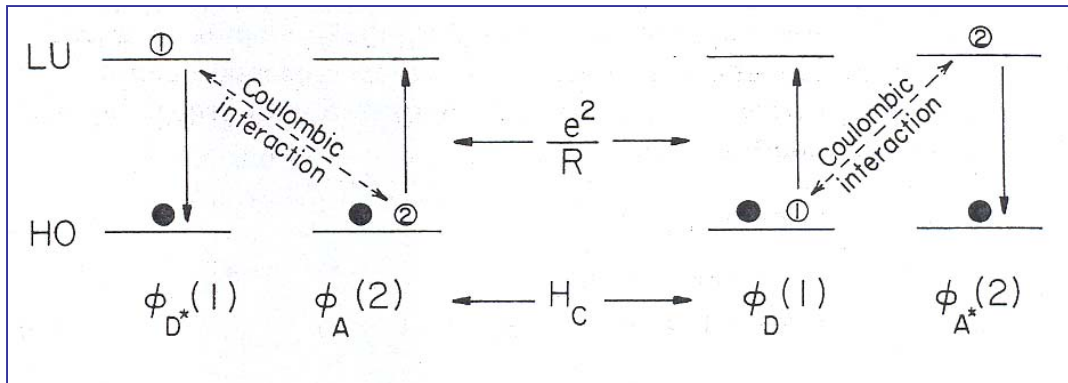


# **Molecular Photonics**

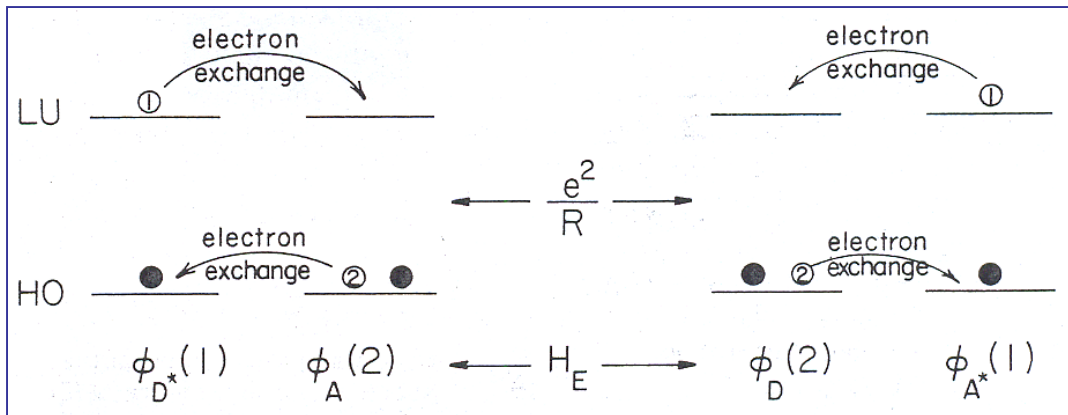
## Lecture 5

# Nonradiative energy transfer: Förster and Dexter mechanisms



**Coulombic mechanism**  
(dipole-dipole) is called  
**Förster energy transfer**  
**mechanism**

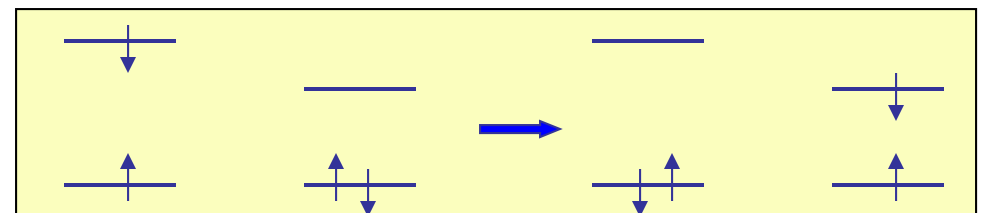
**No direct orbital**  
**overlap necessary**



**Exchange mechanism**  
is called **Dexter energy**  
**transfer mechanism**

**Direct orbital overlap**  
**necessary**

Energy gradient (driving  
force) is important for energy  
transfer observation



# Förster resonance energy transfer (FRET). Dominating mechanism.

The **FRET efficiency** is determined by three parameters:

1. The distance between the donor and the acceptor.
2. The spectral overlap of the donor emission spectrum and the acceptor absorption spectrum.
3. The relative orientation of the donor emission dipole moment and the acceptor absorption dipole moment.

**k (Coulombic ET)  $\sim 1/R^6$ , where R=donor-acceptor distance.**

The FRET efficiency  $E$ , which is defined as

$$E = 1 - \tau'_D / \tau_D$$

where  $\tau'_D$  and  $\tau_D$  are the donor fluorescence lifetimes in the presence and absence of an acceptor, respectively, or as

$$E = 1 - F'_D / F_D$$

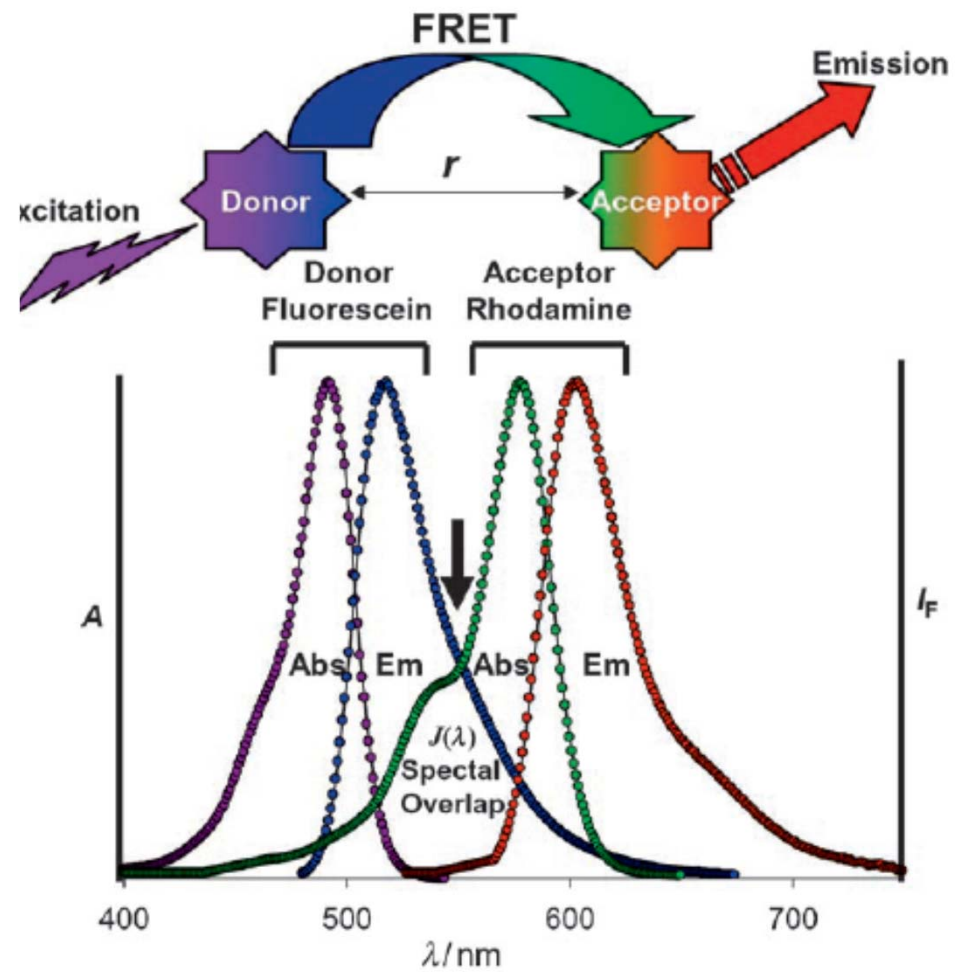
where  $F'_D$  and  $F_D$  are the donor fluorescence intensities with and without an acceptor, respectively.  $E$  depends on the donor-to-acceptor separation distance  $r$  with an inverse 6th order law due to the dipole-dipole coupling mechanism:

