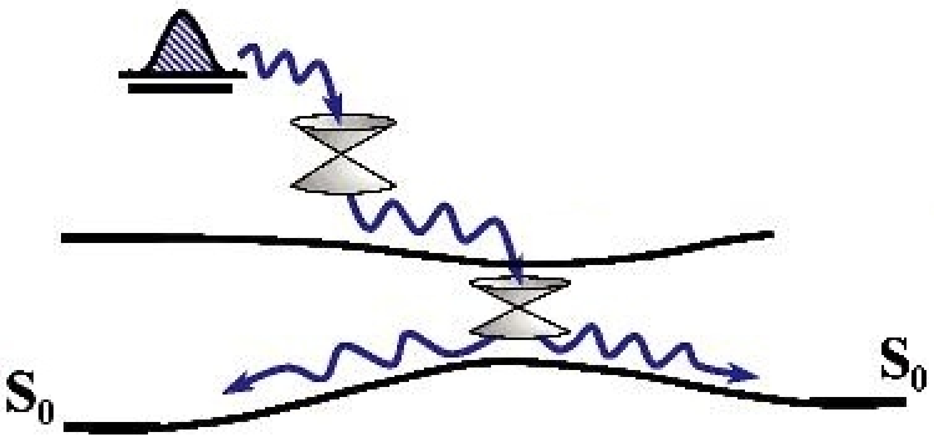
Theoretical Photochemistry WiSe 2016/17

Lecture 10



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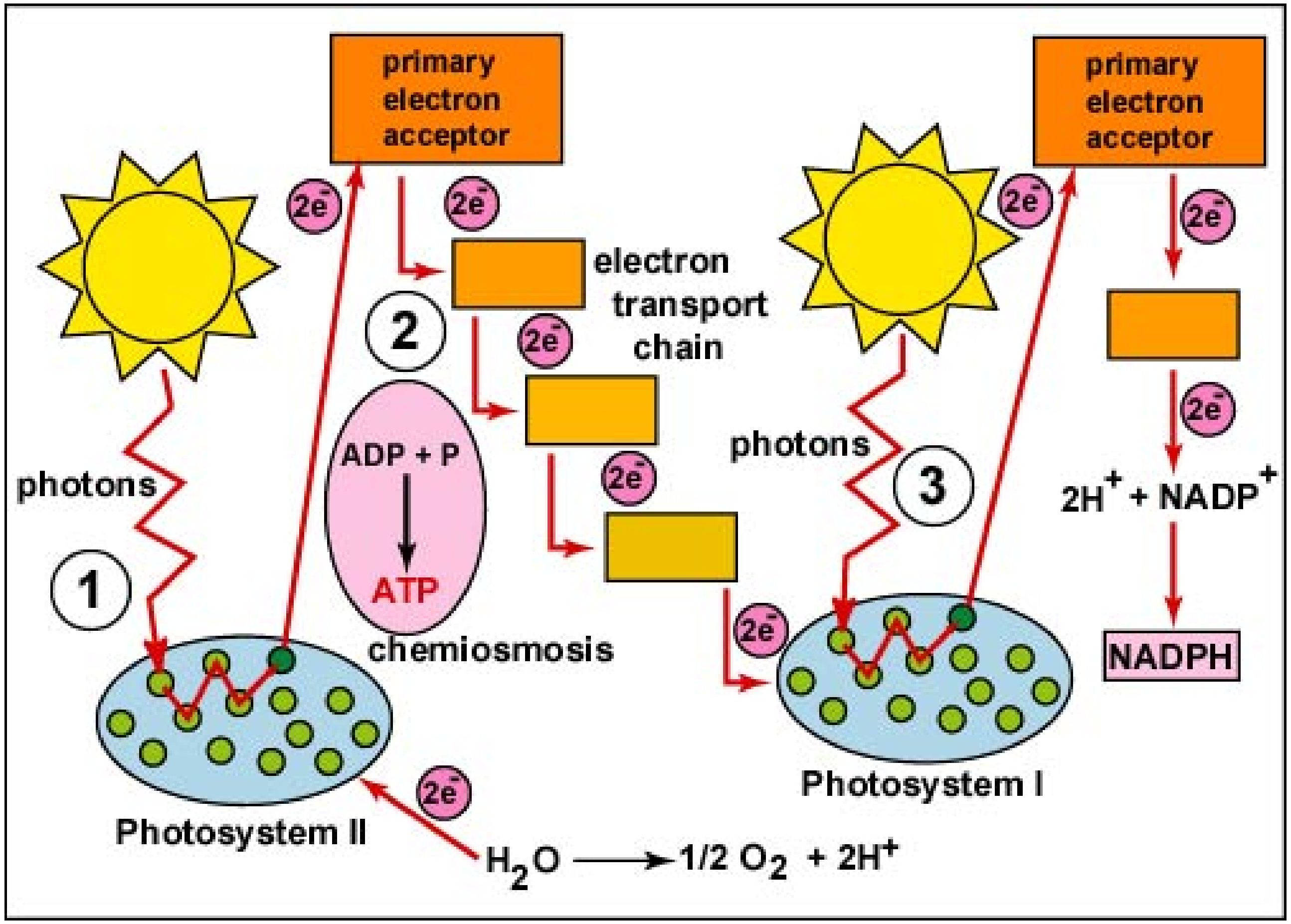
http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

