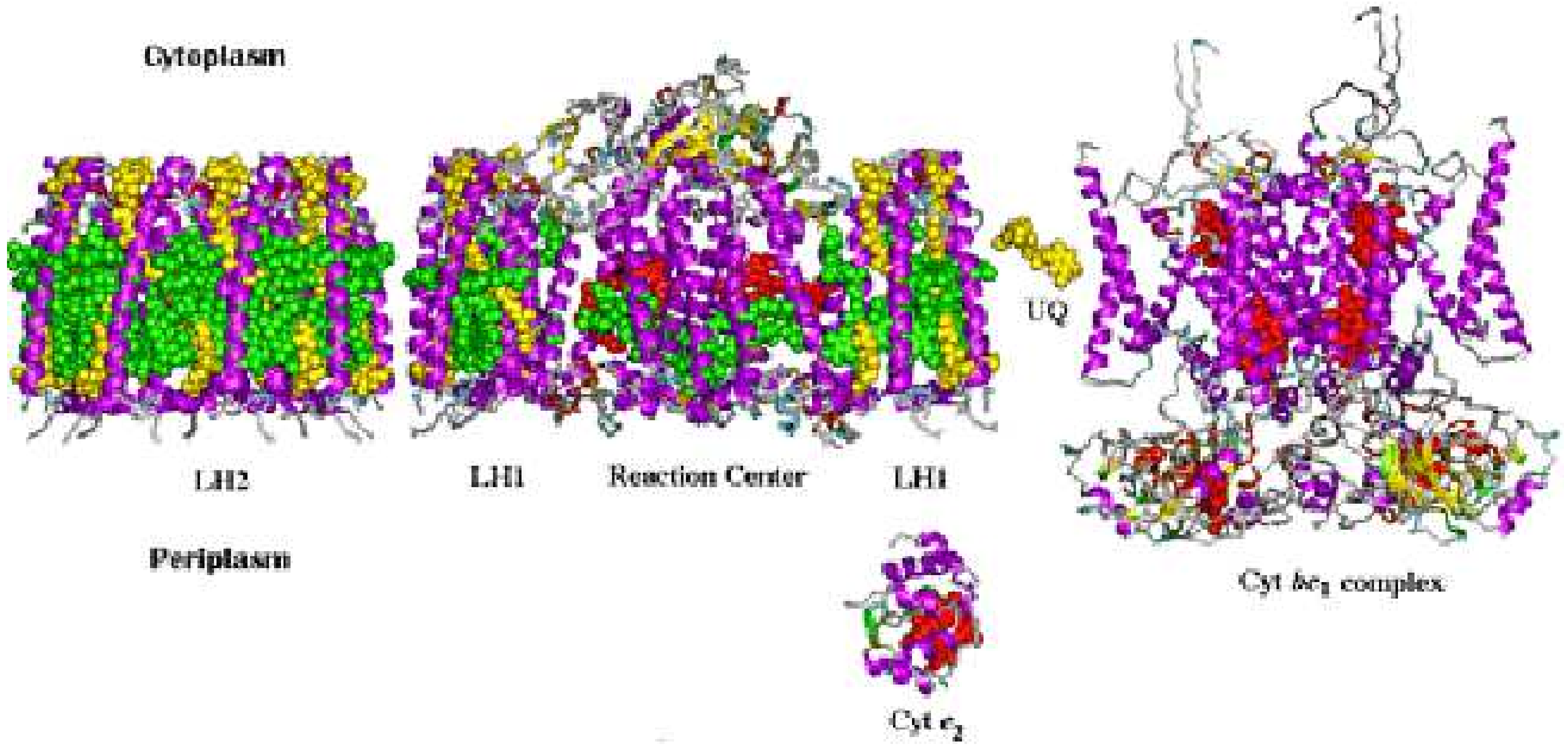
Of Electrons, Energy, and Excitons

Gert van der Zwan

July 17, 2014

Photosynthesis

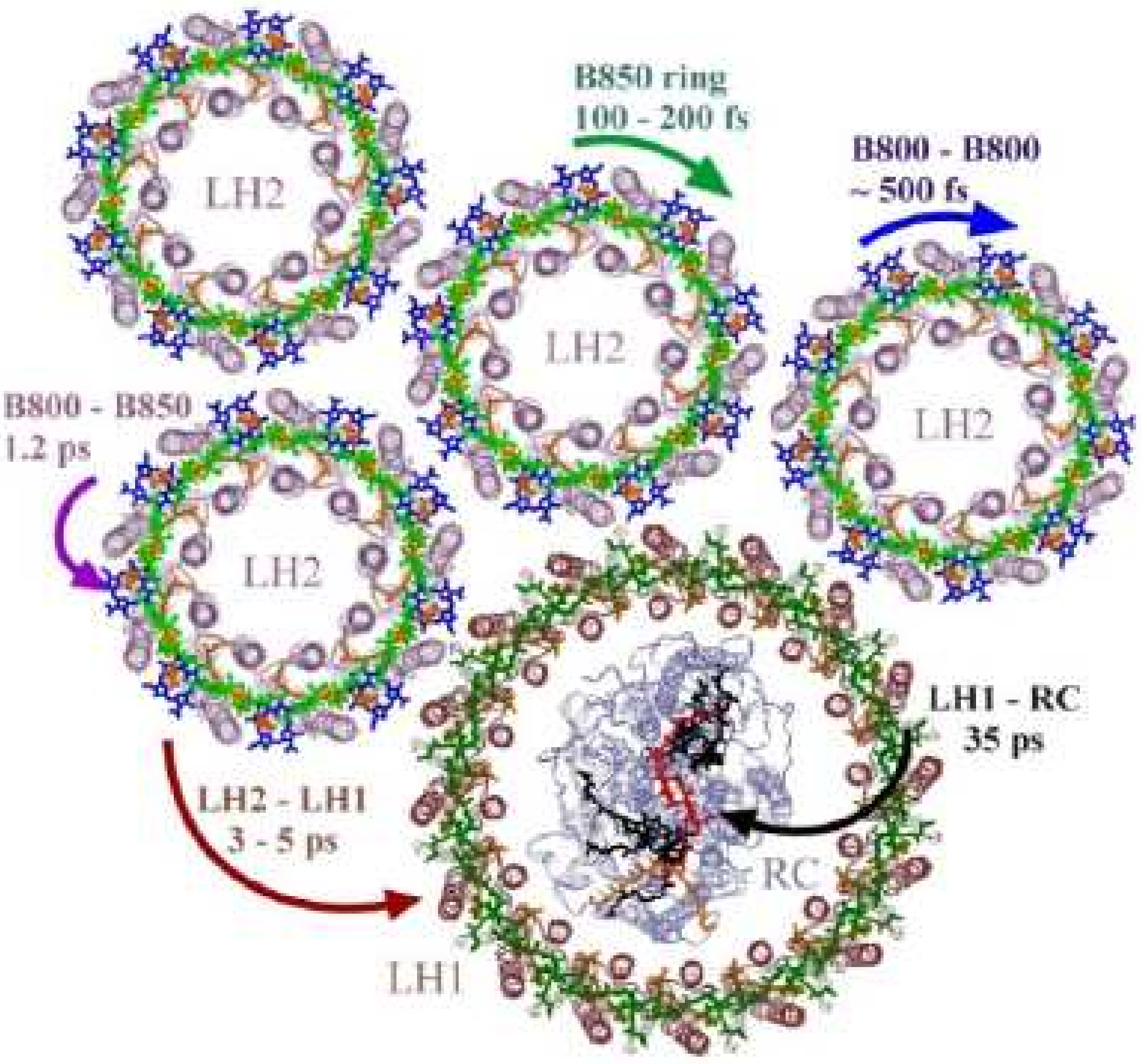
Bacterial Photosynthesis



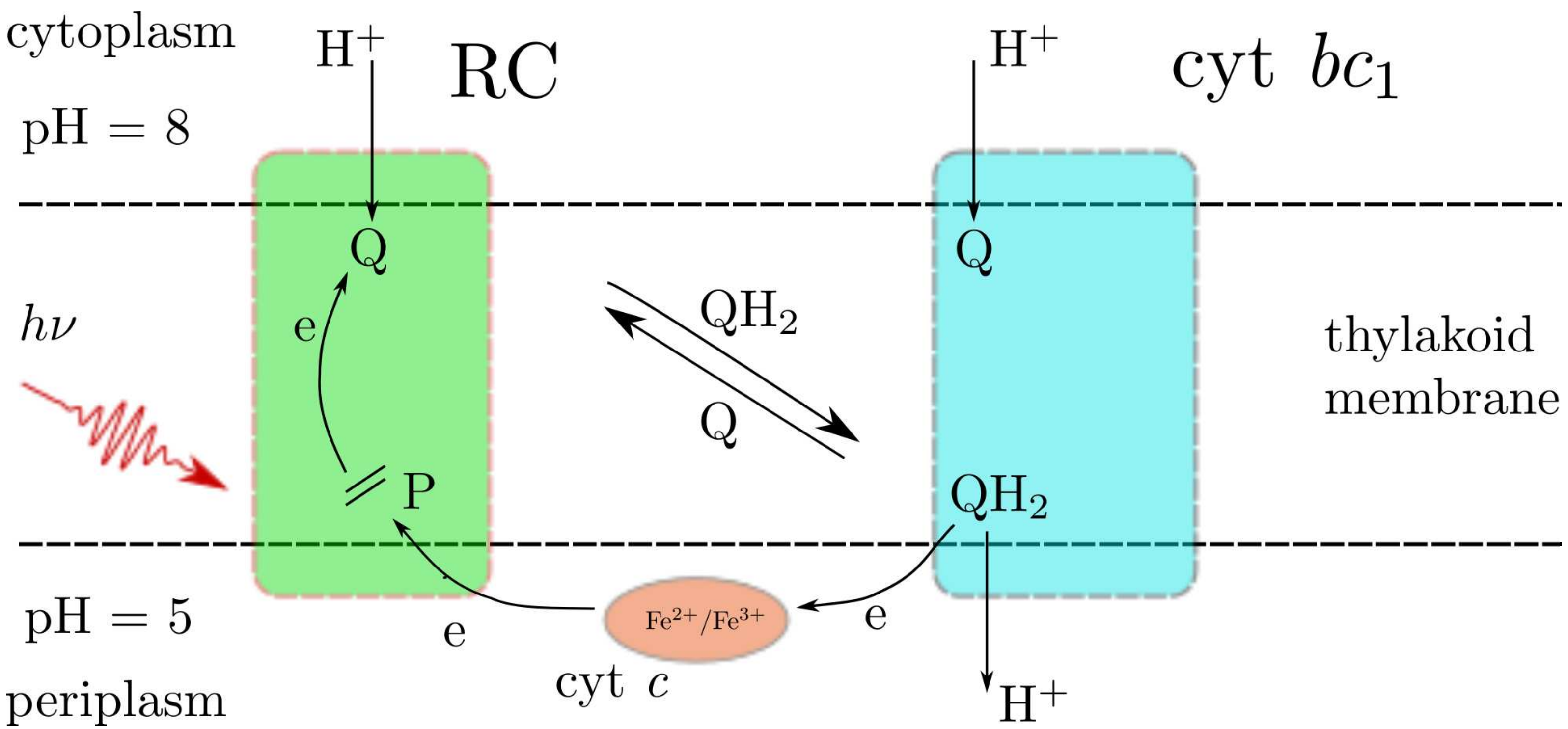
- LH1, LH2: excitonic interaction and energy transfer.
- RC, cytochromes: electron transfer reactions.
- Q, UQ: proton transfer reactions.

Source: M. Brederode, Thesis.