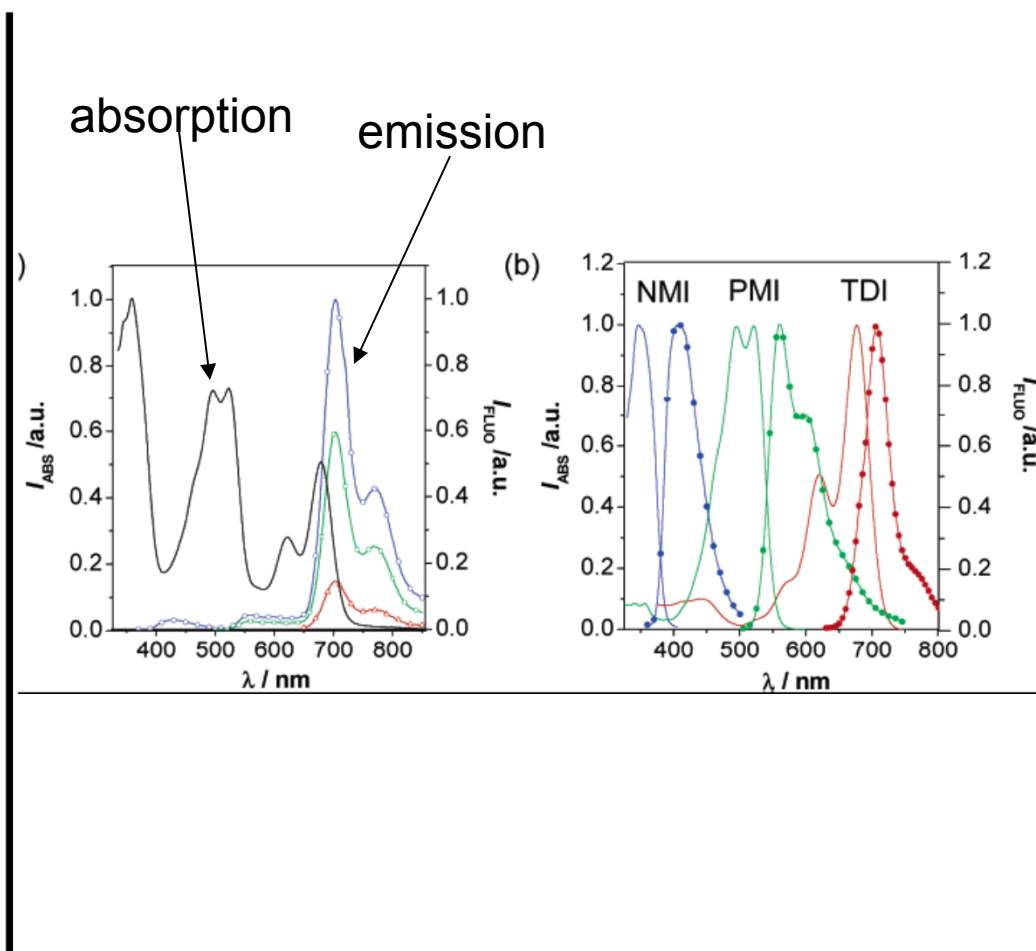
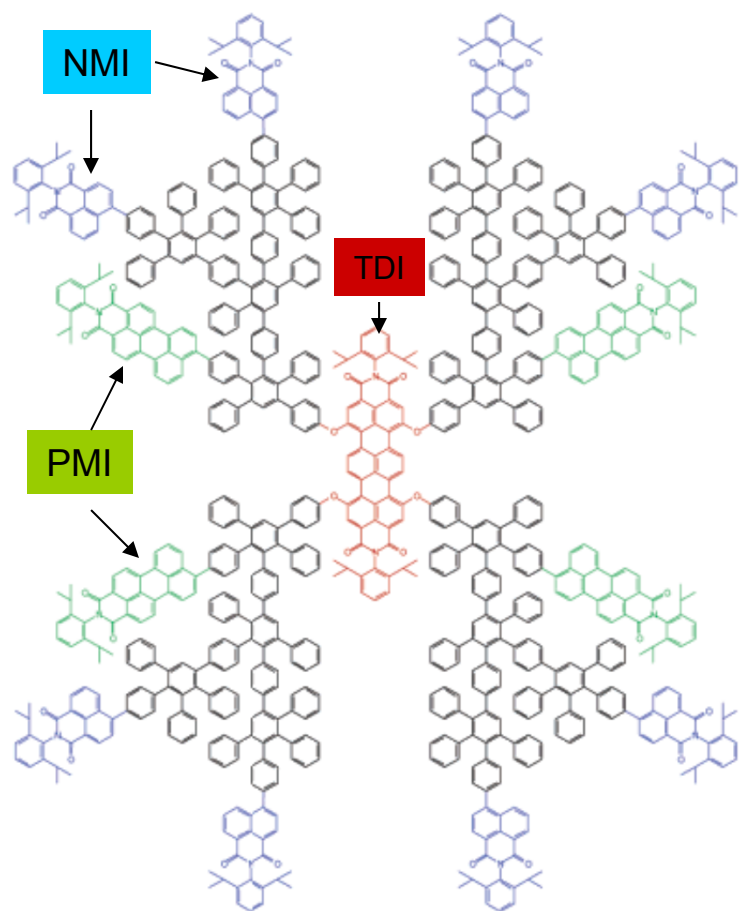
$$E = \frac{1}{1 + (r/R_0)^6}$$

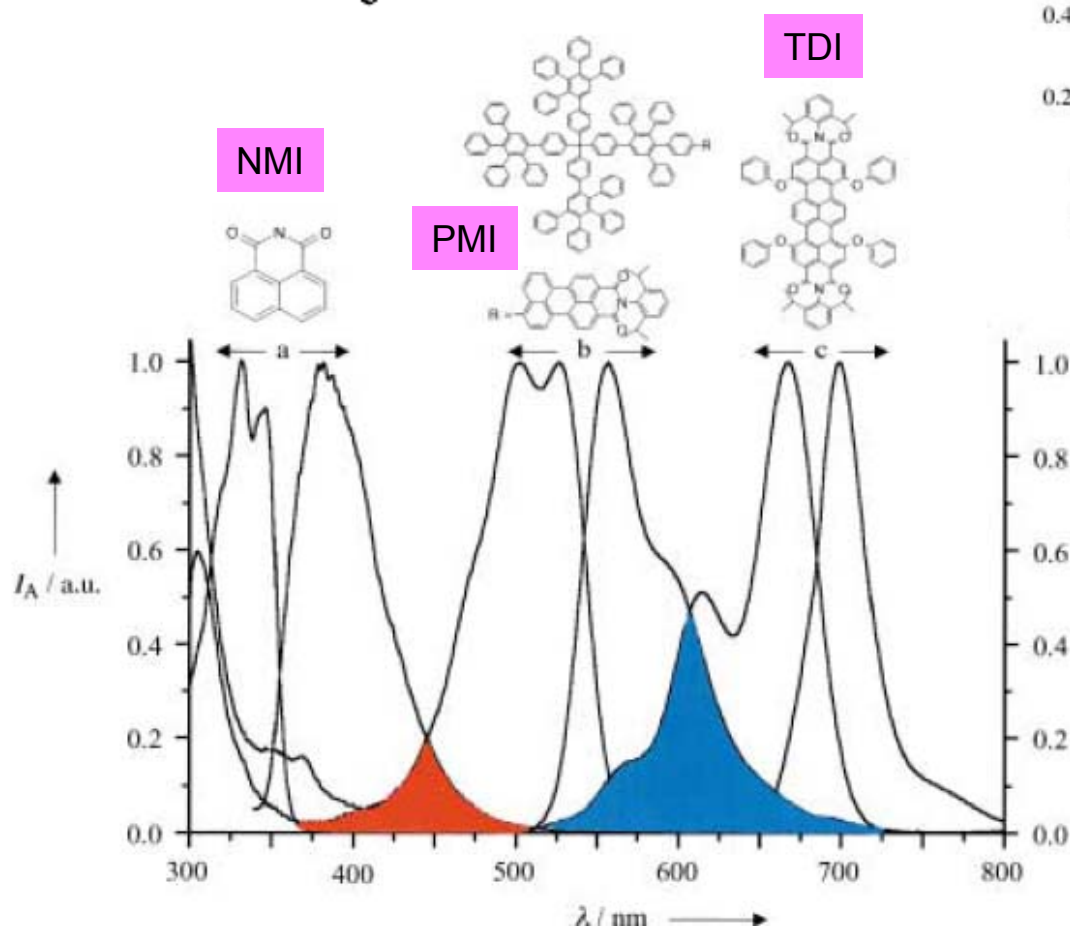
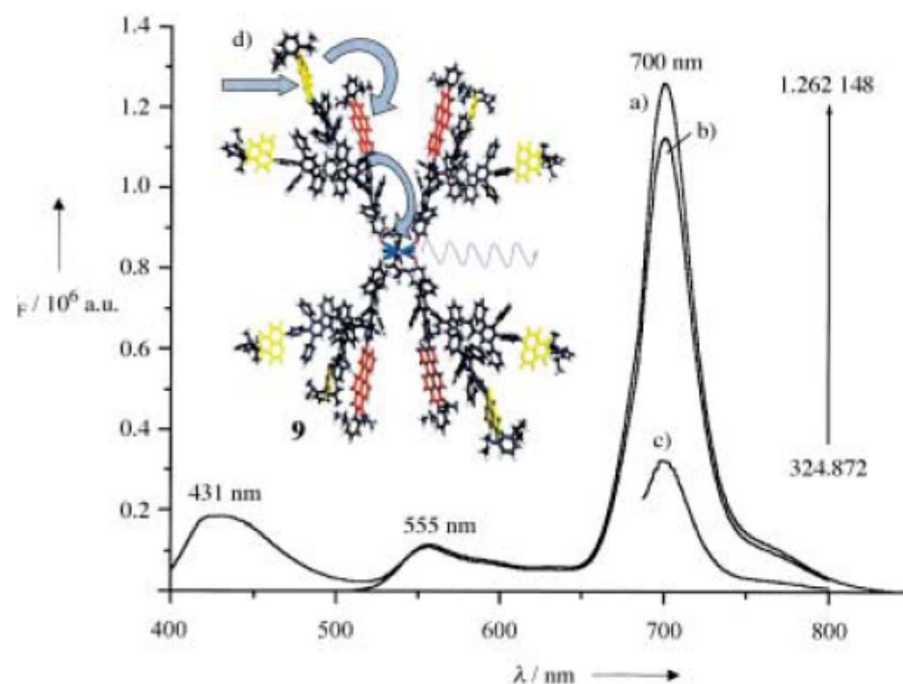
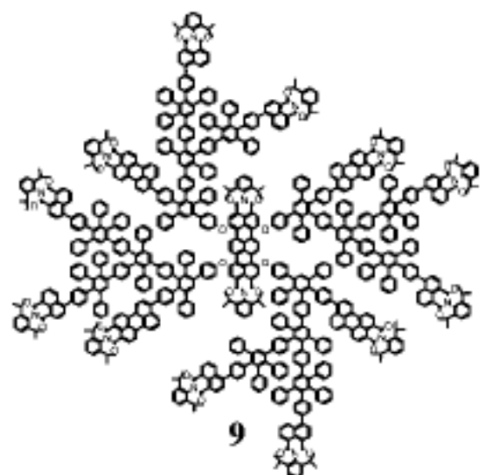
with  $R_0$  being the Förster distance of this pair of donor and acceptor at which the FRET efficiency is 50%. The Förster distance depends on the overlap integral of the donor emission spectrum with the acceptor absorption spectrum and their mutual molecular orientation as expressed by the following equation:

$$R_0^6 = 8.8 \times 10^{23} \kappa^2 n^{-4} Q_0 J$$

where  $\kappa^2$  is the dipole orientation factor,  $n$  is the refractive index of the medium,  $Q_0$  is the fluorescence quantum yield of the donor in the absence of the acceptor, and  $J$  is the spectral overlap integral.

