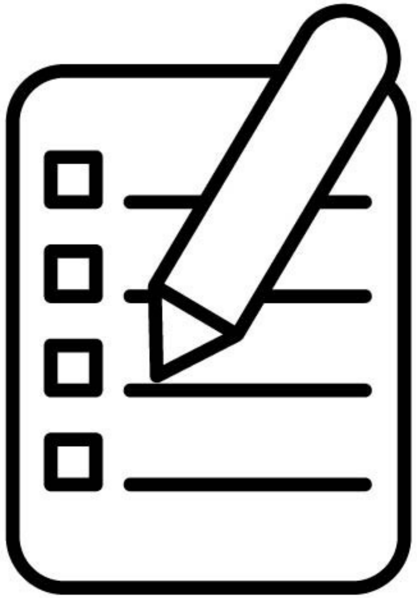
Course Feedback Form

- Please help me to improve :)
- Your feedback is super helpful!
- It will only take a few minutes



Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Recap from last session

Transition State Theory (TST)

$$A + B \rightarrow N^{\ddagger} \rightarrow \text{Products}$$

- *basic assumptions:*

(1) Born-Oppenheimer Approximation

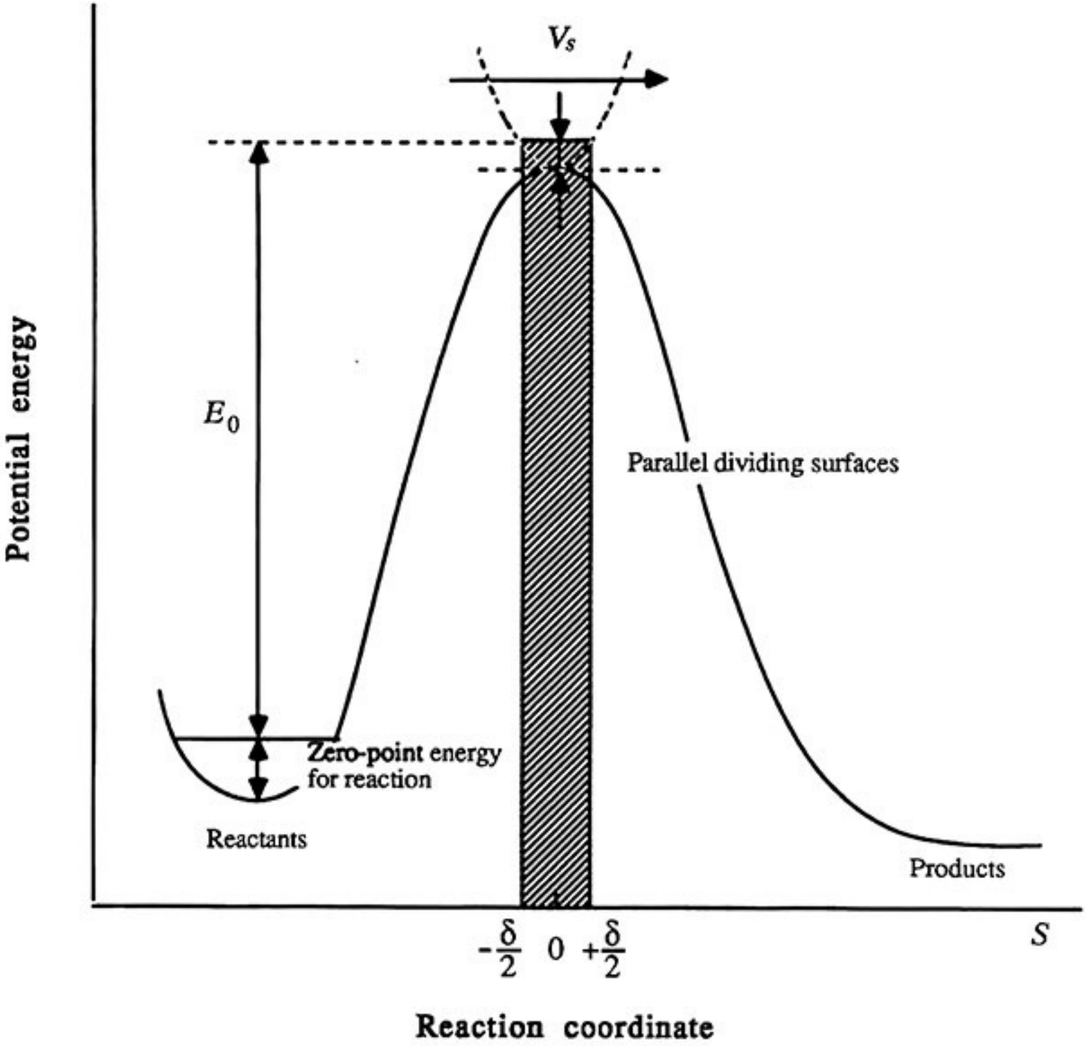
(2) Boltzmann (thermal) distribution

- *specific assumptions:*

(1) no re-crossing

(2) quasi-equilibrium

(3) classical motion along reaction coordinate (pretending no potential at the top and thus ideal gas behavior)



Recap from last session

Transition State Theory (TST)

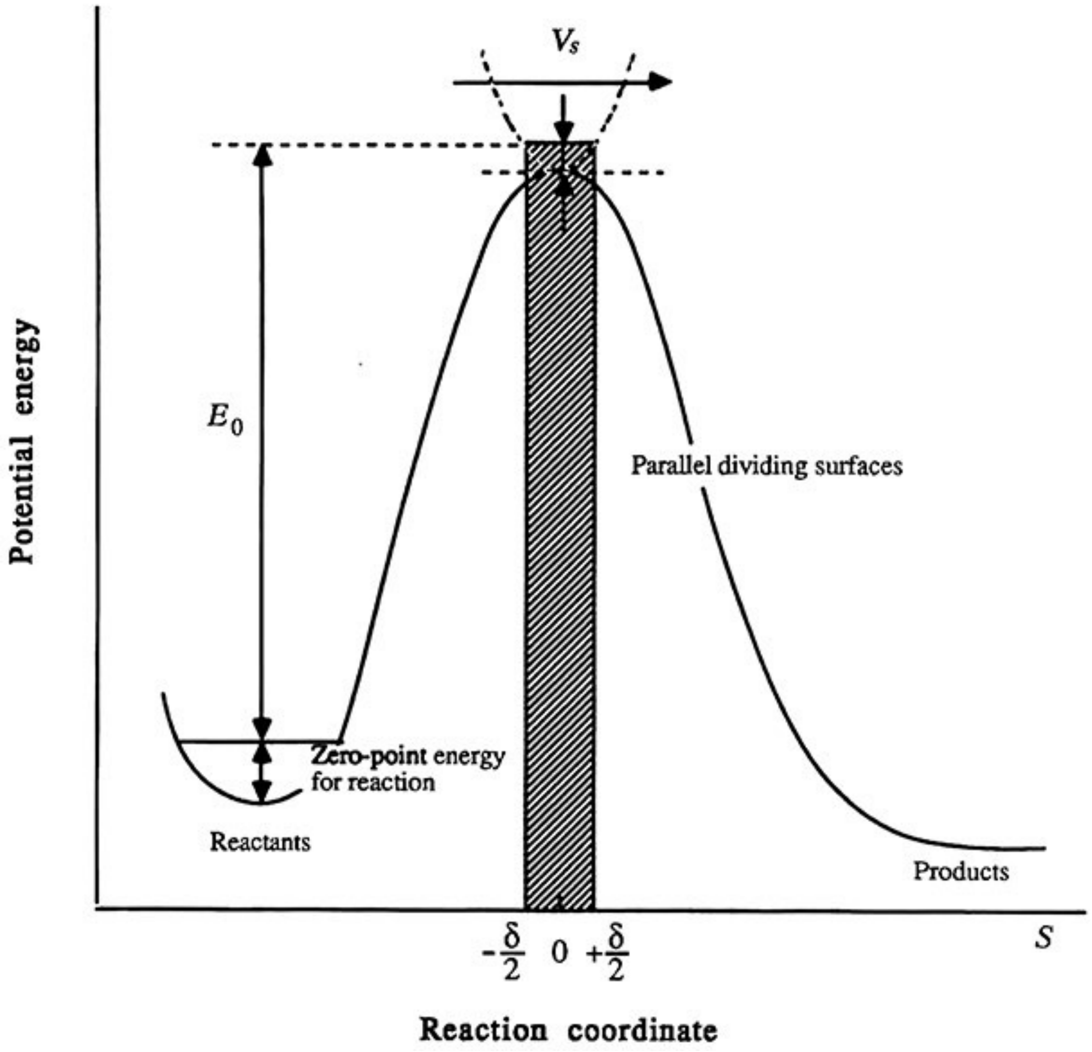
$$k_{TST} = k^{\ddagger}\frac{N_f^{\ddagger}}{[\mathrm{A}][\mathrm{B}]} = \frac{1}{2}k^{\ddagger}K^{\ddagger}$$