Bacterial Photosynthesis II

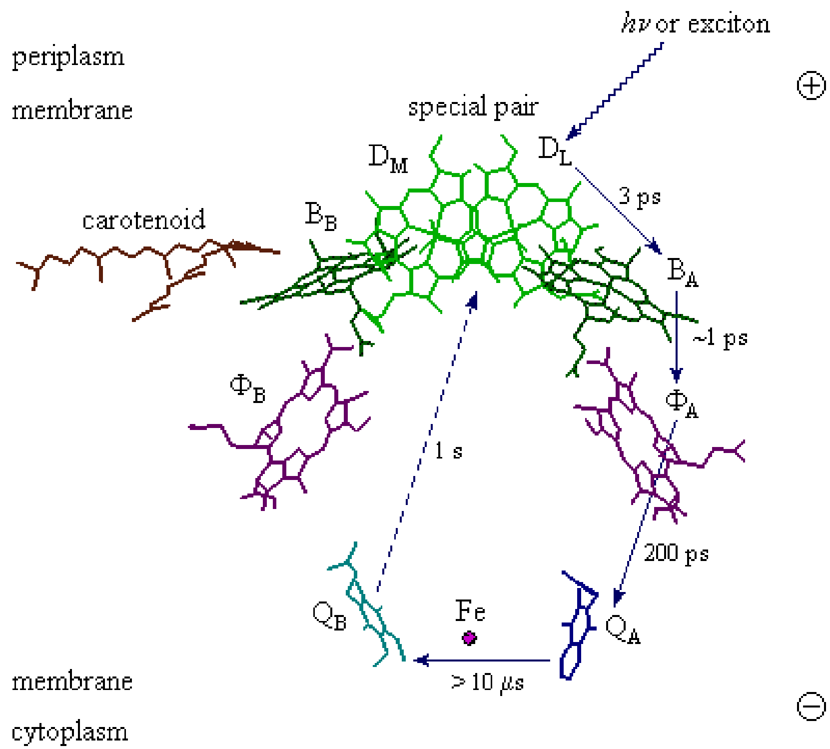


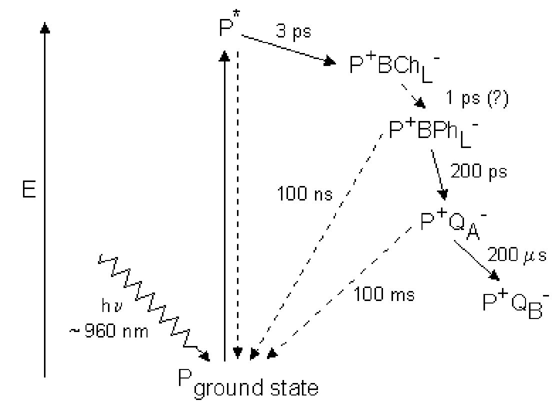
Bacterial Photosynthesis III



Net result: for every 870 nm photon two protons are transported over the membrane against a pH difference of $\Delta\mathrm{pH} = 3$.

Bacterial Photosynthesis IV

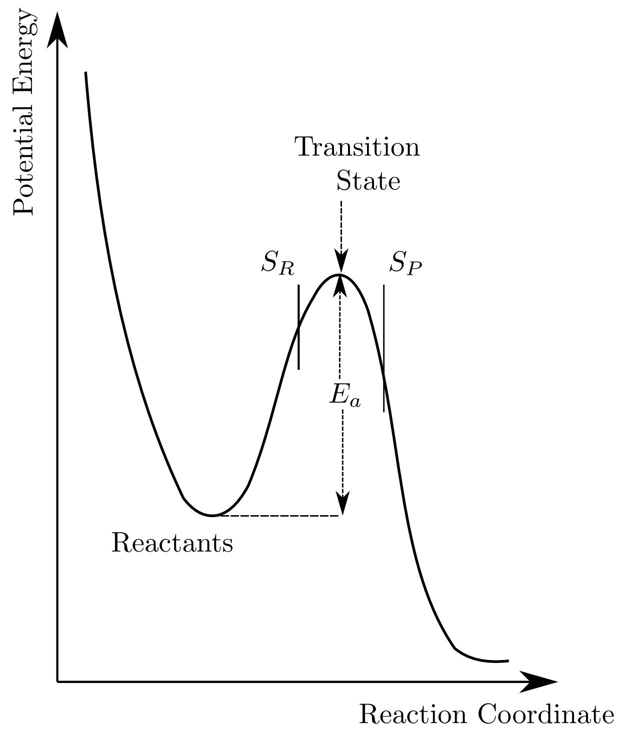




Electron tranfers reactions, redox potentials and transfer times in the RC.

