Problems of Modern Physics

Lecture 7

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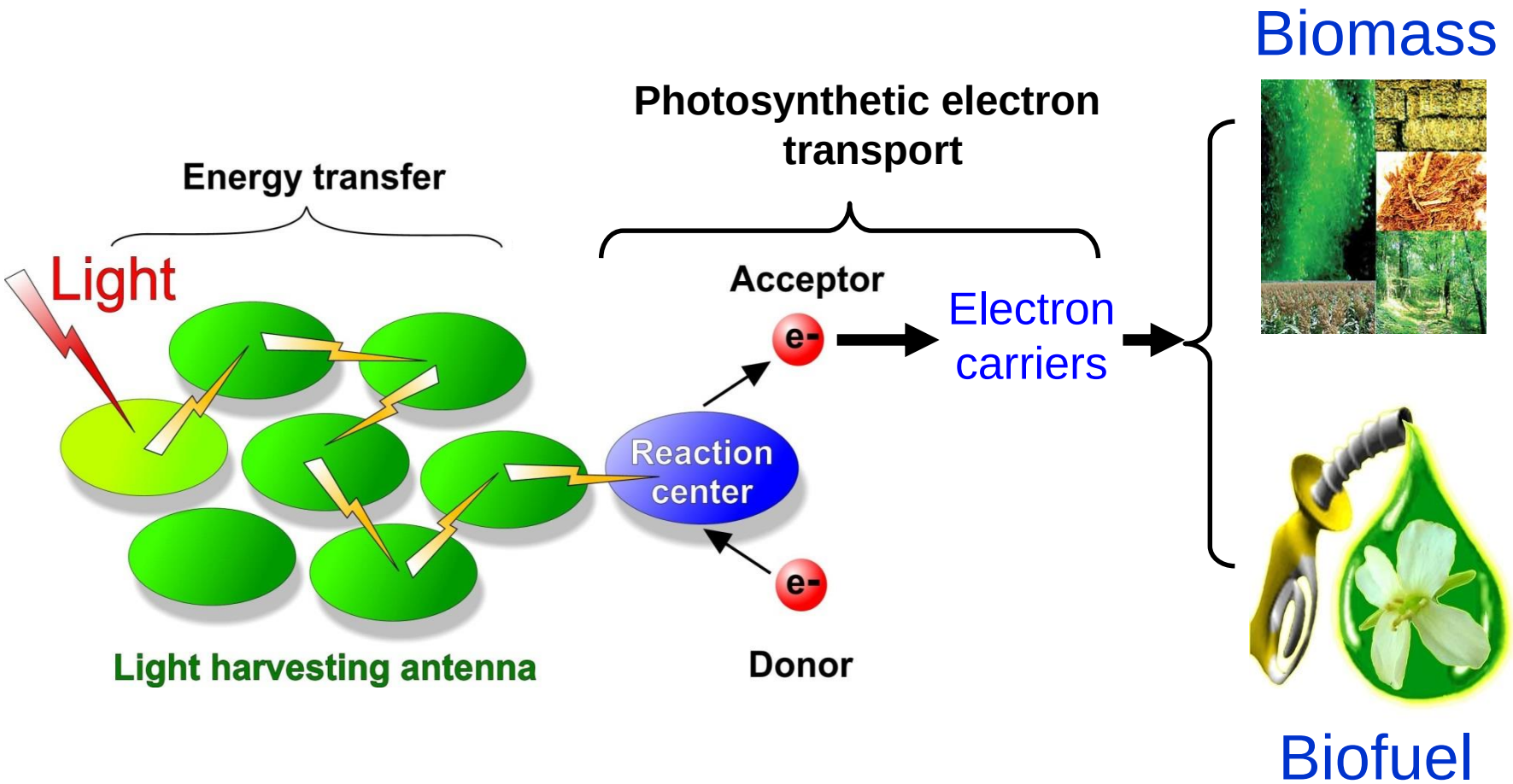
Light-harvesting complexes

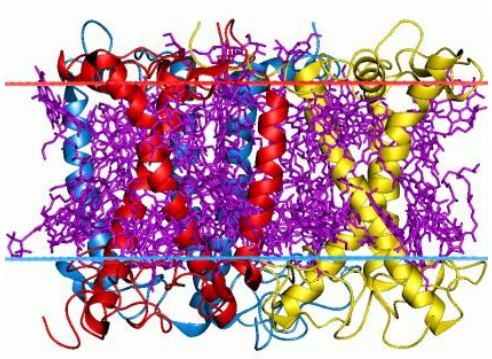
Photosynthesis



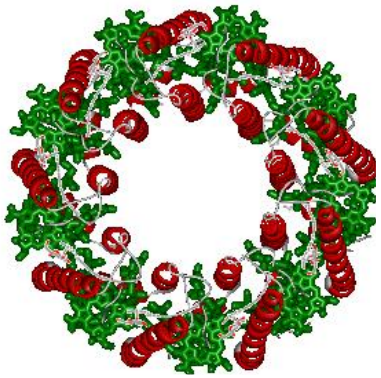
Convert solar energy into biomass and biofuel

Zoo of photosystems

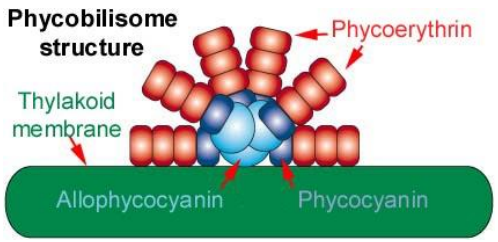
LHCII



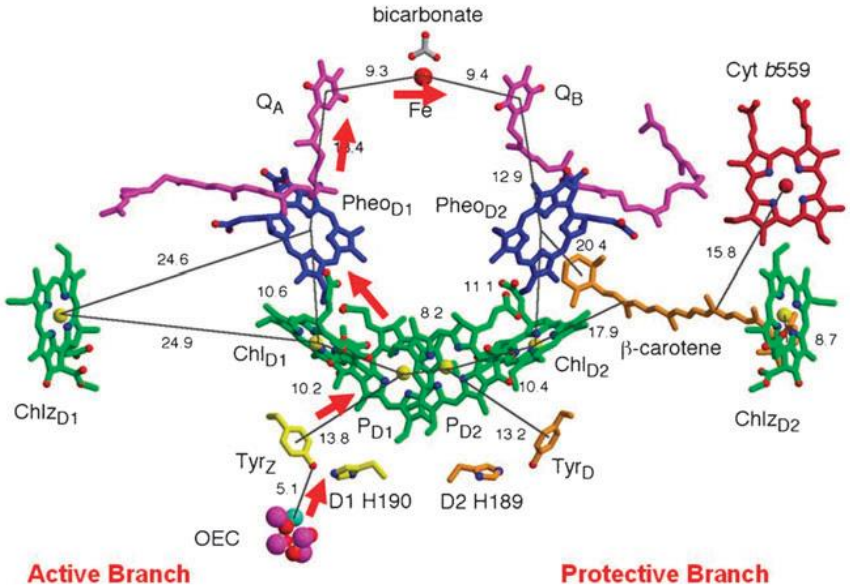
LH2

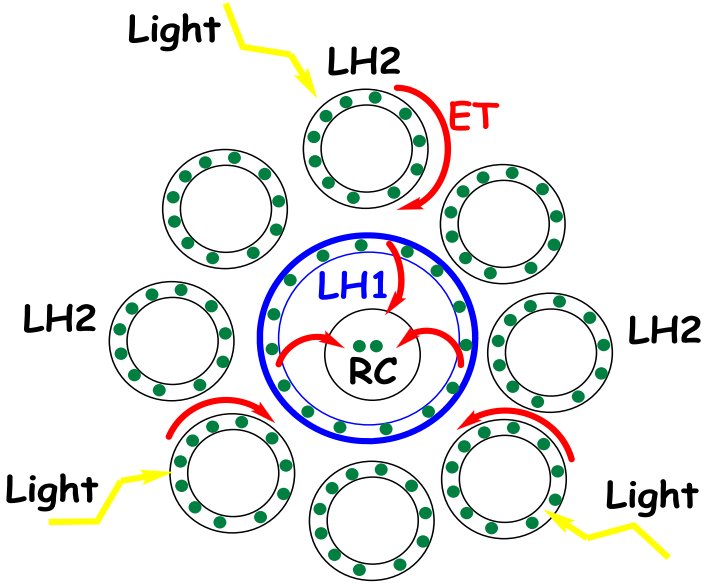


Phycobilisomes



PSII





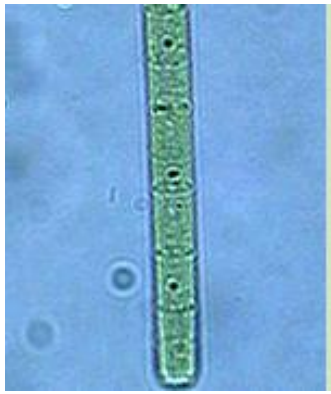
- (bacterio)chlorophylls

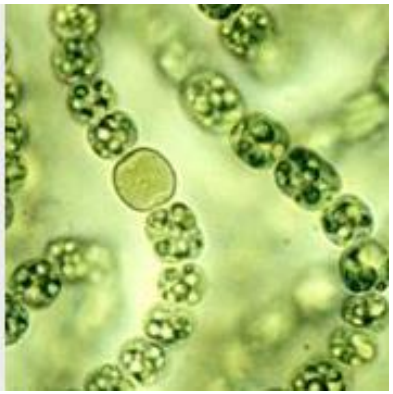
Photosynthetic microbes

Chloroflexus
(Filementous Anoxygenic Phototrophs- FAP)

Green Sulfur Bacteria

Cyanobacteria
(Blue Green Algae, Only oxygenic phototrophic microbes)

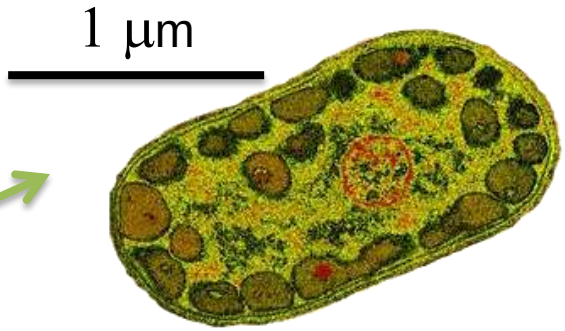




Purple Bacteria

Heliobacteria
(only Gram-(+) photosynthetic microbes)