$K^{\ddagger} = \frac{Q_s\,Q^{\ddagger}}{Q_A Q_B}e^{-\frac{E_0}{k_B T}}$ (stat. thermodynamics)

$Q_s = \frac{\delta}{h}\sqrt{2\pi\mu_s k_B T}$

(translation of particle in 1D box)

$k^{\ddagger} = \frac{1}{\delta t} = \frac{\langle v_s\rangle}{\delta} = \frac{1}{\delta}\sqrt{\frac{2k_B T}{\pi\mu_s}}$ (classical treatment like kinetic gas theory for $\langle v_s\rangle$)

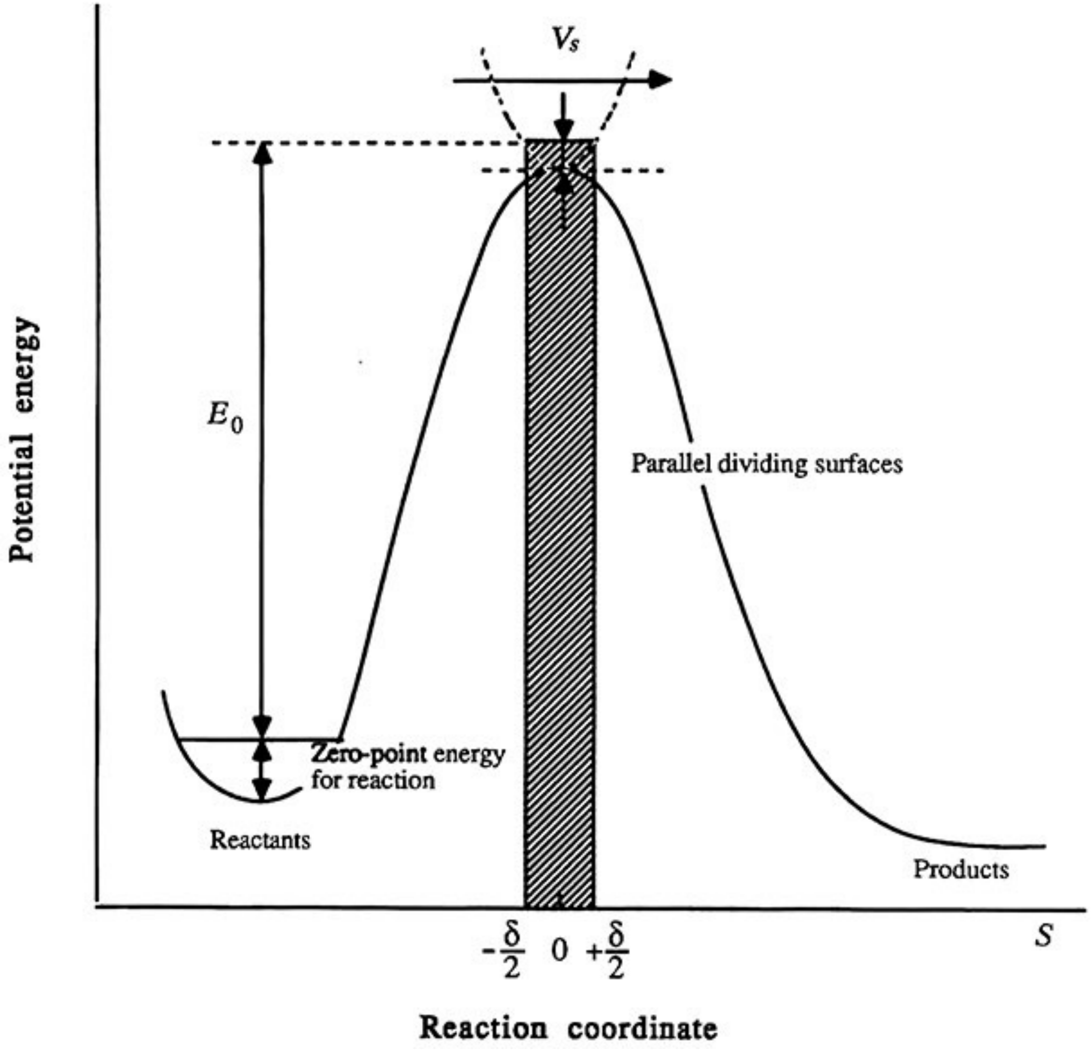


Recap from last session

Transition State Theory (TST)

$$k_{TST} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- reminder that we again made various drastic assumptions in this model



The Kinetics & Dynamics of Photosynthesis

Prof. Sascha Feldmann

École Polytechnique Fédérale de Lausanne

Today’s learning outcomes

- What is photosynthesis?
- Concept of *energy* transfer through FRET
  (we won’t talk about Dexter)
- Concept of *charge* transfer (Marcus theory)

Photosynthesis

$$6\,CO_2 + 6\,H_2O + \text{energy} \rightarrow C_6H_{12}O_6 + 6\,O_2$$

(light)

Challenge: photons → excitons → **free charges** ($e^- + h^+$)

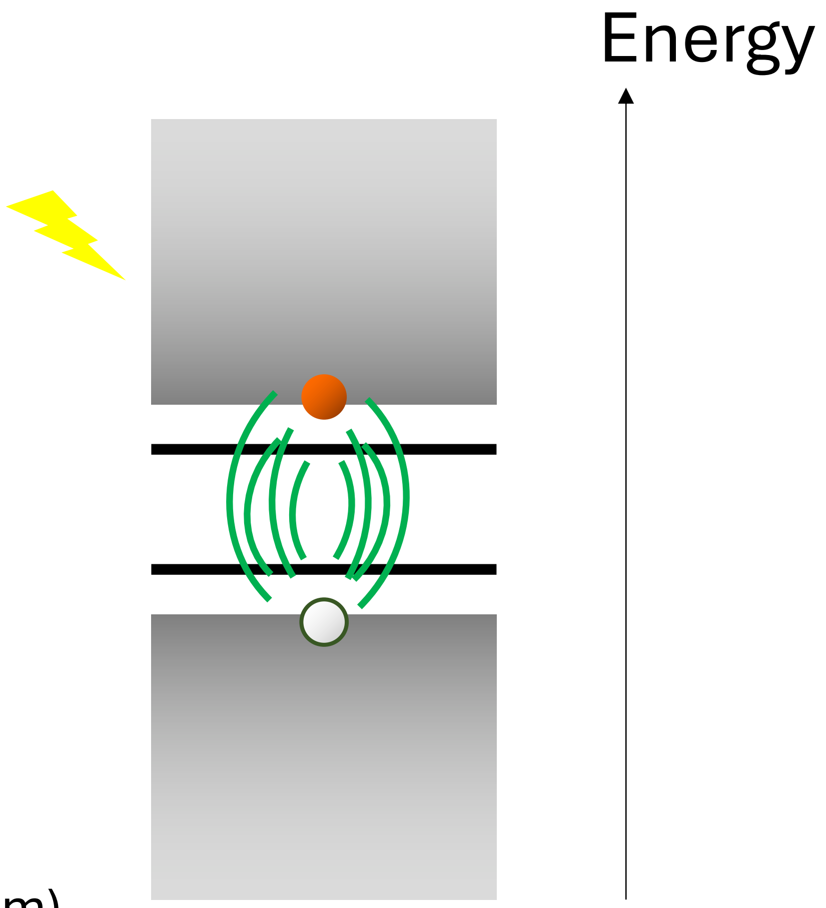
- chemical reactions driven by net <u>positive charge</u>

  e.g. oxidation of water to oxygen

- chemical reactions driven by <u>negative charge</u>

  e.g. reduction of quinones to hydroquinones

Photon absorption in molecules



- optical excitation can generate ***excitons***: electron-hole pairs that are bound together through Coulomb interactions

