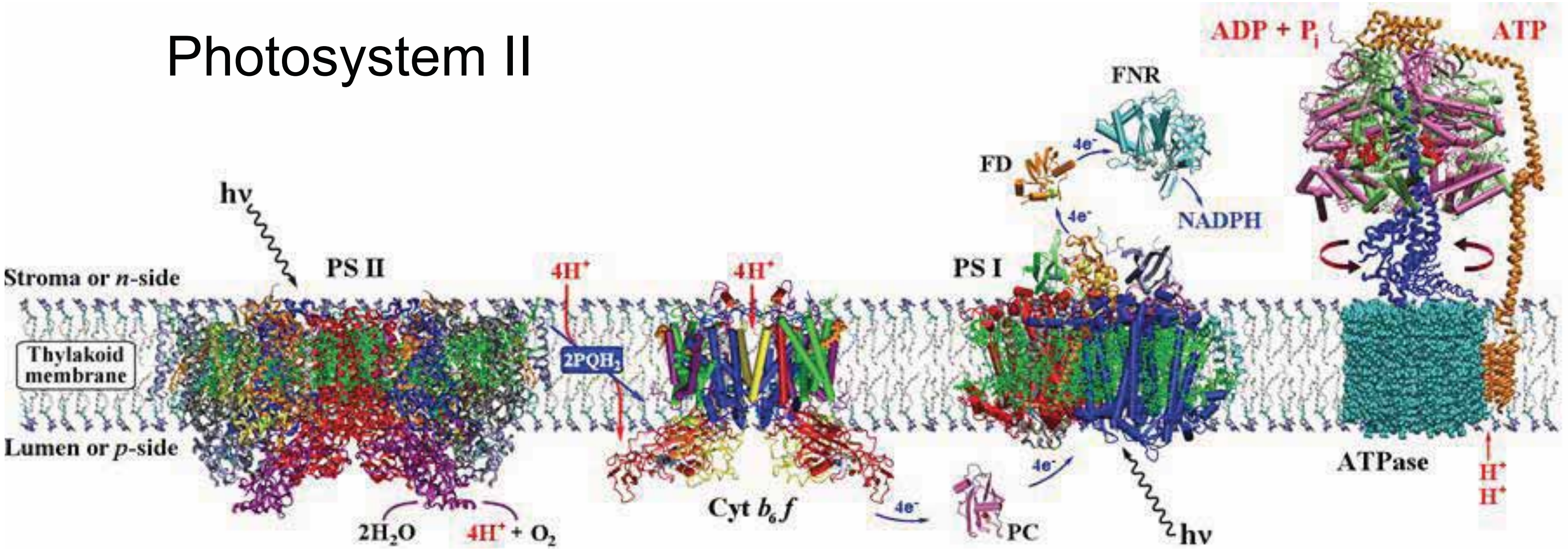
Light-harvesting Apparatus of Higher Plants



*http://www.hpc.unm.edu/~aroberts/main/photosyn.htm

Photosynthetic Membrane

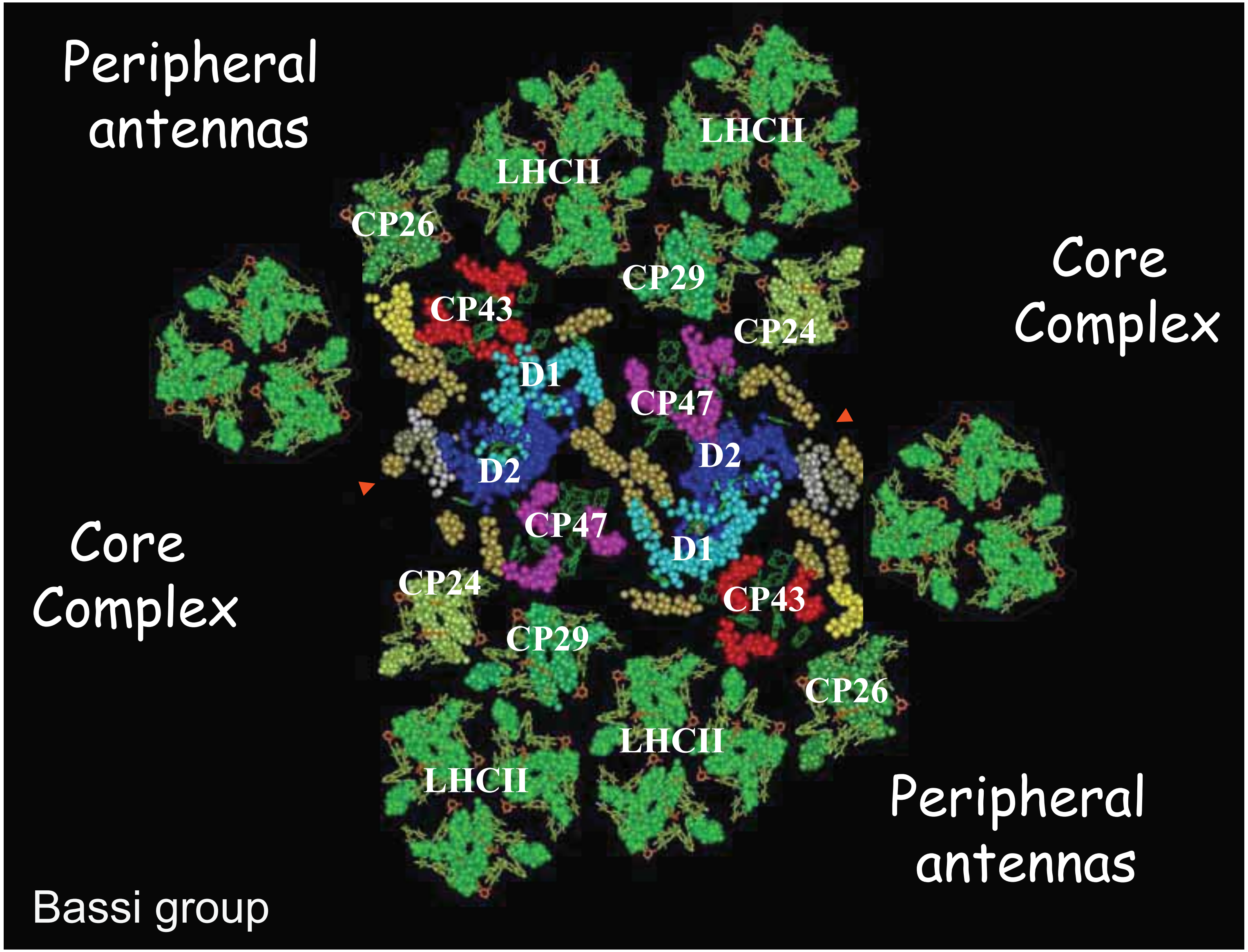
Photosystem II



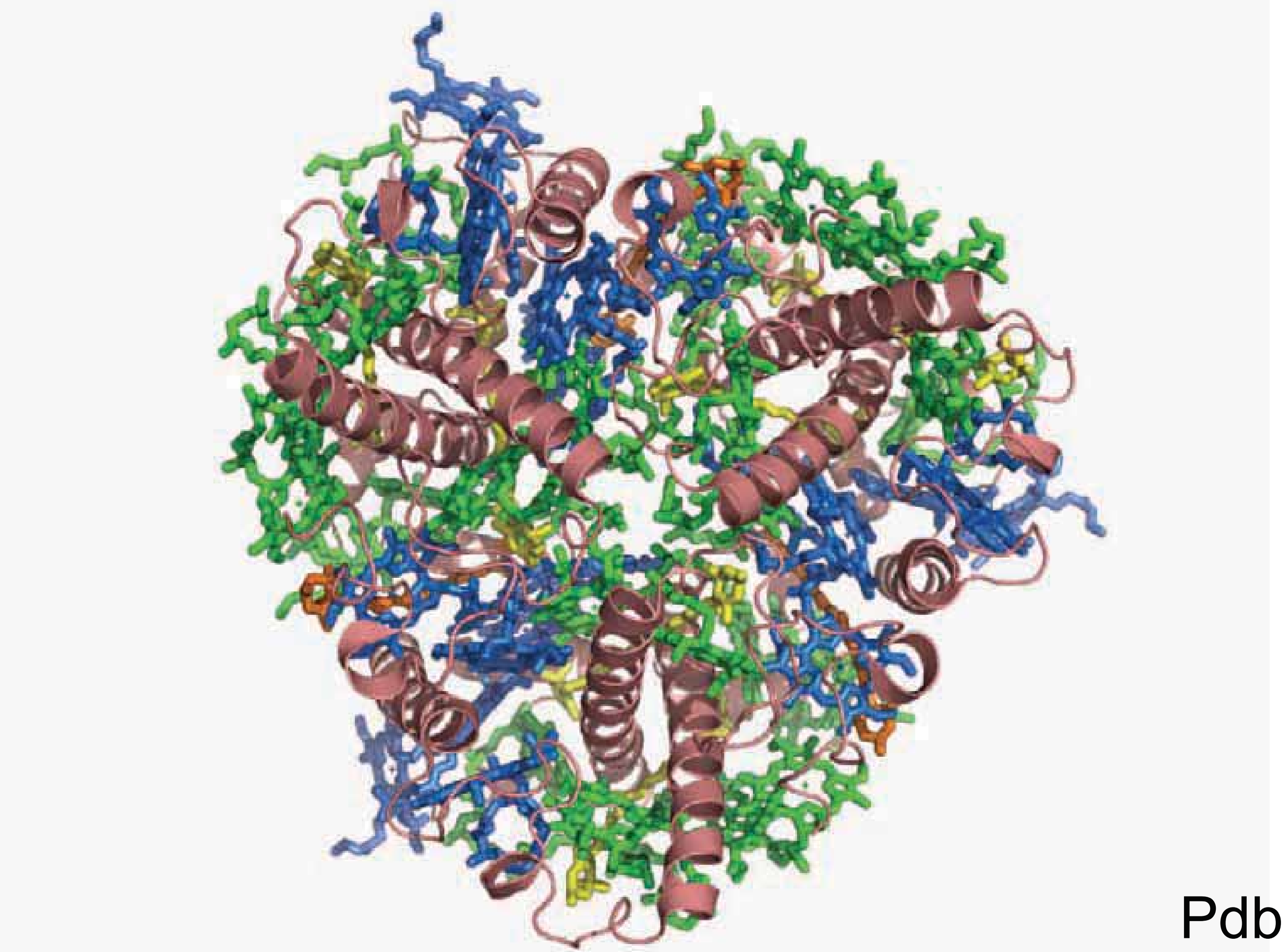
Photosystem I

http://www.physics.purdue.edu/~sergei/Photosynthesis.html

Photosystem II Supercomplex



Light-Harvesting Complex II (LHCII)

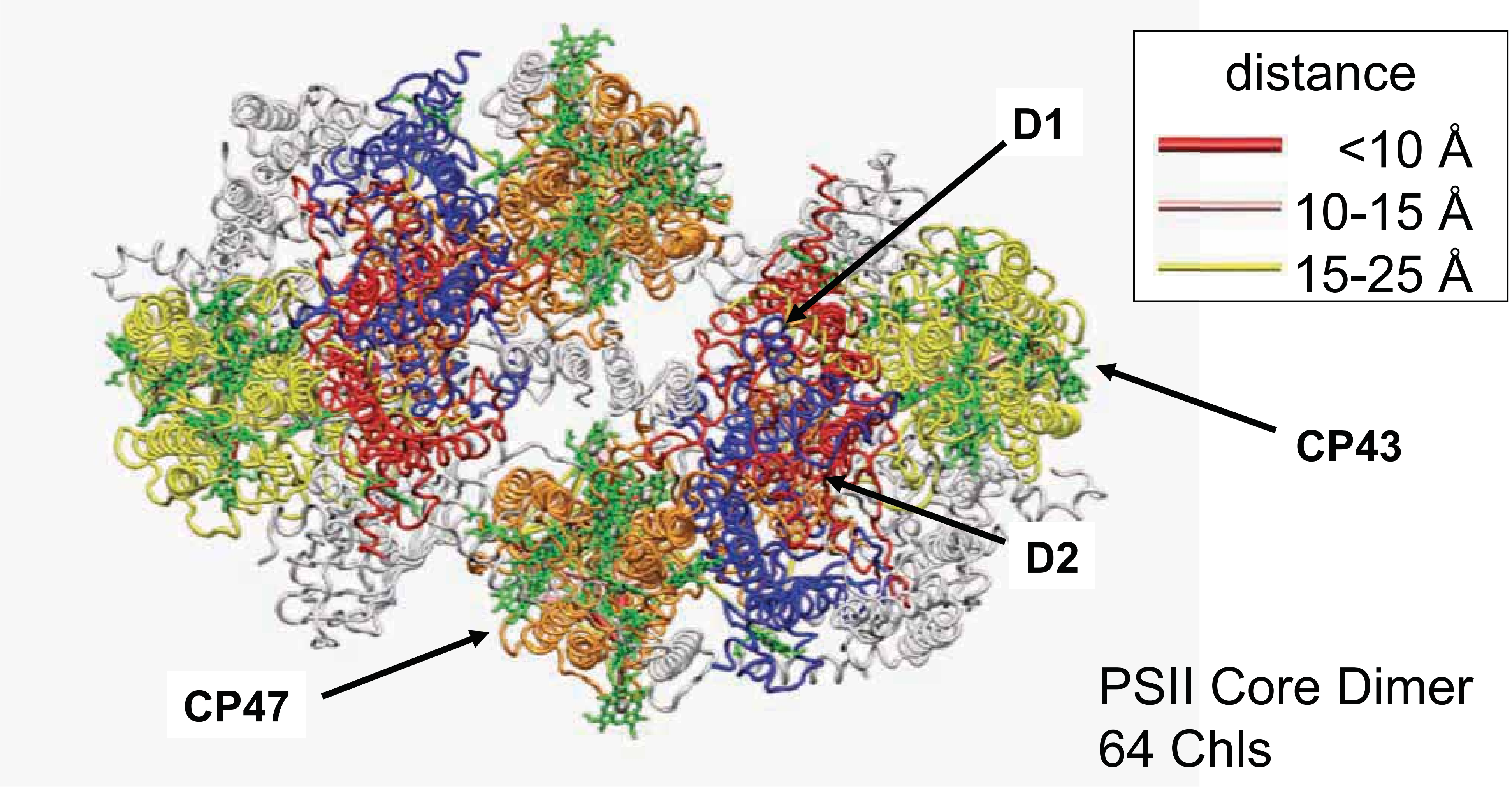


Pdb id: 2bhw

42 Chls; found in plants ; most important LHC on Earth

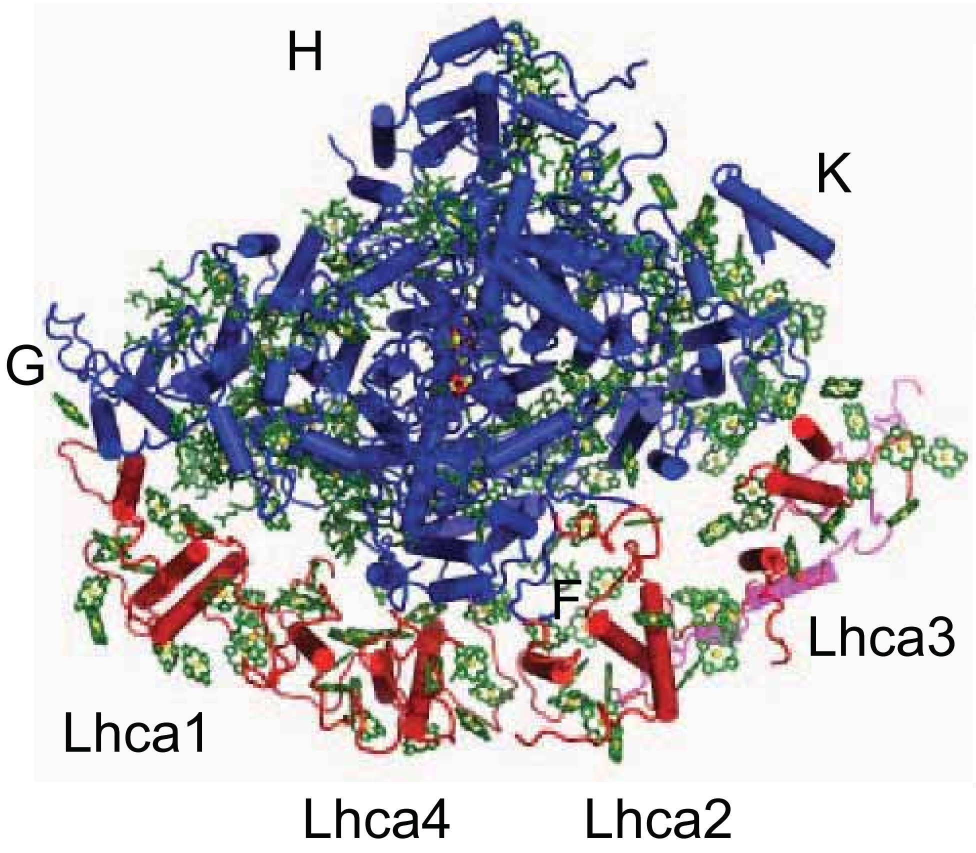
Structure of the PS II Core Complex

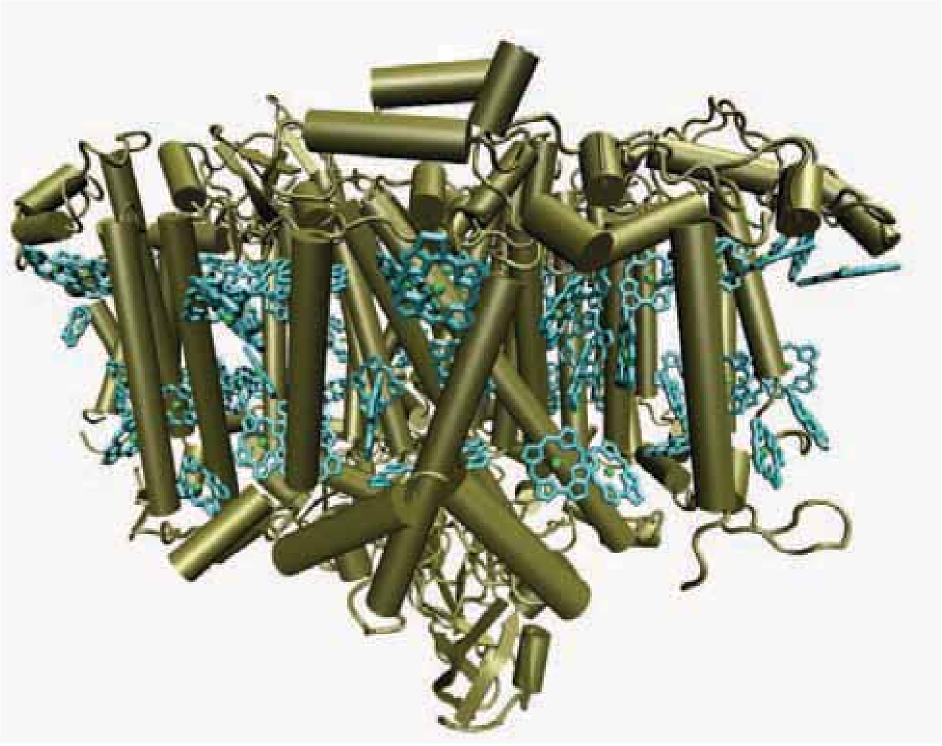
Chlorophyll network in the PSII core complex



PSII Core Dimer
64 Chls

Photosystem I Supercomplex of Plants

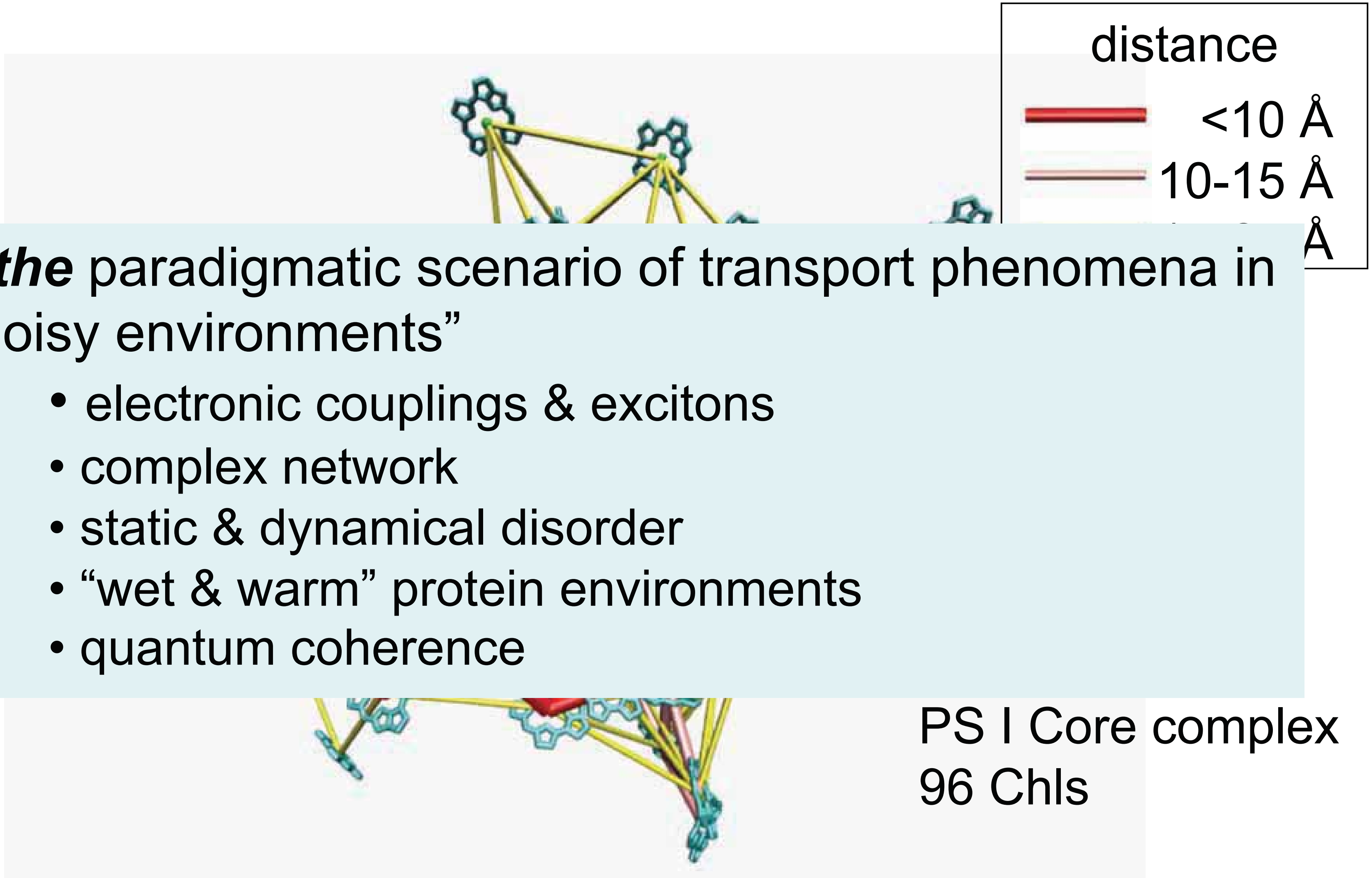




PS I Core complex
96 Chls

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

Chlorophyll Arrangement in the PS I Core



"***the*** paradigmatic scenario of transport phenomena in noisy environments"

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

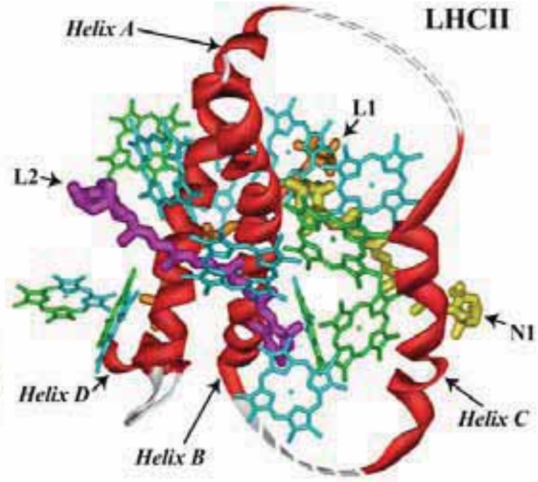
PS I Core complex
96 Chls

Pdb id: 1JB0

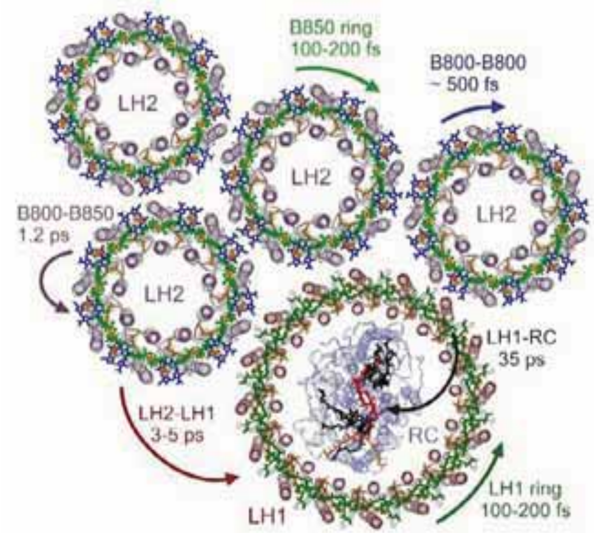
A complex chlorophyll network for light harvesting

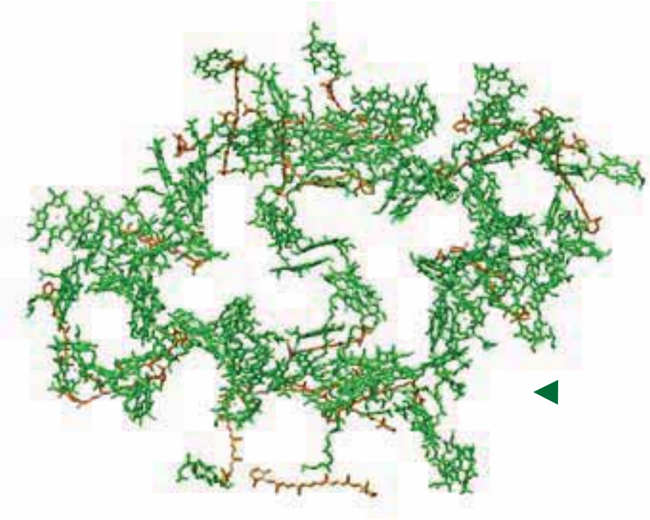
Architecture of Photosynthesis is Optimized to:

Cover the solar spectrum
Protect against photochemical damage

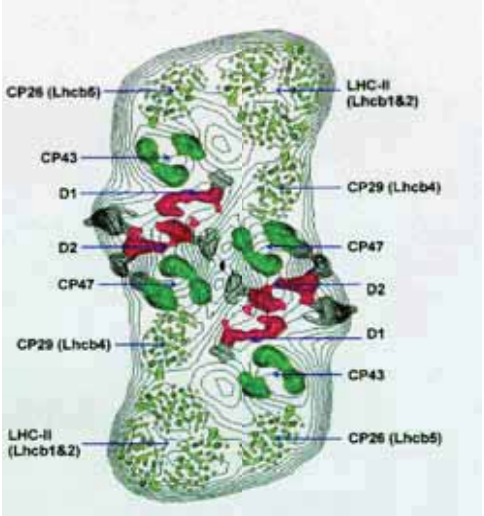


Transmit excitation to the reaction center with near unit efficiency





Achieve robustness & efficiency in highly disordered & complex EET networks



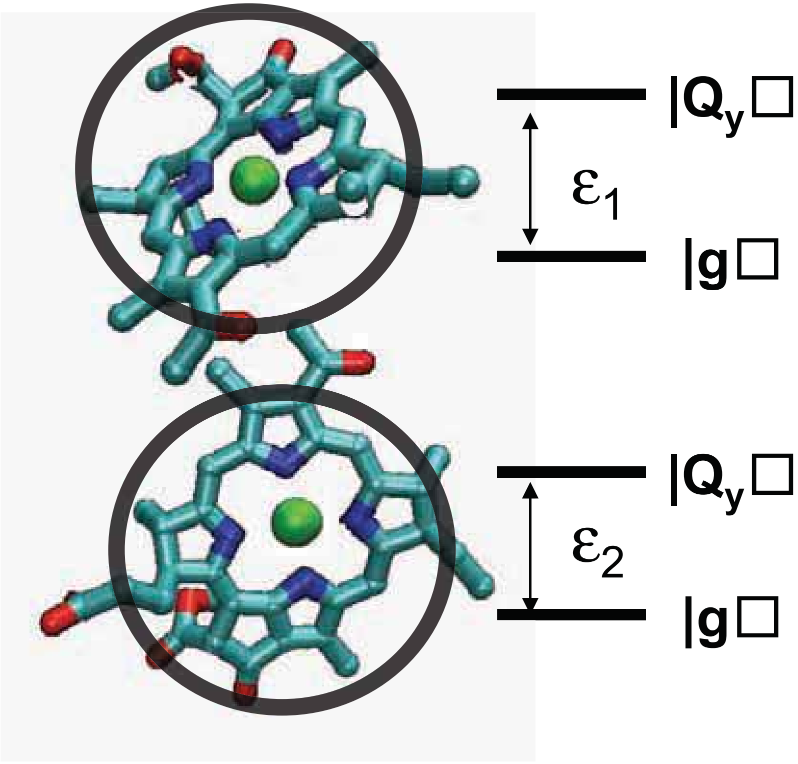
Barber Group, Imperial College (1998)

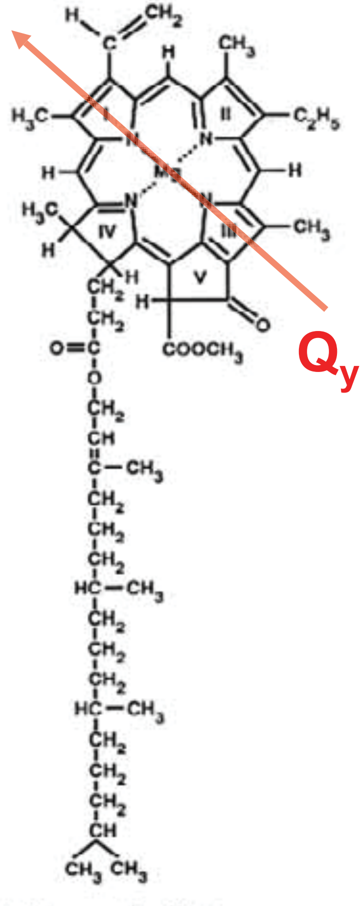
Repair damage and regulate the efficiency of light harvesting (PSII)