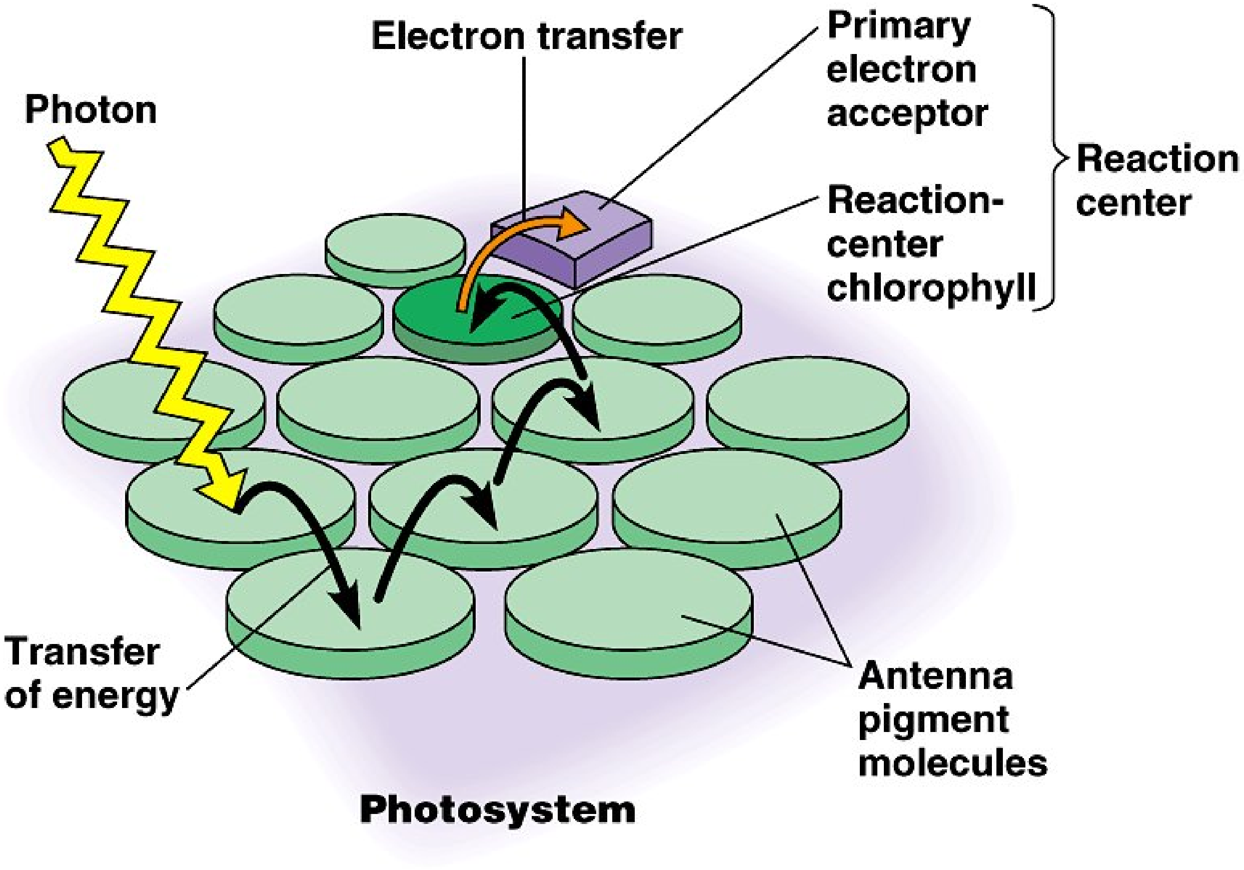
Topics

1. Photophysical Processes
3. Wavepackets
5. The Franck-Condon picture of electronic transitions
6. What do we measure experimentally?
2. The Born-Oppenheimer approximation
4. Beyond Born-Oppenheimer – non-adiabatic transitions
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Intermolecular energy transfer, light-harvesting, and Förster theory
10. Dynamics: trajectories or wavefunctions?
11. Coherence and Dephasing
12. Non-linear optical spectroscopy: calculation of spectroscopic signals
13. Solvent/environmental effects

Photoinduced intermolecular energy transfer

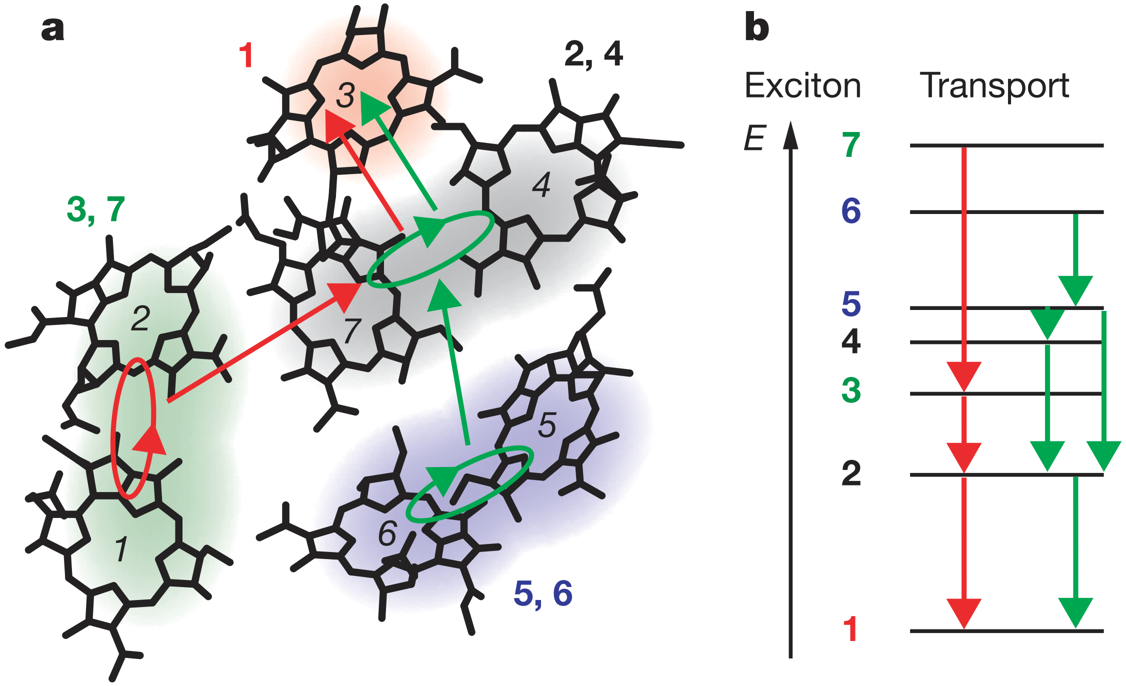


Light-harvesting systems (LH's)



Exciton transfer in the FMO complex

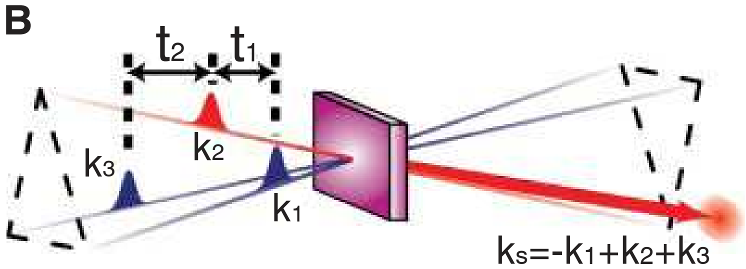
Brixner & collaborators, Nature 434, 625 (2005)

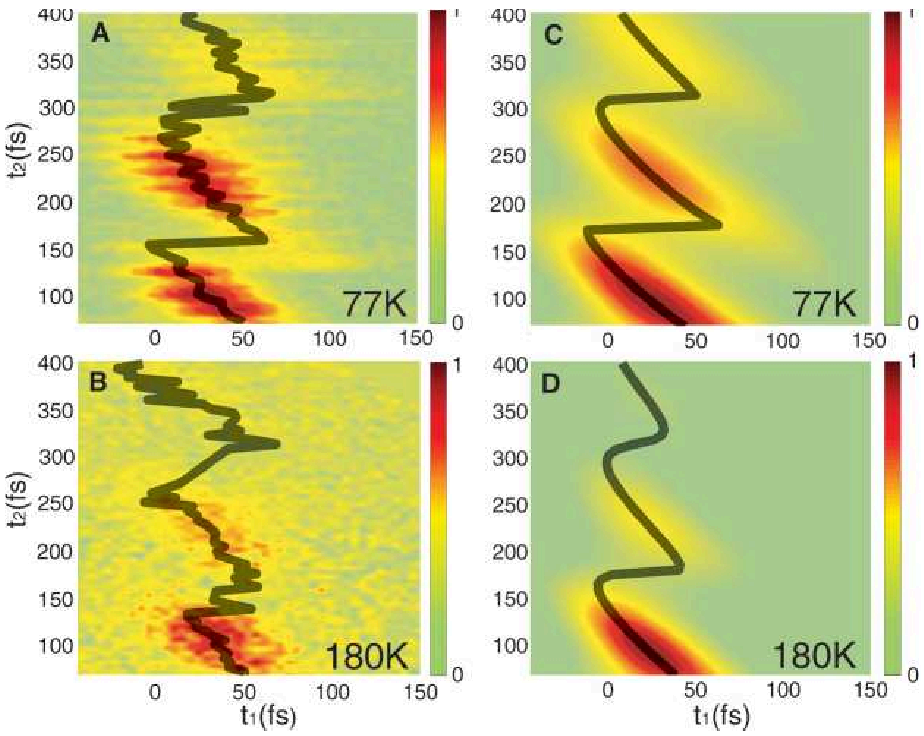


- FMO = Fenna-Matthews-Olson bacteriochlorophyll a (BChl) protein of green sulphur bacteria
- antenna system that collects light and channels excitation to a reaction center where charge transfer takes place