Electrons

Transition State Theory+



- Equilibrium in the reactant well.
- Single reaction coordinate on adiabatic surface.
- Other (vibrational) modes irrelevant.
- No “electronic switching”.
- Classical motion over the barrier.

Rate constant:

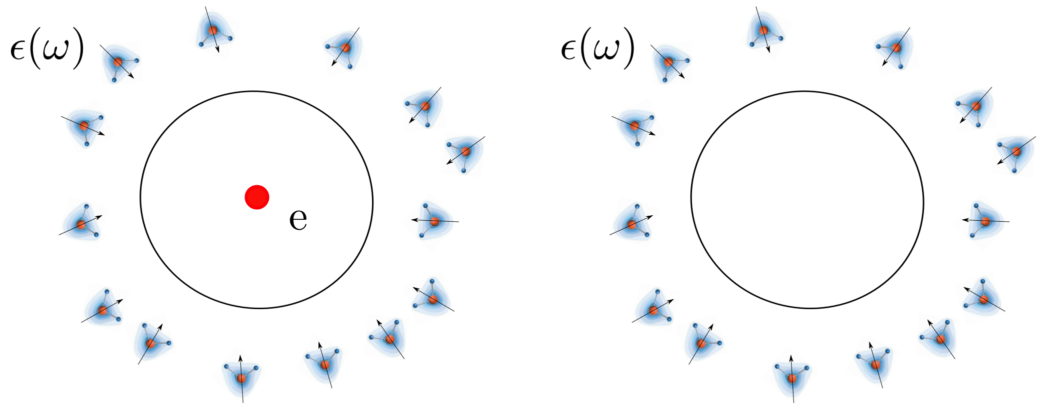
$$k = \kappa e^{-\Delta G^{\ddagger}/k_B T} = \kappa e^{\Delta S^{\ddagger}/k_B} e^{-E_a^{\ddagger}/k_B T}$$

κ depends on dynamics in the barrier region (between S_R and S_P. For TST: $\kappa = \frac{k_B T}{\hbar}$

Trans. Faraday Soc., 1938, 1–1556.

Marcus Theory

Electron transfer reactions do not involve bond–breaking and bond–making, so there is no barrier?



A charge has a reaction potential, (just like a dipole):

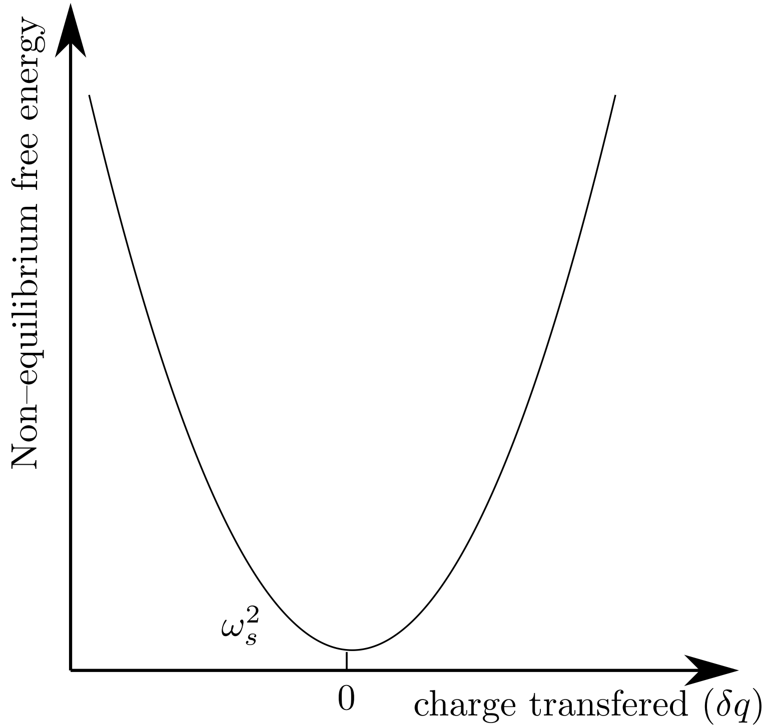
$$\psi_R = \frac{q(\epsilon_r - 1)}{4\pi\epsilon_0\epsilon_r a} \equiv A_q q$$

The free energy of a charge in its own reaction field is

$$G_{\text{eq}} = \frac{1}{2} A_q q^2$$

Marcus Theory II

If the amount of charge in the cavity is changed instantaneously, the order in the solvent remains the same (entropy), but the energy changes.



Non–equilibrium free energy:

$$G_{\text{neq}} = \frac{1}{2}\omega_s^2 (q - \delta q)^2$$

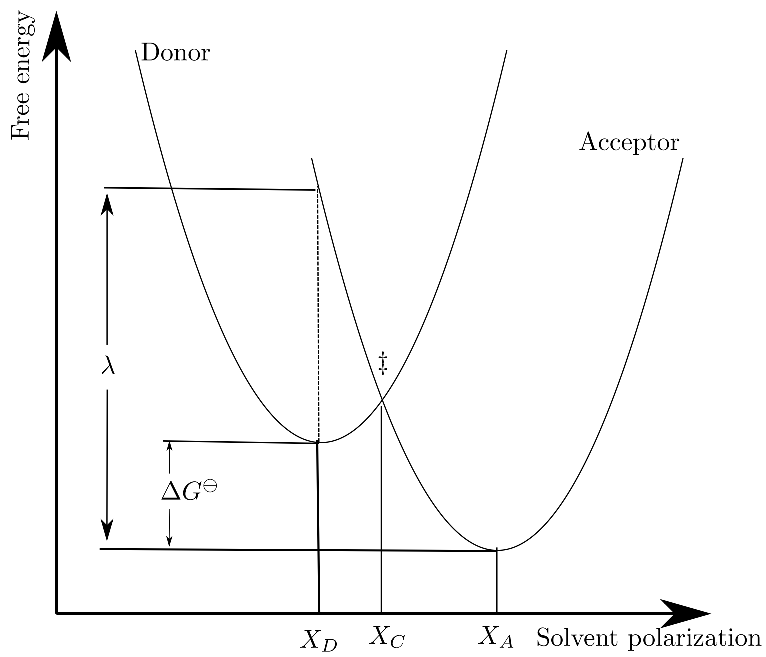
with

$$\omega_s^2 = A_q$$

Reaction Coordinate = Solvent Polarization

Marcus Theory III

Solvent perspective: for a given polarization there is an "equivalent charge".



- $\Delta G^{\ominus} = G_{\mathrm{eq,A}} - G_{\mathrm{eq,D}}$: driving force
- λ: reorganization energy.
- ‡: transition state.
- $X_{D,A}$: Solvent in equilibrium with Donor, Acceptor.

At the crossing point X_C it does not matter for the solvent where the electron is, and transfer can take place.