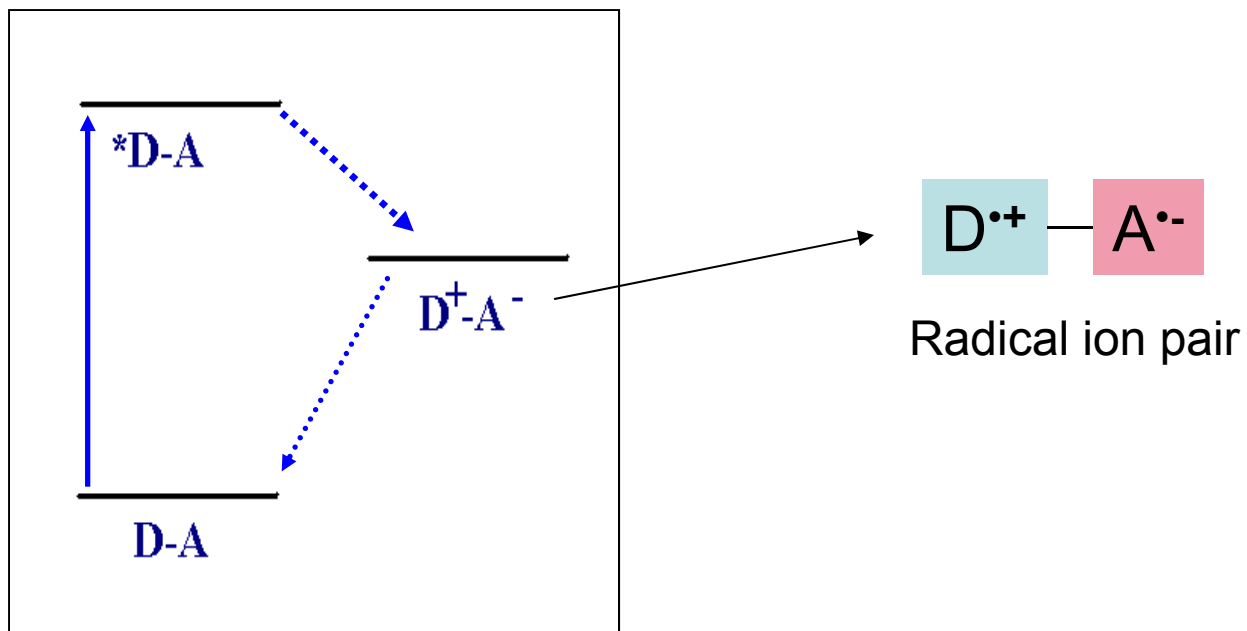






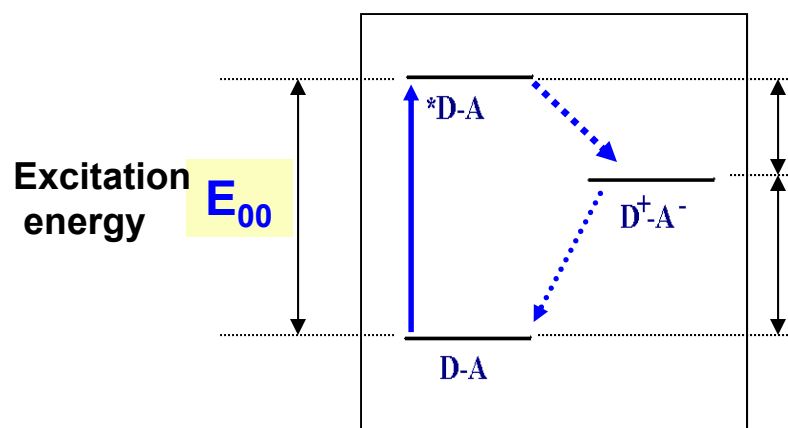
Emission spectra of 9 after excitation of a) the NMI chromophores at the periphery (exc370 nm), b) the PMI chromophores in the scaffold (exc480 nm), and c) the TDI chromophore in the center (exc665 nm). d) 3D structure of 9 obtained from molecular mechanics calculations and visualization of the vectorial energy transfer from the periphery towards the center.

# Photoinduced Electron Transfer



# Driving force for photoinduced electron transfer: Rehm-Weller equation for Thermodynamic analysis

$$\Delta G_{cs} = \underbrace{e(E_{ox}(D) - E_{red}(A)) - E_{00}}_{\text{Coulombic attraction}} - \underbrace{\frac{e^2}{4\pi\epsilon_0\epsilon_s R_c}}_{\text{solvation term}} - S$$



$$S = e^2/8\pi\epsilon_0 (1/r^+ + 1/r)(1/\epsilon_{EC} - 1/\epsilon_s)$$

**$E_{ox}(D)$  and  $E_{red}(A)$  - Redox potentials (obtained electrochemically)**

$e$  = elementary charge,  $e=1$  if units are eV

$R_c$  = distance between D and A

$\epsilon_{EC}$  - Dielectric constant of a solvent used in electrochemistry

$\epsilon_s$  - Dielectric constant of a solvent used in electron transfer system

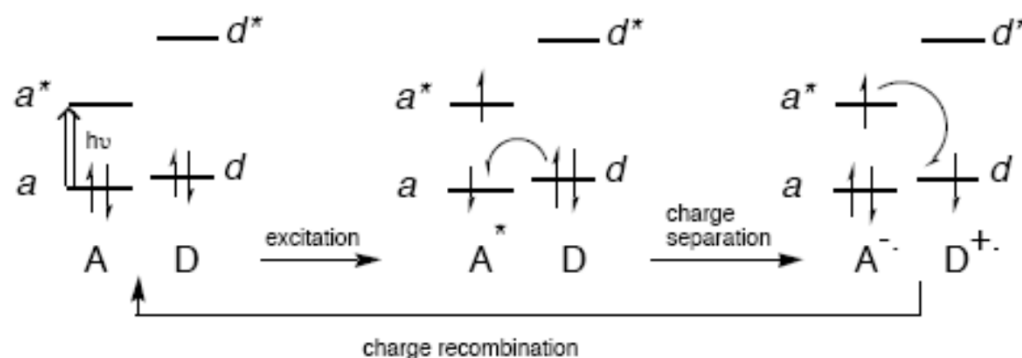




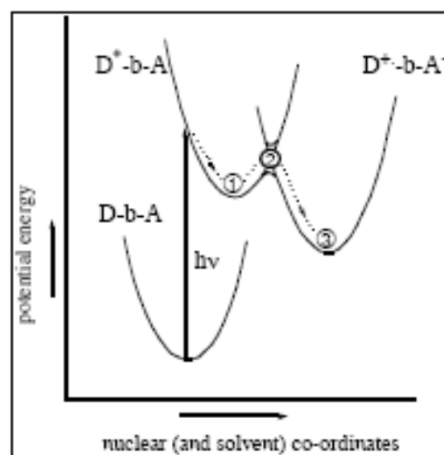
# Rehm-Weller: useful but not precise

- $E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E_{00}$  – gives you an idea if you will get eT at all
- In polar solvents Coulombic term and solvation term are small and can be reliably estimated by Weller.
- In nonpolar solvents we have a problem – Weller does not work well - Coulombic and solvation terms are significant. Weller does not deal well with solvent term in nonpolar solvents.
- Rule of thumb in nonpolar solvents for systems with D-A distance up to 15Å: calculate  $E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E_{00}$  then add 0.5 eV – it will give you a (very) rough estimate of driving force.