Theoretical Background

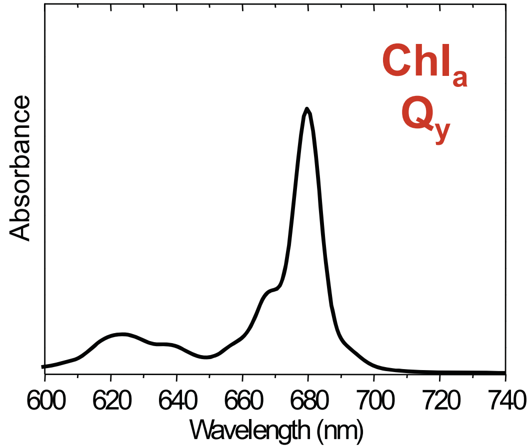
From the perspective of a physical chemist

Frenkel Exciton Model





Chlorophyll *a*



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

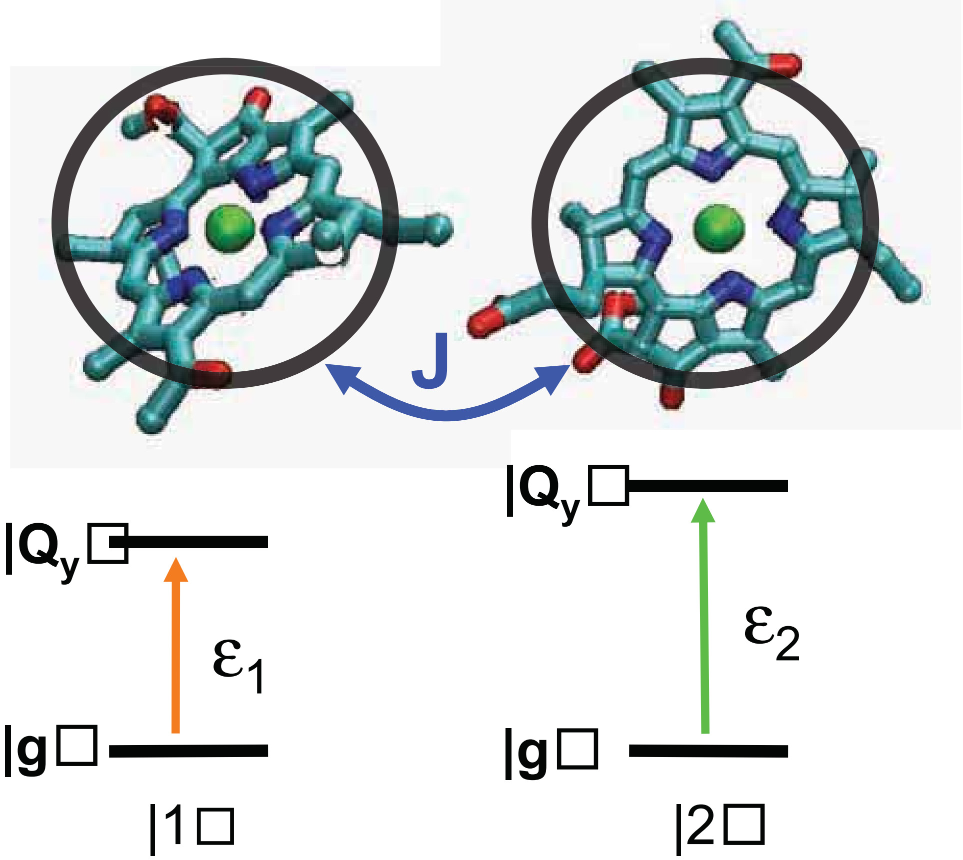
Exciton Hamiltonian and Excitonic Coupling

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

site energy coupling

$$H_e = \begin{bmatrix} \varepsilon_1 & J_{12} & \cdots & J_{1N} \\ J_{12} & \varepsilon_2 & \cdots & J_{2N} \\ \vdots & \vdots & & \vdots \\ J_{1N} & J_{2N} & \cdots & \varepsilon_N \end{bmatrix}$$

“site basis”



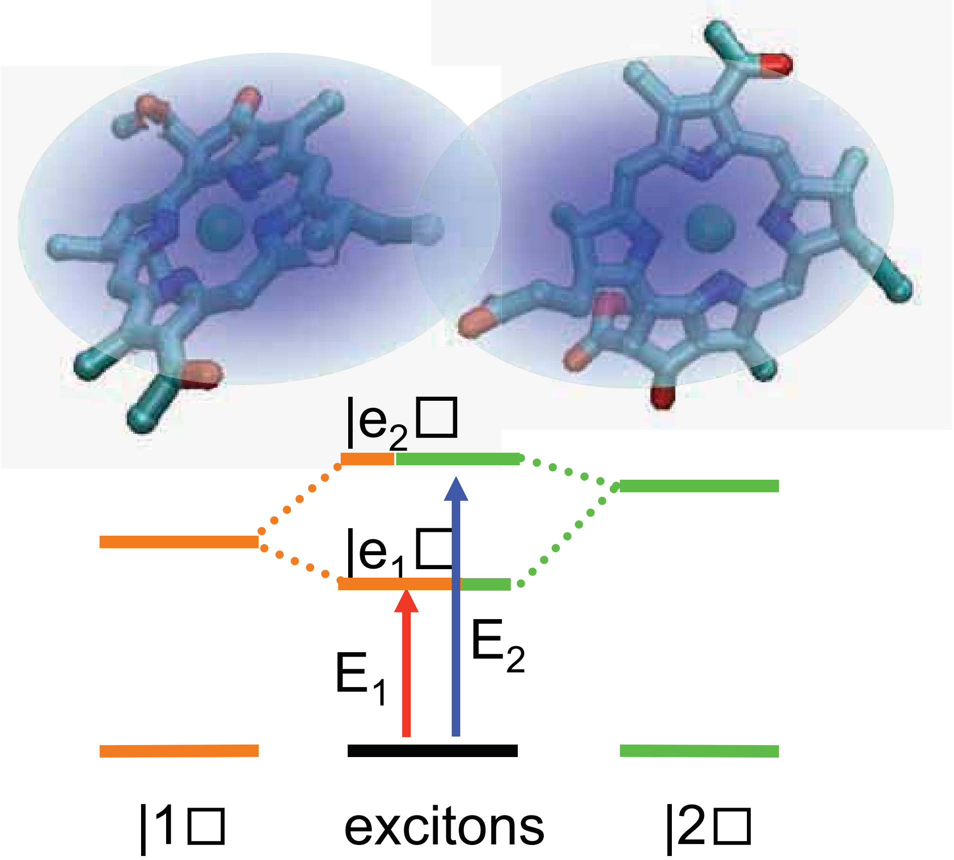
- Excitation energy transfer induced by excitonic coupling J
- When J is significant, the eigenstates of H_e has to be considered ➔ excitons

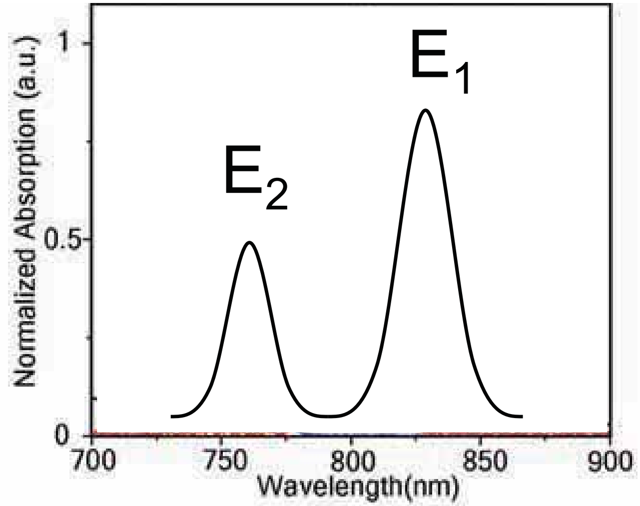
Excitonic Coupling and Photosynthetic Excitons

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

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

“exciton basis”



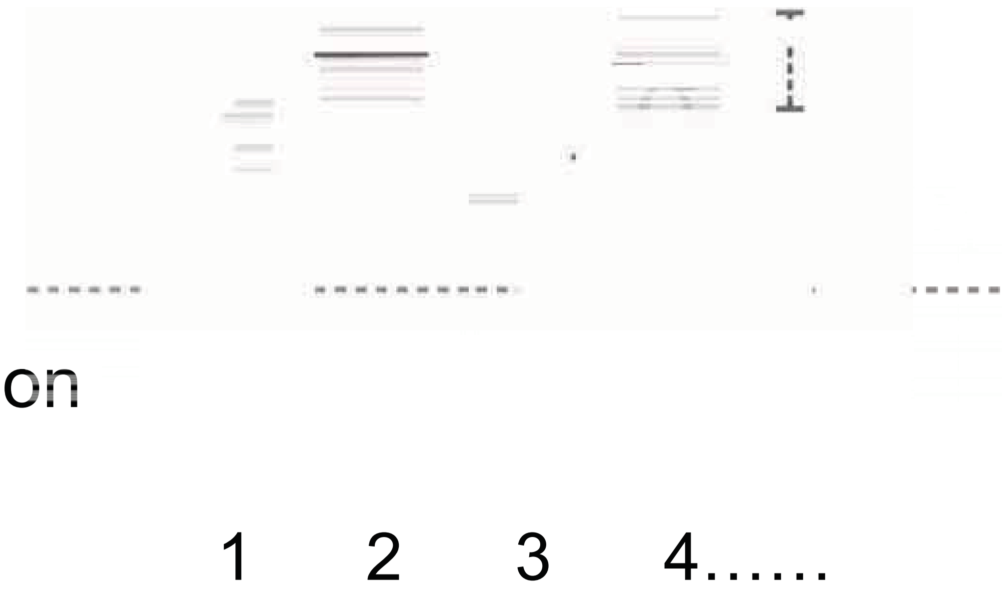


Disordered Exciton Hamiltonian

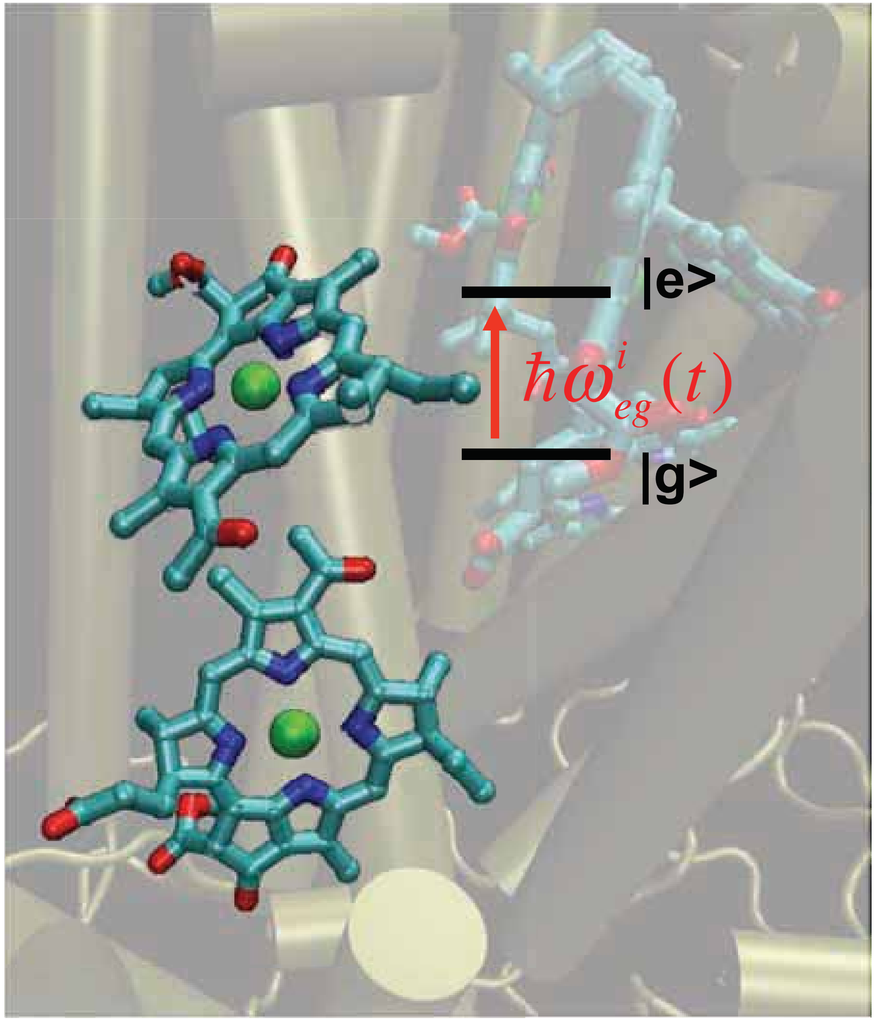
- Static disorder due to heterogeneous protein environments described by Gaussian random variables:

$$\begin{aligned} E_n &= E_0(n) + \delta E_I + \delta E_D(n) \\ J_{nm} &= J_0(n,m) + \delta J(n,m) \end{aligned}$$

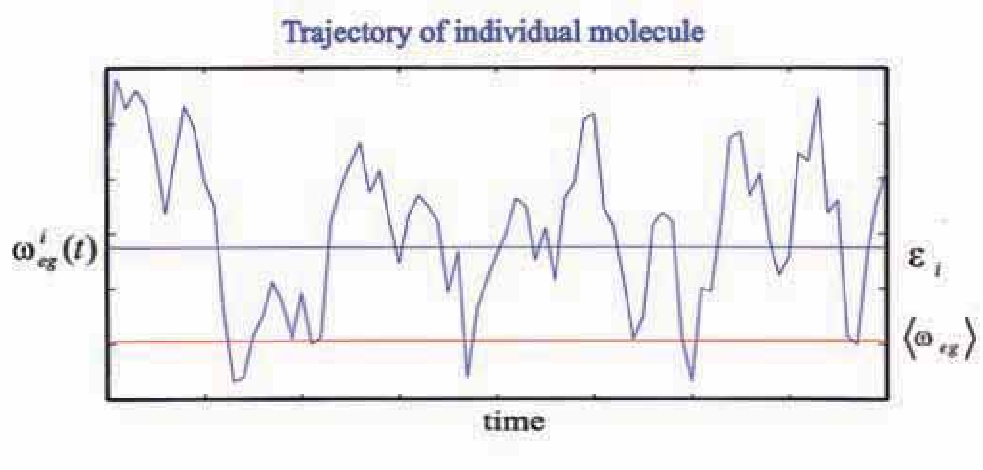
- Often sampled over Gaussian disorder using Monte Carlo simulation method
- Lead to localized exciton states (Anderson localization)



Dynamics in the Condensed Phase



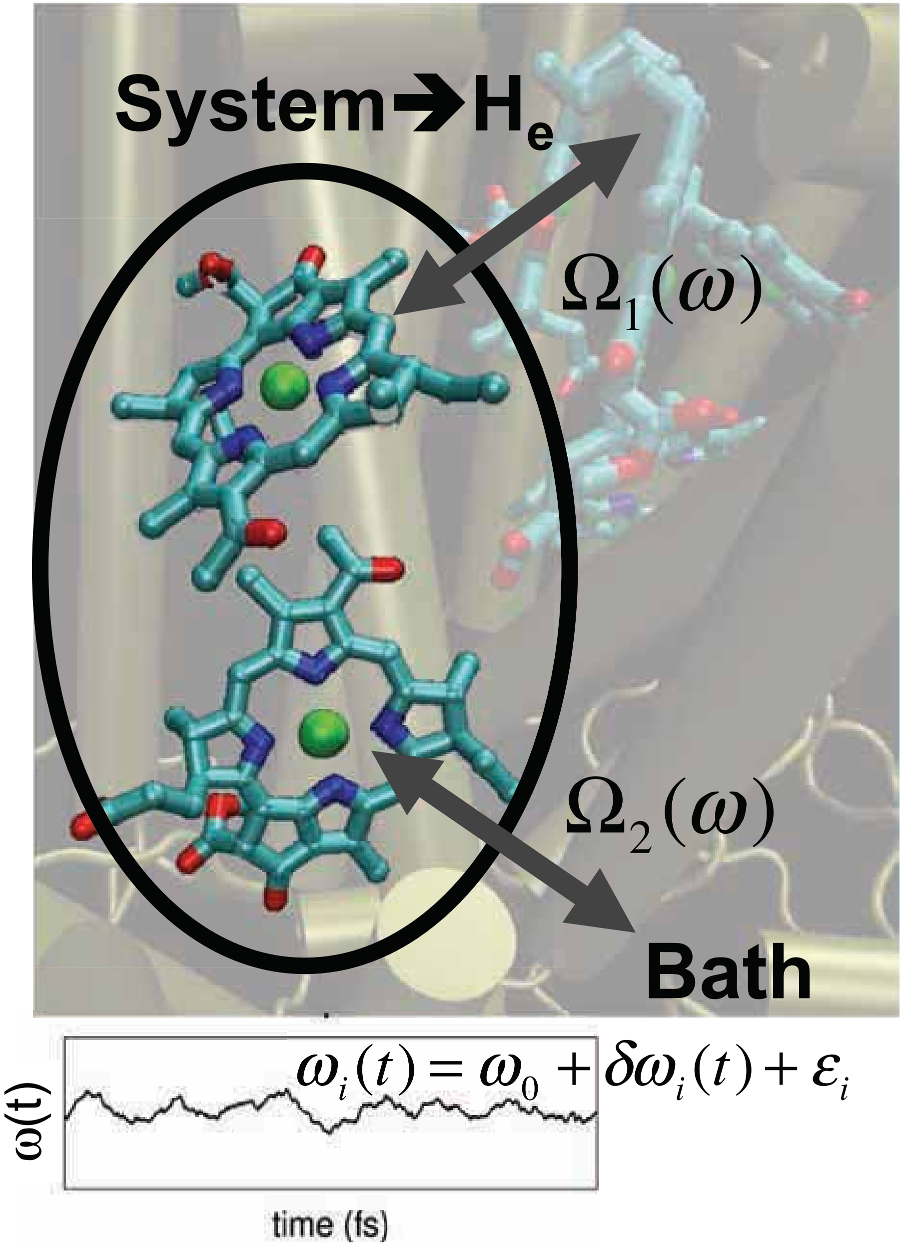
Energy of an individual chromophore *i* modulated by its protein environment:



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

$\delta\omega_i(t)$ ➔ fast, dynamical changes
ε_i ➔ slow, static changes
f(ε_i): inhomogeneous broadening

Modeling Excitation Energy Transfer: System-Bath Model



$$\omega_i(t) = \omega_0 + \delta\omega_i(t) + \varepsilon_i$$

- Environments (baths)
  ➔ harmonic oscillators
- System-bath couplings
  ➔ 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:

$$\rho = \sum_{n} P_n | \psi_n \rangle\langle \psi_n |$$

➔ H_e and Ω(ω) determine the dynamics, ρ(t).

Redfield Picture of Excitation Energy Transfer

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

exciton Hamiltonian

dissipation determined by Ω(ω)

$$\partial_t \rho(t) = -i[H_e, \rho(t)] - \Re[\rho(t)]$$

population

coherence

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

ρ: reduced-system density matrix

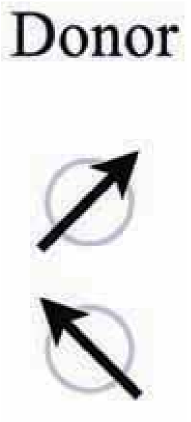
N: number of chromophores

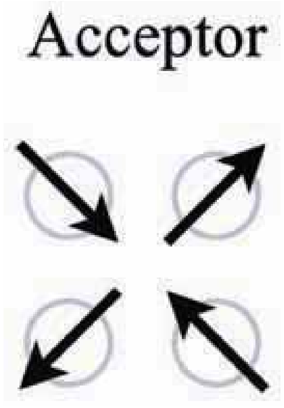
$$\Re[\,]: \quad \begin{array}{l} \rho_{nn} \to \rho_{mm} : \text{ population dynamics (incoherent)} \\ \rho_{nm} \to \rho_{n'm'} : \text{ coherence dynamics} \end{array}$$

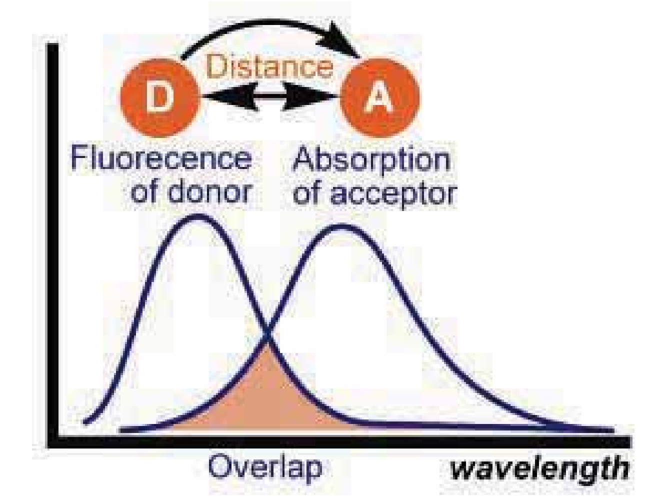
Förster Picture of Excitation Energy Transfer

When electronic coupling is weak, we can use Forster's resonance energy transfer formula (or can we?):

$$k_F = \frac{J^2}{2\pi\hbar^2}\int_{-\infty}^{\infty} d\omega E_D(\omega) I_A(\omega)$$







No EET to/from dark states!

http://www.calctool.org/CALC/chem/photochemistry/fret

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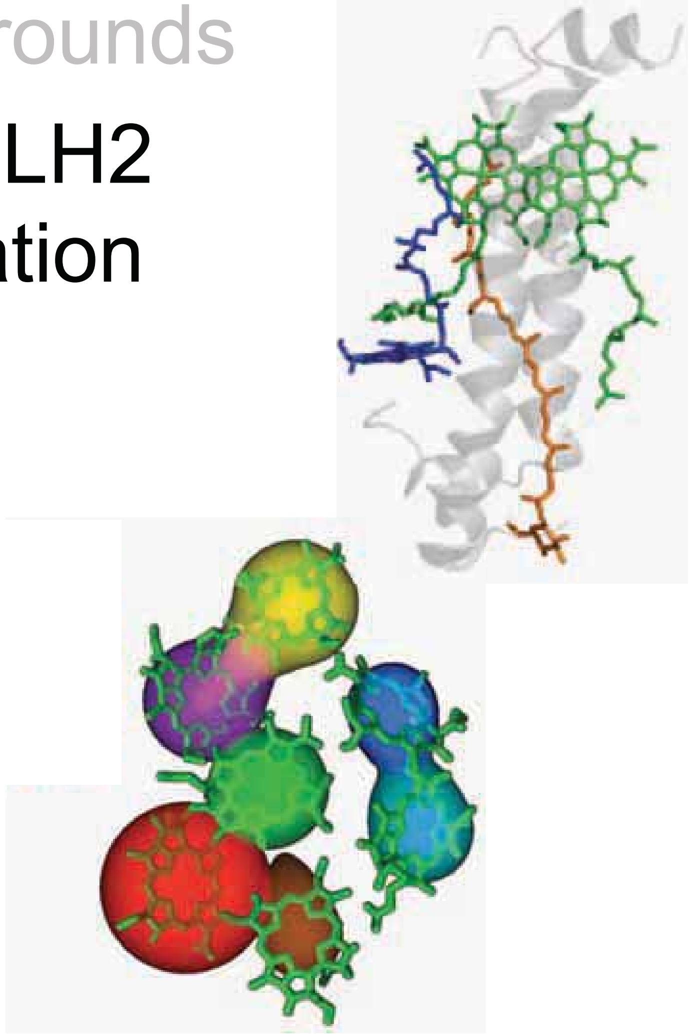
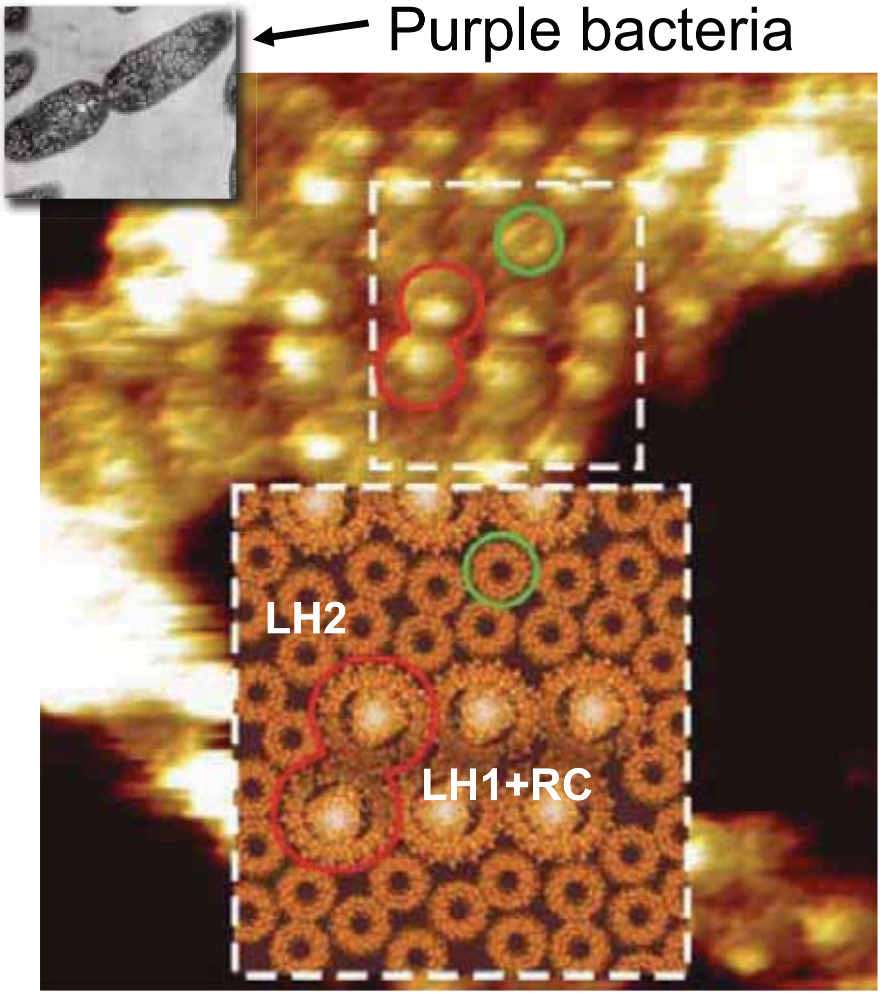


Outline (Part II)

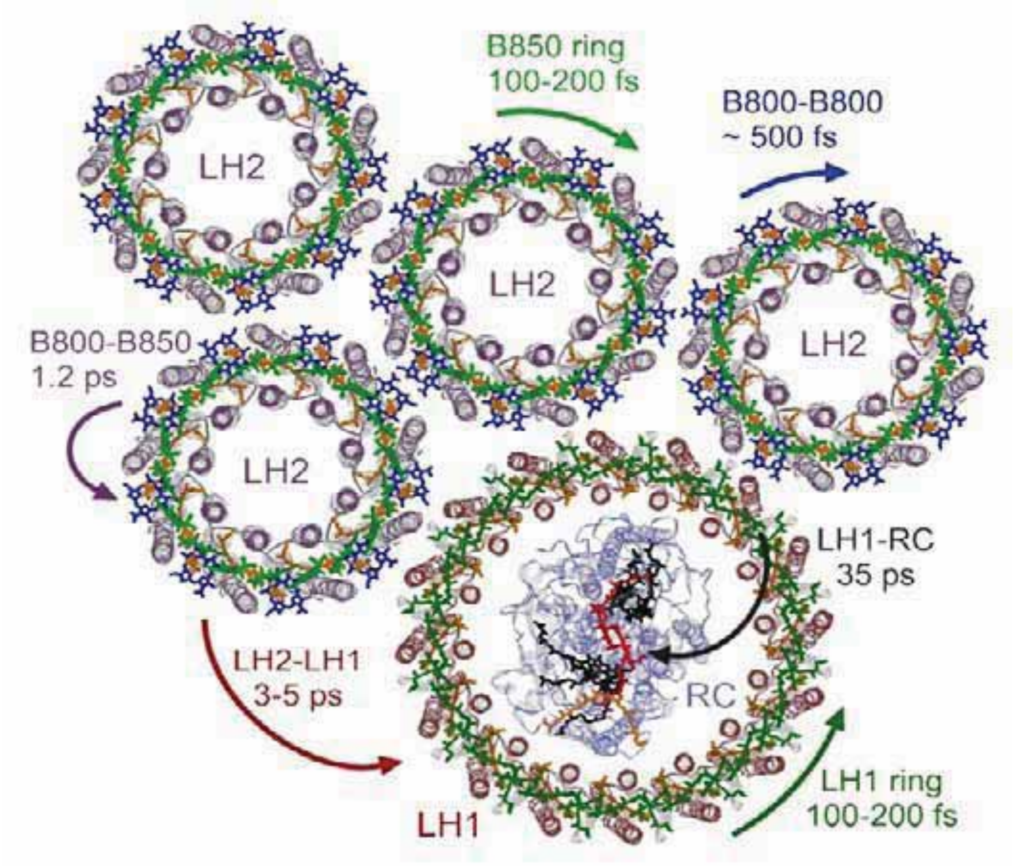
- Light-harvesting apparatus of purple bacteria & the structure of LH2
- Dynamics of light harvesting in the LH2 complex
- B850, B800, and the excitation energy transfer between them
- Optimization of the LH2 complex using quantum coherence
- Concluding remarks