Crossing Point

Donor Potential:

$$G_D = G_{\text{eq,D}} + \frac{1}{2}\omega_s^2 (X - X_D)^2$$

Acceptor potential:

$$G_A = G_{\text{eq,A}} + \frac{1}{2}\omega_s^2 (X - X_A)^2$$

Crossing point:

$$X_C = \frac{1}{2}(X_A + X_D) + \frac{\Delta G^{\ominus}}{\omega_s^2 (X_A - X_D)}$$

Reorganization Energy

$$\lambda = \frac{1}{2}\omega_s^2 (X_A - X_D)^2$$

Activation free energy:

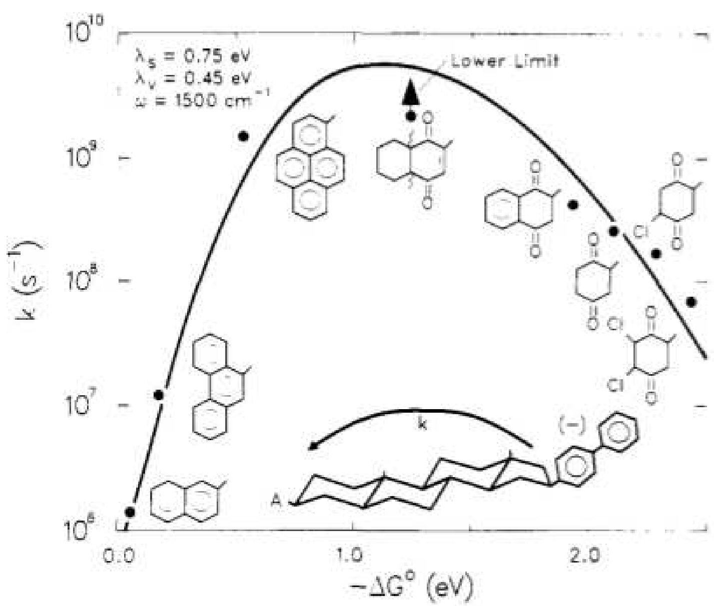
$$\boxed{\Delta G_{\ddagger} = \frac{(\lambda + \Delta G^{\ominus})^2}{4\lambda}}$$

Marcus Rate Constant

The reaction rate is the product of the Arrhenius factor containing the activation free energy, and a transmission coefficient κ:

$$k_{\mathrm{ET}} = \kappa e^{-\frac{(\lambda+\Delta G^{\ominus})^2}{4\lambda k_B T}}$$

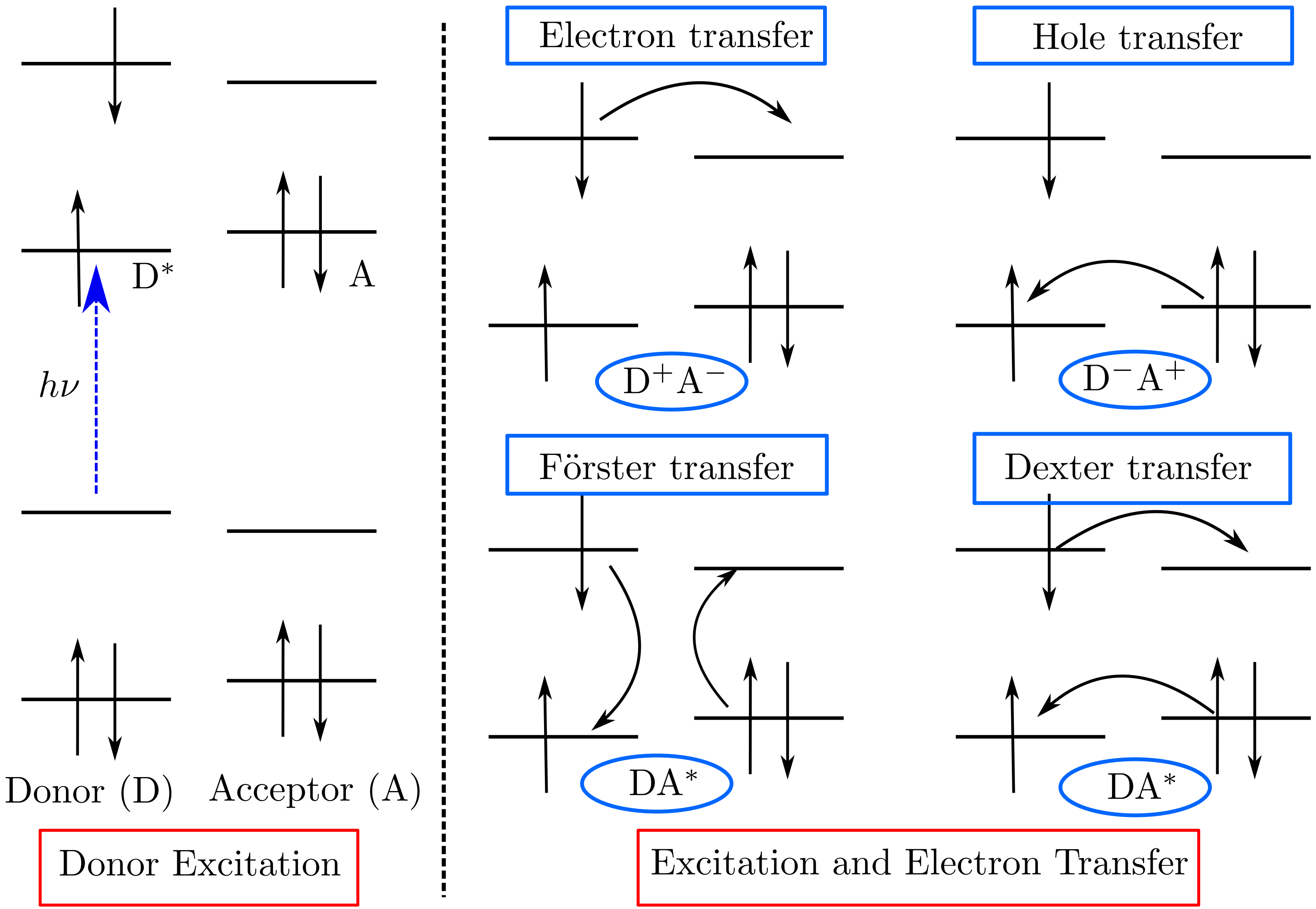
A charge (or charge distribution) creates its own barrier by polarizing the environment.



J. R. Miller , L. T. Calcaterra , G. L. Closs *J. Am. Chem. Soc.*, (1984), **106**, 30473049.

Energy

Transfer


D*
A
$h\nu$
Donor (D)
Acceptor (A)
Donor Excitation
Electron transfer
D^+A^-
Hole transfer
D^-A^+
Förster transfer
DA^*
Dexter transfer
DA^*
Excitation and Electron Transfer

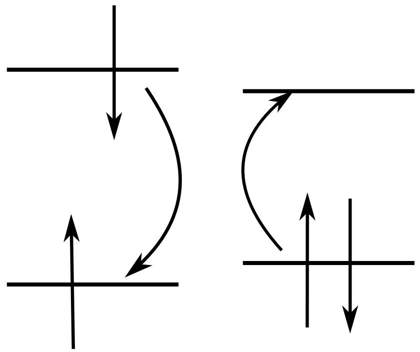
Transfer II

What can happen when a donor gets excited?

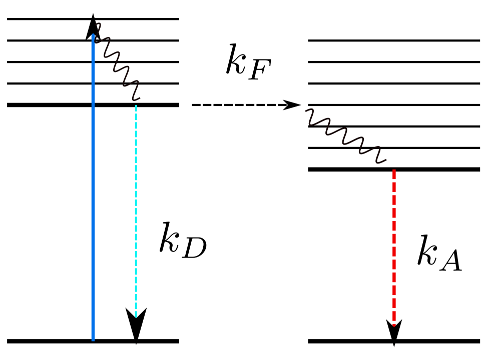
- Fluorescence or radiationless decay.
- Electron and Hole transfer: Marcus Theory.
- Excitation transfer
  - Förster: dipole–dipole interaction, distance between donor and acceptor large.
  - Dexter: overlap of wavefunctions
- Exciton coupling: dipole–dipole interaction, short distance between donor and acceptor.

