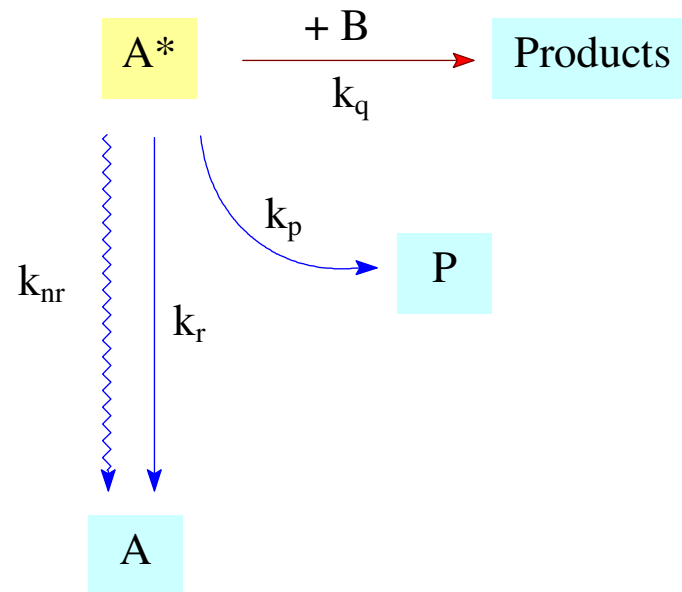


Excited-State Processes



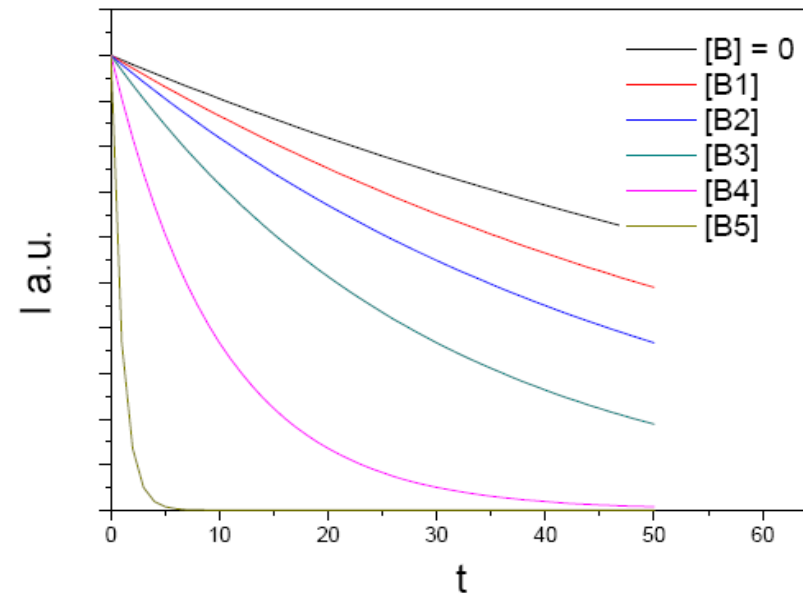
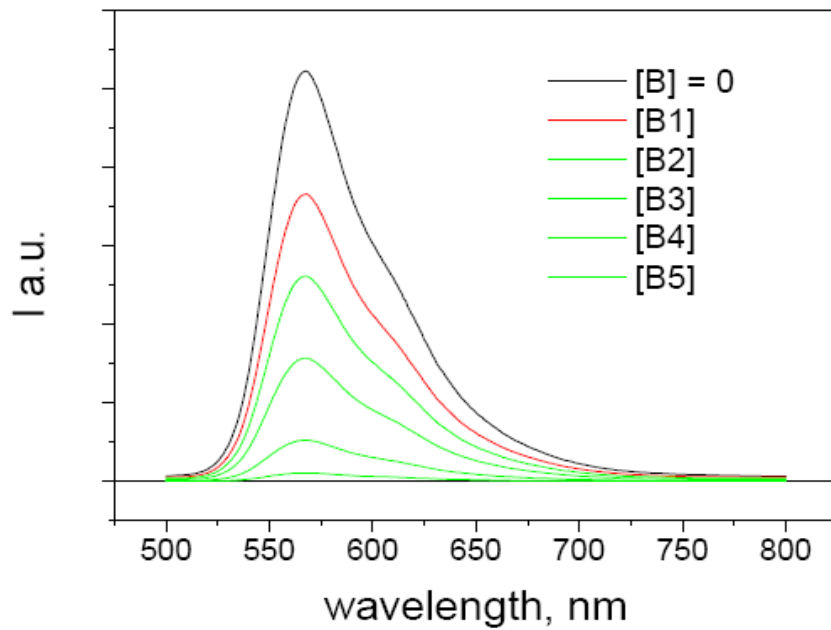
Bimolecular Processes:



.....

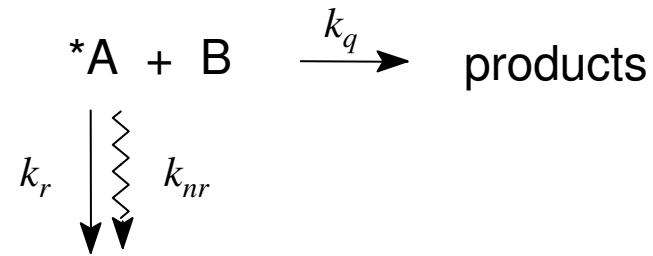
Quenching

Upon addition of B, unimolecular processes of *A (e.g. emission) are **quenched**, both in *intensity* (steady-state) and in *decay kinetics* (time-resolved)



Stern-Volmer kinetics

competition between unimolecular decay and bimolecular process



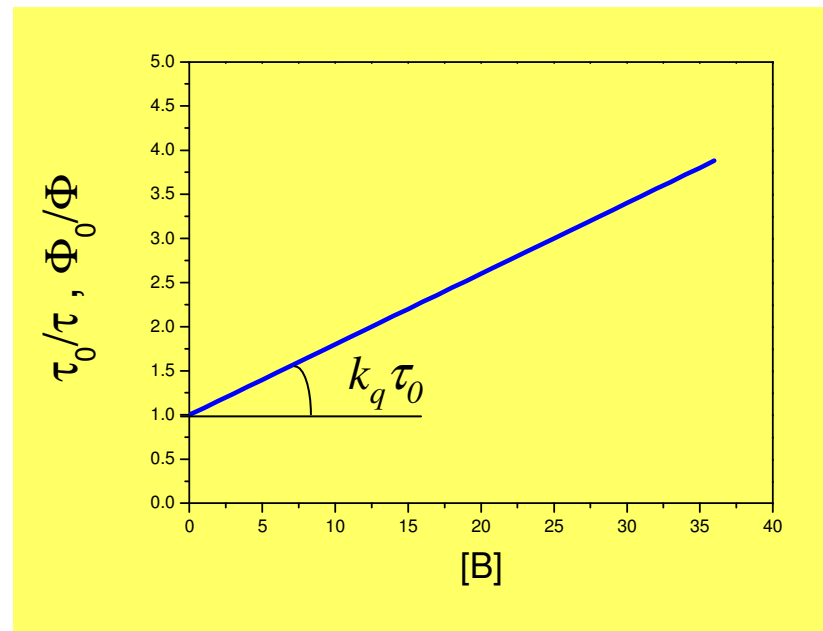
$$\tau_0^A = \frac{1}{k_r + k_{nr}}$$

$$\tau^A = \frac{1}{k_r + k_{nr} + k_q[B]}$$

$$\Phi_0^A = \eta(\rightarrow *A) k_r \tau_0^A \quad \Phi^A = \eta(\rightarrow *A) k_r \tau^A$$

$$\frac{\tau_0^A}{\tau^A} = \frac{\Phi_0^A}{\Phi^A} = 1 + k_q \tau_0^A [B] = 1 + K_{SV} [B]$$

Stern-Volmer equation



$$\frac{\tau_0^A}{\tau^A} = \frac{\Phi_0^A}{\Phi^A} = 1 + k_q \tau_0^A [B] = 1 + K_{SV} [B]$$

Extent of quenching depends on:

- Lifetime of excited state to be quenched
- Rate constant of the quenching process
- Quencher concentration

e.g., for 50% quenching ($k_q \tau_0^A [B] = 1$),

$$\begin{aligned} \tau_0^A &= 1 \text{ ns} \\ k_q &= 10^9 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 1 \text{ M} \end{aligned}$$

$$\begin{aligned} \tau_0^A &= 1 \text{ } \mu\text{s} \\ k_q &= 10^9 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 10^{-3} \text{ M} \end{aligned}$$

$$\begin{aligned} \tau_0^A &= 1 \text{ ms} \\ k_q &= 10^9 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 10^{-6} \text{ M} \end{aligned}$$

$$\begin{aligned} \tau_0^A &= 1 \text{ } \mu\text{s} \\ k_q &= 10^6 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 1 \text{ M} \end{aligned}$$

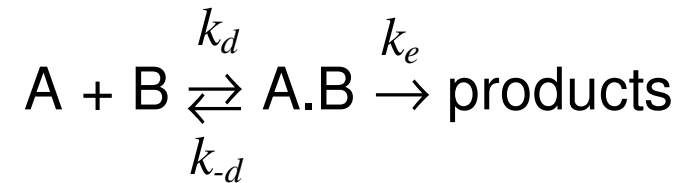
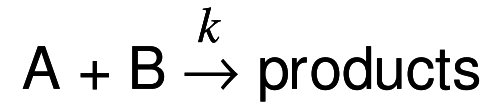
$$\begin{aligned} \tau_0^A &= 1 \text{ ms} \\ k_q &= 10^6 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 10^{-3} \text{ M} \end{aligned}$$

Organic molecules:

- **singlet** excited states (typical τ in the ns range) require very high quencher concentrations
- **triplet** states (typical τ in the μs -ms range) can be easily quenched with low quencher concentrations

$$\begin{aligned} \tau_0^A &= 1 \text{ ms} \\ k_q &= 10^3 \text{ M}^{-1}\text{s}^{-1} \\ [B] &= 1 \text{ M} \end{aligned}$$

Bimolecular processes: role of diffusion and kinetic regimes

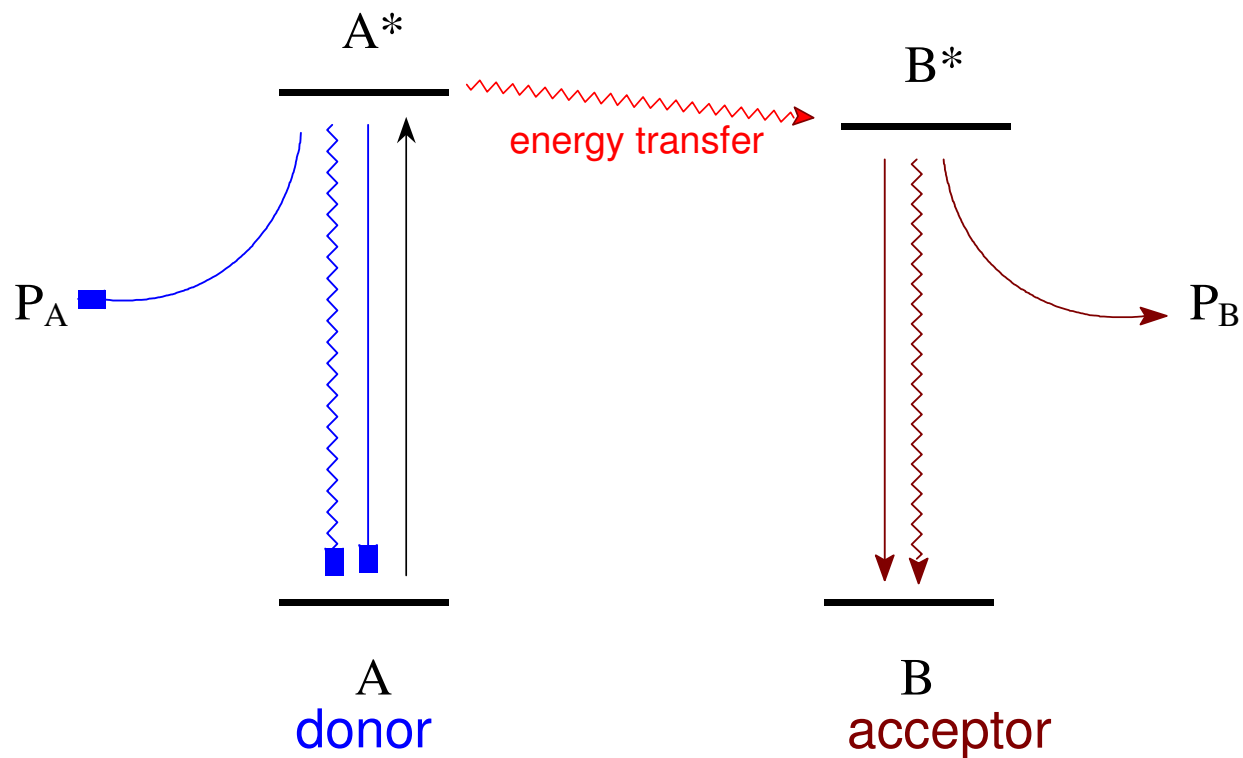
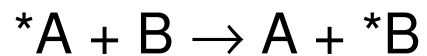


$$k = k_d \frac{k_e}{k_e + k_{-d}}$$

If $k_e \gg k_{-d}$ $k = k_d$ (diffusion-controlled limit)

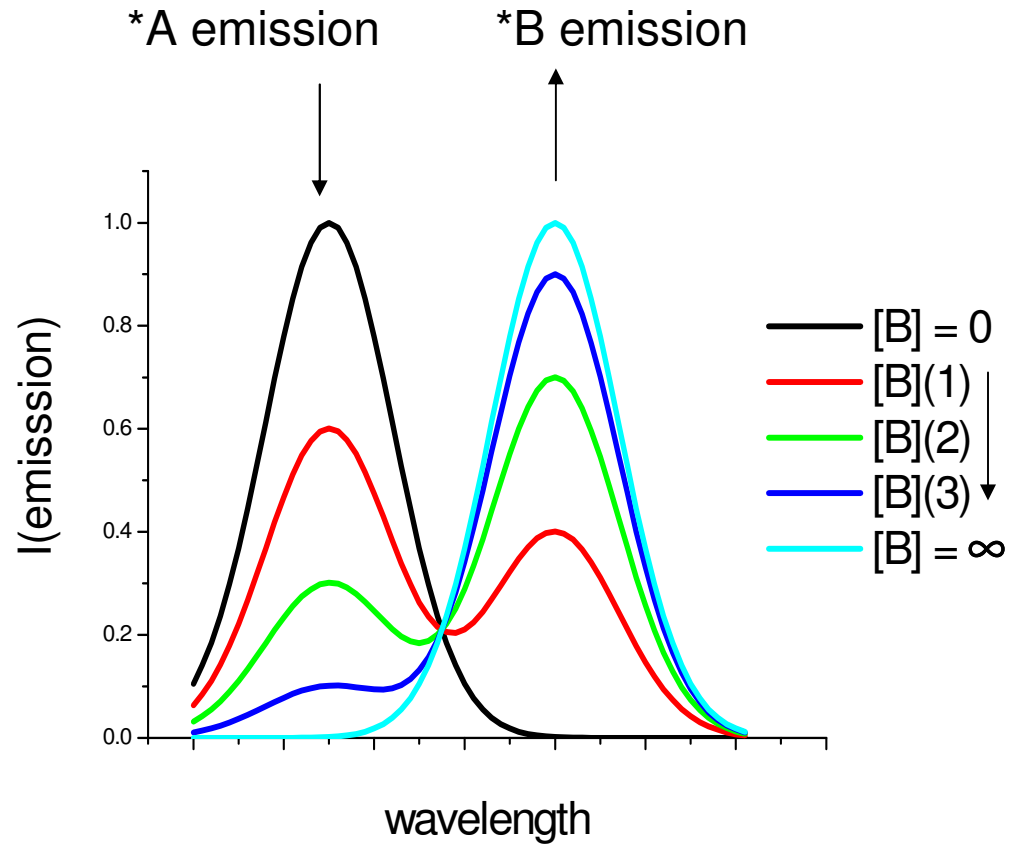
If $k_e \ll k_{-d}$ $k = \frac{k_d}{k_{-d}} k_e$ (reaction-controlled regime)

BIMOLECULAR PROCESSES: ENERGY TRANSFER

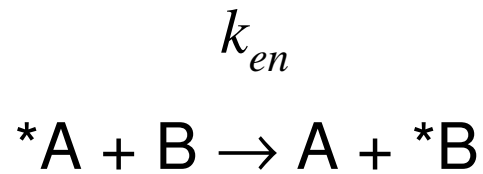


excited-state processes of donor: **quenched.**
excited-state processes of acceptor: **sensitized**

sensitization



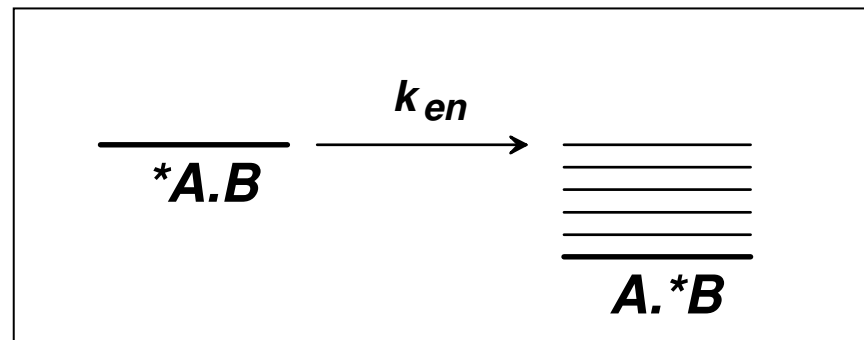
Ideally, A is selectively excited. As the concentration of B increases, the emission from A is quenched and a new emission from B develops



electronic energy transfer can be seen as a

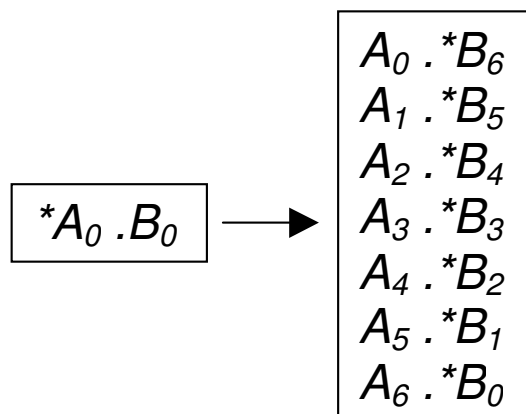
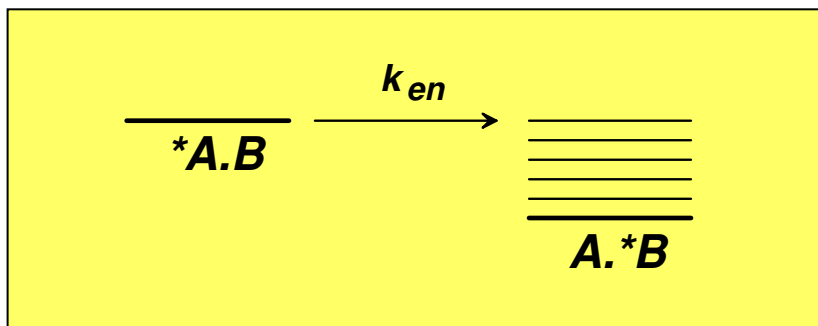
radiationless transition

between “local” excited states of the A.B “supermolecule



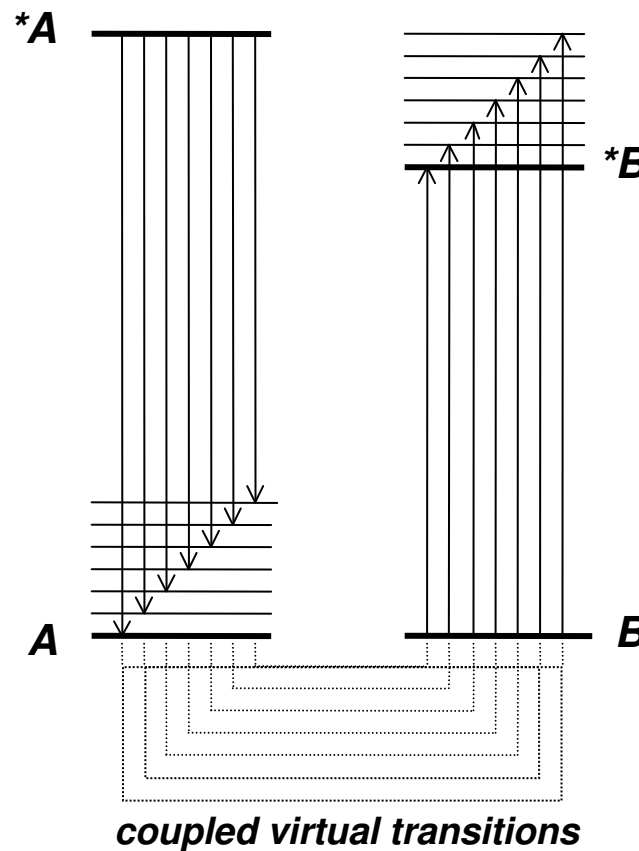
$$k_{en} = (2\pi/\hbar) \langle \Psi_{*A.B} | H' | \Psi_{A.*B} \rangle^2 \text{ FC}$$