Green sulfur bacteria



Can live at extremely low light intensity: 10^{-4} W/m^2~ 300 photons/s

Earth Formation

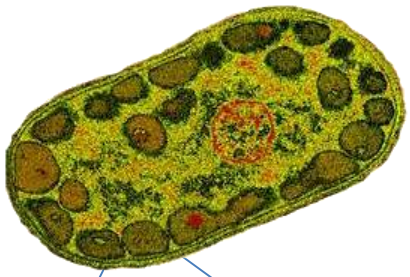
Proterozoic Era

Mesozoic Era

~ 4500 | 2500 | 250

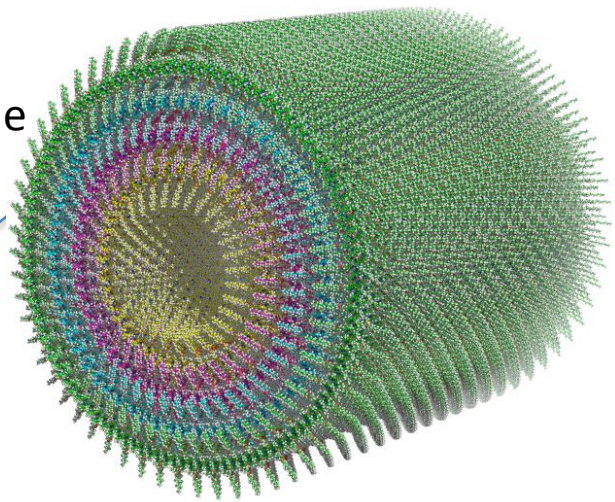
Timeline
million years ago

Light-harvesting complex



Green sulfur bacteria

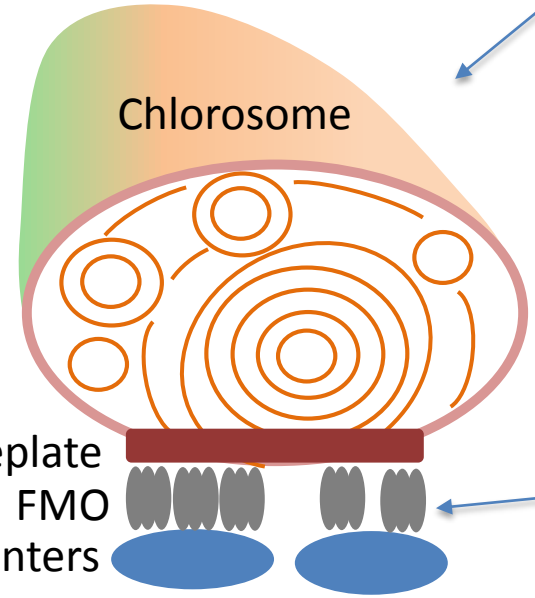
Chlorosome



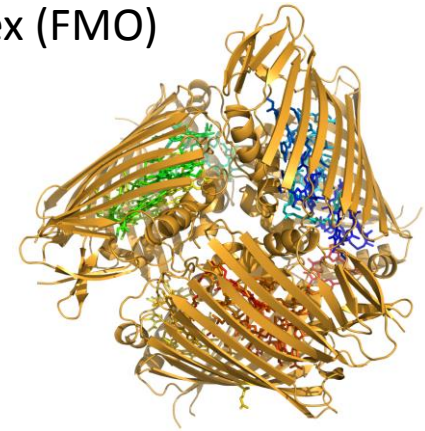
Light-harvesting complex

~ 200,000 molecules

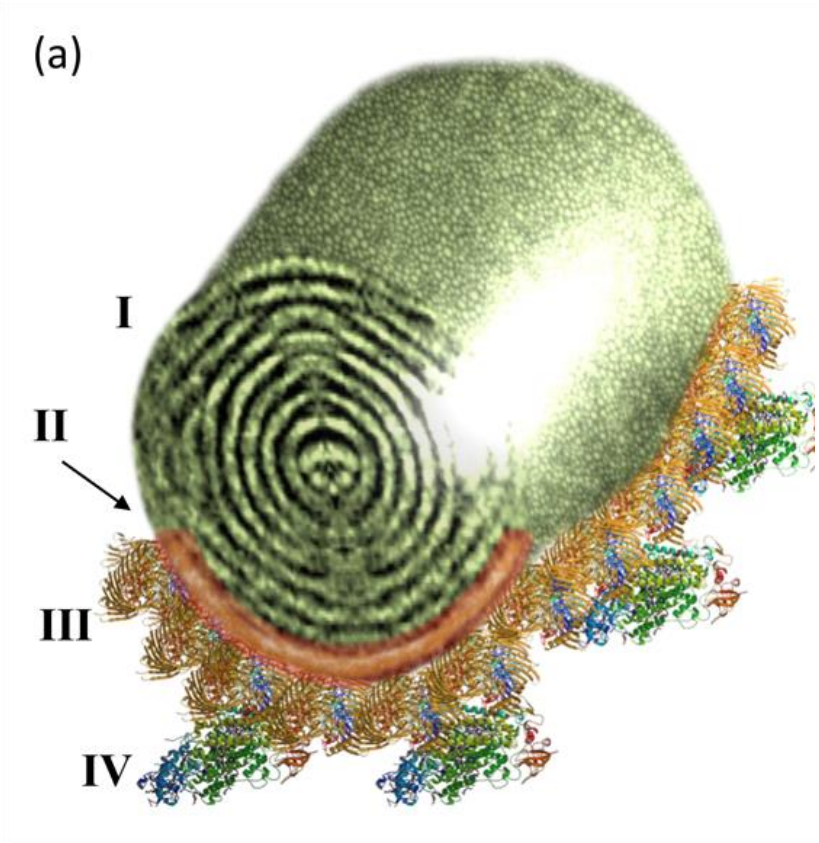
~ 100 – 200 nm

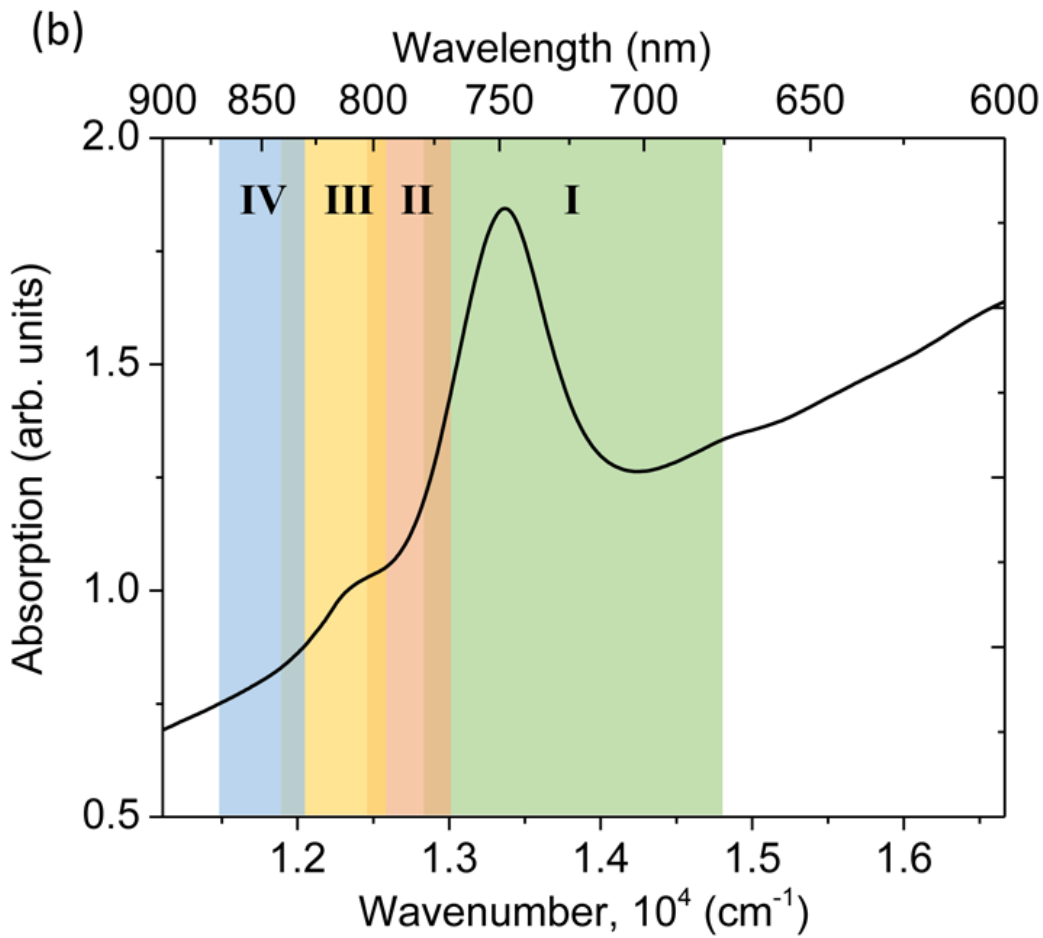


Fenna-Matthews-Olson complex (FMO)



Absorption spectrum of LHC





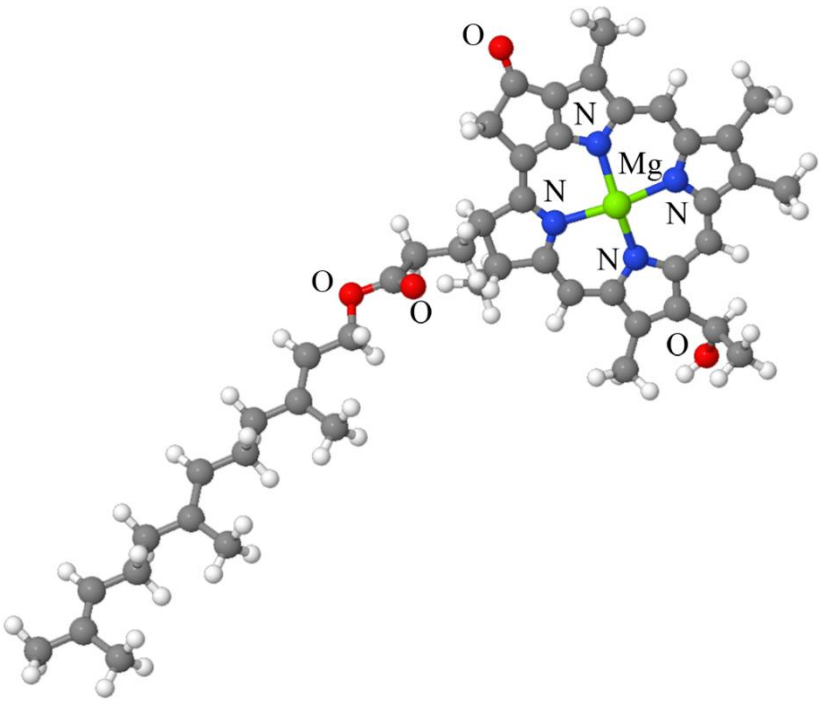
I – chlorosome

II – baseplate

III – FMO complexes

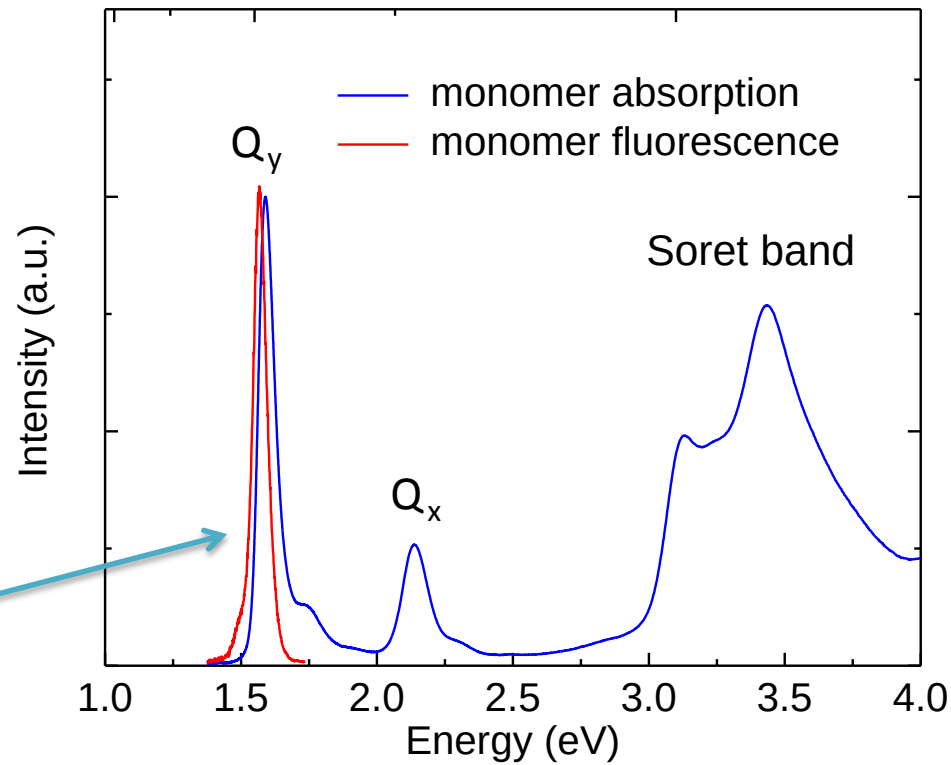
IV – reaction centers

Bacteriochlorophyll



Spectrum

red green violet



This transition is utilized in energy transfer

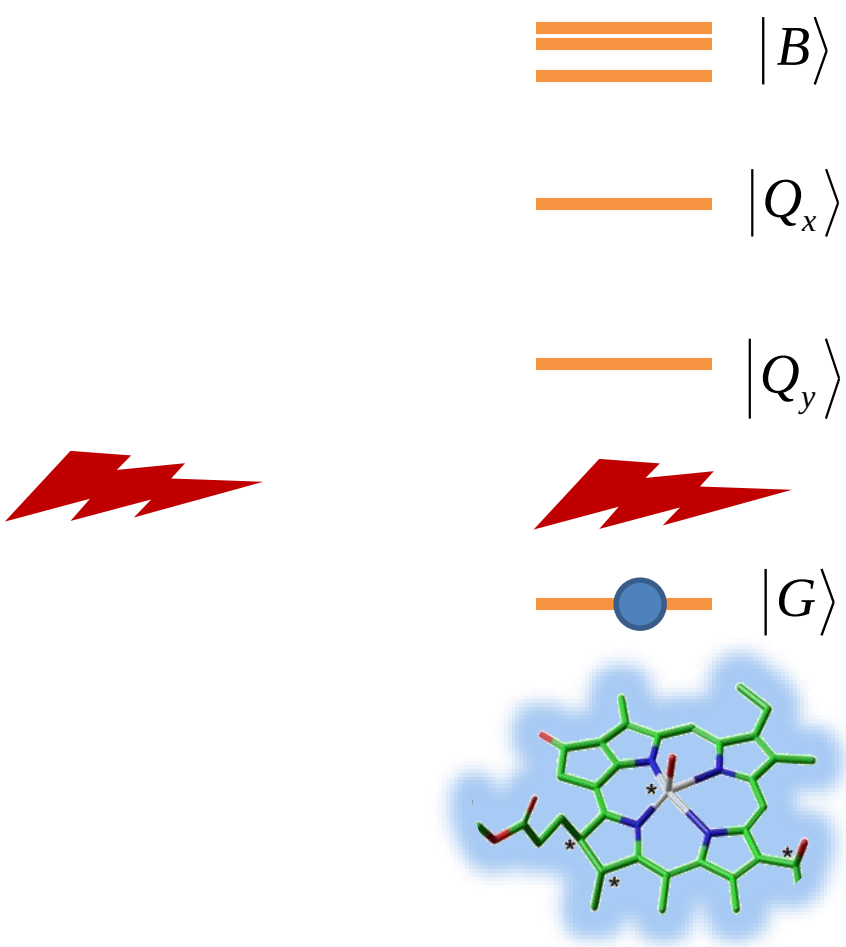
Light absorption

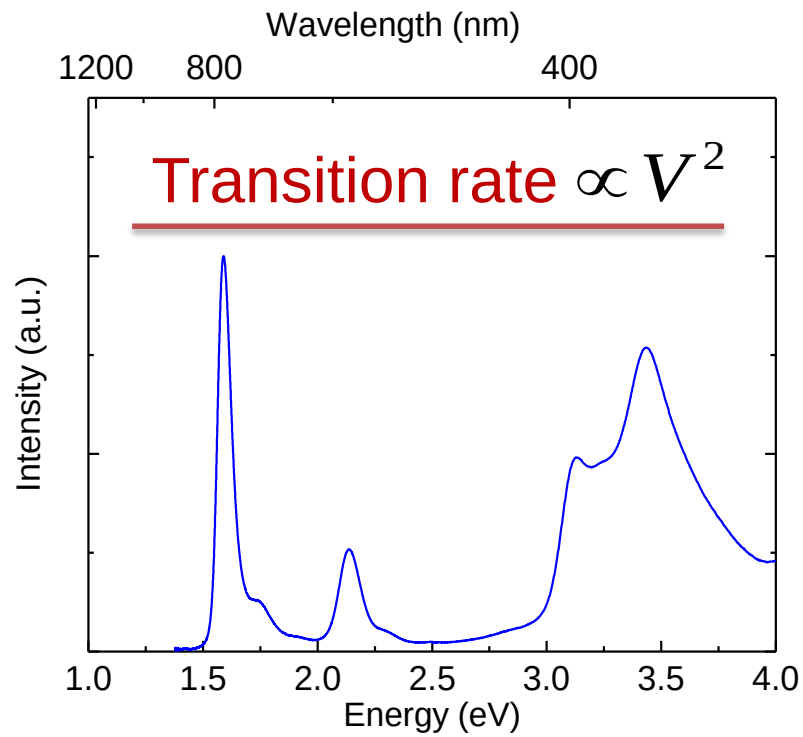
$$V = -\vec{\mu} \cdot \vec{E} = -\langle Q_y | e \cdot \vec{r} | G \rangle \cdot \vec{E}$$