In photosynthesis the chromophores are organized in such a way that energy or electrons are transfered before fluorescence occurs.

Förster Mechanism



$\mathrm{D^*A} \longrightarrow \mathrm{DA^*}$



Fermi's golden rule:

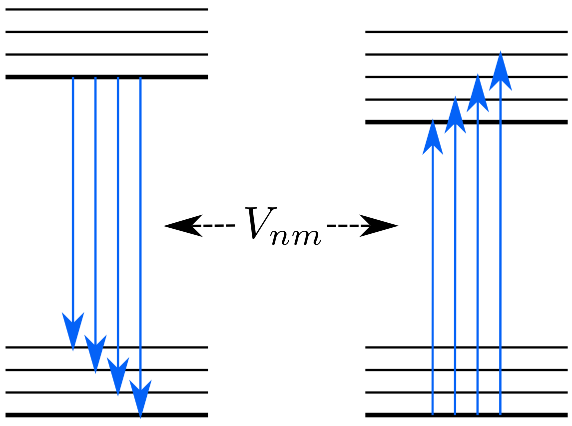
$$\Gamma_{nm} = 4\pi^2 |V_{nm}|^2 \delta(\nu_n - \nu_m)$$

- $\delta(\nu_n - \nu_m)$: energy conservation
- V_{nm}: dipole–dipole interaction.

$$V_{nm} = \frac{f^2}{4\pi\epsilon_0\epsilon_r r^3} \vec{\mu}_n \cdot \left(1 - \frac{3\vec{r}\vec{r}}{r^2}\right) \cdot \vec{\mu}_m$$

Förster Mechanism II

The donor decays mainly from the ground vibrational level in the excited state. The transition moments are $S_m \mu_D$, where S_m is the Franck–Condon overlap and μ_D is the electronic transition moment.



The acceptor is mainly excited from the vibrational and electronic ground state. The transition moments are $S_n \mu_A$ where S_n is the Franck–Condon overlap, and μ_A the electronic transition moment

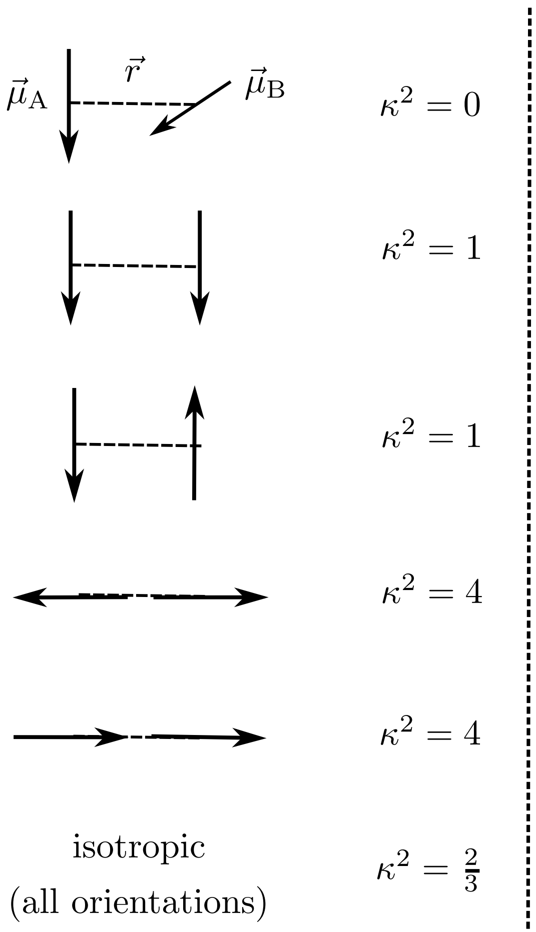
Total transfer rate (sum over all vibrational levels):

$$\Gamma_{\mathrm{DA}} = \frac{f^4 \kappa^2}{4\epsilon_0^2 n^4 r^6} \sum_{n,m} \mu_{\mathrm{D}}^2 \mu_{\mathrm{A}}^2 S_m^2 S_n^2 \delta(\nu_n - \nu_m)$$

with orientation factor (carets denote unit vectors)

$$\kappa = \hat{\mu}_{\mathrm{D}} \cdot (1 - 3\hat{r}\hat{r}) \cdot \hat{\mu}_{\mathrm{A}}$$

Förster Mechanism III



- Normalized Fluorescence Spectrum:

$$F(\nu) = \frac{\sum_m \mu_\mathrm{D}^2 S_m^2 \delta(\nu - \nu_m)}{\sum_m \mu_\mathrm{D}^2 S_m^2}$$

- Absorption spectrum

$$\epsilon_A(\nu) = \frac{8\pi^3 N_a}{3 \times 10^3 \hbar c \ln 10} \frac{\mu_\mathrm{A}^2 f^2}{n} \times \sum_n S_n^2 \delta(\nu - \nu_n)$$

in mol $\mathrm{L}^{-1}\mathrm{cm}^{-1}$

Förster Mechanism IV

Barbatruc

$$\Gamma_{\mathrm{DA}} = \frac{f^4\kappa^2}{4\epsilon_0^2 n^4 r^6} \sum_{n,m} \mu_{\mathrm{D}}^2 \mu_{\mathrm{A}}^2 S_m^2 S_n^2 \delta(\nu_n - \nu_m)$$

$$= \frac{f^4\kappa^2}{4\epsilon_0^2 n^4 r^6} \int d\nu \underbrace{\left[\sum_m \mu_{\mathrm{D}}^2 S_m^2 \delta(\nu_n - \nu)\right]} \underbrace{\left[\sum_n \mu_{\mathrm{A}}^2 S_n^2 \delta(\nu_n - \nu)\right]}$$

Proportional to the fluorescence spectrum

Proportional to the absorption spectrum

After all the dust has settled:

$$\boxed{\Gamma_{\mathrm{DA}} = 8.8 \times 10^{17} \frac{\kappa^2}{n^4 \tau_D R^6} \int d\nu \, \frac{F_{\mathrm{D}}(\nu)\epsilon_{\mathrm{A}}(\nu)}{\nu^4}}$$

Properties of Förster energy transfer

- Overlap integral:

$$J_{\mathrm{DA}} = \int d\nu \, \frac{F_{\mathrm{D}}(\nu)\epsilon_{\mathrm{A}}(\nu)}{\nu^4}$$

Overlap between the spectra is needed, otherwise energy can not be conserved. Overlap is usually small for the same molecule due to Stokes shift.

- Förster Length:

$$R_0^6 = 8.8 \times 10^{17} \frac{\kappa^2}{n^4}$$

R_0 is usually of the order 10 nm.