- can be treated in first approx. like a hydrogen atom

$$E_{binding} = \frac{e^4\mu}{2(4\pi\varepsilon\varepsilon_0\hbar)^2} = \frac{\mu/m}{\varepsilon^2}\times 13.6\,eV$$

μ is the reduced mass for the e$^-$ - h$^+$ system:

● ○

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

- dielectric constant low: $\varepsilon_r \sim 3-4$
- for $m_e^* = m_h^*$ yields $E_{binding} \sim 0.75$ eV (& Bohr radius $a_r \sim 0.3$ nm)

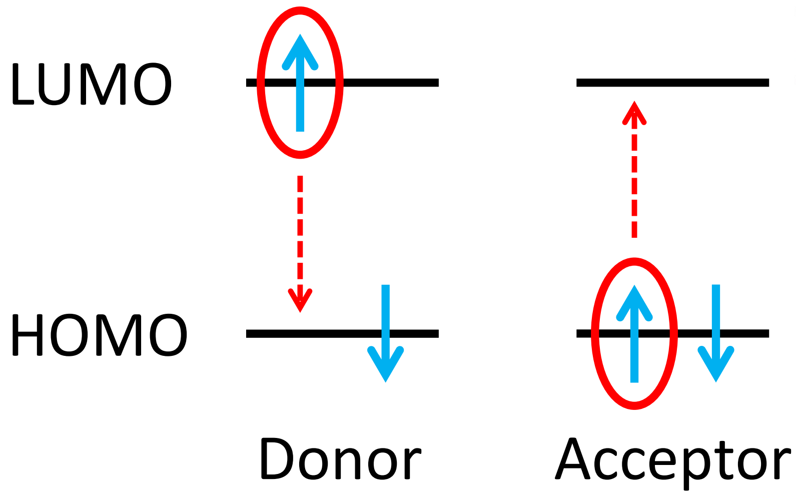
→ in organic materials: difficult to generate free electrons & holes at r.t.!

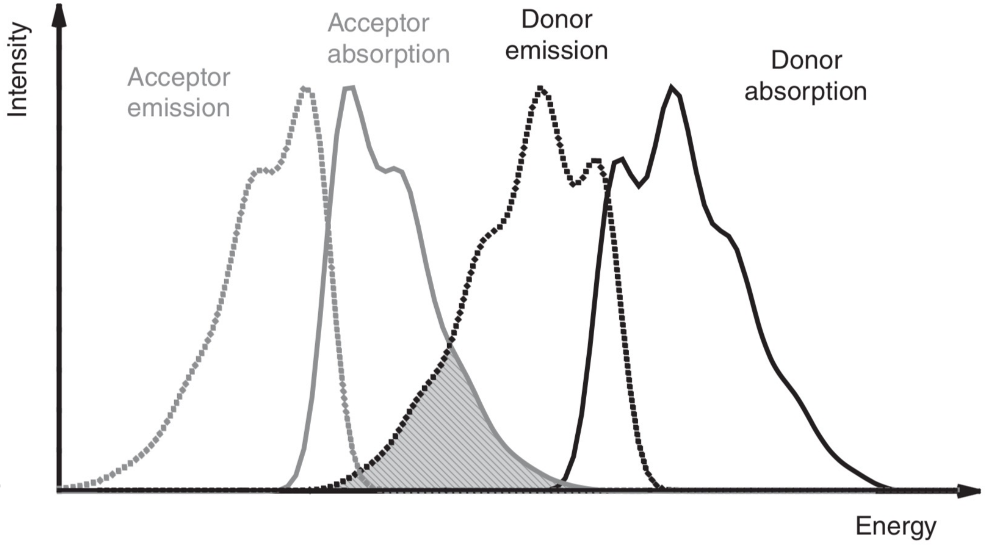
→ excitons are the dominant species, and we must break them up later for PV

Energy transfer & exciton motion *via* FRET

- excitons can 'diffuse' to lower energy sites *via* Förster resonant energy transfer (FRET)
- dipole-dipole coupling
- can be long-range interaction (few nm)
- can be very fast (sub-ps)

Förster transfer (singlet)





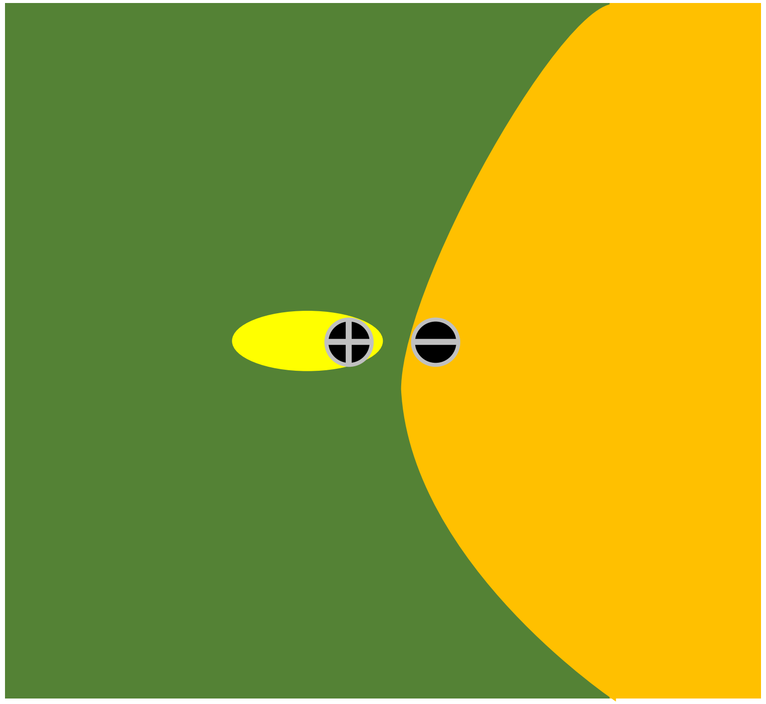
$$I_{DA} \propto \int_0^\infty \frac{F_D(\nu)\varepsilon(\nu)}{\nu^4}\,d\nu$$

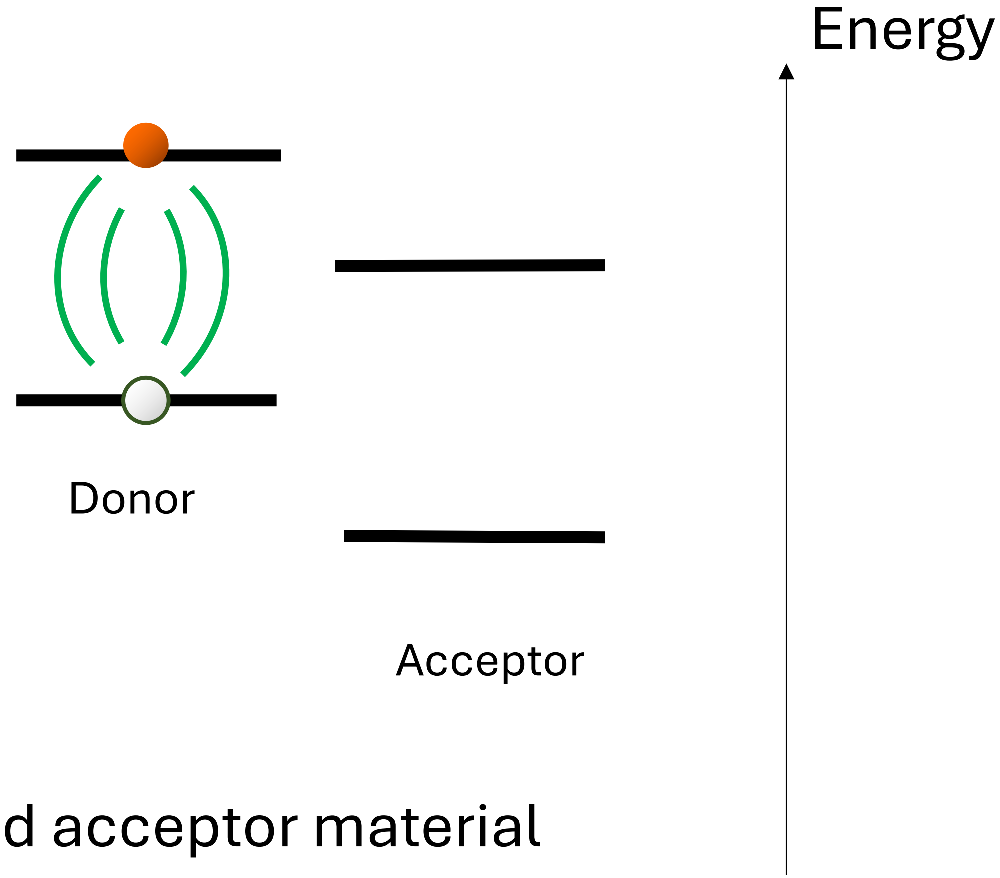
$$k_{DA} = \frac{1}{\tau_D}\,\frac{9\ln(10)\phi_D}{128\pi^5 N_A n_{solv}^4}\,c^4 I_{DA}\kappa_{DA}\,\frac{1}{R_{DA}^6}$$