transition dipole

electromagnetic field

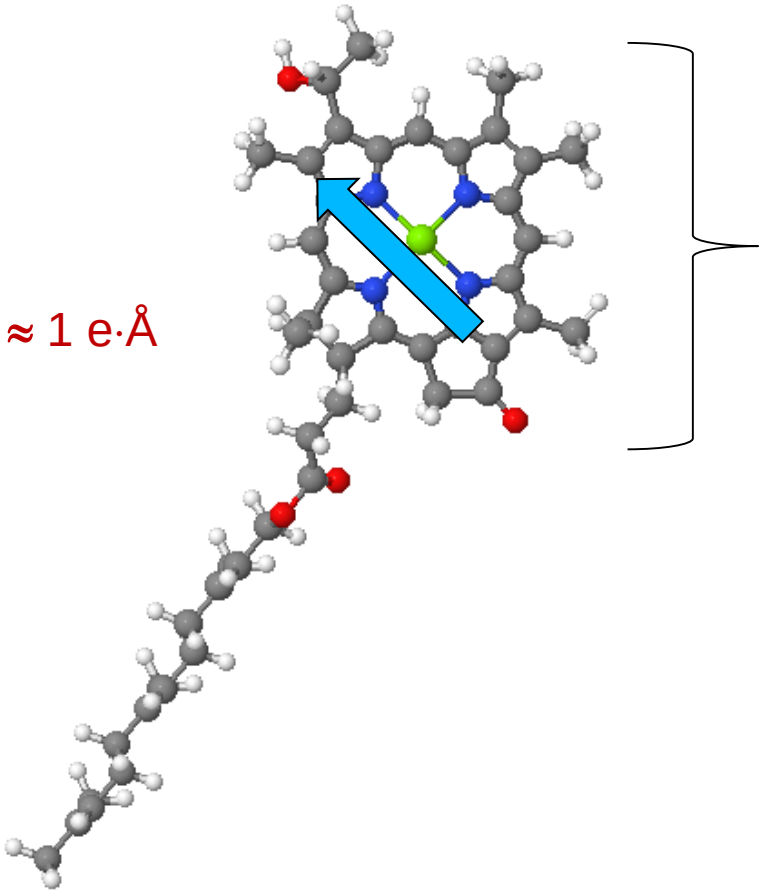
Molecule states





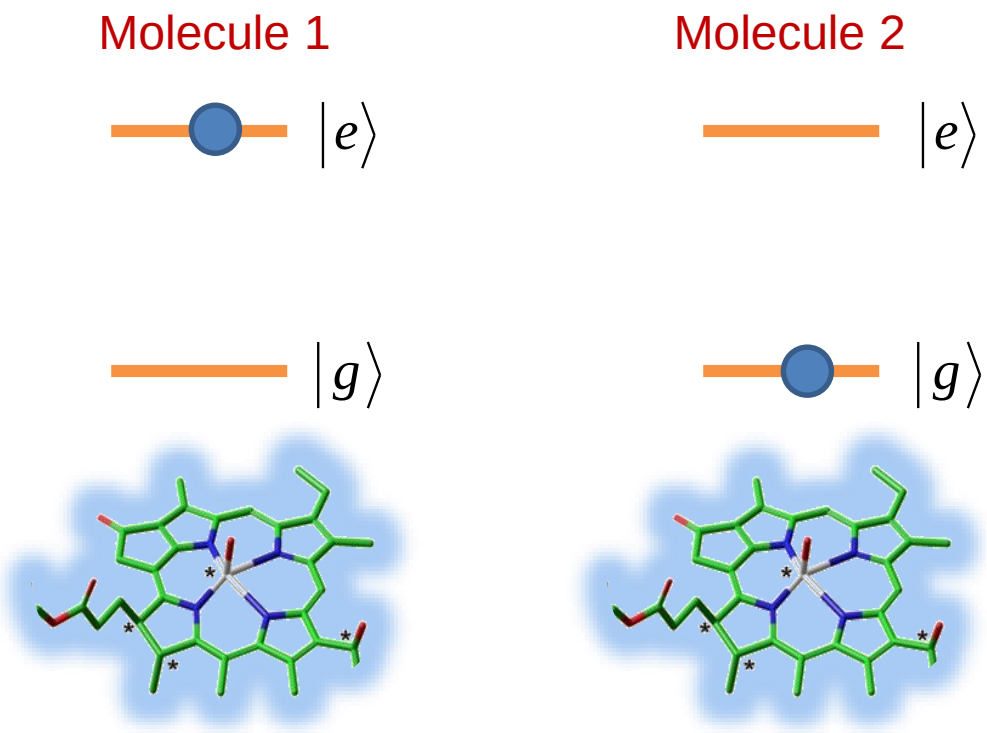
Transition dipoles

$\mu_{Qy} \approx$ 4-5 Debye $\approx$ 1 e·Å



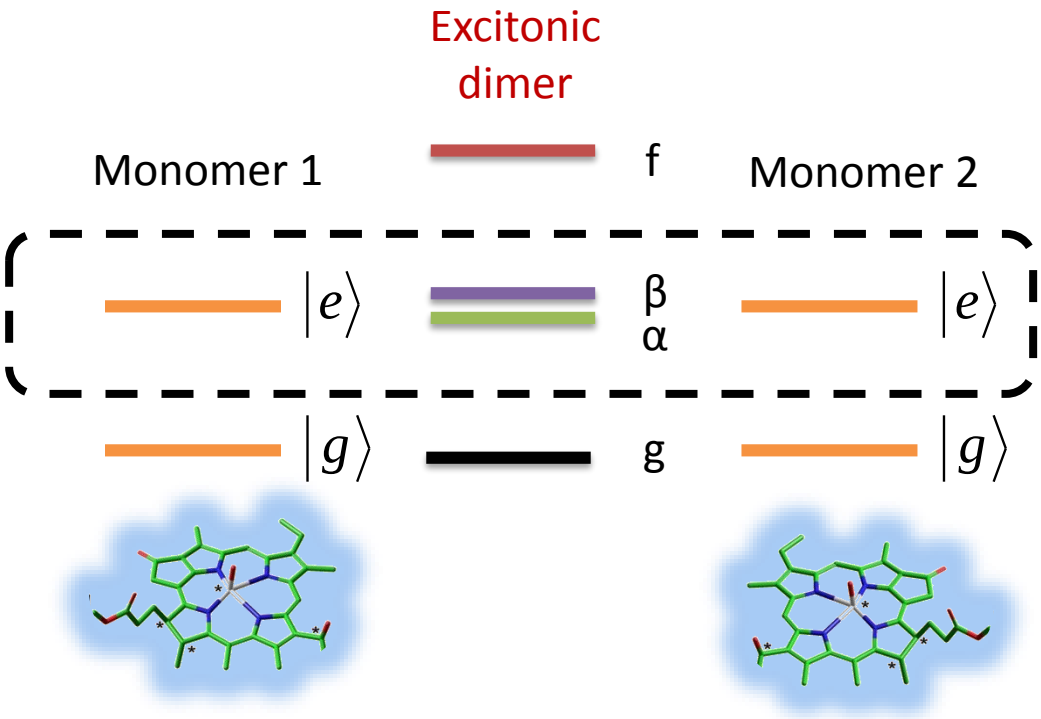
The main electron excitation is here

Intermolecular energy transfer



Förster interaction: $V_{\mathrm{F}} = \frac{1}{R_{12}^3}\left(\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3\left(\vec{\mu}_1 \cdot \vec{R}_{12}\right)\left(\vec{\mu}_2 \cdot \vec{R}_{12}\right)}{R_{12}^2}\right)$

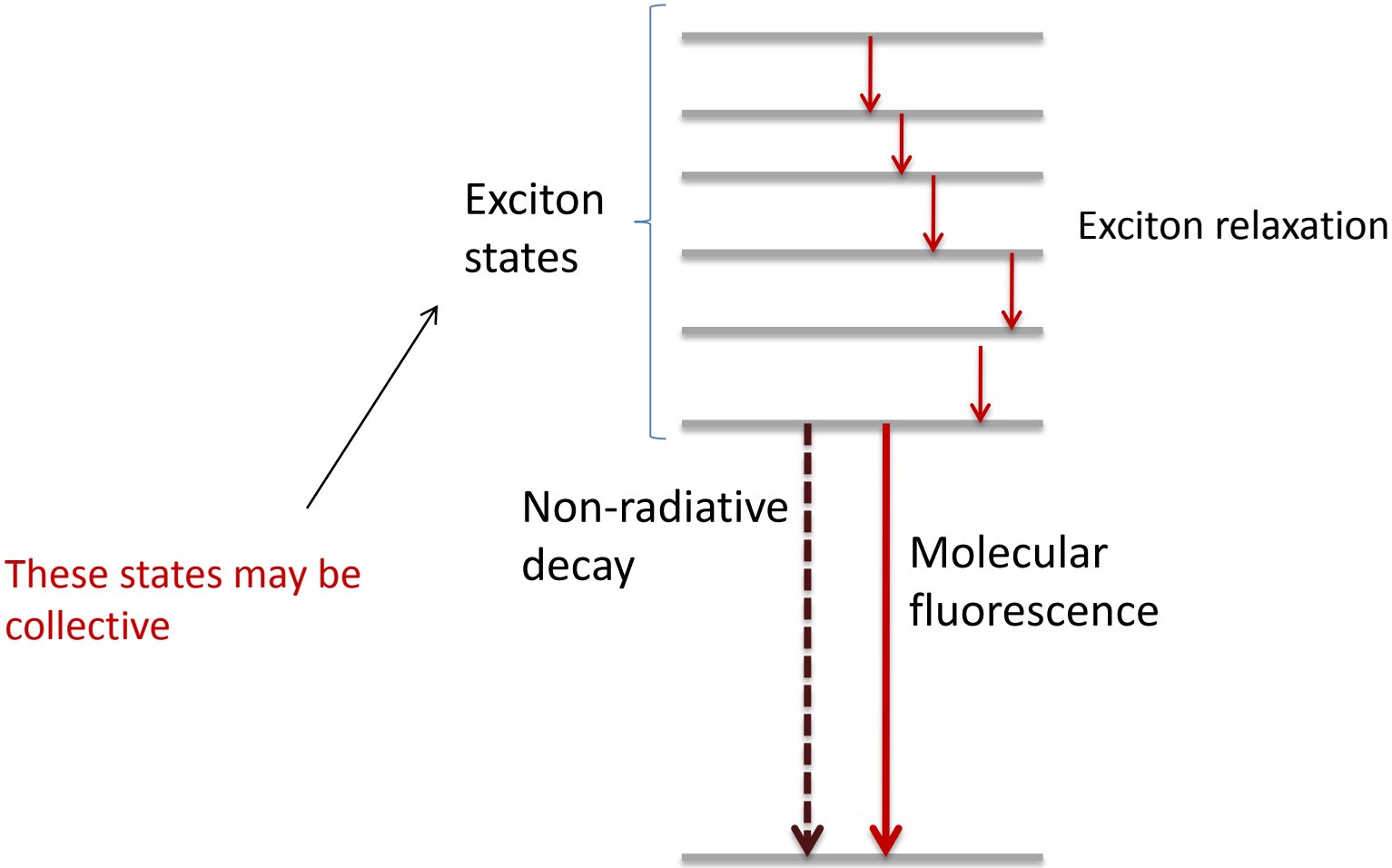
State hybridization



$$|\alpha\rangle = \frac{1}{\sqrt{2}}\left(|e_1\rangle|g_2\rangle - |g_1\rangle|e_2\rangle\right)$$

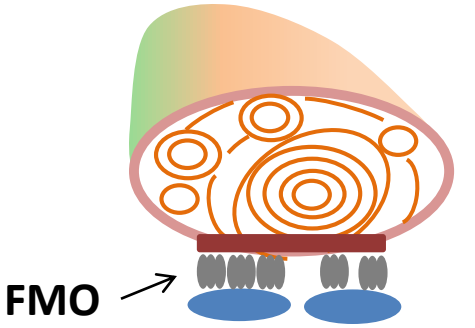
$$|\beta\rangle = \frac{1}{\sqrt{2}}\left(|e_1\rangle|g_2\rangle + |g_1\rangle|e_2\rangle\right)$$

