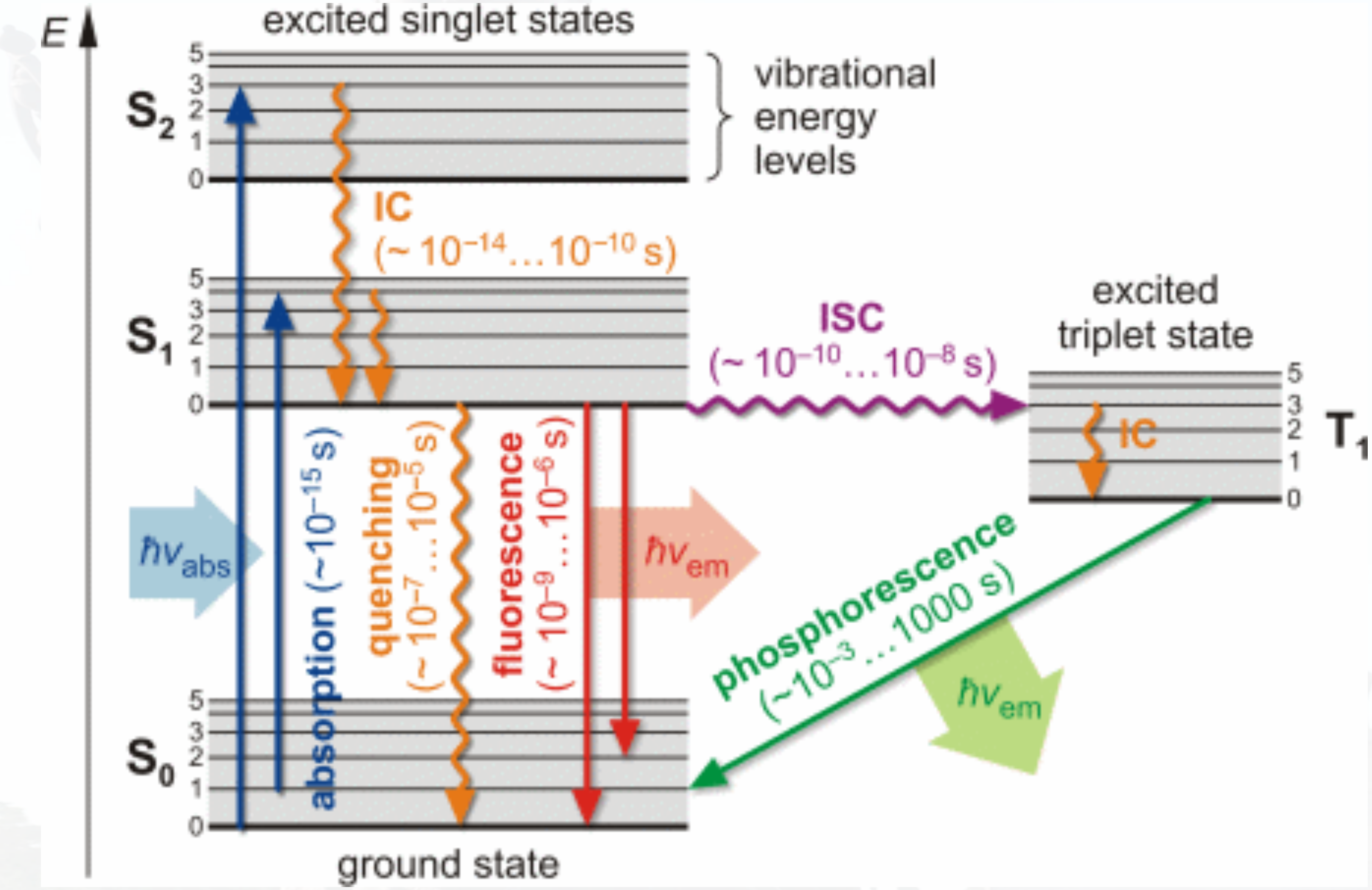
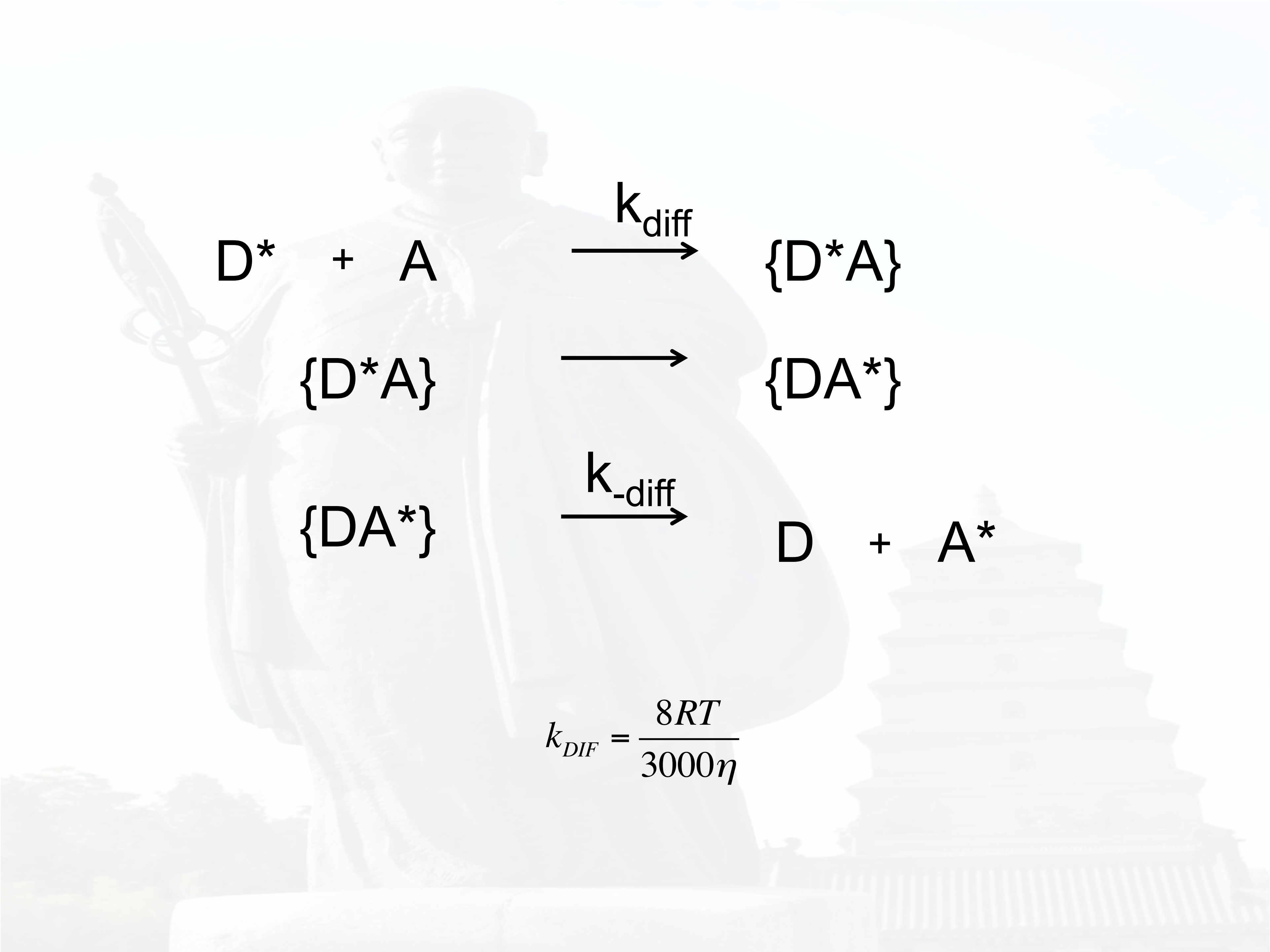
Energy and Electron Transfer


E
excited singlet states
vibrational energy levels
S$_2$
S$_1$
S$_0$
T$_1$
5
3
2
1
0
IC
(~ 10^{-14}…10^{-10} s)
ISC
(~ 10^{-10}…10^{-8} s)
excited triplet state
IC
$\hbar\nu_{abs}$
absorption (~10^{-15} s)
quenching (~ 10^{-7}…10^{-5} s)
fluorescence (~ 10^{-9}…10^{-6} s)
$\hbar\nu_{em}$
phosphorescence (~10^{-3}…1000 s)
$\hbar\nu_{em}$
ground state



$$D^* + A \xrightarrow{k_{diff}} \{D^*A\}$$

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

$$\{DA^*\} \xrightarrow{k_{-diff}} D + A^*$$

$$k_{DIF} = \frac{8RT}{3000\eta}$$

Possibilities

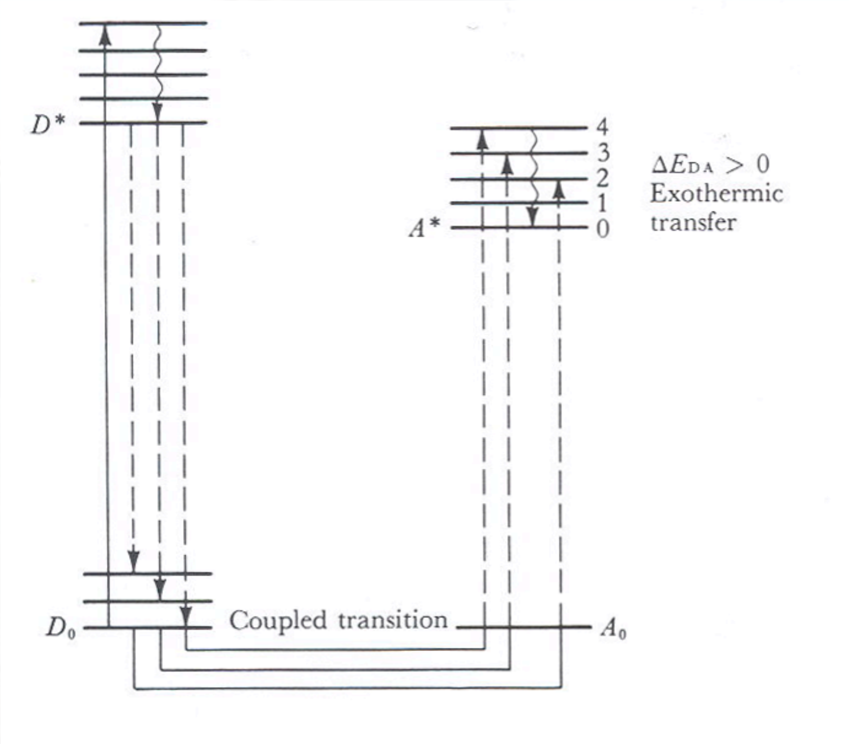
$$^1D^* + A \longrightarrow D + {}^1A^*$$

$$^1D^* + A \longrightarrow D + {}^3A^*$$

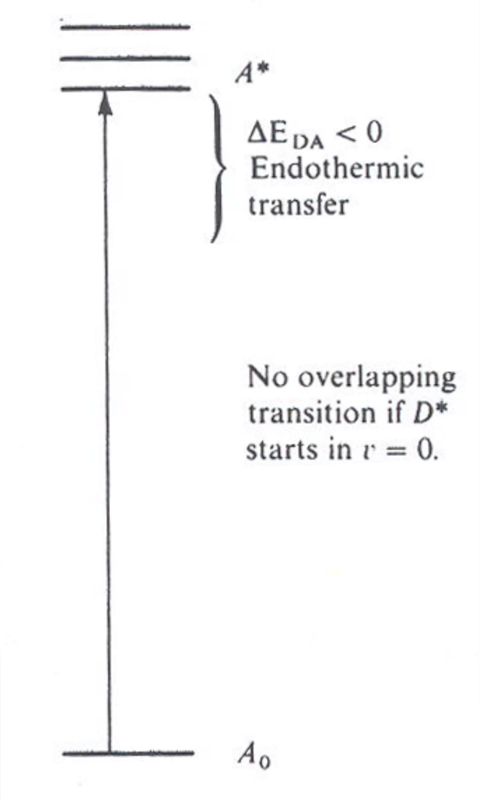
$$^3D^* + A \longrightarrow D + {}^1A^*$$