$$\boxed{k_{DA}(R) = \frac{1}{\tau}\left(\frac{R_F}{R_{DA}}\right)^6}$$

$F_D$is the normalized donor emission rate, ε is molar absorption coefficient, Φ_D is the quantum efficiency of luminescence of the donor and τ_D its lifetime, N_A Avogadro's number, k_D an orientational factor for the dipole, n_{solv} the refractive index in the medium, R_{DA} the donor-acceptor separation

How do we generate free charges from excitons?





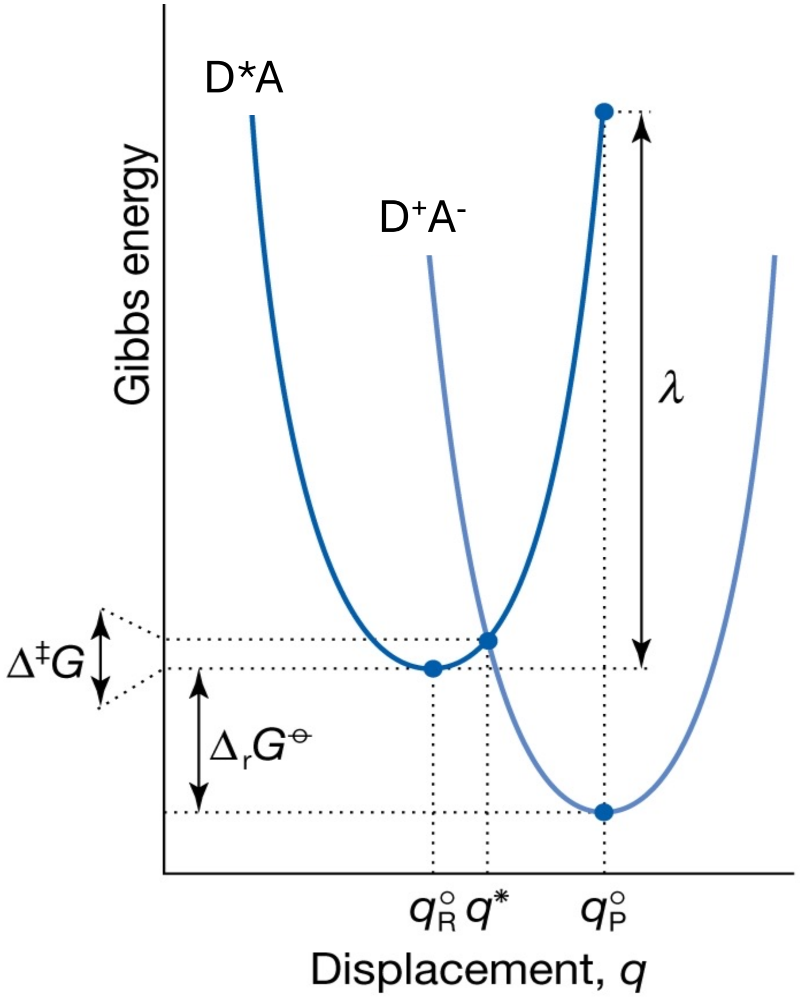
Two steps:

1) Set up a (hetero)junction between a donor and acceptor material

2) Electron (hole) transfer from donor (acceptor) to acceptor (donor) breaks the excitons up and generates charges

Electron transfer: Marcus theory

Idea: presence of charge rearranges optimal molecular geometry



- isoenergetic electron transfer requires thermal excitation to crossing point
- activation barrier: $\Delta G^{\dagger} = (\Delta G^0 + \lambda)^2 / 4\lambda$

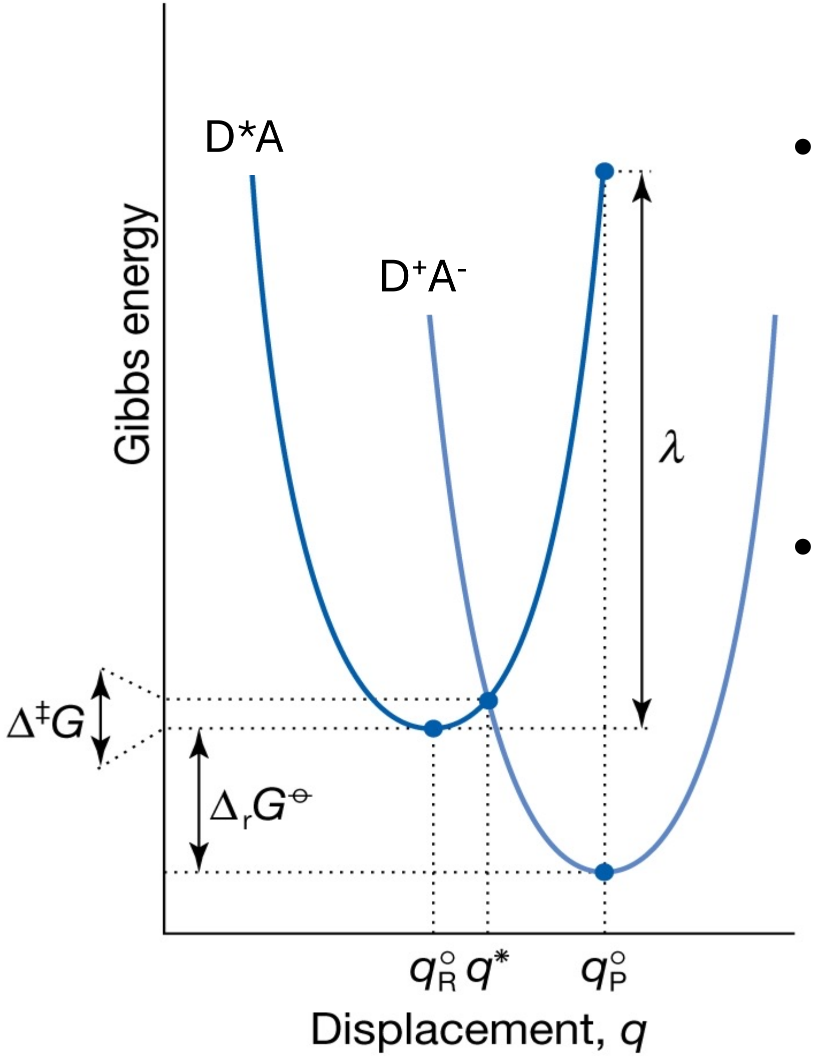
λ is the ‘reorganization energy’: energy change associated with molecular rearrangements such that $^1D^*A$ takes up the equilibrium geometry of D^+A^-

$$V^2_{tunnelling} \propto \langle \psi_{1D*} | \psi_A \rangle^2 \propto \exp\left(\frac{-2r\sqrt{2mV}}{\hbar}\right) = \exp(-\beta r)$$

$$\boxed{k_{transfer\quad rate} \propto V^2_{tunnelling}\, e^{-\left(\frac{\left(\Delta G^0+\lambda\right)^2}{4\lambda k_B T}\right)}}$$