(Fermi Golden Rule)



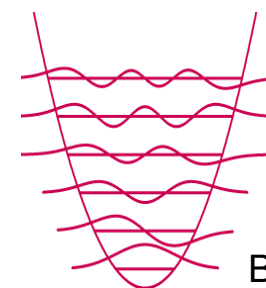
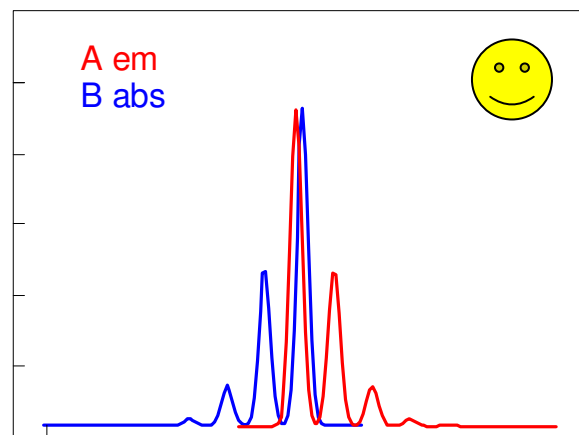
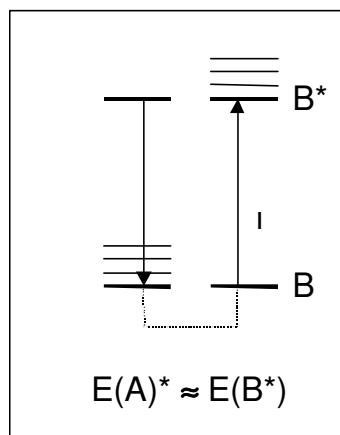
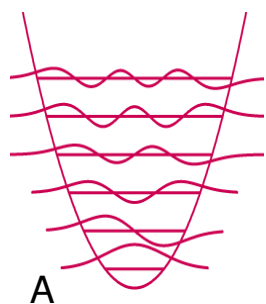
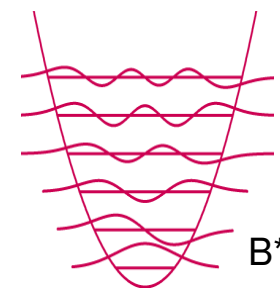
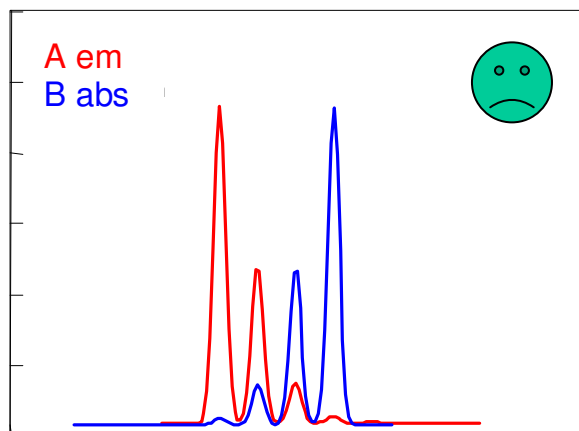
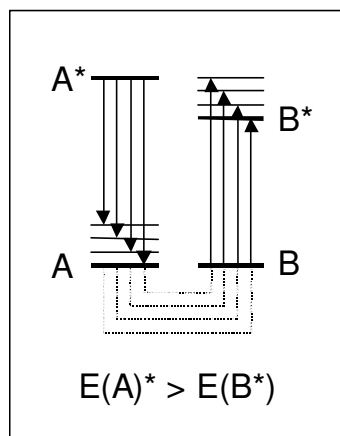
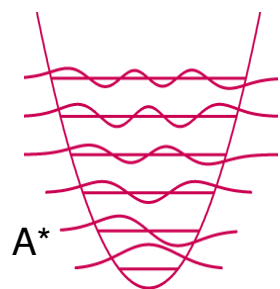
$FC \propto J = \int_0^\infty I_A(\nu) \varepsilon_B(\nu) d\nu$
 spectral overlap

$FC = \sum \langle \chi_{*A.B} / \chi_{A.*B} \rangle^2$
 (isoenergetic levels)



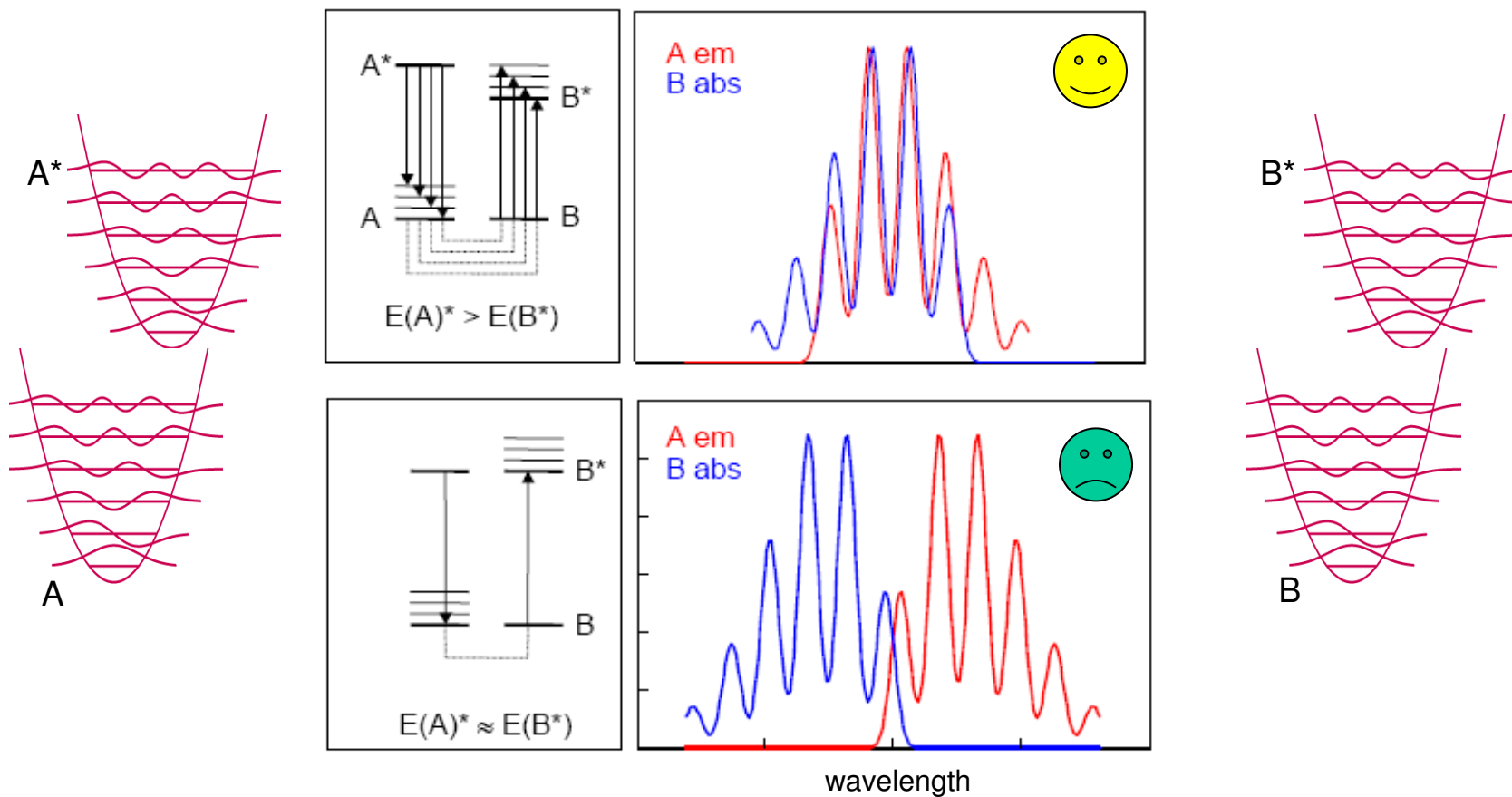
$FC = \sum_{m,n} \langle \chi_{*A}^0 \chi_B^0 / \chi_A^m \chi_{*B}^n \rangle^2 = \sum_{m,n} \langle \chi_{*A}^0 / \chi_A^m \rangle^2 \langle \chi_B^0 / \chi_{*B}^n \rangle^2$

Franck-Condon Factors and spectral overlap:
energy transfer between molecules with “undistorted” excited states



wavelength

Franck-Condon Factors and spectral overlap:
energy transfer between molecules with “undistorted” excited states



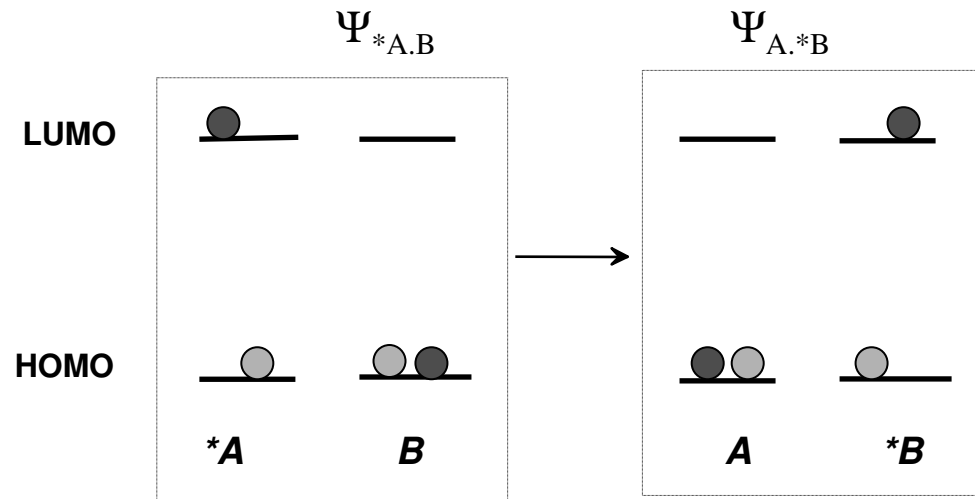
Question: Is there an optimum driving force for an EnT process?

Answer: No. It depends on the degree of distortion of the excited states involved

- Energy can be transferred efficiently between almost **iosenergetic** states only if the molecules involved have **small excited-state distortion**
- With **distorted excited states**, a **driving force** is required for EnT. The larger the excited-state distortion, the larger is the price to pay in terms of driving force

$$k_{en} = (2\pi/\hbar) \langle \Psi_{*A.B} | H' | \Psi_{A.*B} \rangle^2 FC$$

ELECTRONIC COUPLING

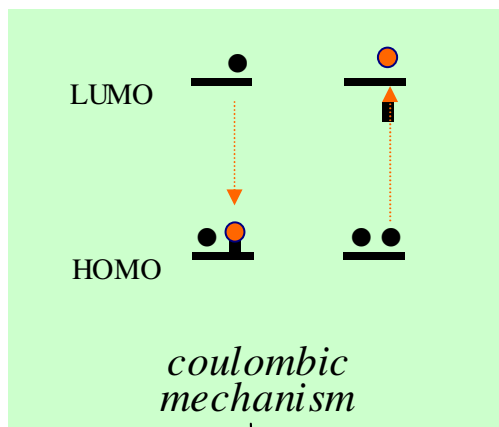
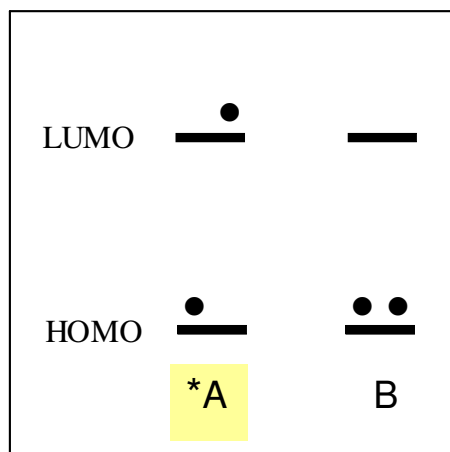


$$\langle \Psi_{*A.B} | (e^2/r_{AB}) | \Psi_{A.*B} \rangle =$$

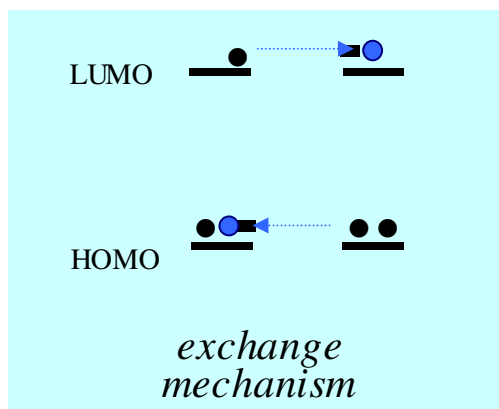
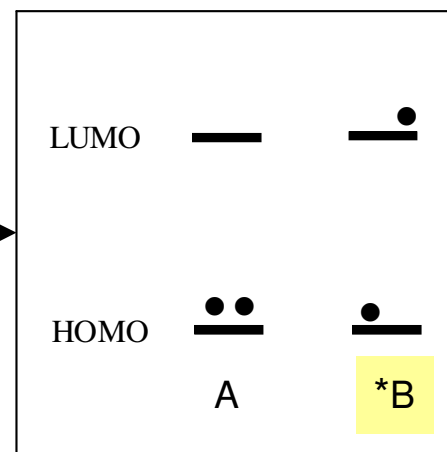
exchange

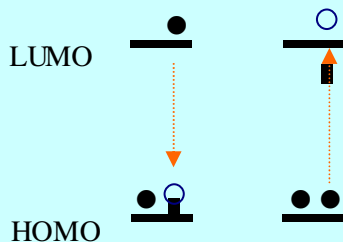
$$= (1/2) \langle [\phi_{*A}^*(1)\phi_B(2) \pm \phi_{*A}^*(2)\phi_B(1)] | (e^2/r_{AB}) | [\phi_A(1)\phi_{*B}^*(2) \pm \phi_A(2)\phi_{*B}^*(1)] \rangle$$

Coulomb



energy transfer





Coulombic (Förster) Mechanism

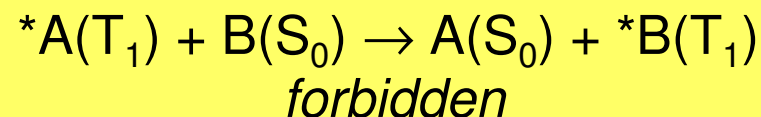
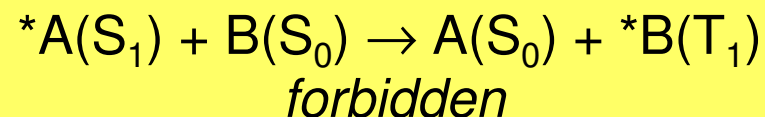
Dipole-dipole, **long-range mechanism** (in favorable conditions, efficient over 50 Å)

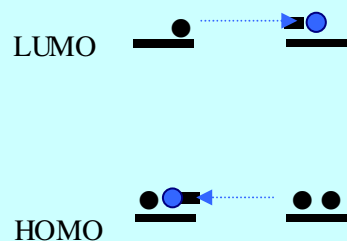
- Can be efficient between electronically isolated chromophores (spatially separated, saturated bridges)
- Fast when there is good spectral overlap between donor emission and acceptor absorption **and both are allowed**
- Förster formula for calculating en. tr. rate constants from experimental data on A and B

$$k_{en}^{coul} = 1.25 \times 10^{17} \left(\frac{\Phi_A}{n^4 \tau_A r^6} \right) \int_0^\infty F_A(\bar{\nu}) \epsilon_B \frac{d\bar{\nu}}{\bar{\nu}^4}$$

Spin selection rule
(spin conservation *within each molecule*):

e.g.,





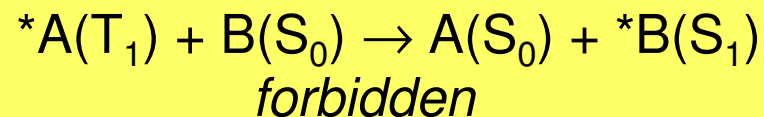
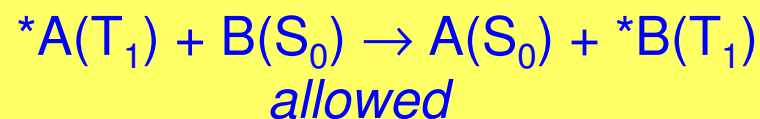
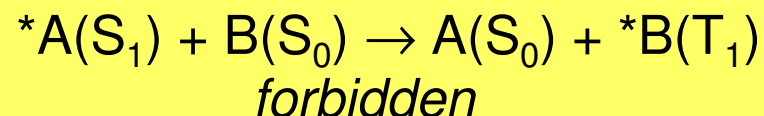
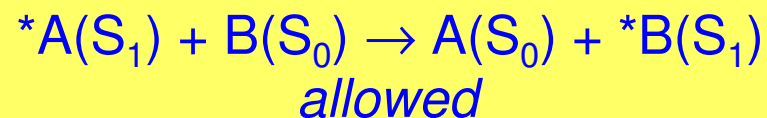
Exchange (Dexter) mechanism

- Requires orbital overlap (HOMO-HOMO and LUMO-LUMO) between donor and acceptor (direct or bridge-mediated)
- Short-range mechanism, exponential dependence on distance
- In fluid solution, requires diffusional encounters. Blocked in rigid media

Spin selection rule:

(spin conservation *within the A.B supermolecule*)

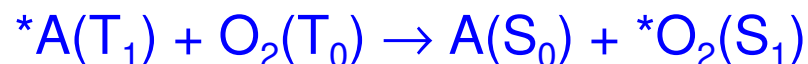
e.g.,



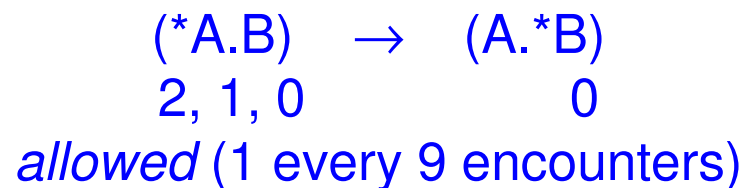
Spin selection rule:

(spin conservation *within the A.B supermolecule*)

e.g.,



Total Spin: $|S_A + S_B|, |S_A + S_B - 1|, \dots |S_A - S_B|$

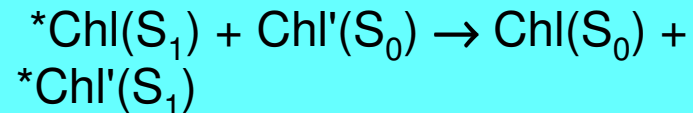


- Oxygen, with its low-lying singlet excited state, is a very efficient quencher of triplet states of organic molecules.
- In order to study triplet states: (i) remove oxygen from solution or (ii) block diffusion (e.g., by using glassy solvents at 77K)

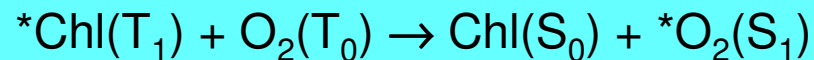
Importanza dei processi di trasferimento di energia

In natura:

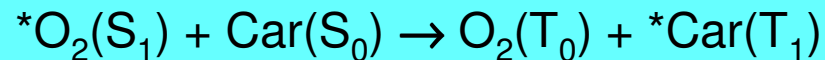
- Forster S-S nelle antenne fotosintetiche



- Dexter nella formazione di ossigeno singoletto

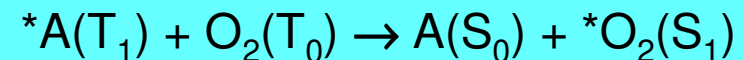


- Dexter nella protezione da ossigeno singoletto da parte di carotenoidi

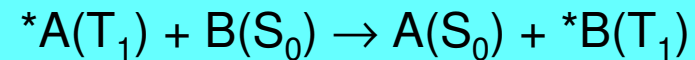


In laboratorio:

- Dexter nello spegnimento dei tripletti (e.g., da parte di ossigeno)