Light-harvesting Apparatus of Purple Bacteria


Purple bacteria

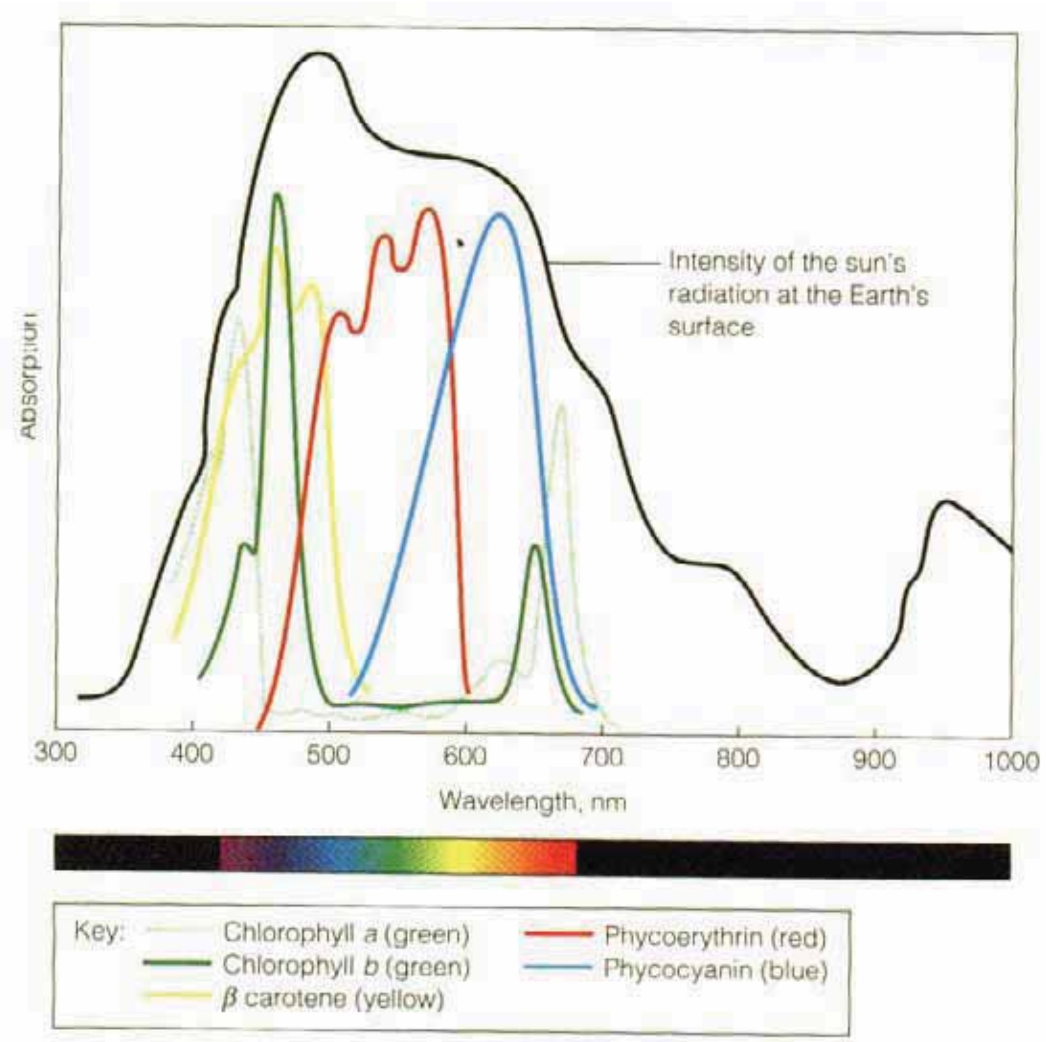
AFM of native photosynthetic membranes of a purple bacterium

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

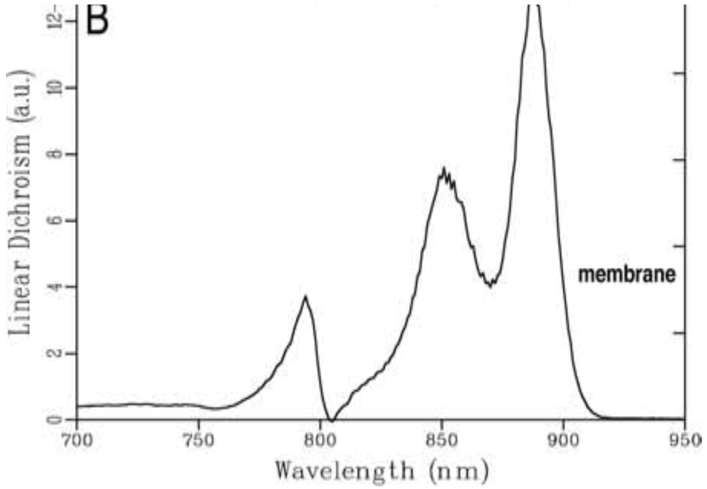


Hu et al., *Q. Rev. Biophys.* **35**, 1 (2002)

Sun Light Absorption by Photosynthetic Pigments



Photosynthetic membranes of purple bacteria

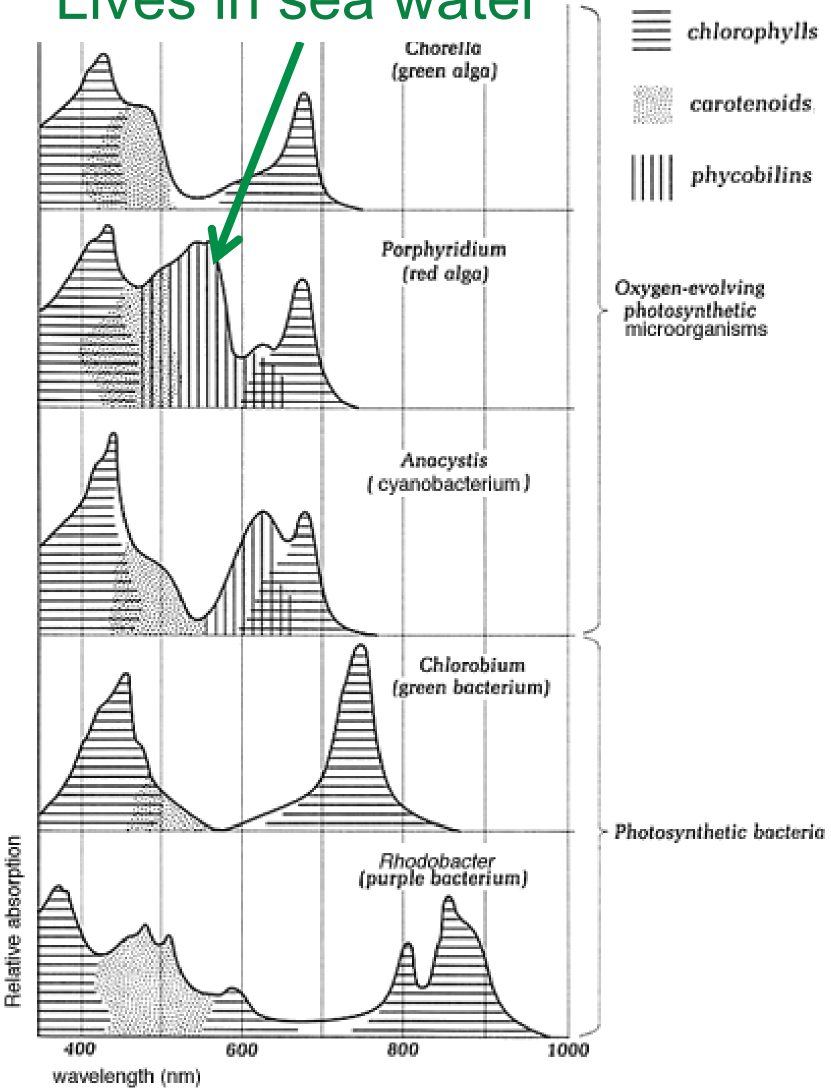


Frese R N et al. PNAS 2004;101:17994-17999

http://course1.winona.edu/sberg/

Pigment Distribution of Photosynthetic Organisms

Lives in sea water

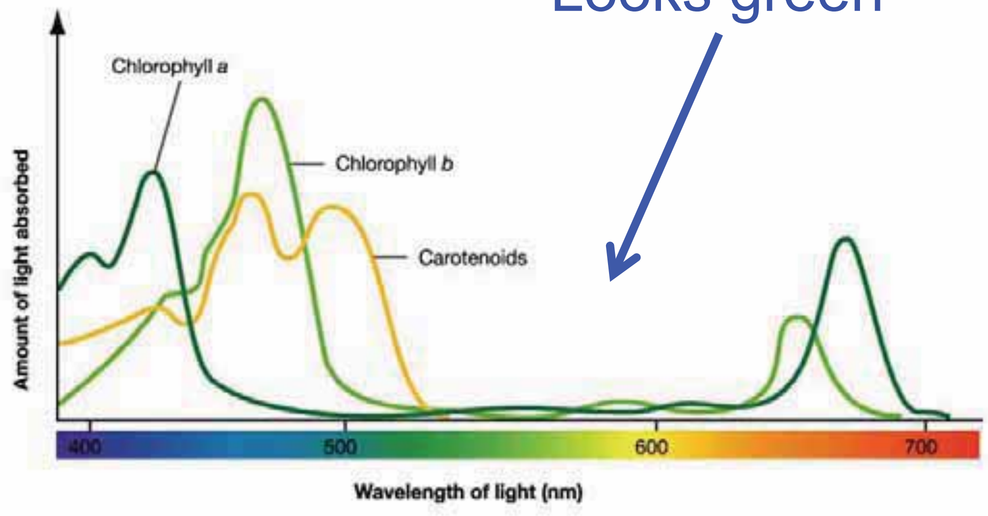


Photosynthetic microorganisms

http://www.textbookofbacteriology.net

Each photosynthetic organism has its own “niche” light-absorption band

Looks green



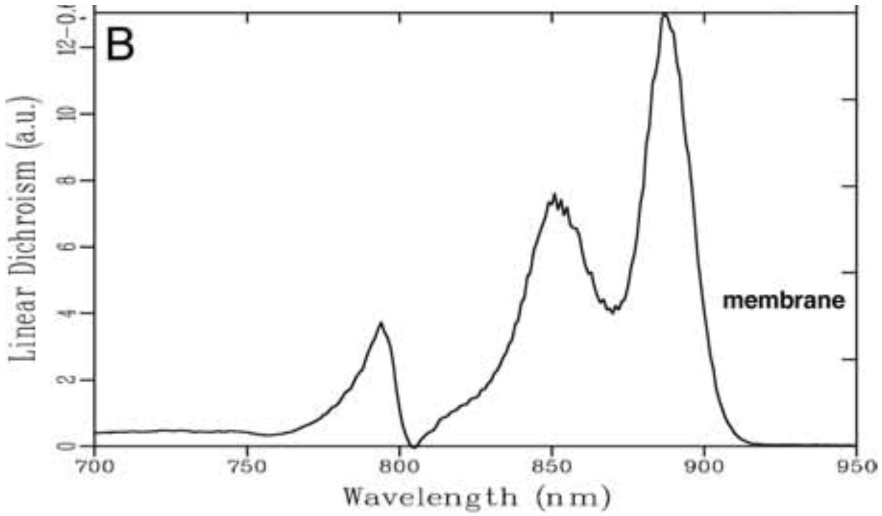
Higher plants

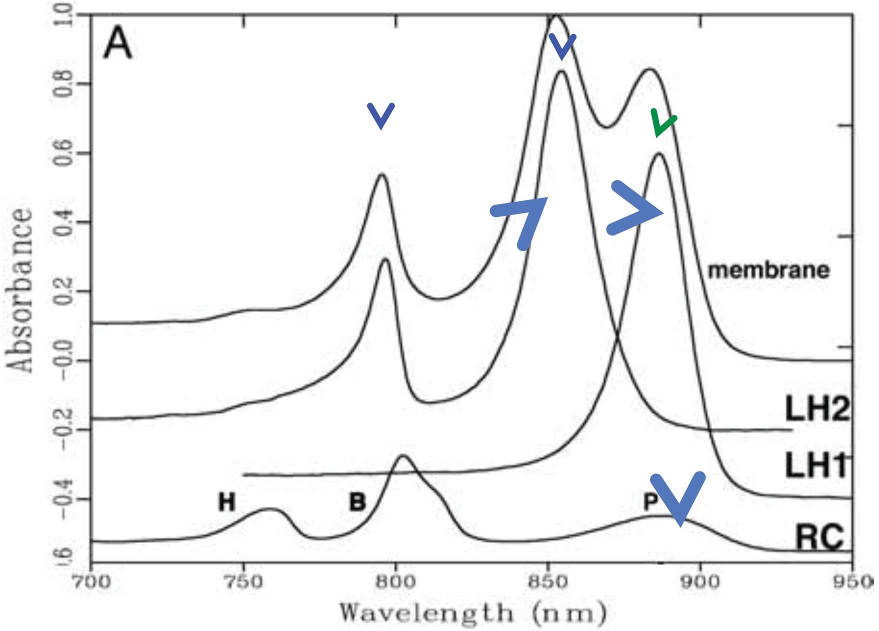
Components of Purple Bacteria Photosynthetic Membranes

Three pigment-protein complexes

B800   B850   B875

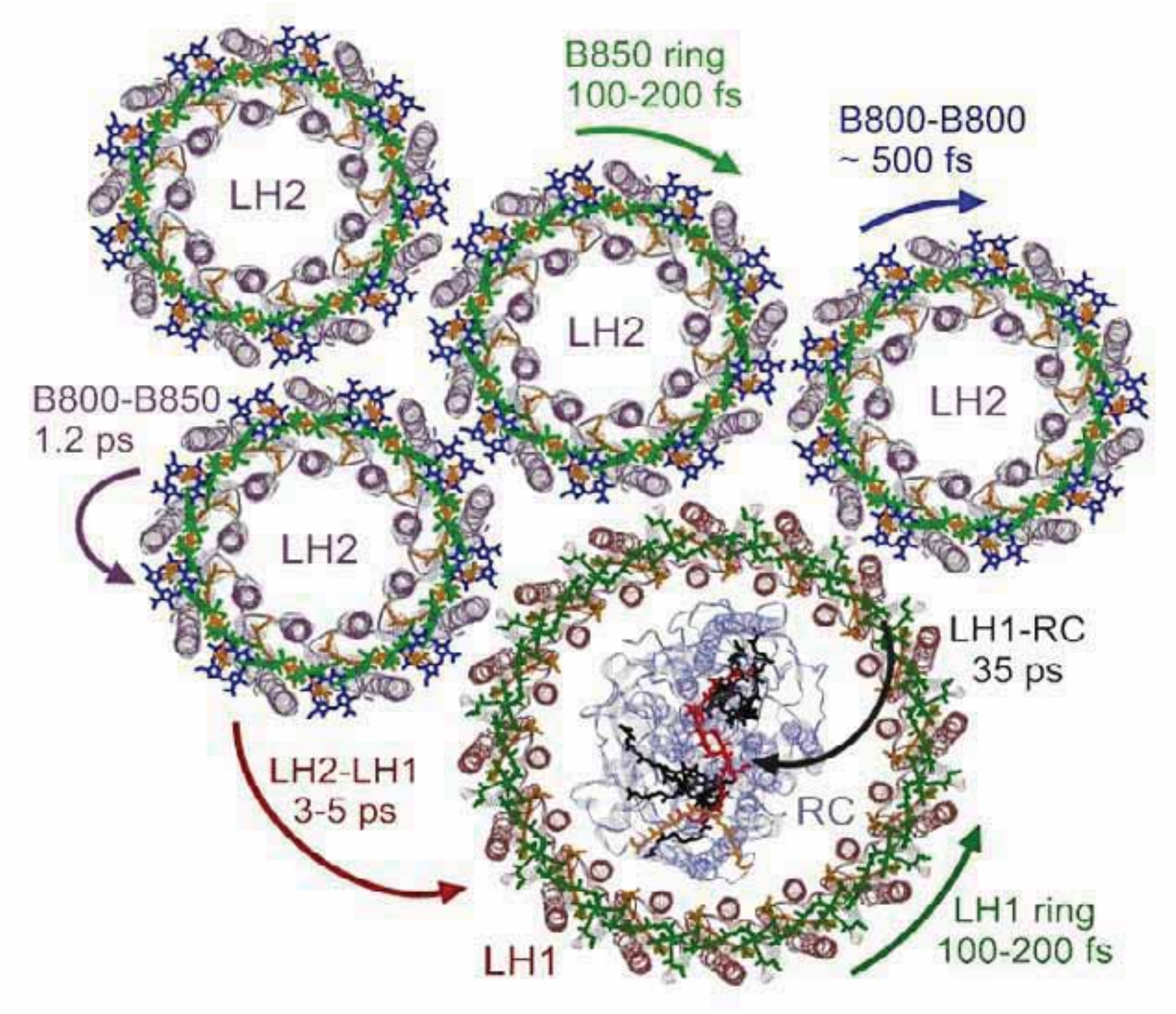
Clear energy transfer pathways from high to low energies
B800➔B850➔B875➔P





Frese R N et al. PNAS 2004;101:17994-17999

Light-harvesting Apparatus of Purple Bacteria



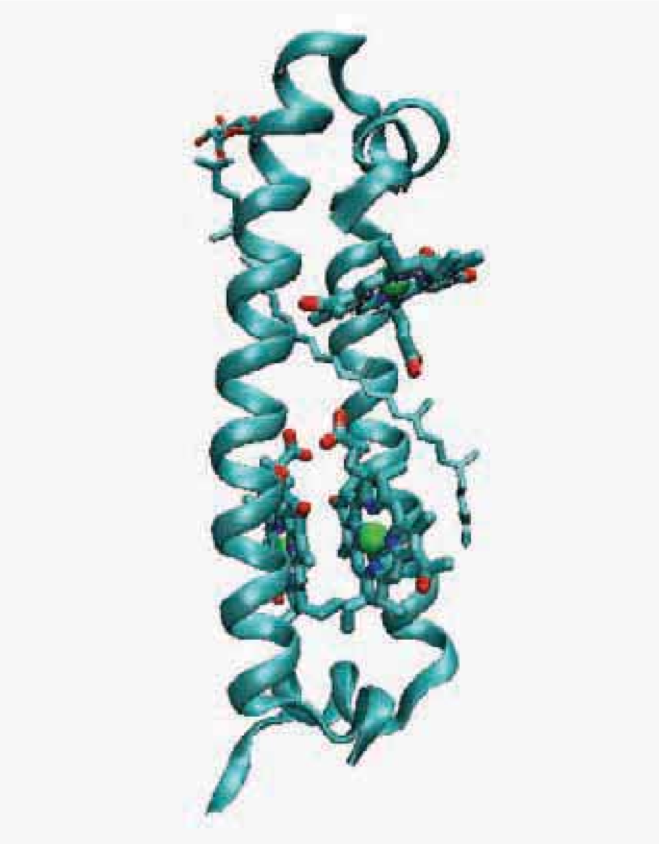
- Rapid excitation energy transfer (EET) $\tau_{EET} << \tau_{fluorescence}$
- Almost unity quantum yield (>95%)
- Architecture highly tuned to gain optimal light harvesting efficiency

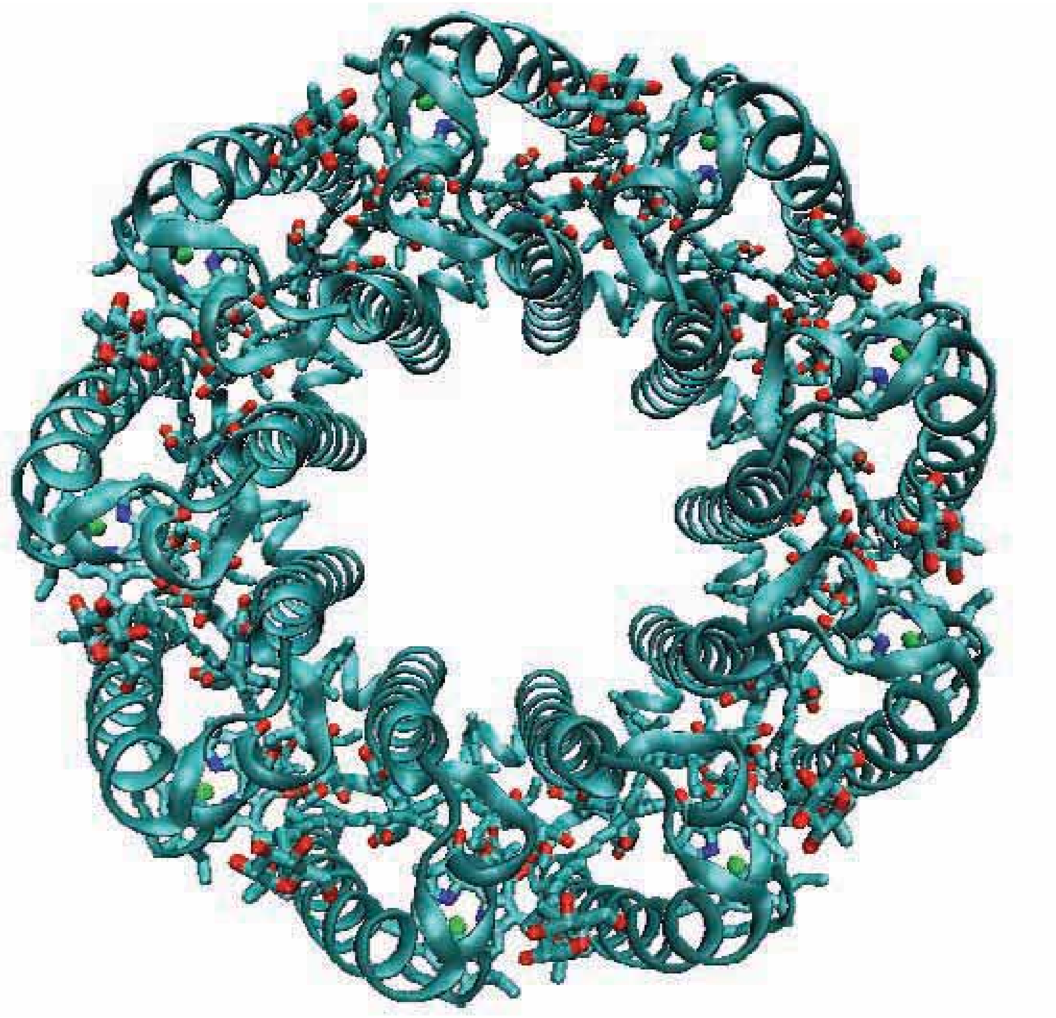
Take LH2 as an illustrative example!

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

LH2 from *Rps. acidophila*: Structure

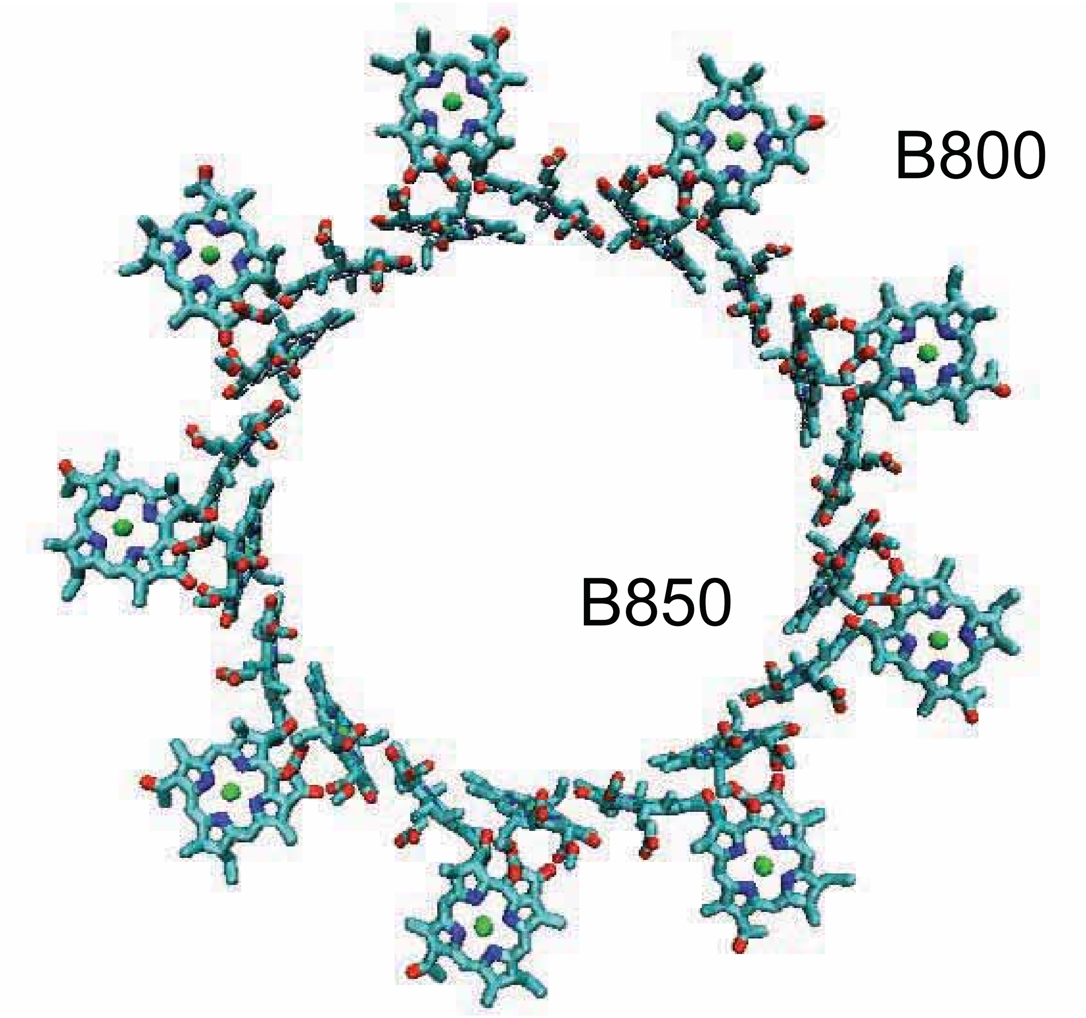
- Pigment-protein complex
- 9-fold symmetry





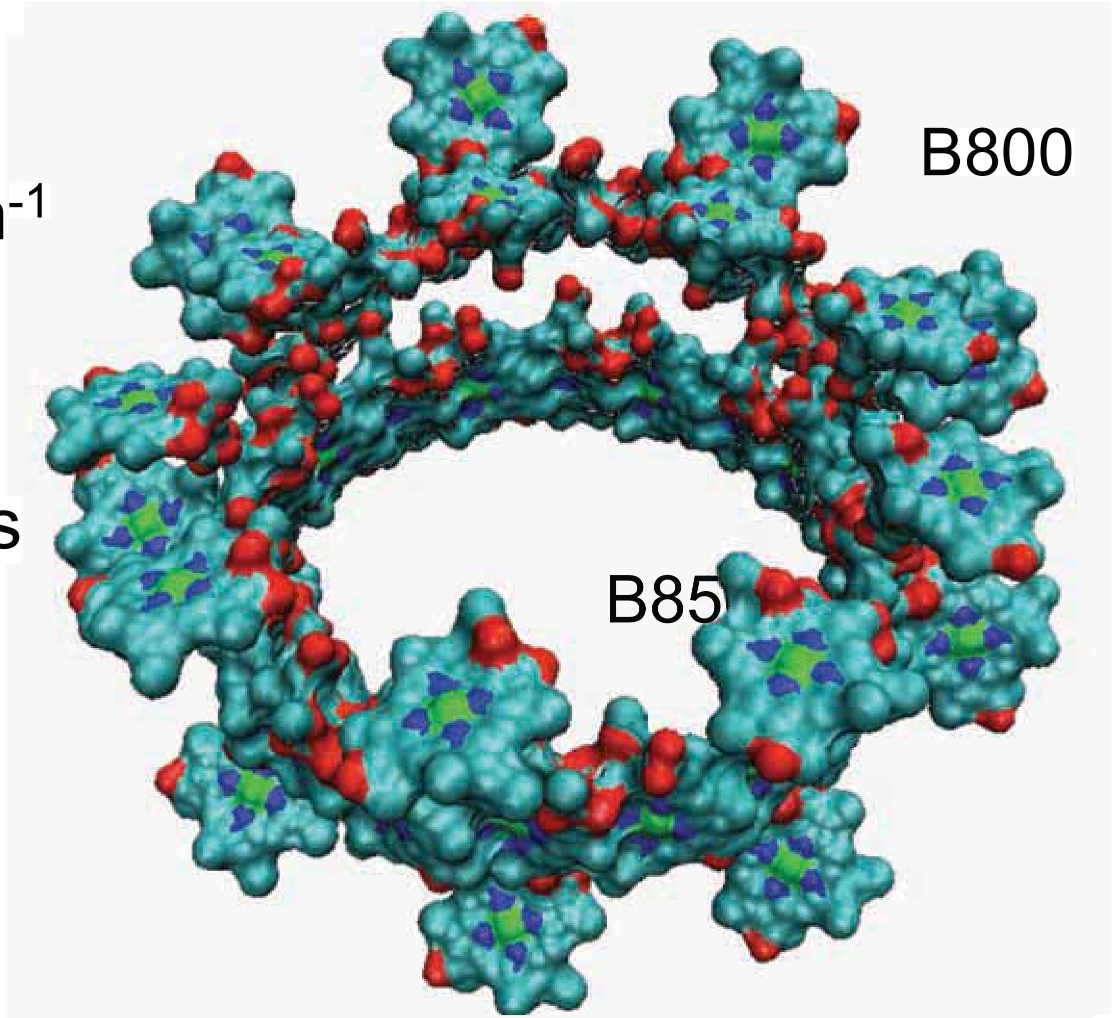
LH2 from *Rps. acidophila*: Structure

- Pigment-protein complex
- 9-fold symmetry
- B800 ring:
  - 9 BChl *a* molecules
  - Mg-Mg ~ 21Å
- B850 ring:
  - 18 BChl *a* molecules
  - Mg-Mg ~ 9Å



LH2 from *Rps. acidophila*: Excitations

- Excitonic couplings
  - $J_{B800} \sim -30\ cm^{-1}$
  - $J_{B800\text{-}850} \sim 20\ cm^{-1}$
  - $J_{B850} \sim 300\ cm^{-1}$
- The system exhibits significant disorder
  - Dynamical
  - Quasi-static
  - Static



So, how do we describe EET in such complex systems?