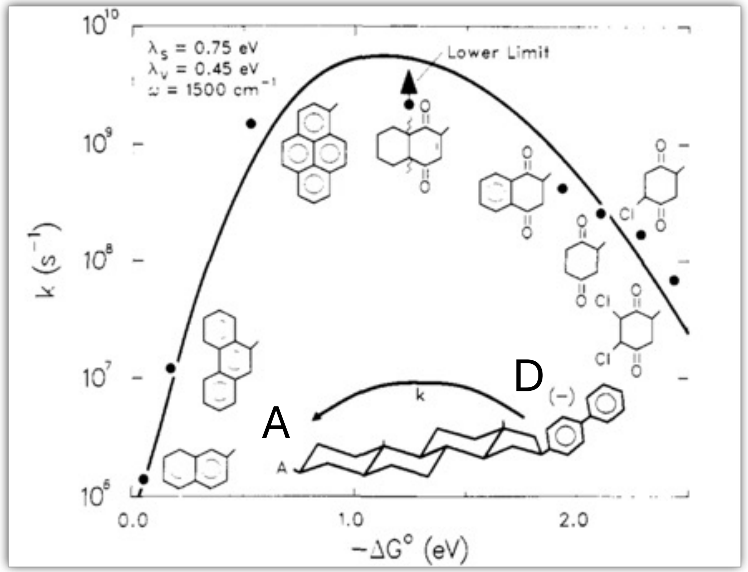
R. Marcus, *J. Chem. Phys*. **24** (5), 966 (1956)

Transfer rate *vs* free energy ΔG



- $\Delta G^0 < 0$ for downhill electron transfer
- as ΔG^0 is reduced, at some point $|\Delta G^0| = \lambda$ and 'Boltzmann factor' = 1

  →'***activationless***' electron transfer!
- as $|\Delta G^0| > \lambda$, the Boltzmann factor becomes < 1 and rate slows down again: the '***inverted* Marcus regime**'



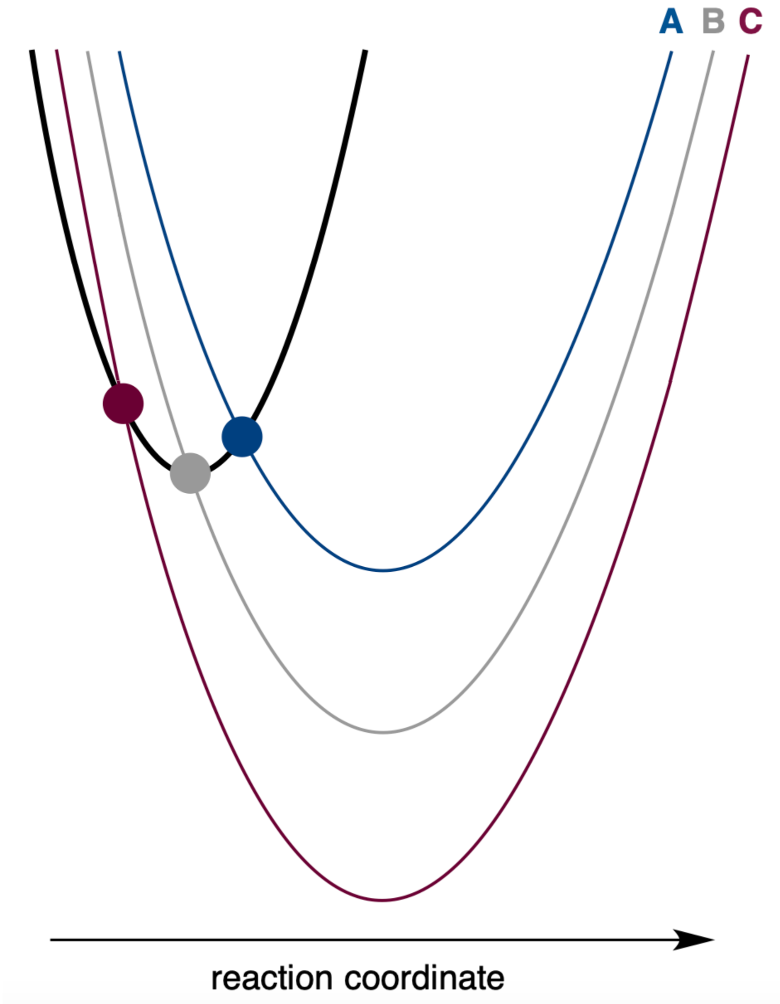
Data for covalently attached D/A pair [1]

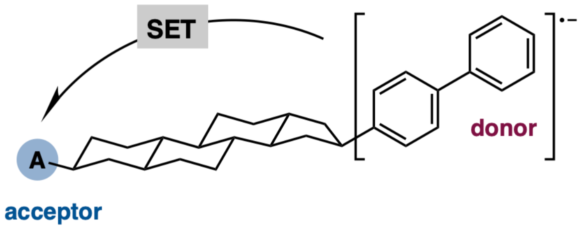
$$\boxed{k_{transfer\quad rate} \propto V_{tunnelling}^{2}\, e^{-\left(\frac{\left(\Delta G^{0}+\lambda\right)^{2}}{4\lambda k_{B}T}\right)}}$$

R. Marcus, *J. Chem. Phys*. **24** (5), 966 (1956)

[1] Miller, Calcaterra & Closs, *JACS* **106**, 3047 (1984)

More about the “Marcus Inverted Region”





A $\Delta G^\circ < 0$ (somewhat negative)
● $\Delta G^\ddagger > 0$, rate k_A

B $\Delta G^\circ = -\lambda$ (quite negative)
● $\Delta G^\ddagger = 0$, rate $k_B > k_A$

C $\Delta G^\circ << 0$ (very negative)
● $\Delta G^\ddagger > 0$, rate $k_C < k_B$

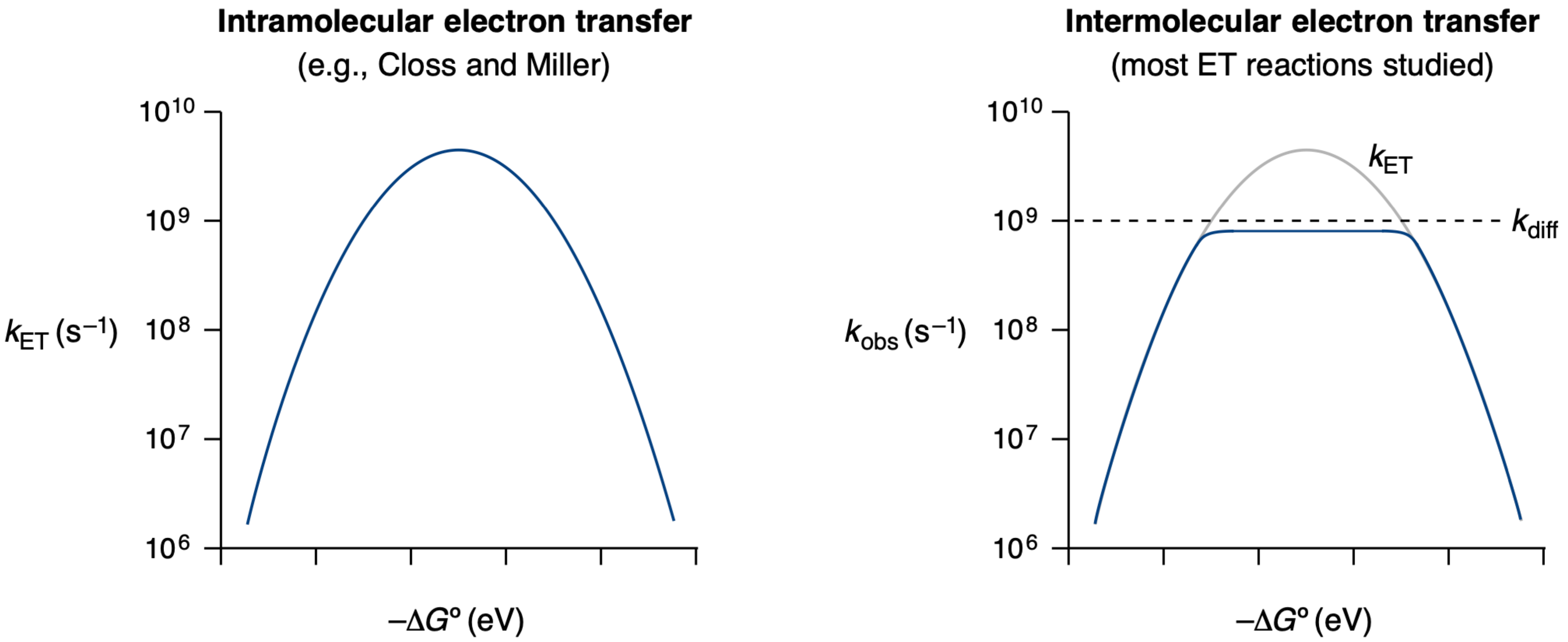
As ΔG° approaches $-\lambda$, the rate of reaction *increases*