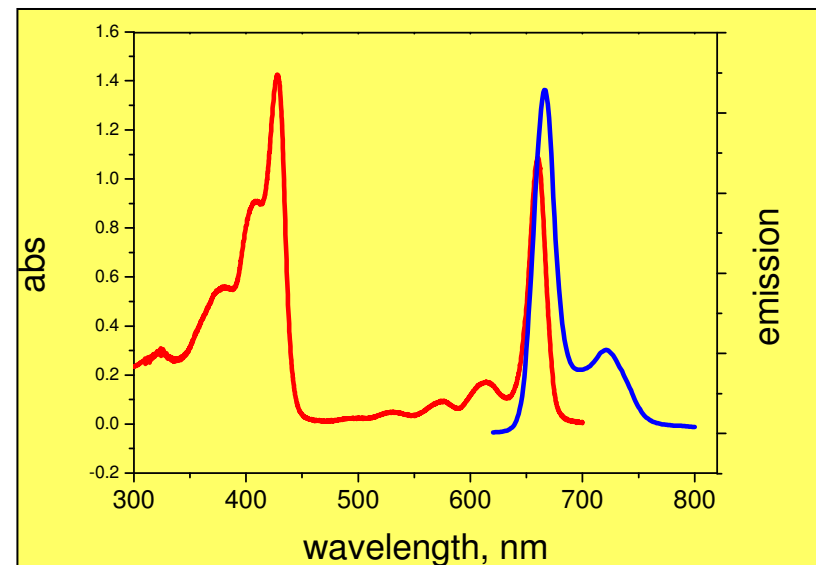
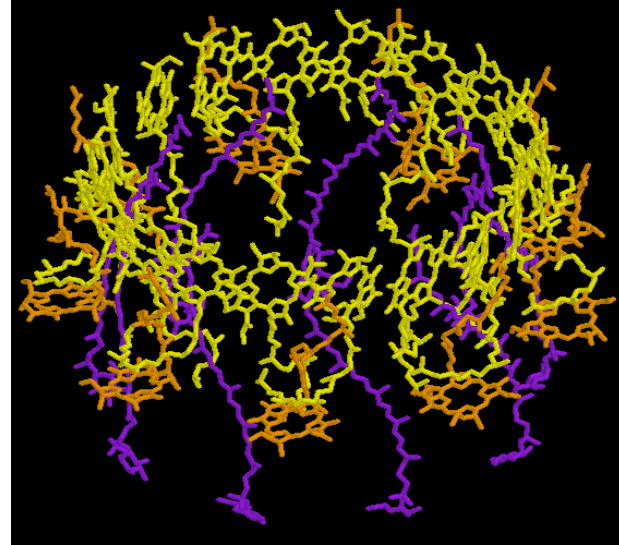
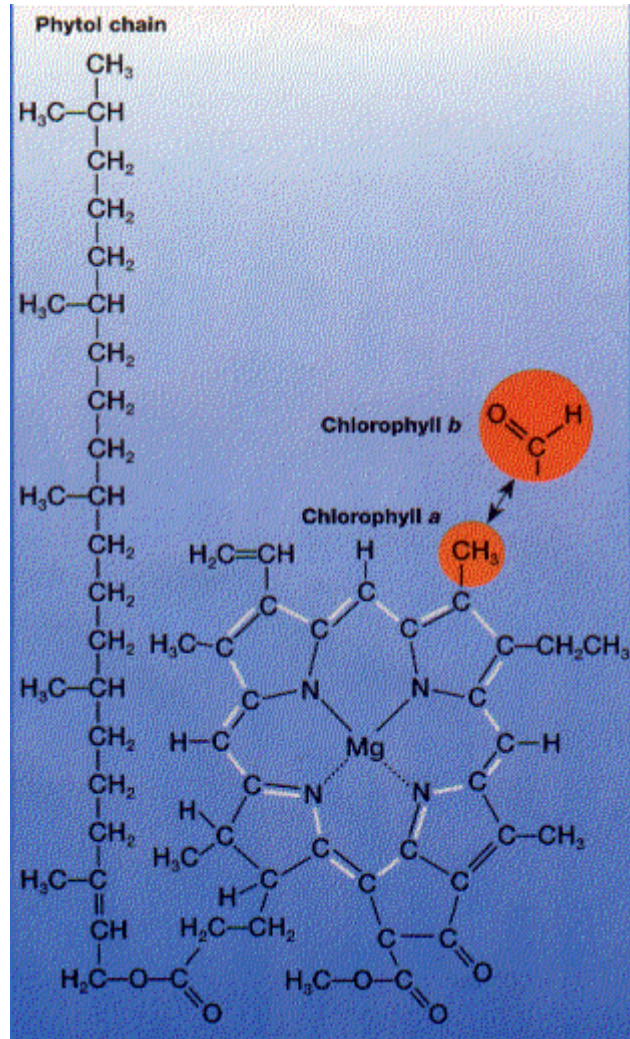
- Dexter nella sensibilizzazione a scopi meccanicistici



- Forster in fluorescence labelling

- Forster e Dexter nella progettazione e costruzione di "antenne artificiali"

Forster energy transfer between identical chromophores in light harvesting antennas

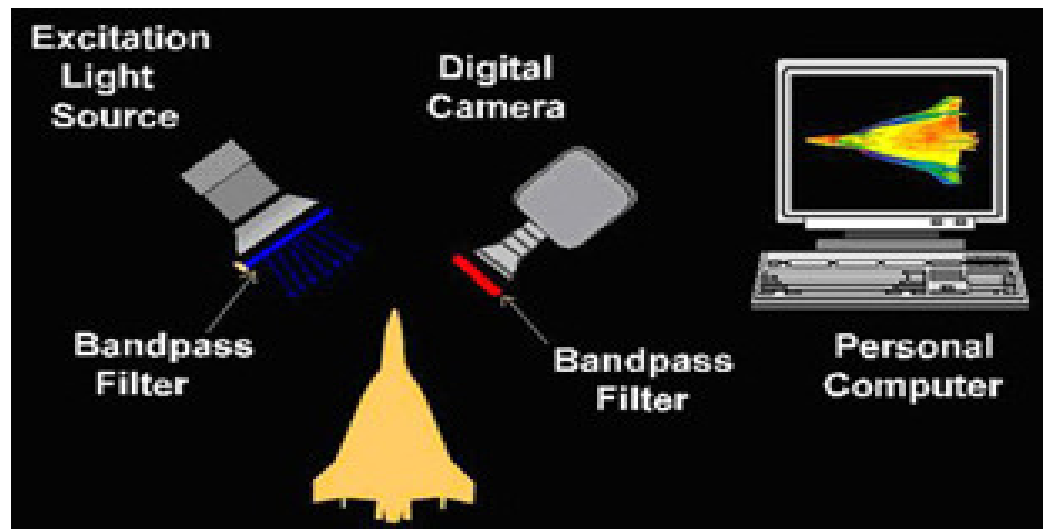


Pressure-Sensitive Paint (PSP)

Although most aircraft and automobiles are currently designed using computational fluid dynamics (CFD), wind tunnel testing is still necessary to validate CFD models. In the past, pressure measurements were limited to a few key locations on the model where mechanical pressure transducers could be placed.

Now optical measurements of pressure can be taken using pressure-sensitive paint (PSP). A wind tunnel model is covered with a paint formulation that fluoresces under short-wavelength excitation. As pressure is increased, collisions between oxygen and fluorescing paint quench the fluorescence. The change in fluorescence intensity can be used to calculate a pressure map of the surface.

Both steady-state as well as lifetime (time-resolved) imaging techniques are used in wind tunnels around the world.



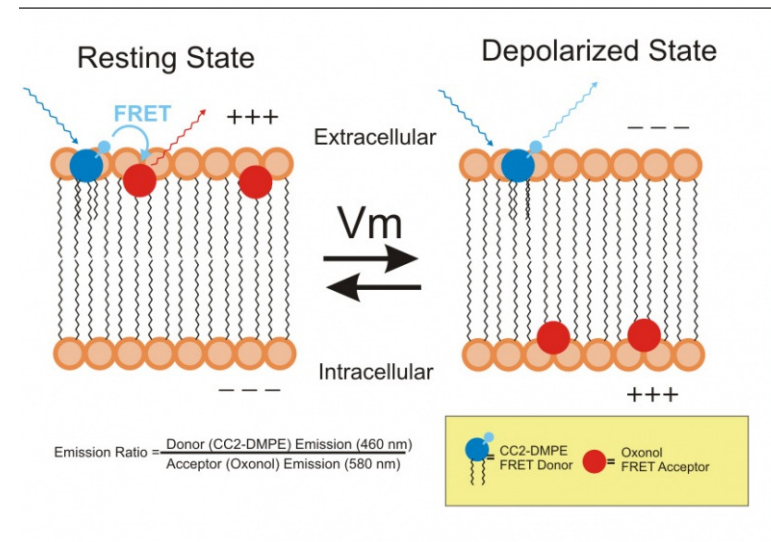
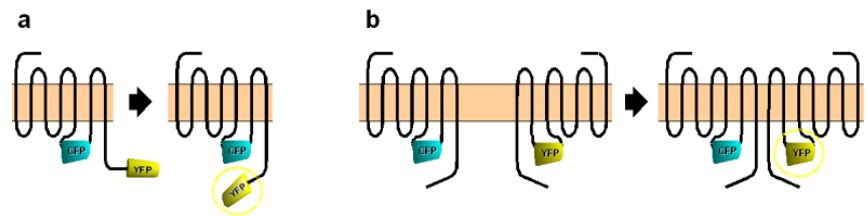
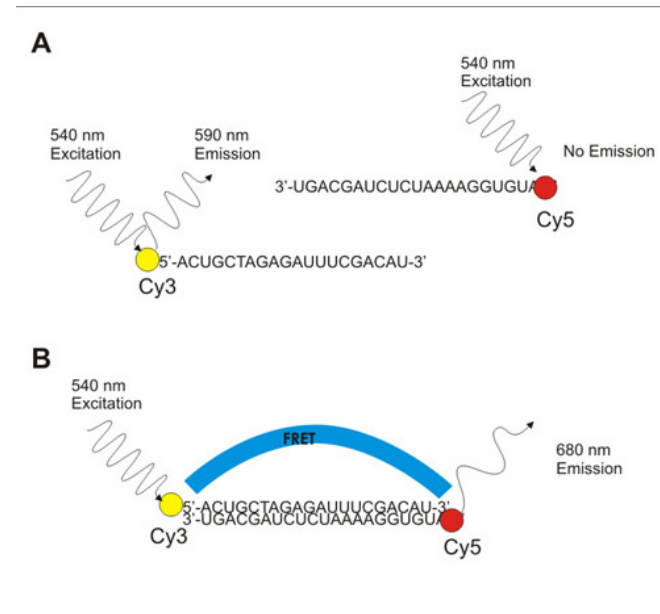
Photodynamic therapy

A photosensitizer (or a metabolic precursor of) is administered to the patient. The tissue to be treated is exposed to suitable light. The excited photosensitizer, following interystem crossing, is quenched by oxygen, with formation of **singlet oxygen**. Singlet oxygen is a very aggressive chemical species and rapidly reacts with any nearby biomolecules. Ultimately, these destructive reactions will kill the targeted cells.

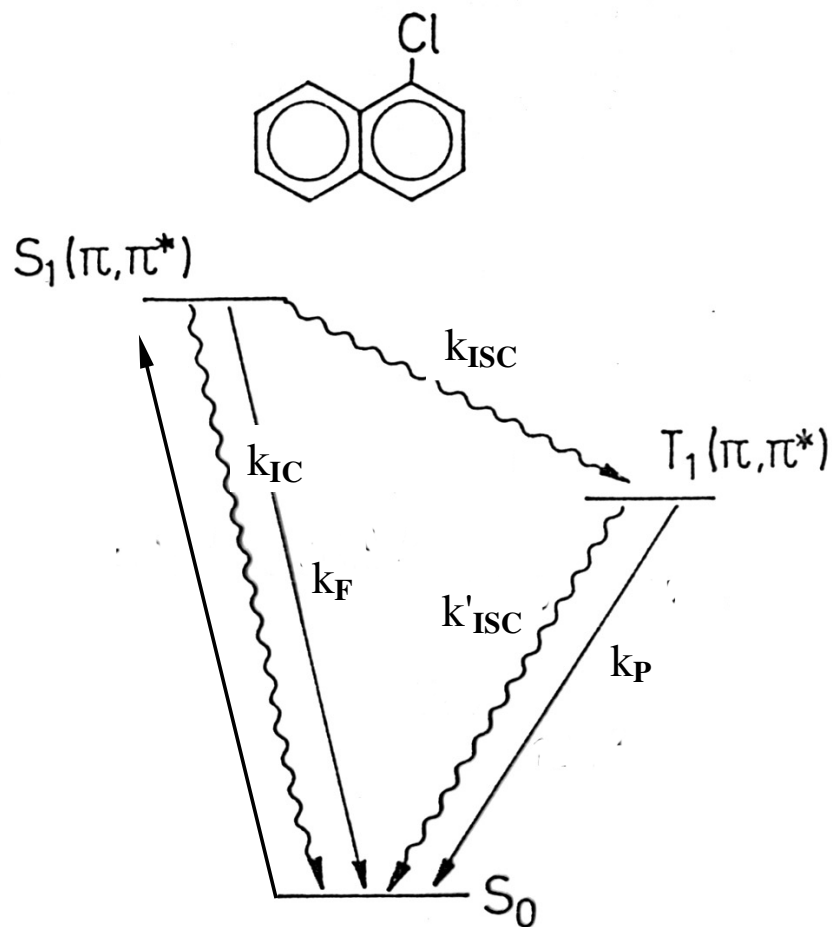


Fortster Resonance Energy Transfer (FRET) in Biology

- Structure and conformation of proteins
- Spatial distribution/assembly of proteins
- Receptor/ligand interactions
- Immunoassays
- Structure and conformation of nucleic acids
- Nucleic acid hybridization
- Membrane potential sensing
-



Use of triplet-triplet energy transfer for mechanistic purposes



Experimental Data:

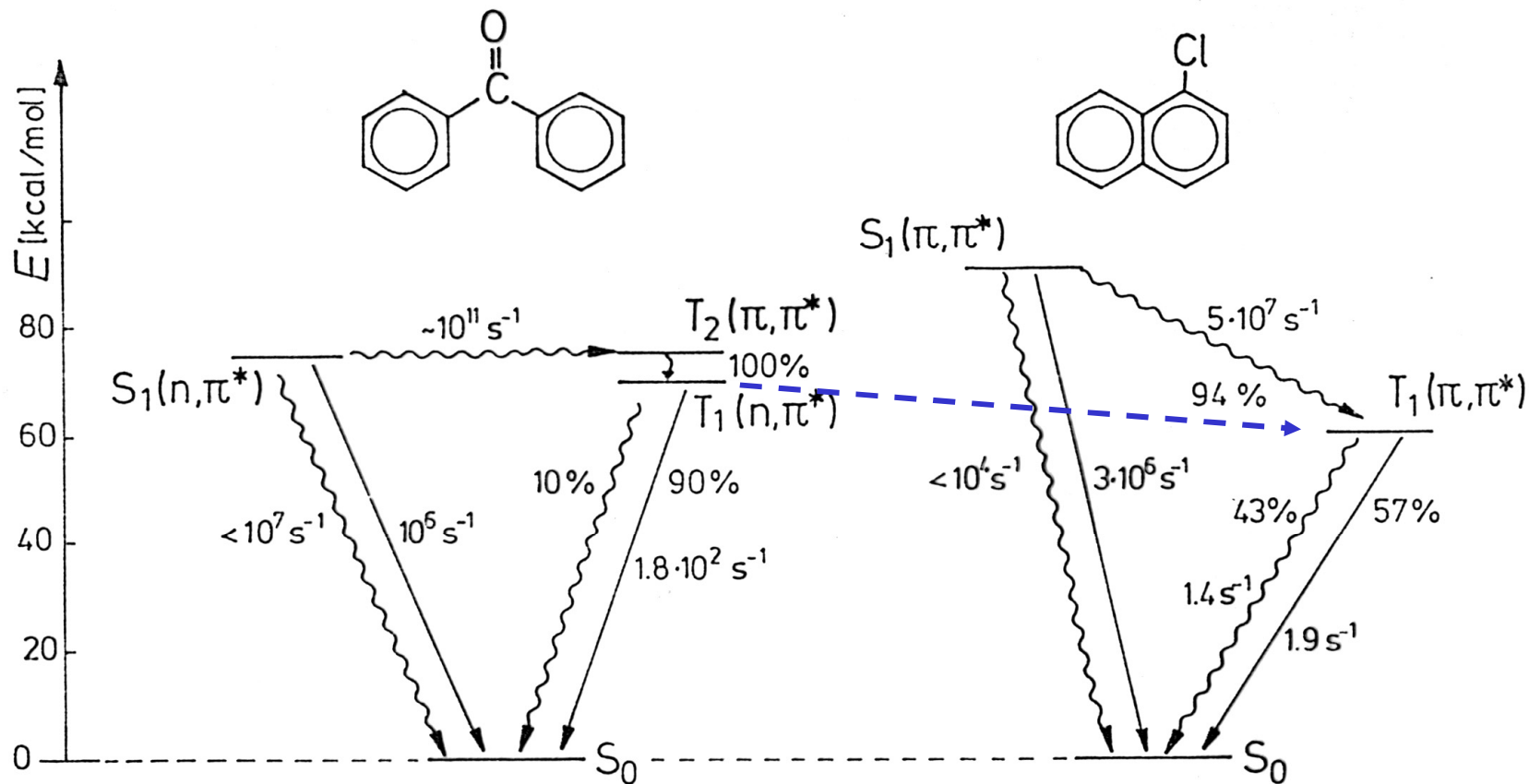
$$\Phi_F = 0.056 \quad \tau(S_1) = 19 \text{ ns}$$

$$\Phi_P = 0.54 \quad \tau(T_1) = 0.4 \text{ s}$$

For a complete definition (k_F , k_{IC} , k_{ISC} , k_P , k'_{ISC}) from exptl data, a measure of η_{ISC} is required

In order to measure η_{ISC} , one should be able to *selectively excite* T_1 . This cannot be performed spectroscopically

Use of triplet-triplet energy transfer for mechanistic purposes

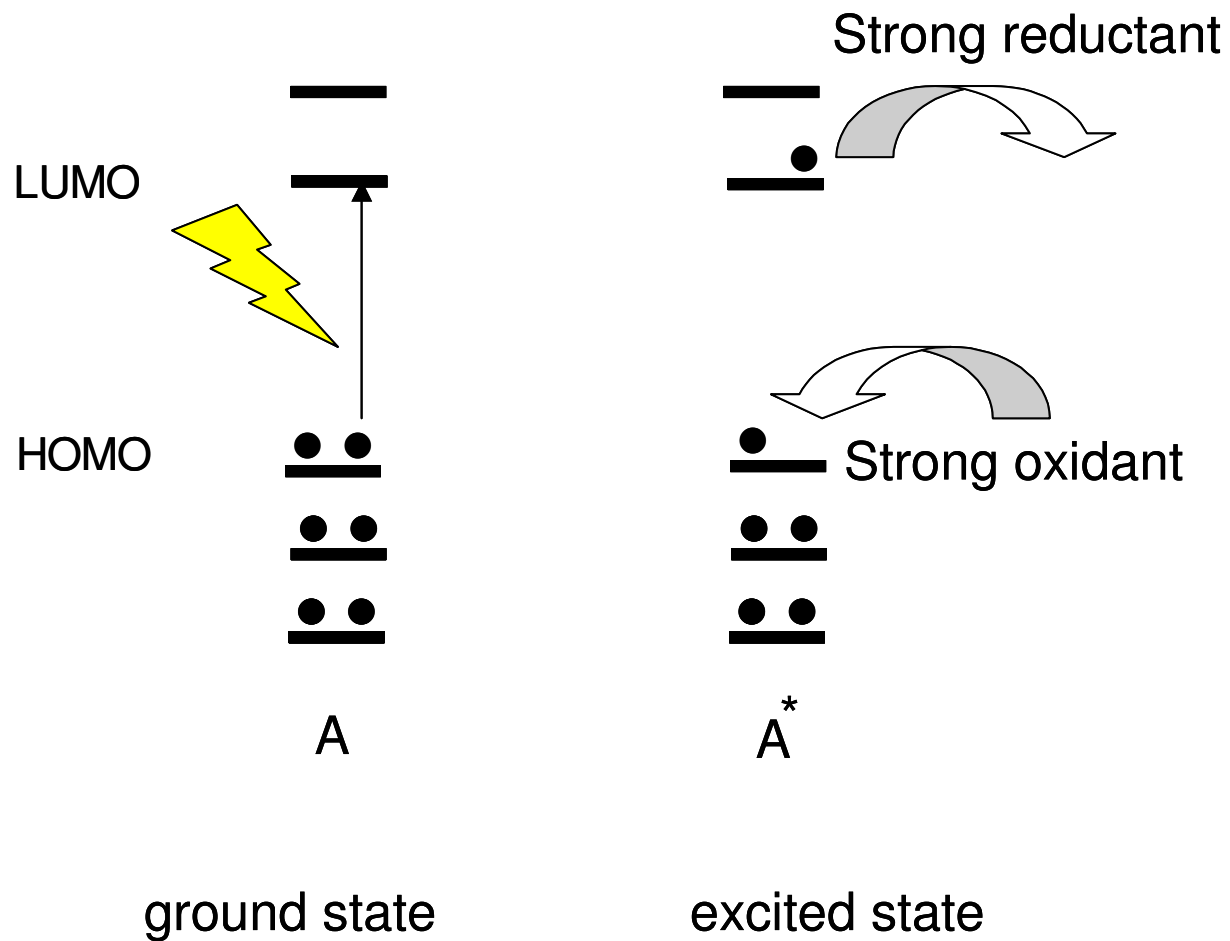


From a comparison between direct and sensitized photophysics, the efficiency of intersystem crossing in the acceptor can be obtained (sensitization data extrapolated to infinite acceptor concentration, known intersystem crossing efficiency of the donor)

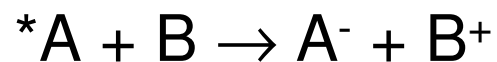
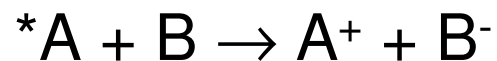
BIMOLECULAR PROCESSES: ELECTRON TRANSFER



- thermodynamic aspects
- kinetic aspects



An excited state is always expected to be *both a better oxidant and a better reductant* than the corresponding ground state



An evaluation of ΔG requires the knowledge of **excited-state redox potentials**.