# Frontier Molecular Orbital Description

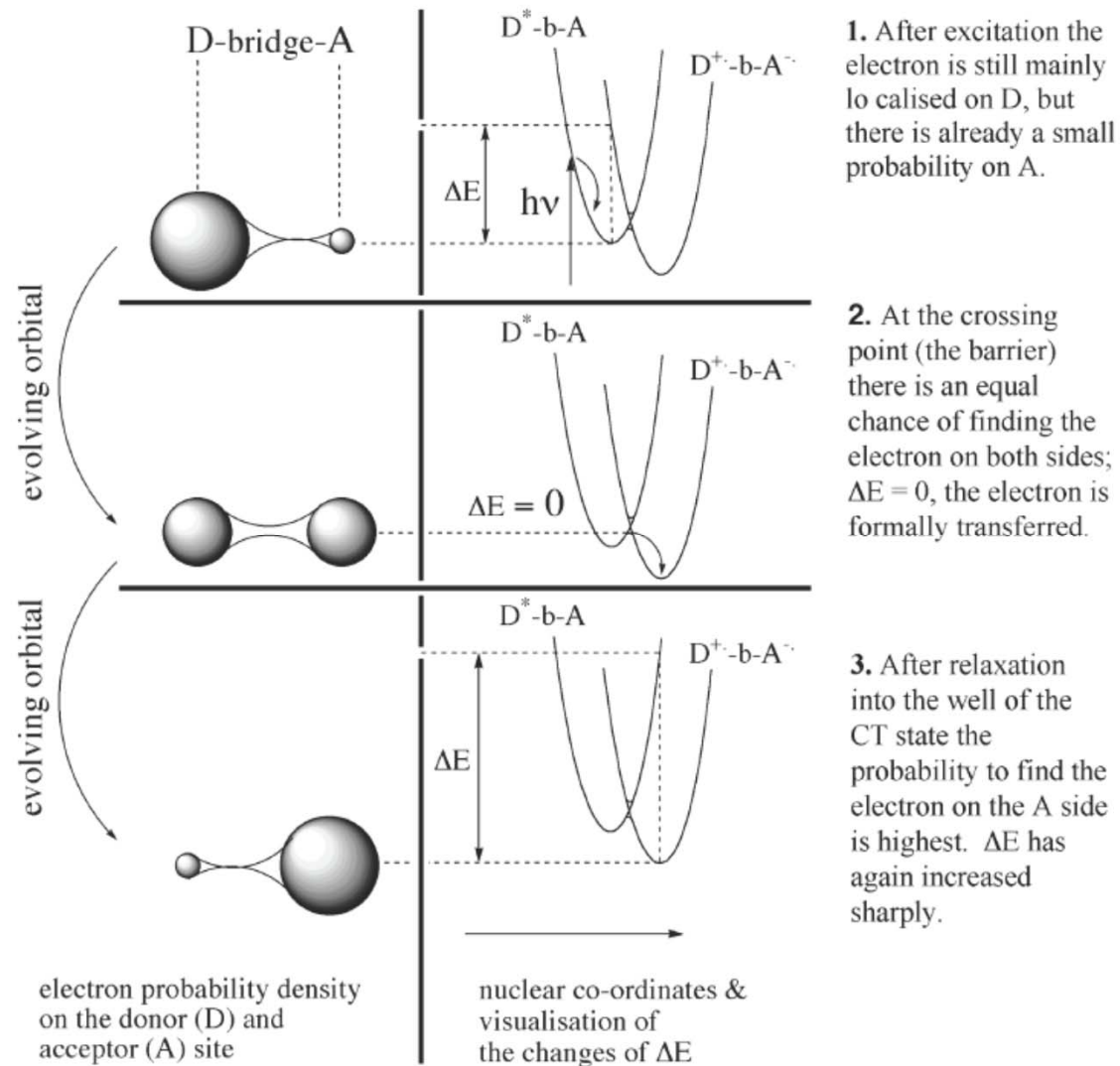


# Parabolas Description



# **Electron transfer dynamics**

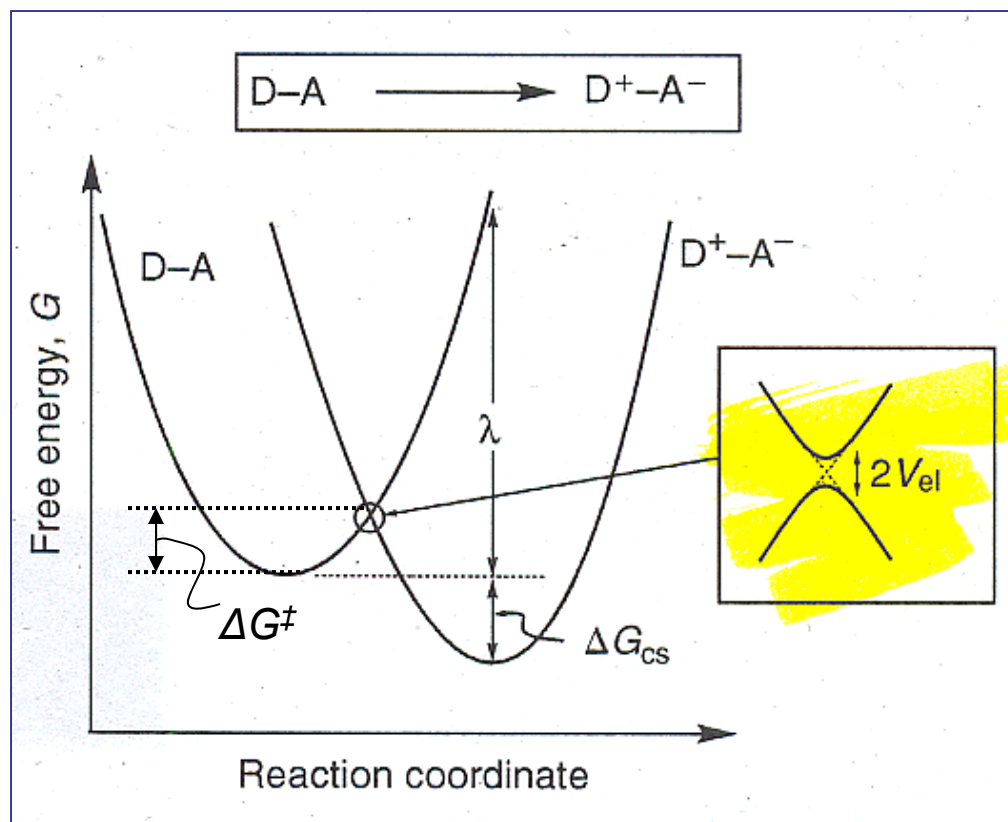
# Visualization



# Marcus Theory (The Nobel Prize in Chemistry 1992)



From the analytical  
geometry of parabolas:  
 $\Delta G^\ddagger = (\lambda + \Delta G_{cs})^2 / 4\lambda$



## Classical Transition State Theory

$$k_{\text{ET}} = \kappa_{\text{el}} \nu_n \exp \left[ \frac{-\Delta G^\ddagger}{k_B T} \right] \quad (4)$$

where  $\nu_n$  is the frequency of passage (nuclear motion) through the transition state  $(D|A)^\ddagger$  ( $\nu_n \sim 10^{13} \text{ s}^{-1}$ ),  $\Delta G^\ddagger$  is the Gibbs energy of activation for the ET process,  $\kappa_{\text{el}}$  is the electronic transmission coefficient,  $k_B$  is the Boltzmann constant, and  $T$  is temperature. In the classical treatment  $\kappa_{\text{el}}$  is usually taken to be unity.

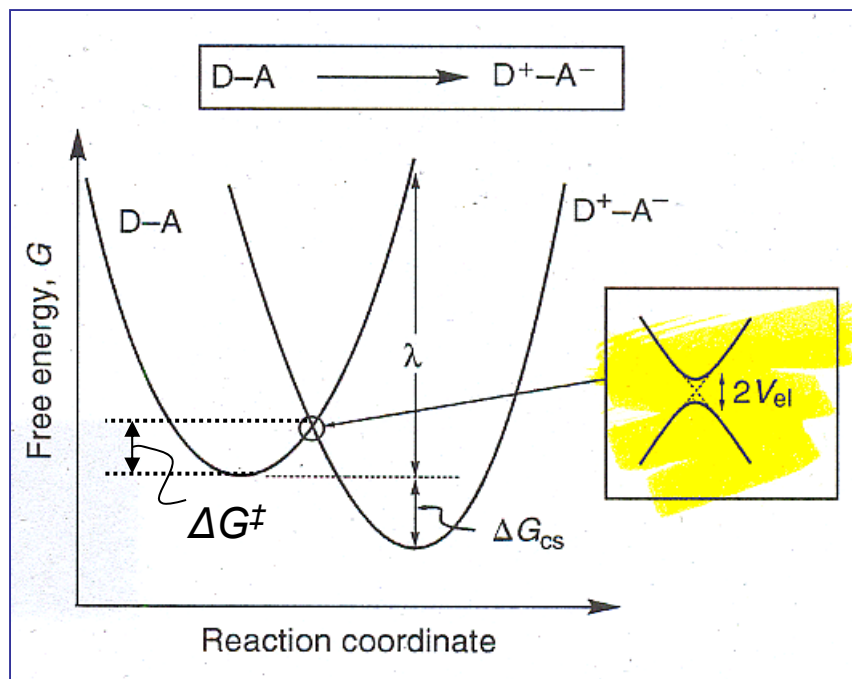
**From the analytical geometry of parabolas:**

$$\Delta G^\ddagger = (\lambda + \Delta G_{\text{cs}})^2 / 4\lambda$$

## Marcus-Hush equation for electron transfer rate

$$k_{\text{et}} = \frac{4\pi^2 |V_{\text{el}}|^2}{h} \left\{ \frac{1}{4\pi\lambda k_B T} \right\}^{1/2} \exp \left( \frac{-(\Delta G_{\text{cs}} + \lambda)^2}{4\lambda k_B T} \right)$$

Three important quantities that affect the magnitude of  $k_{\text{et}}$  are  $V_{\text{el}}$ ,  $\Delta G_{\text{cs}}$ , and  $\lambda$ , the reorganization energy. The reorganization energy is an important concept in ET theory and is defined as the energy required to distort the reactant and its associated solvent molecules from their relaxed nuclear configurations to the relaxed nuclear configurations of the product and its associated solvent molecules.



# Reorganization Energy

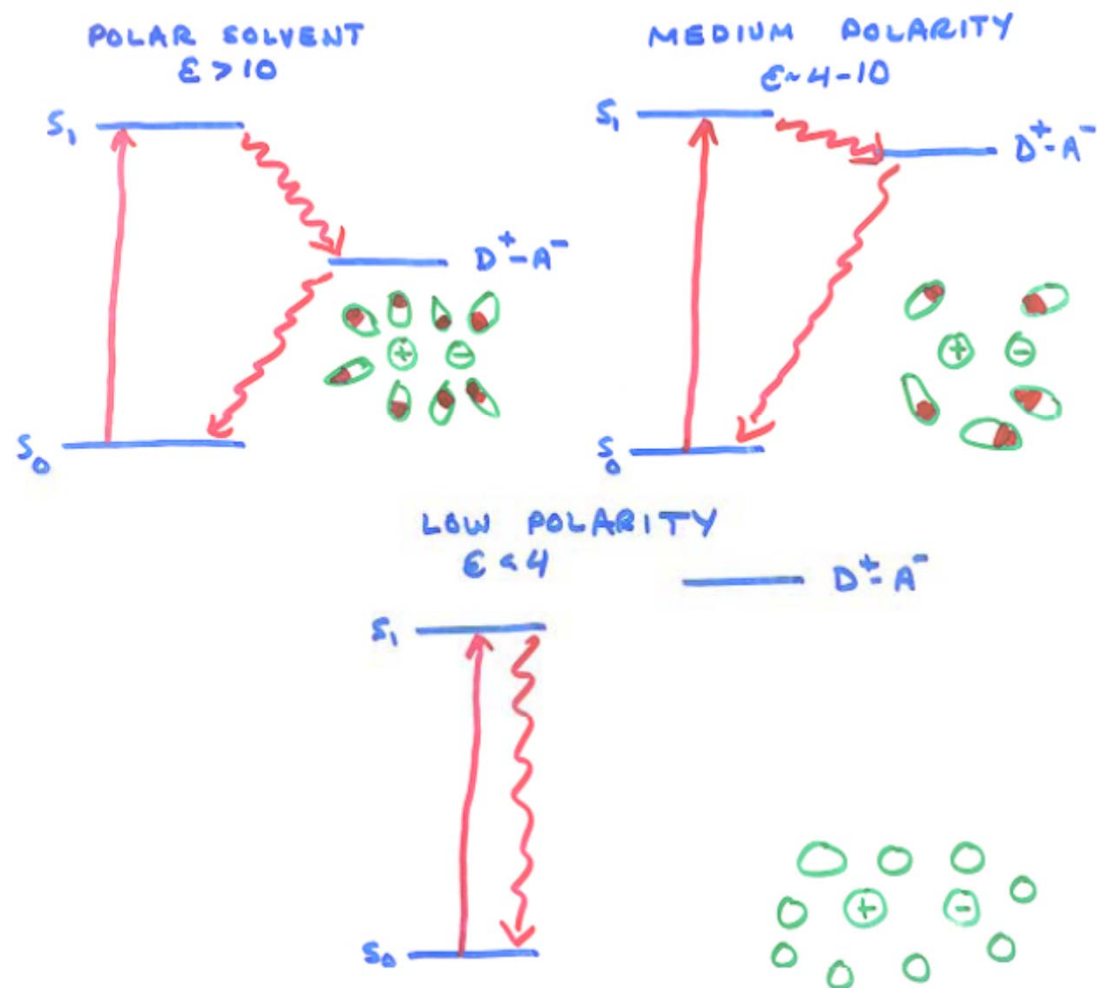
$$\lambda_{\text{total}} = \lambda_{\text{int}} + \lambda_{\text{s}}$$

$\lambda_{\text{int}}$  – inner sphere reorganization energy. Called *intramolecular* reorganization energy. Arises from structural differences between the relaxed nuclear geometries of the reactant and product.