When $\Delta G^\circ = -\lambda$, the reaction becomes barrierless

As ΔG° becomes even more negative ($\Delta G^\circ < -\lambda$), the rate of reaction *decreases* ($\Delta G^\ddagger > 0$)

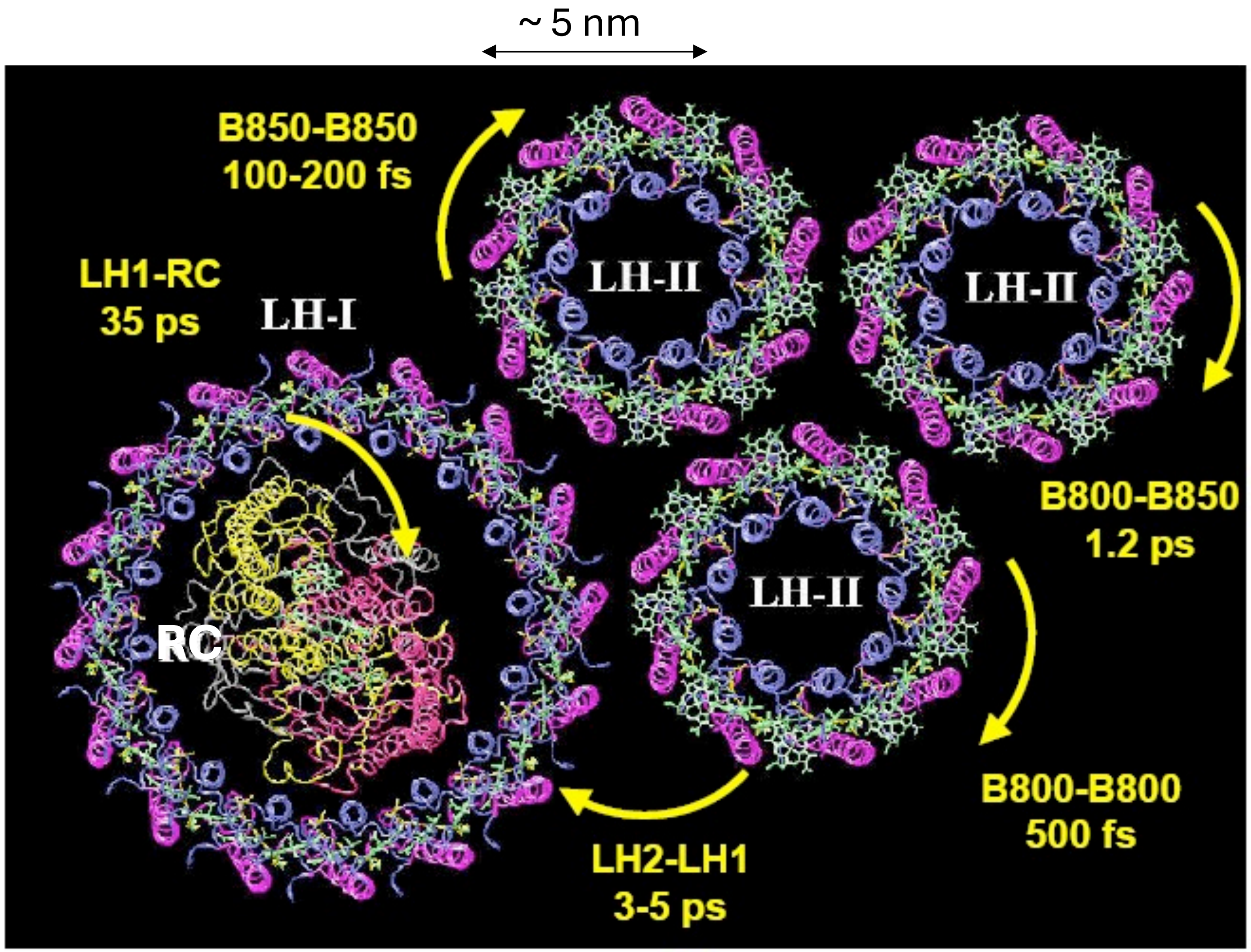
Marcus inverted region

Why did it take 30 years to verify the existence of the Marcus inverted regime?!



1. *For intermolecular ET, observed rate is limited by diffusion* ($k_{obs} = k_{diff}$ when $k_{ET} >> k_{diff}$)
2. *To escape the diffusion "leveling effect,"* $\Delta G°$ *must be very, very negative (difficult to achieve)*

The photosystem

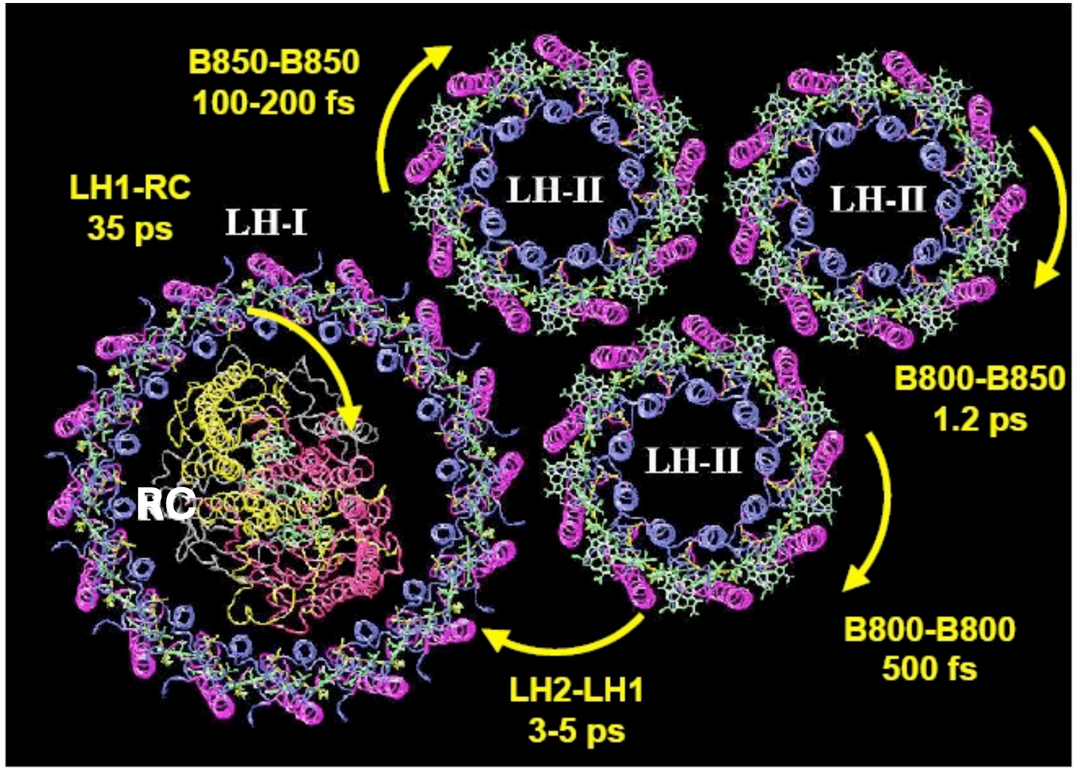


Top view of bacterial photosynthetic membrane
green = chlorophylls

- Photosystem consists of 2 different light-harvesting complexes: **LH-I** and **LH-II**
- Ultimately charge separation at the **Reaction Center (RC)**

- electronic energy transfer cascade to RC
- up to 200 chromophores per RC
- concept common to all photosynthetic organisms; detailed structure varies

Step 1: Energy transfer

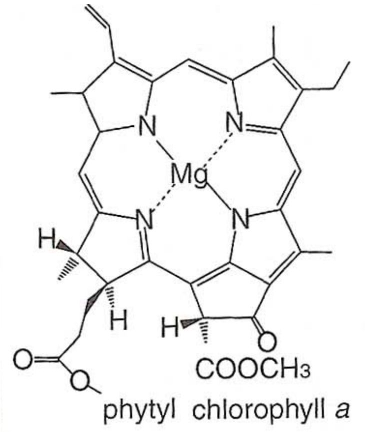


- antennae molecules
  - absorb incident photons (creating excitons)
  - transfer energy quickly towards Reaction Center (RC), avoiding non-radiative decay channels