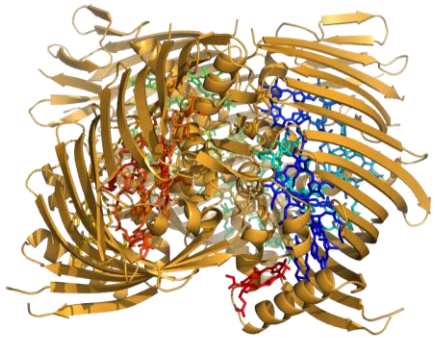
Exciton states

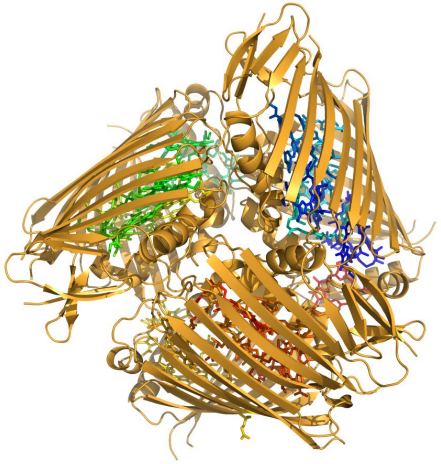


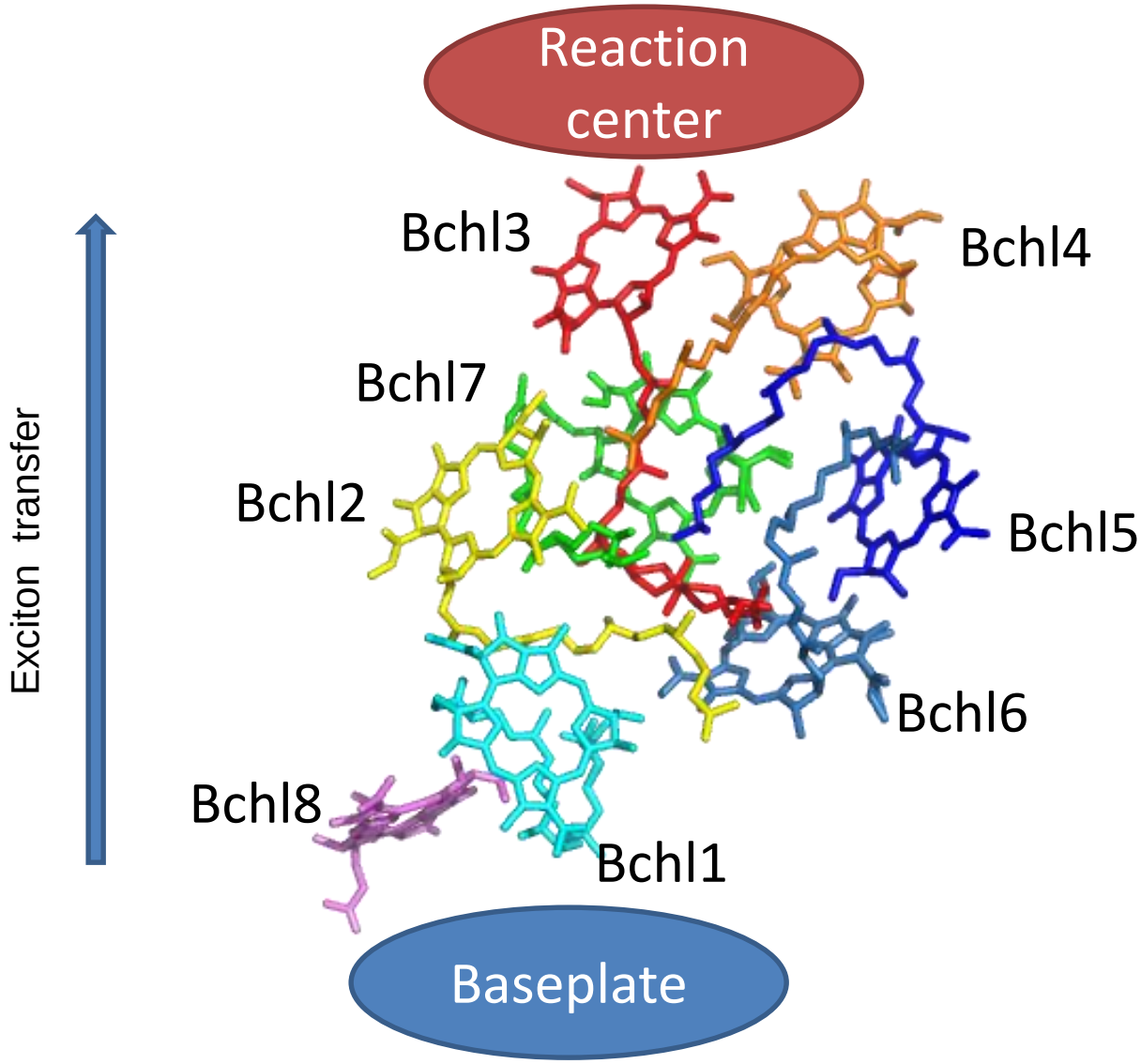
Coherent excitation dynamics

Fenna-Matthews-Olson protein complex





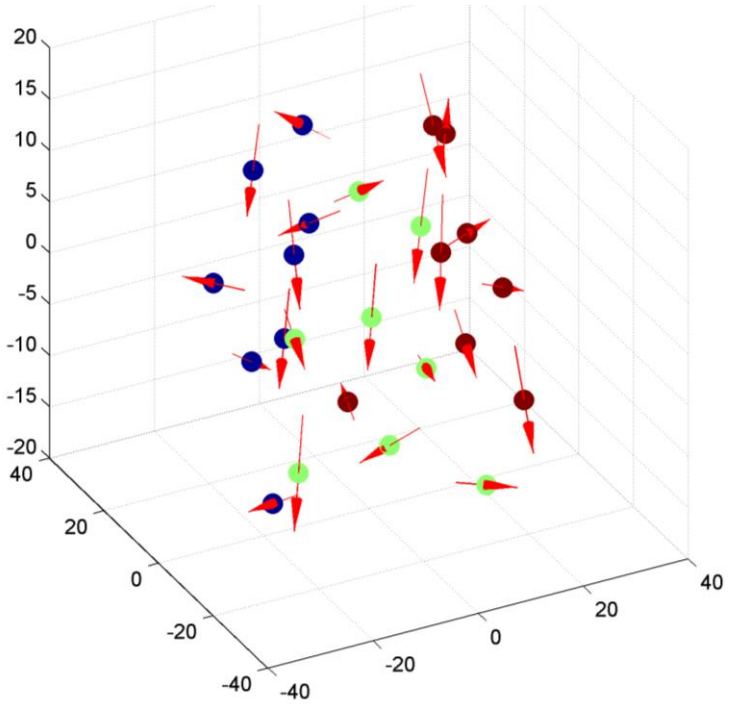




Hamiltonian

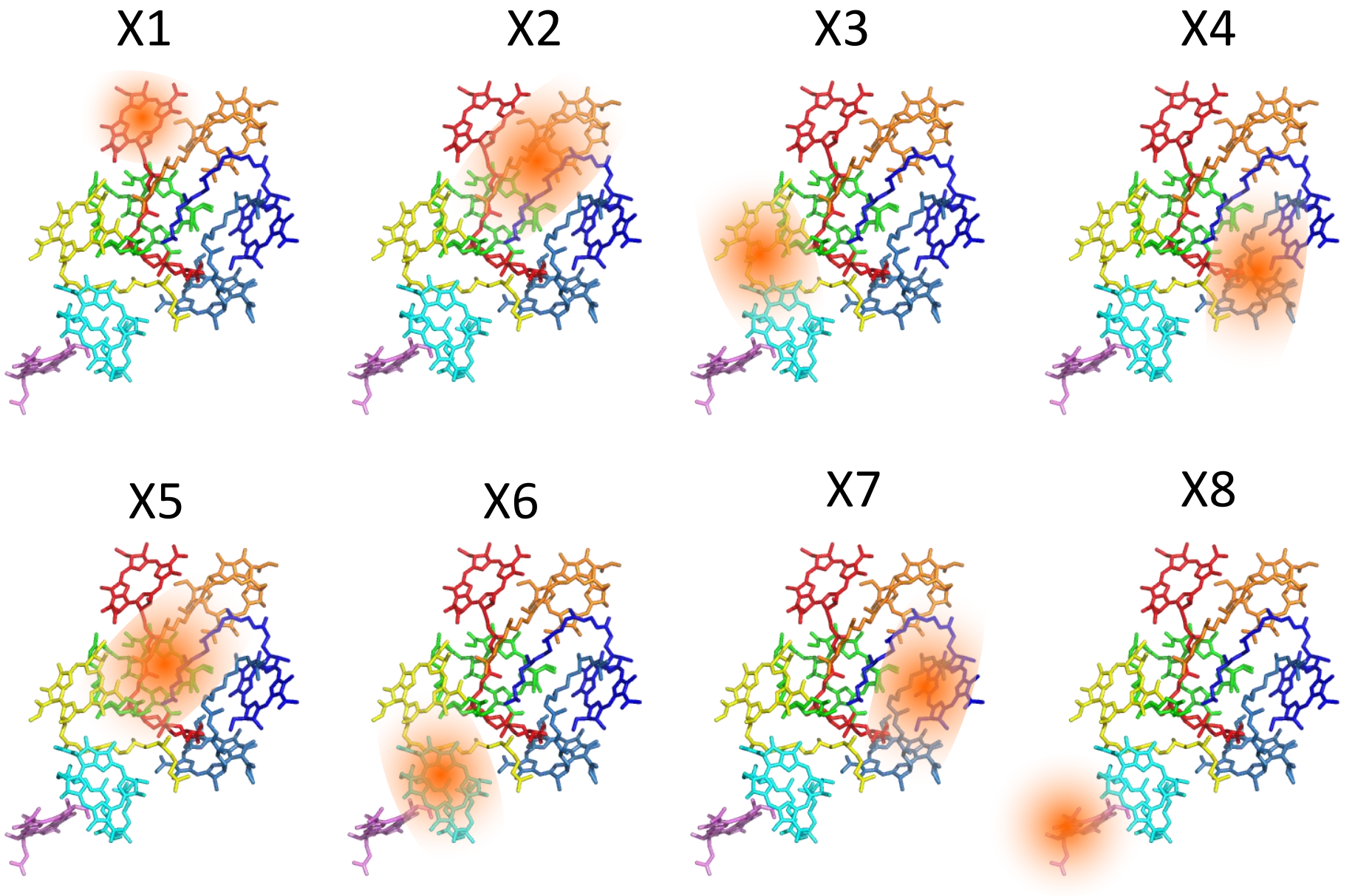
24 molecules with Förster coupling

24 interacting transition dipoles

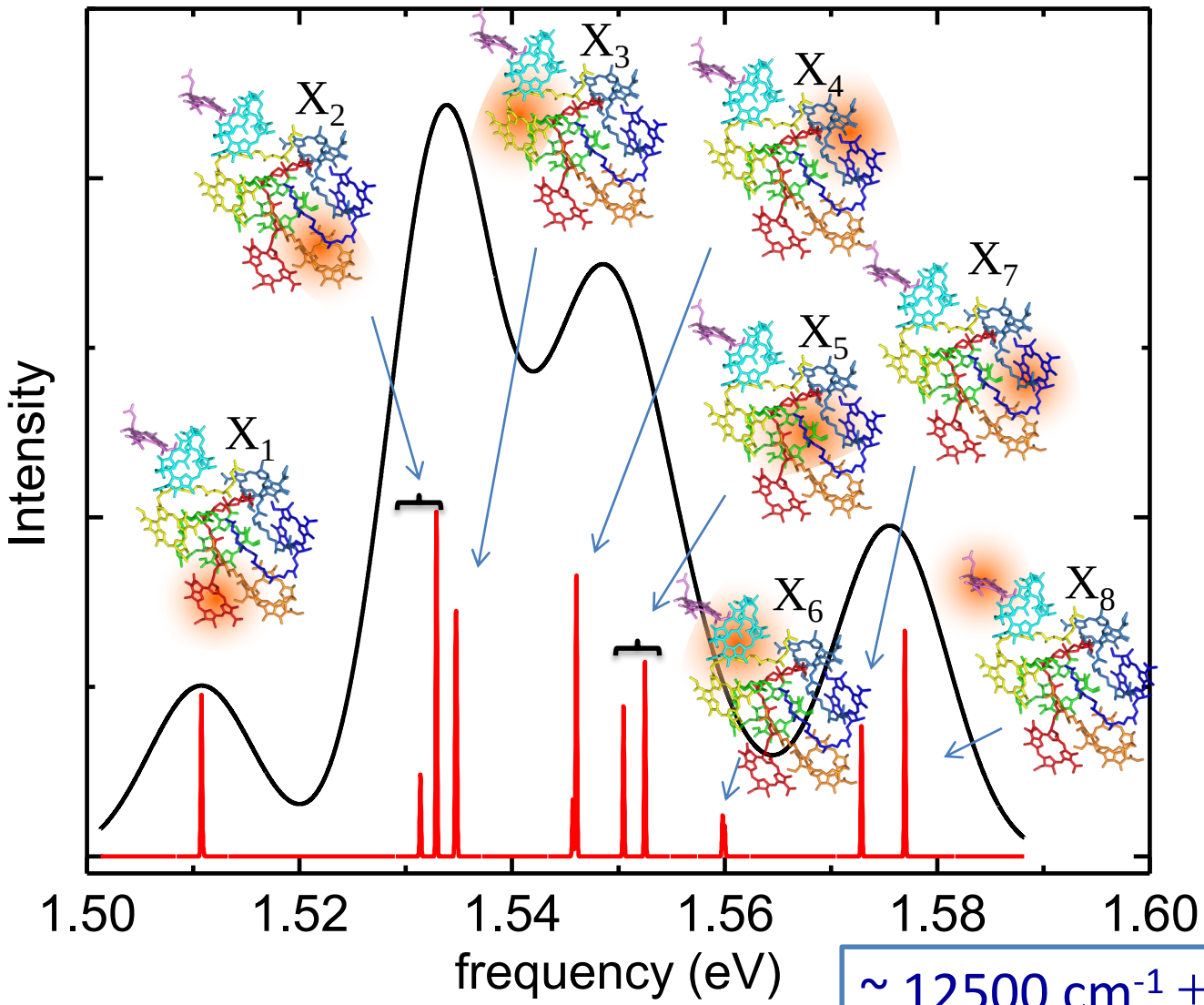


- The dipoles and the transition frequencies estimated using TDDFT
- Protein introduces additional corrections that usually extracted from experimental spectra

Exciton states



Absorption spectra

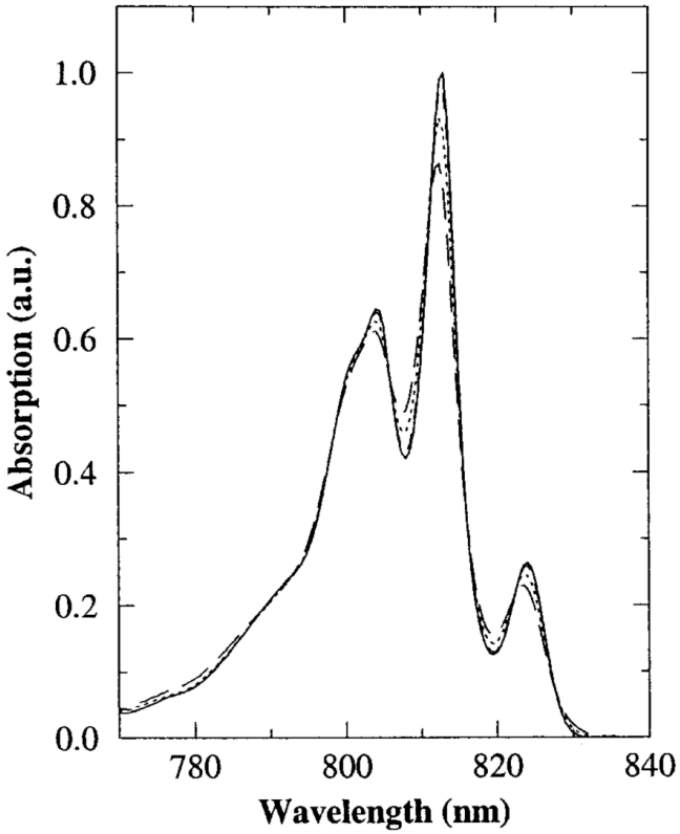


~ 12500 $cm^{-1} \pm 300$ cm^{-1}

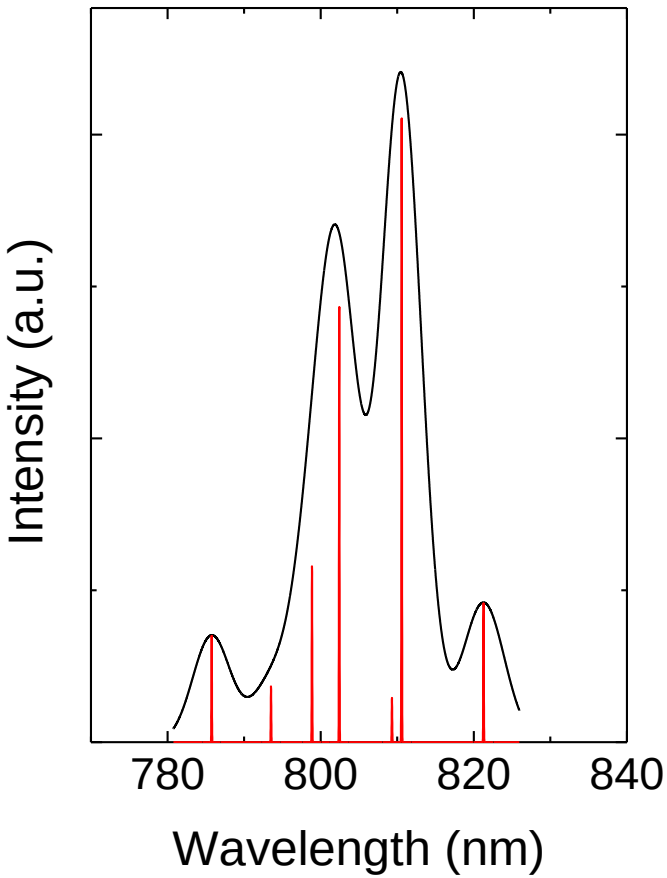
- Exciton states are partly delocalized over 2-3 BChl molecules