$$^3D^* + A \longrightarrow D + {}^3A^*$$

Energy Requirement



ENERGY TRANSFER



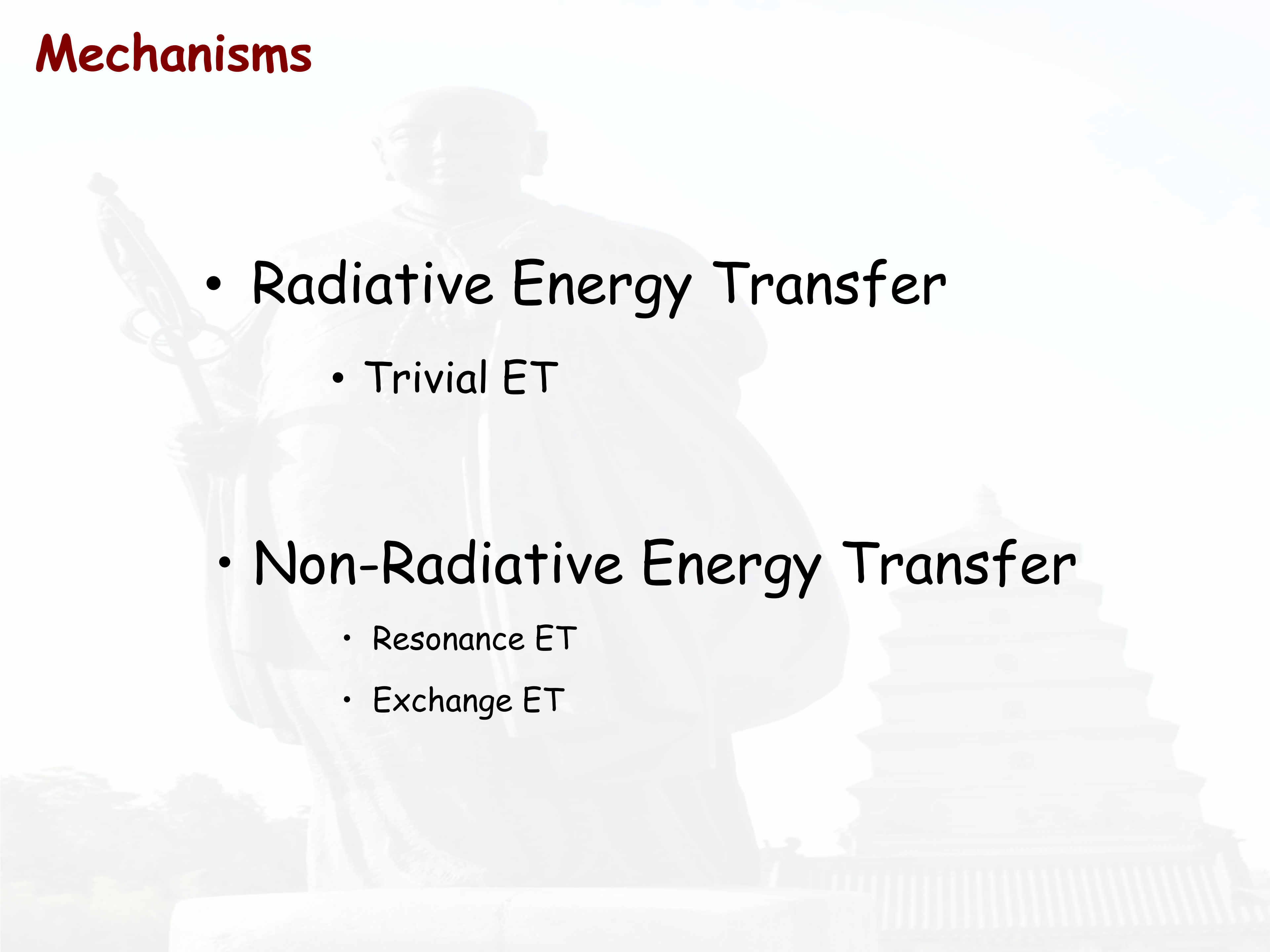
Allowed

$E_D > E_A$

Forbidden

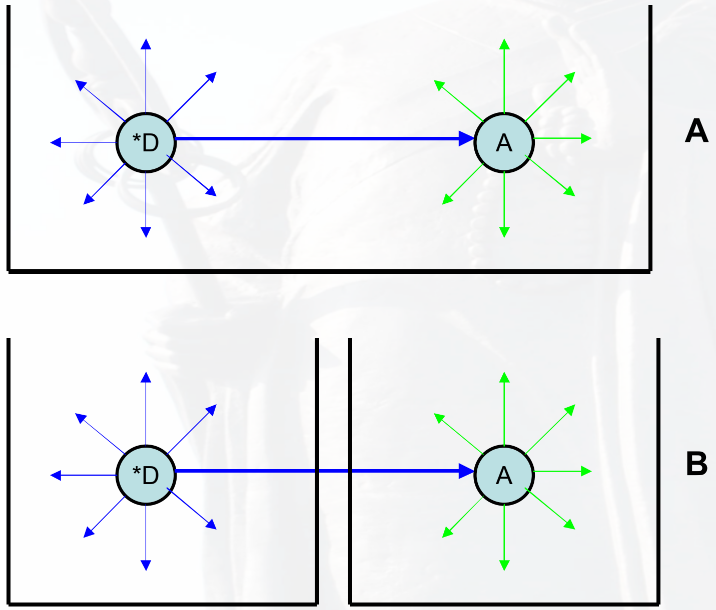
$E_D < E_A$

Mechanisms



- Radiative Energy Transfer
  - Trivial ET
- Non-Radiative Energy Transfer
  - Resonance ET
  - Exchange ET

Trivial energy transfer (*radiative energy transfer*)



$$D^* \longrightarrow D + h\nu$$

$$A + h\nu \longrightarrow A^*$$

- no electronic interaction between D* and *A*
- D* emits a quantum of light which is absorbed by *A*

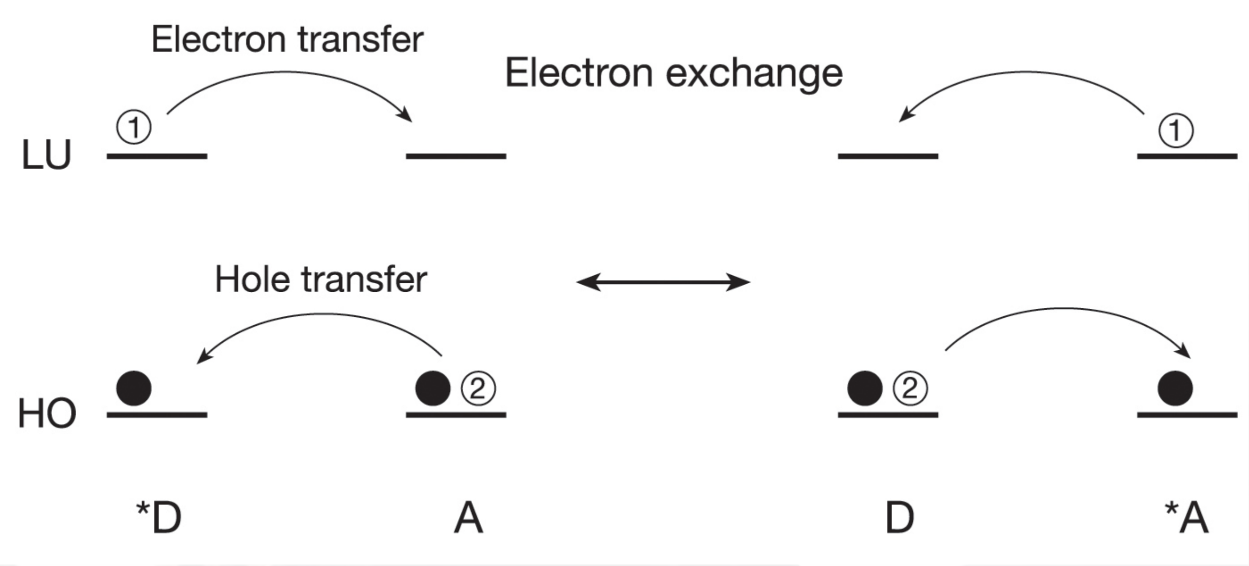
A physical encounter between *A* and D* is not required, the photon must only be emitted in an appropriate direction and the medium must be transparent in order to allow transmission.