Förster Transfer Examples

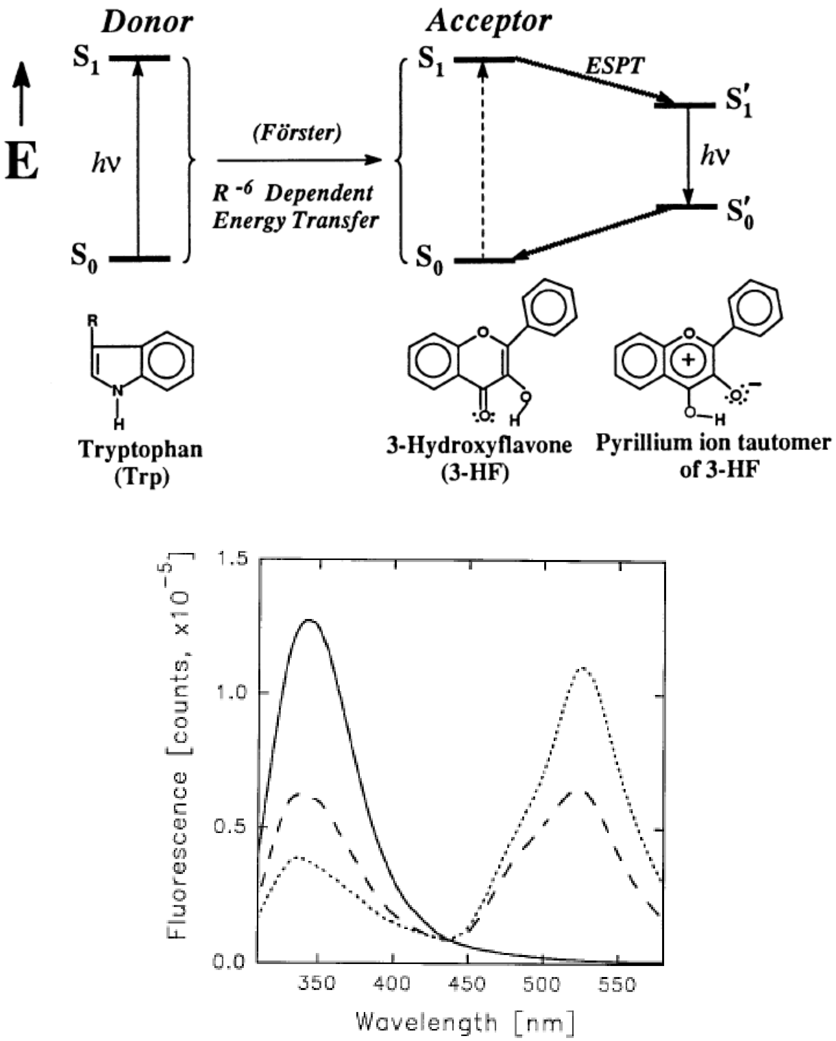


FIG. 4. Fluorescence spectra of HSA (40 μM) in absence (——) and presence of 40 μM (---) and 80 μM (···) 3-HF. λ_{ex} = 297 nm.

- Two 6.3 D dipoles at 10 nm:

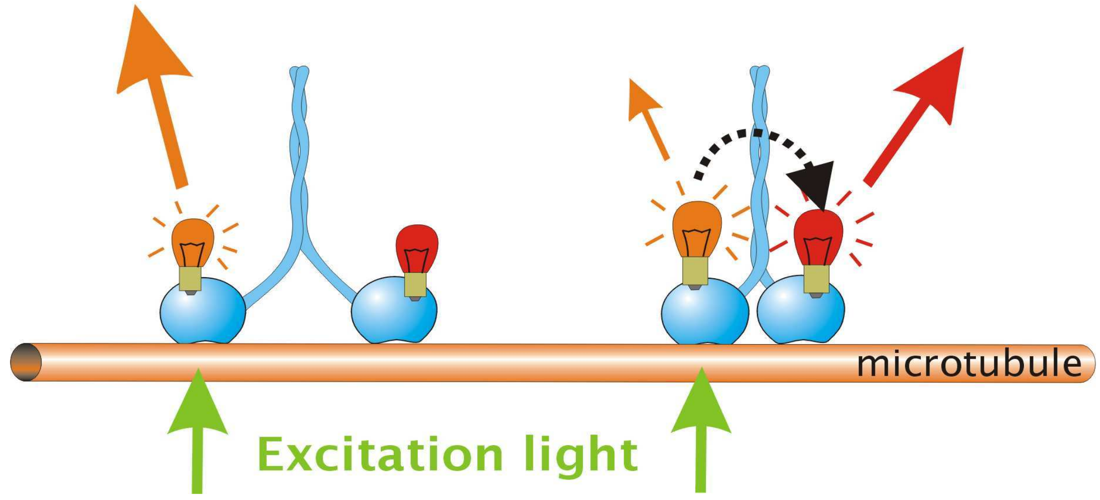
  $V \approx 0.2\,\mathrm{cm}^{-1}$.

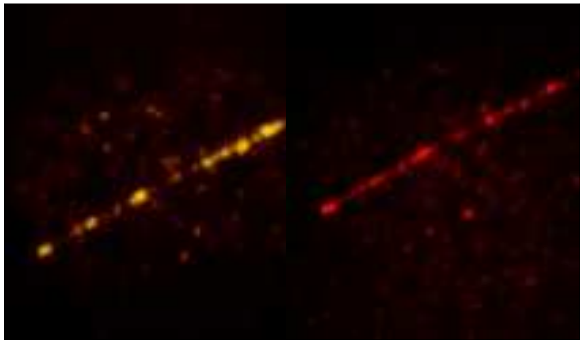
- κ can range from 0 to 4 for fixed orientations.

- It is usually possible to find good labels for energy transfer.

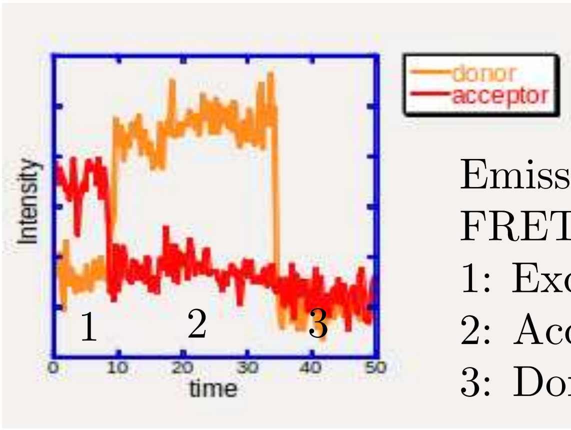
Förster Transfer Examples II

Kinesin: two–headed motor protein. Mobility is driven bu conformational changes induced by ATP hydrolysis