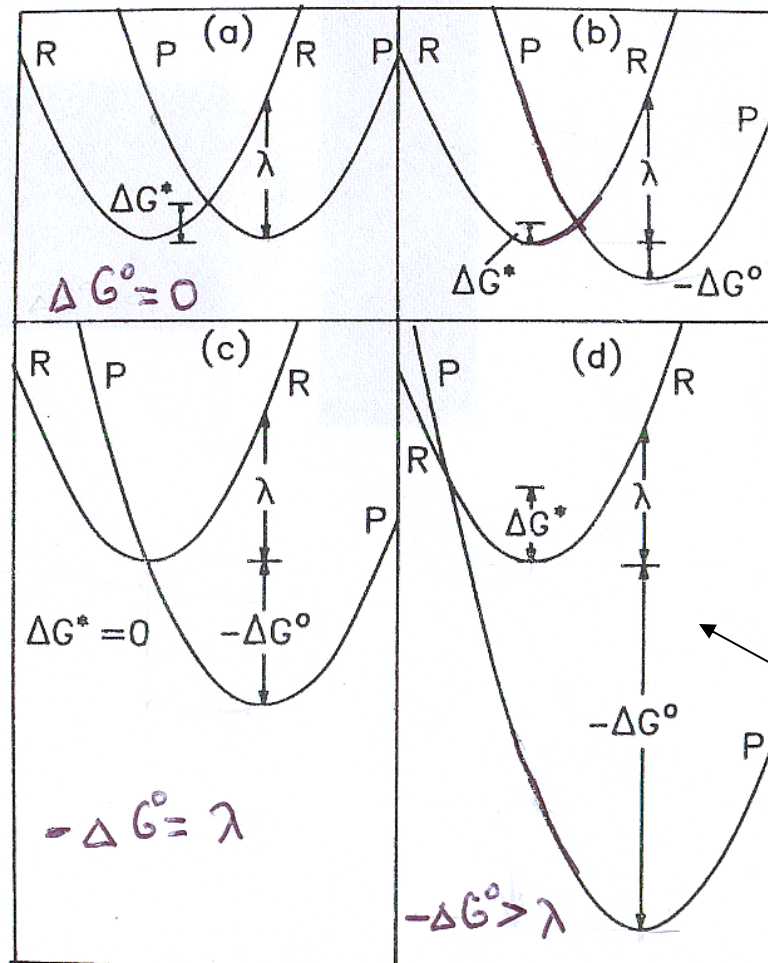
$\lambda_{\text{s}}$  – outer sphere reorganization energy. Called *solvent* reorganization energy. Arises from differences between the orientation and polarization of the solvent molecules surrounding the reactant and product.



SOLVATION OF CHARGES BECOMES  
AN IMPORTANT ISSUE IN ELECTRON  
TRANSFER REACTIONS



# Inverted Region



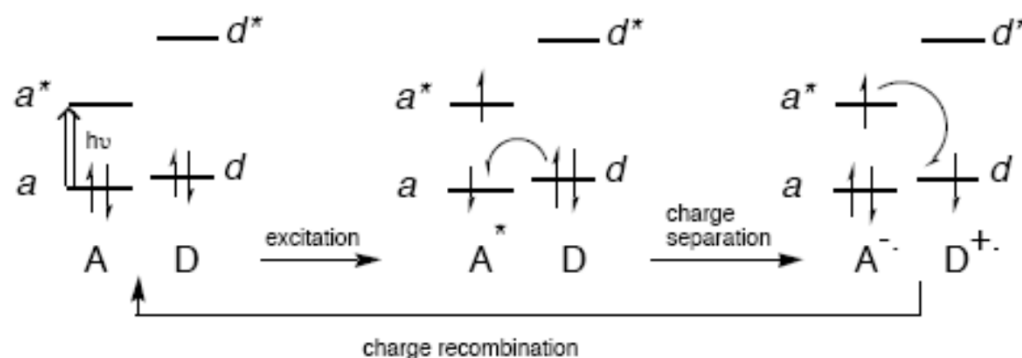
$$\Delta G^\ddagger = (\lambda + \Delta G_{cs})^2 / 4\lambda$$

Marcus predicted something completely counter-intuitive:

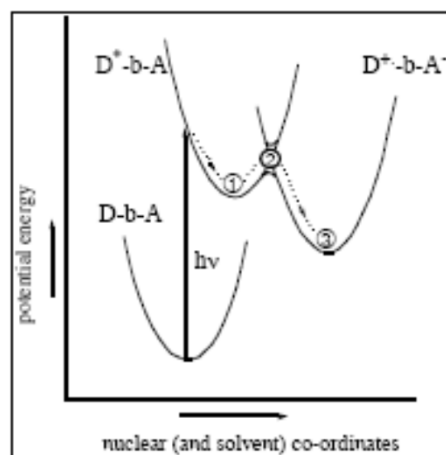
***If there is a really huge driving force for the electron transfer, larger than reorganization energy, the reaction will become slower!***

This was the reason that for several years people were skeptical regarding his theory.

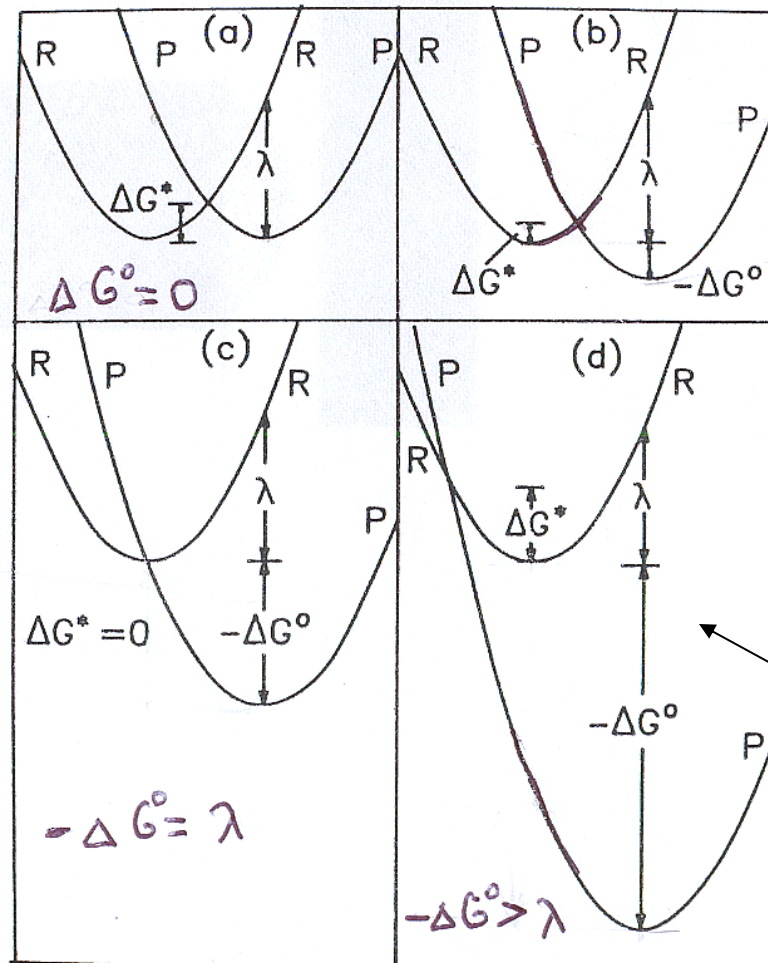
# Frontier Molecular Orbital Description



# Parabolas Description



# Inverted Region



$$\Delta G^\ddagger = (\lambda + \Delta G_{cs})^2 / 4\lambda$$

Marcus predicted something completely counter-intuitive:

***If there is a really huge driving force for the electron transfer, larger than reorganization energy, the reaction will become slower!***

This was the reason that for several years people were skeptical regarding his theory.

# Inverted region - continued

Marcus predicted something completely counterintuitive:

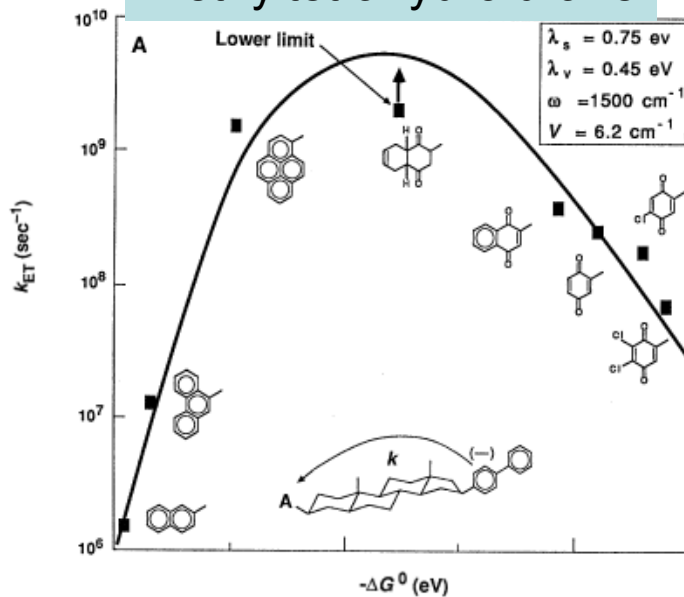
***If there is a really huge driving force for the electron transfer, larger than reorganization energy, the reaction will become slower!***

This was the reason that **for 30 years** (!) people were skeptical regarding his theory...until Closs and Miller demonstrated very clearly that inverted region exists.

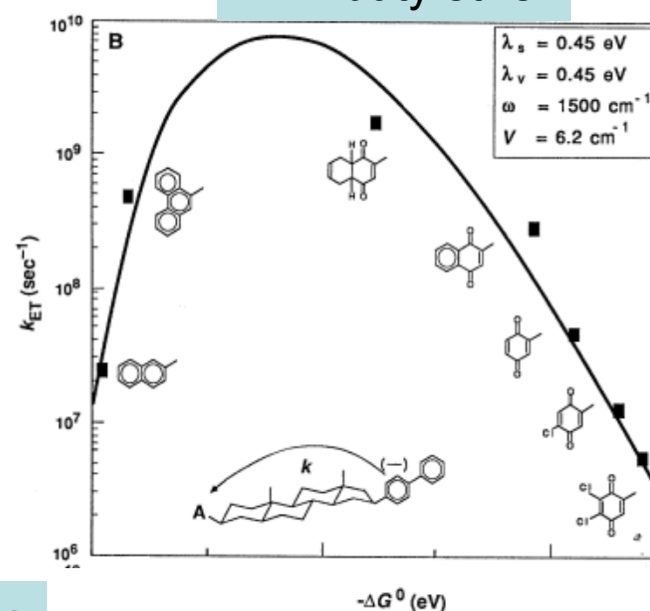
They got Nobel Prize... for Marcus.