Non-Radiative Energy Transfer

Exchange Energy Transfer

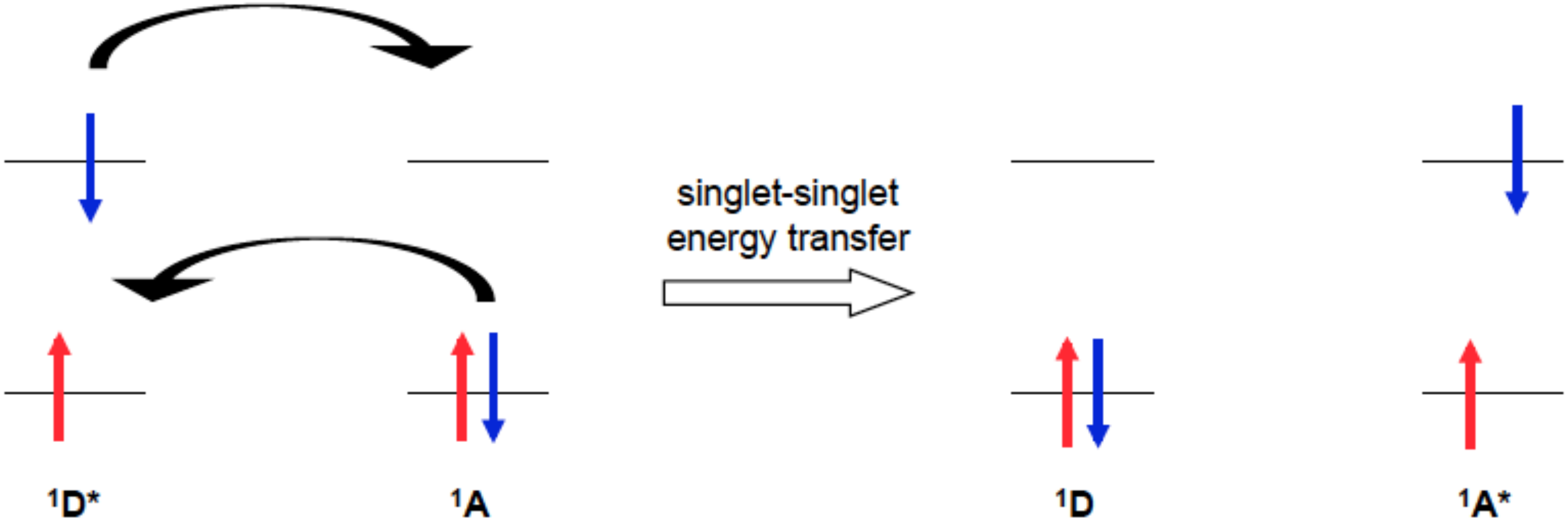
Collisional Energy Transfer

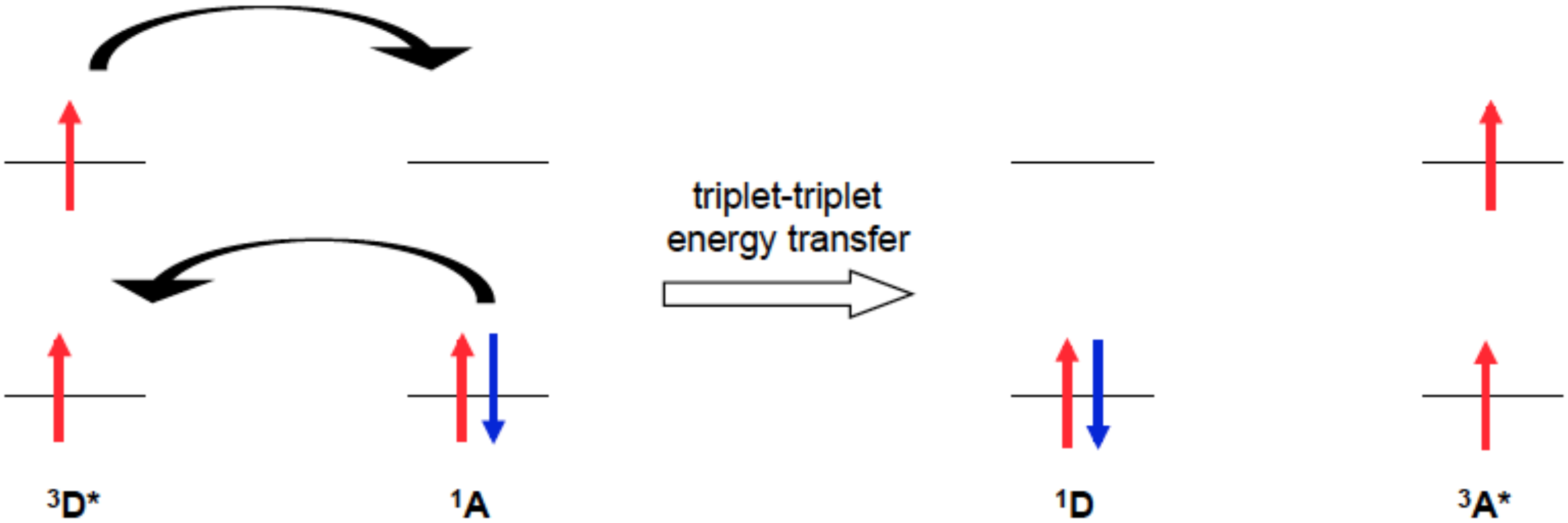
Dexter Energy Transfer



$$k_{ET}\ (\text{exchange}) = KJ\ \exp(-2\ r_{DA}/L)$$

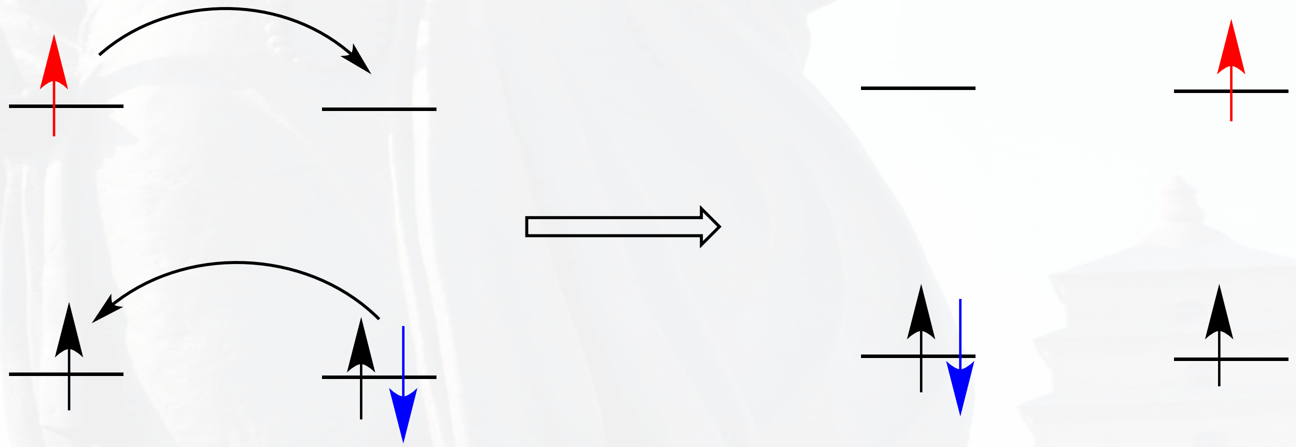
Exchange Energy Transfer





Triplet-Triplet Energy Transfer

$$^{3}D^{*} + A \qquad D + {}^{3}A^{*}$$



$$k_{ET}\ (\text{exchange}) = KJ\,\exp(-2\,r_{DA}/L)$$

Exchange Energy Transfer

$$k_{\mathrm{ET}}\,(\text{exchange}) = KJ\exp(-2\mathrm{r}_{\mathrm{DA}}/\mathrm{L})$$

where K is related to the specific orbital interactions such as the dependence of orbital overlap to the instantaneous orientations of *D and A.

J is the normalized spectral overlap integral, where normalized means that both the emission intensity (I_{D}) and extinction coefficient (ε_A) have been adjusted to unit area on the wavenumber scale. It is important that J, by being normalized does not depend on the actual magnitude of ε_A.

r_{DA} is the donor-acceptor separation relative to their van der Waals radii, L

Non-Radiative Energy Transfer

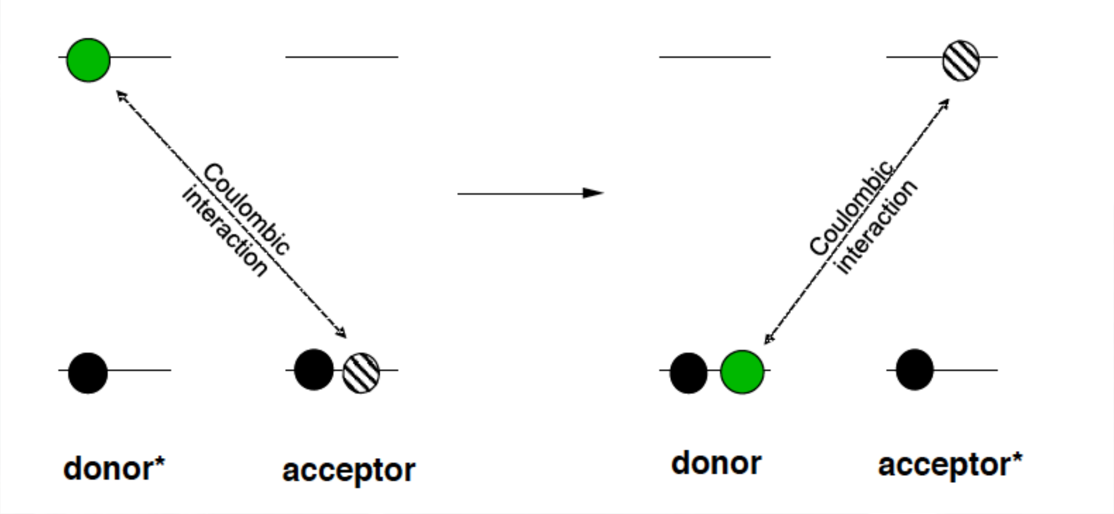
Dipole-Dipole Energy Transfer

Coulombic Energy Transfer

Resonance Energy Transfer

Förster Energy Transfer

Förster Resonance Energy Transfer (FRET)

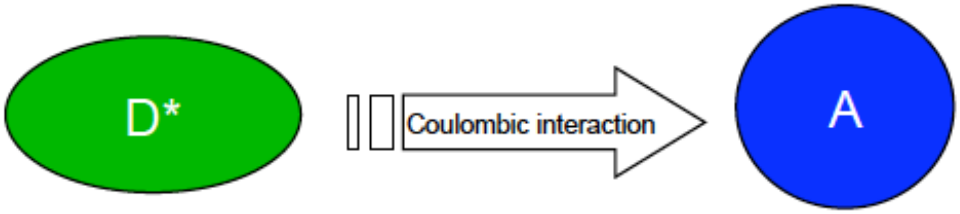


$$k_{ET}\text{ (Dipole - dipole)} \propto E^2 \approx \left(\frac{\mu_D \mu_A}{R_{DA}^3}\right)^2 = \frac{\mu_D^2 \mu_A^2}{R_{DA}^6}$$

Resonance Energy Transfer

The dipole-dipole interaction represents a classical Coulombic interaction so we can make a classical analogy

the electric field
around an excited
molecule D*
behaves like a
field generated by
a classical
oscillating dipole



the electrons in
the ground state
of A are assumed
not to be
oscillating at all

- the oscillating field of D* causes the excitation of nearby electronic systems (provided certain resonance conditions are met)
- this is analogous to absorption of a photon by A to generate A* as a result of coupling between A_{e-} and and the oscillating electric field of the light wave