Optimization of LH2 via Quantum Coherence

Electronic coherence manifested as excitation delocalization are heavily utilized for optimal efficiency in **LH2**:

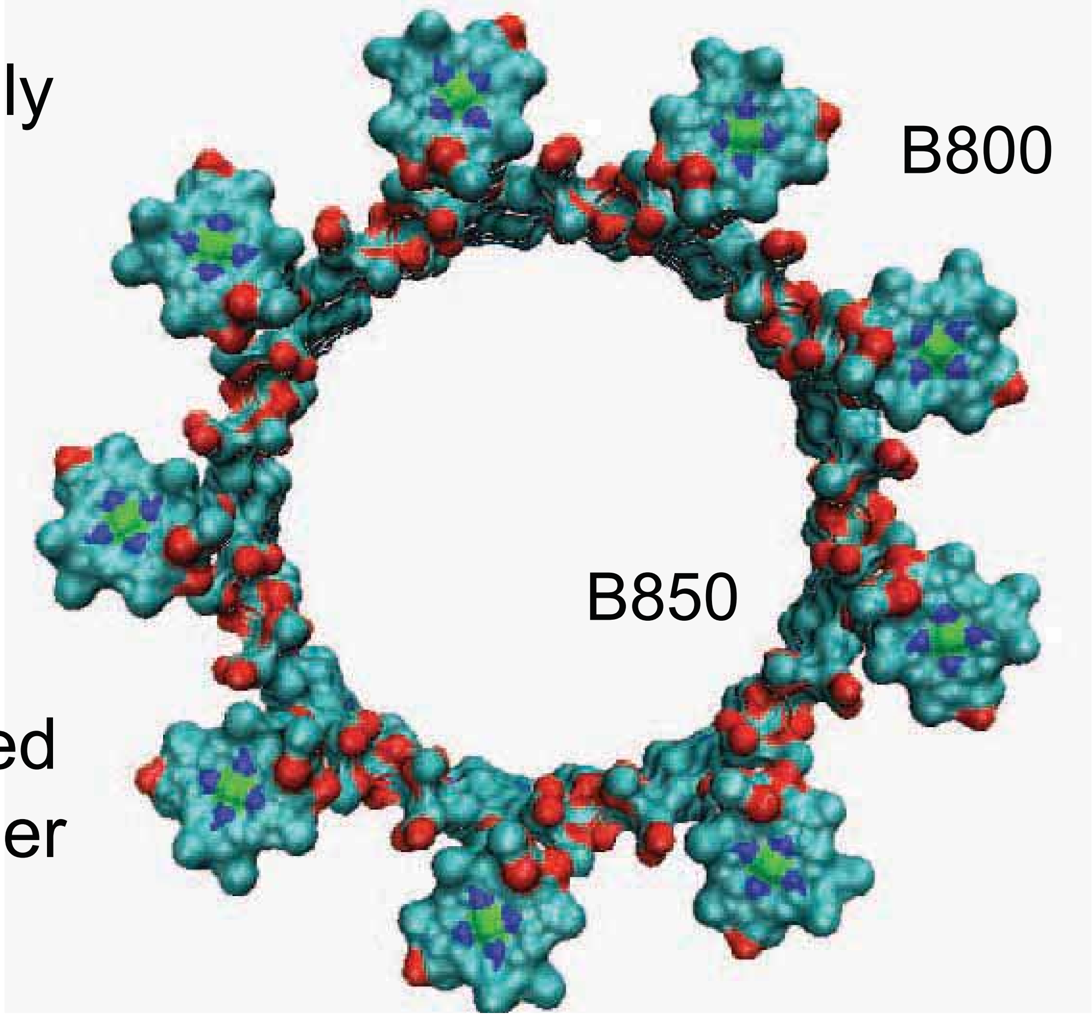
- Ultrafast coherent dynamics and spectral tuning mechanism in the B850 system
- Multichromophoric effects in the B800 to B850 inter-ring energy transfer
- Coherence signatures in the B800 system and robustness of light harvesting

B850 Intra-Ring EET

B850 Intra-Ring Couplings

- B850 BChl a molecules are closely packed and exhibit strong couplings $J_{B850} \sim 300\ \mathrm{cm}^{-1}$

- The exciton states are highly delocalized despite static disorder



B850 Transition Dipole Arrangements

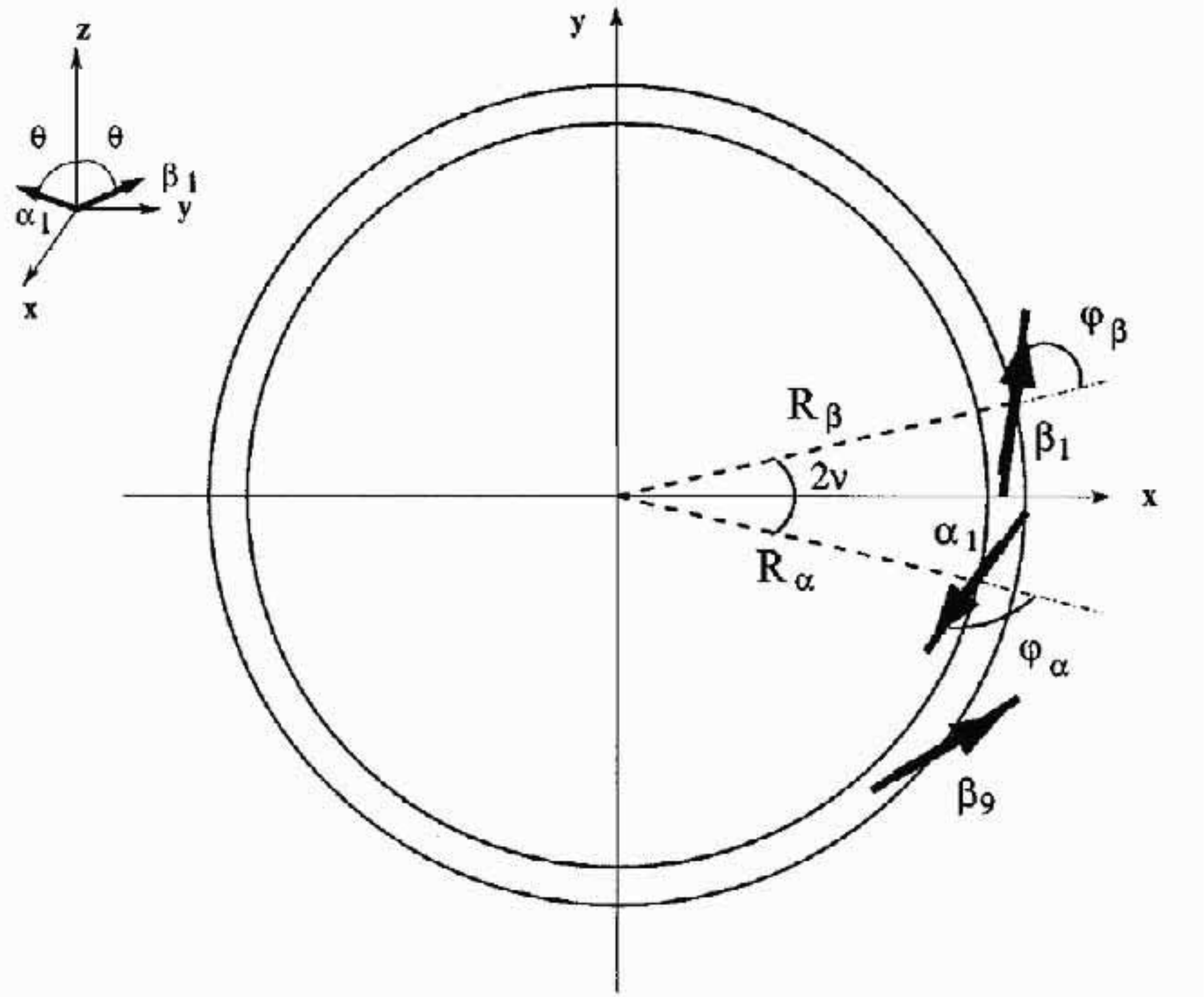
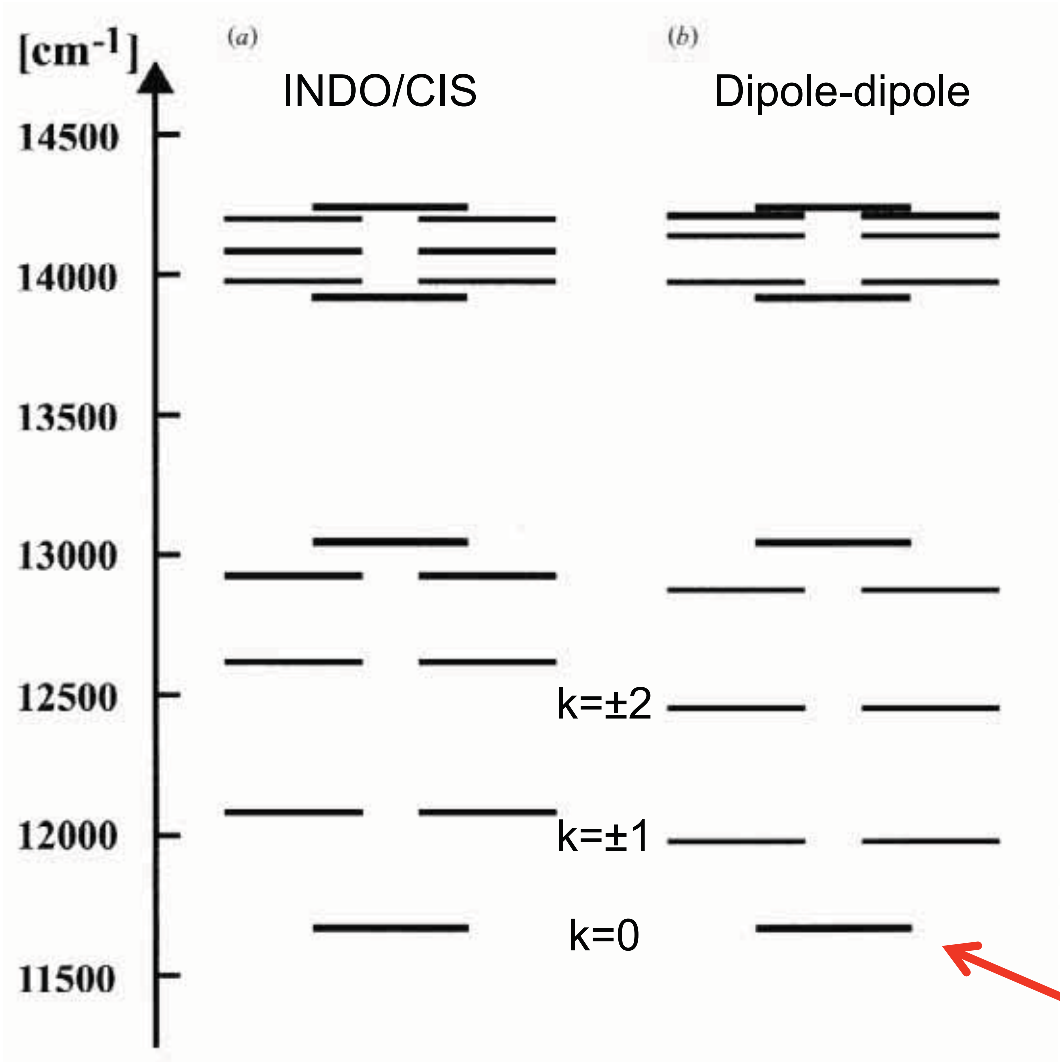


FIG. 1. Model of the arrangement of BChls for the B850 band of LH2 in *Rps. Acidophila*. The arrows represent the transition dipole moment vectors

Jang & Silbey

B850 Energy Levels & Spectrum

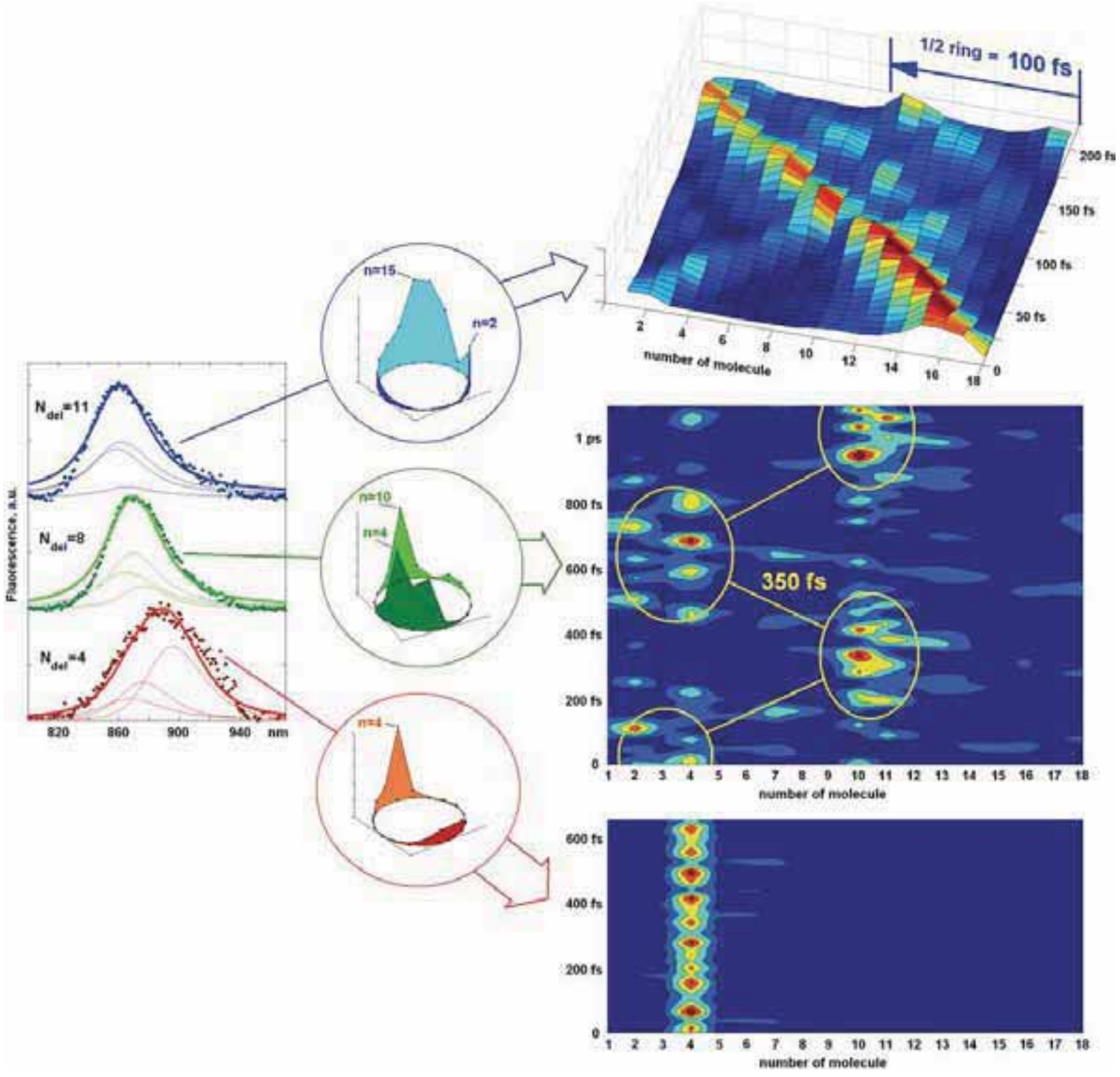


- Large spacing due to electronic couplings
- Only k=±1 states have significant absorbance

k=0 is a dark state,
low fluorescence lost!

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

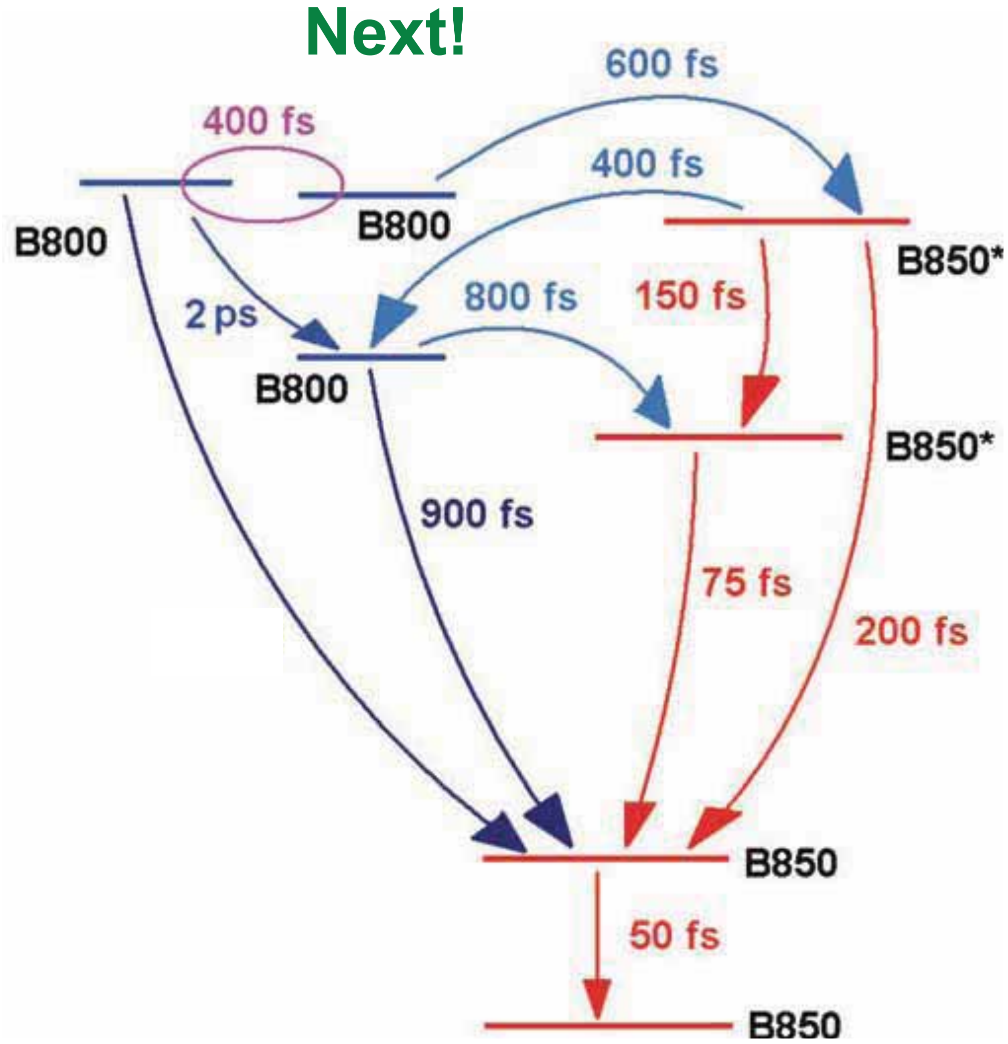
B850 Intra-Ring Dynamics



- Coherent EET dynamics depending on disorder
- Rapid inter-ring relaxation
- Exciton delocalized on 4 BChls on average

van Grondelle & Novoderezhkin, PCCP 2005.

Dynamics of LH2 Light Harvesting

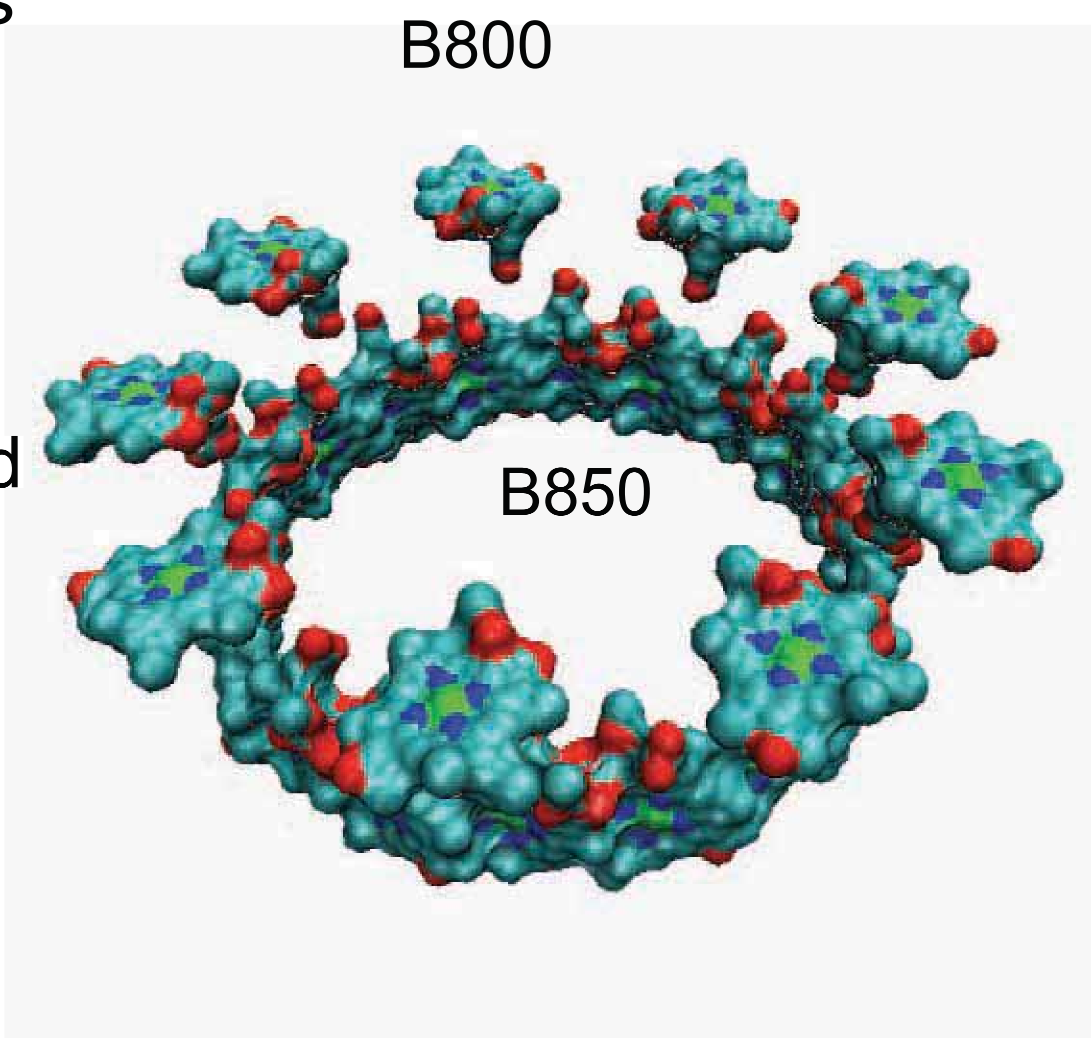


- Energy tuning to efficiently accept energy from B800
- Rapid inter-ring relaxation
- Lowest one-exciton state with very weak fluorescence – ideal for ***energy storage***
- All made possible by electronic coherence

Van Grondelle & Novoderezhkin, PCCP 2005.

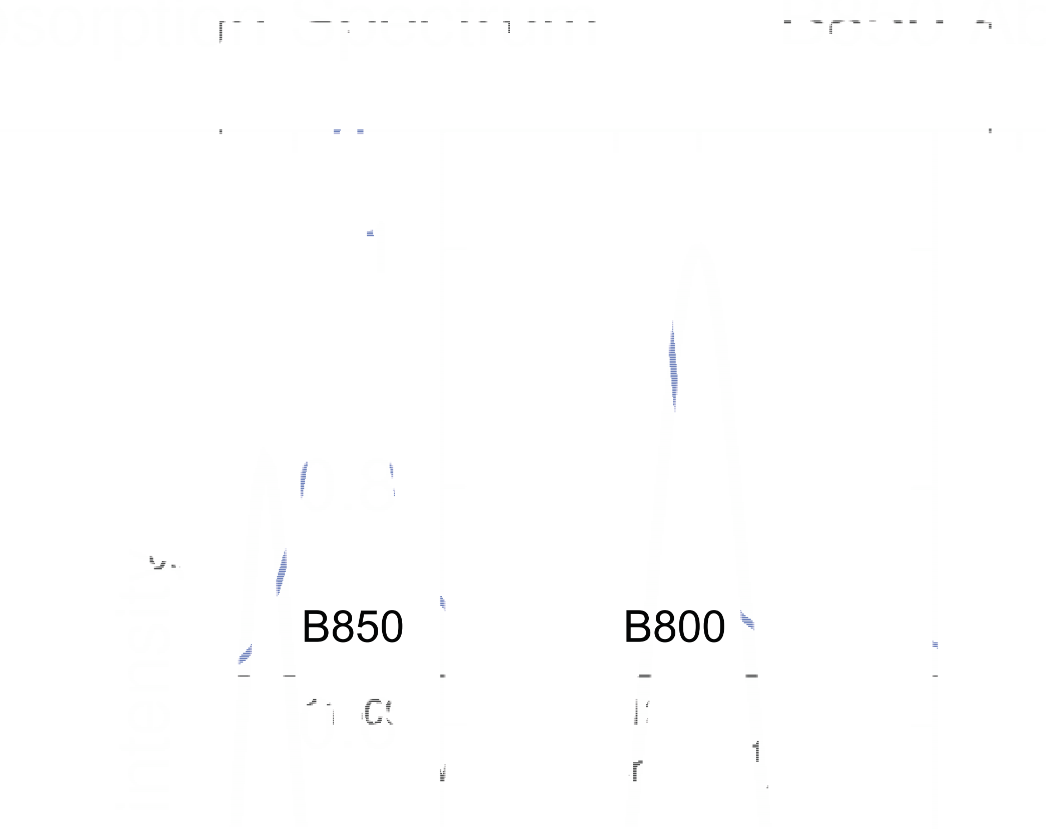
B800-B850 Inter-Ring Couplings

- B800 & B850 BChls are weakly coupled $J_{B800\text{-}850} \sim 20\ \mathrm{cm}^{-1}$
- The EET dynamics should be described by the Forster resonance energy transfer theory



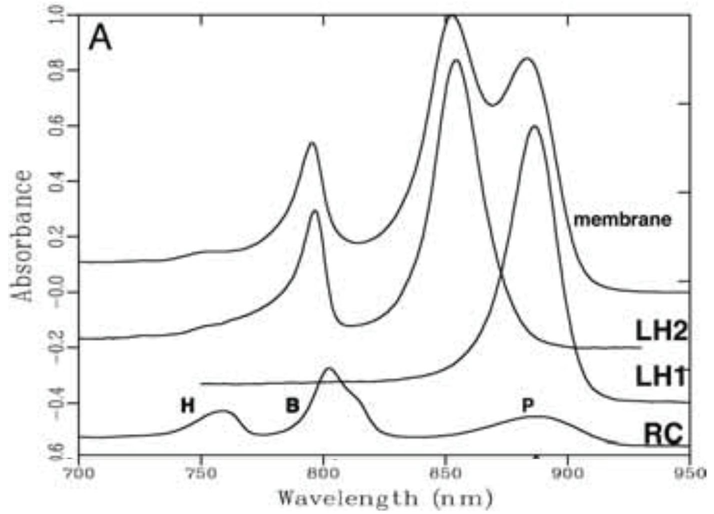
Problems with the Forster Theory

LH2 spectrum



Extremely small spectral overlap

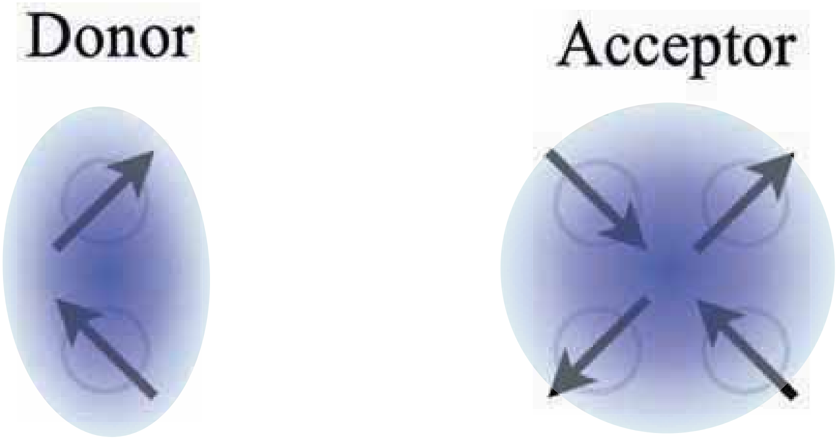
- B800->B850 EET rate predicted by simple Forster theory is 10 times slower than observed
- Also in H➔B➔P, Car S1➔BChl,…



Generalized Forster Theory

- Includes multichromophoric effects in the FRET formula (MC-FRET):

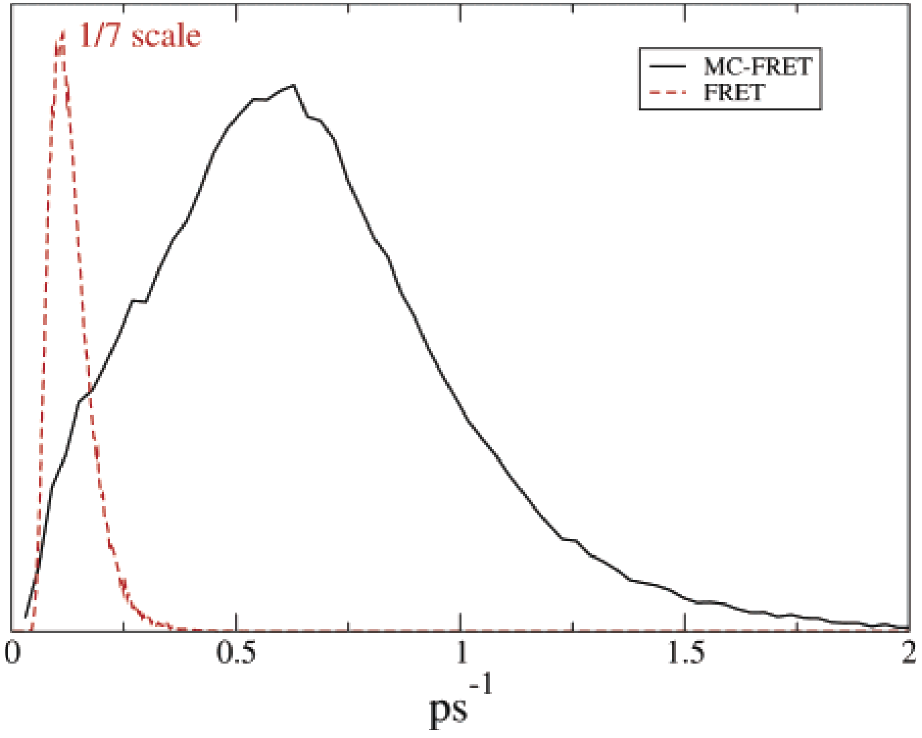
$$k_F^{MC} = \sum_{j'j''} \sum_{k'k''} \frac{J_{j'k'} J_{j''k''}}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D^{j''j'}(\omega) I_A^{k'k''}(\omega)$$



The cross terms represent coherence effects within the donor and the acceptor, respectively.

Sumi, Scholes & Fleming, Jang, Newton, and Silbey…

MC-FRET Theory for B800-B850 EET



- Distribution of EET rate calculated using the MC-FRET theory is in excellent agreement with experiments

- The most effective channel involves EET from B800 to **dark** k= ±2 B850 states

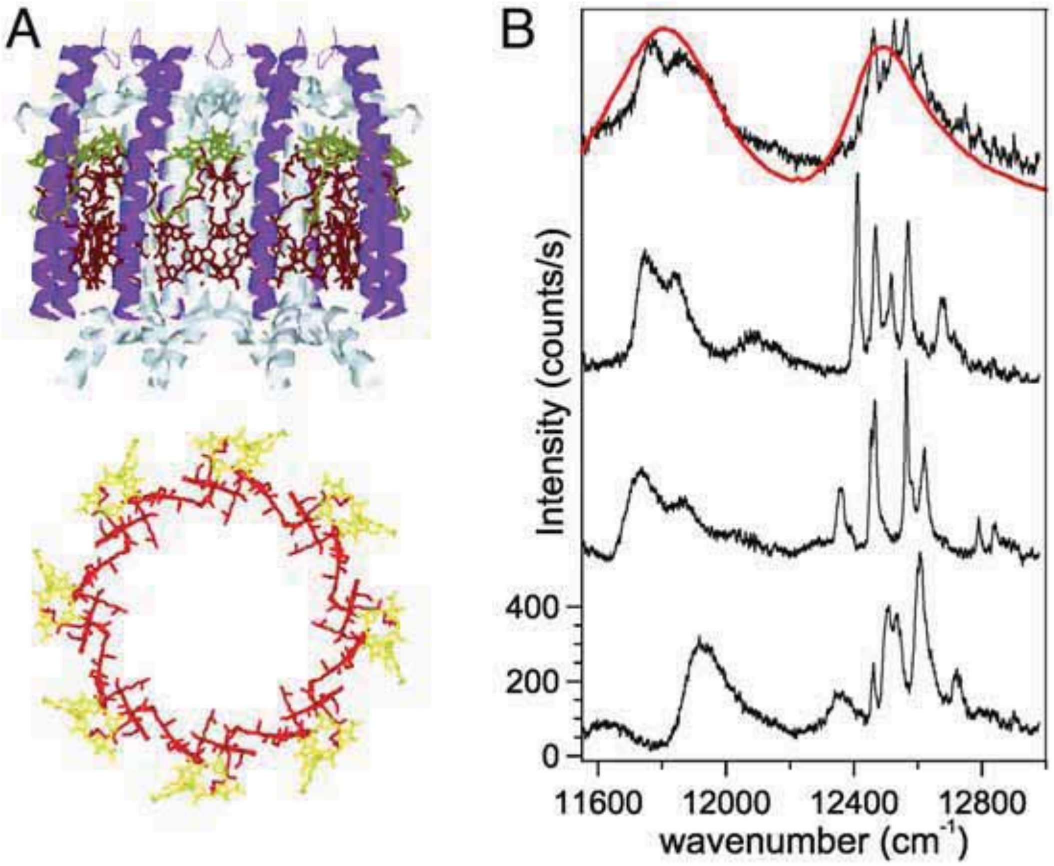
Jang, Newton, and Silbey, JPCB 2007.