- transfer from B800 to B850 in LH-2, from LH-2 to LH-1, and from LH-1 to the RC is by FRET
  - “downhill” energy transfer to give overlap of absorption and emission spectra
  - distances carefully controlled by protein structure to control rates
  - avoids very close contact – wavefunction tunnelling would lead to non-radiative states

More about the light-harvesting antennae

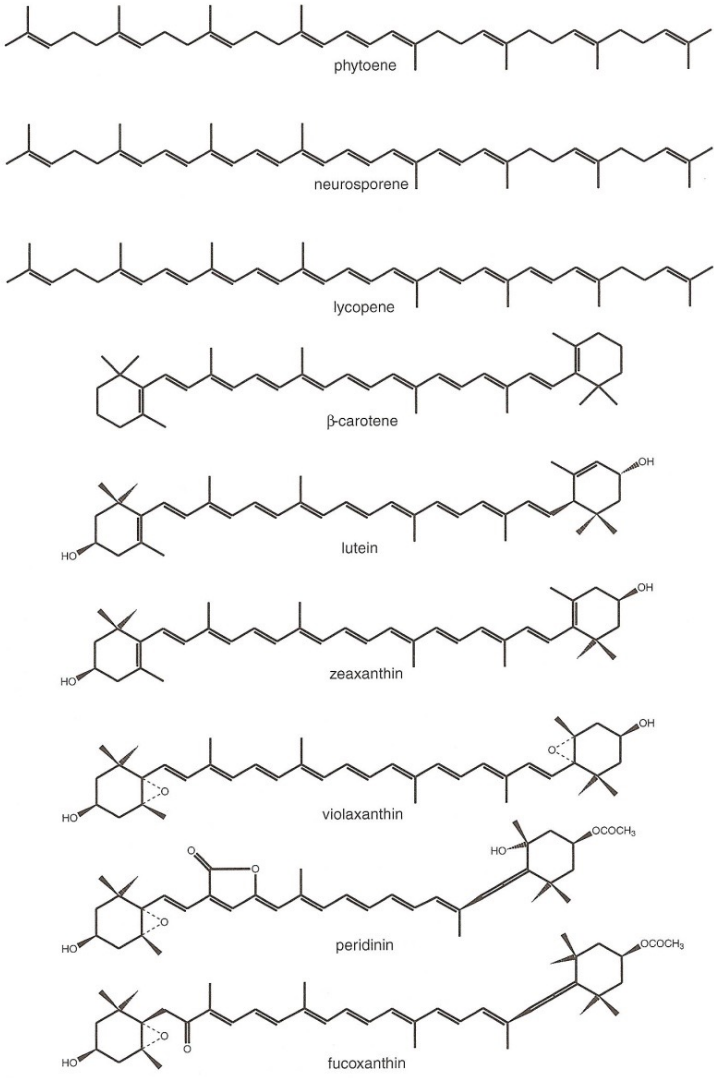
- Typically a few *hundred* light-absorbing molecules per RC
- Various types, incl. chlorophylls and carotenes



Why even bother with antennae?

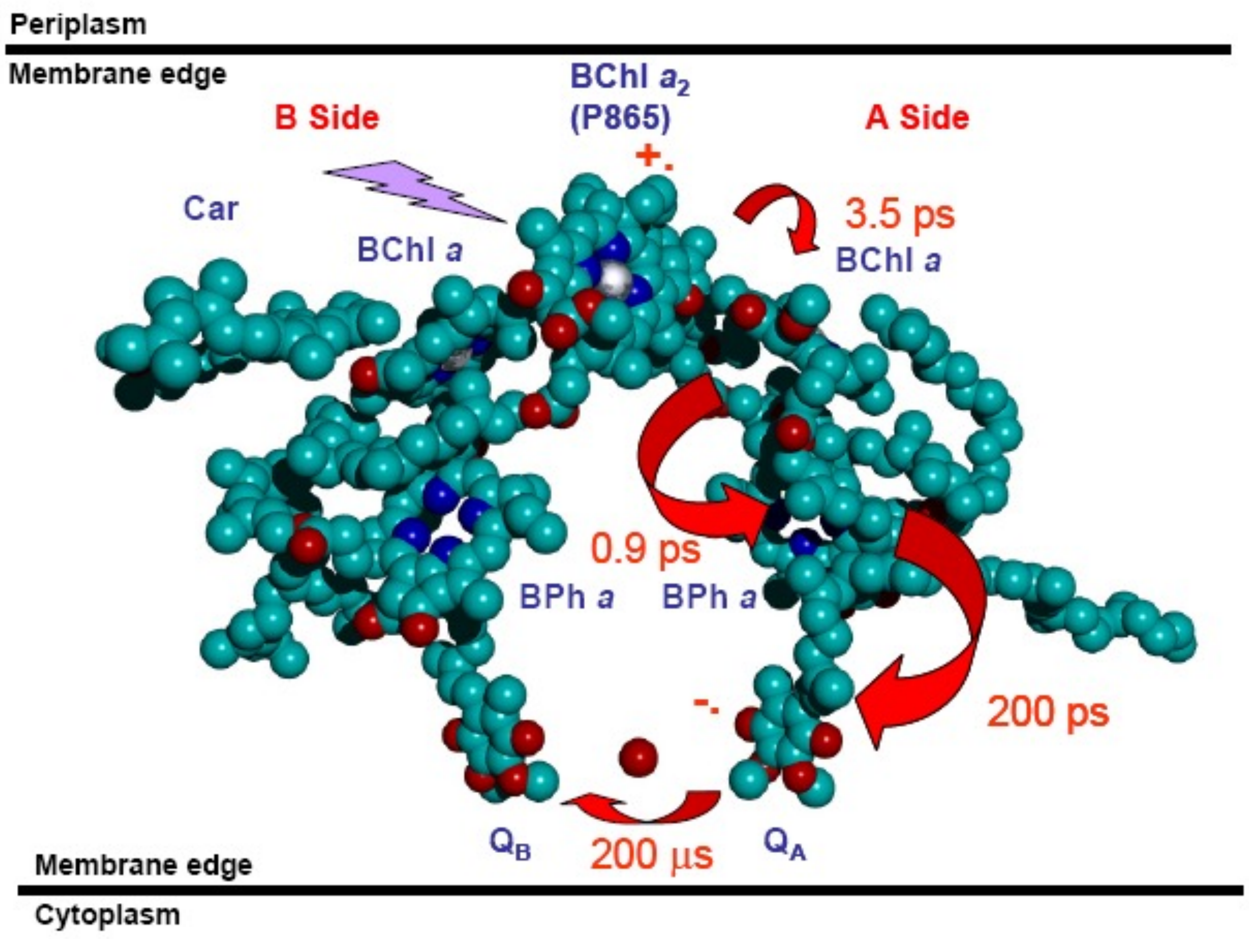
1) about 10 photons/s absorbed under full sunlight in one chlorophyll – much slower than rate at which the RC can operate!