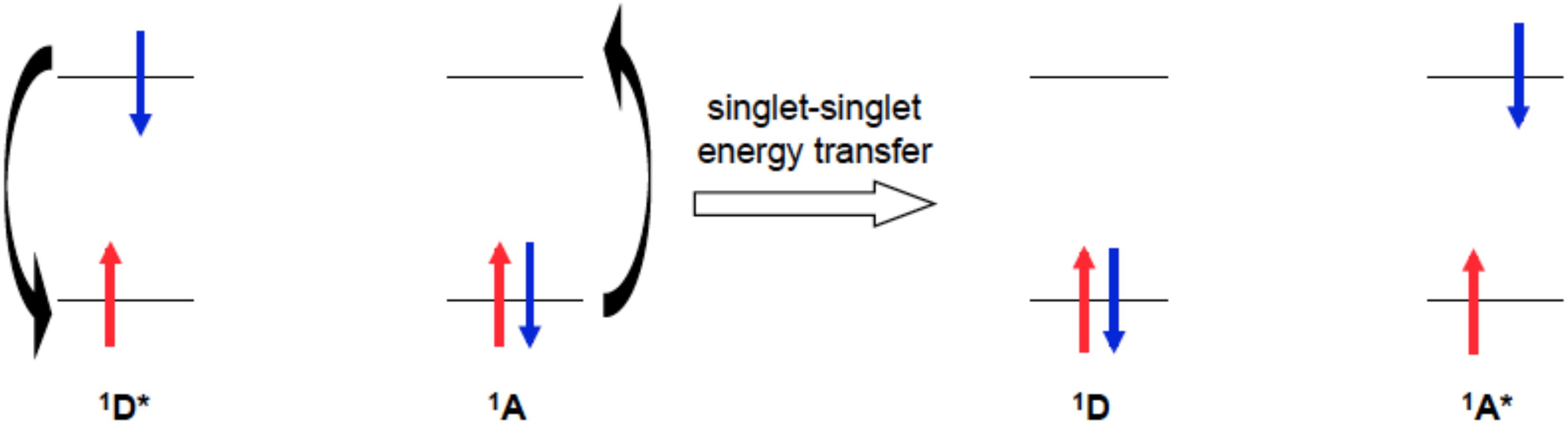
induced dipole time

transition dipole

$$\mu = \mu_0 \cos(2\pi\nu t)$$

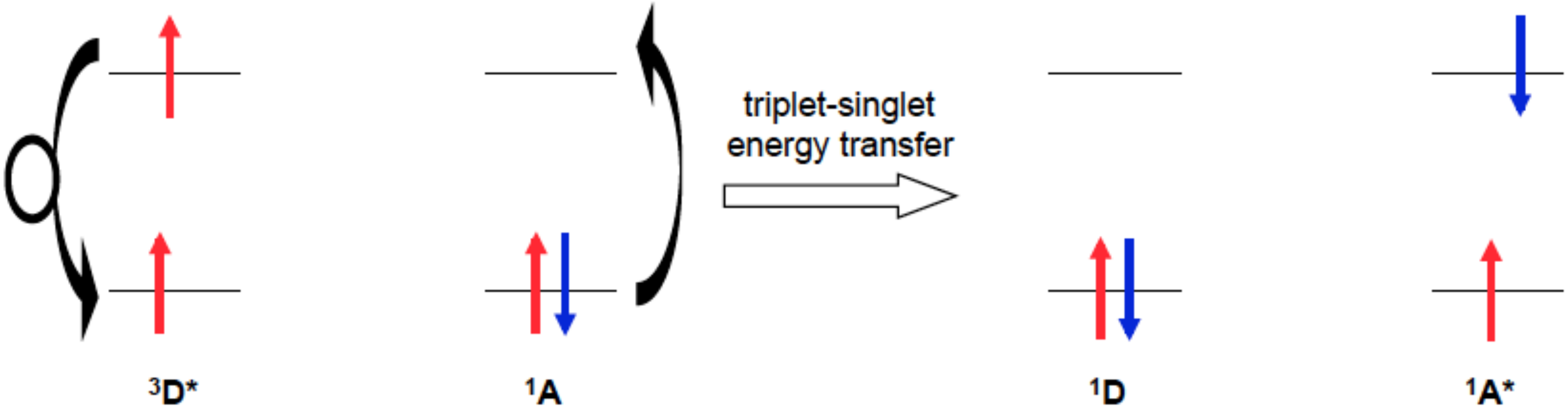
oscillation frequency

Resonance Energy Transfer



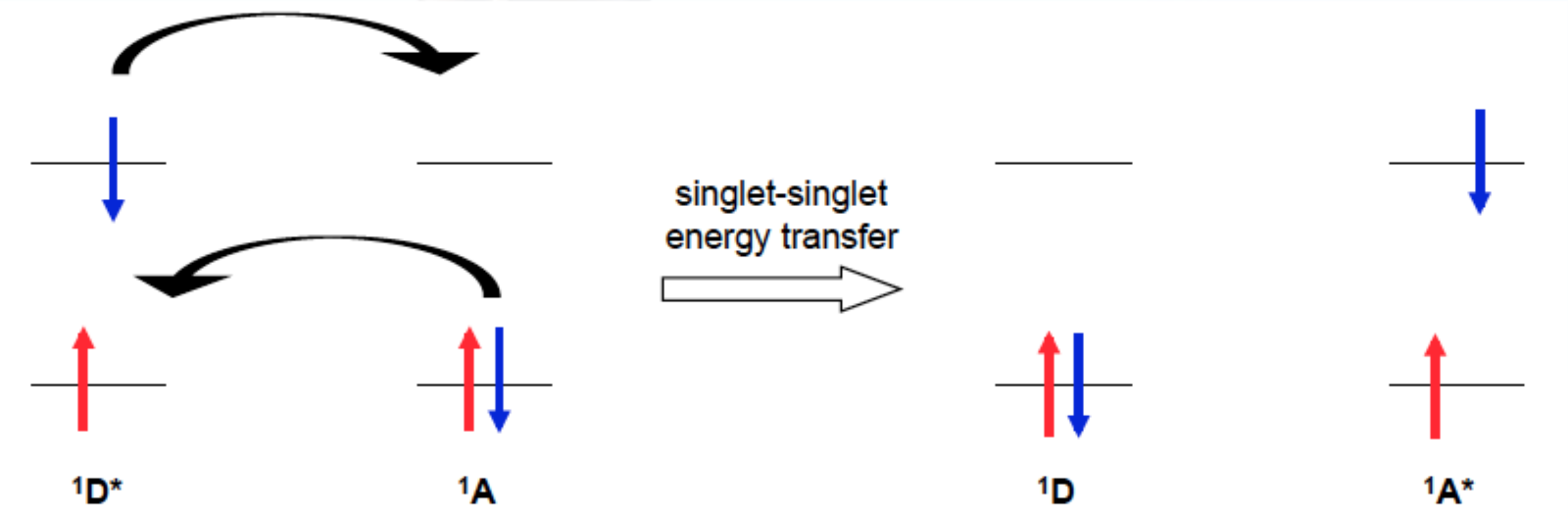
singlet-singlet energy transfer

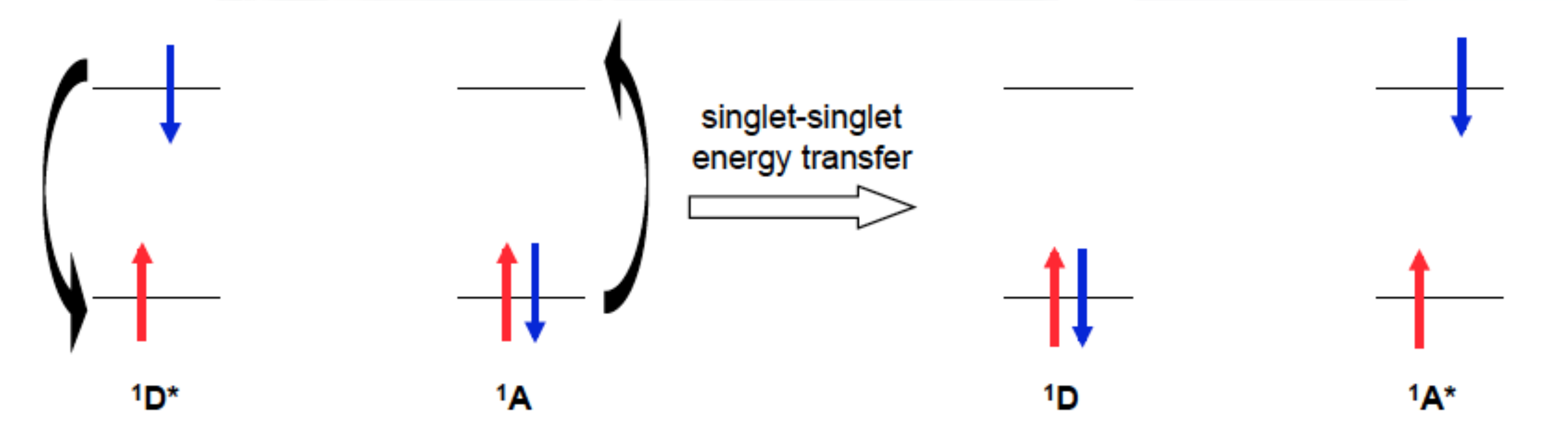
very rare in solution!



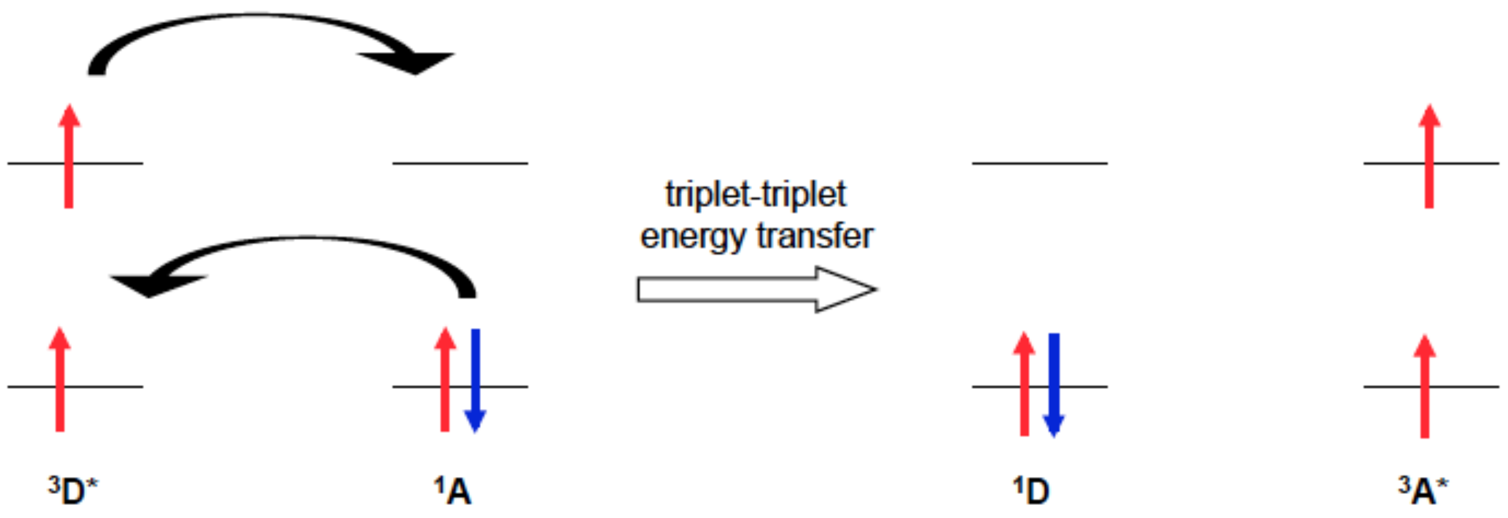
triplet-singlet energy transfer

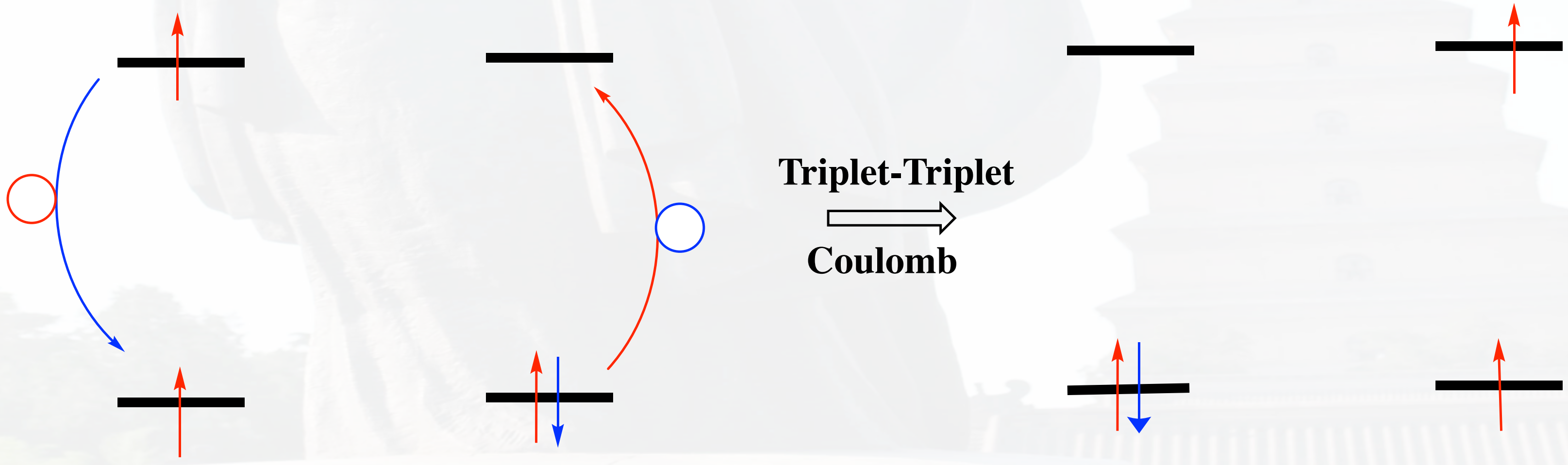
Exchange vs Coulomb (Singlet-Singlet)