“Coherence dynamics in photosynthesis: protein protection of excitonic coherence”

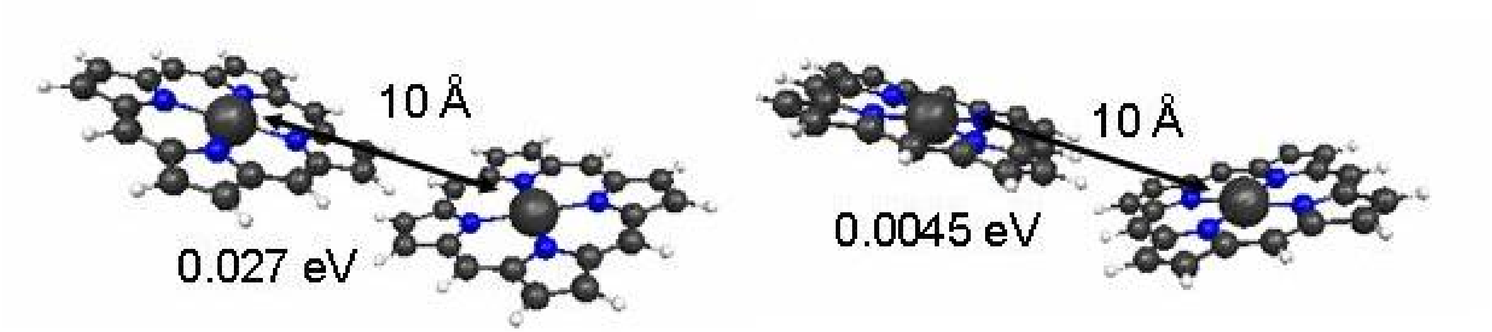
Lee, Cheng, Fleming, Science 316, 1462 (2007)





- **2CECPE = two-color electronic coherence photon echo experiment**

Multi-chromophoric systems



- **Two basic (single-excited) configurations:**

$$|\phi_1\rangle = |e^{(1)}\rangle \otimes |g^{(2)}\rangle \qquad |\phi_2\rangle = |g^{(1)}\rangle \otimes |e^{(2)}\rangle$$

- **For two identical, non-interacting monomers, these configurations are degenerate**
- **once an excitonic coupling is included, the degeneracy is removed**
- **Frenkel exciton state = superposition of these configurations:**

$$|\Psi_{\text{exciton}}(t)\rangle = c_1(t)|\phi_1\rangle + c_2(t)|\phi_2\rangle$$

What is the excitonic coupling?

- Coulomb coupling matrix element between donor (D) and acceptor (A) permitting transitions between single-excited configurations:

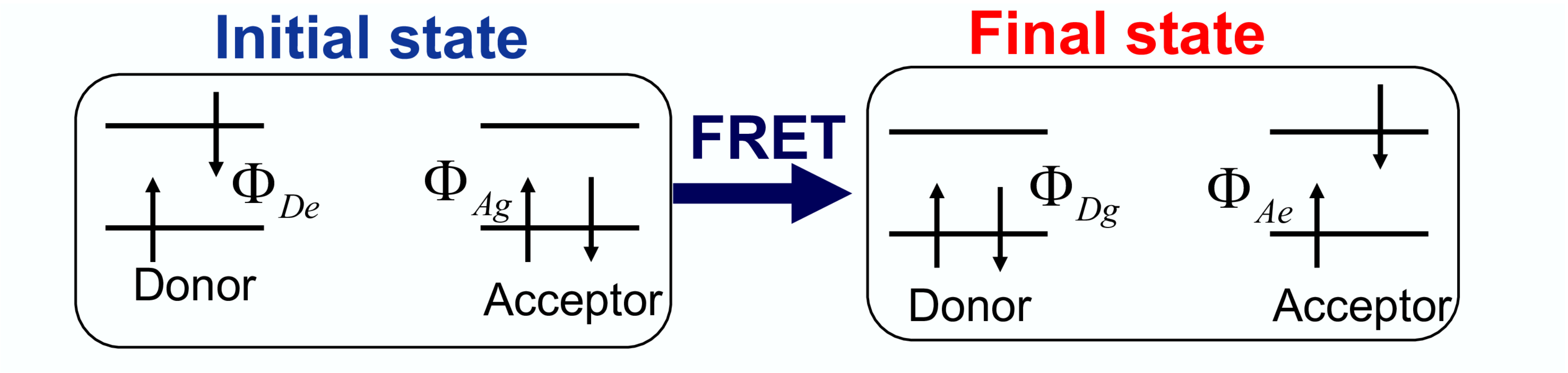
$$j = \langle e^D g^A | V_{\text{Coulomb}} | g^D e^A \rangle$$

- this can be re-written in terms of coupled transition densities $\rho_A^{(ge)}$ and $\rho_D^{(eg)}$ (noting that D/A exchange interactions have been disregarded!):

$$j = \int d\mathrm{r}_D^3 d\mathrm{r}_A^3 \frac{\rho_D^{(eg)}(\mathrm{r}_D)\rho_A^{(ge)}(\mathrm{r}_A)}{|\mathrm{r}_D - \mathrm{r}_A|}$$

- at large D-A distances, one can approximate transition densities by transition dipoles: $\rho_D^{(eg)} \longrightarrow \mu_D^{(eg)}$

Dipole Approximation



Initial state

Φ_{De}

Donor

Φ_{Ag}

Acceptor

FRET

Final state

Φ_{Dg}

Donor

Φ_{Ae}

Acceptor

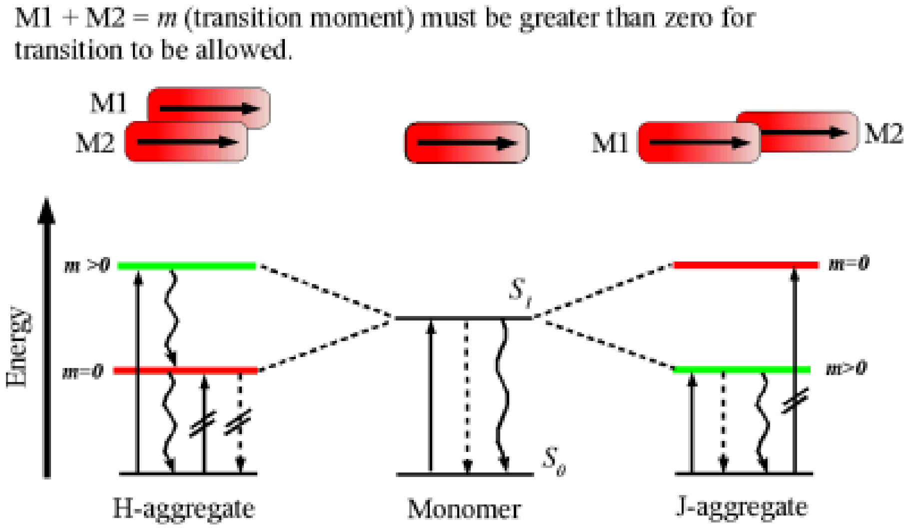
$$\langle \psi^*_D \psi^0_A | V^{\mathrm{dip}}_{DA} | \psi^0_D \psi^*_A \rangle = \langle \psi^*_D \psi^0_A | \frac{\hat{\mu}_D \cdot \hat{\mu}_A}{|r_{DA}|^3} - 3 \frac{(r_{DA} \cdot \hat{\mu}_D)(r_{DA} \cdot \hat{\mu}_A)}{|r_{DA}|^5} | \psi^0_D \psi^*_A \rangle$$