B800 Coherence & B800-B850 Inter-Ring EET

B800 Intra-Ring Couplings

- B800 BChls are weakly coupled $J_{B800} \sim -30\ \mathrm{cm}^{-1}$
- B800 band is inhomogeneously broadened, static disorder $\sigma > 60\ \mathrm{cm}^{-1}$
- Conventional wisdom considers B800 excitations as localized on a single site, i.e. no coherence

Single-molecule fluorescence-excitation spectroscopy



Kohler & coworkers, PNAS 2003.

Spectrum of the B800 System

- B800 exhibits an asymmetric shape that was difficult to explain based on localized excitations
  - Non-Gaussian form
  - Pronounced blue tail

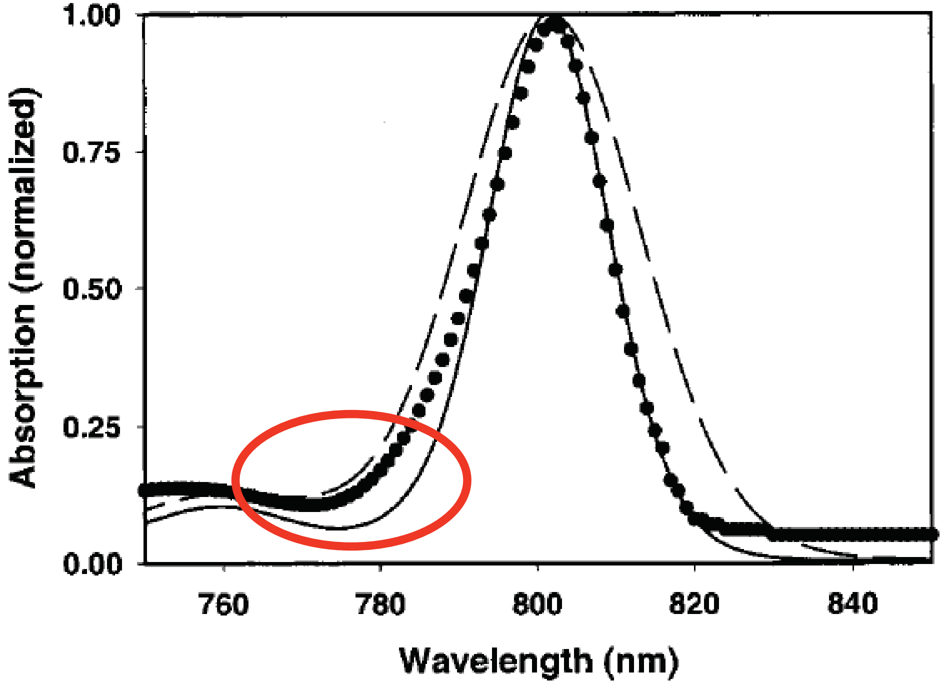
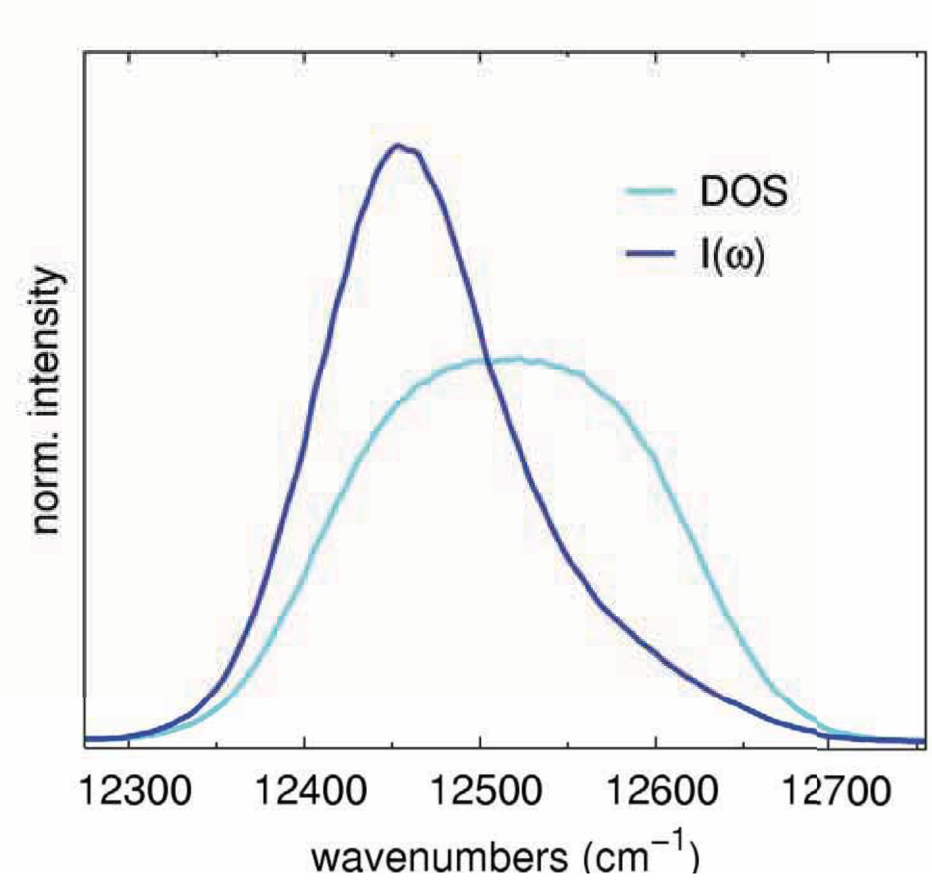


Figure 7. B800-only absorption spectrum (solid circles) obtained after removing the contribution from the B850 absorption spectrum. The dashed line shows the simulated B800 absorption spectrum with a disorder width of 150 cm^{-1}, and the solid line is the simulated spectrum with a disorder width of 100 cm^{-1}.

Agarwal et al., JPCB 2001.

Coherence Signature of B800

- Simulation including coherence effects is in excellent agreement with experiments

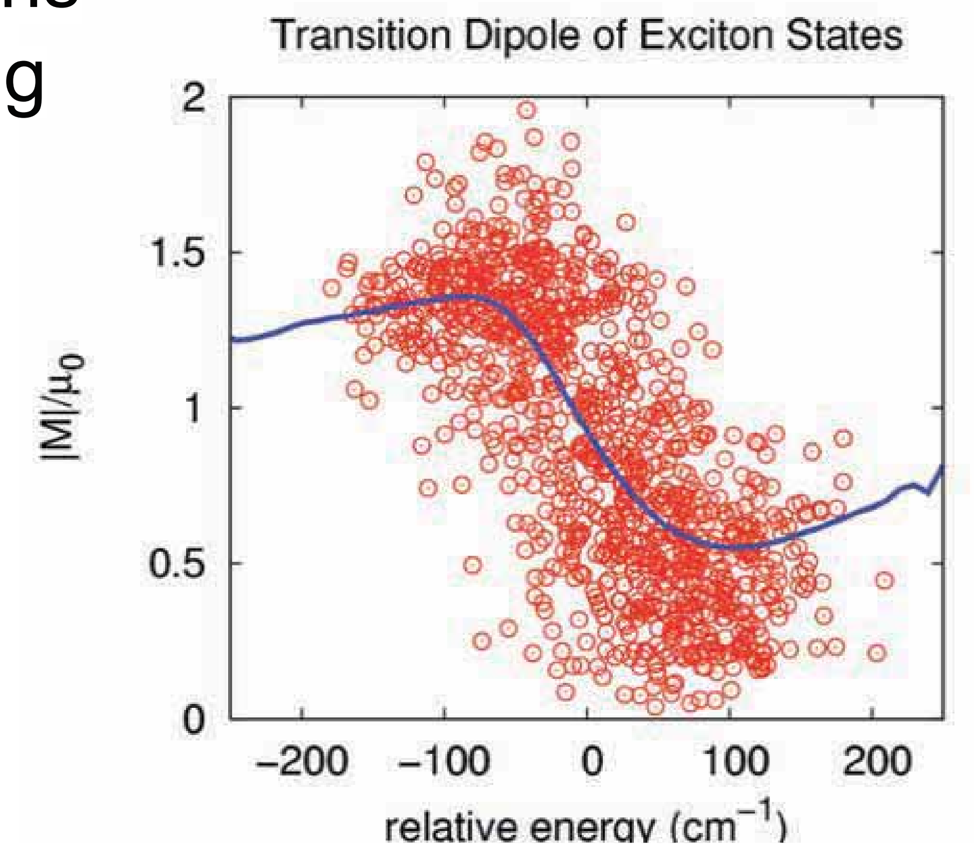


Asymmetric lineshape because coherences re-distribute oscillator strengths in the B800 excitons

Cheng & Silbey, PRL 2006.

Coherence Signature of B800

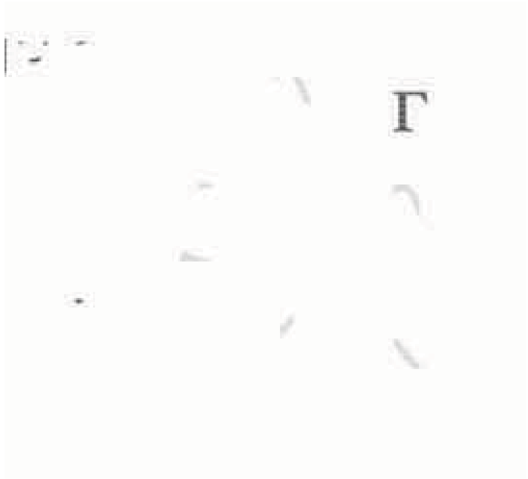
- Transition dipoles of B800 states show anti-correlated energy dependence
- On average, excitations are delocalized among dimers

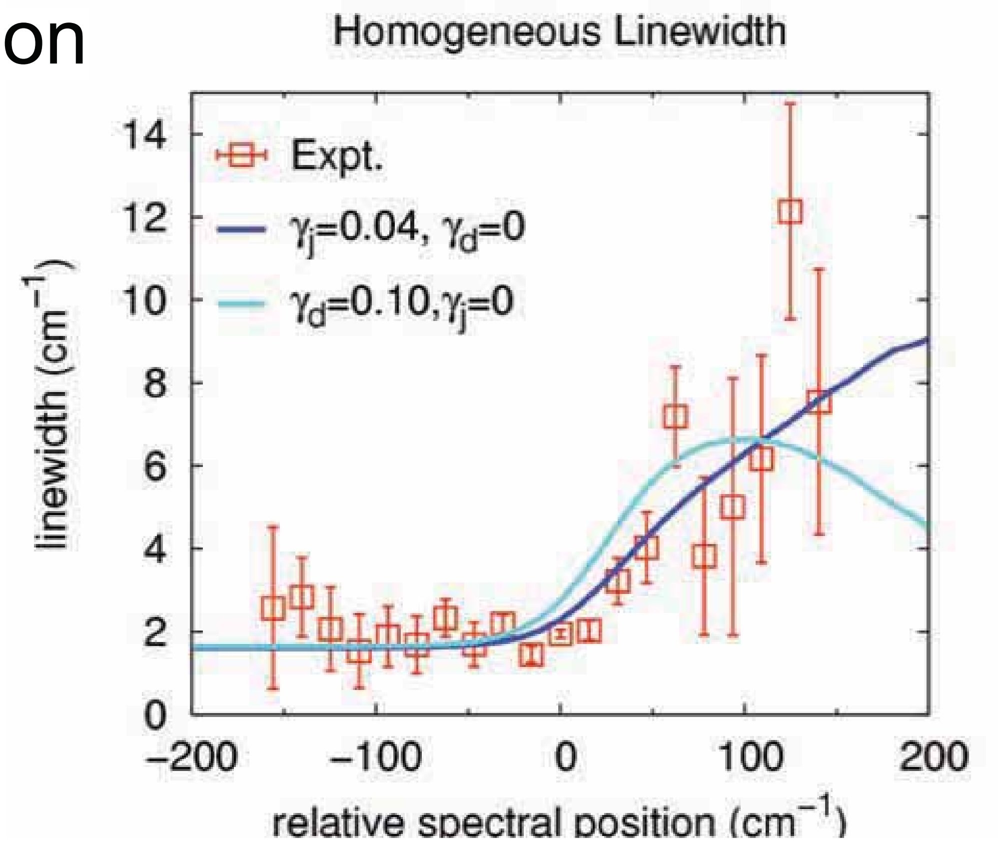


Cheng & Silbey, PRL 2006.

Coherence Effects in B800 Intraband EET

- Hole-burning & single-molecule experiments indicate energy dependent homogeneous linewidth in the B800 band
- Explained by relaxation within dimer states





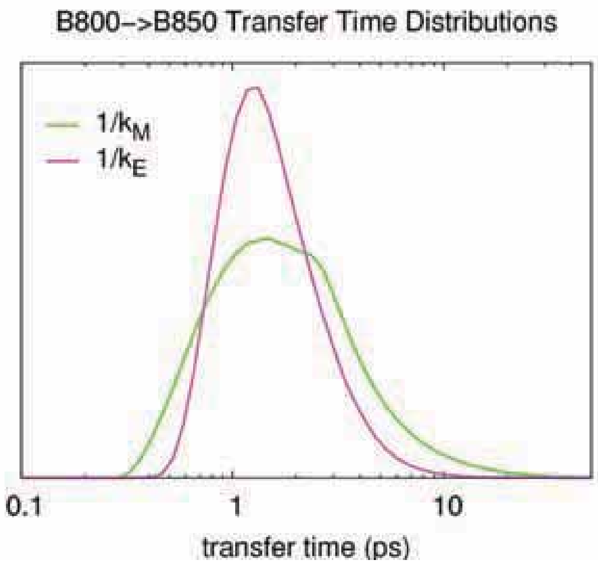
Cheng & Silbey, PRL 2006.

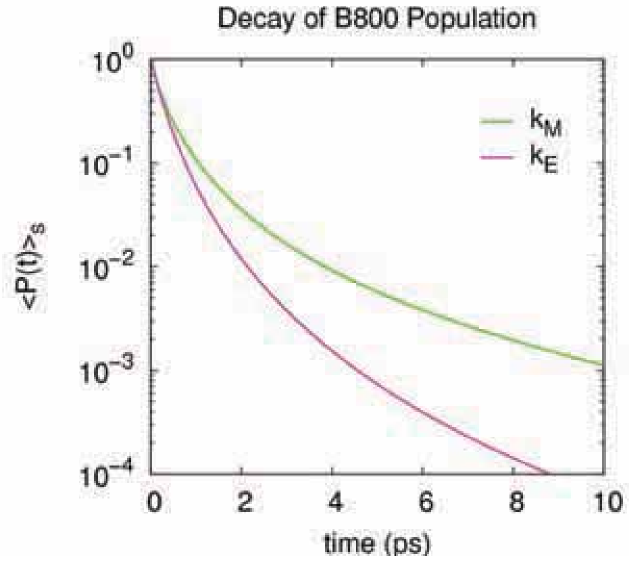
Coherence Effects in B800-B850 Interband EET

- Monomer model

- Dimer Model

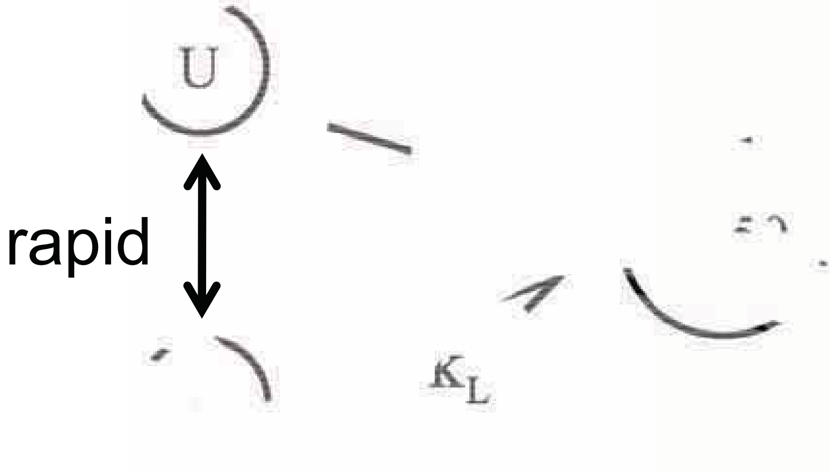
$$k_{B800\to B850} \sim (k_L + k_U)/2 \equiv k_E$$

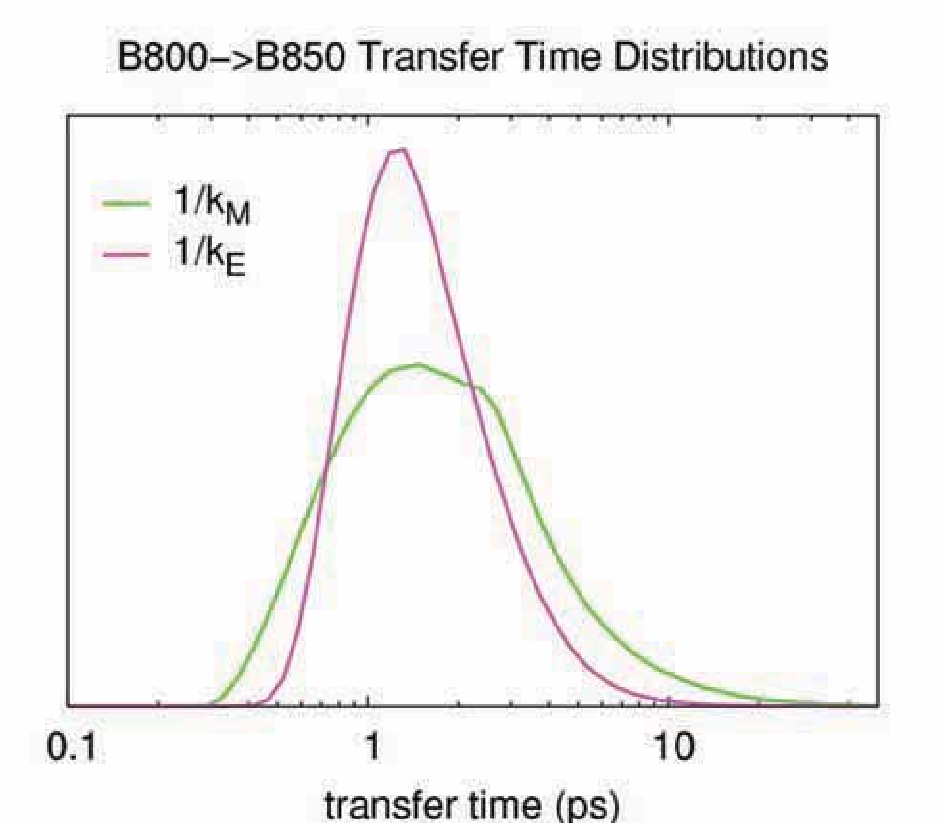




Coherence Effects in B800-B850 Interband EET

- Narrower distribution of B800->B850 EET rates enabled by rapid EET between B800 dimer states
- Quantum coherence in B800 makes light harvesting more robust!



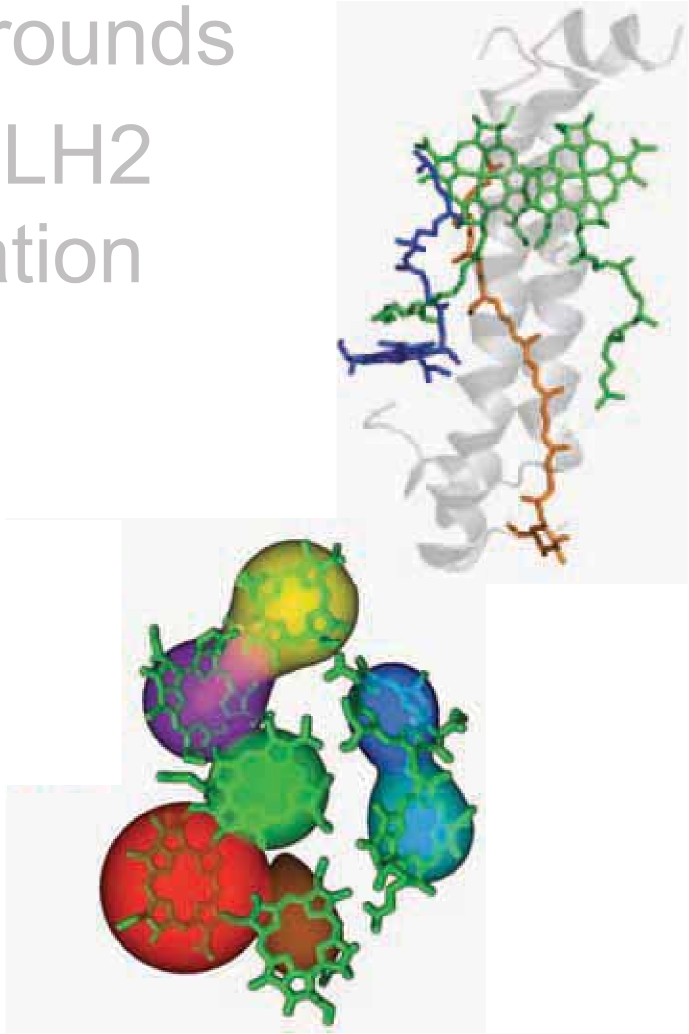


Remarks

- Quantum coherences as represented in delocalized exciton states are necessary for the understanding of LH2 light harvesting: photosynthetic excitons!
- Purple bacteria have employed quantum mechanical rules to optimize the efficiency of light harvesting

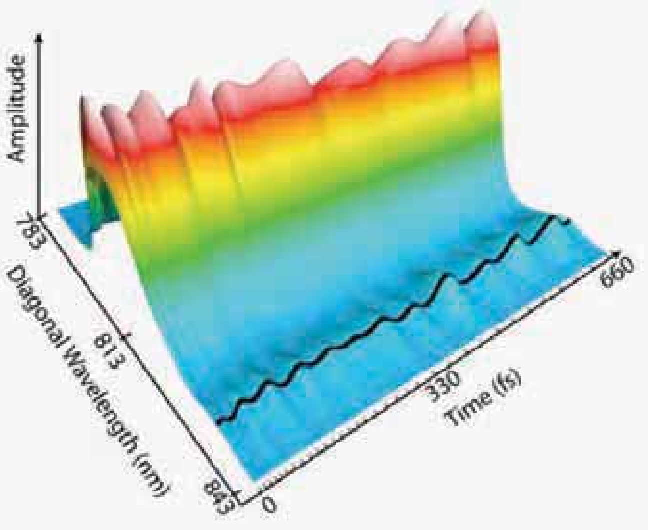
Outline

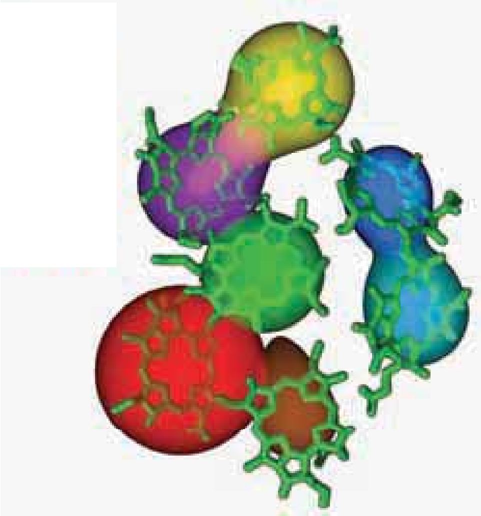
- Part I: Introduction to photosynthetic light harvesting & theoretical backgrounds
- Part II: Quantum coherence in LH2 from purple bacteria – optimization of light harvesting through delocalization of excitons
- Part III: Excitonic quantum coherence in light harvesting – coherence assistant excitation energy transfer



Outline (Part III)

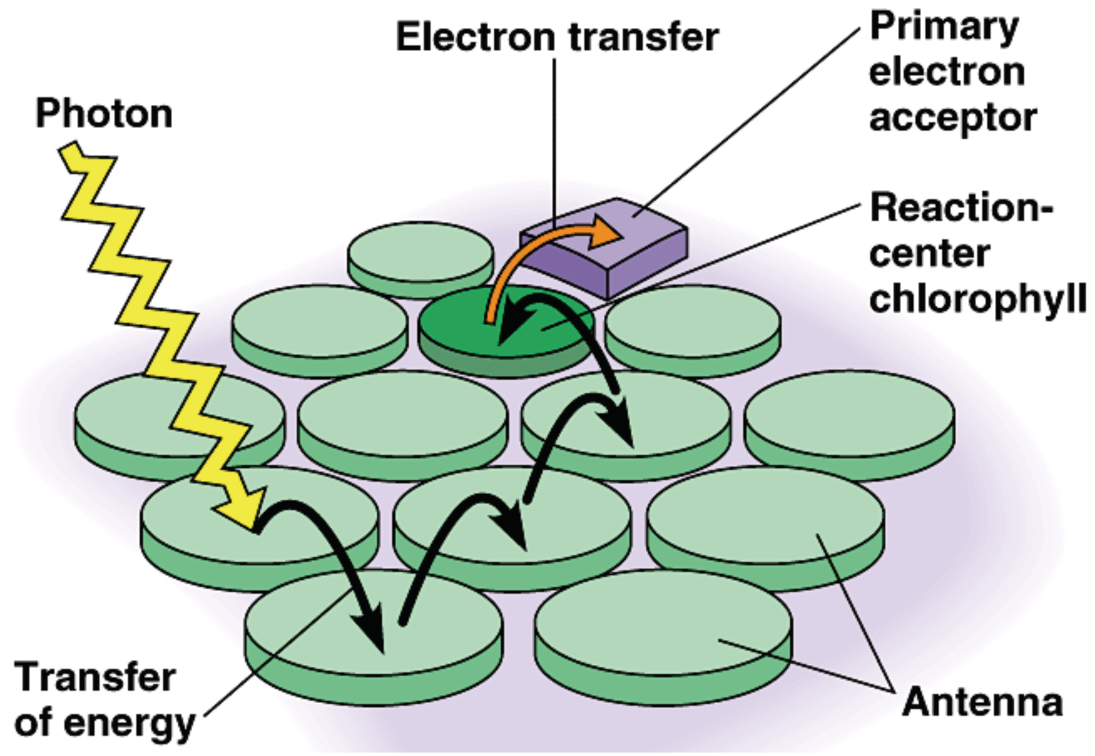
- Light harvesting & excitonic coherence
- Experimental evidences for quantum coherence effects in photosynthetic light harvesting
- Quantum dynamical modeling of coherent excitation energy transfer (EET) in light harvesting
- Coherence assisted excitation energy transfer
- Concluding remarks





Incoherent Hopping Model of Light Harvesting

- The conventional paradigm of light harvesting



- Quantum effects in coherent dynamics?