Exchange vs Coulomb (Triplet-Triplet)





$$k_{D^* \rightarrow A} = \frac{8.8 \times 10^{-25} K^2 \phi_D}{n^4 \tau_D R^6} \int_0^\infty F_D(\nu)\epsilon_A(\nu)\,\frac{d\nu}{\nu^4}$$

κ^2 mutual orientation of the dipoles in space

ϕ_D = quantum yield of donor emission

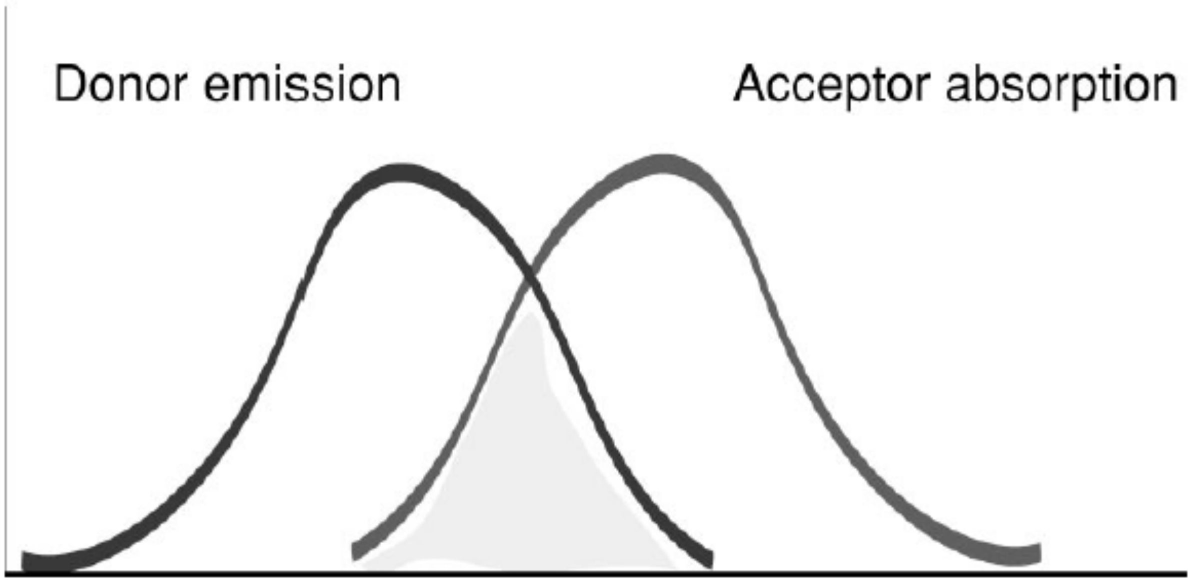
n = refractive index of the solvent

τ_D = actual donor lifetime

R = distance between donor and acceptor

$\int_0^\infty F_D(\nu)\epsilon_A(\nu)\,\frac{d\nu}{\nu^4}$ = spectral overlap integral

$$\int_0^\infty F_D(\nu)\epsilon_A(\nu)\,\frac{d\nu}{\nu^4}$$ = spectral overlap integral



Förster theory predicts that k_{ET} for an energy transfer via dipole-dipole interactions will be proportional to the following quantities:

- The square of the transition dipole moment $\boldsymbol{\mu}_D$, corresponding to the *D → D transition.

- The square of the transition dipole moment $\boldsymbol{\mu}_A$ corresponding to the A → *A transition.

- The inverse sixth power of the separation between *D and A (i.e. $1/R_{DA}^6$).

Dipole-dipole mechanism will be most favored for *D and A pairs such that:

- The *D → D and A → *A processes correspond to a large (spectral) overlap integral, *J*.
- The radiative rate constant, k°_{D}, is as large as possible.
- The magnitude of ε_A is as large as possible.
- There is a small spatial separation between *D and A.
- There will be a preferred orientation for which energy transfer is most favorable.

Differences between Förster (dipole-dipole interaction) and Dexter (electron exchange) energy transfer processes

- The rate of dipole-induced energy transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as $\mathit{exp}-(2r/L)$. Quantitatively, this means that k_{ET}(exchange) drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å)

- The rate of dipole-induced transfer depends on the oscillator strength of the *D → D and A → *A radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the *D → D and A → *A transitions

$D^* + A \longrightarrow D + A^*$

$$k_{ET}\ (\text{total}) \propto \left[\alpha\left\langle \Psi(D^*)\Psi(A)\right| H_e \left| \Psi(D)\Psi(A^*)\right\rangle^2\right.$$

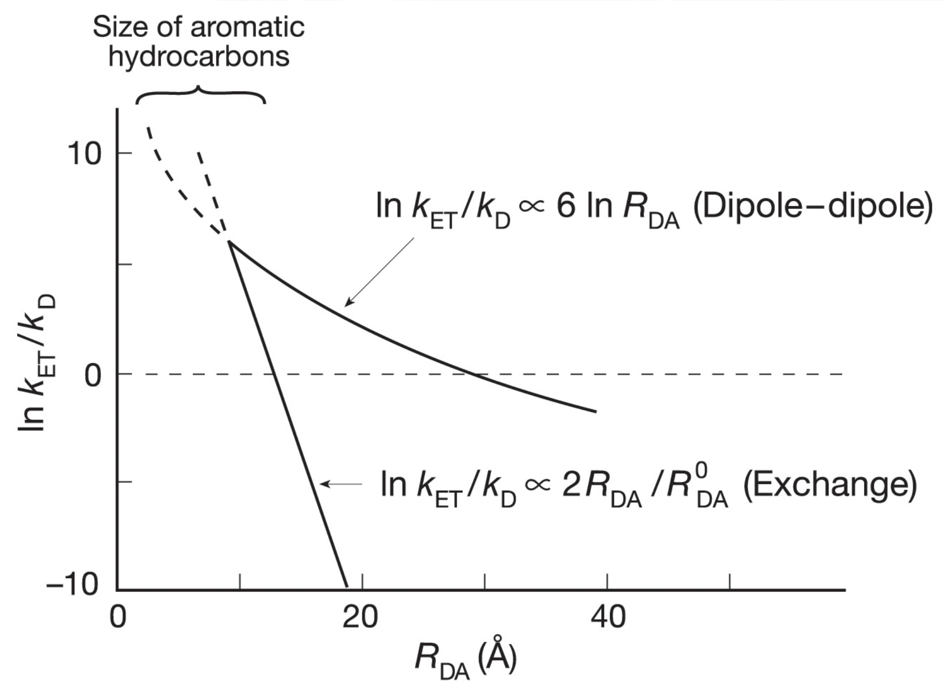
Electron exchange

$$\left. + \beta\left\langle \Psi(D^*)\Psi(A)\right| H_c \left| \Psi(D)\Psi(A^*)\right\rangle^2\right]$$

Electron dipole-dipole interactions

$$k_{ET}\ (\text{Dipole-dipole}) \propto E^2 \approx \left(\frac{\mu_D\mu_A}{R_{DA}^3}\right)^2 = \frac{\mu_D^2\mu_A^2}{R_{DA}^6}$$

$$k_{ET}\ (\text{exchange}) = KJ\ \exp(-2\ r_{DA}/L)$$



Distance dependence, when it can be measured accurately, is a basis for distinguishing energy transfer that occurs by dipole–dipole interactions from electron exchange interactions, since the latter generally falls off exponentially with the separation $\mathbf{R_{DA}}$

Spin in Energy Transfer

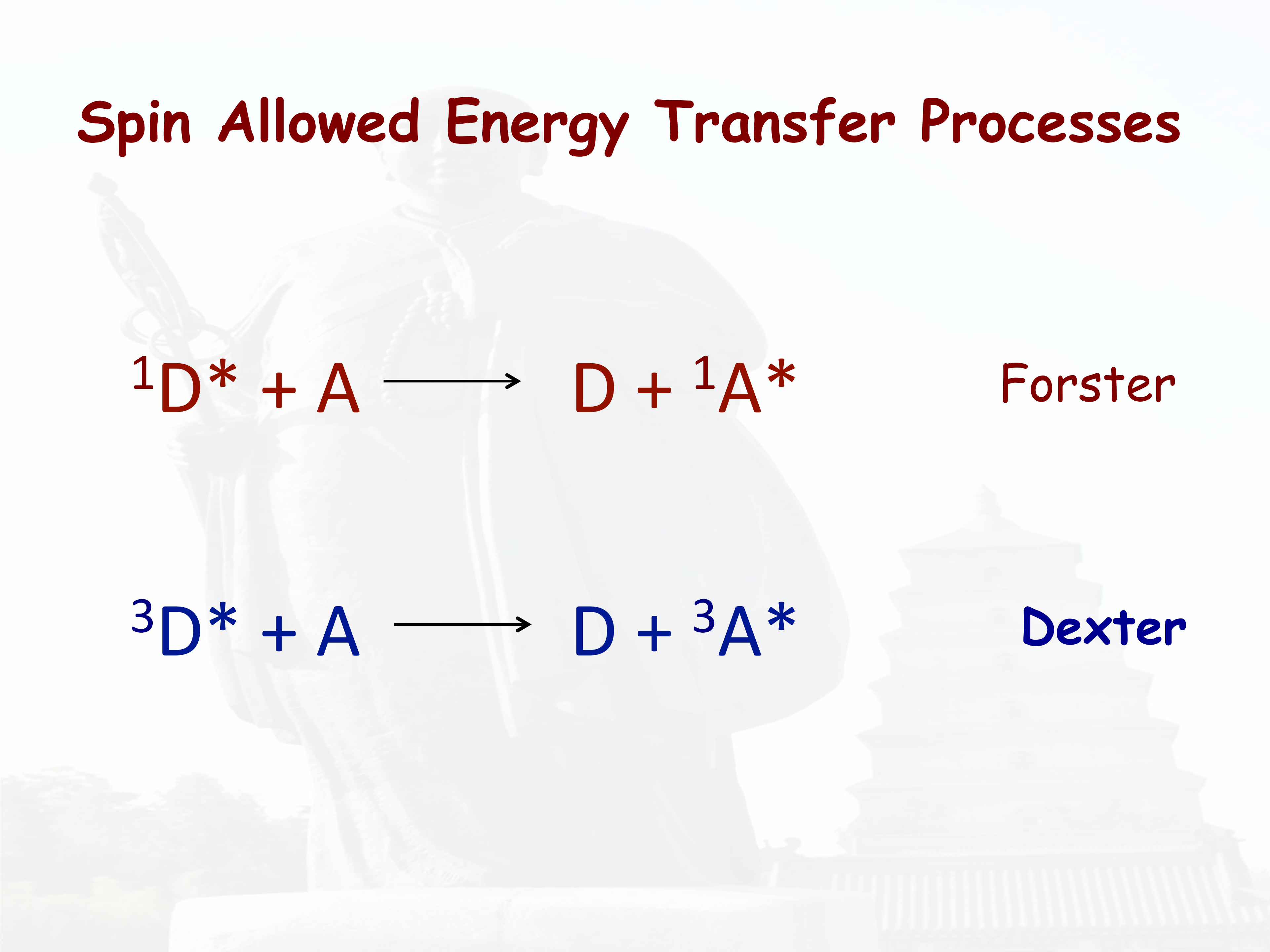
$$ {}^1D^* + A \longrightarrow D + {}^1A^* $$