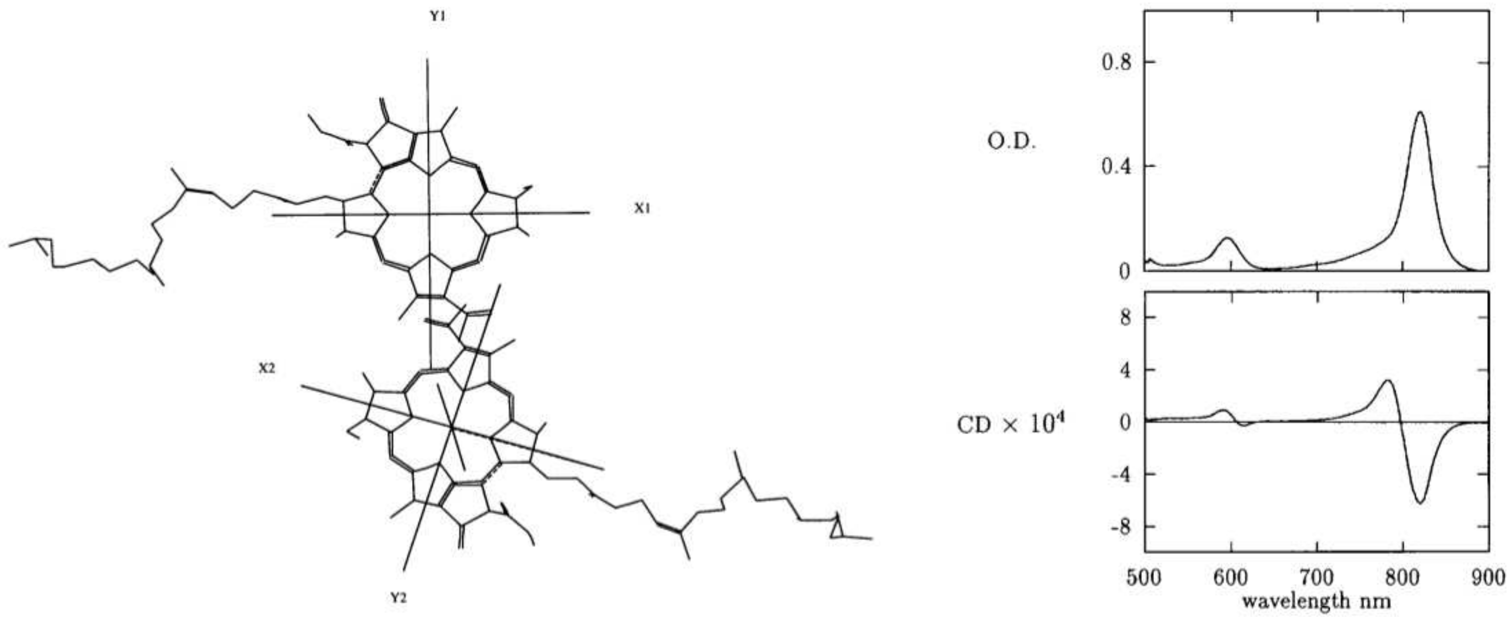
Donor Image Acceptor Image



Emission of Single FRET pair:
1: Excitation transfer;
2: Acceptor Bleached;
3: Donor bleached.

Excitons

B820



- The LH1 antenna consists of 16 B820 dimers. A dimer binds two bacteriochlorophyll*a* pigments.
- CD spectroscopy measures optical activity. Bacteriochlorophyll*a* is not optically active.

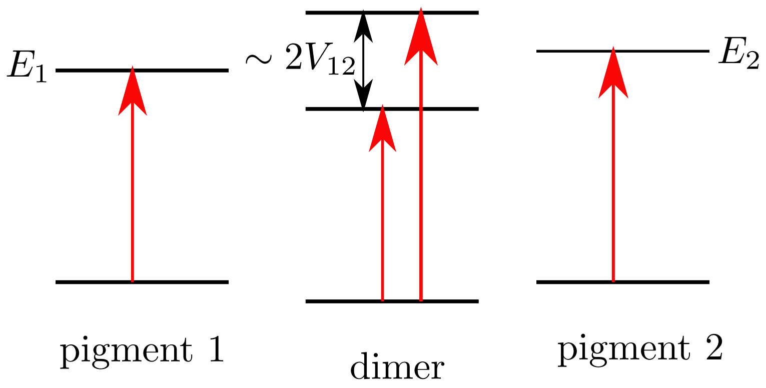
C. Koolhaas *et al*, *Biophysical J.*, (1997), **72**, 1828.

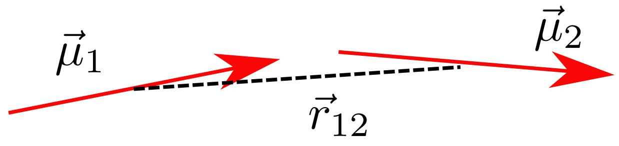
Excitonic Interaction

- When pigments are close together, the interaction between transition dipoles starts to influence the electronic states. The pigments are no longer independent.
- In B820, the dipole–dipole interaction is approximately 300 cm^{-1}.
- As a consequence the absorption spectrum changes and the pigment pair becomes optically active, because rotational invariance is broken.
- This so–called *excitonic interaction* plays an important role in energy transfer within the antenna systems, and in the optical properties of J–aggregates.

Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{pigment 1}} + \mathcal{H}_{\text{pigment 2}} + V_{12}$$