$$= \kappa_{DA} \frac{\langle \psi^*_D | \hat{\mu}_D | \psi^0_D \rangle \langle \psi^0_A | \hat{\mu}_A | \psi^*_A \rangle}{|r_{DA}|^3}$$

κ_{DA} = orientational factor

J and H Aggregates

$$H = \begin{pmatrix} \epsilon_0 & j \\ j & \epsilon_0 \end{pmatrix}$$



M1 + M2 = m (transition moment) must be greater than zero for transition to be allowed.

- $j < 0$: J-aggregates, $j > 0$: H-aggregates
- absorption spectra are red-shifted (J-aggregates) and blue-shifted (H-aggregates)

J and H Aggregates

Solve for the eigenvalues and eigenvectors of the matrix Hamiltonian (in the basis of excitonic configurations $|\phi_1\rangle, |\phi_2\rangle$):

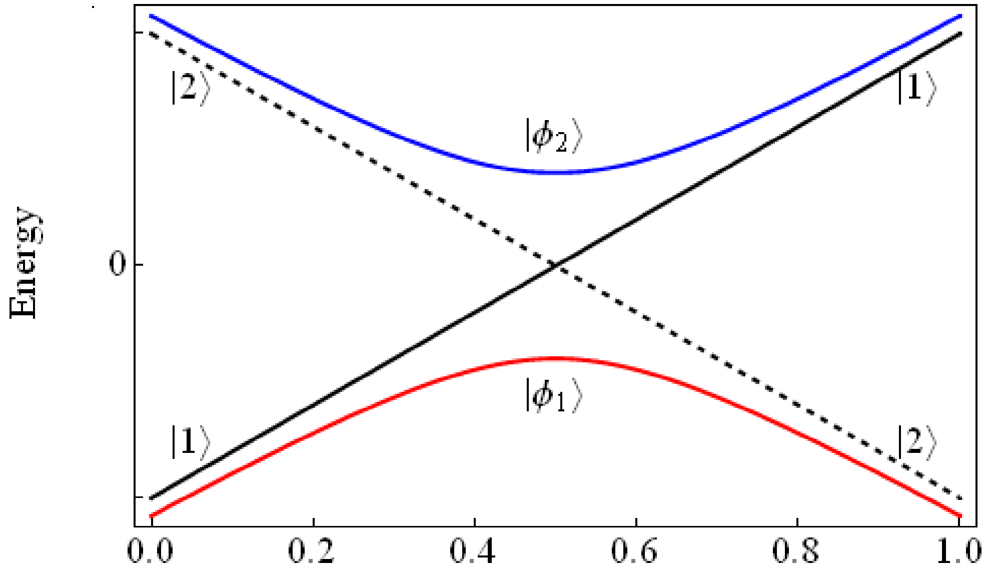
$$H = \begin{pmatrix} \epsilon_0 & j \\ j & \epsilon_0 \end{pmatrix}$$

eigenvalues: $E_\pm = \epsilon_0 \pm j$ **eigenvectors:** $|\phi_\pm\rangle = 1/\sqrt{2}(|\phi_1\rangle \pm |\phi_2\rangle)$

- **for the eigenvector $|\phi_+\rangle$, the monomer transition dipole moments $M_i = \langle e^{(i)}|\hat{\mu}|g^{(i)}\rangle$, $i = 1, 2$, add up constructively, while the opposite is the case for the $|\phi_-\rangle$ eigenvector $\longrightarrow$ "bright" vs. "dark" states**

- **the sign of the coupling j determines which eigenvalue is the lower one. Therefore, the sign of the coupling j also determines whether the upper or lower state is dark – distinction between J and H aggregates!**