Absorption spectra: measured vs. computed

Measured



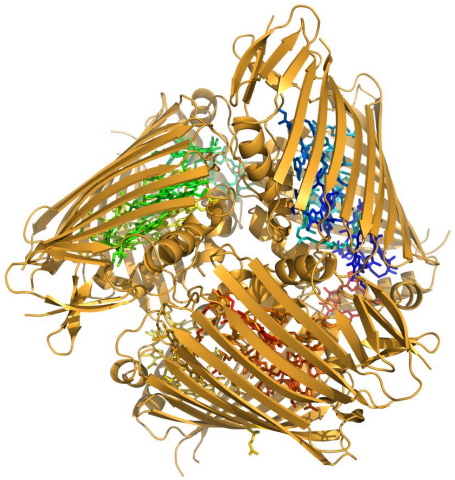
Computed

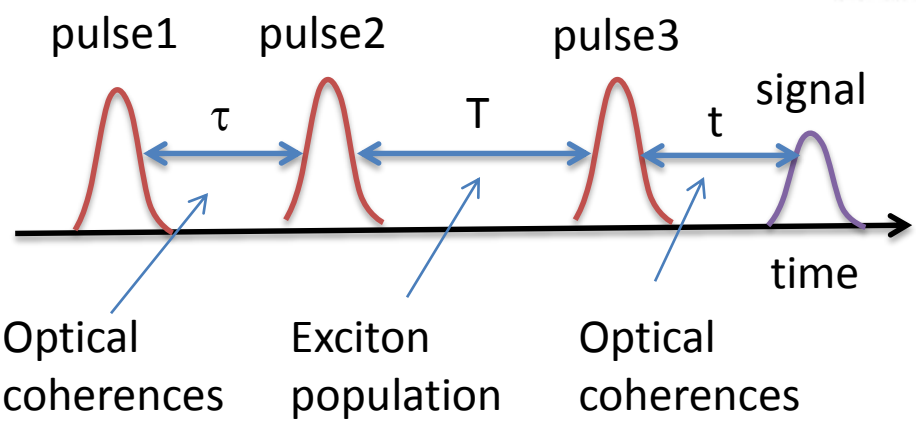


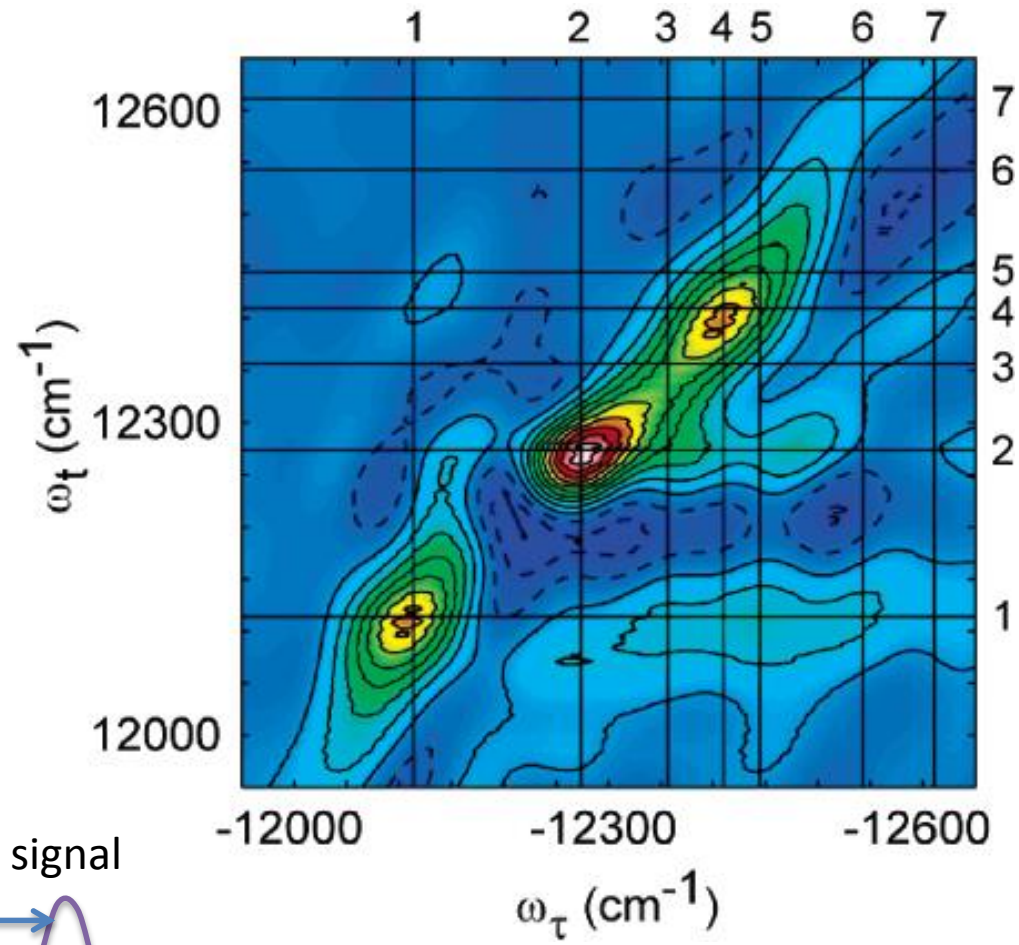
- Computed peak intensities are proportional to $|\mu_z|^2$ averaged over different molecular orientations
- Computed lines are broadened with 40 cm^{-1} linewidth

Pump-probe spectroscopy

Fenna-Mathew-Olson (FMO)
Protein complex

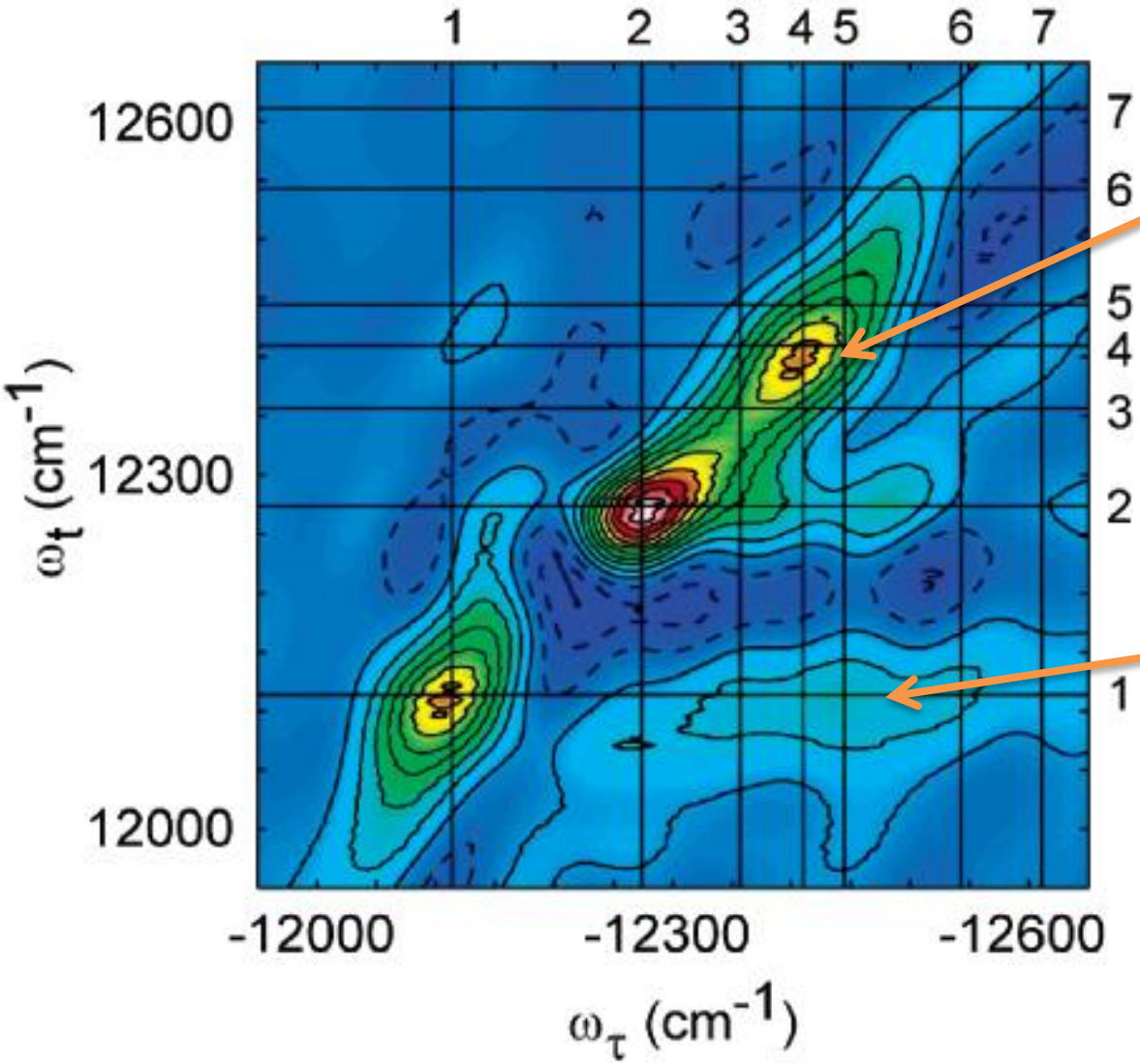






Brixner, et. al. Nature **625**, 434 (2005)