# Miller and Closs

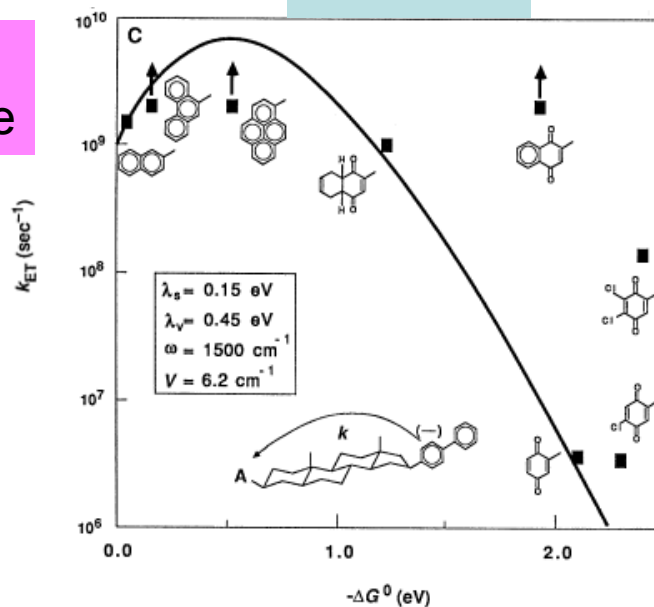
methyltetrahydrofurane



Di-n-butylether



isooctane

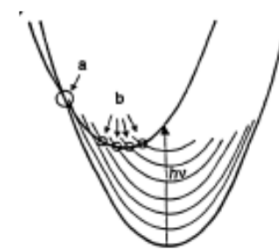
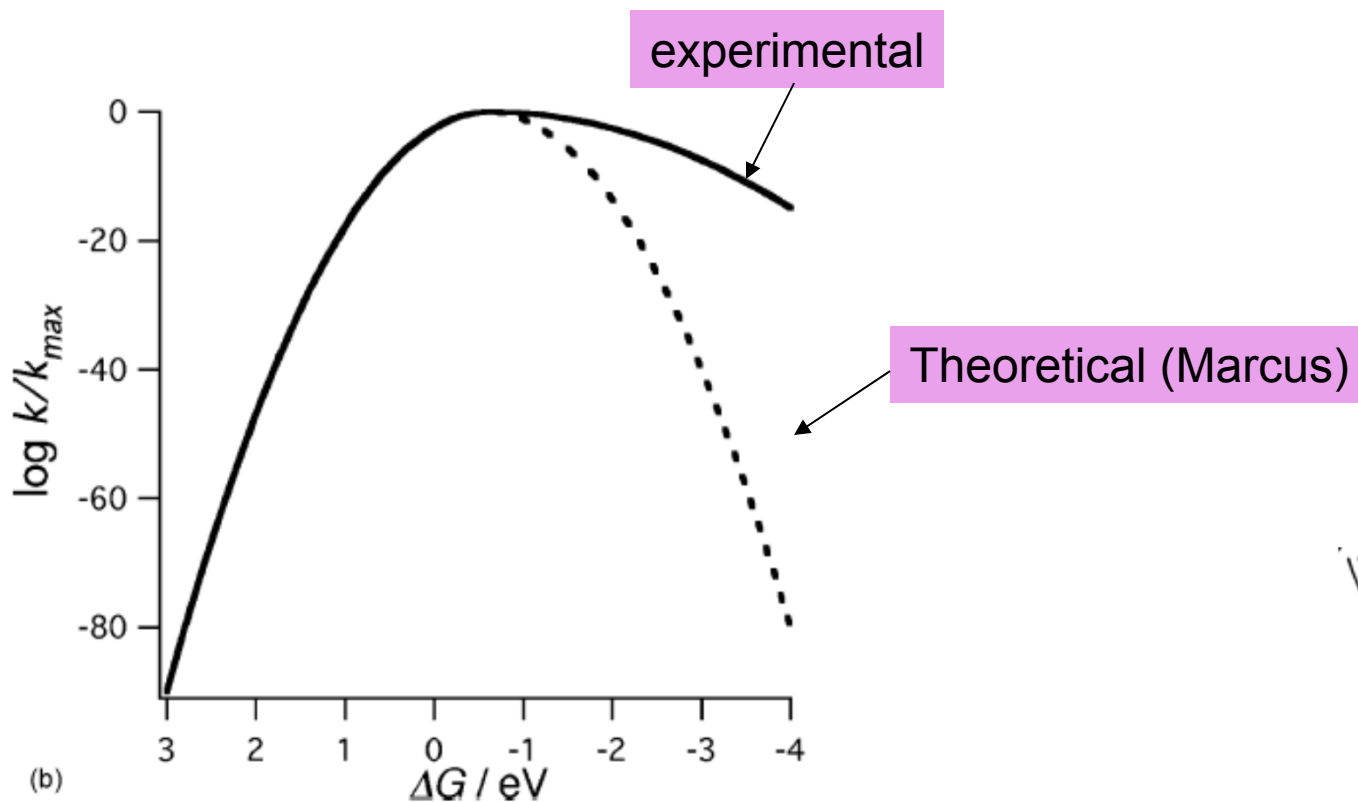


Solvent polarity:  
MTHF>DBE>isooctane

Closs et al.  
*JACS* **1983**, 105, 670

Closs, Miller,  
*Science* **1988**, 240, 440.

# Inverted region and electronic coupling.

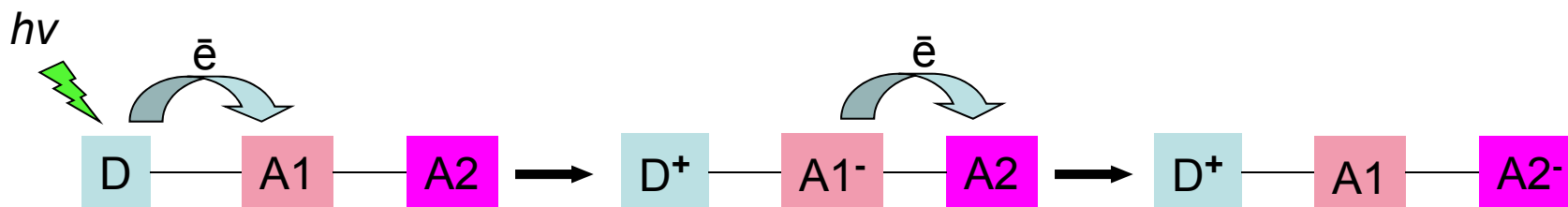


Inverted region:  
embedded curves, good  
vibrational coupling

# Importance of the inverted region

The Marcus theory predicts that, for a family of related reactants,  $k_{ET}$  should decrease with driving force ( $-\Delta G^0$ ), reach a maximum at  $-\Delta G^0 = \lambda$ , and decrease as the driving force is increased further.

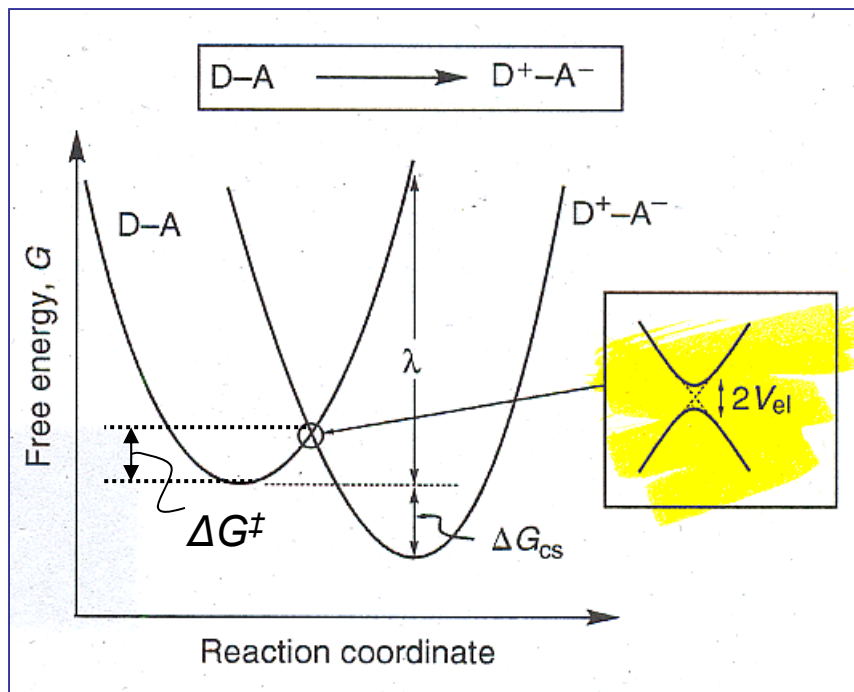
This is the *inverted region*, one key to photochemical energy conversion and storage in natural photosynthetic systems and to the design of molecular assemblies for artificial photosynthesis.



Electron transfer creates transiently stored, oxidative and reductive equivalents at the oxidized donor and reduced acceptor. If “recombination” by back electron transfer occurs in the inverted region, it is inhibited. This allows the redox equivalents to be transferred away from the initial site of excitation and utilized elsewhere. The role of the inverted region is paramount. The greater the energy stored, the greater the barrier to back electron transfer (the further electron goes the better – it will return slower due to larger driving force).