2×2 system – Backup Slide

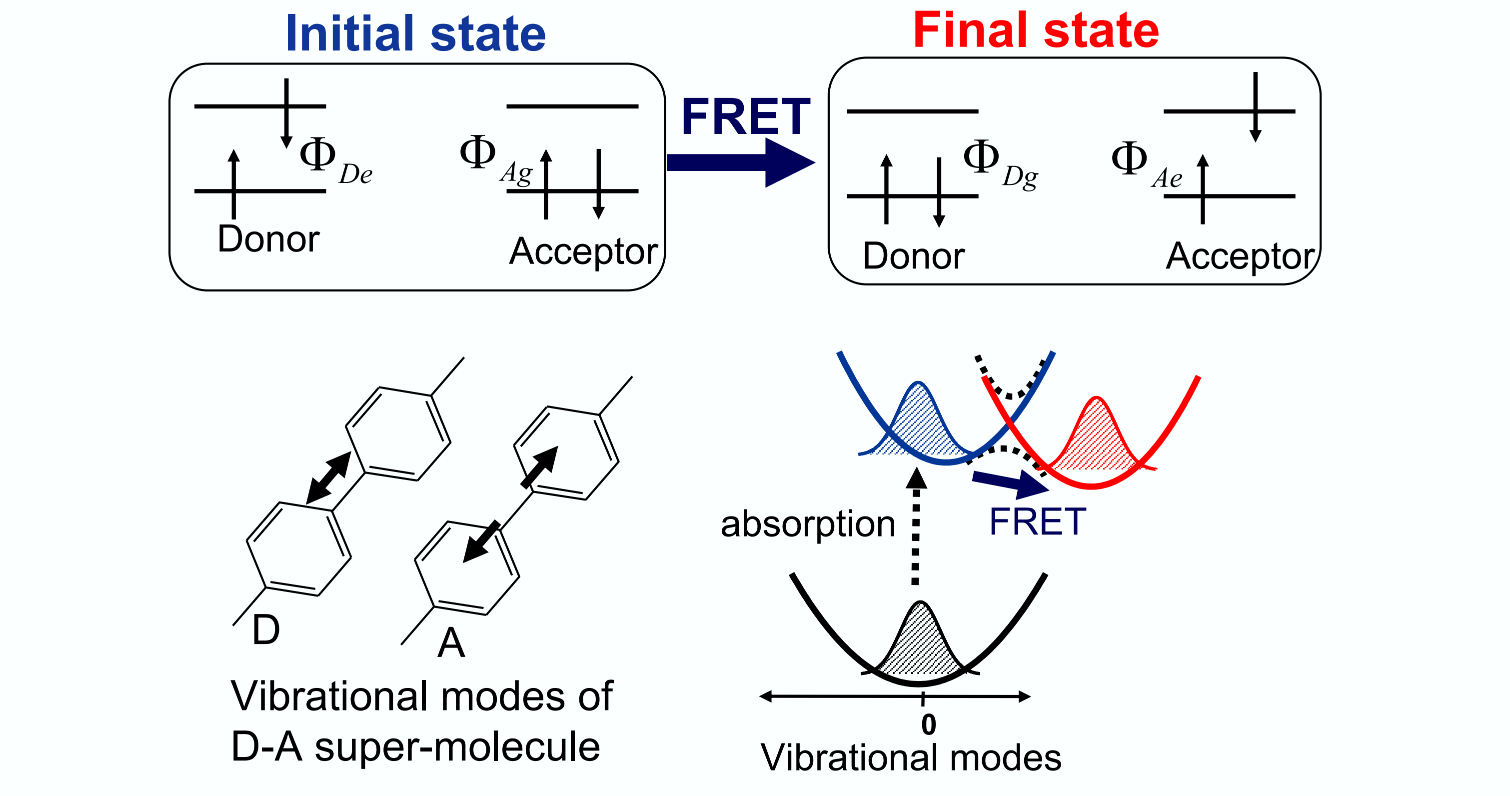


$$\begin{vmatrix} E_1 - E & \Delta \\ \Delta & E_2 - E \end{vmatrix} = 0$$

$$\longrightarrow \quad E_\pm = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}[(E_2 - E_1)^2 + 4\Delta^2]^{1/2}$$

If $E_1 = E_2 = E_0 \quad \longrightarrow \quad E_\pm = E_0 \pm \Delta$

Vibronic coupling picture of excitation energy transfer (EET)



Initial state

Φ_{De} Φ_{Ag}

Donor Acceptor

FRET

Final state

Φ_{Dg} Φ_{Ae}

Donor Acceptor

D A

Vibrational modes of
D-A super-molecule

absorption

FRET

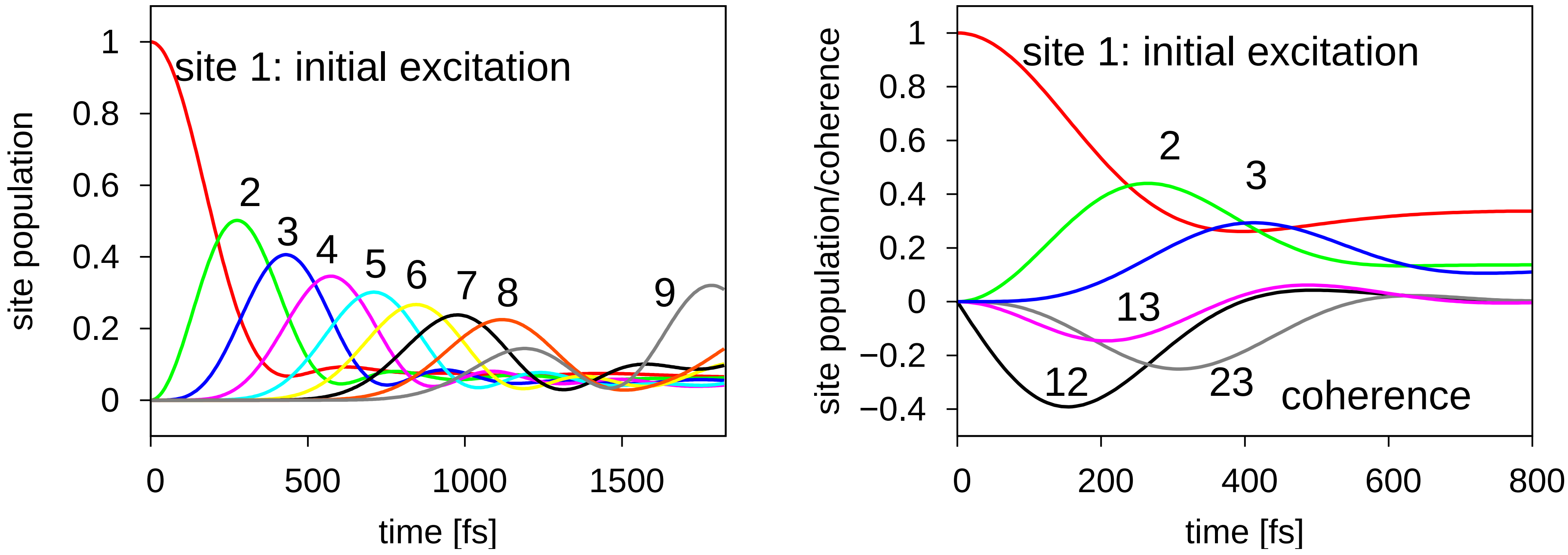
0

Vibrational modes

- **FRET = fluorescence resonance energy transfer (equivalent to EET)**

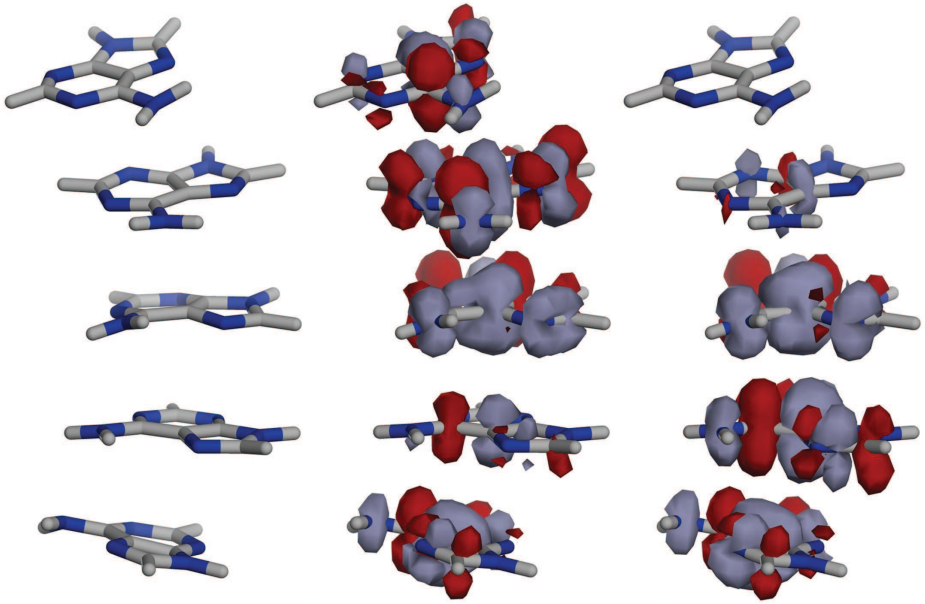
Exciton transfer can be coherent and ultrafast

quantum dynamics simulation:



- **site-site excitation energy transfer** $|\phi_n\rangle \longrightarrow |\phi_{n+1}\rangle$
- **transfer is mediated by coherences** $|\phi_n\rangle\langle\phi_{n+1}|$
- **but the environment could rapidly induce "decoherence"**
- **coherent transfer can be observed experimentally!**

Excitonic eigenstate picture



electronic densities of stacked adenine pentamer corresponding to two $\pi\pi^*$ states with different degrees of localisation

Bittner & co-workers, in: *Energy Transfer Dynamics in Biomaterial Systems*, Burghardt et al. (eds), Springer (2009).