~~$ {}^1D^* + A \longrightarrow D + {}^3A^* $~~

~~$ {}^3D^* + A \longrightarrow D + {}^1A^* $~~

$$ {}^3D^* + A \longrightarrow D + {}^3A^* $$

Spin Allowed Energy Transfer Processes



$^{1}D^{*} + A \longrightarrow D + {}^{1}A^{*}$ Forster

$^{3}D^{*} + A \longrightarrow D + {}^{3}A^{*}$ **Dexter**

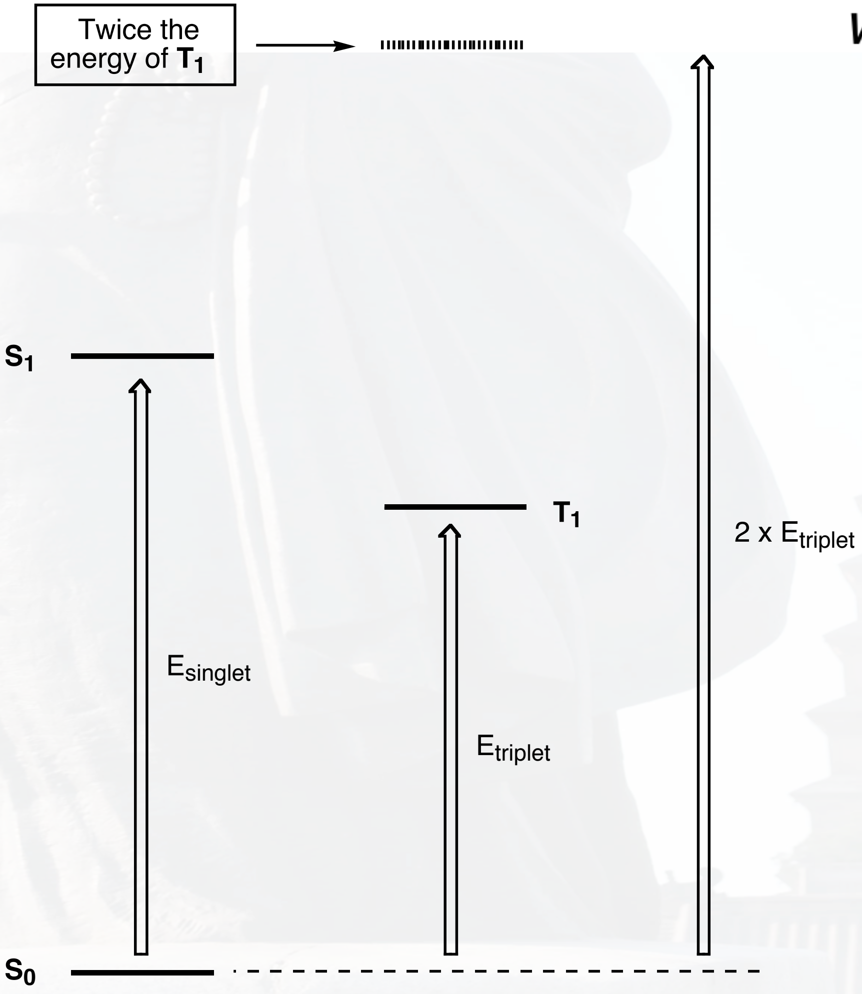
A Theory of Sensitized Luminescence in Solids, D. L. Dexter*, J. Chem. Phys.* 21, 836 (1953)

Transfer mechanisms of electronic excitation, Th. Forster, *Discussions Faraday Soc.* 27, 7, (1959)

Triplet-Triplet Annihilation

$$^*D(T_1) + {}^*D(T_1) \xrightarrow{k_{TTA}} {}^*D(S_1) + D(S_0)$$

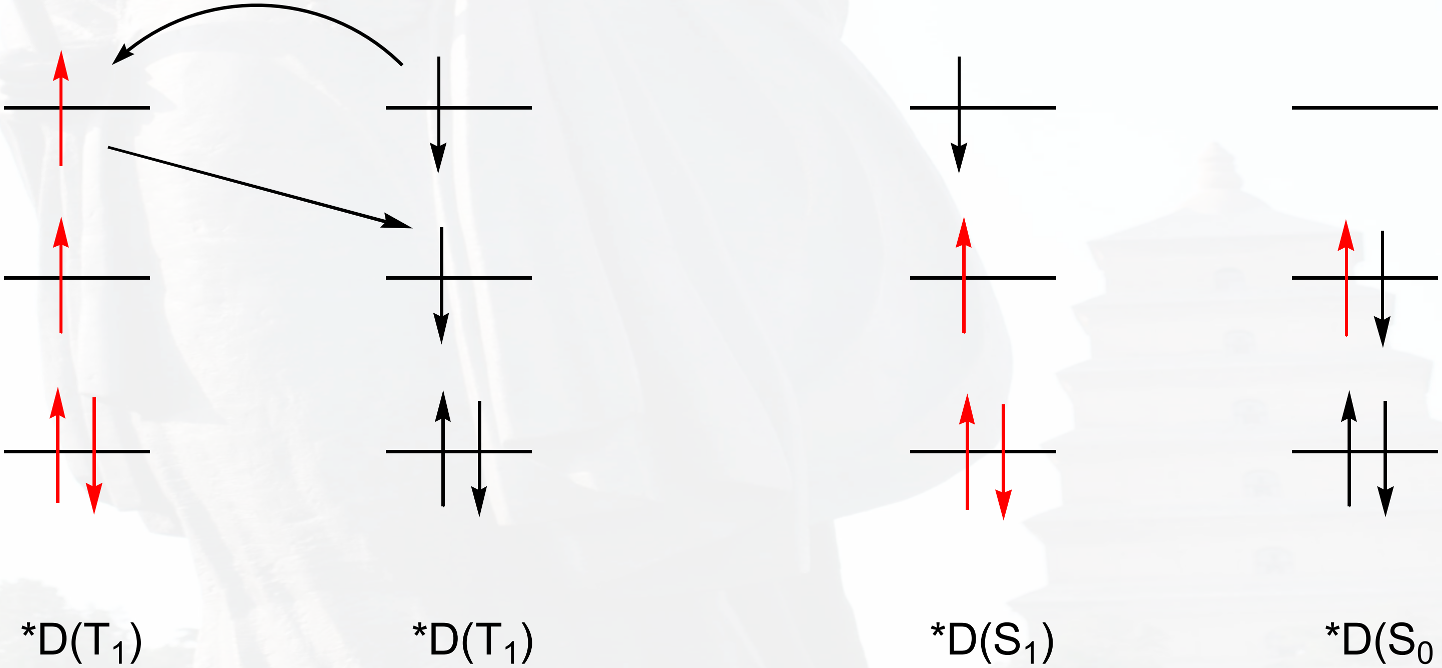
with $\Delta H < 0$



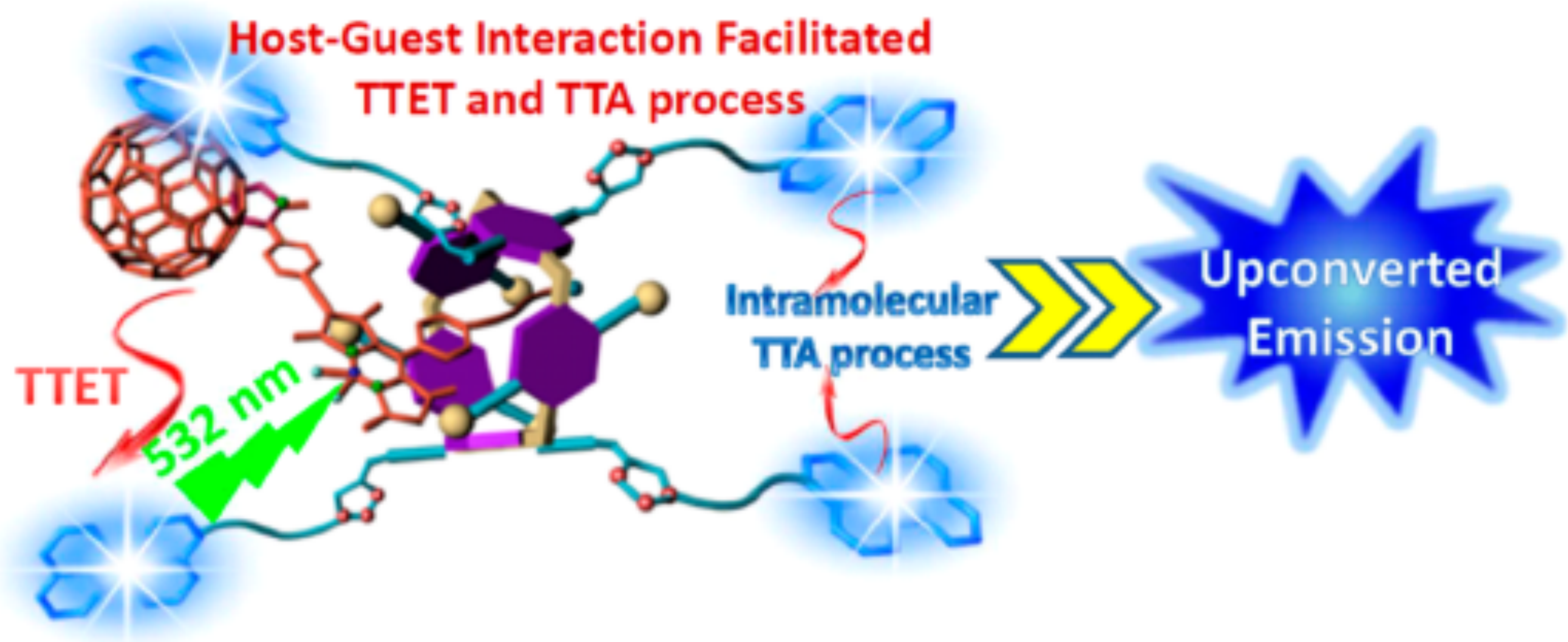
$$^{*}D(T_1) + {}^{*}D(T_1) \xrightarrow{k_{TTA}} {}^{*}D(S_1) + D(S_0)$$

with $\Delta H < 0$

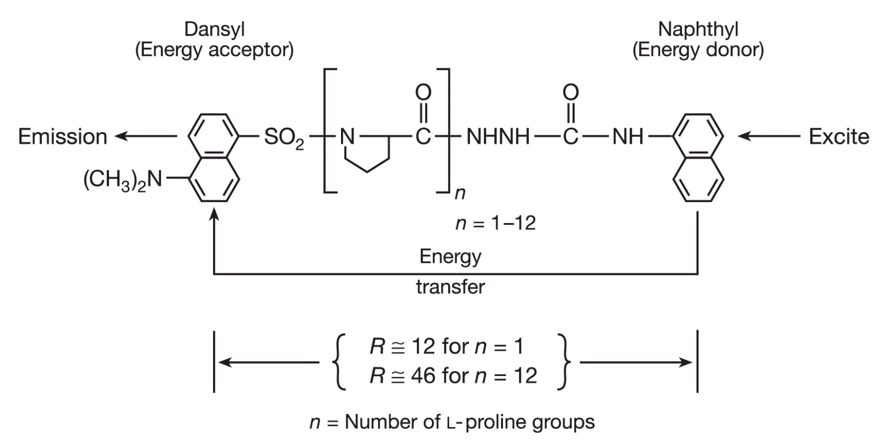
Initial states **Final states**



Upconversion Through Triplet-Triplet Annihilation



Energy Transfer: A Spectroscopic Ruler
L. Stryer and R. Hauhland,
PNAS, 58, 719 (**1967**)