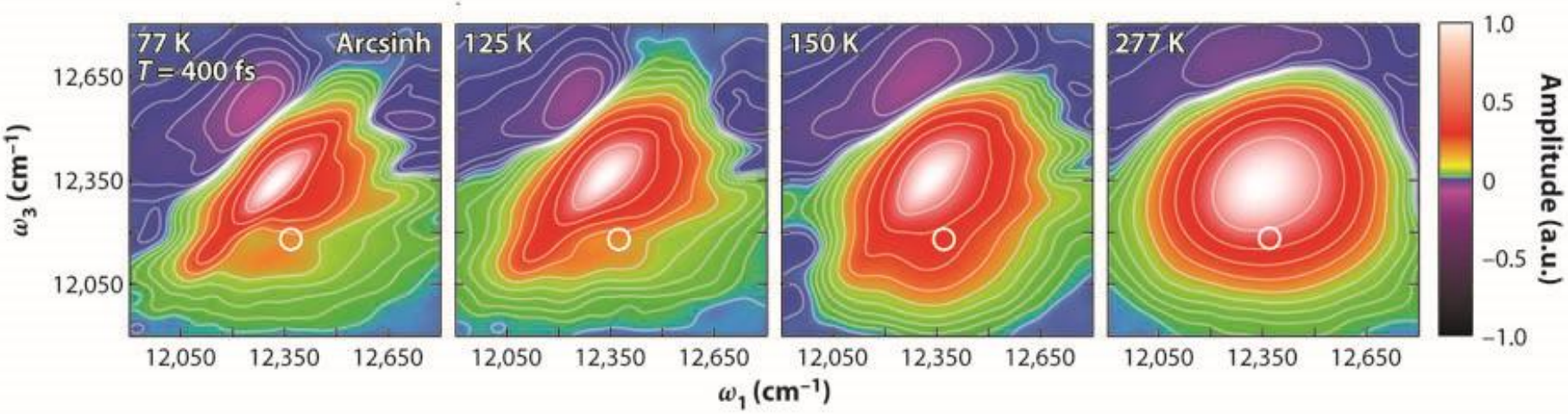
Pump-probe spectroscopy

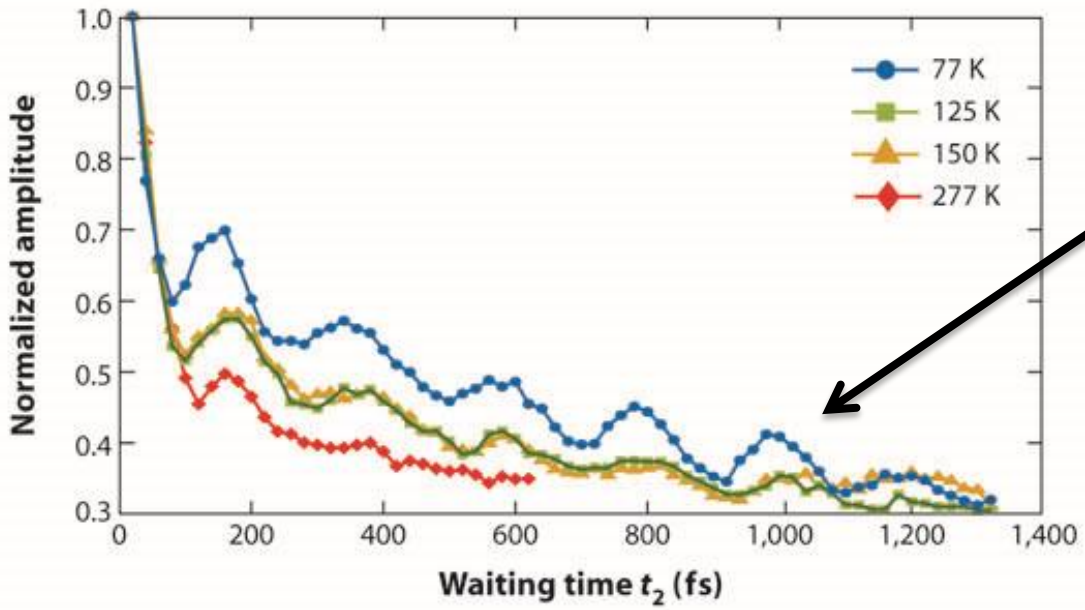


Exciton states

Energy transfer
~ exciton-exciton
coherences

Coherent dynamics





Extremely long timescales for electronic coherences

A. Ishizaki, G.R. Fleming, Annu. Rev. Condens.Matter Phys. 2012. 3:333

Coherent dynamics

Electronic coherences

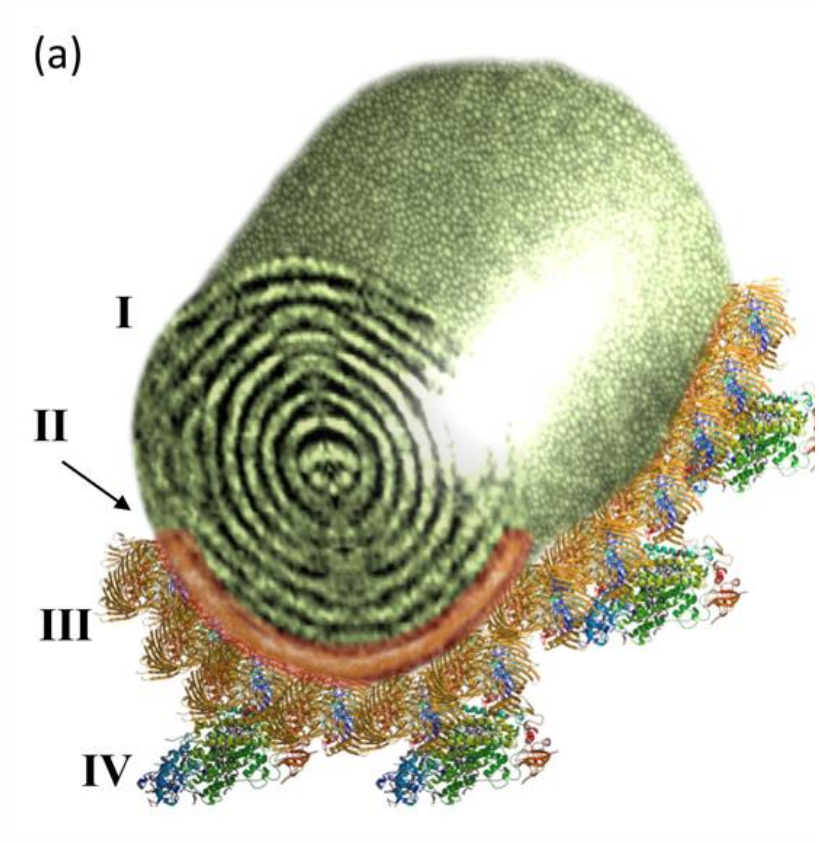
vs.

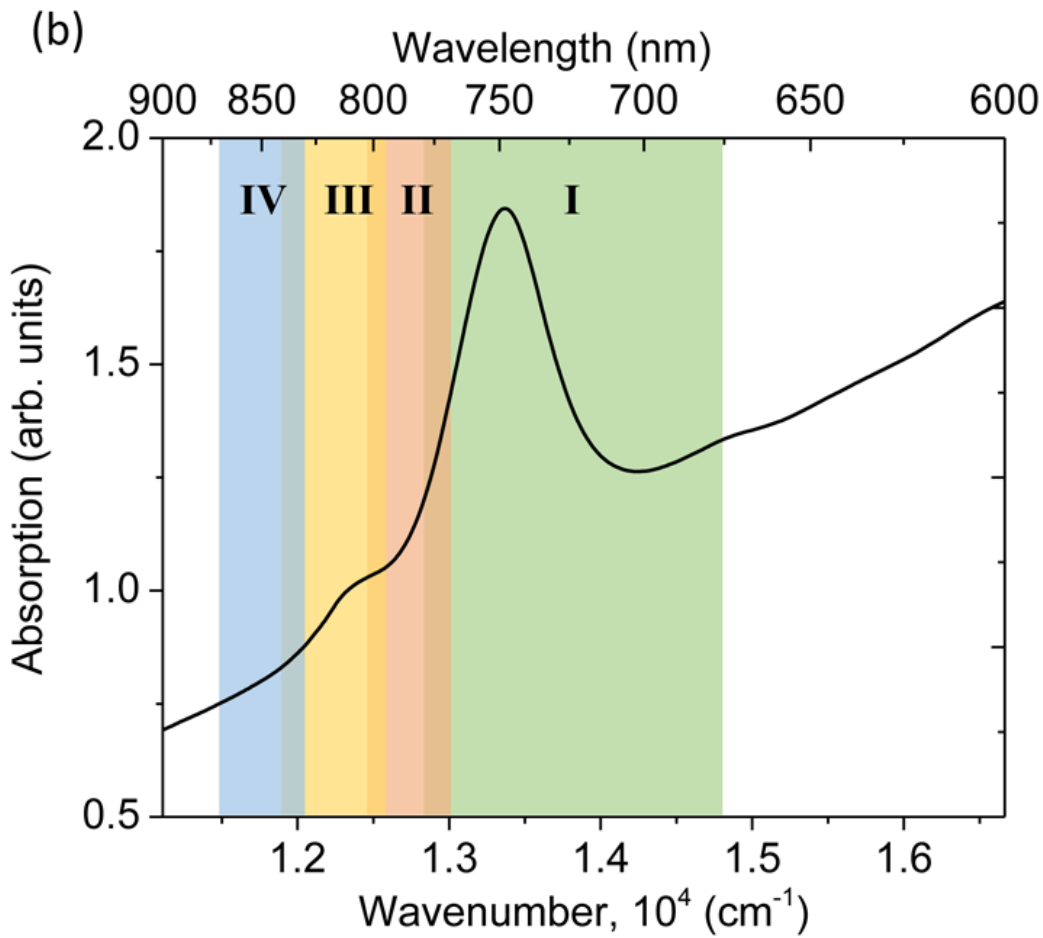
Vibronic coherences

How relevant these oscillations to light harvesting in living organisms?

Chlorosomes

Absorption spectrum of LHC





I – chlorosome

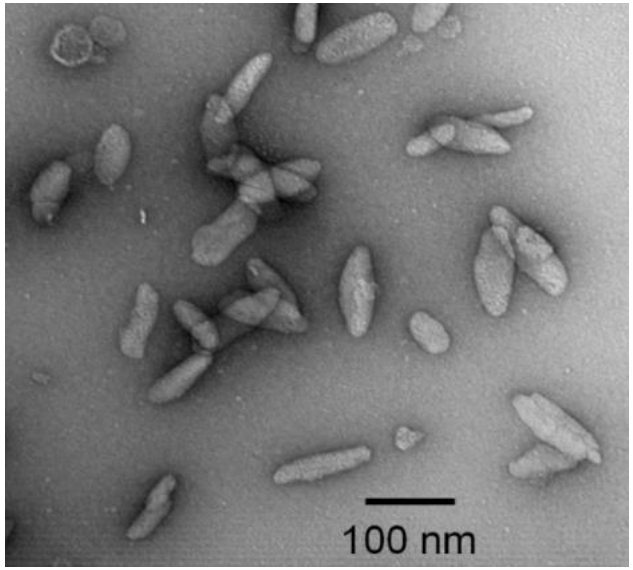
II – baseplate

III – FMO complexes

IV – reaction centers

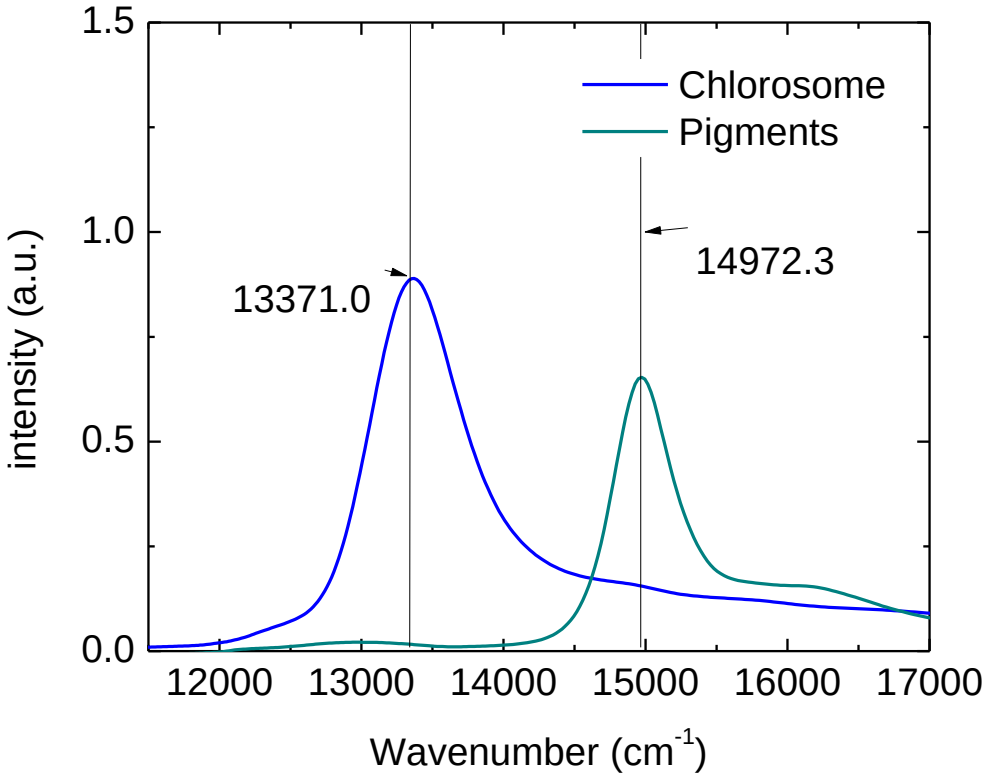
Chlorosomes as biological quantum dots

Image



Tunneling electron microscopy images of chlorosomes (Tang lab, Clark U)