- **the excitonic eigenstates are obtained by diagonalizing the exciton Hamiltonian, as a function of the nuclear coordinates:**

$$|\Psi_{\text{exciton}}(R;t)\rangle = \sum_n c_n(R,t)|\phi_n\rangle$$

Can we use perturbative limits?

consider site-site coupling (J) vs. electron-phonon coupling (κ)

- case 1: $J \ll \kappa$

Förster theory – non-coherent hopping between sites

e.g., Scholes & collaborators, J. Phys. Chem. B, 113, 656 (2009): EET in semiconducting polymers

- case 2: $\kappa \ll J$

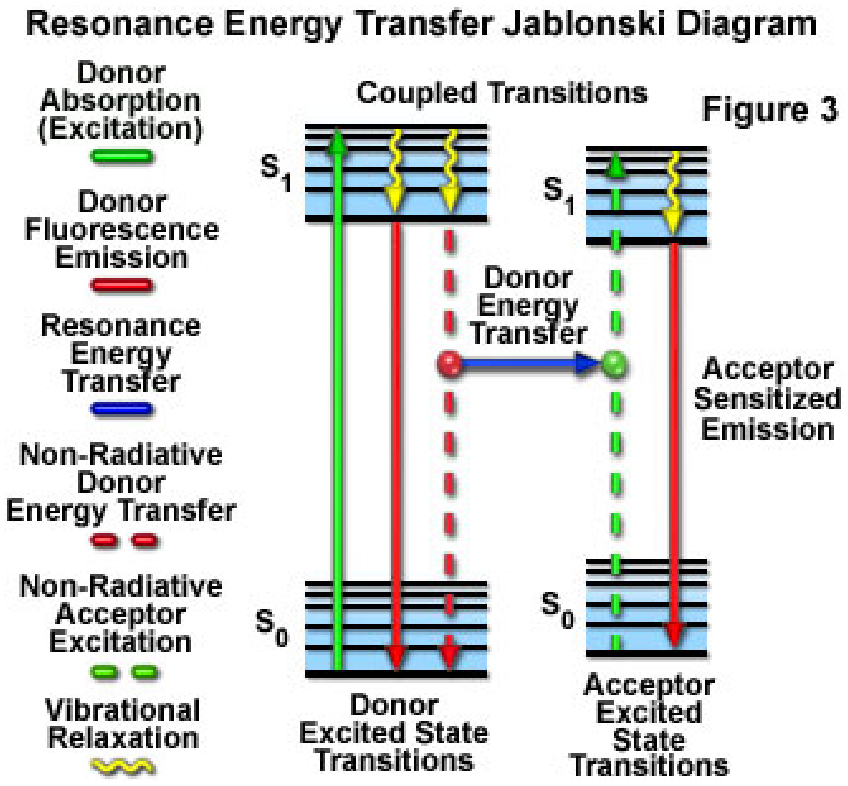
excitonic eigenstates in a vibrational bath

e.g., Abramavicius & Mukamel, J. Chem. Phys. 133, 064510 (2010): EET in Photosystem II

- but in most systems of interest: $\kappa \sim J$

in principle, we need the full dynamics on the Born-Oppenheimer surfaces of the oligomer/aggregate species

Excitation Energy Transfer (EET): Förster rates



- resonant donor-acceptor transfer
- also denoted FRET = fluorescence resonance energy transfer
- interacting transition dipole moments
- standard description: Förster rate

Scholes & collaborators, J. Phys. Chem. B, 113, 656 (2009)

Fluorescent markers in biological applications

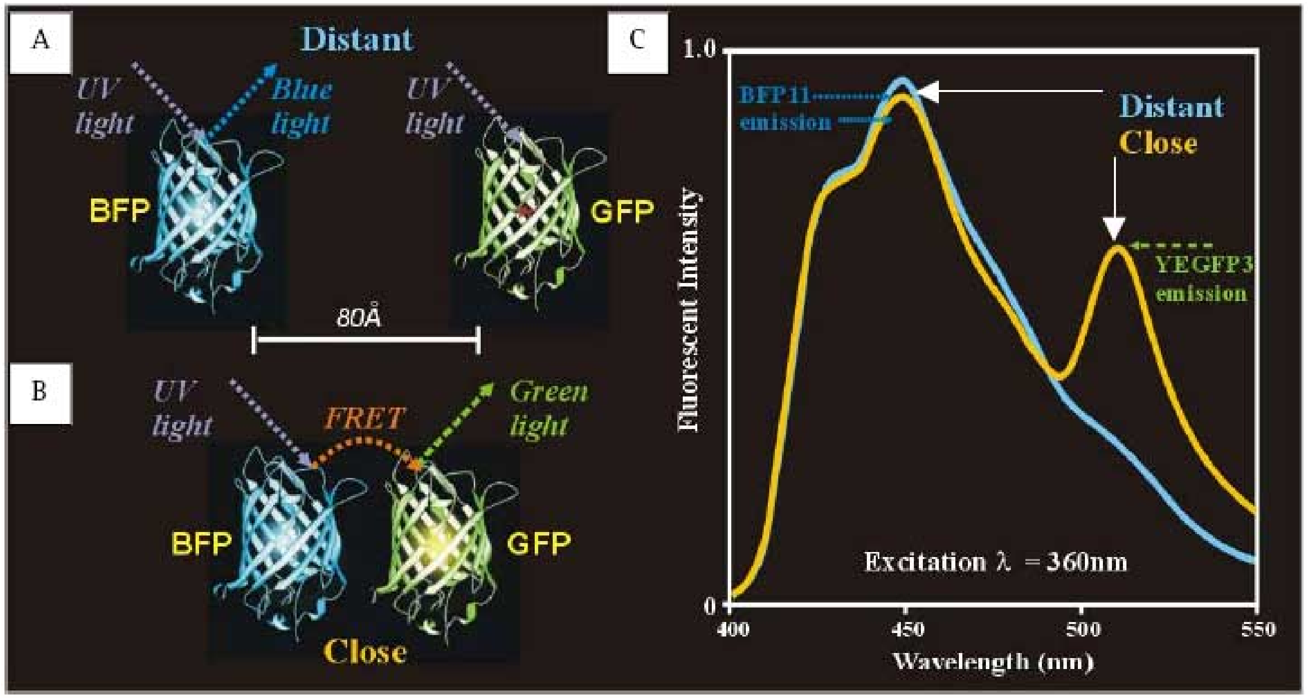
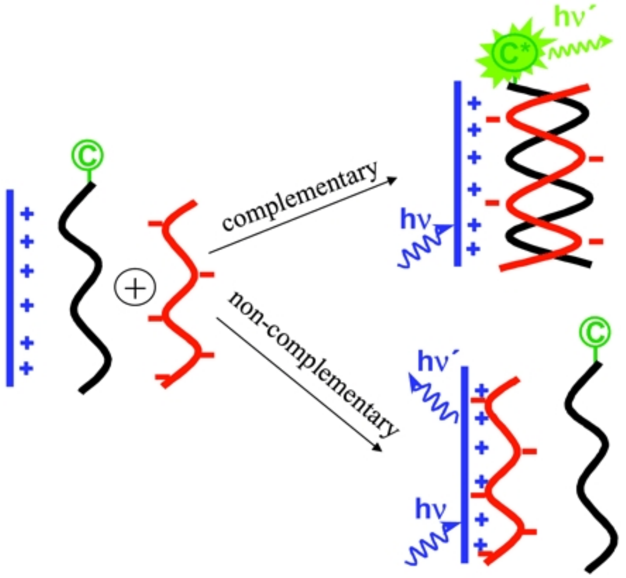
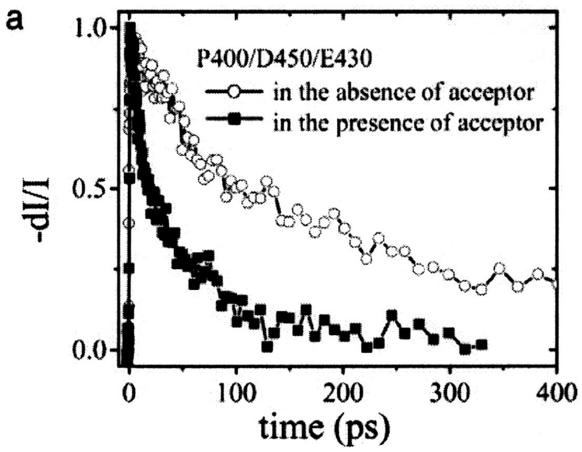