Coherent Evolution of Density Matrix

- Time-evolution of a superposition of

stationary

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

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

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

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

- Coherence oscillation results in energy population moving rever ophores

- Cohe sing 2-D photon echo spectroscopy: quantum beats in 2-D signals

phase oscillation

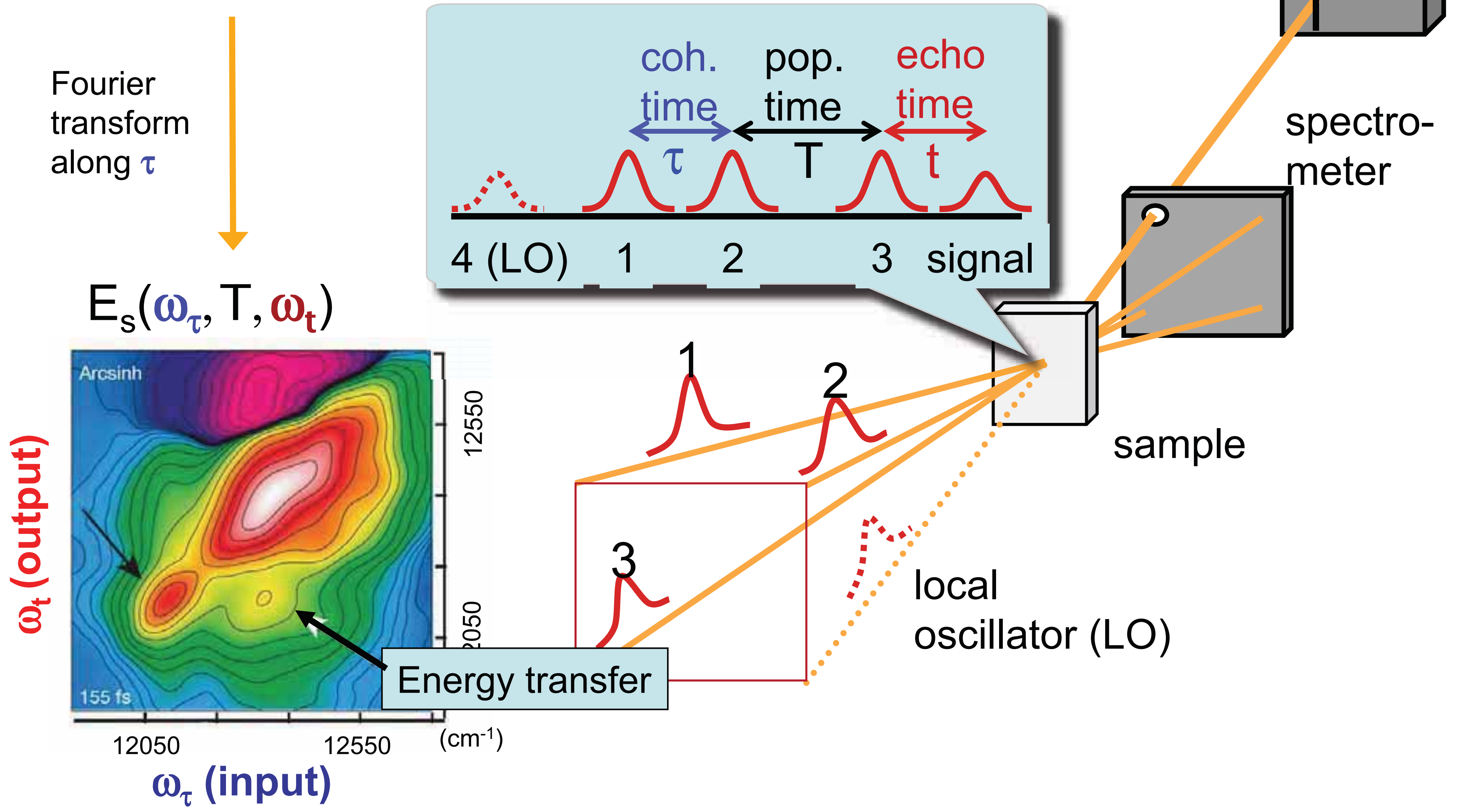
ence

Two-dimensional Electronic Spectroscopy

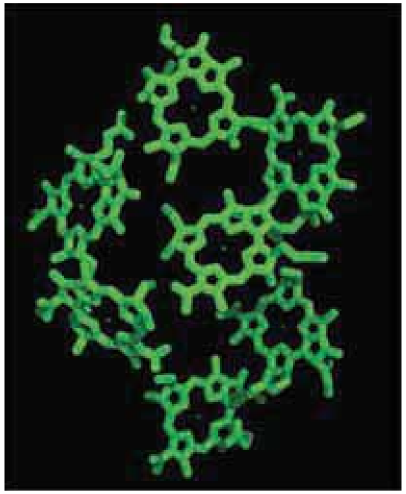
$$E_s(\tau, T, \omega_t) \sim iP^{(3)}(\tau, T, \omega_t)$$

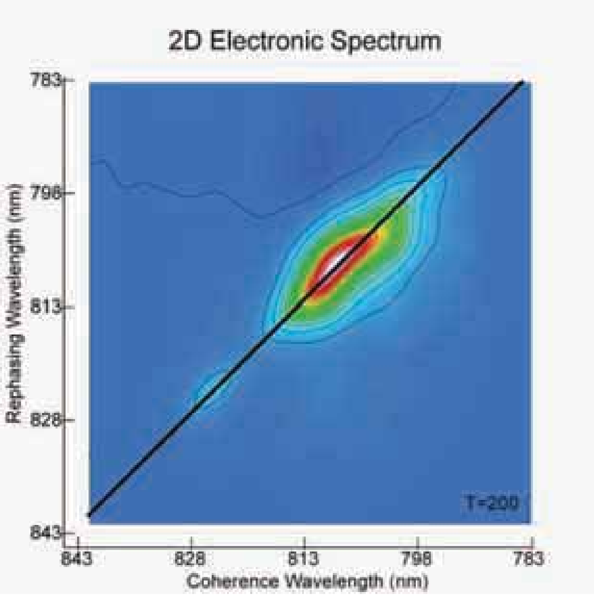
Fourier transform along τ

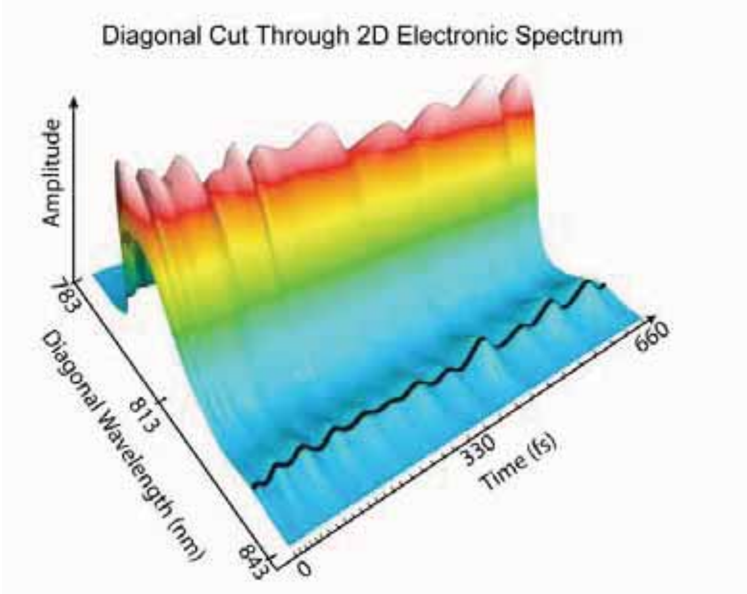
$$E_s(\omega_\tau, T, \omega_t)$$



Electronic Coherence in FMO (77K)





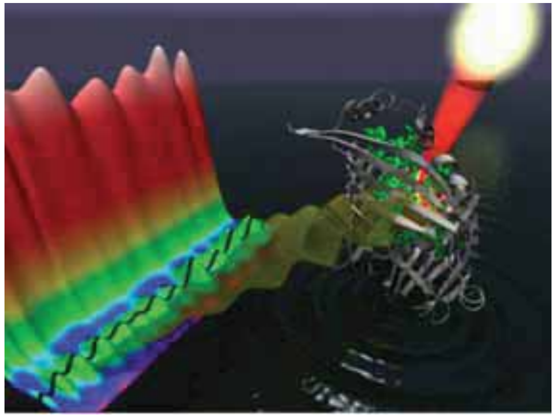


- 2D electronic spectra show quantum beats on the diagonal cuts
- Strong evidence for long-lasting excitonic coherence (> 600 fs) in the Fenna-Matthews-Olson Complex
  ➔ coherent wavelike energy transfer
- True electronic quantum effect may play a role in energy transfer

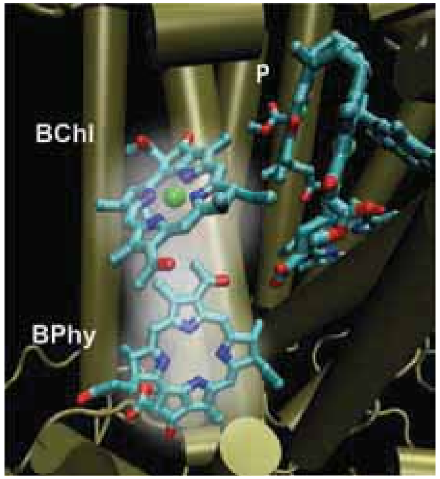
G.S. Engel, T.R. Calhoun, E.L. Read, T. Ahn, T. Mancal, **Y.-C. Cheng**, R.E. Blankenship & G.R. Fleming, *Nature* **446**, 782 (2007)

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).

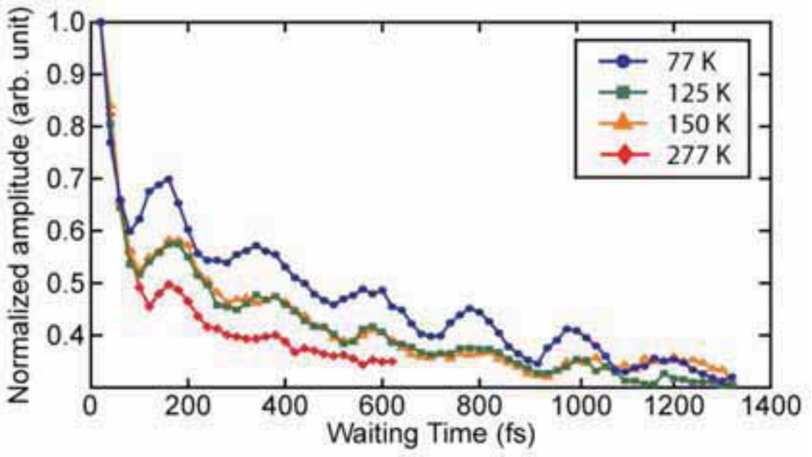


- **Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence**, H. Lee, Y.-C. Cheng & G.R. Fleming, *Science* **316**, 1462 (2007).

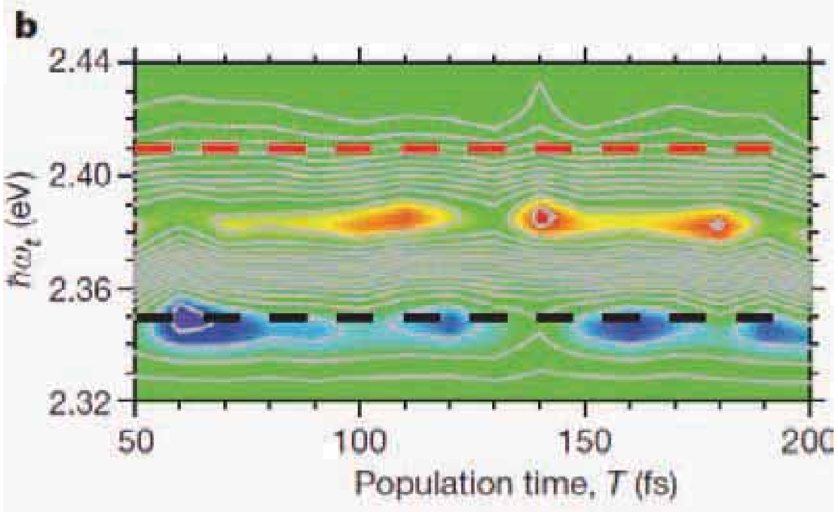
New Insights into Photosynthetic Light Harvesting

- 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).



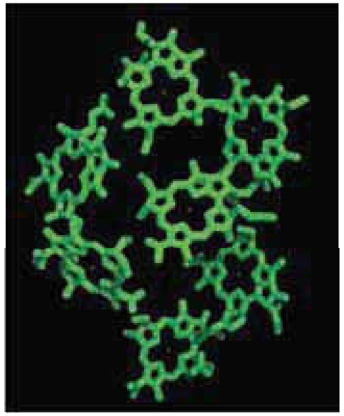
- **Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature**, G. D. Scholes and coworkers, *Nature,* **463**, 644 (2010).

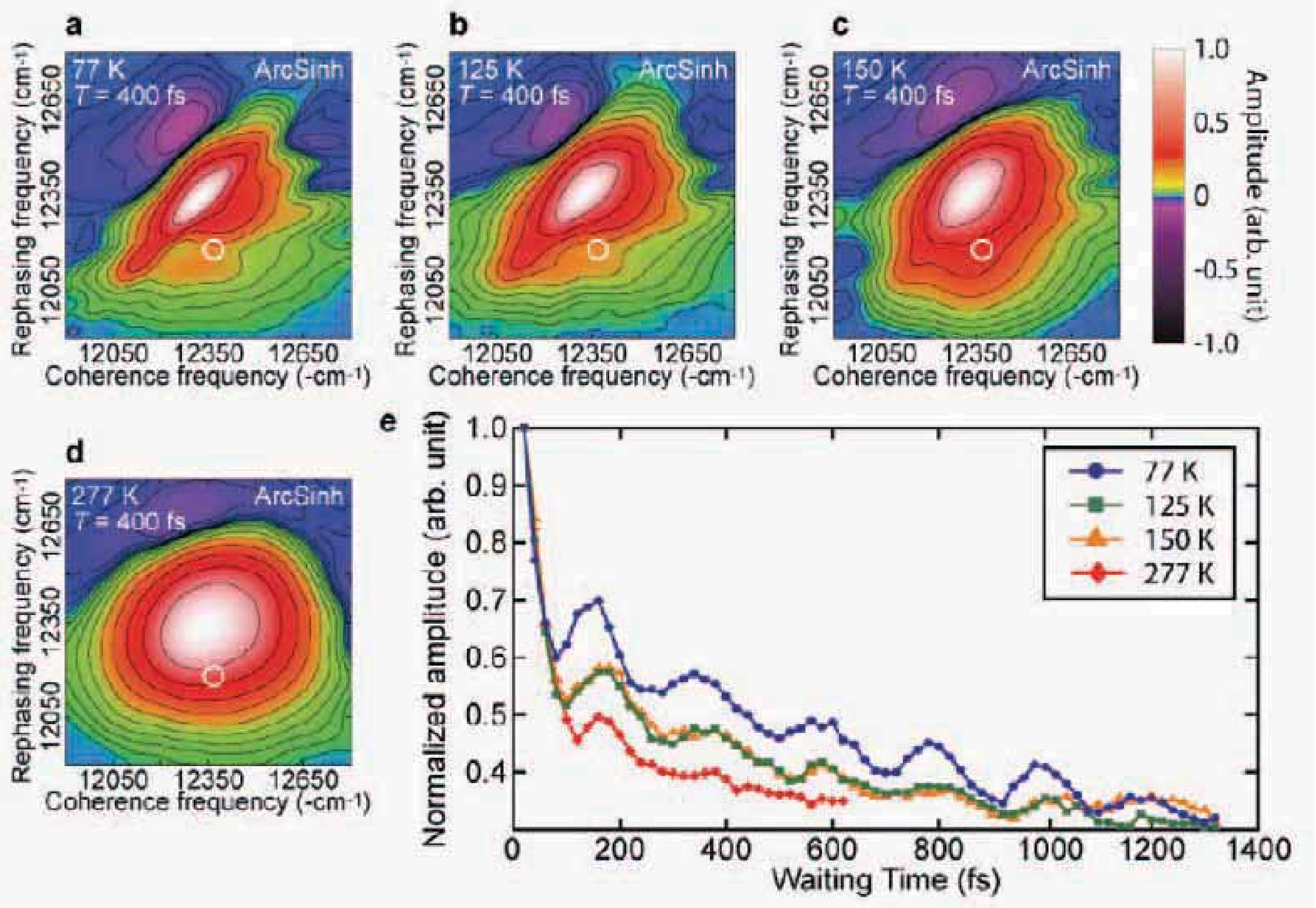


Quantum Coherence in FMO at Physiological Temperature

FMO

2DES
Spectra





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

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

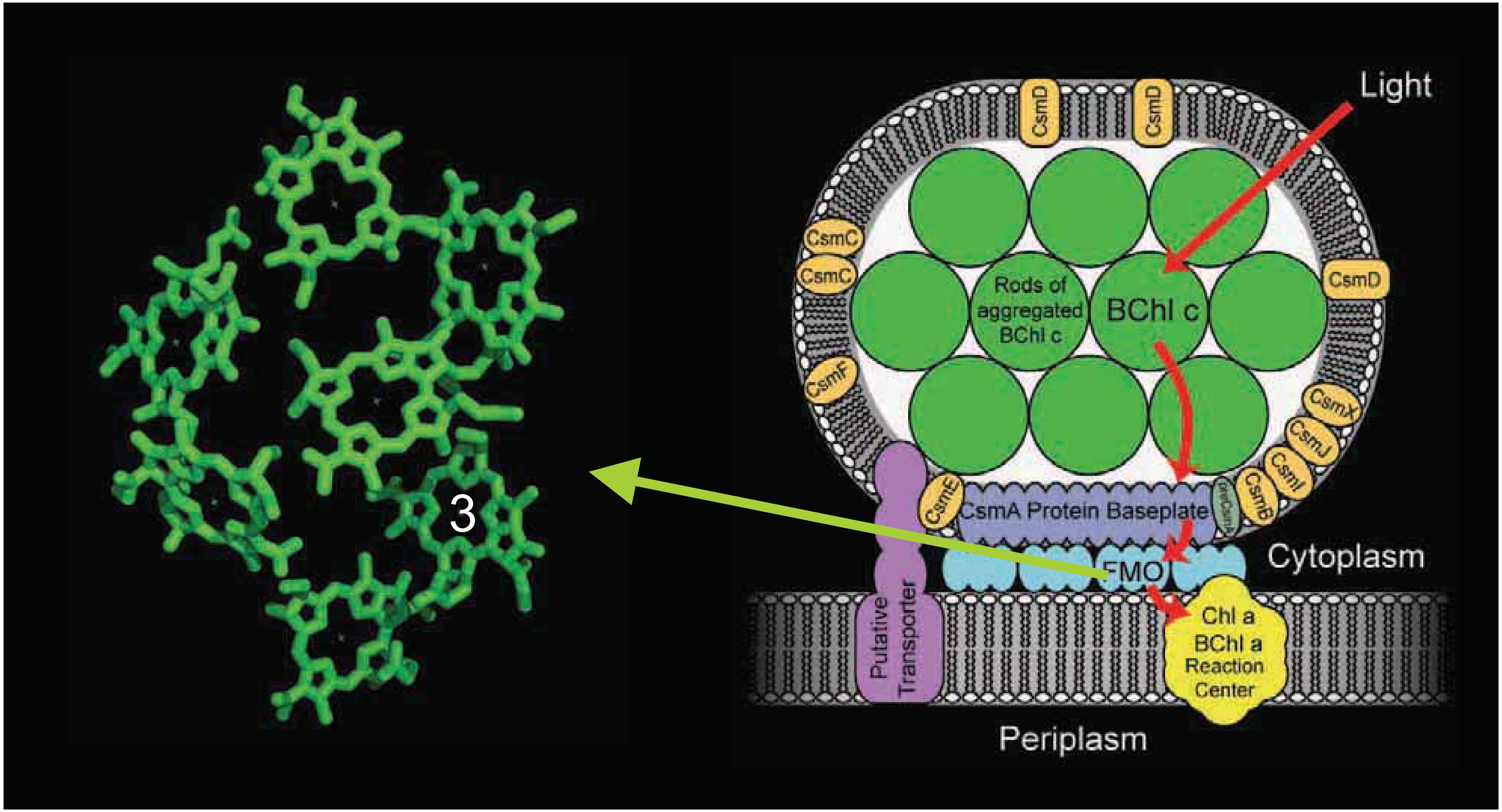
Combine experimental results & theoretical modeling to find out!

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

The Fenna-Matthews-Olson Complex

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



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

FMO Complex: Electronic Interactions

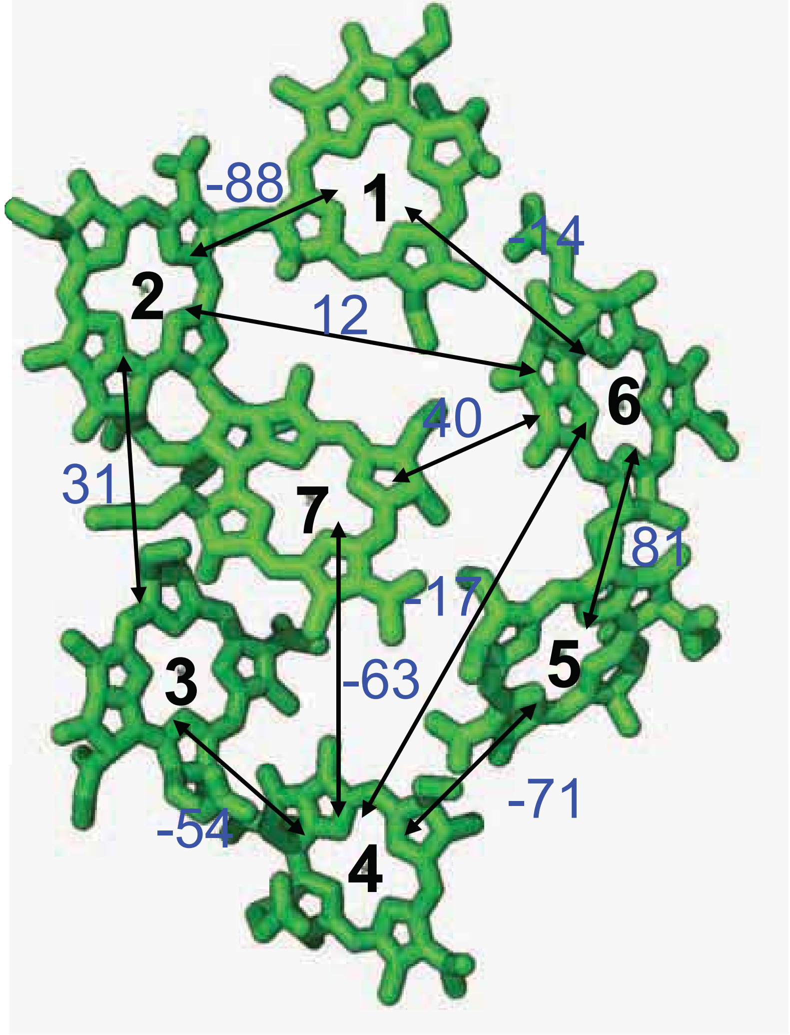
- There is a good starting point for the model of FMO Hamiltonian
- Couplings from quantum chemistry + transition density cube calculations
- Site energies from fitting to optical spectra

Site energies

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

J. Adolphs & T. Renger, Biophys. J. 91, 2778 (2006).

Excitonic couplings



* For C. Tep. FMO, unit in cm^{-1}

Redfield Picture of Excitation Energy Transfer

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

exciton Hamiltonian

dissipation determined by system-bath couplings

$$\partial_t \rho(t) = -i[H_e, \rho(t)] - \Re[\rho(t)]$$

population coherence

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

ρ: reduced-system density matrix

N: number of chromophores

$$\Re[\,]: \quad \begin{array}{l} \rho_{nn} \to \rho_{mm} : \text{ population dynamics (incoherent)} \\ \rho_{nm} \to \rho_{n'm'} : \text{ coherence dynamics} \end{array}$$

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

Meier & Tannor, *J. Chem. Phys.* **111**, 3365 (1999); Cheng, Lee & Fleming, JPCA (2007).

Calculate Nonlinear Spectrum

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

exciton Hamiltonian

dissipation

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

light-matter interactions

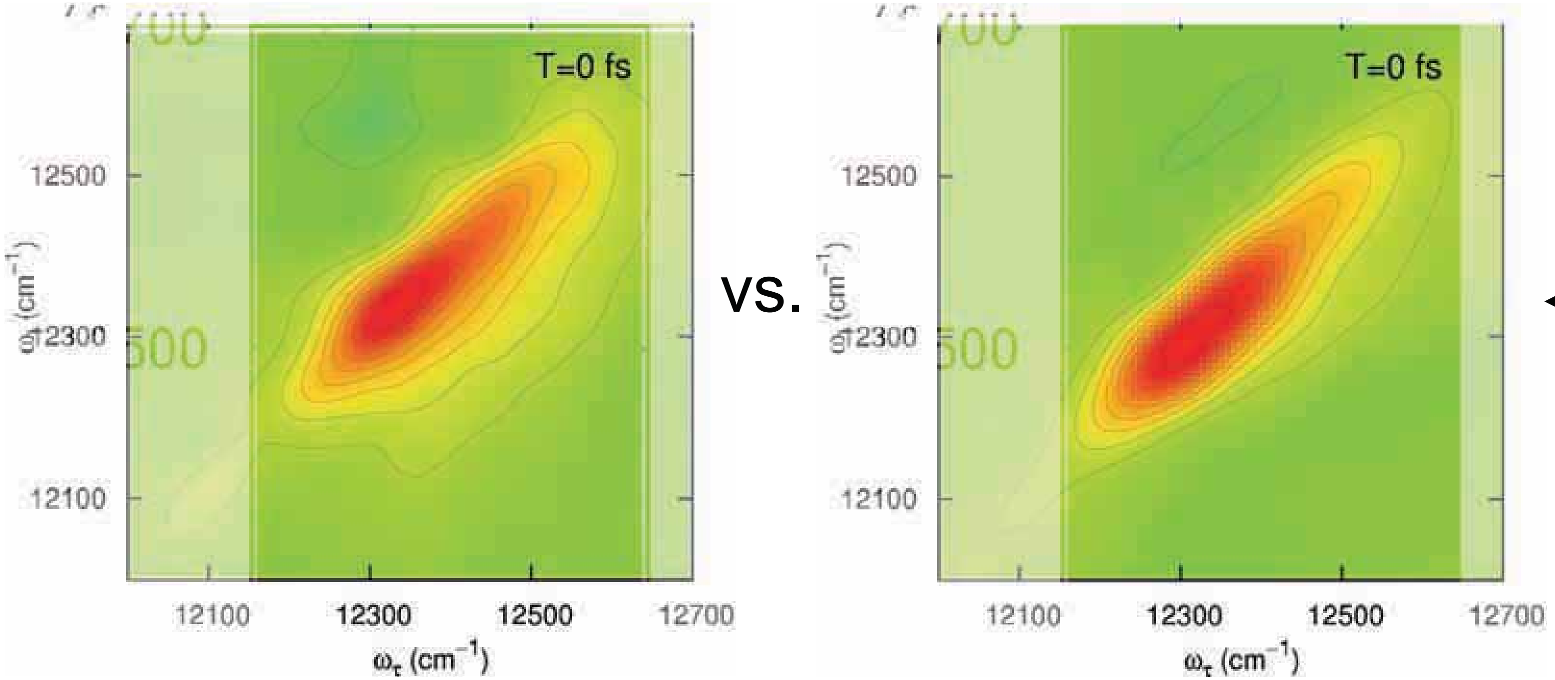
$$H_{\text{int}}(t) = -\mu \cdot \sum_{a=1}^{3} \mathbf{E}_a(t)$$

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

M. F. Gelin, D. Egorova, W. Domcke, JCP **123**, 164112 (2005);
Y.-C. Cheng, H. Lee, G. R. Fleming, JPCA **111**, 9499 (2007).

Simulated 2D Spectrum for FMO

Experiment Theory Model



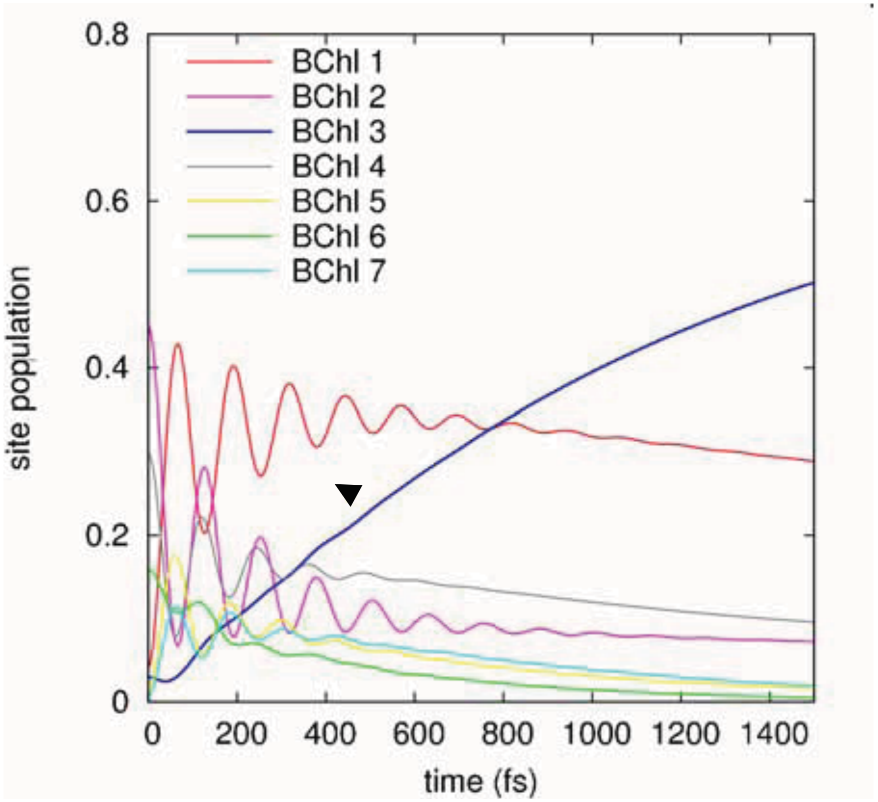
$$\longleftrightarrow \quad H_e + \Omega(\omega)$$

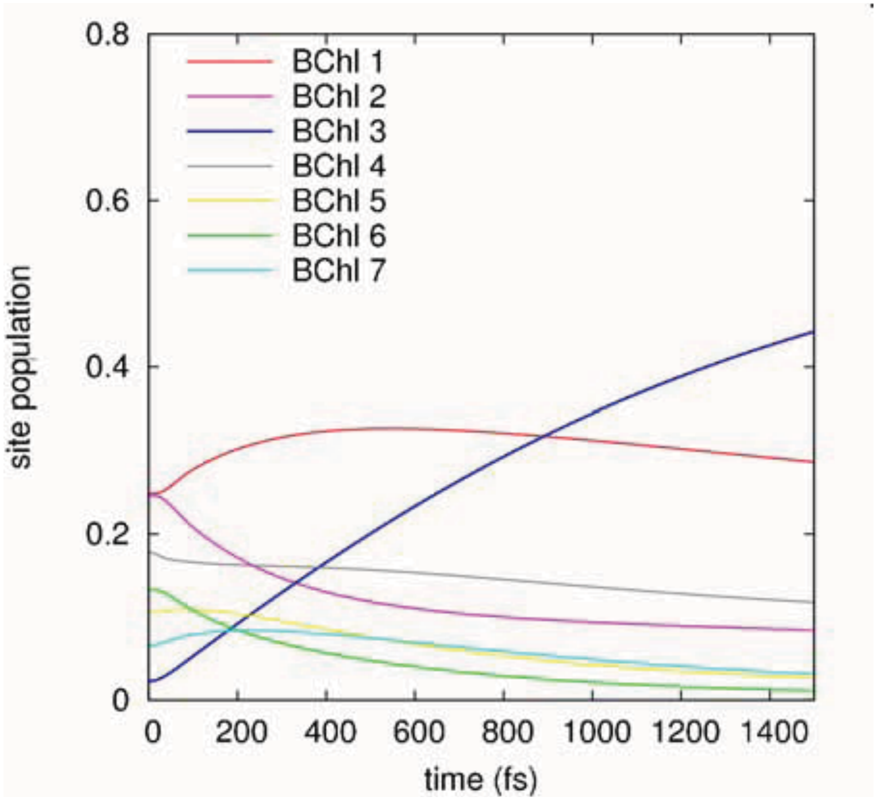
- Iterate to reach good agreement between experiment & theory (starting from Renger's model)
- Require inclusion of doubly excited states and average over a Gaussian distribution of disordered energies
- Provide refined model ➔ basis for studying coherence effects