# Electronic coupling

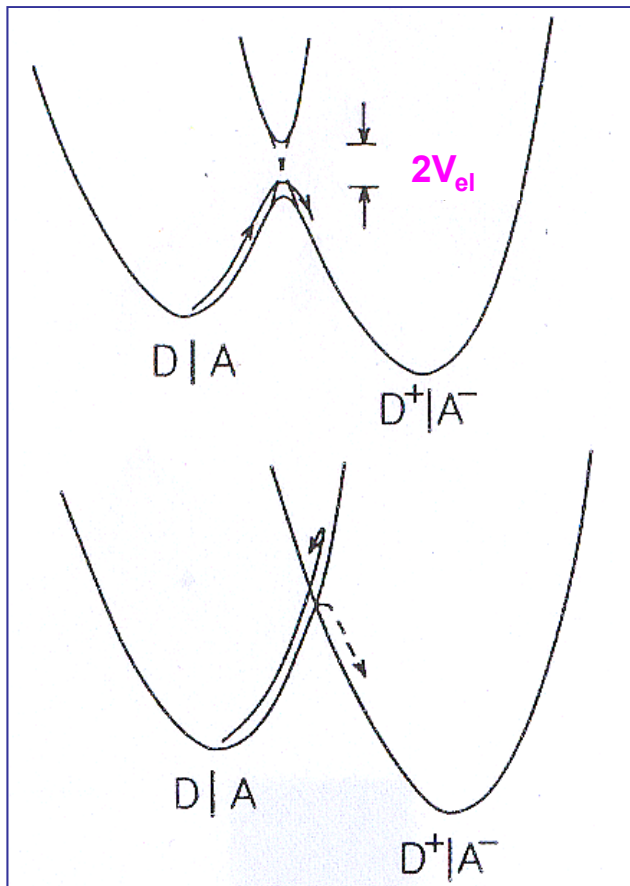


$$k_{et} = \frac{4\pi^2 |V_{el}|^2}{h} \left\{ \frac{1}{4\pi \lambda k_B T} \right\}^{1/2} \exp \left( \frac{-(\Delta G_{cs} + \lambda)^2}{4\lambda k_B T} \right)$$

The matrix element  $V_{el}$  (*electronic coupling energy*) scales with the interaction energy between the donor orbital and the acceptor orbital that are associated with the migrating electron. This term depends on the overlap between two orbitals.

$V_{el}$  fall off exponentially with increased interchromophore separation because of decreasing orbital overlap.

# Adiabatic vs. Nonadiabatic Electron Transfer



The dividing line for electron transfer reactions can be roughly estimated by comparison the matrix element  $V_{el}$  with the thermal energy

**Adiabatic:**  $V_{el} \gg kT$

**Nonadiabatic:**  $V_{el} \ll kT$

**Adiabatic case:** all species that have energy higher than activation energy will cross to the product state.

**Nonadiabatic case:** not all the species that reach the activation barrier cross over to the product surface.

# Quantum Mechanical Corrections for Marcus Theory: vibronic (phonon) theory

## Problems:

- Classical Marcus theory works well only if  $V_{el} \geq kT$
- Marcus theory does not predict temperature dependence correctly.
- Marcus theory does not explain electron transfer at very low temperatures.

## Conclusion:

The assumption that the barrier should be always crossed is not always holds.

Tunneling should be taken into account.

Vibrational overlap is of primary importance: electron transfer can occur above or below crossing point provided there is good vibrational overlap. Quantum corrections to Marcus theory dealing with vibrations (phonons) were introduced by Jortner and others.

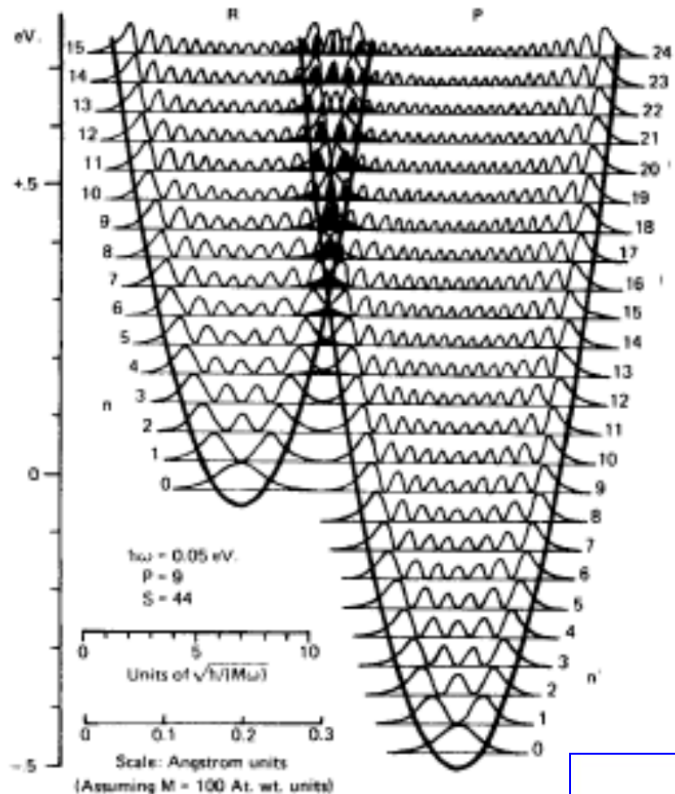
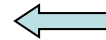


Figure 8. Schematic one-dimensional representation of the between reactant and product vibrational levels. The opti of the  $v = 0$  initial vibrational level is with the  $v' = 9$  pr Reproduced with permission from: DeVault, D. *Quantum Tunneling in Biological Systems*; Cambridge University Press, 1984. Copyright 1984 Cambridge University Pre

### Semiclassical eT theory (Jortner's theory):

$$k_{cs} = \frac{2\pi^{3/2}}{h\sqrt{\lambda_s k_B T}} (V)^2 \sum_{m=0}^{\infty} \frac{e^{-S} S^m}{m!} \exp\left[-\frac{(\lambda_s + \Delta G_{cs} + m\hbar\nu_i)^2}{4\lambda_s k_B T}\right]$$

with the electron-vibronic (phonon) coupling  $S = \lambda_i/\hbar\nu_i$ . Here  $\nu_i$  is the average skeletal (IR)-vibration (in general between 300 and 2300  $\text{cm}^{-1}$ ). The “ $\Sigma$ ” term indicates a summation over all “m” levels.



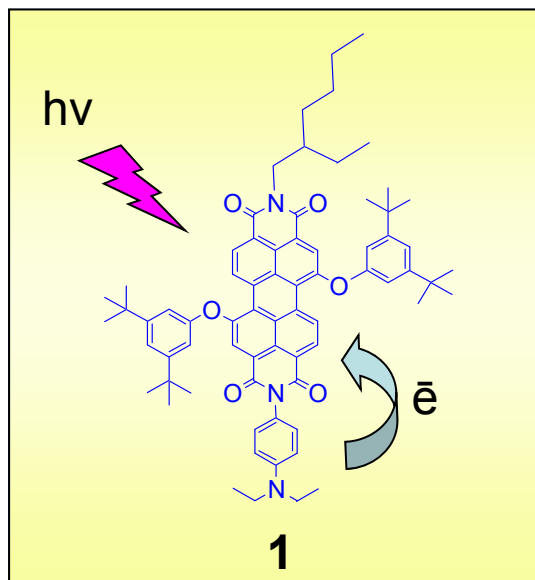
Barbara et al. describe it well

# Factors that Influence Electron Transfer

## Electron transfer rates depend on

- Driving force  $\Delta G^0$
- Reorganization energy  $\lambda$
- Solvent ( $\Delta G^0$ ,  $\lambda$ )
- Electronic coupling  $V_{el}$
- Distance between donor (D) and acceptor (A) ( $\Delta G^0$ ,  $\lambda$ ,  $V_{el}$ )
- Orientation of D relative to A ( $V_{el}$ )
- Temperature

# Driving Force and Solvents



From Rehm-Weller equation

	$E_{1/2}^{RED}$ (V)	$E_{1/2}^{OX}$ (V)	$E_{SI}$ (eV)	$\Delta G_{CS}$ (eV)		$\Delta G_{CR}$ (eV)	
				MTHF	Toluene	MTHF	Toluene
<b>1</b>	-0.70	0.97	2.21	-0.67	-0.14	-1.58	-2.11

From transient absorption

Compound	CS Time Constant (ps)		CR Time Constant (ps)	
	Toluene	MTHF	Toluene	MTHF
<b>1</b>	$0.7 \pm 0.1$	$0.8 \pm 0.3$	$16 \pm 3$	$3.4 \pm 0.5$

Slower charge recombination in less polar solvent indicates inverted region regime.

Rybitchinski, B., Sinks, L. E. & Wasielewski, M. R.  
*J. Phys. Chem. A* **2004**, 108, 7497-7505.

# Distance dependence

$V_{el}$  is proportional to  $e^{-0.5\beta r}$

$k_{ET}$  is proportional to  $e^{-\beta r}$

$\beta$  = damping factor

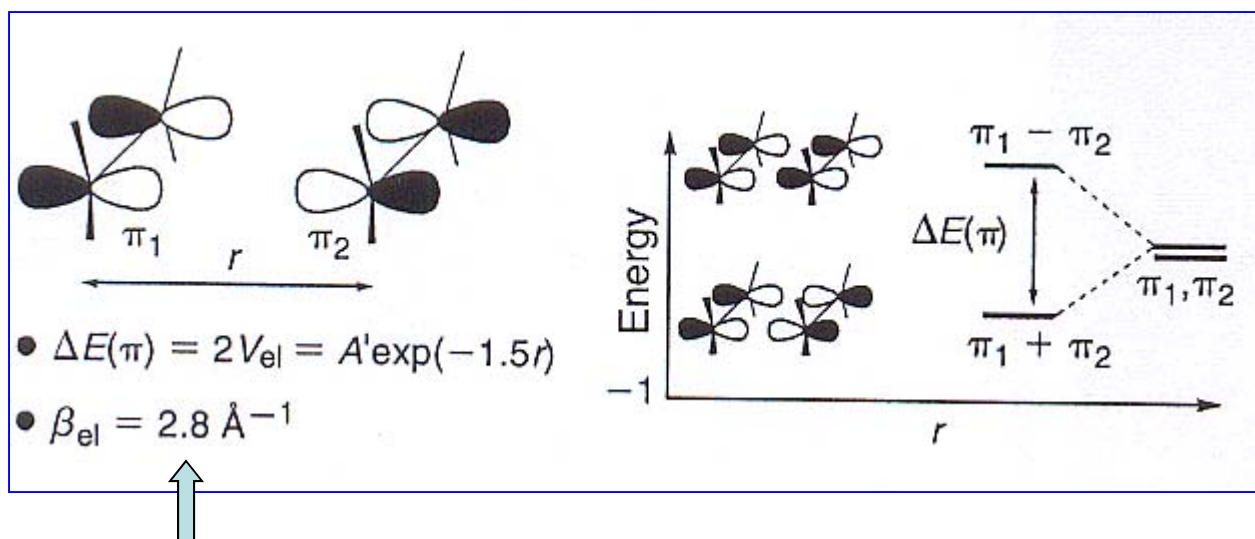
$r$  = distance

Large  $\beta$  – significant falloff of rates with distance

Small  $\beta$  – rates are almost independent of distance  
(molecular wire)