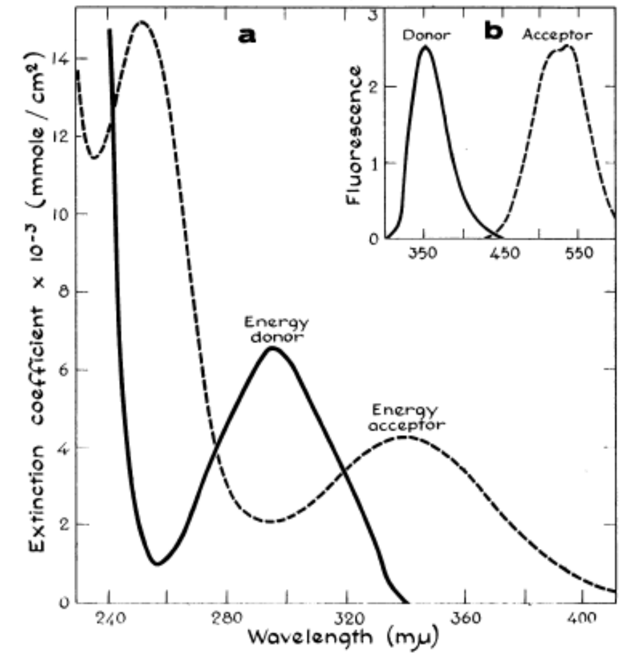
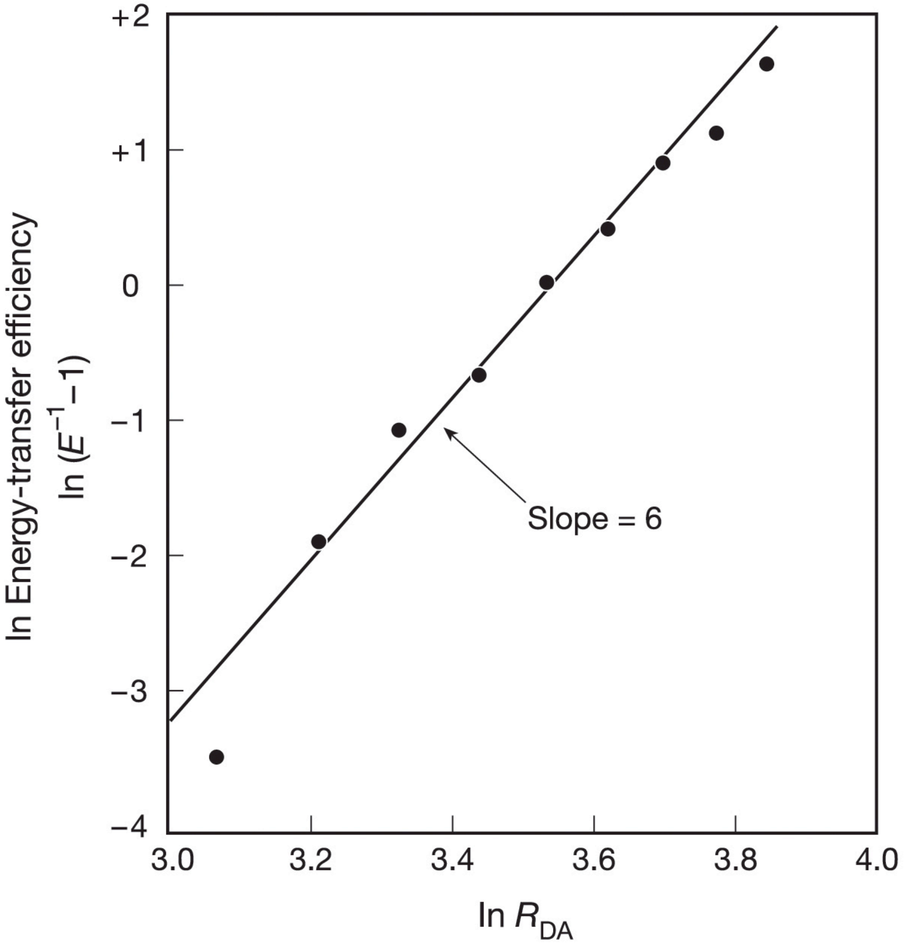
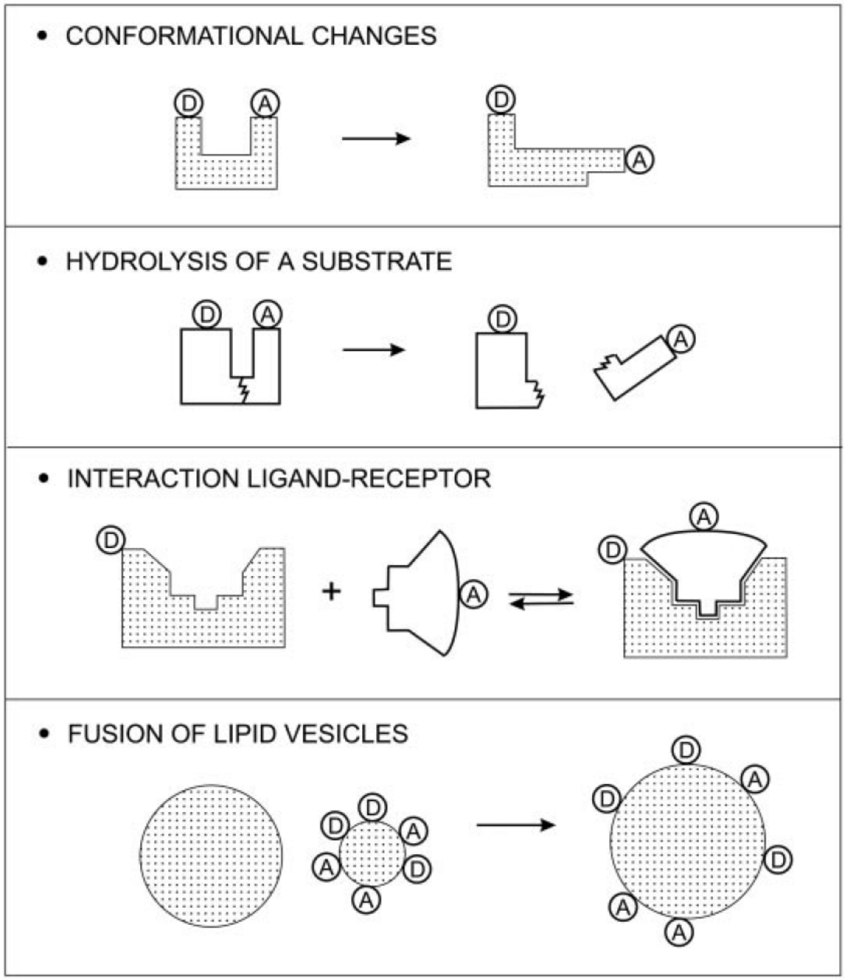
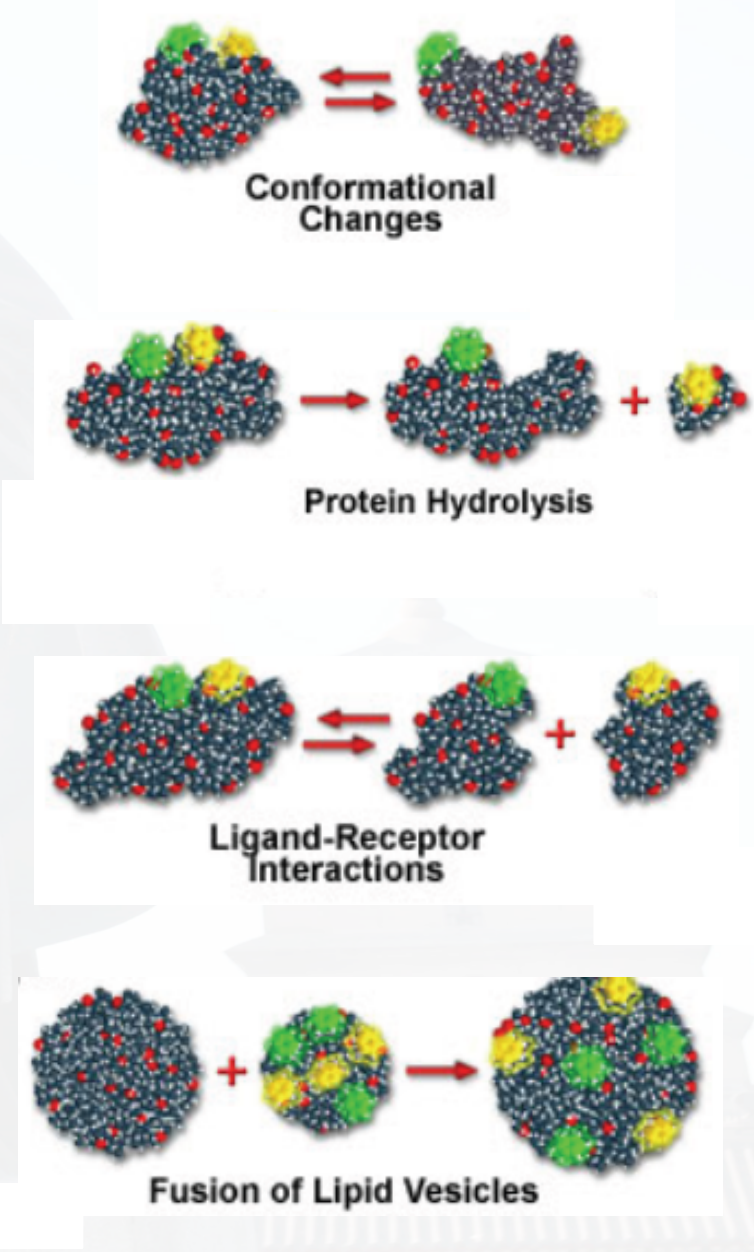


FIG. 2.—(*a*) Absorption spectrum of the energy donor (1-acetyl-4-(1-naphthyl) semicarbazide, ———) and the energy acceptor (dansyl-L-prolyl-hydrazide, - - - - -) in ethanol; (*b*) emission spectrum of the energy donor (———) and the energy acceptor (- - - - -) in ethanol.