2) RC much more expensive to synthesize!



various carotenoid molecules used in photosynthesis

Step 2: Charge transfer



side view of bacterial Reaction Center, with protein not shown

Exciton transfers from antennae to pair of chlorophylls which are arranged to have correct exciton energy to collect from the antennae – the ***"Special Pair"***

– usually labelled by this energy (in nm) in its name

– electron transfer 'across the heterojunction' – in green plants to a pheophytin; subsequent transfer to lower-energy sites

$$k_{transfer\quad rate} \propto V_{tunnelling}^{2}\, e^{-\left(\frac{\left(\Delta G^{0}+\lambda\right)^{2}}{4\lambda k_{B}T}\right)}$$

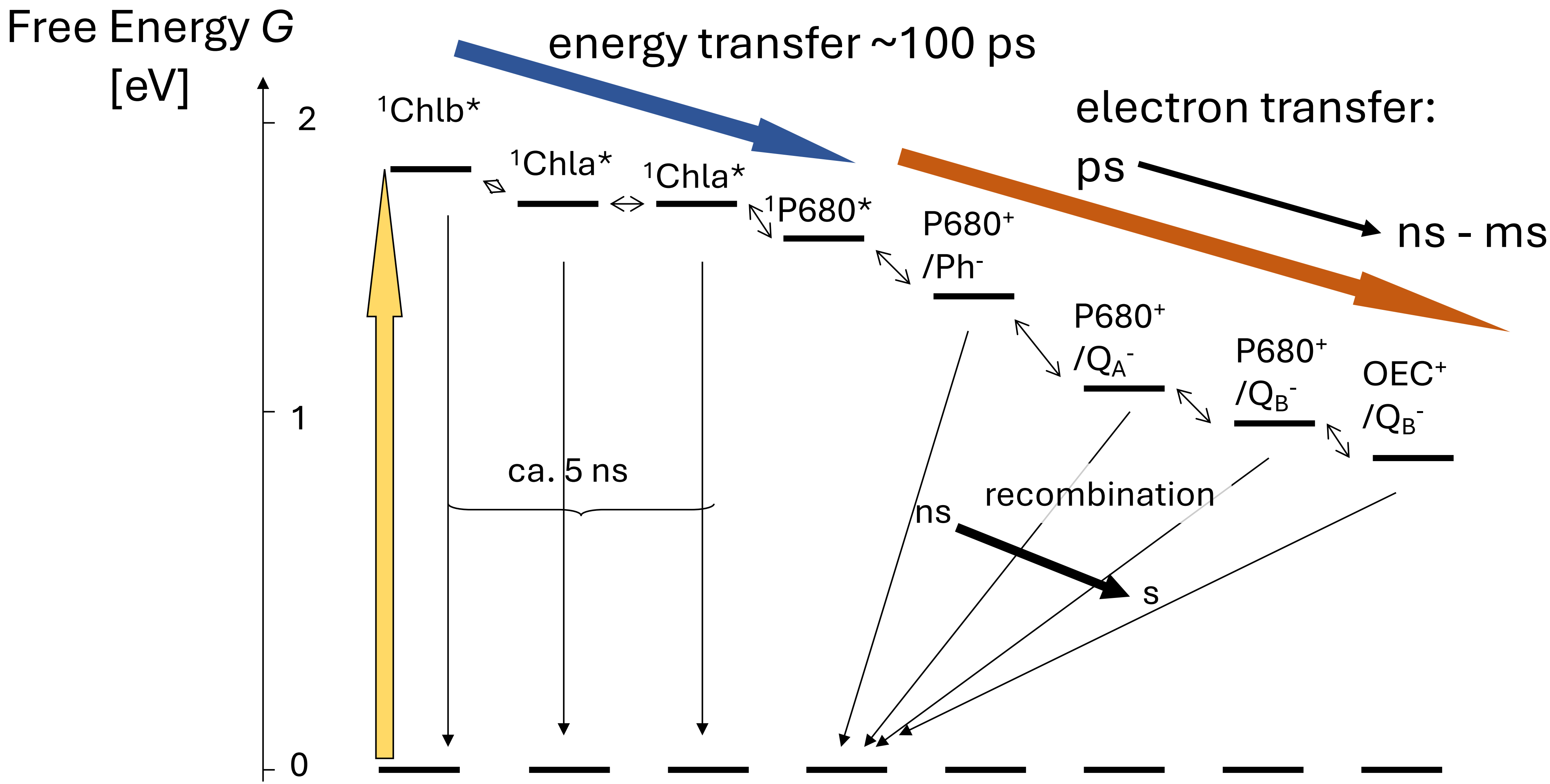
Photosynthetic Reaction Centers evolved such that:

✓non-polar interior (λ ≤ 1 eV)

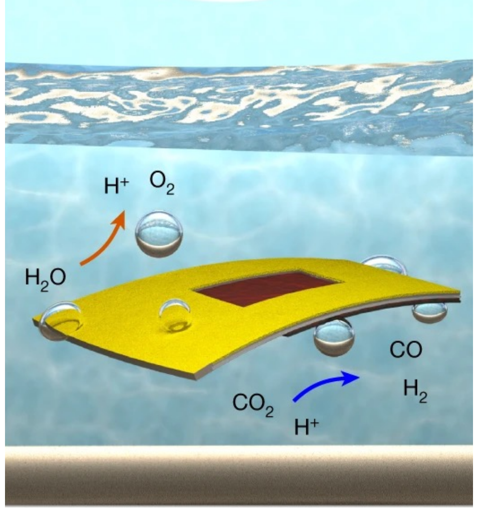
✓forward reactions activation-less: |ΔG^0| = λ : fast

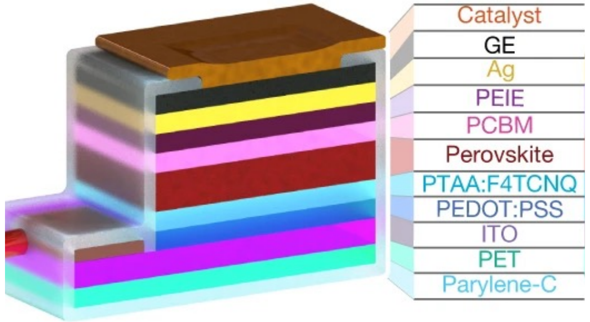
✓reverse reactions in inverted region: |ΔG^0| > λ : slow

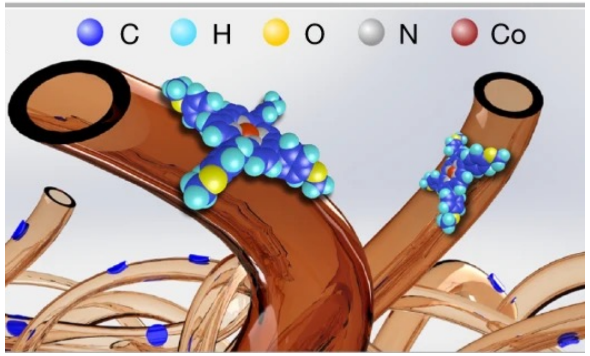
Energetics & kinetics in green plants



Outlook: Artificial leaves to save the planet?







0.58% efficiency of H_2 production

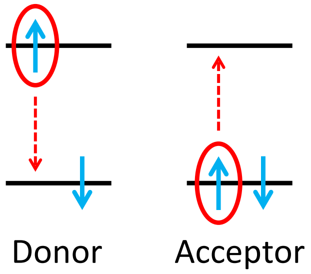
...and quite expensive to make

Nature **608**, 518–522 (2022)

Summary

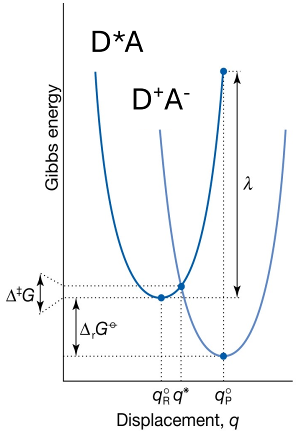
- **What is photosynthesis?**

Cleverly engineered system of dyes to turn light energy into chemical energy, by generating and transferring excitons, before breaking them up into free charges for redox reactions



- **Concept of *energy* transfer (FRET)**

Excitons 'diffuse' *via* Förster transfer to sites of lower energy, dependent on spectral overlap and distance ($\sim R^{-6}$)



- **Concept of *charge* transfer (Marcus theory)**

Rates governed by trade-off between free energy (ΔG) and reorganization energy (λ)

Further reading

If you are interested in learning more on…

- **Electronic structure and processes in molecular systems:**

Electronic Processes in Organic Semiconductors and processes: An Introduction
by A. Köhler and H. Bässler, Chapter 1

- **Photosynthesis:**

Molecular Mechanisms of Photosynthesis
by R. E. Blankenship, Chapters 5-7

- **Marcus theory:**

Recent lecture (Feb. 2022) by Rudolph Marcus (Nobel Prize 1992)
youtube.com/watch?v=CR2gPgpUWxk

Reminder: Submit your questions to your TAs by today!

- Submit any specific questions about the lecture and exercise contents *via* Moodle or *via* email by the end of today, if you want them to be discussed by your TAs!

- A final reminder that the examinable course contents consist of *both* the lectures and the exercise sessions, covering complementary aspects

- Next week: Q&A session with your TAs