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

Dynamics in the Site Basis

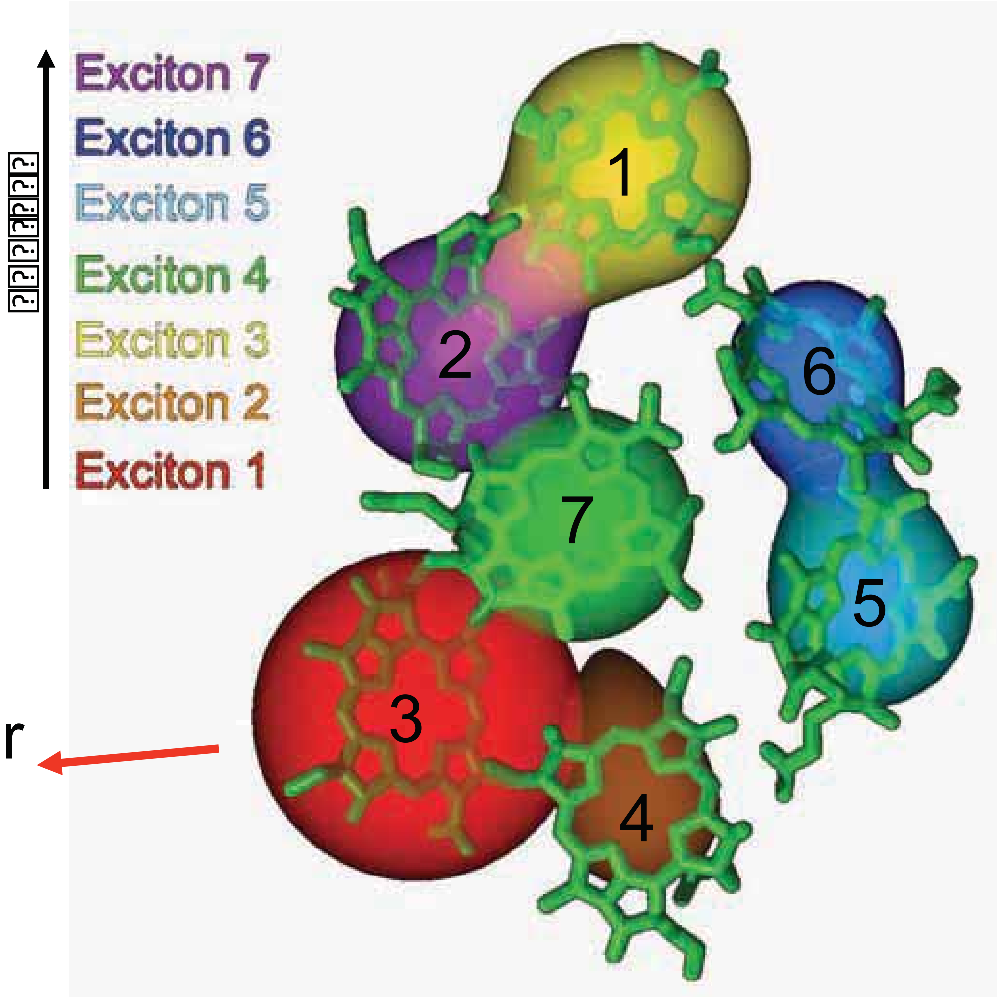

Coherent Picture


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

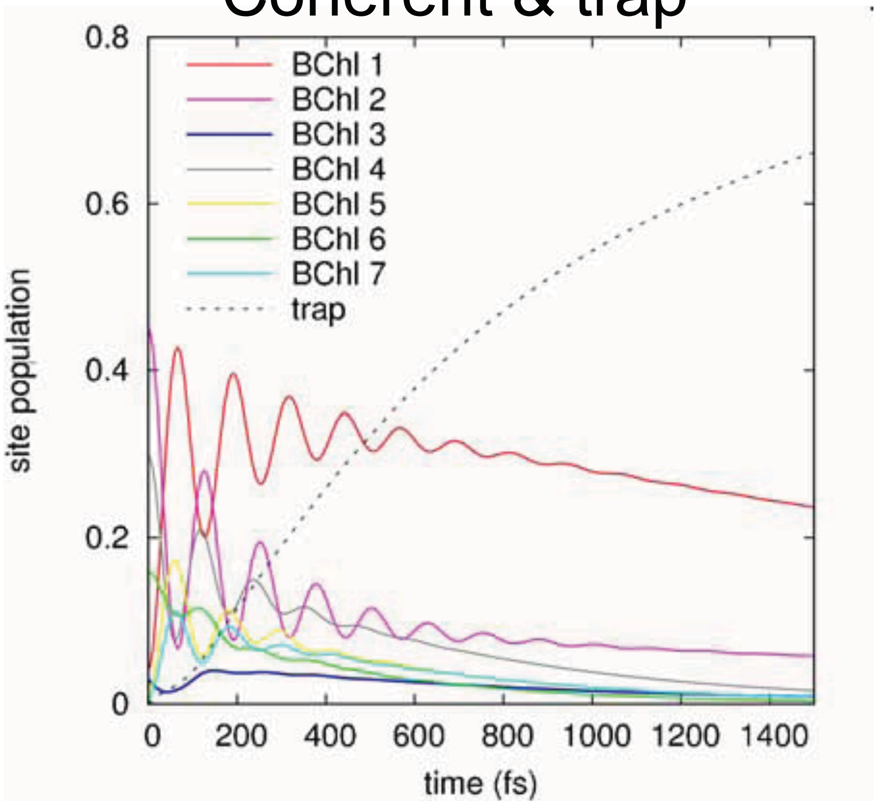
FMO complex is a energy wire connected to RC through BChl 3

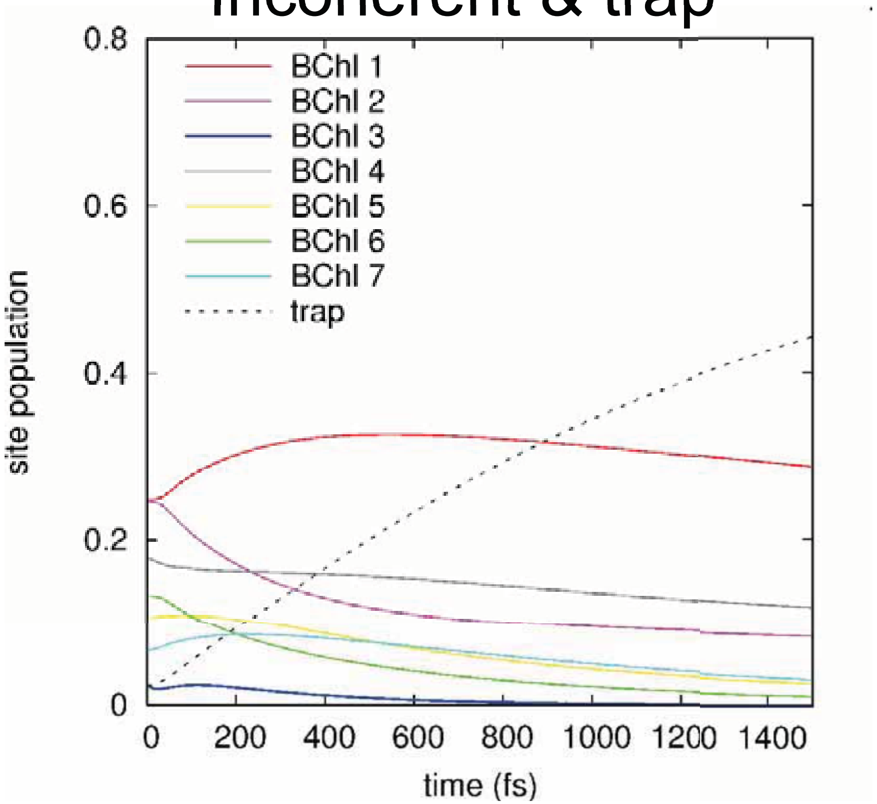


Reaction center
(energy trap)

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

Coherence Assisted Energy Trapping

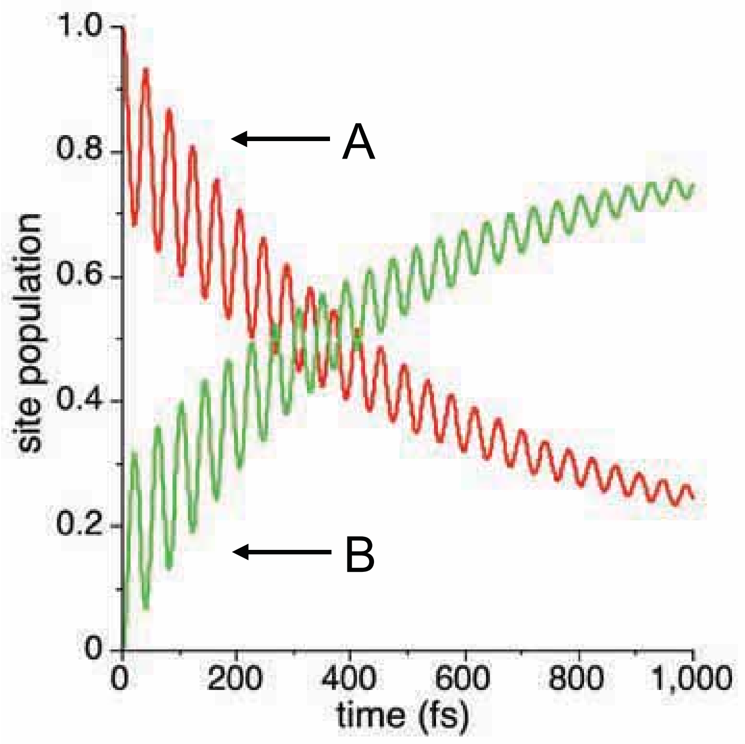

Coherent & trap

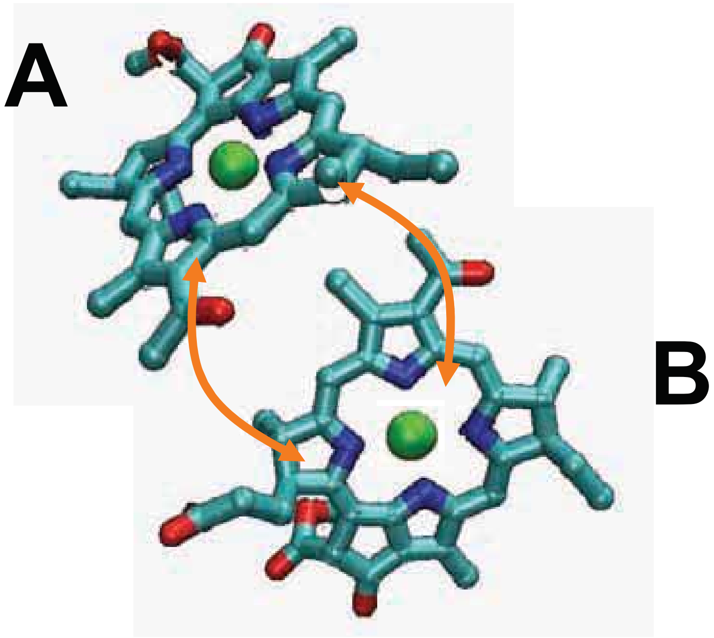

Incoherent & trap

- 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*

Simple Model for Coherence Assisted Energy Trapping

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



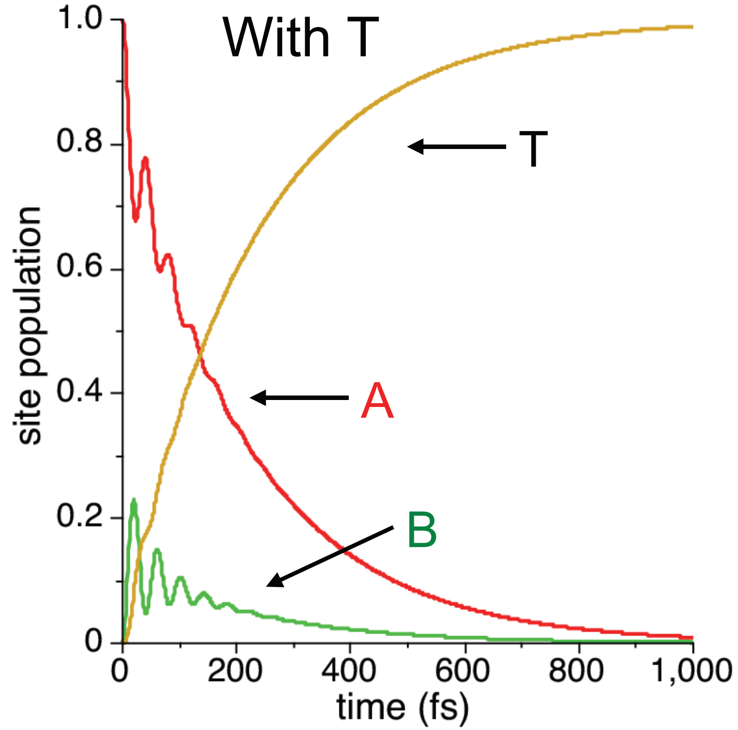


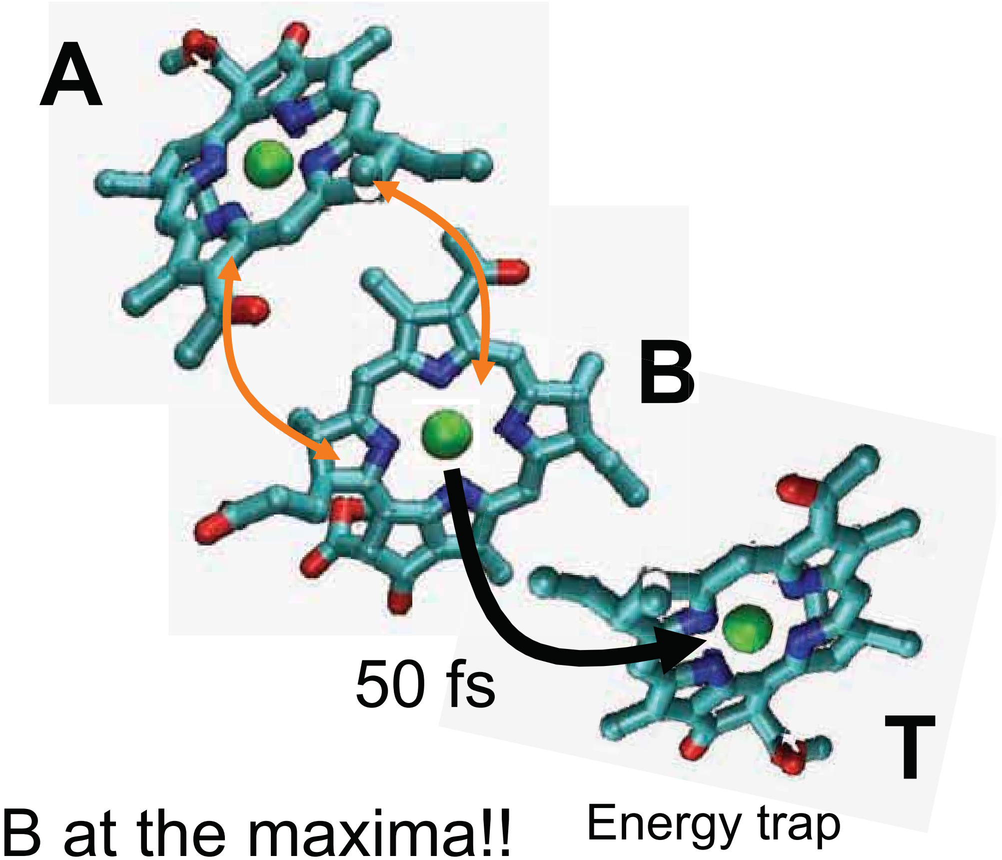
Effective A➔B time: 500 fs

Bloch dynamics using 450 fs A/B dephasing time, 500 fs intrinsic A➔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



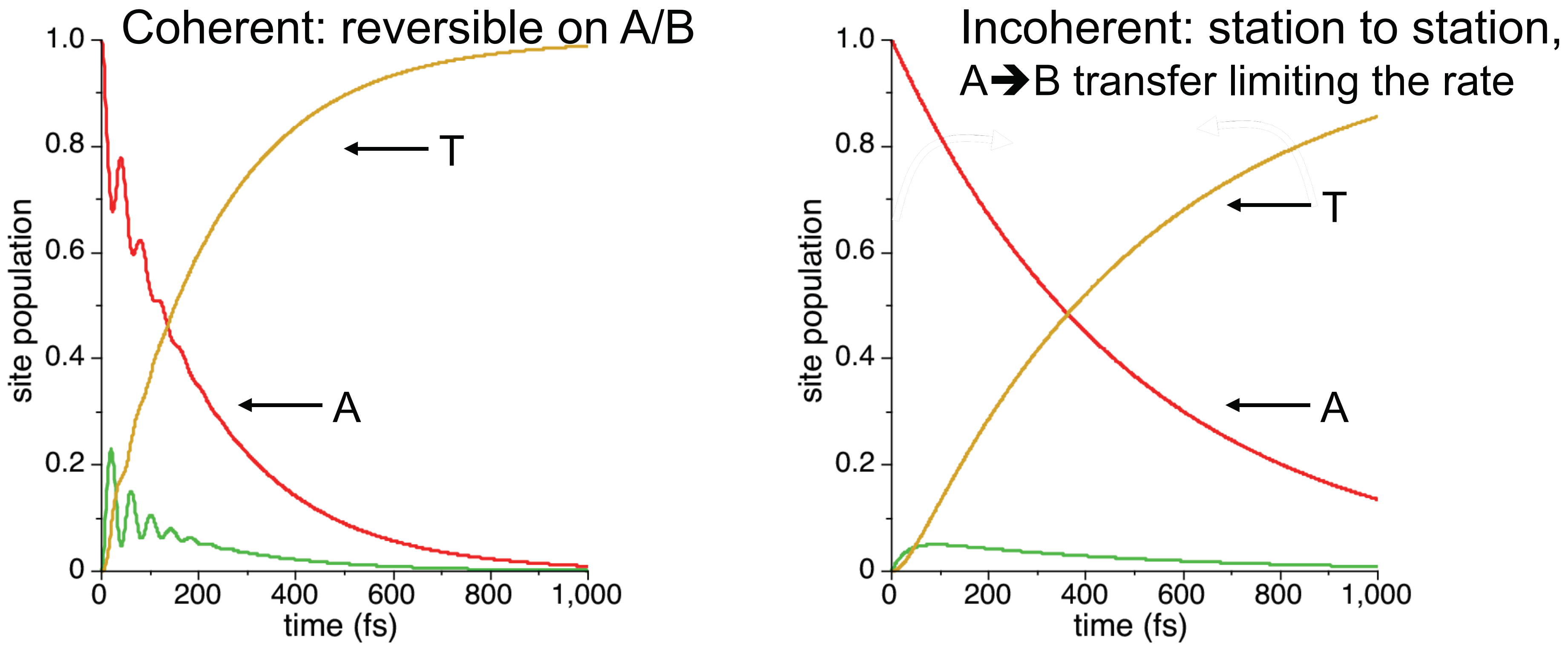


T efficiently captures energy on B at the maxima!!

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



Coherent: reversible on A/B

Incoherent: station to station, A➔B transfer limiting the rate

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

Lee, Cheng & Fleming, UP2008

Coherence Assisted Energy Trapping

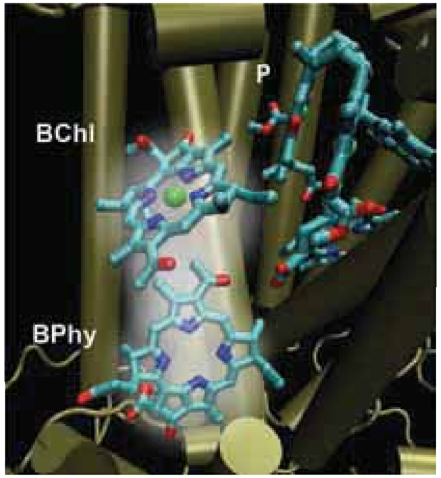
- Long-lived electronic coherence enables the system to perform rapid and reversible sampling in space to search for the trap site
- Efficient trapping process dissipates the energy and localizes the excitation
- The scheme can be more efficient than incoherent hopping and is likely to be more robust 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?

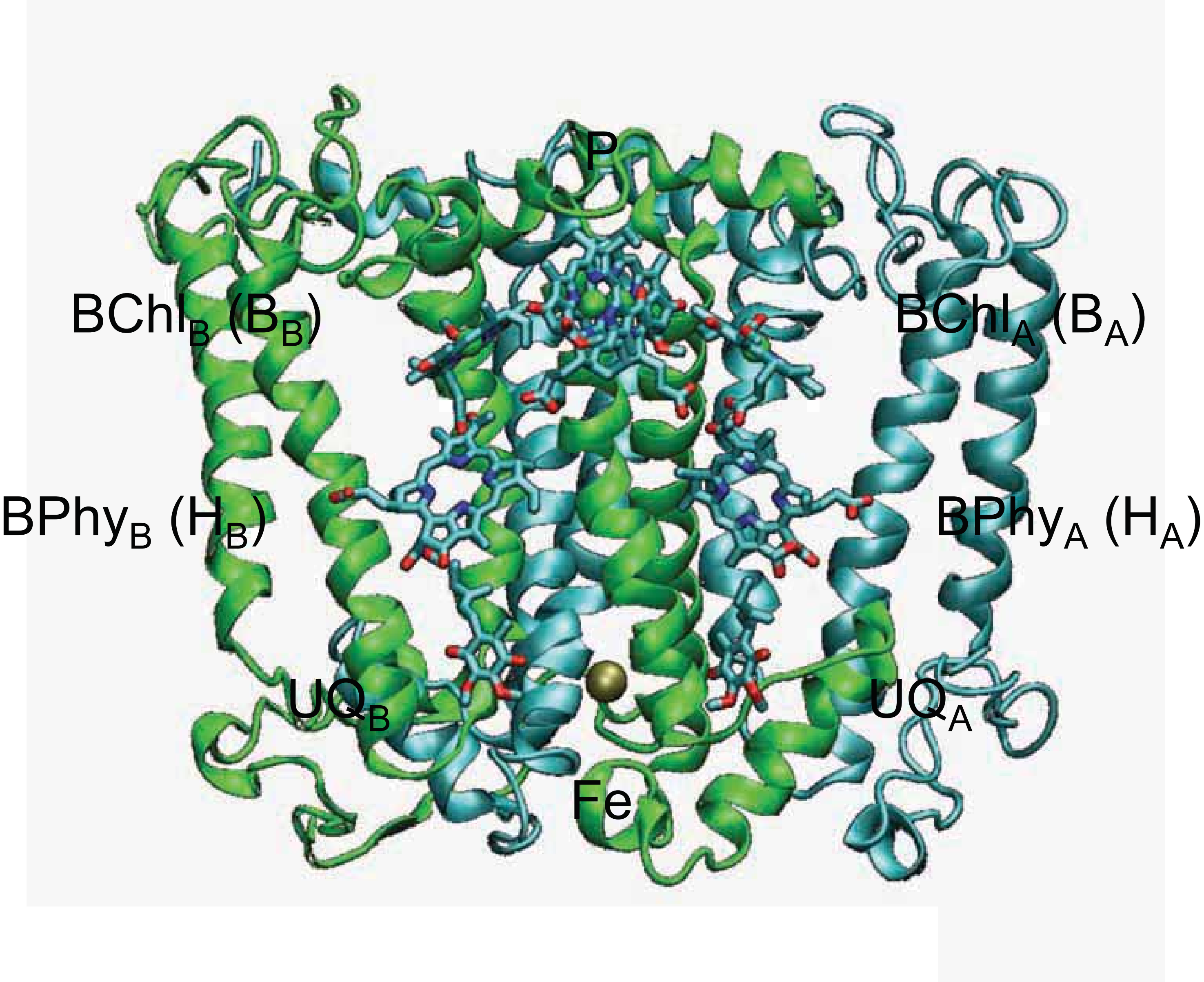
1. Protein environment & correlated motions
2. Non-equilibrium effects in energy transfer

Coherence Photon Echo of Bacterial Reaction Center

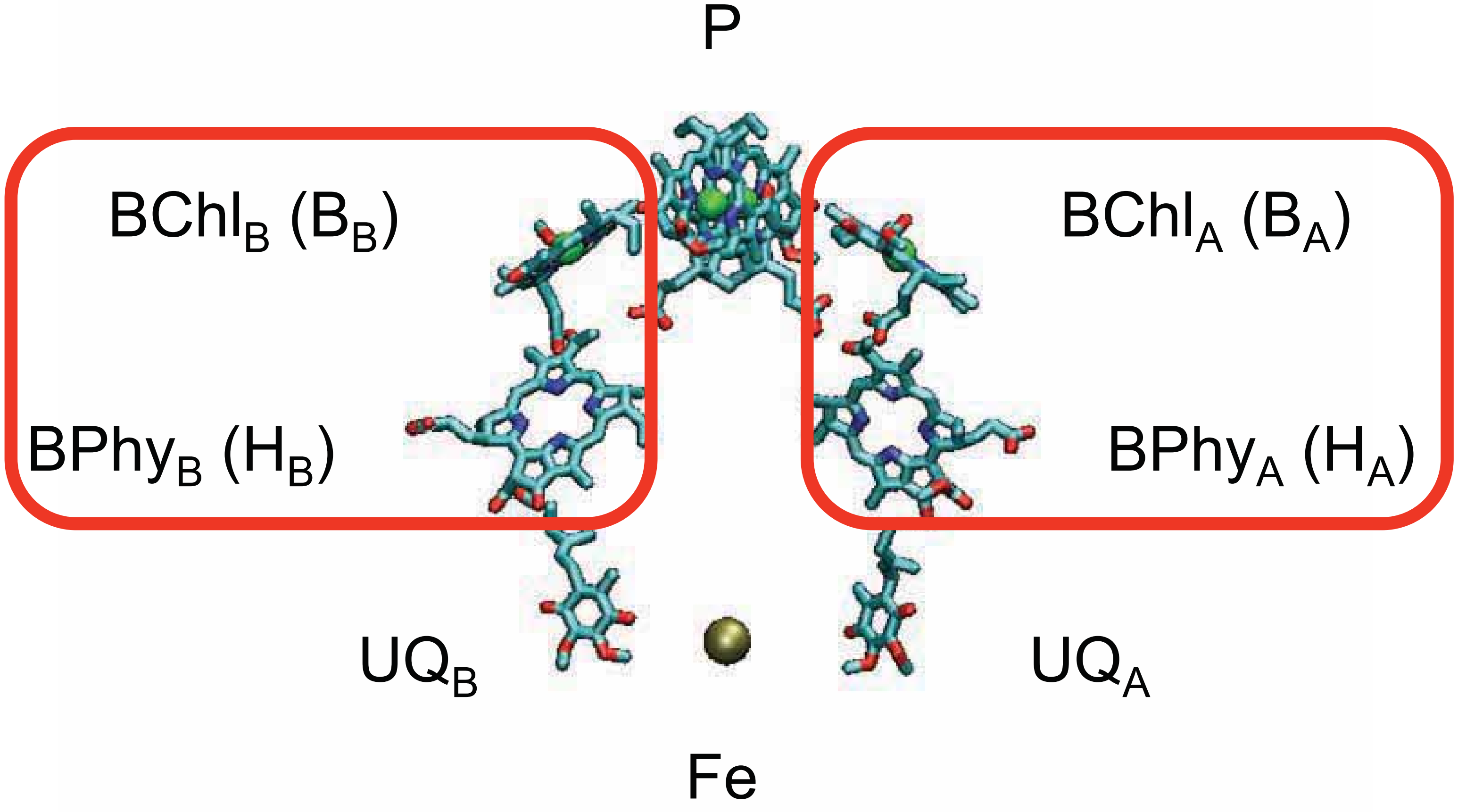
- Protein protection of electronic quantum coherence:
  - H. Lee, Y.-C. Cheng & G.R. Fleming, *Science* **316**, 1462 (2007).