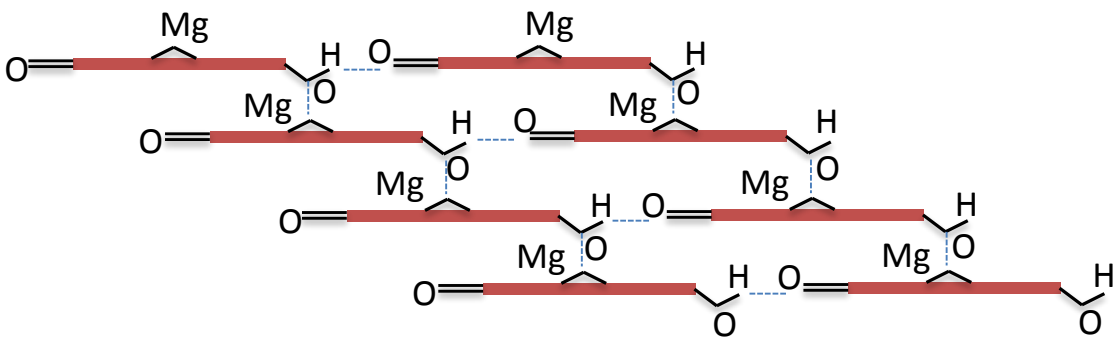
Absorption

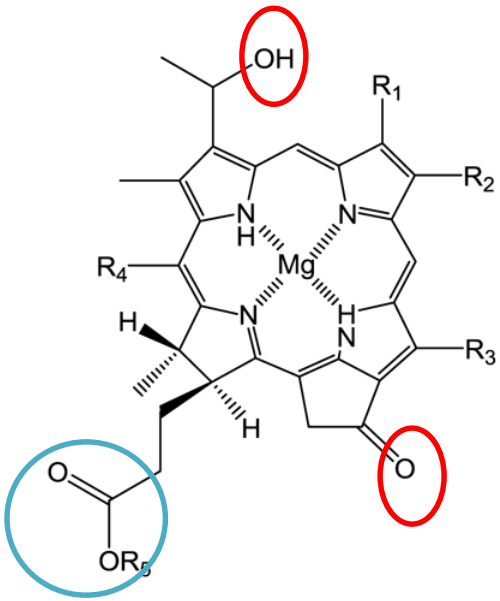


Red shift ~2000 cm^{-1}

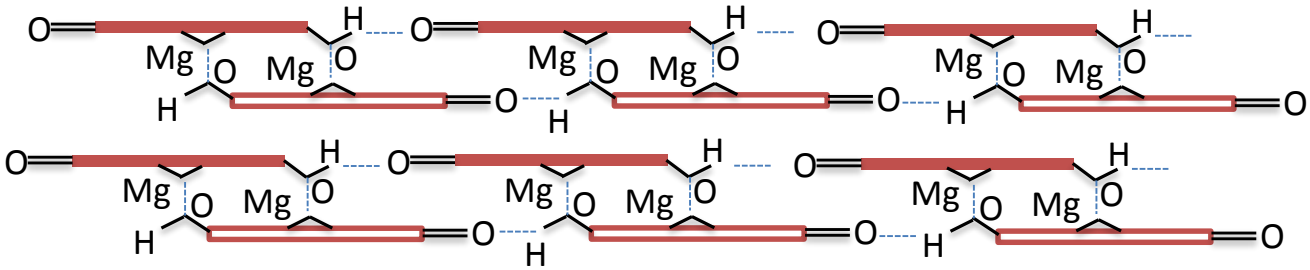
Molecular aggregation

Chain-like structure





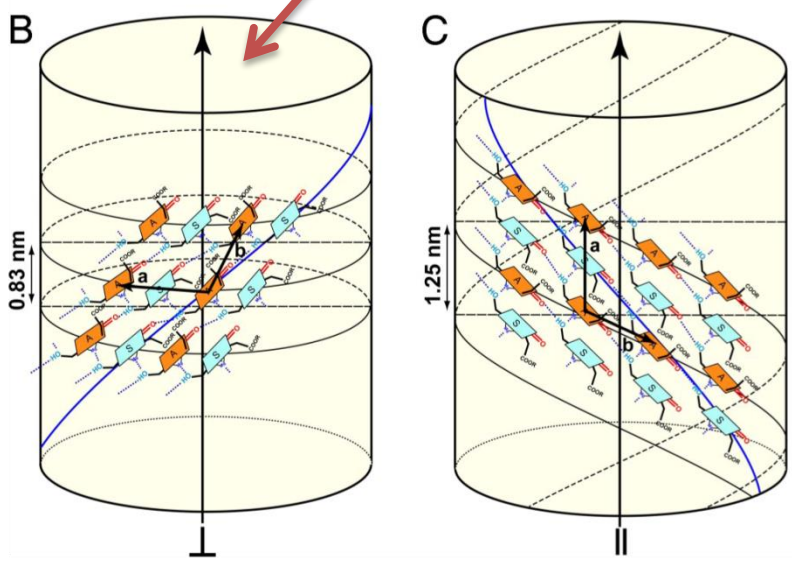
Piggyback structure



Holzwarth, Photosynth. Res. 1994

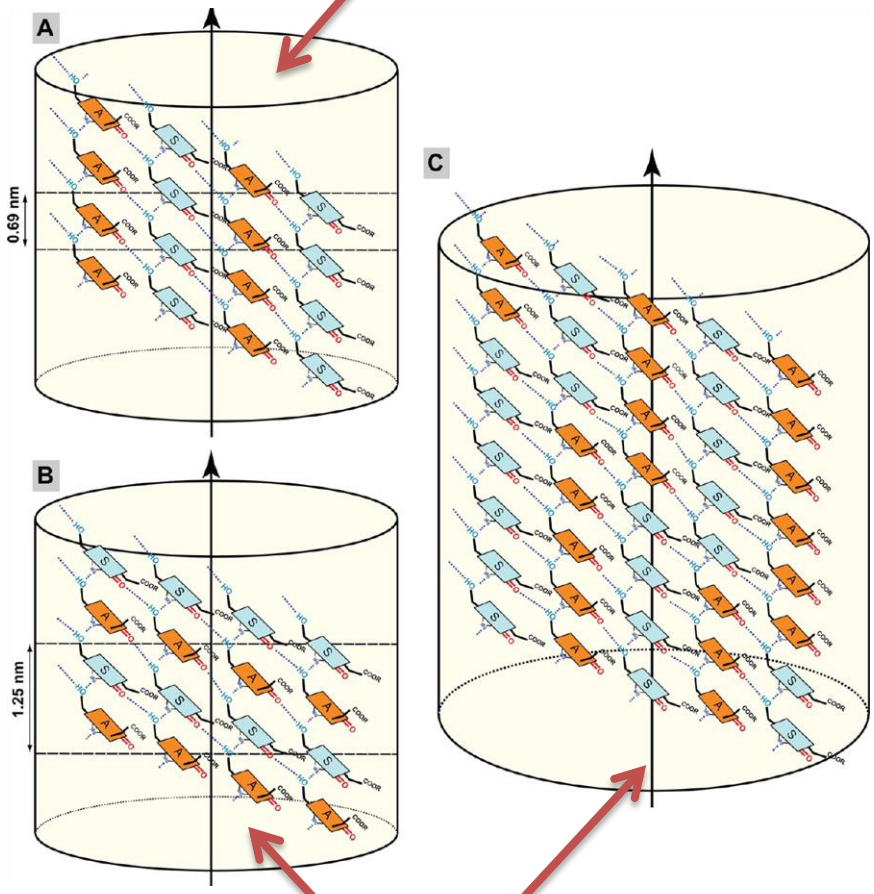
Aggregation: rolls

Bchl d – triple point mutant



PNAS 2009 – Ganapathy,… Bryant, … Holzwarth,…de Groot

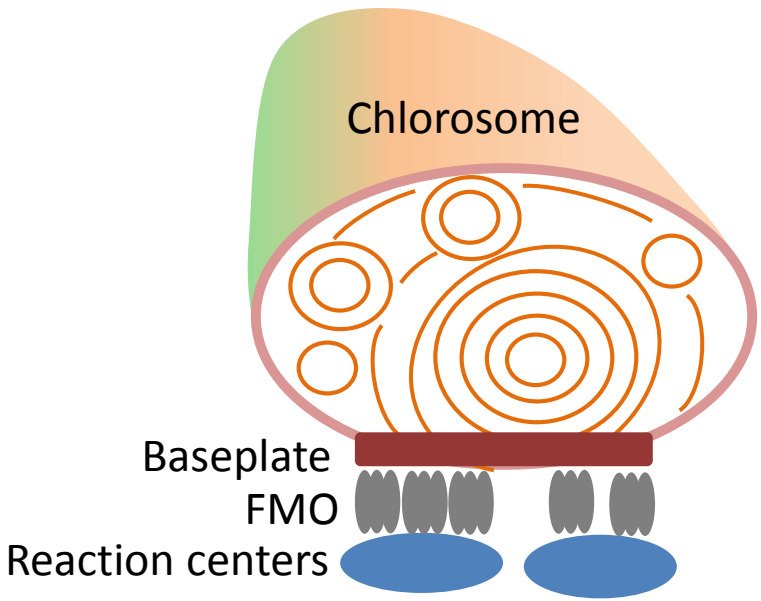
Bchl c –mutant

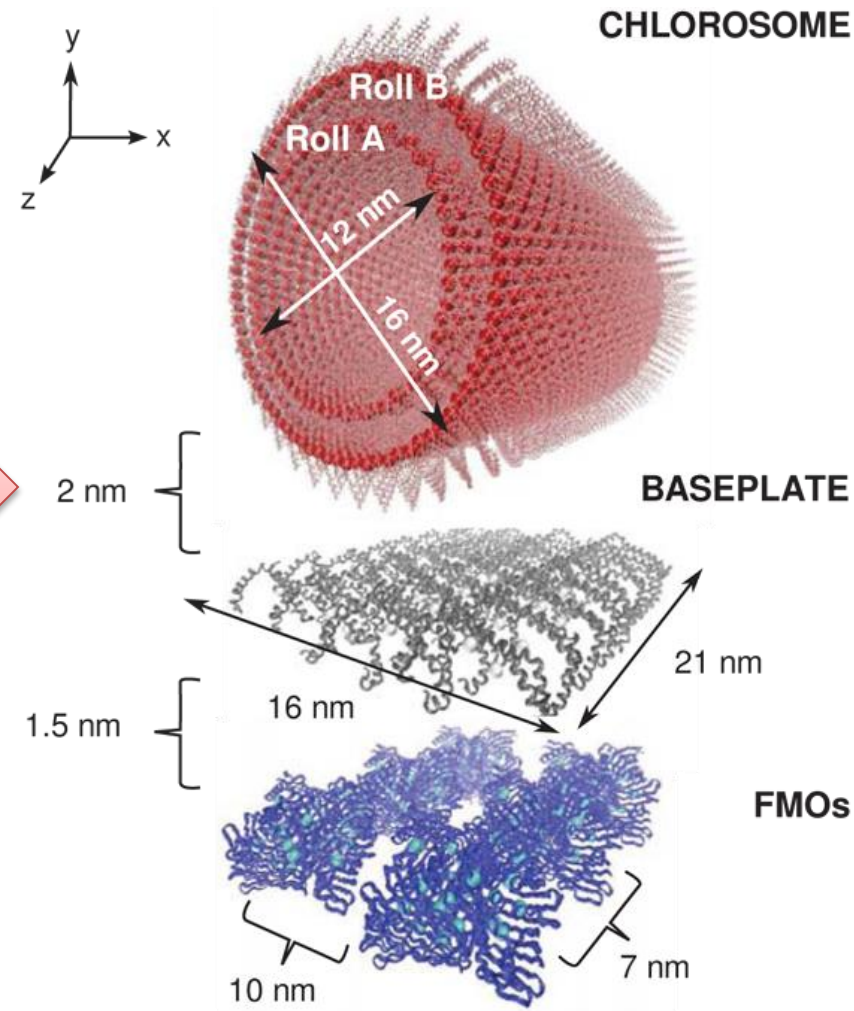


Wild type

Biochemistry 2012 – Ganapathy,… Bryant, … Holzwarth,…de Groot

From the organism to a model

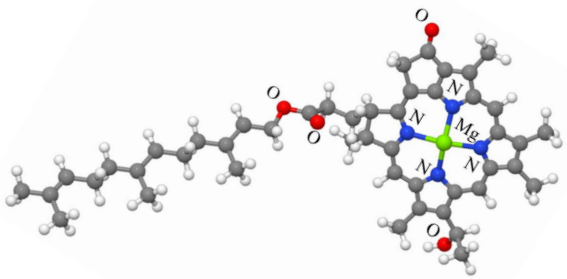




J. Huh, S. K. Saikin, J. C. Brookes, S. Valleau, T. Fujita, A. Aspuru-Guzik, *J. Am. Chem. Soc.* 136, 2048–2057 (2014).

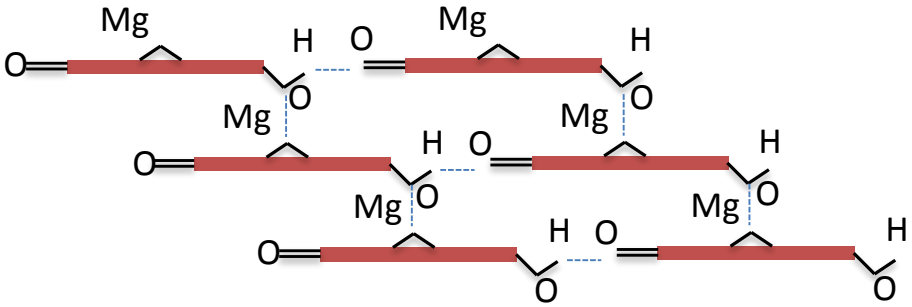
Multiscale disorder

Single molecules: Bacteriochlorophyll



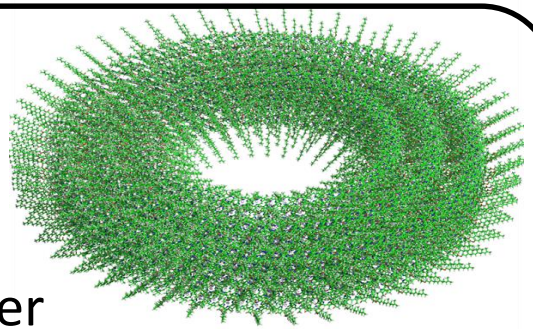
- Intramolecular vibrations
- Homologues composition

Aggregates: Local structure



- Intermolecular vibrations
- Near-neighbor structural disorder

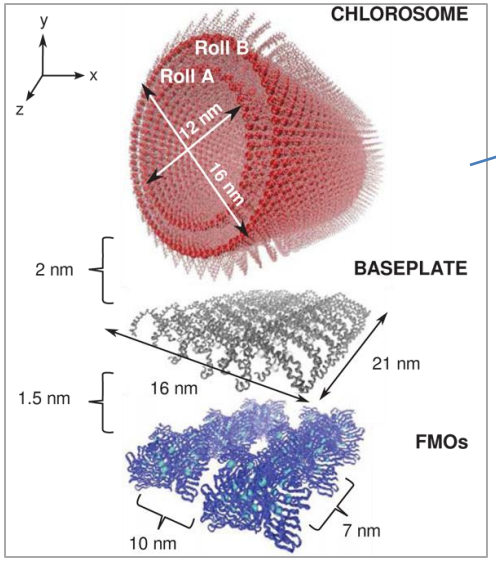
Aggregation: Global structure

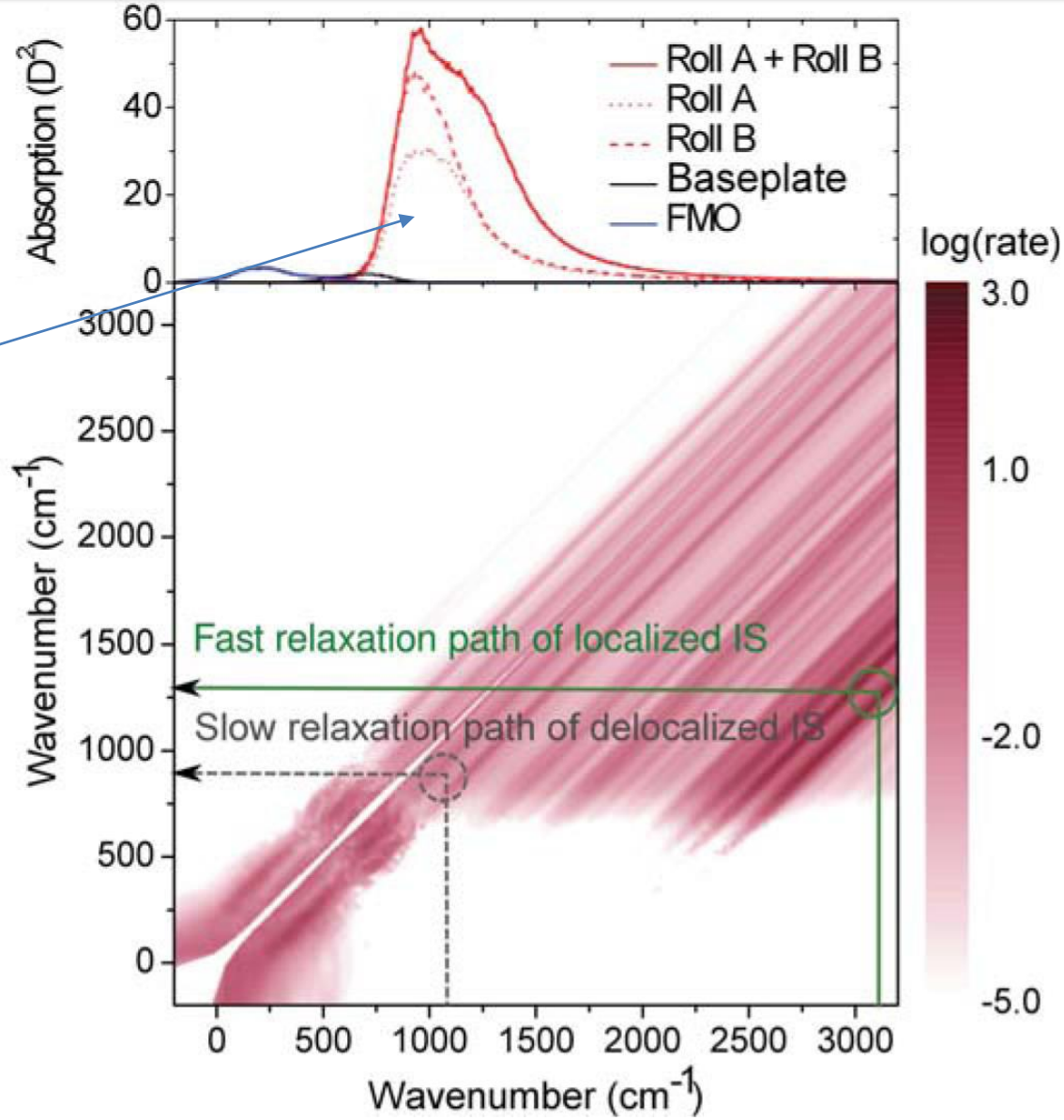


- Long-range disorder
- Fluctuations in surrounding proteins

J. K.-H. Tang, S. K. Saikin, S. V. Pingali, M. M. Enriquez, J. Huh, H. A. Frank, V. S. Urban, A. Aspuru-Guzik *Biophys. J.* 105, 1346 (2013)