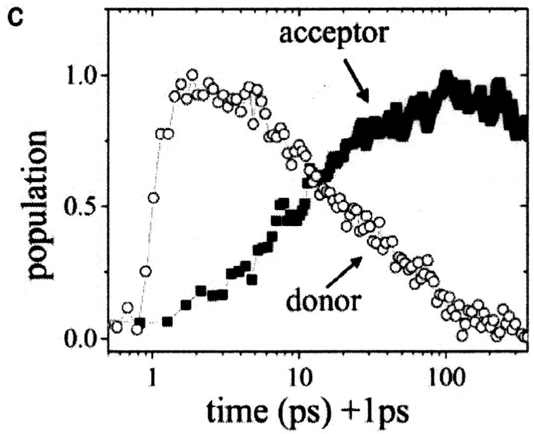
Figure 1. *The use of GFP variants to produce FRET. In A, Distant; UV light excites BFP (donor fluorophore) to emit blue light (peak emission = 450nm), but GFP (acceptor) is not close enough to draw energy from the excited donor. In B, Close; proximity of GFP to BFP allows non-radiative energy transfer, the stimulated BFP exciting GFP to fluoresce green (peak emission = 510nm). Figure 1C shows the expected emission spectra when the GFP fluorophores are either close or distant.*

Time-resolved FRET

Heeger & co, PNAS 101, 11634 (2004), PNAS 102, 530 (2005)







CCP (cationic conjugated polymer) ⟶
PNA-C (peptide nucleic acid + chromophore
C=fluorescein)

Derivation of Förster theory, in a nutshell: Fermi's Golden Rule + dipole-dipole interaction

thermally averaged rate (2nd order perturbation theory):

$$k_{DA} = \frac{2\pi}{\hbar} \sum_{\text{D/A vib. states}} f(E_D^*) f(E_A^0)\, |\langle \psi_D^* \psi_A^0 | V_{DA}^{\text{dip}} | \psi_D^0 \psi_A^* \rangle|^2 \delta(E_D^* + E_A^0 - E_A^* - E_D^0)$$

$$\langle \psi_D^* \psi_A^0 | V_{DA}^{\text{dip}} | \psi_D^0 \psi_A^* \rangle = \langle \psi_D^* \psi_A^0 | \frac{\hat{\mu}_D \cdot \hat{\mu}_A}{|r_{DA}|^3} - 3 \frac{(r_{DA} \cdot \hat{\mu}_D)(r_{DA} \cdot \hat{\mu}_A)}{|r_{DA}|^5} | \psi_D^0 \psi_A^* \rangle$$

$$= \kappa_{DA} \frac{\langle \psi_D^* | \hat{\mu}_D | \psi_D^0 \rangle \langle \psi_A^0 | \hat{\mu}_A | \psi_A^* \rangle}{|r_{DA}|^3}$$

Now identify the ingredients of this formula with the expressions for the donor emission / acceptor absorption spectra $\longrightarrow$ spectral overlap

Fermi's Golden Rule

Transition probability between quantum states that are subject to a perturbation

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

e.g., $\hat{V}(t) = -\hat{\mu}\, E_0\, (e^{i\omega t} + e^{-i\omega t})$ "perturbation"

Transition rate between two states $a \rightarrow b$
(in 2nd order perturbation theory):

$$\Gamma_{a\rightarrow b} = \frac{2\pi}{\hbar} |\langle\psi_b^{(0)}|\hat{\mu}|\psi_a^{(0)}\rangle|^2\ \delta(E_b^0 - E_a^0 \pm \hbar\omega)$$

where $E_b^0 - E_a^0 = \hbar\omega_{ba}$ - resonance condition!

Förster theory = rate theory for resonant energy transfer between two dipoles

$$k_{DA}(r_{DA}) = k_D^{\mathrm{rad}} \left(\frac{r_F}{r_{DA}}\right)^6$$

$$r_F^6 = \frac{9c^4\,\kappa_{DA}^2}{8\pi\eta^4} \int_0^\infty d\omega\ \frac{1}{\omega^4} I_D(\omega)\alpha_A(\omega)$$

"Förster radius" $r_F \propto$ orientational factor × spectral overlap

$I_D(\omega)$ = donor emission spectrum

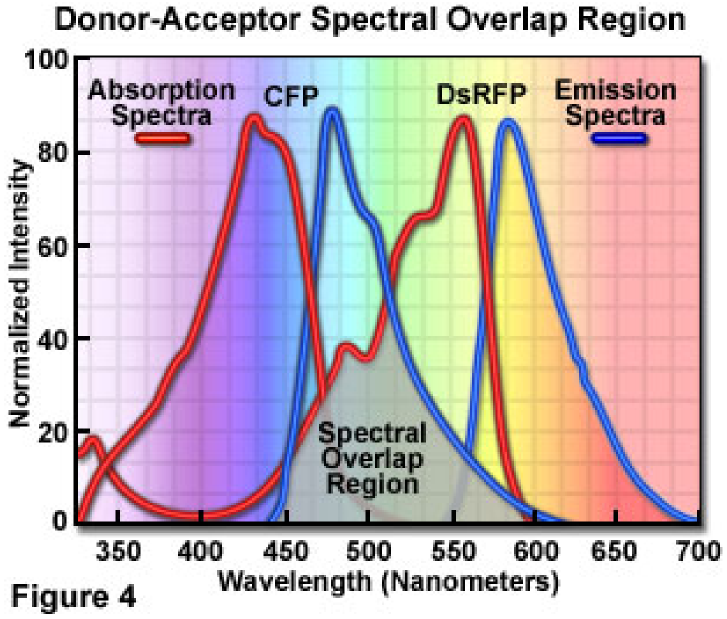
$\alpha_A(\omega)$ = acceptor absorption spectrum