Excited-state redox potentials can be calculated from ground-state values and excitation energy as follows:

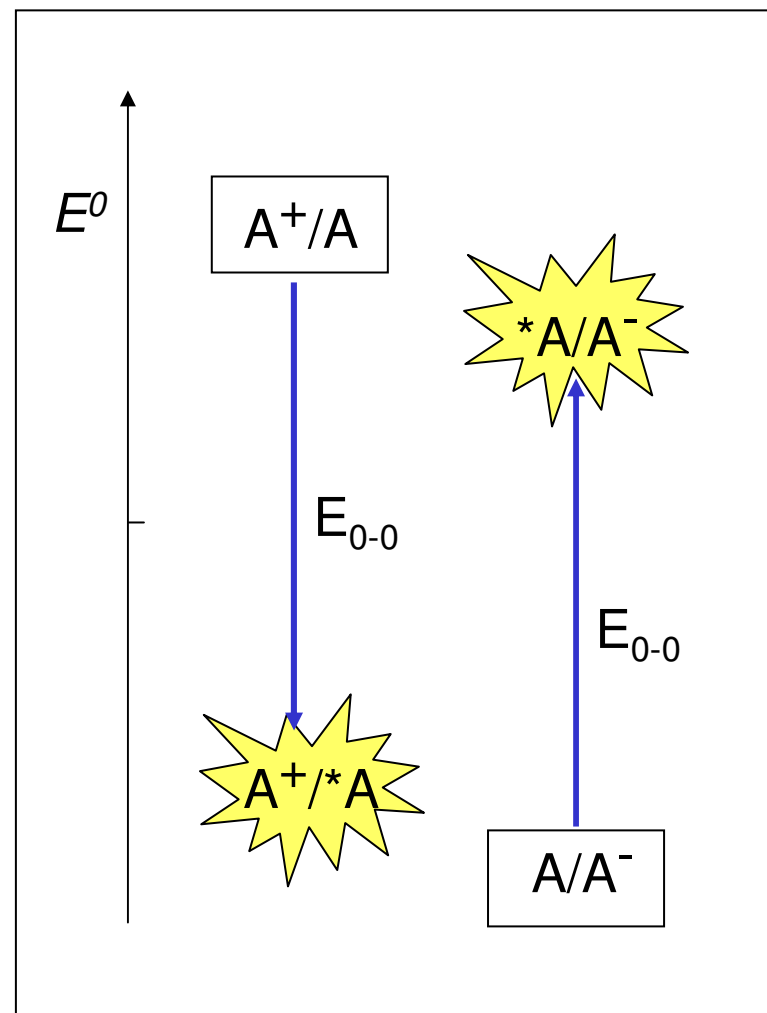
$$\Delta G^0(X^*/X) = \Delta H^0(X^*/X) - T\Delta S^0(X^*/X)$$

$$\Delta H^0(X^*/X) \approx E_{0-0} \gg T\Delta S^0(X^*/X),$$

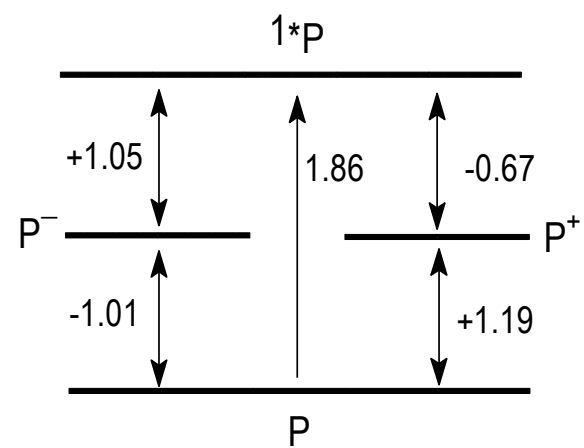
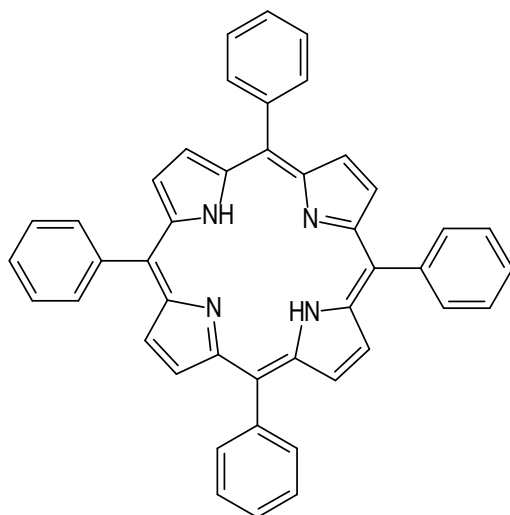
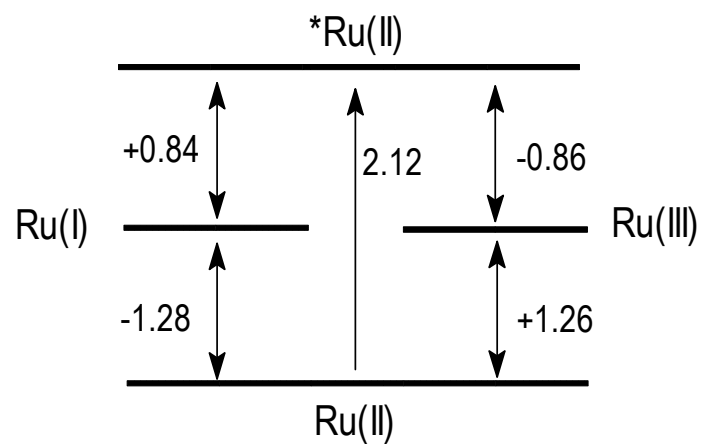
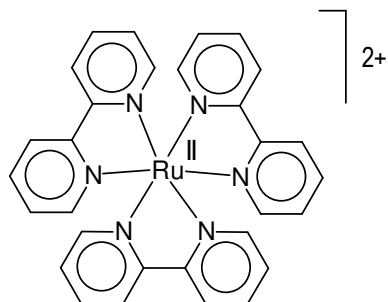
$$\Delta G^0(X^*/X) \approx E_{0-0}$$

$$E^0(A^+/^*A) = E^0(A^+/A) - E_{0-0}(A)$$

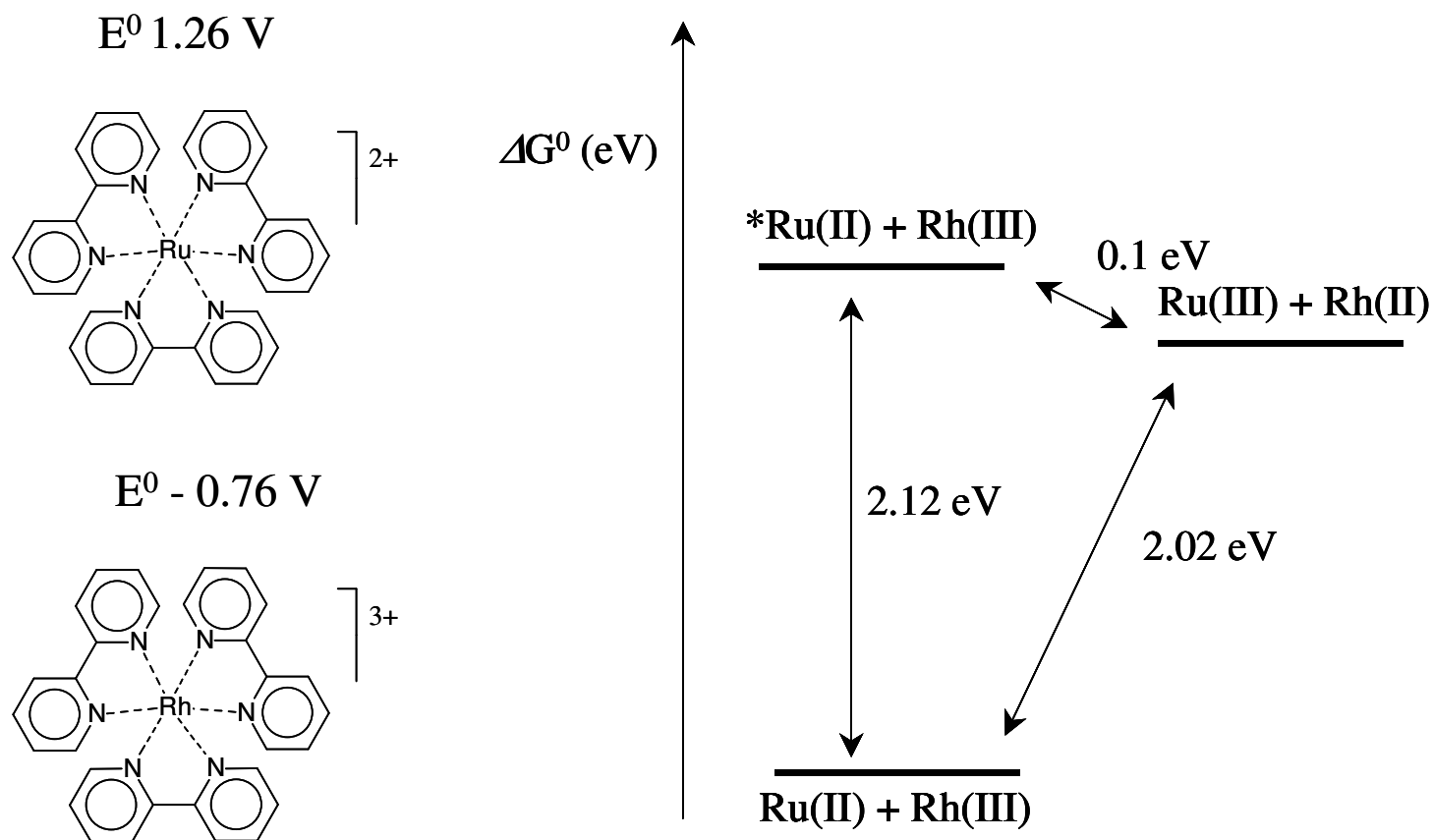
$$E^0(^*A/A^-) = E^0(A/A^-) + E_{0-0}(B)$$



Typical inorganic and organic chromophores



An example):



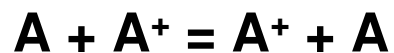
- A strongly forbidden ground-state process becomes thermodynamically allowed upon excitation of one reactant
- Once formed, the products inevitably tend to undergo back electron transfer to ground-state reactants (*charge recombination*)

Kinetic aspects

- One-electron redox processes are usually considered to be “fast” (on conventional time scales)
- However, their rates may vary over a substantial kinetic range (see next)
- Kinetics is important when short-lived excited states are involved

A very simple class of ET reactions:

Self-Exchange ($\Delta G = 0$)



Reaction	k_{obs} ($\text{M}^{-1}\text{s}^{-1}$)
$\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$	4.2
$\text{Ru}(\text{H}_2\text{O})_6^{2+} + \text{Ru}(\text{H}_2\text{O})_6^{3+}$	$\sim 10^2$
$\text{Ru}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$	3×10^3
$\text{Co}(\text{NH}_3)_6^{2+} + \text{Co}(\text{NH}_3)_6^{3+}$	$\sim 10^{-7}$
$\text{Co}(\text{bpy})_3^{2+} + \text{Co}(\text{bpy})_3^3$	20
$\text{Ru}(\text{bpy})_3^{2+} + \text{Ru}(\text{bpy})_3^3$	4×10^8

Note: 15 orders of magnitude difference in k!

Classical ET Model (“Marcus model”)

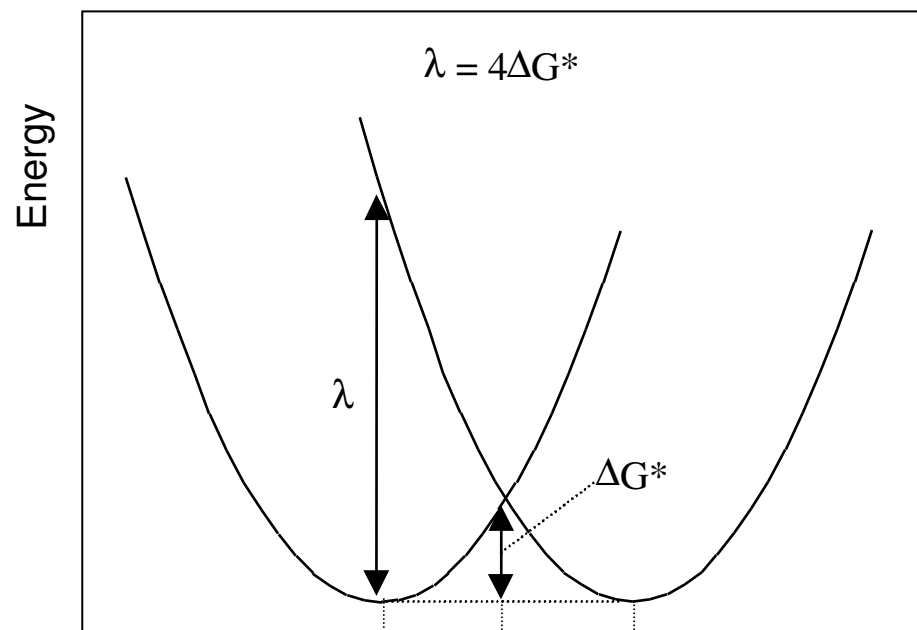
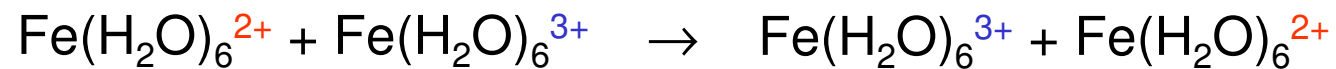
$$k = \nu_N \kappa_e \exp\left(\frac{\Delta G^*}{RT}\right)$$



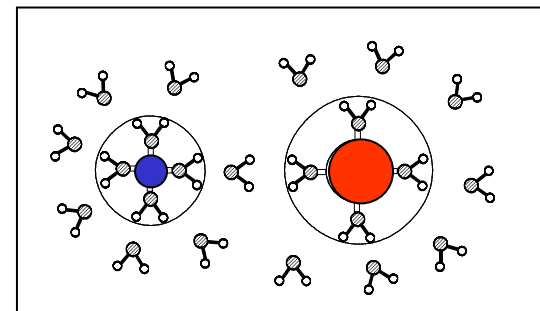
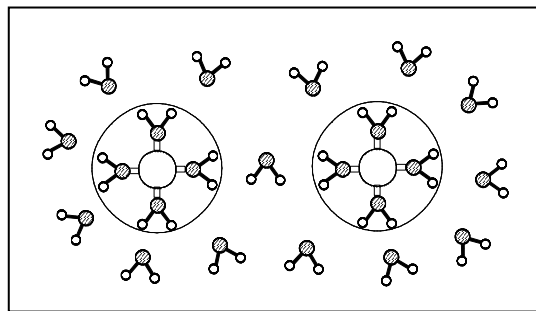
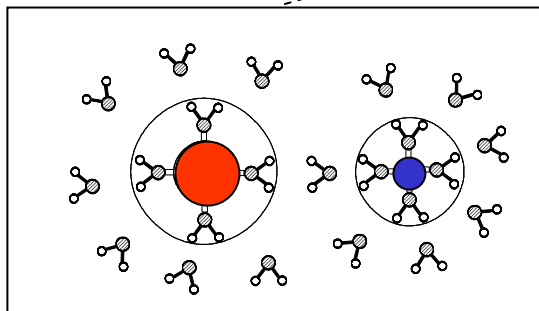
R. A. Marcus (Nobel Prize 1992)

Reaction coordinate and activation energy

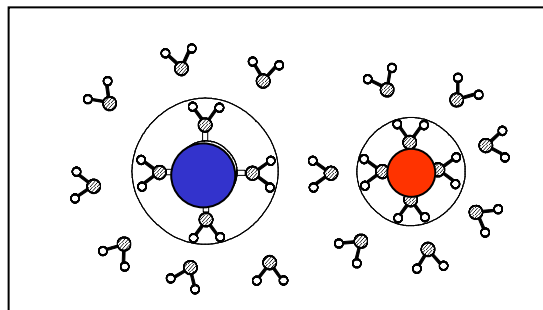
$$k = \nu_N \kappa_e \exp\left(\frac{\Delta G^*}{RT}\right)$$



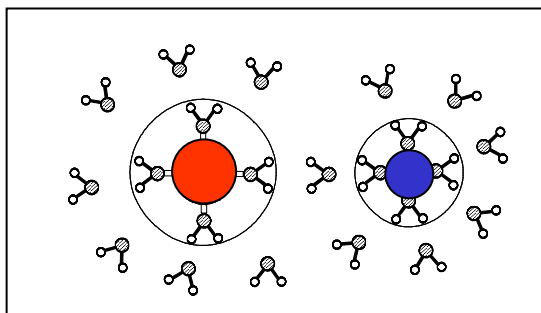
nuclear geometry



$\lambda = \text{reorganizational energy}$



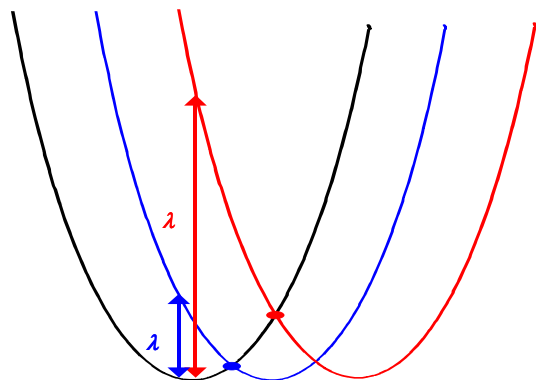
λ



$$\lambda = \lambda_i + \lambda_o$$

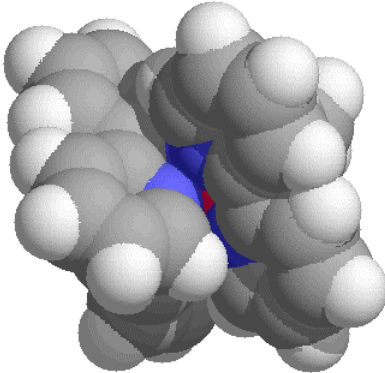
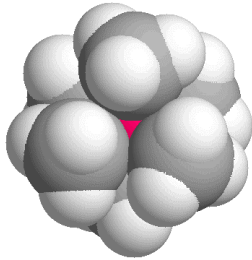
$$\lambda_o = e^2 \left(\frac{1}{2r_A} + \frac{1}{2r_B} - \frac{1}{r_{AB}} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right)$$

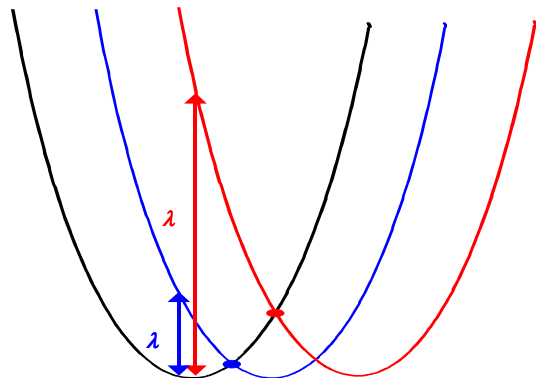
$$\lambda_i = \frac{1}{2} k \Delta Q^2$$



Effect of λ_0

Reaction	$k_{\text{obs}} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\text{Fe(H}_2\text{O)}_6^{2+} + \text{Fe(H}_2\text{O)}_6^{3+}$	4.2
$\text{Ru(H}_2\text{O)}_6^{2+} + \text{Ru(H}_2\text{O)}_6^{3+}$	$\sim 10^2$
$\text{Ru(NH}_3\text{)}_6^{2+} + \text{Ru(NH}_3\text{)}_6^{3+}$	3×10^3
$\text{Co(NH}_3\text{)}_6^{2+} + \text{Co(NH}_3\text{)}_6^{3+}$	$\sim 10^{-7}$
$\text{Co(bpy)}_3^{2+} + \text{Co(bpy)}_3^3$	20
$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^3$	4×10^8