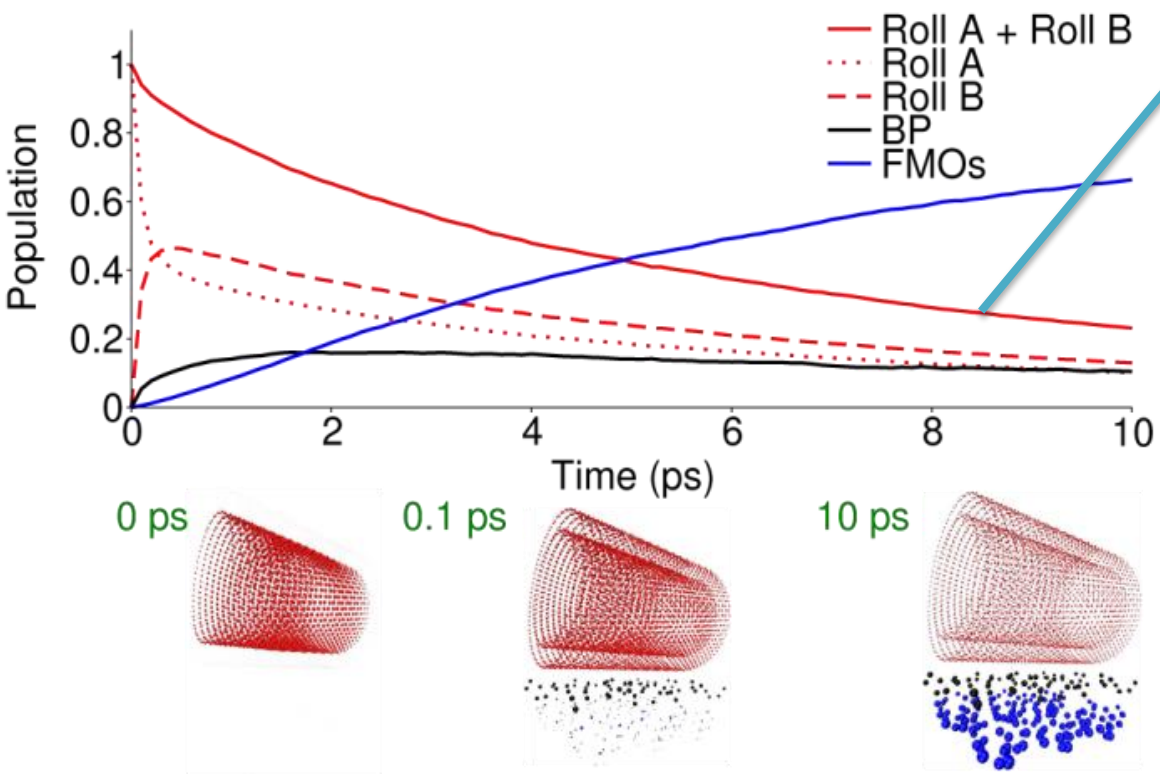
Exciton relaxation rates





J. Huh, S. K. Saikin, J. C. Brookes, S. Valleau, T. Fujita, A. Aspuru-Guzik, *J. Am. Chem. Soc.* 136, 2048 (2014)

Exciton dynamics



Population dynamics timescales:

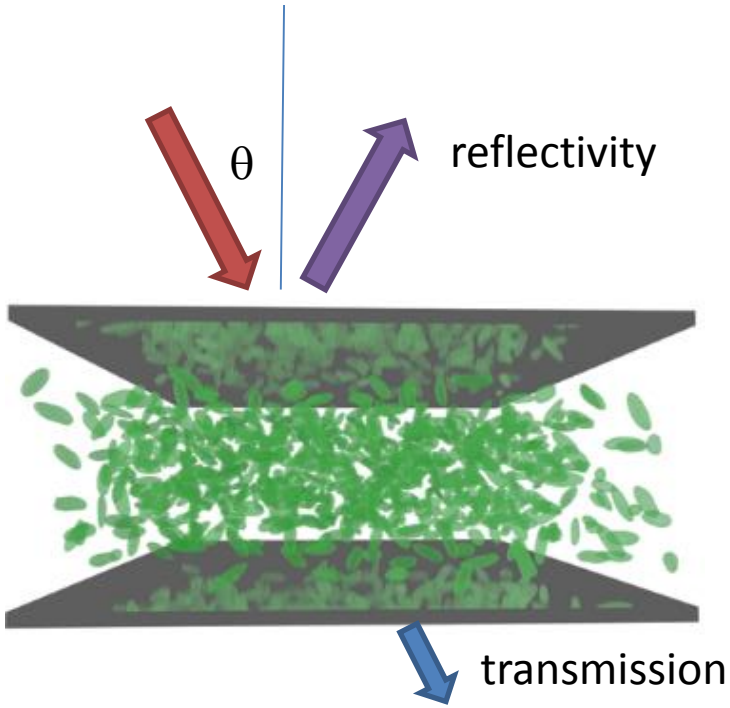
$$p = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$

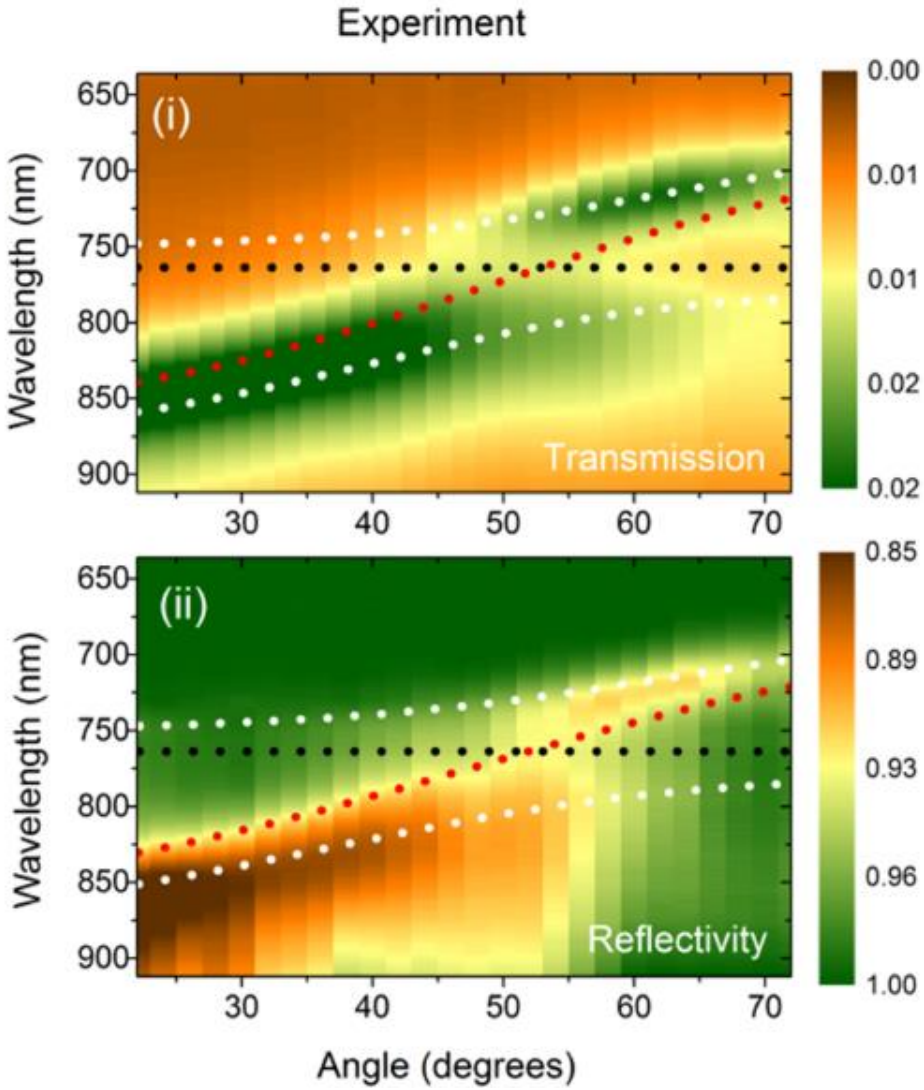
	Model	Experiment*
τ_1(fs)	91.2	
A_1	6.0	
τ_2(ps)	1.9	1.1
A_2	22.0	42.0
τ_3(ps)	8.7	12.1
A_3	72.0	58.0

***Photochem. Photobiol. 88, 675 (2012)**

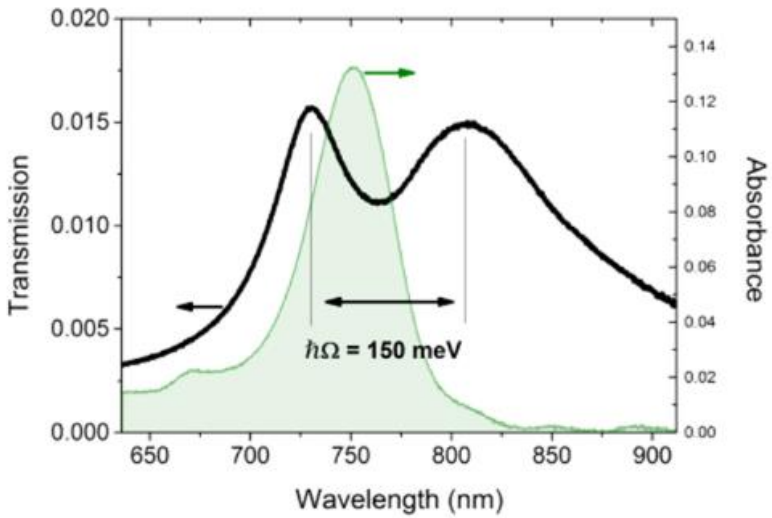
J. Huh, S. K. Saikin, J. C. Brookes, S. Valleau, T. Fujita, A. Aspuru-Guzik, *J. Am. Chem. Soc.* 136, 2048–2057 (2014).

Chlorosomes in a cavity





Chlorosome cavity coupling



Coupling strength

$$\hbar\Omega = 2\left(\vec{\mu}\cdot\hat{E}\right)\sqrt{N}\left(\frac{\pi\hbar c}{n_{\text{eff}}^2\lambda\epsilon_0 V}\right)^{\frac{1}{2}}$$

Laser field

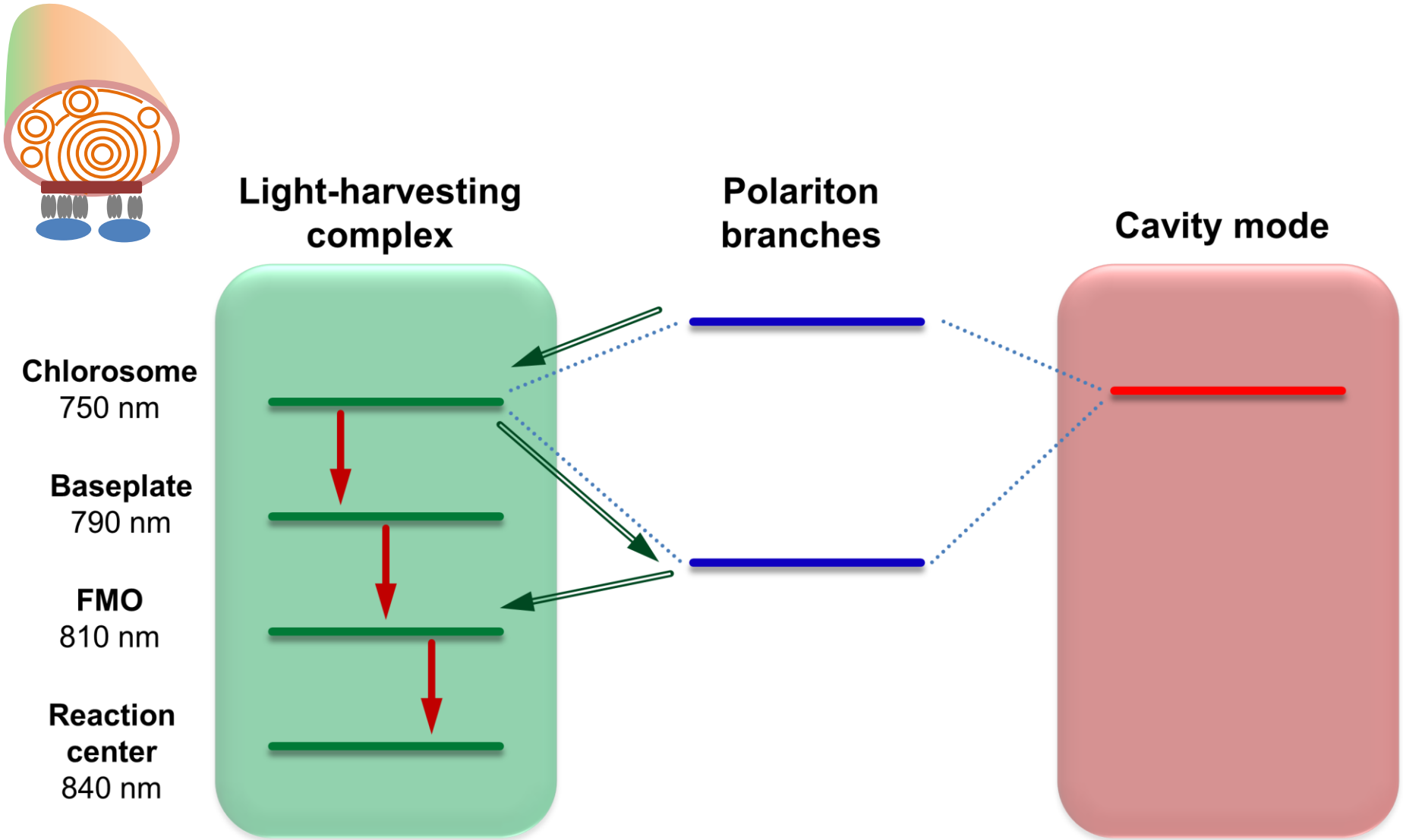
Rabi frequency

Molecular transition dipole

Number of molecules in the cavity

About 1000 chlorosomes are coherently coupled to the cavity mode

Modifying energy transfer paths in LHCs



D. M. Coles, et. al., Nat. Commun. (2014)