The Reaction Center of Purple Bacteria

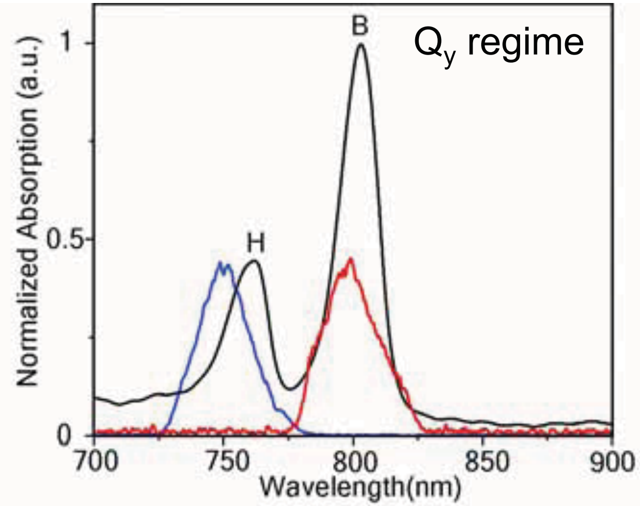


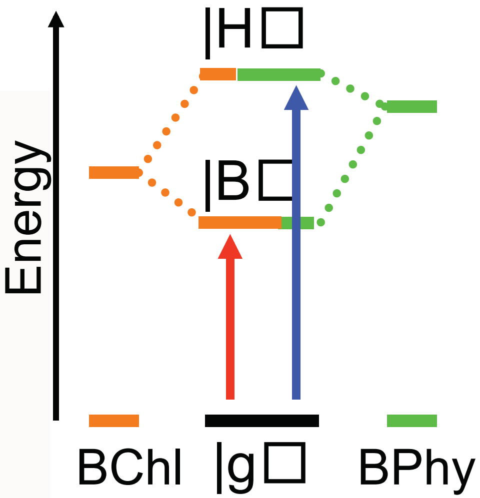
The Reaction Center of Purple Bacteria

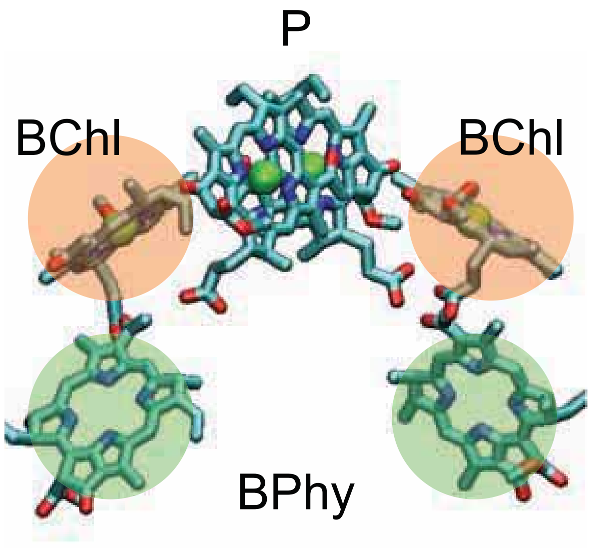


Probing H/B Coherence Dynamics: Two-color Electronic Coherence Photon Echo

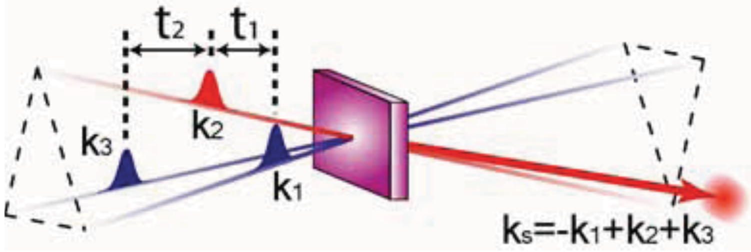
Spectrum of the RC



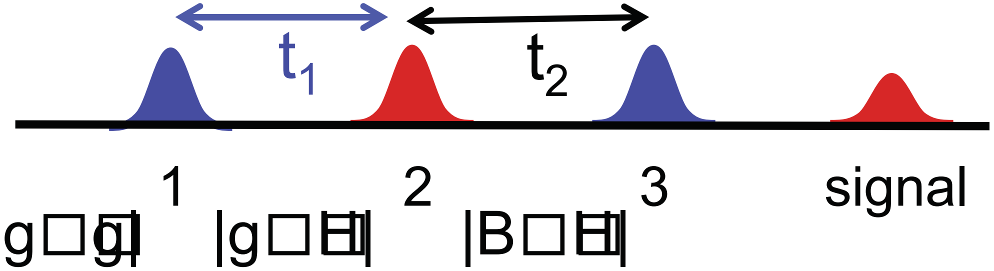




- $|H\rangle$ and $|B\rangle$ selectively excited
- Design to probe coherence specifically
  $|g\rangle\langle H|$ in t_1, $|B\rangle\langle H|$ in t_2

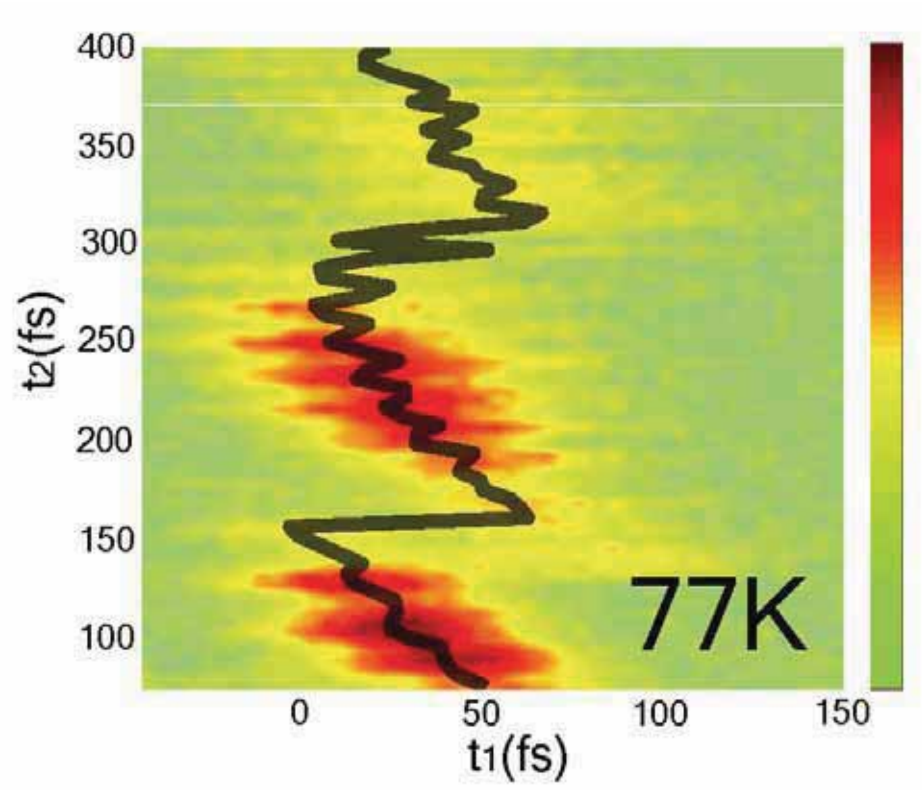


Ordering: 750-800-750 (nm)



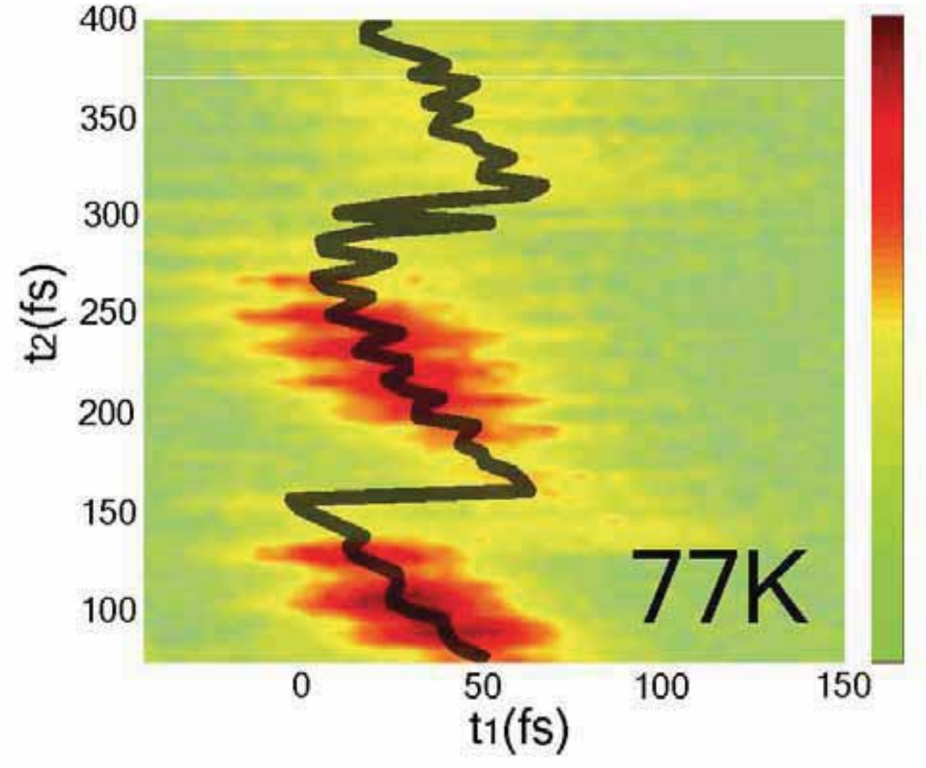
Experimental Data @ 77K

Photon-echo Intensity



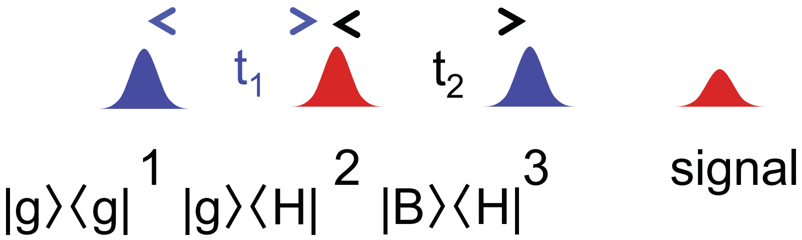
Mapping Coherence Dynamics in the RC

Photon-echo Intensity



$|B\rangle\langle H|$ dephasing

$|g\rangle\langle H|$ dephasing

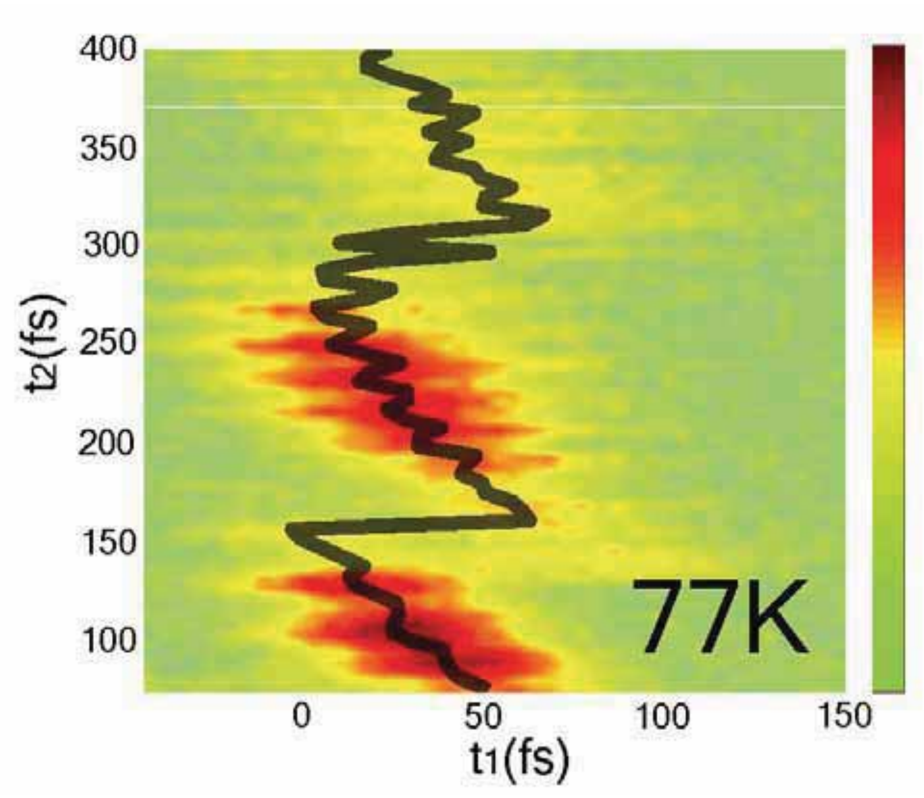


- Photon-echo intensity measured in this two-color experiment follows coherence dynamics.
- Along t_1: $|g\rangle\langle H|$ dephasing
- Along t_2: $|B\rangle\langle H|$ dephasing

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

Mapping Coherence Dynamics

$|B\rangle\langle H|$ dephasing

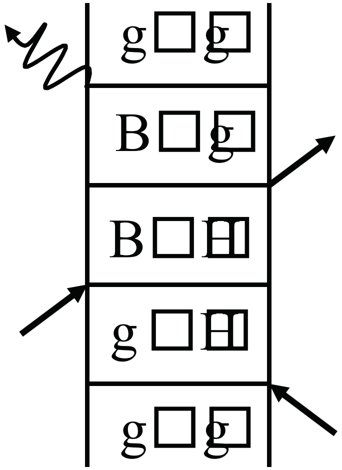


$|g\rangle\langle H|$ dephasing

- 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!

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

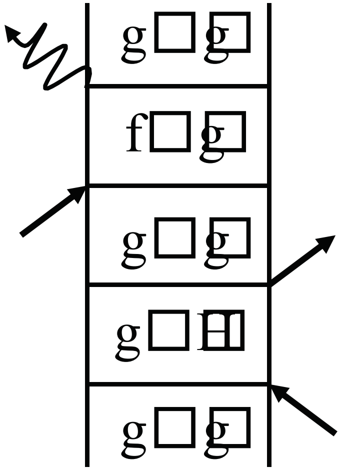
Theoretical Modeling



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

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

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

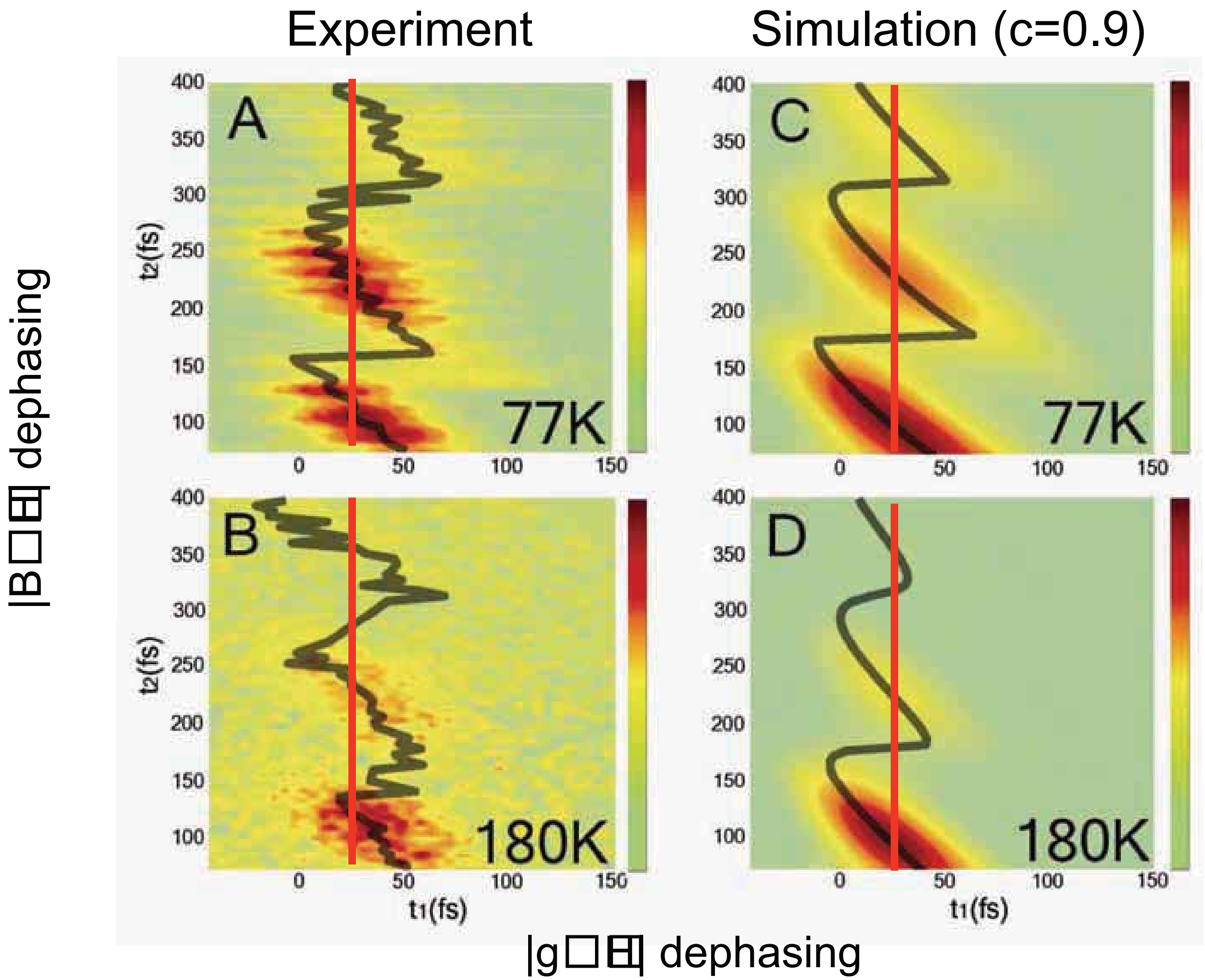


Cross-correlation between BPhy and BChl fluctuations (described by c):

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

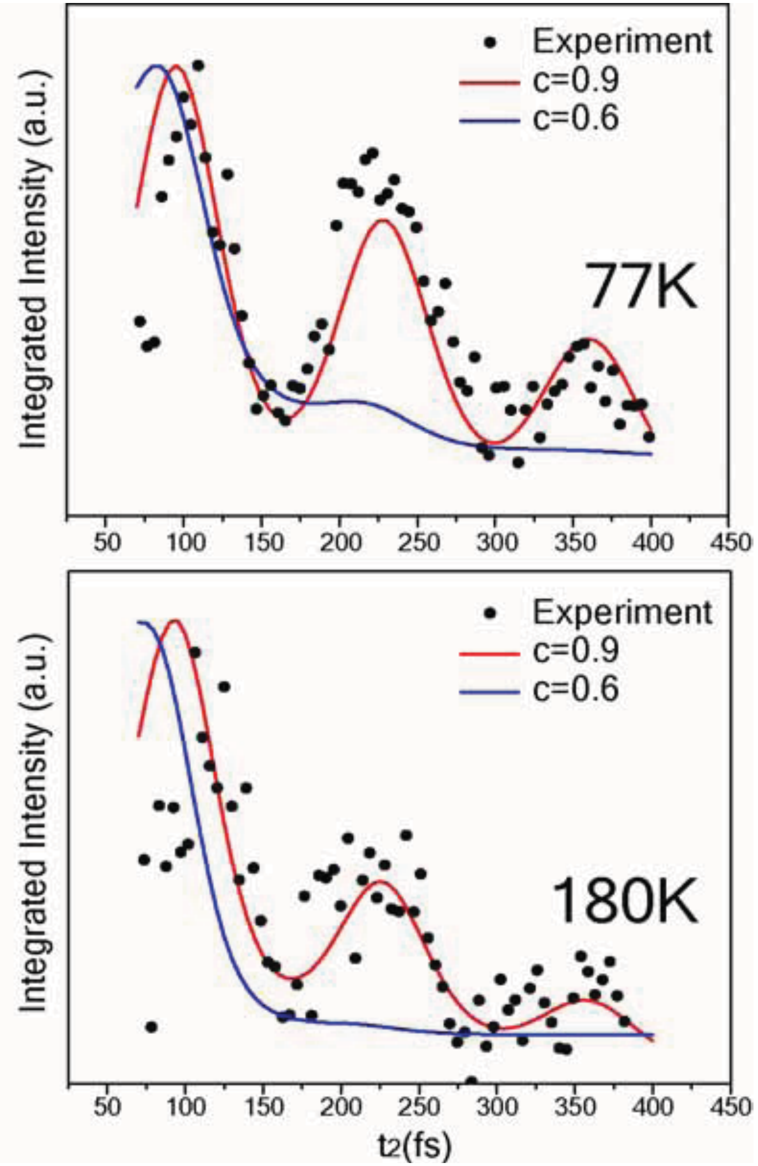
250 cm^{-1} vibrational mode coupled to BPhy (sawtooth pattern).

Experiment vs. Theory



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

Protein Protection of Electronic Coherence



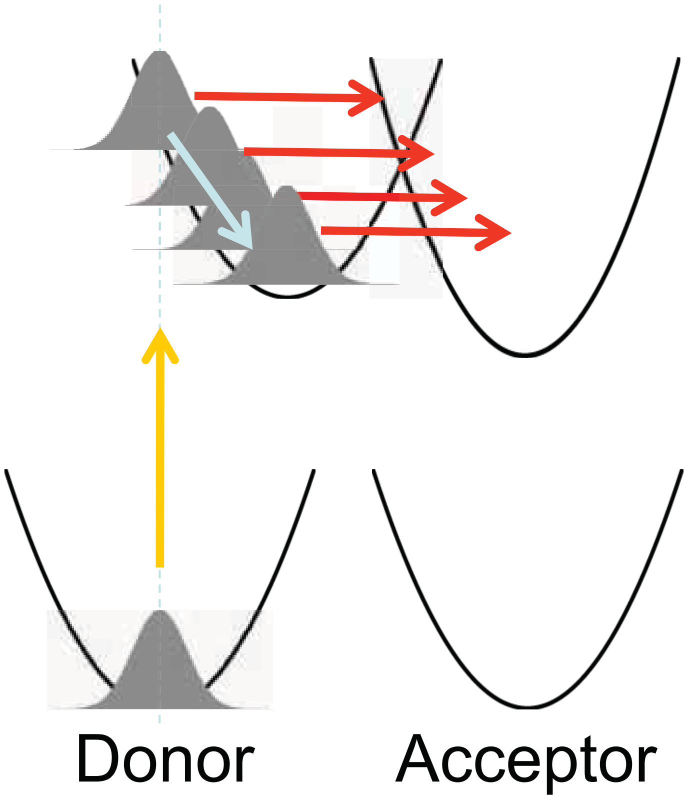
- Electronic coupling alone (c=0.6) cannot explain the long dephasing time
- Strong cross-correlations (c~0.9) between protein environments responsible for long-lived |B〉〈H| coherence
- ➔ “*Protein protection of excitonic coherence*”

|B〉〈H| dephasing times: $t_{g,77K}$ =440fs, $t_{g,180K}$=310fs

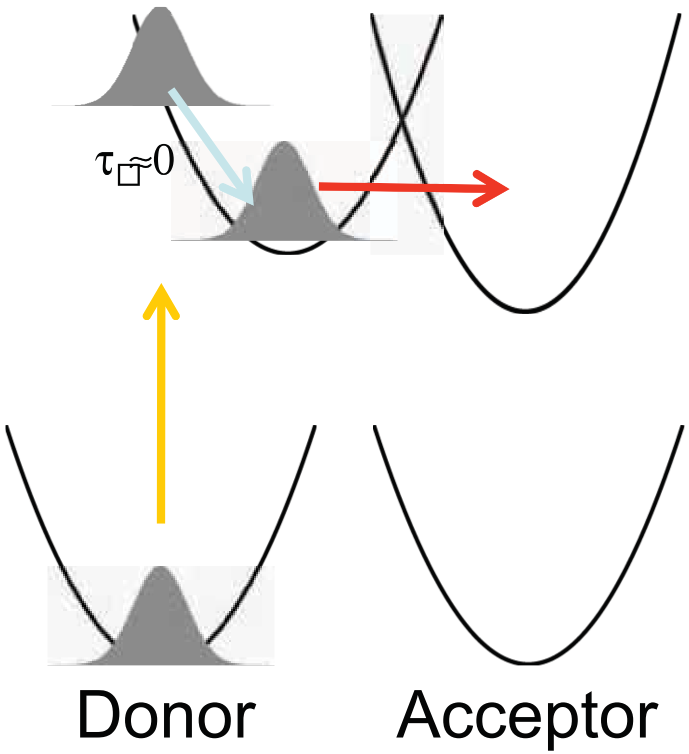
Non-equilibrium Effects in Excitation Energy transfer

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

Photon-induced dynamics

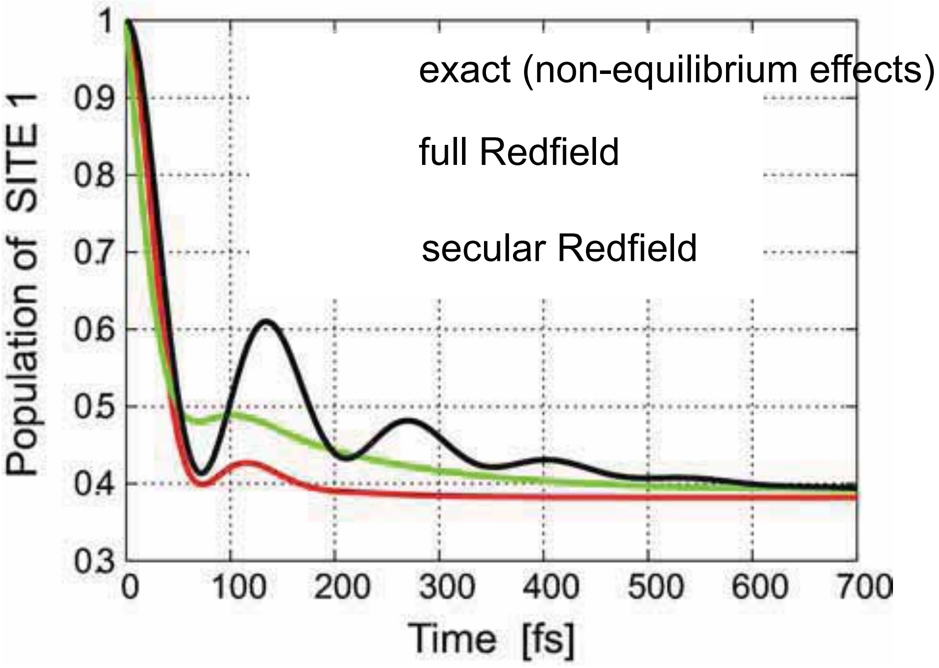


Redfield/Forster picture



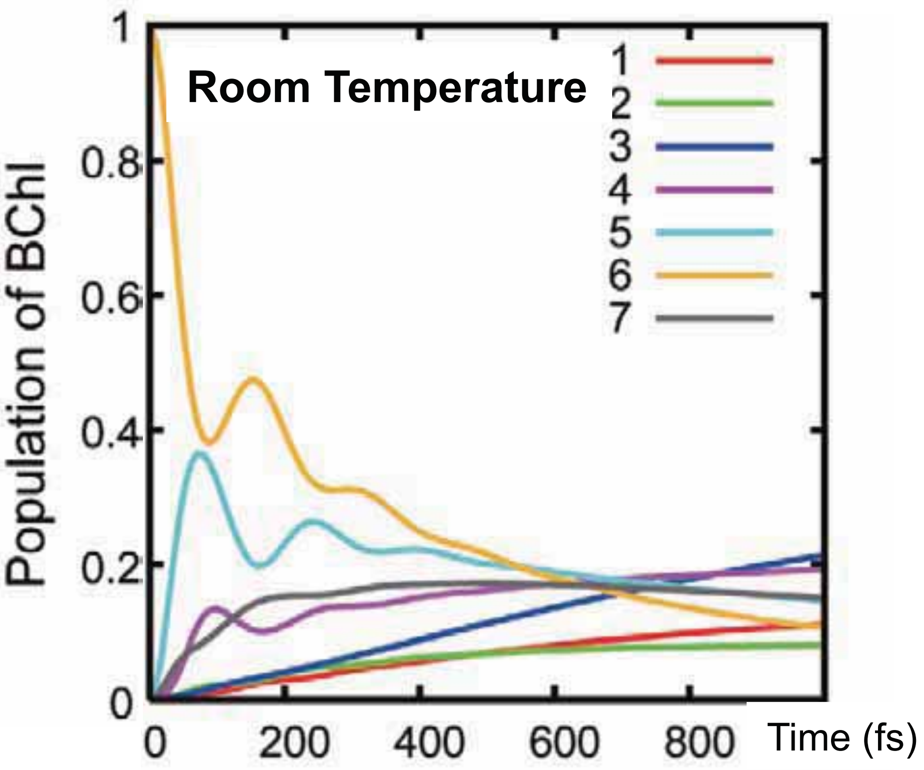
Non-equilibrium Effects Lead to Longer Decoherence Time

- 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)

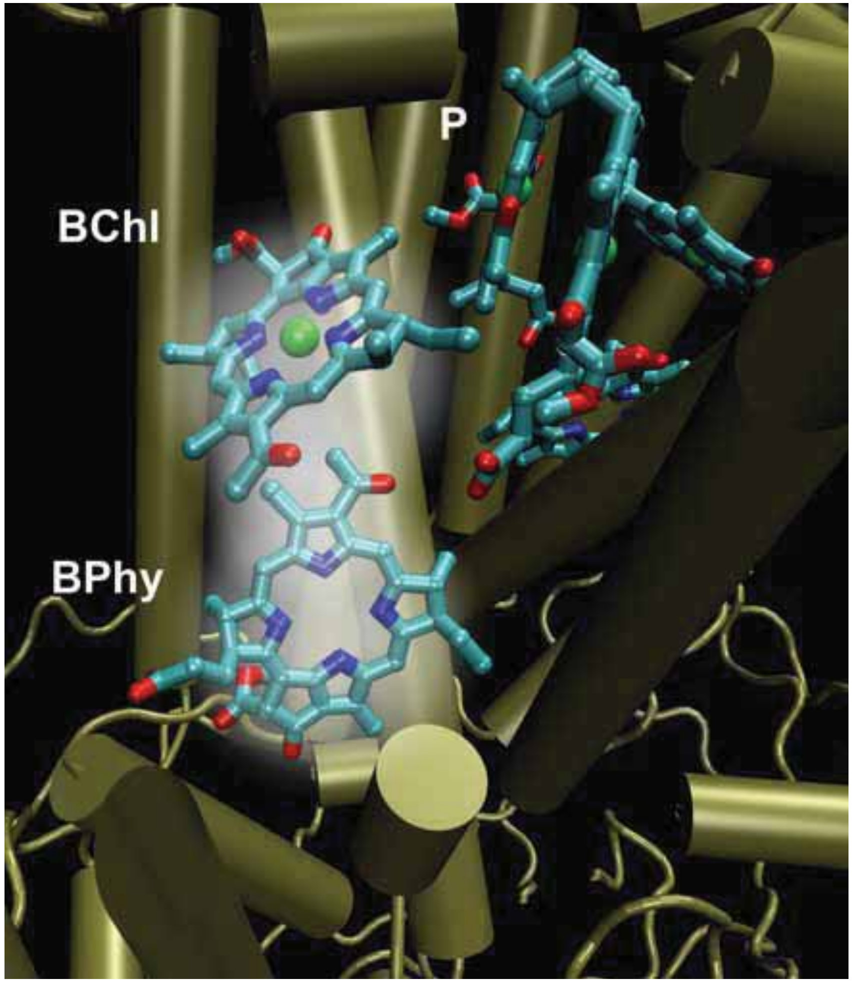


Benchmark calculations on a spin-boson model.
Ishizaki &Fleming, JCP 2009.

Coherent EET Dynamics the FMO



Concluding Remarks



Pigments and proteins in the reaction center of a purple bacteria

- Energy transfer through quantum coherence has been revealed in photosynthetic complexes
- Coherent dynamics may promote energy trapping in light harvesting
- Correlations in protein dynamics & non-equilibrium bath effects contribute to the preservation of coherence
- More challenges ahead in gaining full understanding and applying to artificial systems

Acknowledgements

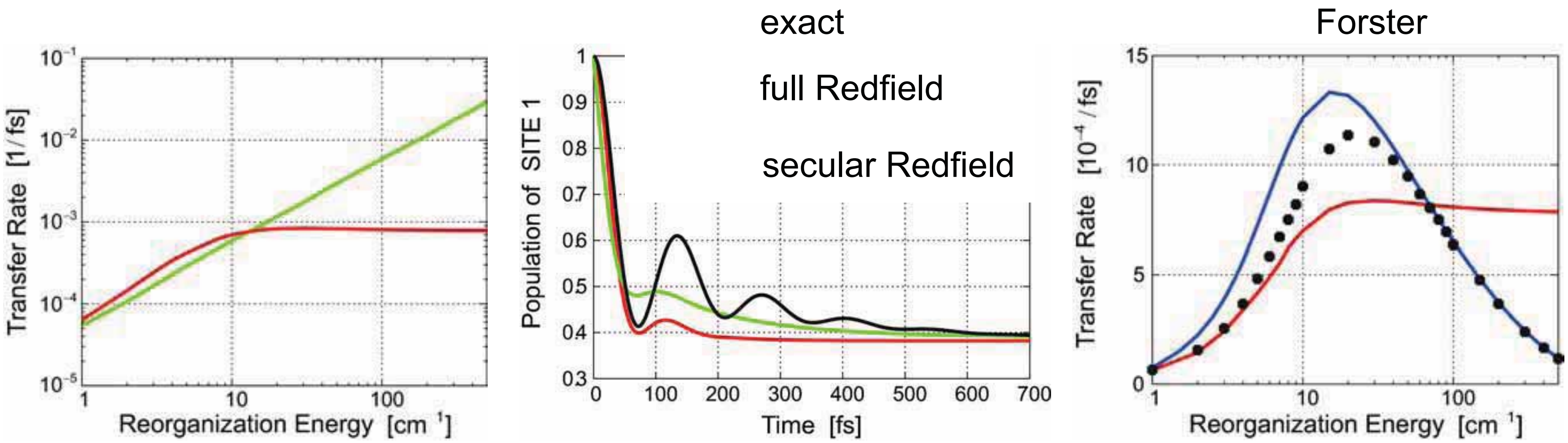
- Bob Silbey (MIT)
- Graham Fleming (UC Berkeley)
- Seogjoo Jang (Queens College, CUNY)
- The Fleming Group (UC Berkeley)

- National Science Council of Taiwan

Thank You!

Quantitative Description Still Not Available

To describe the dynamics in the the intermediate regime and the long-lasting coherence dynamics require new theoretical developments. We have to go beyond the secular approximation and Redfield equation.



Benchmark calculations on a spin-boson model using several different theories. Ishizaki and Fleming, *unpublished data*.

Propagating Dynamics with Bath Memory

- Redfield theory ➔ 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:

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

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

Meier & Tannor, *J. Chem. Phys.* **111**, 3365 (1999); Cheng, Lee & Fleming, JPCA (2007).