<p>$\text{Ru(bpy)}_3^{2+/3}$</p> <p>$4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$</p>  <p>$d = 14 \text{ \AA}$ $\lambda_0 = 12.8 \text{ kcal/mol}$</p>	<p>$\text{Ru(NH}_3\text{)}_6^{2+/3+}$</p> <p>$3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$</p>  <p>$d = 7 \text{ \AA}$ $\lambda_0 = 25.6 \text{ kcal/mol}$</p>
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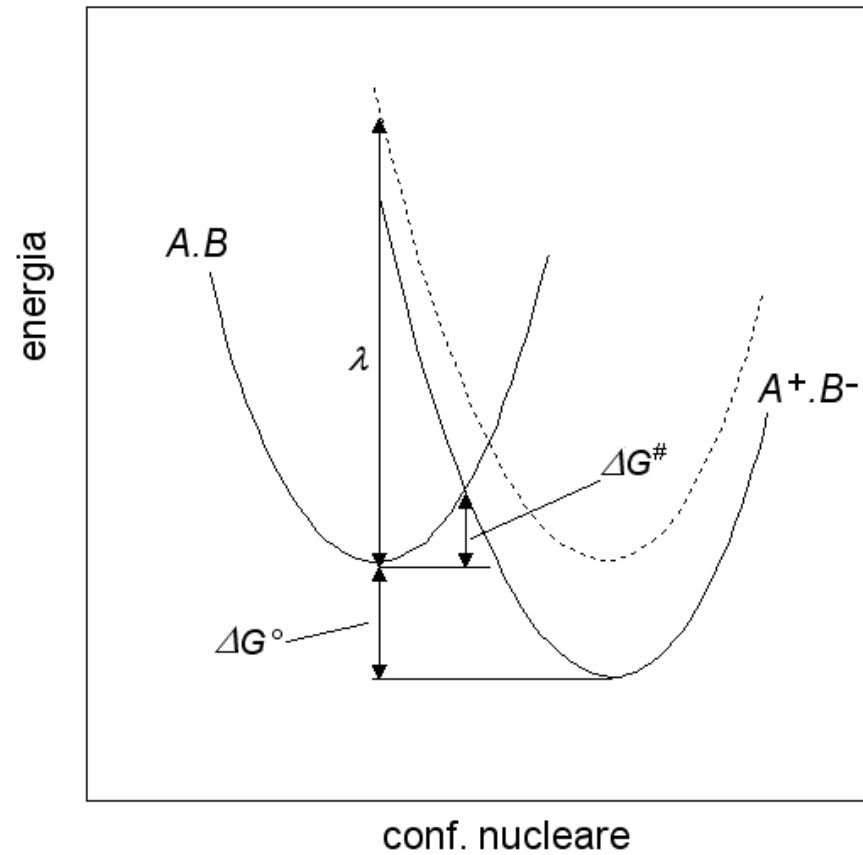


Effect of λ_i

Reaction	k_{obs} ($\text{M}^{-1}\text{s}^{-1}$)
$\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$	4.2
$\text{Ru}(\text{H}_2\text{O})_6^{2+} + \text{Ru}(\text{H}_2\text{O})_6^{3+}$	$\sim 10^2$
$\text{Ru}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$	3×10^3
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$\text{Ru}(\text{bpy})_3^{2+} + \text{Ru}(\text{bpy})_3^3$	4×10^8

$\text{Ru}(\text{NH}_3)_6^{2+/3+}$	$\text{Co}(\text{NH}_3)_6^{2+/3+}$
$3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	$\sim 10^{-7} \text{ M}^{-1}\text{s}^{-1}$
<div style="border: 1px solid blue; padding: 5px;"> $\begin{array}{c} e_g^* \text{ --- } \\ t_{2g} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \\ \text{Ru(III)} \end{array}$ </div>	<div style="border: 1px solid blue; padding: 5px;"> $\begin{array}{c} e_g^* \text{ --- } \\ t_{2g} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \\ \text{Co(III)} \end{array}$ </div>
<div style="border: 1px solid blue; padding: 5px;"> $\begin{array}{c} e_g^* \text{ --- } \\ t_{2g} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \\ \text{Ru(II)} \end{array}$ </div>	<div style="border: 1px solid blue; padding: 5px;"> $\begin{array}{c} e_g^* \uparrow \uparrow \\ t_{2g} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \\ \text{Co(II)} \end{array}$ </div>
$\lambda_i = \text{small}$	$\lambda_i = \text{very large}$

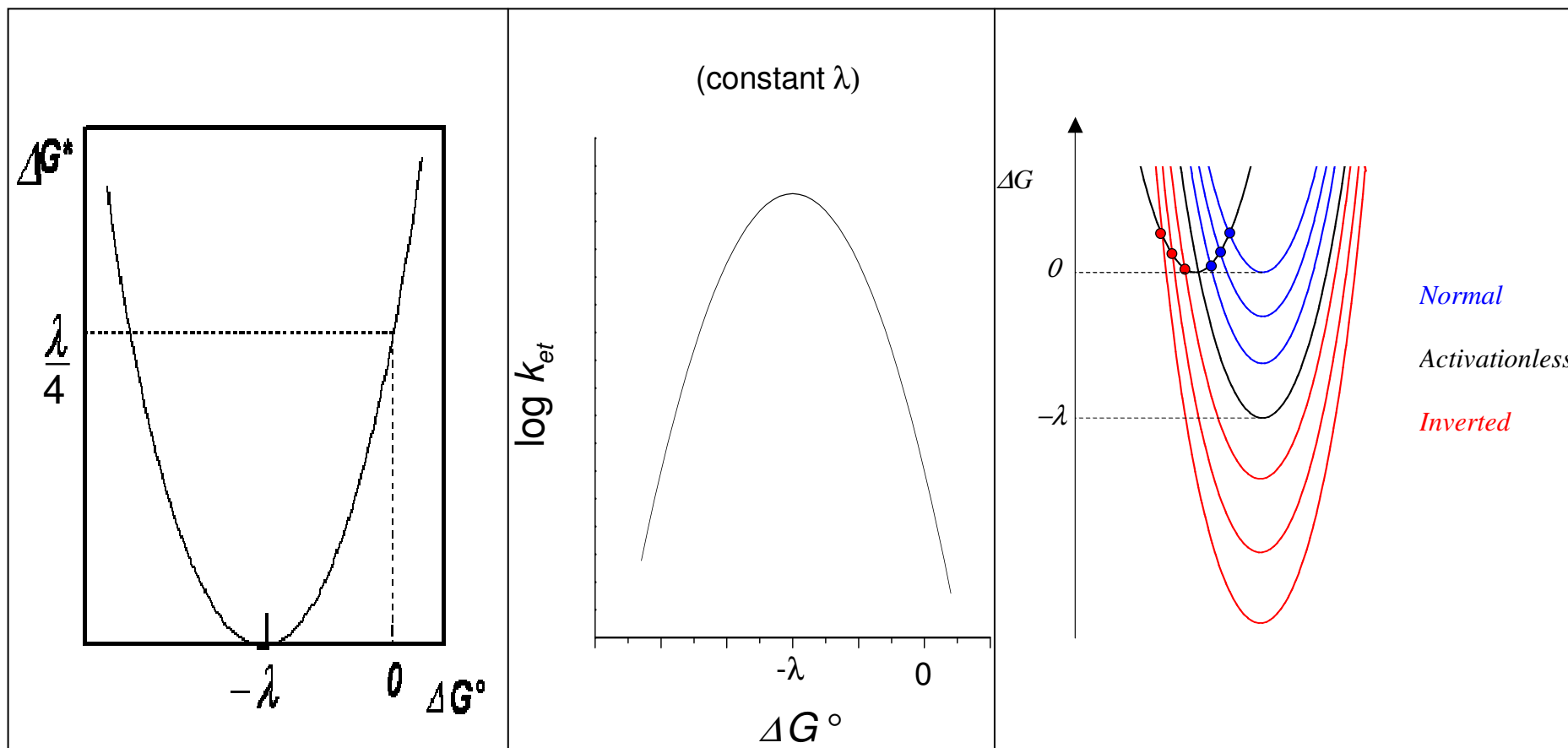
Cross-reaction ($\Delta G \neq 0$)



$$\Delta G^\# = f(\Delta G, \lambda)$$

Marcus free-energy relationship (FER)

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4\lambda}$$

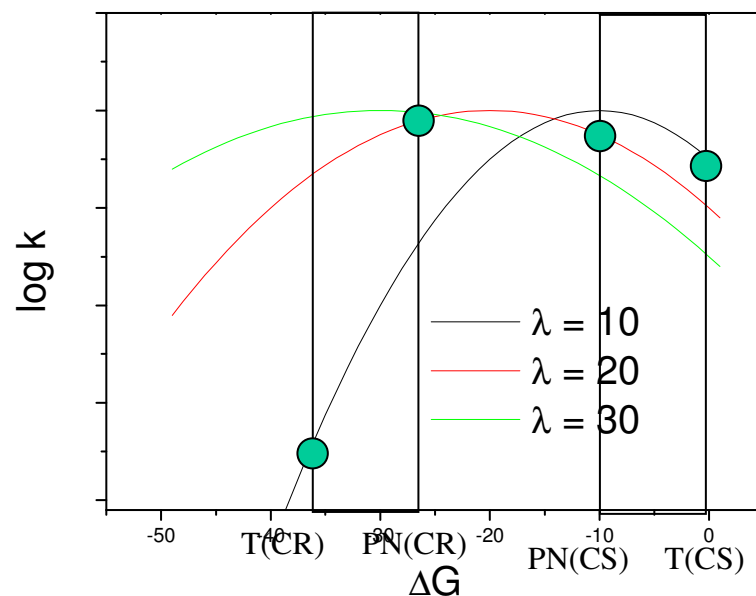


Summary: combined effects of ΔG and λ (nuclear factor)

For moderately exergonic processes (normal region), fast ET requires small λ (less polar solvents, large molecules, delocalized redox orbitals)

For highly exergonic processes (inverted region), the role of λ is reversed: with small λ the process slows down as it gets more inverted

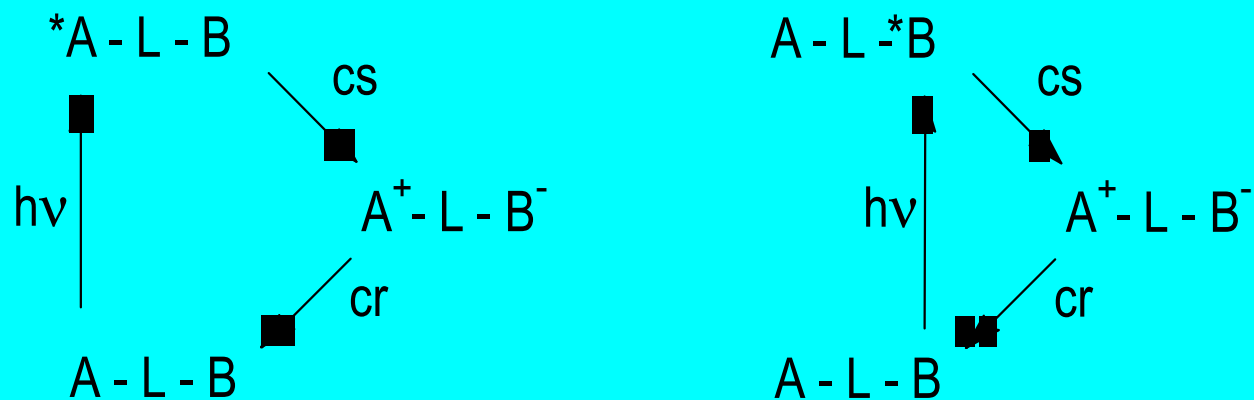
In order to obtain very fast (activationless) ET processes, the driving force must be chosen so as to match the reorganizational energy $\Delta G = -\lambda$



Photoinduced bimolecular ET processes



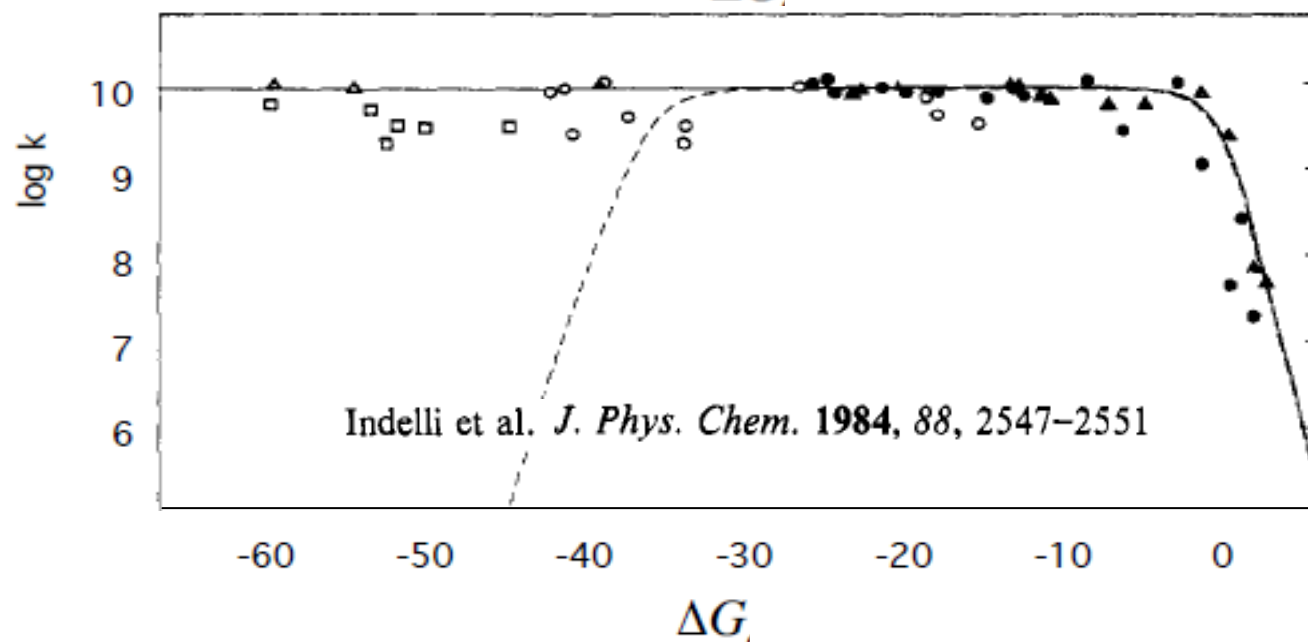
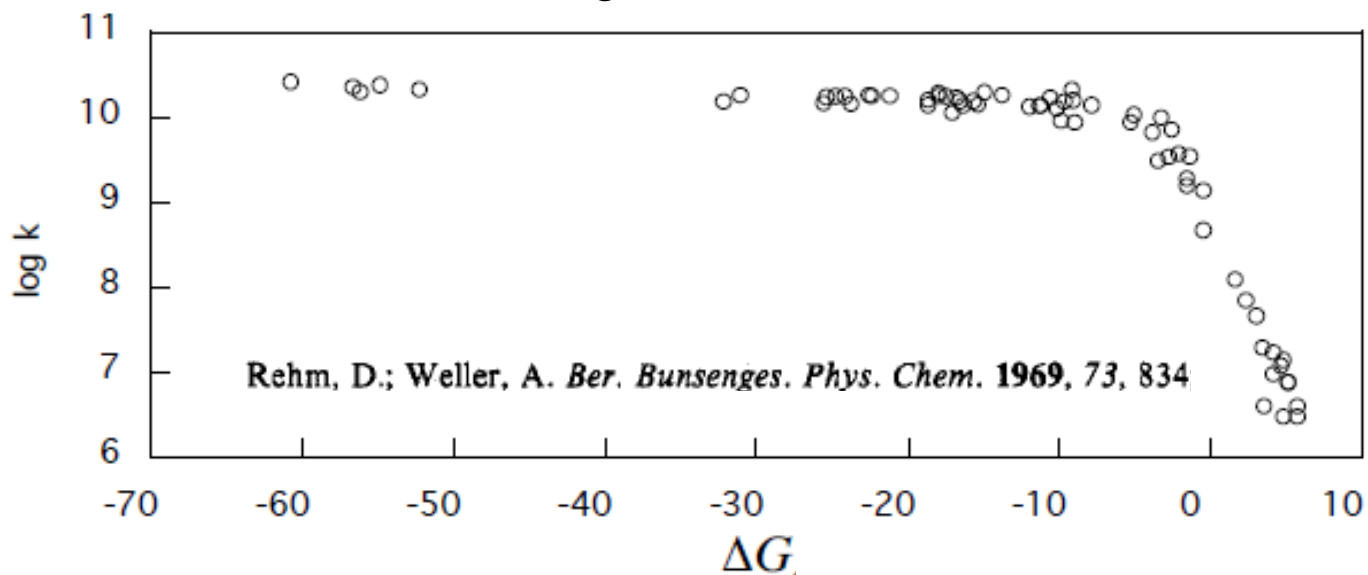
Photoinduced ET processes in covalently linked donor-acceptor systems ("dyads")



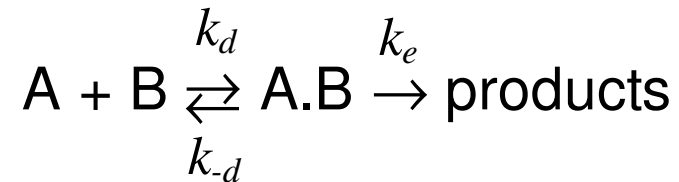
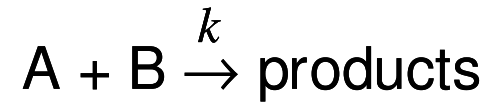
Advantages: well-defined geometry, lack of diffusional cut-off, possibility to tune electronic coupling (bridge effects)

Tests of the Marcus Inverted Region in $A + B + h\nu$ systems

negative results



Bimolecular processes: role of diffusion and kinetic regimes

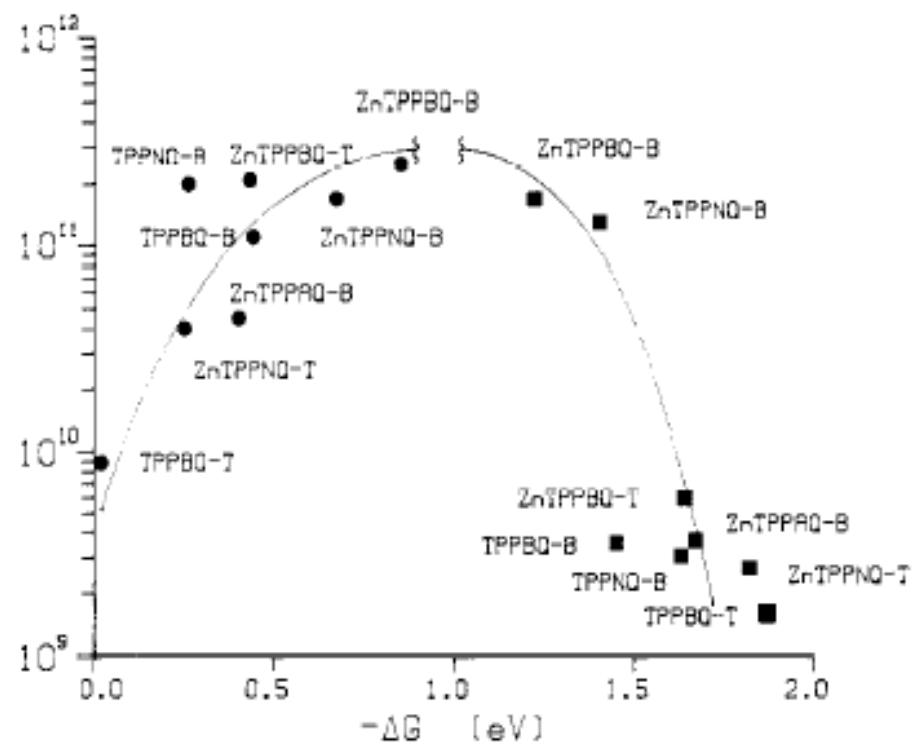
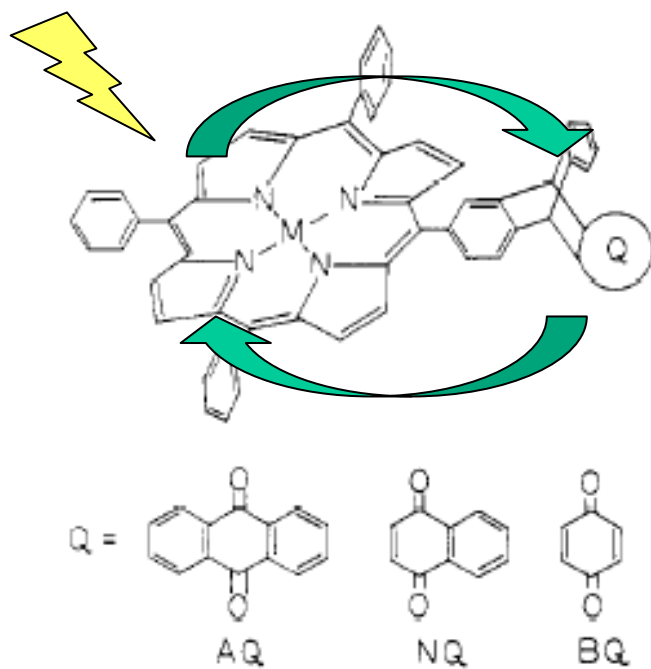
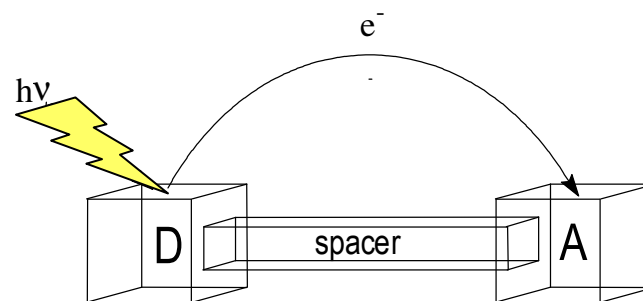