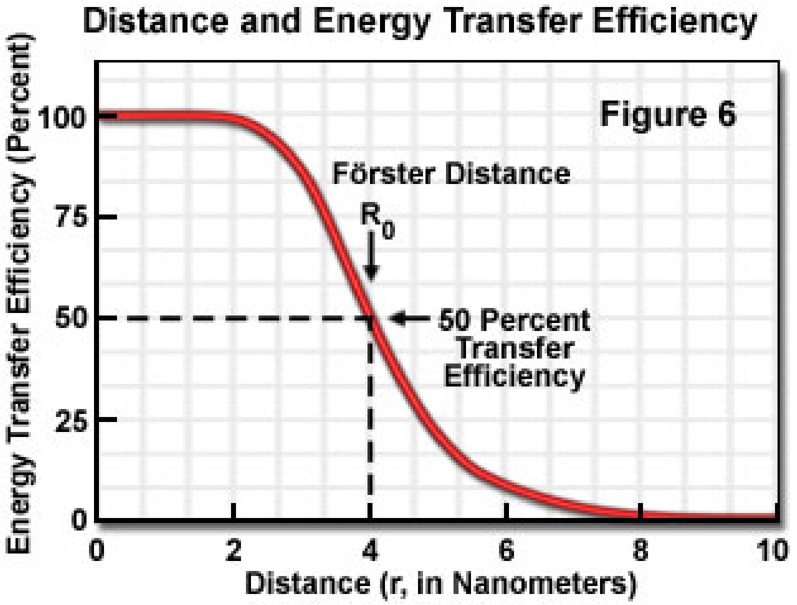
κ_{DA} = orientational factor:

$$\kappa_{DA} = \sin\theta_D \sin\theta_A \cos\Phi_{ARD} - 2\cos\theta_D \cos\theta_A$$

Standard Förster expression: isotropic average $\kappa_{DA}^2 = 2/3$

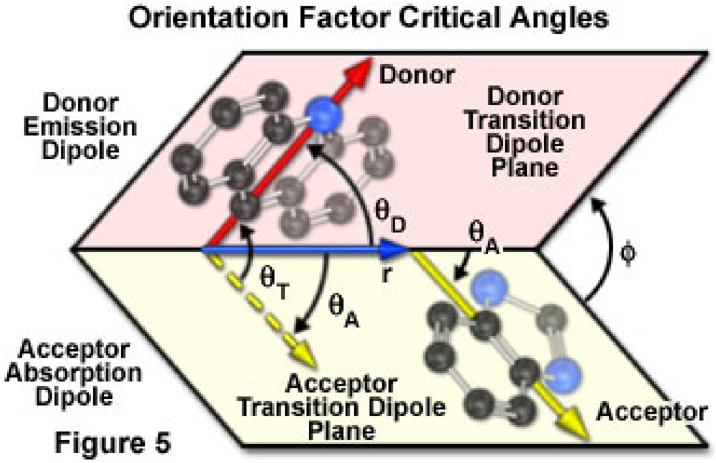
Förster theory, cont'd





$$k_{DA}(r_{DA}) = k_D^{\mathrm{rad}}\Big(\frac{r_F}{r_{DA}}\Big)^6 \quad ; \quad r_F^6 = \frac{9c^4\,\kappa_{DA}^2}{8\pi\eta^4}\int_0^\infty d\omega\;\frac{1}{\omega^4}\,I_D(\omega)\alpha_A(\omega)$$

Isotropic orientational average often inappropriate

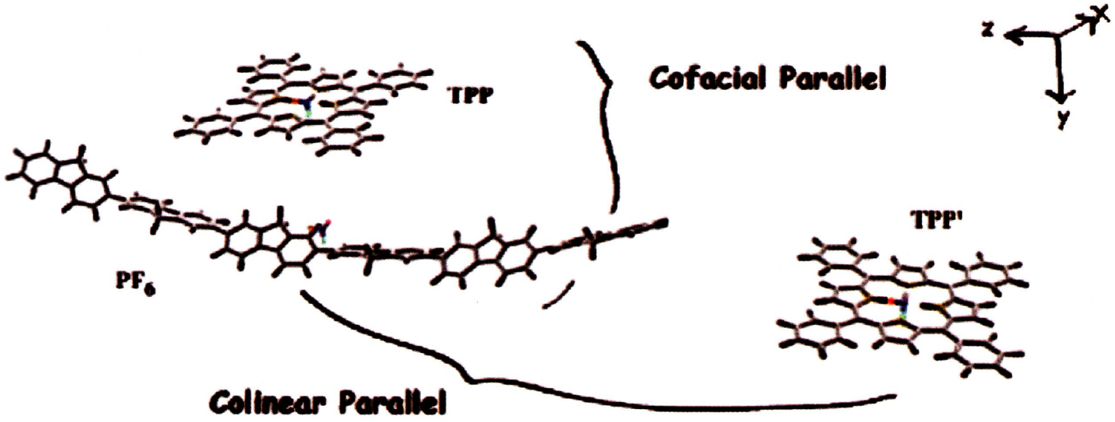


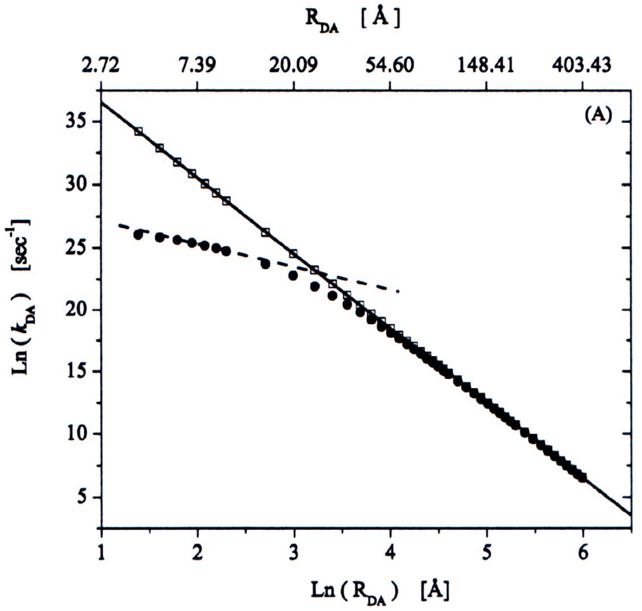
- standard Förster expression works if rotational motion is very fast as compared with transfer rate
- in general: compute $k_{DA}(r_{DA}, \theta_{DA})$
- if transfer is much faster than rotational motion: static average

Non-Förster behavior due to orientation effects

Wong, Bagchi, and Rossky, J. Phys. Chem. A, 108, 5752 (2004)

polyfluorene (PF_6) $\longrightarrow$ tetraphenylporphyrin (TPP)





The Förster rate is recovered at large distances, $\sim$ 100 $\AA$

At shorter distances, r^{-2} gives a better fit

We'd expect deviations from Förster theory, for various reasons:

- if EET time scales are short, and similar to the time scale of molecular rearrangements: exciton dynamics picture necessary
- at short distances, exchange effects need to be accounted for (Dexter, 1953) $\longrightarrow$ exponential variation of the rate with r
- for extended donor/acceptor entities, the point dipole approximation is often not sufficient $\longrightarrow$ multipole expansions
- for molecules near surfaces, the energy transfer is carried by (i) plasmons (collective electronic excitation modes) and (ii) electron-hole excitations