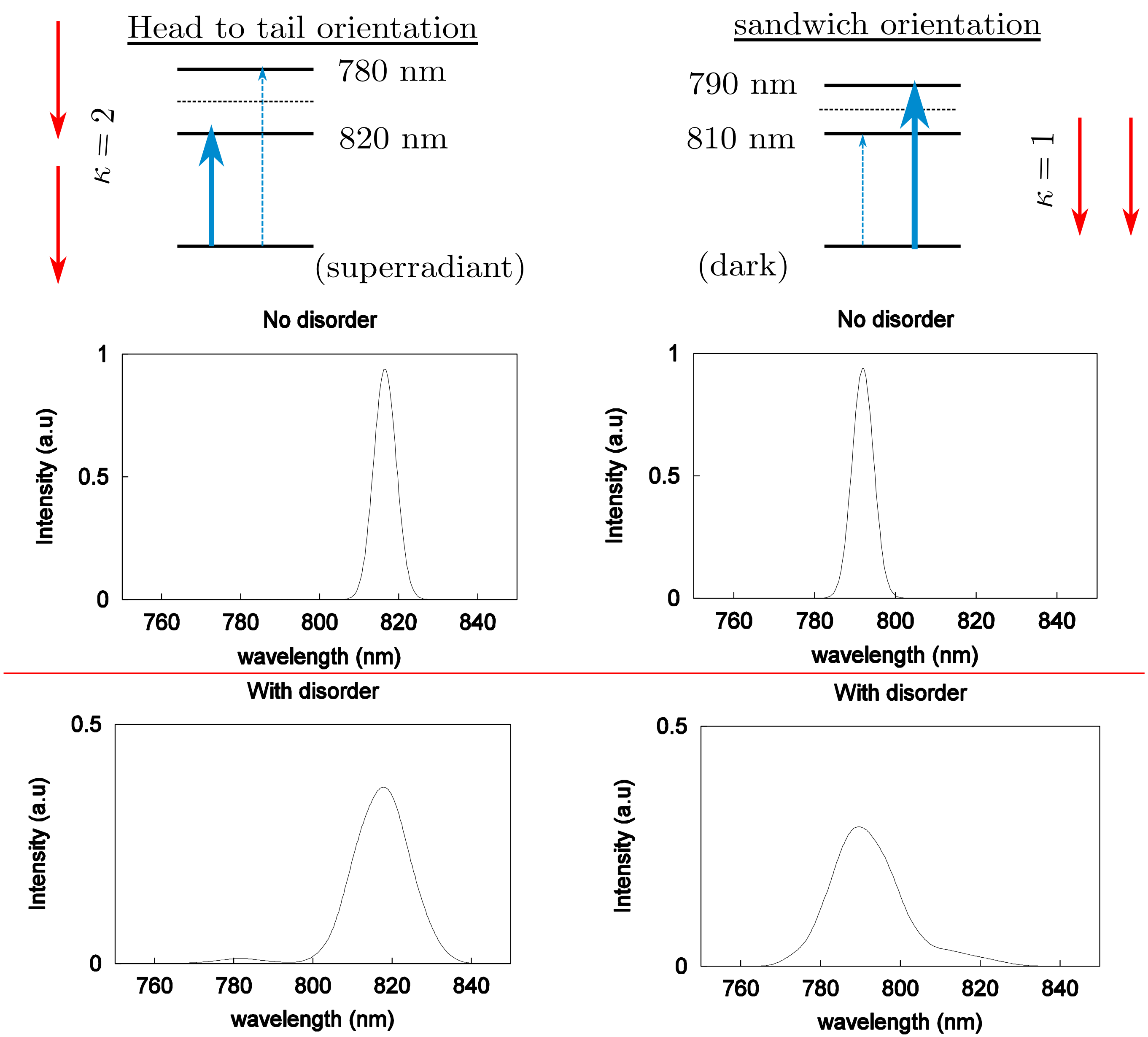




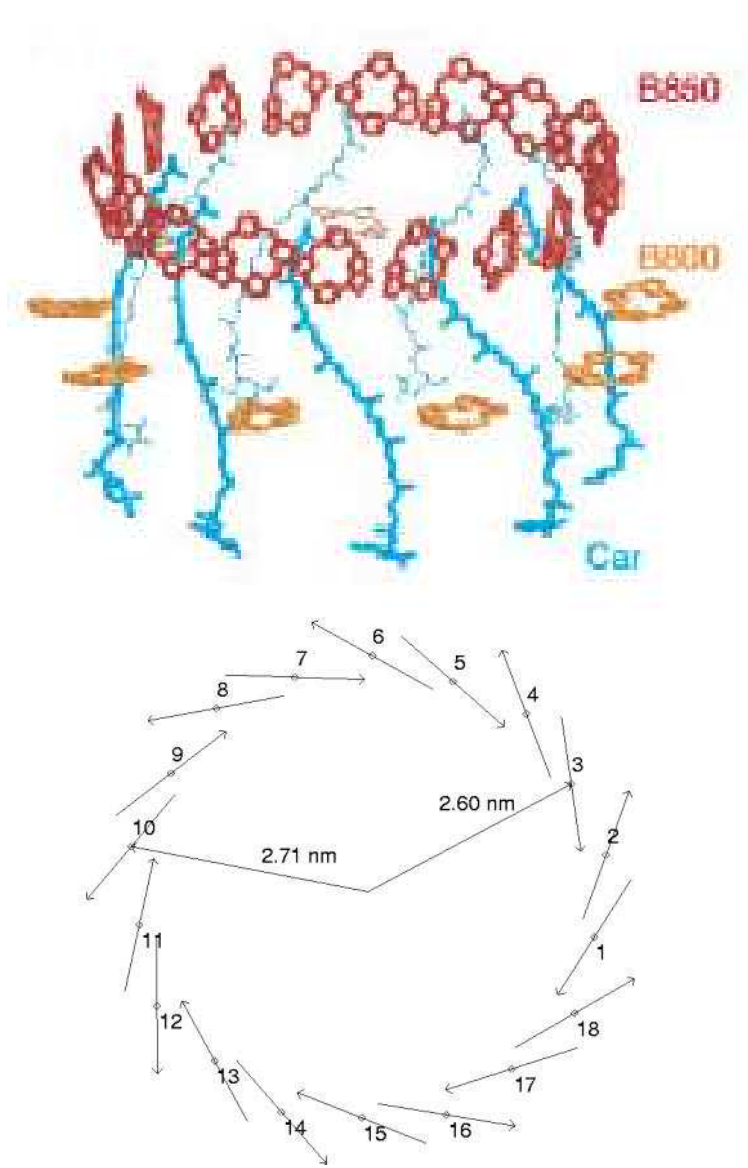
In B820 the interaction strength is about 300 cm^{-1}, and the orientation of the dipoles is almost parallel.

An energy difference of 600 cm^{-1} at a wavelength of 800 nm (absorption of BChl), is about 40 nm. Therefore one transition is at 780 nm, the other at 820 nm.

Excitonically Coupled Pigment Pairs II



LH2



Hamiltonian:

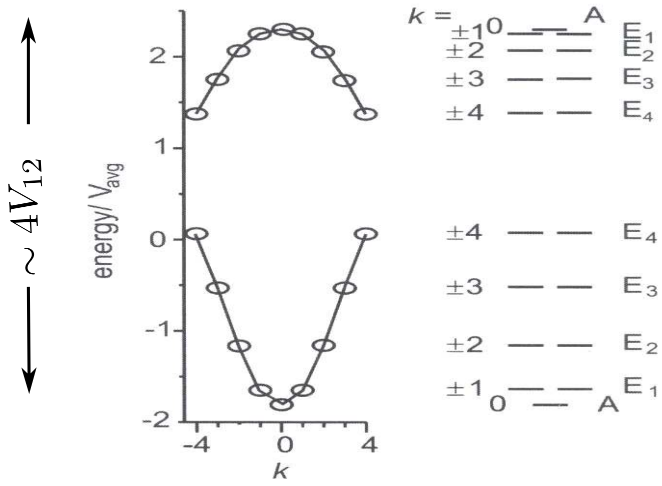
$$\mathcal{H} = \sum_{n} \mathcal{H}_{\text{pigment n}} + \sum_{n,m} V_{nm}$$

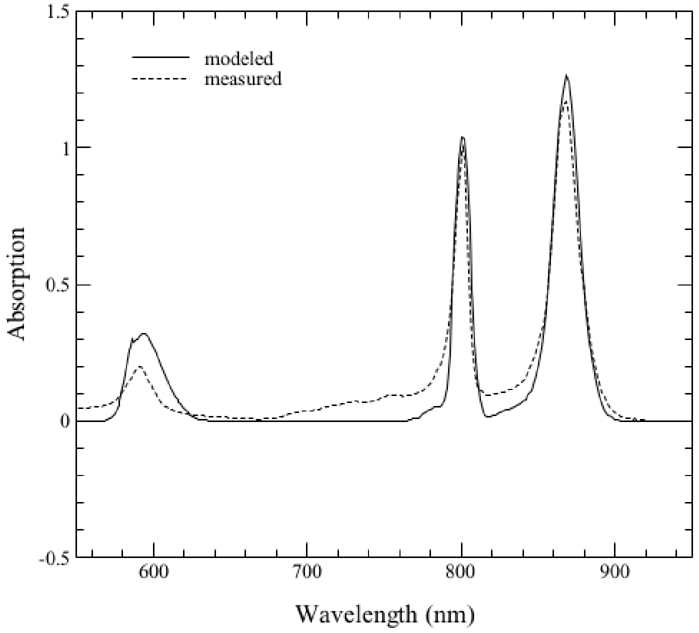
V_{nm}: dipole–dipole interactions between all the pigment.

Excitonic states are delocalized states, where all the pigments are taking part in the excitation.

C. Koolhaas *et al*, *J. Phys. Chem. B*, (1997), **101**, 7262.

LH2





- Spectrum is shifted to the red. These bacteria live at the bottom of ponds where only red light penetrates.
- Lowest excitonic state is dark. This prevents fluorescence before energy is transfered to the RC.

S. Georgakopoulou *et al*, *Biophysical J.*, (2002), **82**, 2184.

Conclusions

- Molecules can be considered collections of state dipole moments and transition dipole moments. These are measurable quantities.
- Solvents can be considered collections of dipolar, polarizable molecules, described by their macroscopic dielectric properties.
- Much of the spectroscopy of molecules in solution or embedded in protein structures can be understood this way.
- Two main problems: dynamics of the interaction and protons. Want to know more: come to Finland.

Exercises and Problems

Exercises

1. How much work does it take to transport a proton over a membrane against a pH difference of 3?
2. Explain the behavior of the Marcus rate when the reorganization energy λ goes to zero.
3. Explain the behavior of the rate *vs* the driving force in the figure of p. 13.
4. Explain the second figure on p. 22, What value does the paper use for κ^2? Can this be justified?
5. What causes the bleaching shown in the bottom right figure of p. 23.
6. Explain how diagonal disorder (energy disorder) leads to the side peaks in the botton figure of p. 28

Literature

1. J. Léonard, E. Portuondo–Campa, A. Cannizzo, F. van Mourik, G. van der Zwan, J. Tittor, S. Haacke, and M. Chergui, Functional electric field changes in photoactivated proteins revealed by ultrafast Stark spectroscopy of the Trp residues, *PNAS*, (2009), **106**, 7718–7723.
2. J. Joy R.T. Cheriya, K. Nagarajan, A. Shaji, and M. Hariharan, Breakdown of Exciton Splitting through Electron DonorAcceptor Interaction: A Caveat for the Application of Exciton Chirality Method in Macromolecules, *J. Phys. Chem. C*, (2013), **117**, 17927–17939.
3. A. Sytnik and I. Litvinyuk, Energy transfer to a proton–transfer fluorescence probe: Tryptophan to a flavonol in human serum albumin, *Proc. natl. Acad. Sci. USA*, (1996) **93**, 12959–12963.
4. B. Prevo and E.J.G. Peterman, Förster resonance energy transfer and kinesin motor proteins, *Chem. Soc. Rev.*, (2014), **43**, 1144.