$$k = k_d \frac{k_e}{k_e + k_{-d}}$$

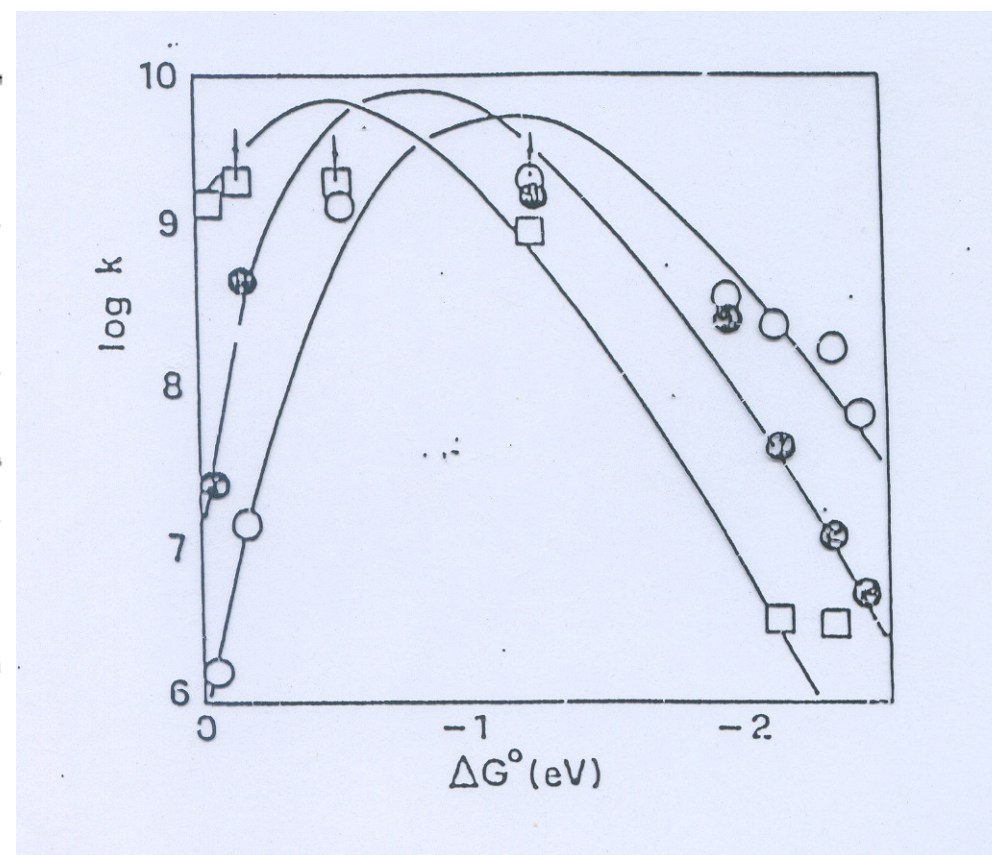
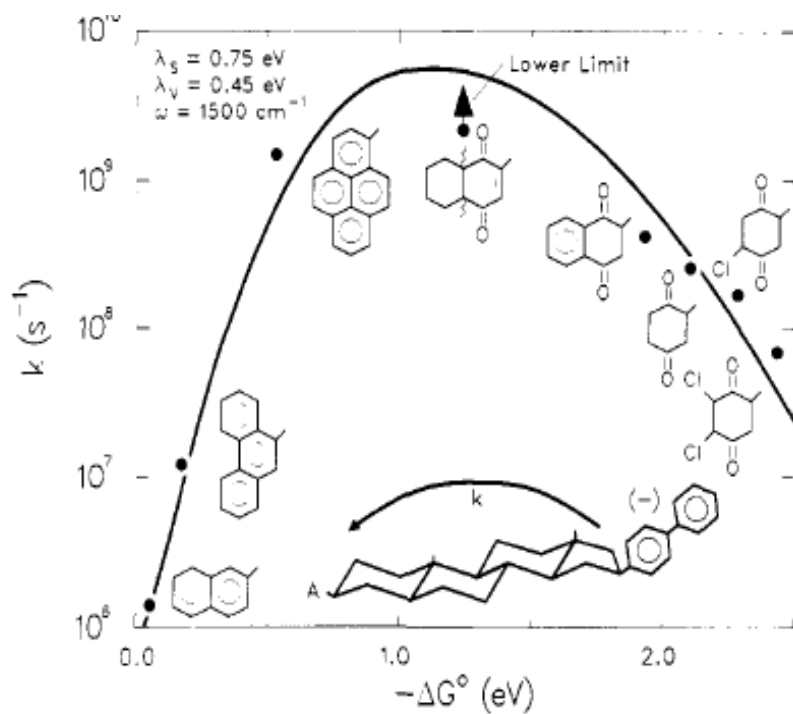
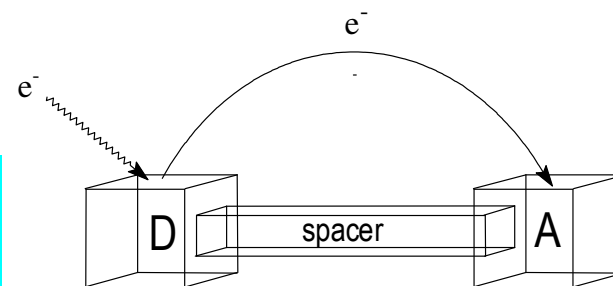
If $k_e \gg k_{-d}$ $k = k_d$ (diffusion-controlled limit)

If $k_e \ll k_{-d}$ $k = \frac{k_d}{k_{-d}} k_e$ (reaction-controlled regime)

Experimental evidence for the Marcus inverted region (M. R. Wasielewski, 1984)



Experimental evidence for the Marcus inverted region (G. L. Closs & J. R. Miller, 1988)



$$k = \nu_N \kappa_e \exp\left(\frac{\Delta G^*}{RT}\right)$$

ν_N = “weighted” average nuclear frequency

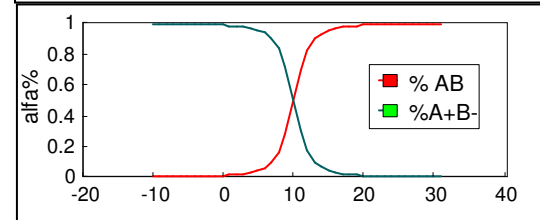
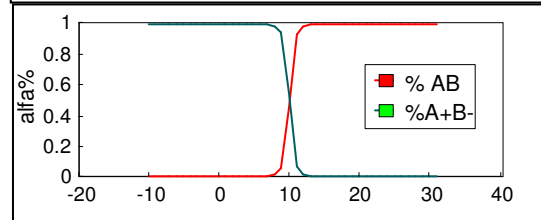
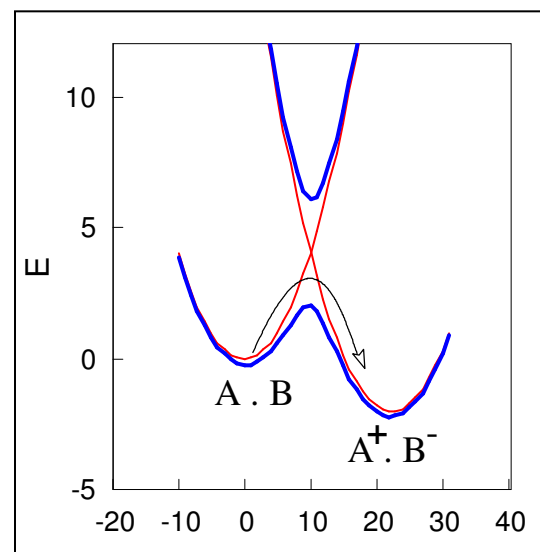
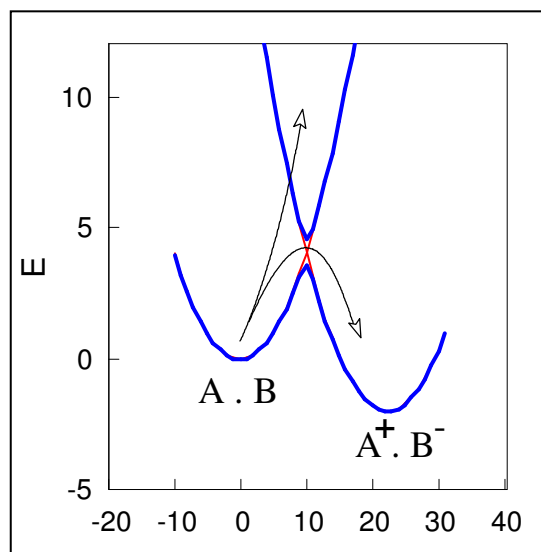
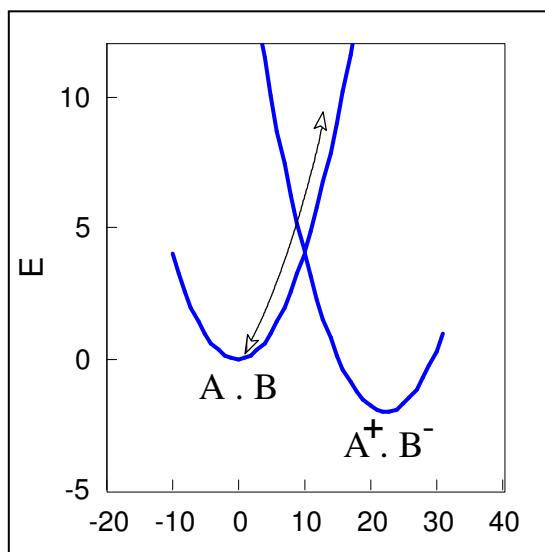
$$\nu_N = \frac{(\nu_i \lambda_i + \nu_o \lambda_o)}{\lambda}$$

Molecular vibrations, ν_i of the order of 10^{13} s^{-1})

Solvent repolarization, ν_i of the order of 10^{10} s^{-1}

$$k = \nu_N \kappa_e \exp\left(\frac{\Delta G^*}{RT}\right)$$

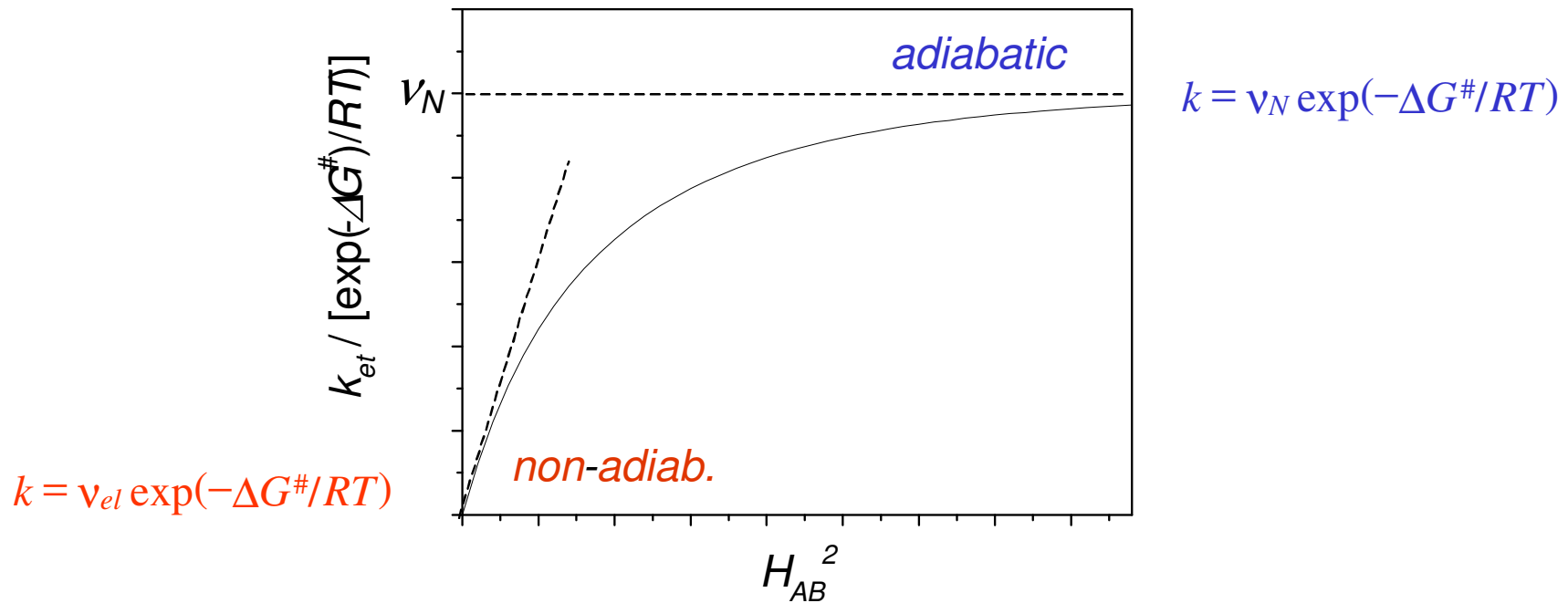
The transmission coefficient κ_e is related to the magnitude of the **electronic interaction** between reactants, i.e., on the details of the intersection region (avoided crossing) of reactants and product curves.



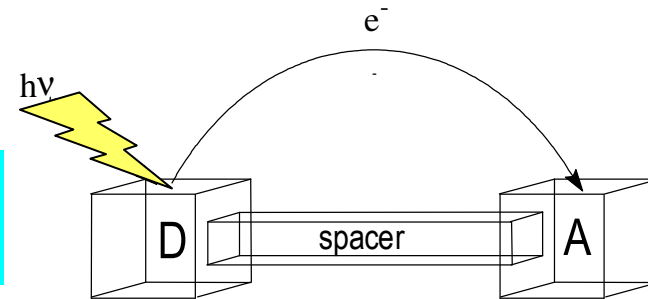
$$k = \nu_N \kappa_e \exp(-\Delta G^\# / RT)$$

Landau-Zener

$$k_e = \frac{2[1 - \exp(-\nu_{el}/2\nu_N)]}{2 - \exp(-\nu_{el}/2\nu_N)} \quad \nu_{el} = \frac{2\pi H_{AB}^2}{h} \left(\frac{1}{4\pi\lambda RT} \right)^{1/2}$$

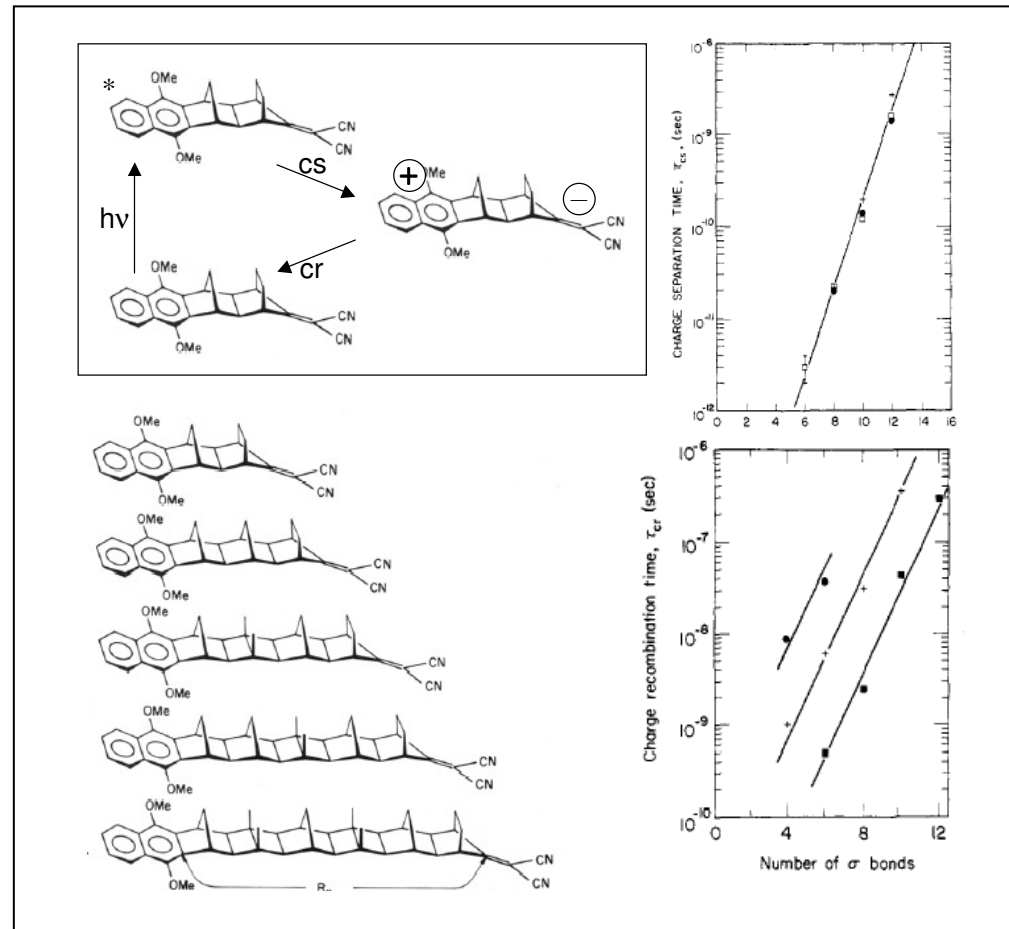


Donor-acceptor distance effects (J. Verhoeven & M. N. Paddon-Row, 1988)



$$H_{AB} = H_{AB}(0) \exp\left[-\frac{\beta}{2}(r_{AB} - r_0)\right]$$

$$k_{el} = k_{el}(0) \exp[-\beta(r_{AB} - r_0)]$$

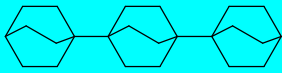
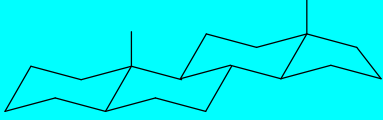
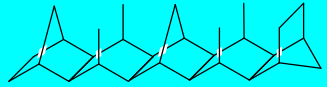
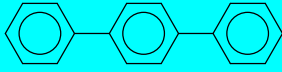
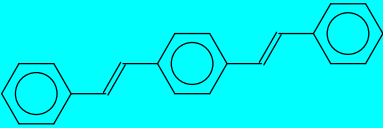
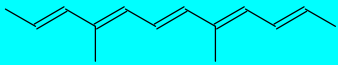


Dependence of attenuation factor β on chemical nature of the bridge

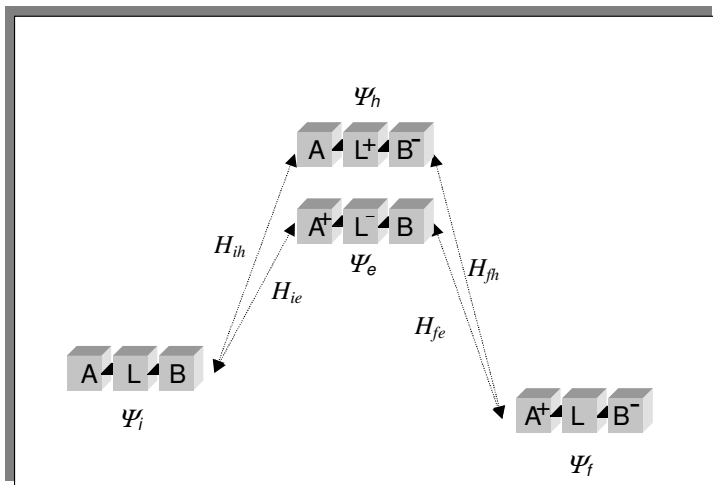
β depends on the chemical nature of the bridge

Saturated bridges are less “conductive” than unsaturated ones

NOTE: bridge “conduction” is not ohmic. The redox orbitals of the bridge are too high in energy. The electron goes in one coherent step from donor to acceptor, without being localized at any time on the bridge.