# Through-space distance dependence

In the absence of any intervening medium (vacuum) the electronic coupling depends on direct through space overlap between the active orbitals of the donor and acceptor. Calculation for two ethylene molecules:

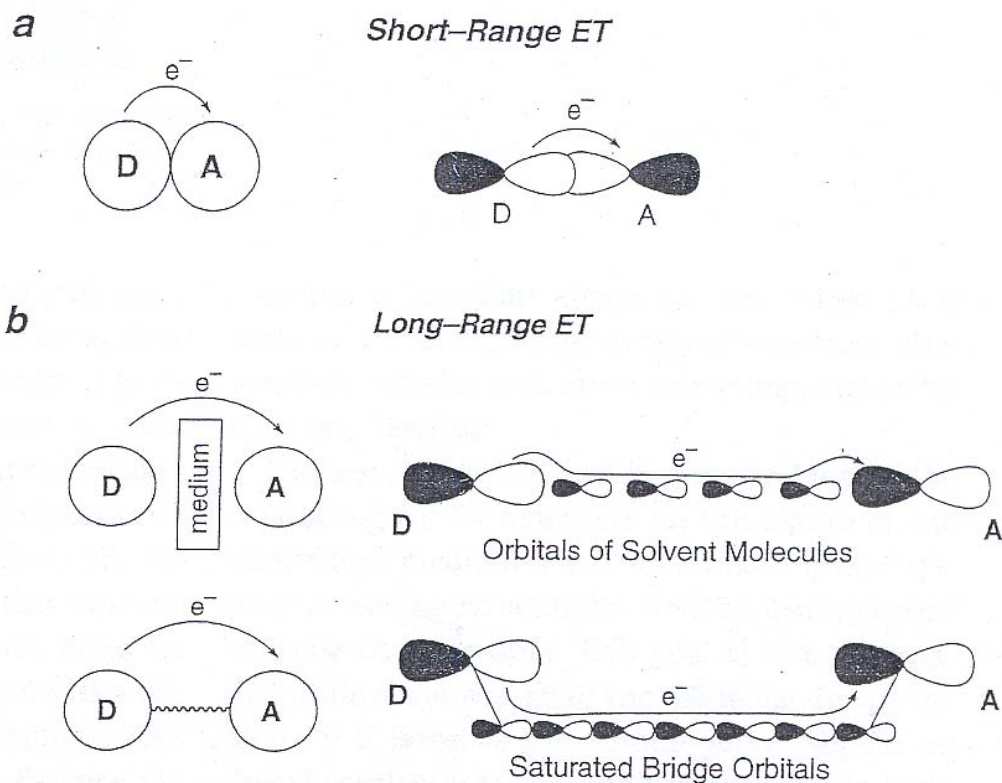


Large value for damping factor, which means that the eT rate occurring by a through-space mechanism should be attenuated by a factor as large as 20 per 1Å



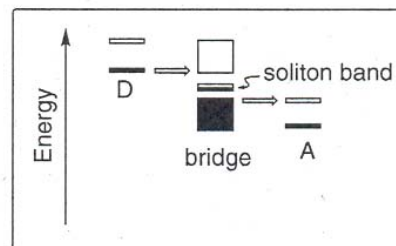
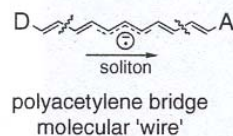
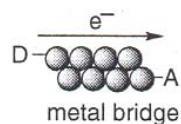
# Bridge between donor and acceptor: how it influences eT

**Figure 2.** (a) Short-range ET. The donor and acceptor orbitals overlap strongly and ET takes place by a direct, through-space mechanism. (b) Long-range ET. Direct overlap between the donor and acceptor orbitals is negligible and ET occurs by an indirect mechanism involving electron tunnelling through the orbitals of the intervening medium, e.g. solvent molecules (upper) or a covalently linked saturated bridge (lower).

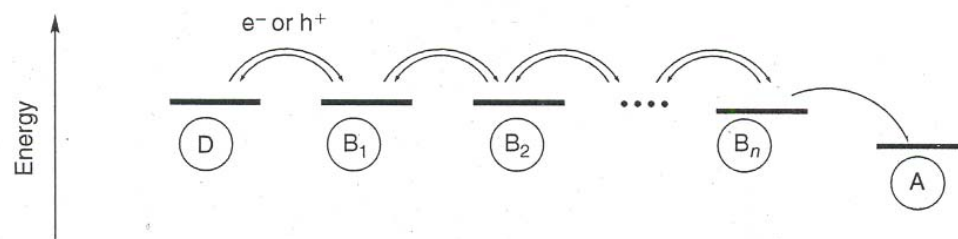


# Hopping vs Superexchange

(a) Electrically conducting bridges: electron transport

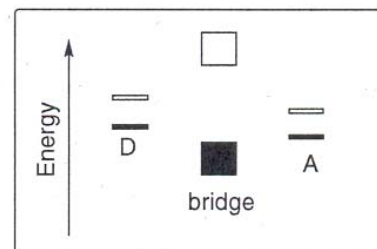
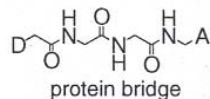
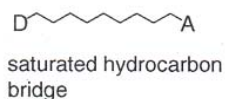


(b) Charge-hopping bridges: electron transport



Hopping: charges reside on the bridge

(c) Electrically insulating bridges ('saturated' bridges): electron transfer



Superexchange: the bridge mediates electron transfer, although the charges never reside on it. One can say that the electron tunnels through the bridge.

# Superexchange example: saturated bridge

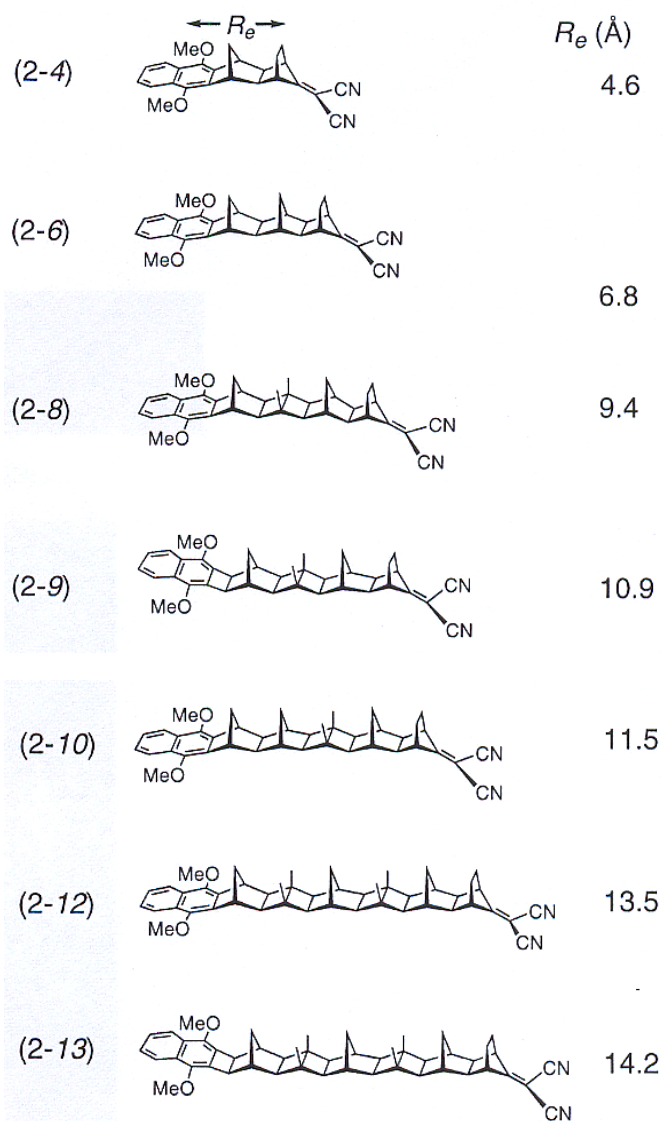
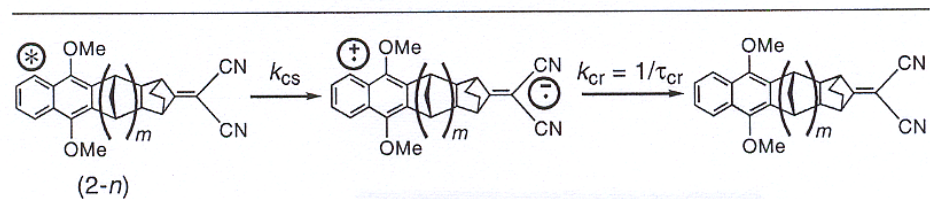
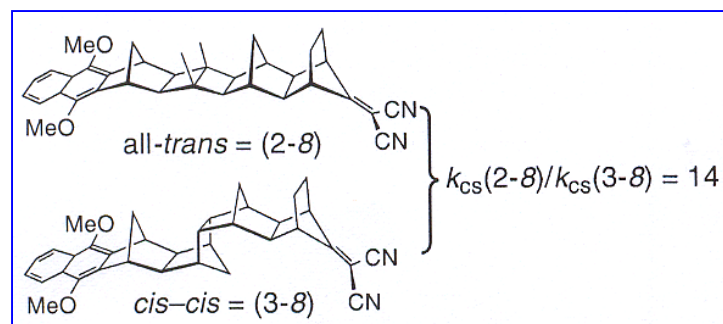


Table 1. Rate data for photoinduced charge separation and subsequent charge recombination in the dyads (2-*n*)



System	Charge separation rates $k_{\text{cs}}$ [ $10^8 \text{ s}^{-1}$ ] <sup>A</sup>		Mean lifetime towards charge recombination $\tau_{\text{cr}}$ [ns] <sup>B</sup>
	Fluorescence measurements <sup>[68,70]</sup>	Pump-probe measurement <sup>[81]</sup>	
(2-4)	$\gg 5000$	28 000	–
(2-6)	3000	4890	0.5
(2-8)	670	1160	2.5
(2-9)	250	647	–
(2-10)	120	180	43
(2-12)	13	–	297
(2-13)	1.2	–	1050

<sup>A</sup> Measured in THF at 20°C. <sup>B</sup> From time-resolved conductivity measurements in 1,4-dioxane.<sup>[67,77,79,80]</sup>



Paddon-Row et al.