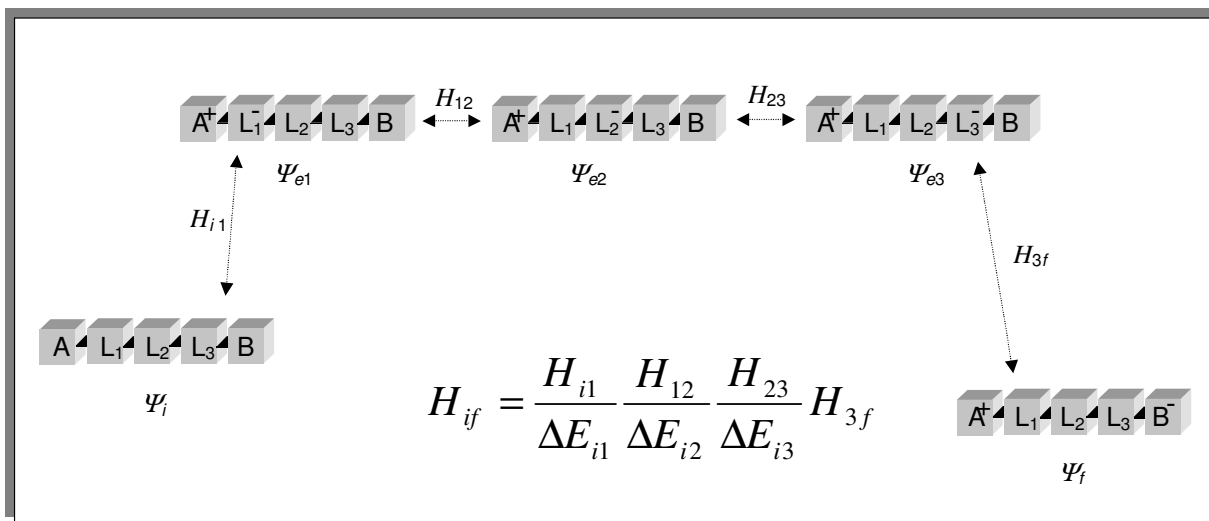
bridge	β (\AA^{-1})
	1.2
	0.80
	0.77
	0.50
	0.40
	0.1-0.2

Dependence of attenuation factor β on bridge chemical nature and length



Superexchange: indirect mixing of reactant and product states via high-energy ligand-localized charge transfer states ("virtual states")

$$H_{if} = \frac{H_{ie} H_{fe}}{\Delta E_e} + \frac{H_{ih} H_{fh}}{\Delta E_h}$$



$$H_{if} = \frac{H_{i1}}{\Delta E_{i1}} \frac{H_{12}}{\Delta E_{i2}} \frac{H_{23}}{\Delta E_{i3}} H_{3f}$$

Modular bridges:
exponential distance dependence arises from inter-module interactions

Summary: role of the electronic factor

Many bimolecular electron transfer reactions, where the reactants can diffuse to encounters with good orbital overlap, are generally assumed to be in the adiabatic regime, with rates exclusively regulated by the activation term (nuclear factor).

Unimolecular processes taking place in systems where the reactants are held at fixed distance (e.g., in a protein matrix, in a polymeric material, or in covalently linked donor-bridge-acceptor systems) usually behave in the non-adiabatic regime, with rates controlled by electronic factors and thus sensitive to distance, orientation, chemical nature of interposed material)

NOTE: one-electron transfer processes have only been considered. The simultaneous transfer of two (or more) electrons is a low-probability (small H_{AB}) phenomenon. Thus, multi-electron transfer processes are intrinsically very slow.

Quantum aspects

The simple Marcus theory is based on a **classical** model (classical motion along the reaction coordinate, continuous energy changes). Appropriate only *if* the relevant nuclear motions have $h\nu \ll k_B T$ (at room temperature, $k_B T \gg 200 \text{ cm}^{-1}$).

- OK for solvent reorganization ($\nu_o \gg 1\text{-}2 \text{ cm}^{-1}$)
- not for molecular rearrangements ($\nu_i \gg 200\text{-}2000 \text{ cm}^{-1}$)

Quantum models (of various complexity) are available that:

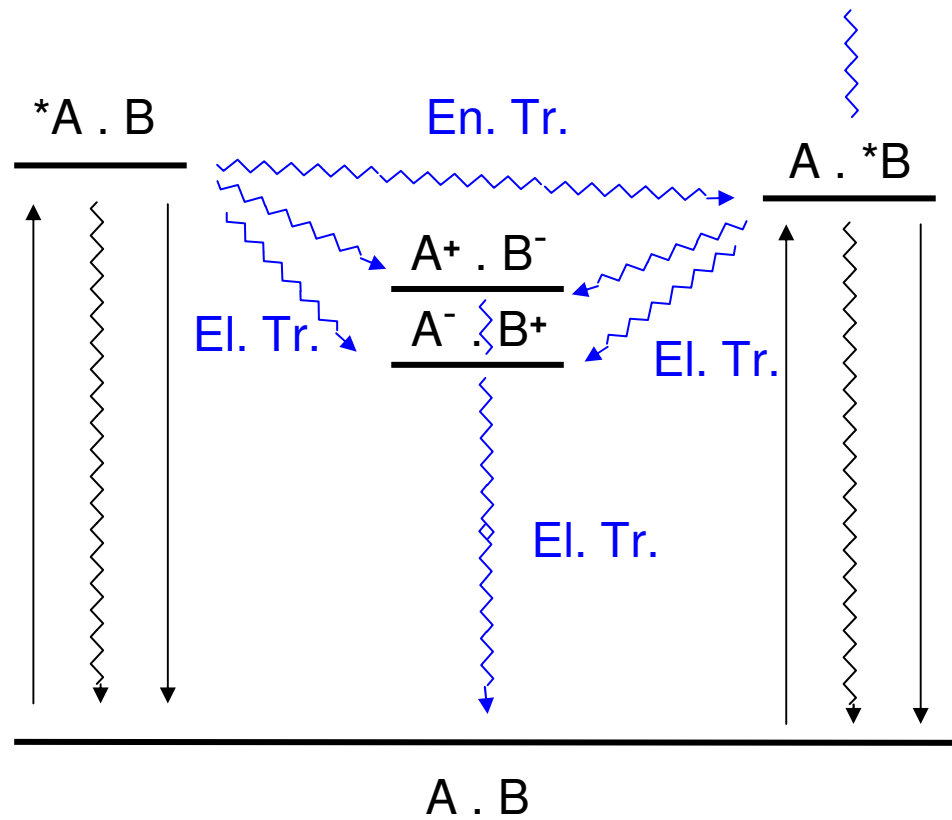
- Explicitly consider discrete energy levels for high energy nuclear motions
- Treat ET as radiationless transition (Fermi Golden Rule) between reactant and product states

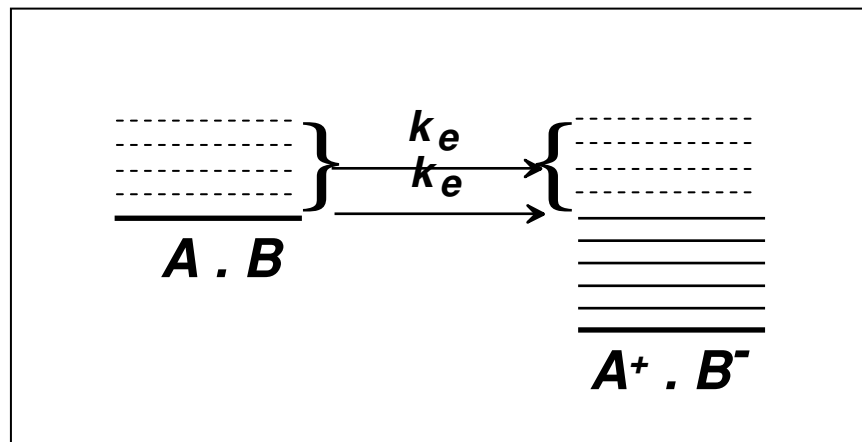
$$k_{el} = \frac{2\pi}{\hbar} H_{AB}^{el\ 2} FCWD^{el}$$

$FCWD$ = Franck-Condon term

(thermally weighted average over the reactant vibrational levels)

Electron Transfer
as a radiationless Transition
(within the A.B "supermolecule")





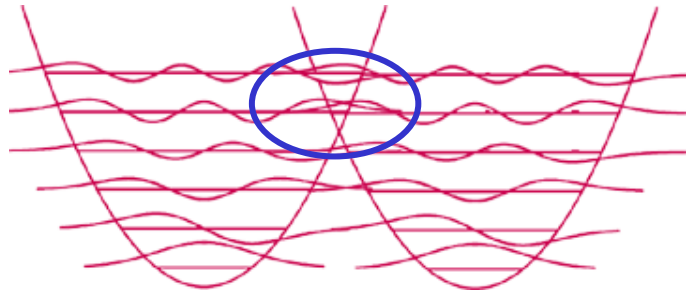
$$k_{el} = \frac{2\pi}{\hbar} H_{AB}^{el\ 2} FCWD^{el}$$

$FCWD$ = Franck-Condon term

(thermally weighted over the reactant vibrational levels)

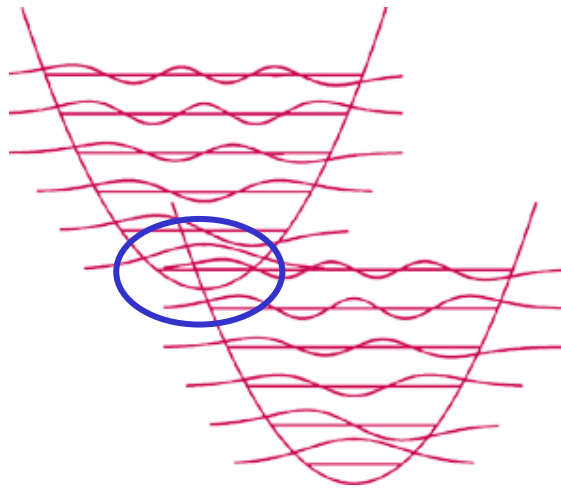
$$FCWD = \sum_n \exp\left(-\frac{nh\nu}{k_B T}\right) \int X_{A \cdot B}^n X_{A^+ \cdot B^-}^{m+n} dQ$$

$$mh\nu = \Delta E(A \cdot B - A^+ \cdot B^-)$$

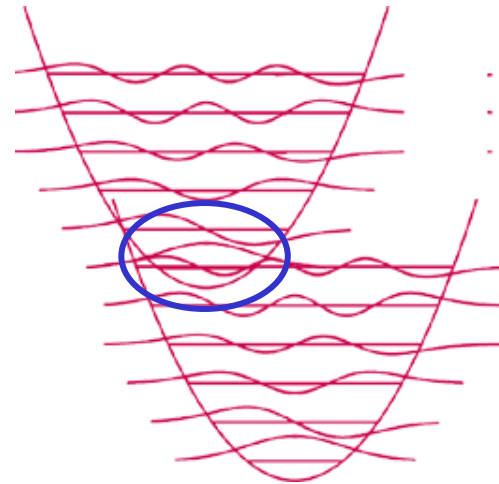


“normal” (activated)

“activationless”



“inverted”



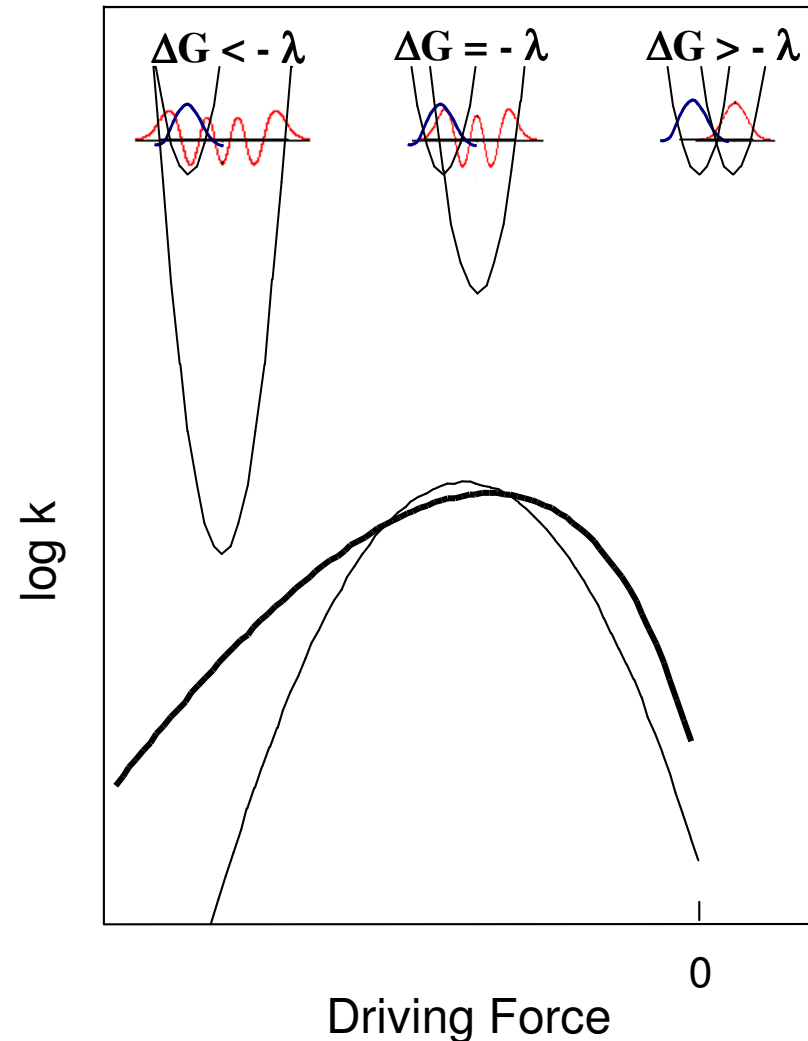
$$FCWD^{el} = \left(\frac{1}{4\pi\lambda_o k_B T} \right)^{\frac{1}{2}} \sum_m S^m \frac{e^{-S}}{m!} \exp \left[-\frac{(\Delta G^0 + \lambda_o + mh\nu_i)^2}{4\lambda_o k_B T} \right]$$

(single mode ν_i , harmonic, $\lambda_i = S \times \nu_i$)

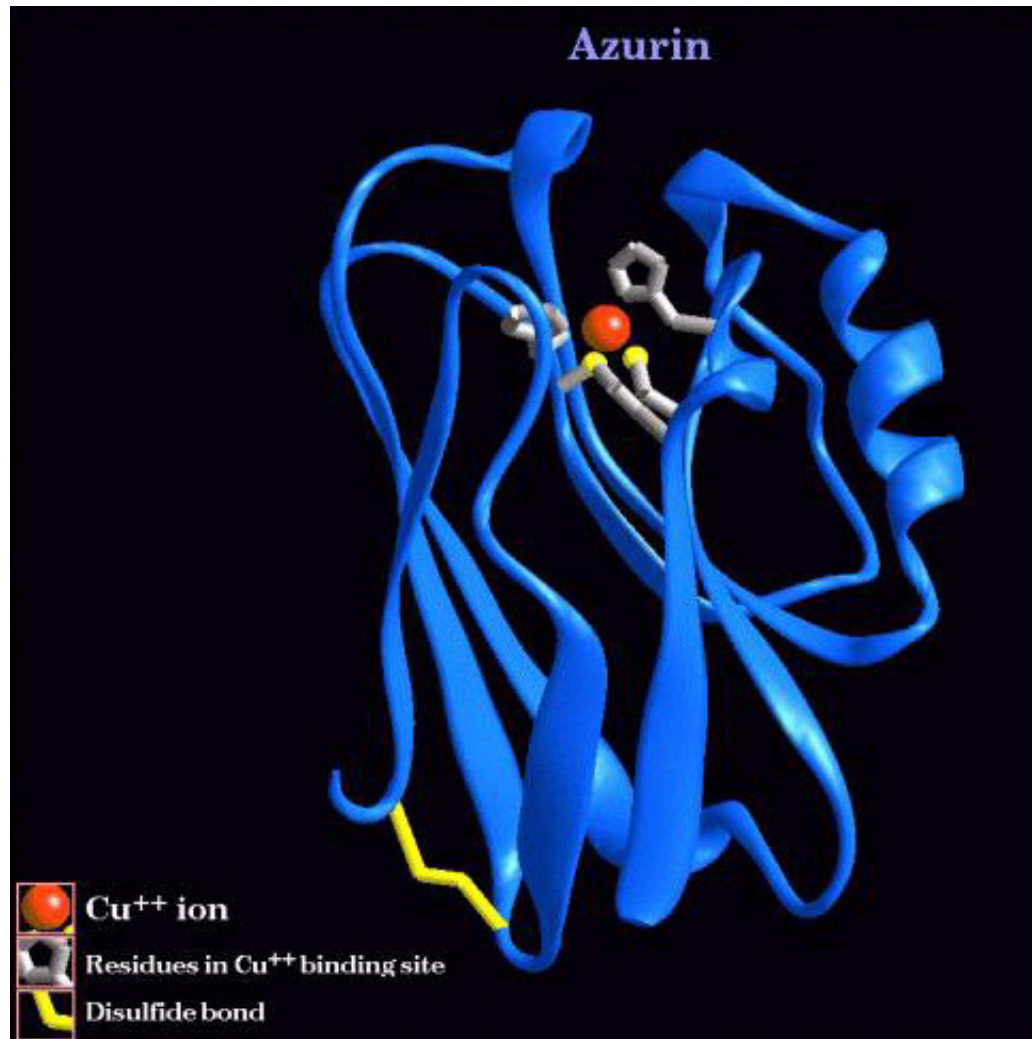
Quantum models

General behavior: qualitatively similar to classical Marcus theory

Inverted region somewhat less pronounced: linear (energy-gap law) instead of parabolic log k decrease



Blue copper-containing proteins function as electron transfer agents in nature (12). Azurin, a single blue copper protein, serves as an electron carrier in several bacteria and is a useful model system for investigating structure-function relationship in copper proteins

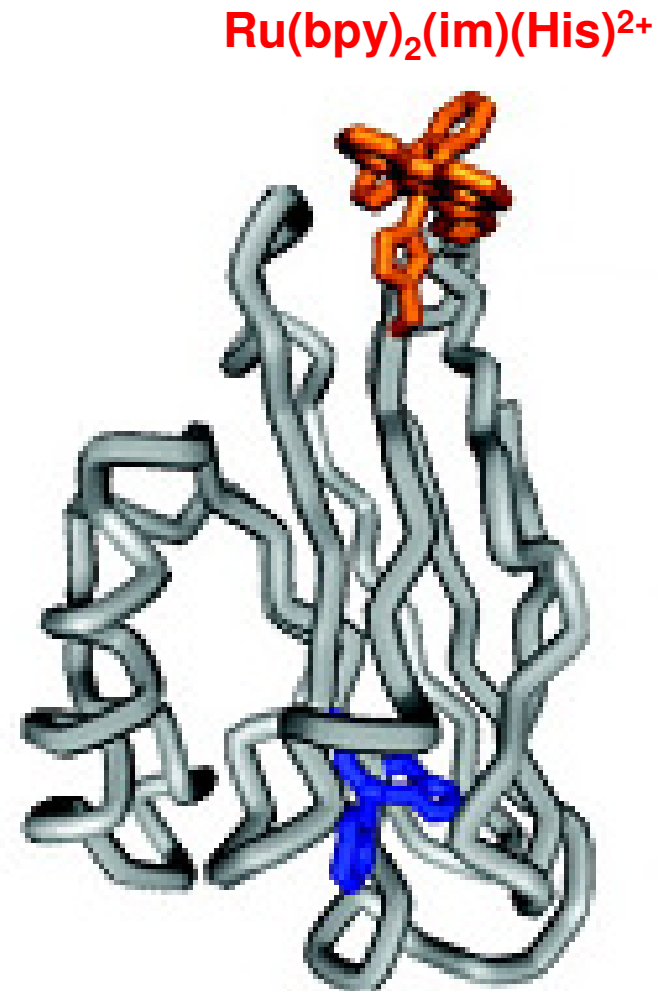


The geometry is somewhere between the preferred tetragonal geometry of Cu(II) and the (distorted) tetrahedral coordination preferred by Cu(I) . This means that there is no need for a significant structural change to accompany the redox reaction, accounting for the small reorganization energy and hence the high rate of electron transfer in azurin and its relatives.

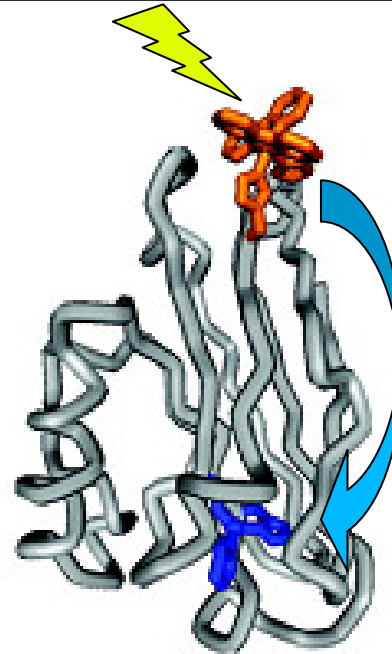
Azurin can be functionalized with a Ru(II) photoactive unit by coordination of a histidine residue (His129 in the Figure) to the metal.

Photoexcitation of the Ru(II) unit can be used to monitor electron transfer to/from the Cu center in two ways:

- PET**
- Flash-Quench**



Photoinduced Electron Transfer



Flash-Quench Experiment

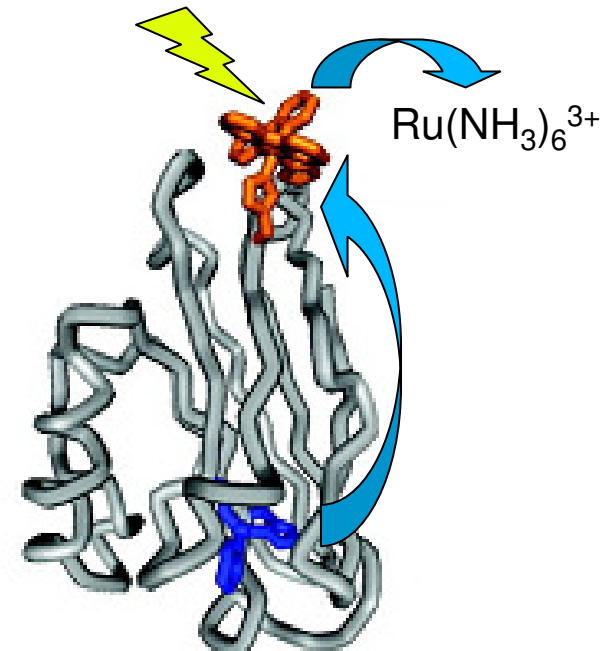
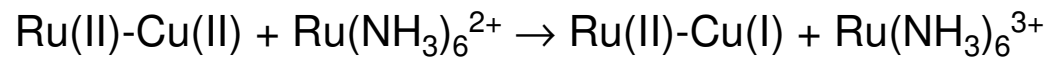
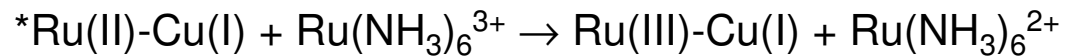
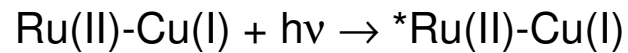
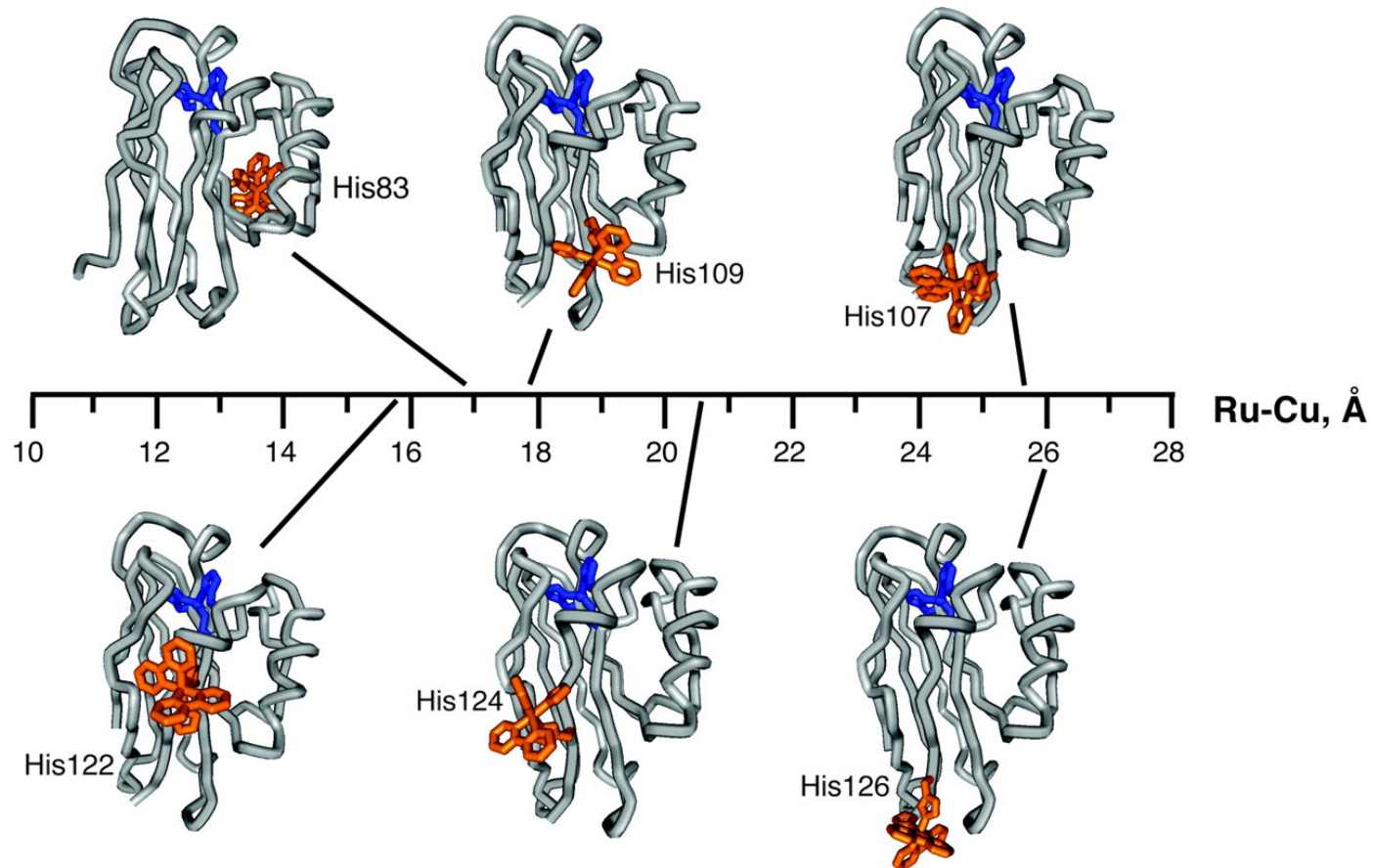


Fig. 2. Tunneling distances and backbone structure models showing locations of the Cu active site (blue) and the Ru(bpy)2(im)(HisX)2+ label (orange) in Ru-azurins: Ru-Cu (A), HisX (X = 122, 15.9; 83, 16.9; 109, 17.9; 124, 20.6; 107, 25.7; 126, 26.0)



Gray, Harry B. and Winkler, Jay R. (2005) Proc. Natl. Acad. Sci. USA 102, 3534-3539

Detailed through-bond electronic coupling pathways (“ET pathways”) can be identified by a variety of theoretical methods. In this case, parallel β -strands bridged by hydrogen bonds.

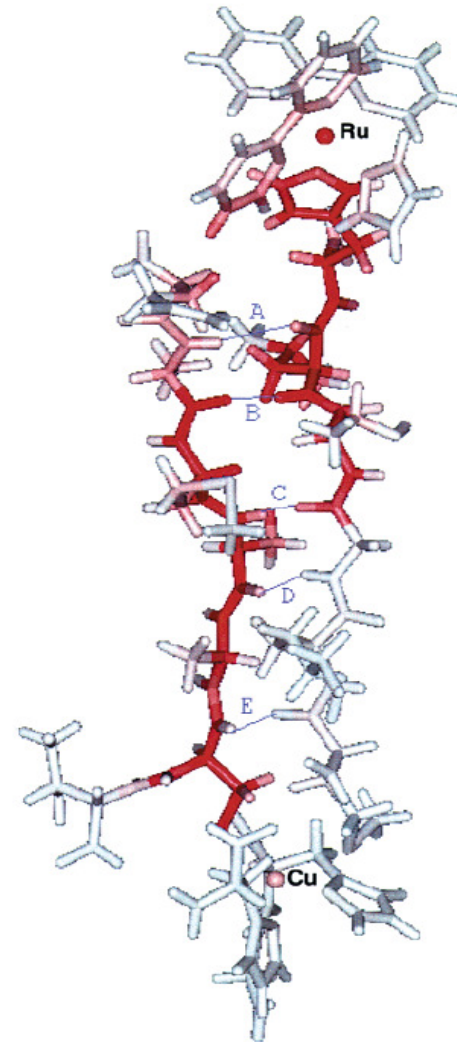
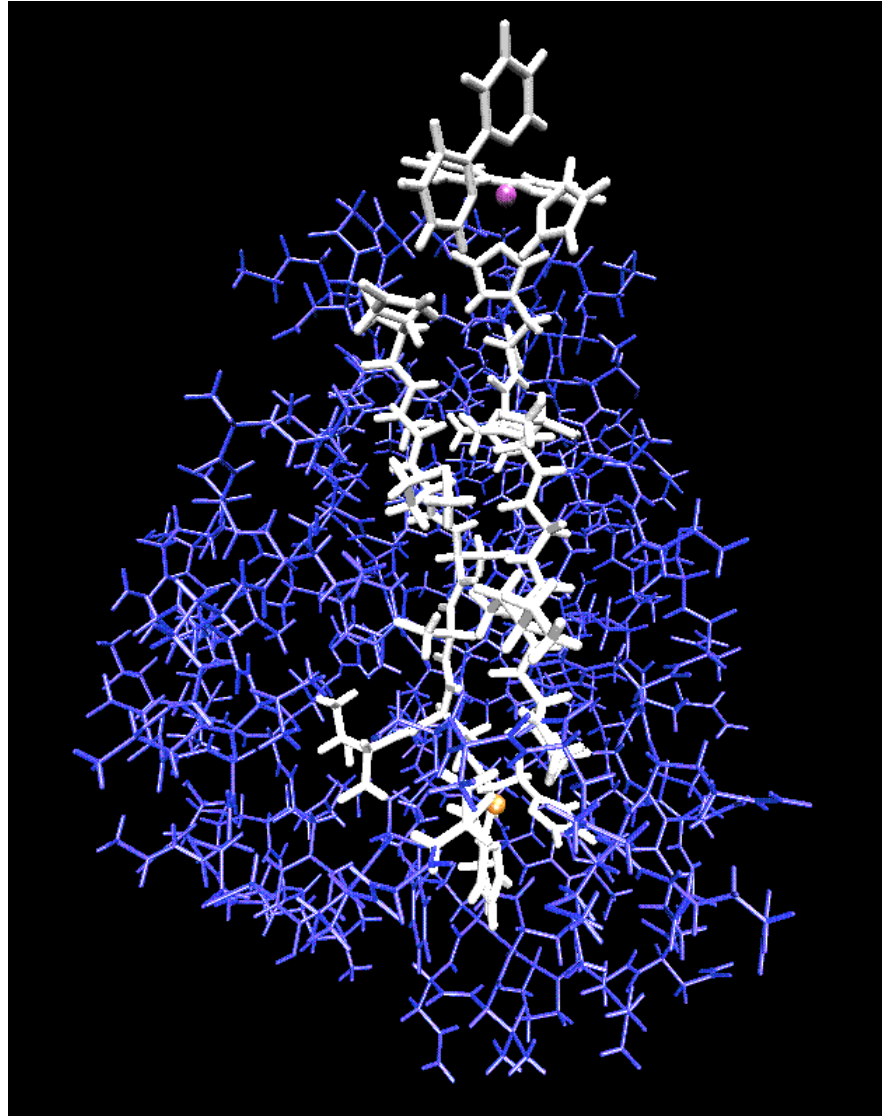
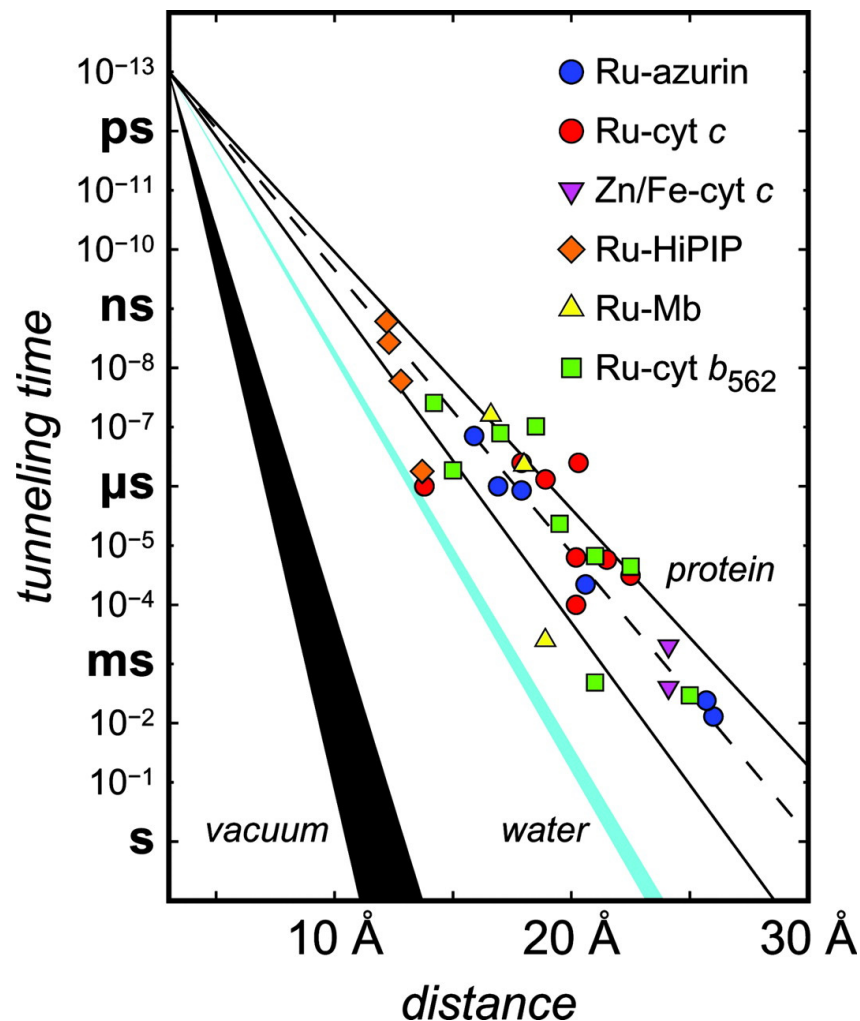
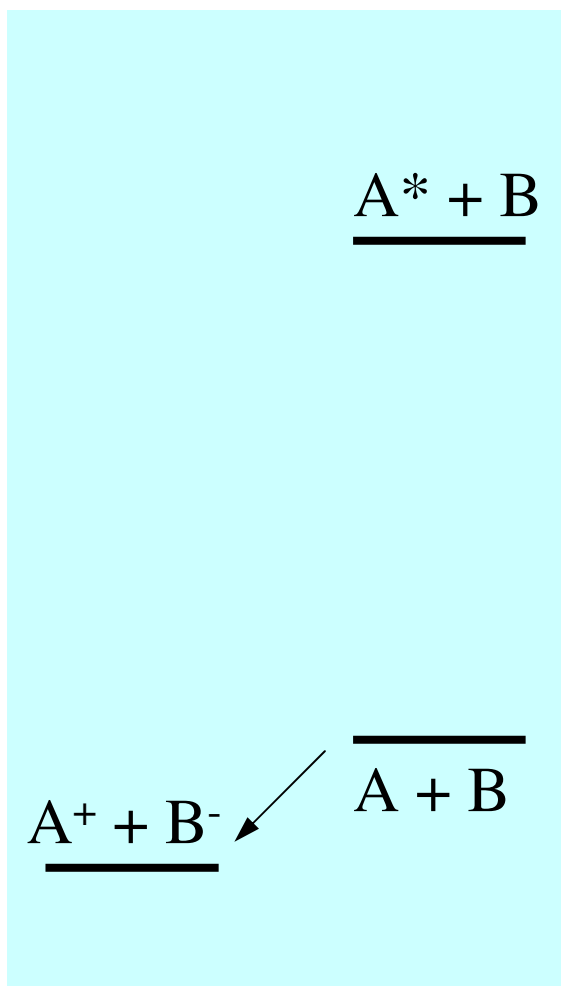


Fig. 3. Tunneling timetable for intraprotein ET in Ru-modified azurin (blue circles), cyt c (red circles), myoglobin (yellow triangles), cyt b562 (green squares), HiPIP (orange diamonds), and for interprotein ET Fe:Zn-cyt c crystals (fuchsia triangles)

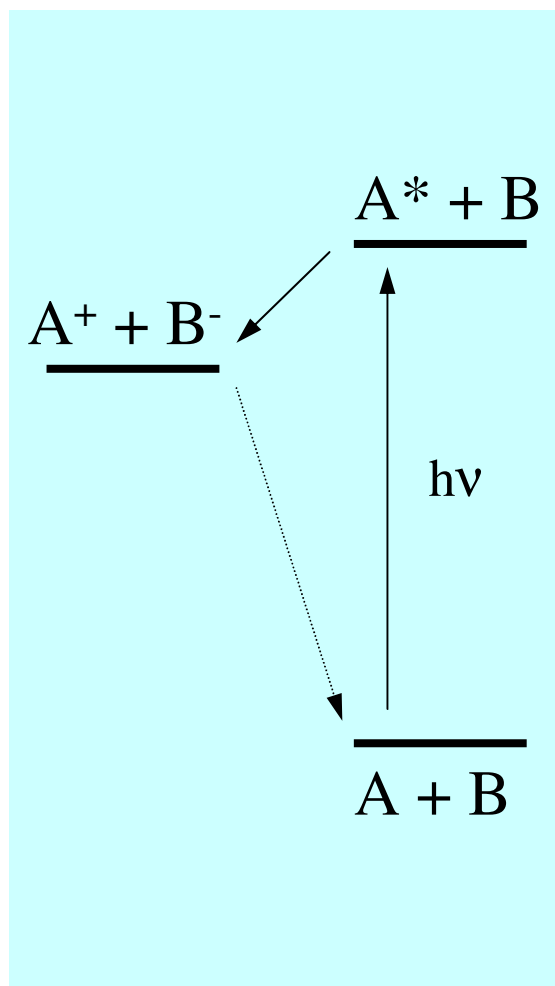


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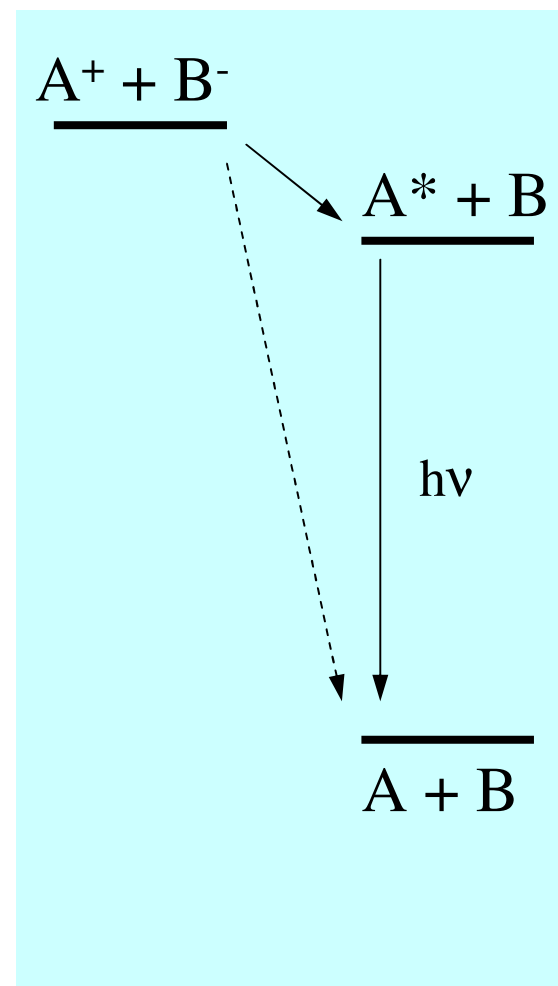
Thermal ET



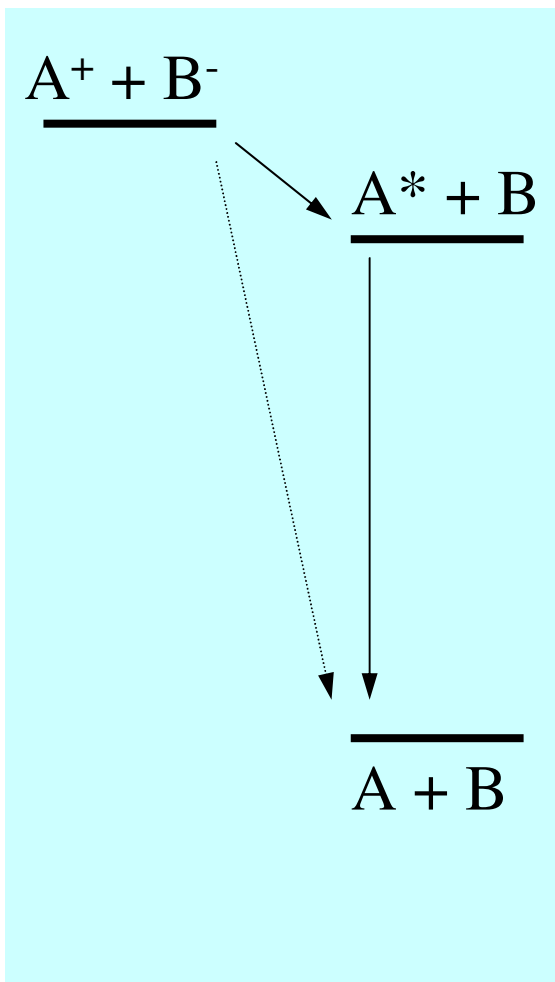
Photoinduced ET



Chemiluminescence



Chemiluminescent Reactions



Photoinduced Electron Transfer

- Photosynthesis
- Artificial solar energy conversion
- Molecular devices and machines
- Luminescent sensors
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