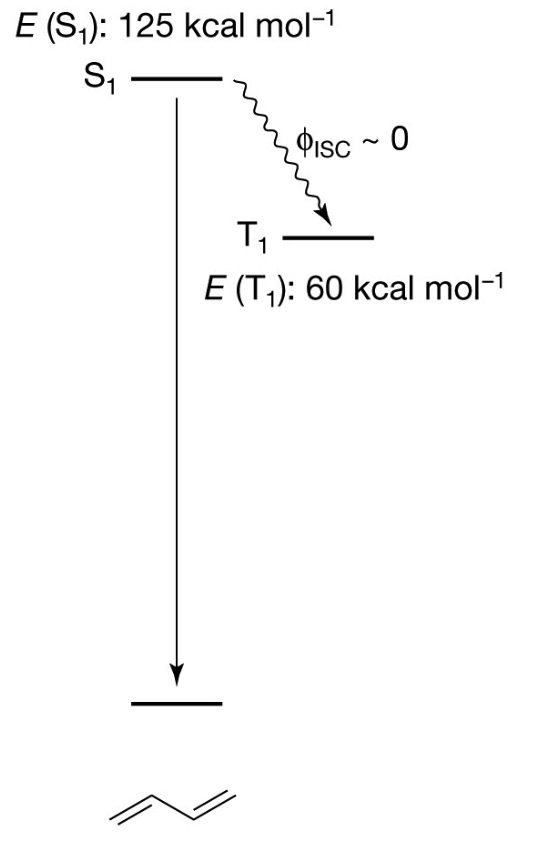


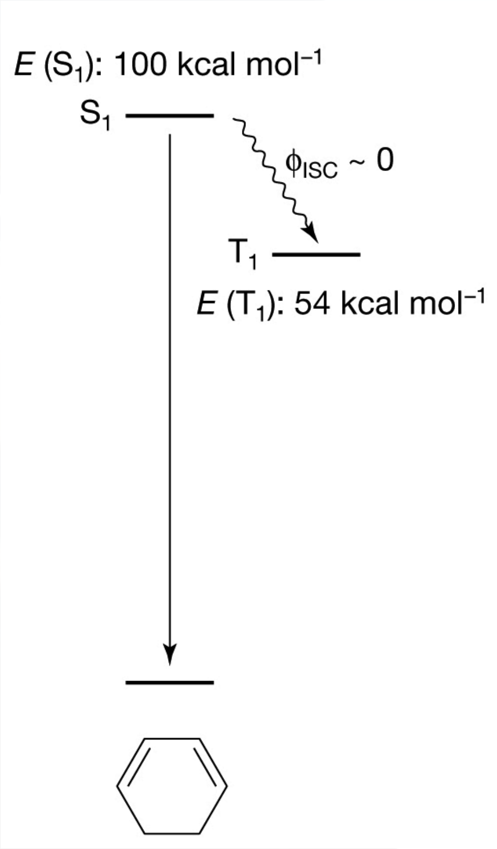
Making Use of Förster Resonance Energy Transfer

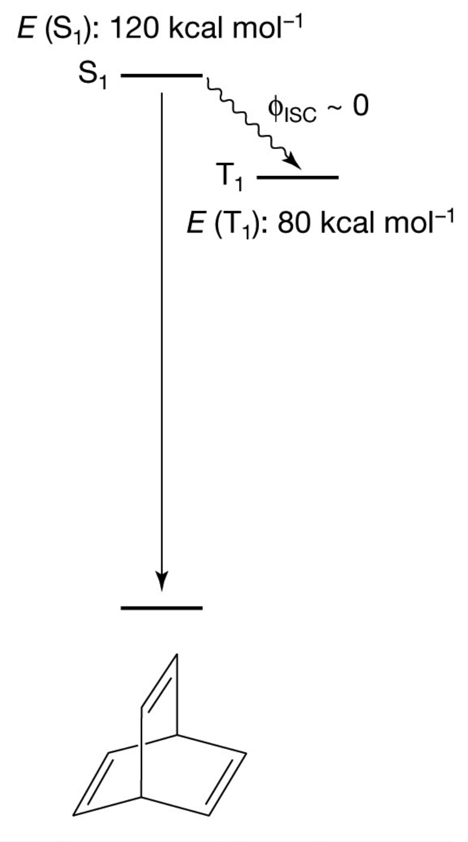




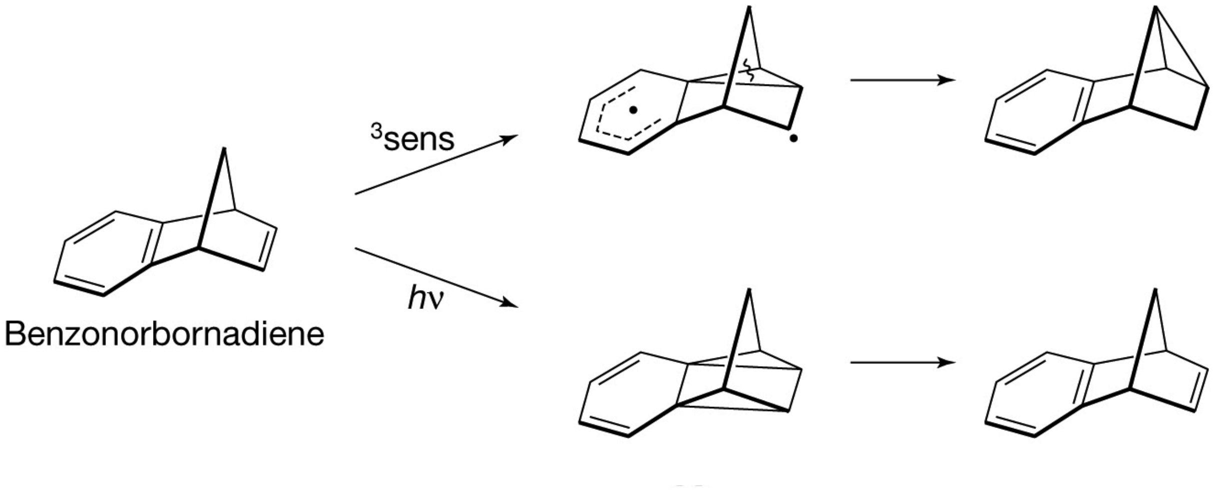
Need for Triplet Sensitization







Triplet Sensitization



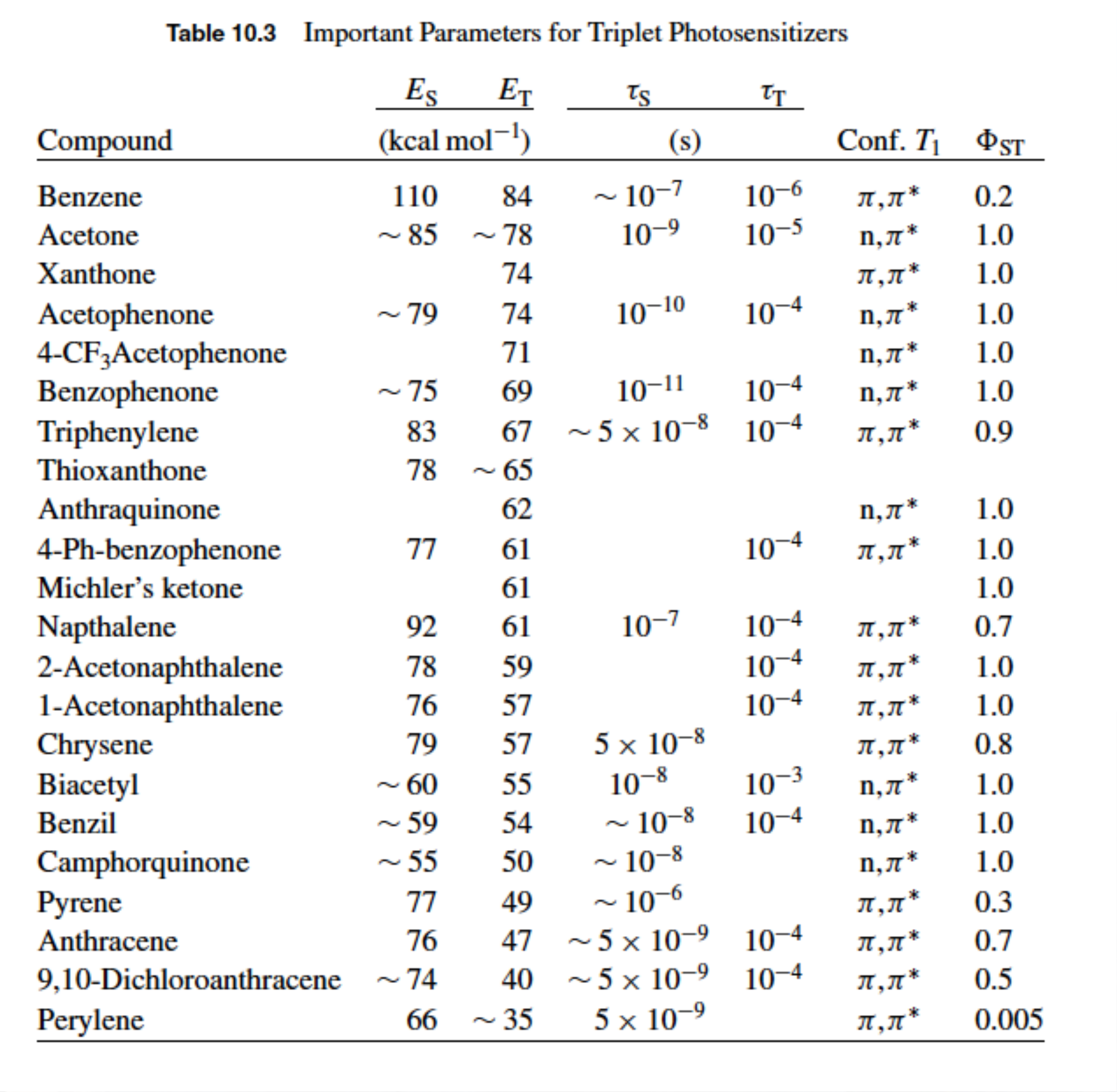
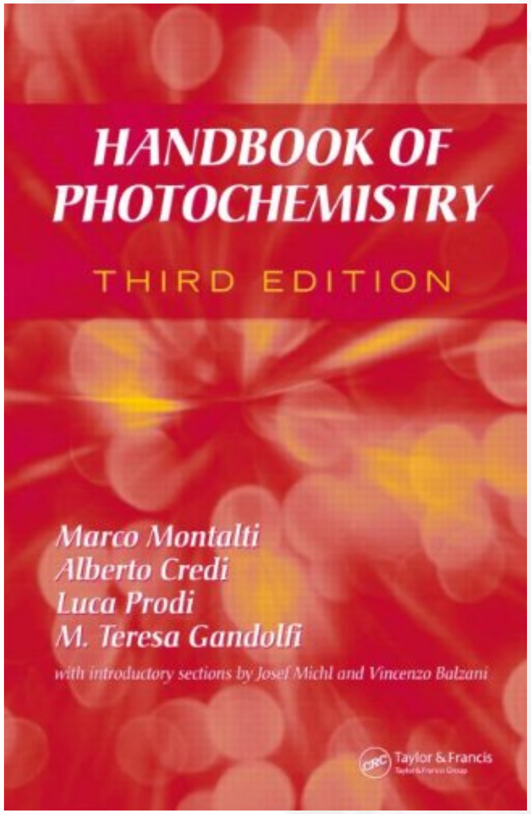


Table 10.3 Important Parameters for Triplet Photosensitizers

	E_S	E_T	τ_S	τ_T		
Compound	(kcal mol^{-1})		(s)		Conf. T_1	Φ_{ST}
Benzene	110	84	$\sim 10^{-7}$	10^{-6}	π,π^*	0.2
Acetone	~ 85	~ 78	10^{-9}	10^{-5}	n,π^*	1.0
Xanthone		74			π,π^*	1.0
Acetophenone	~ 79	74	10^{-10}	10^{-4}	n,π^*	1.0
4-CF_3Acetophenone		71			n,π^*	1.0
Benzophenone	~ 75	69	10^{-11}	10^{-4}	n,π^*	1.0
Triphenylene	83	67	$\sim 5 \times 10^{-8}$	10^{-4}	π,π^*	0.9
Thioxanthone	78	~ 65				
Anthraquinone		62			n,π^*	1.0
4-Ph-benzophenone	77	61		10^{-4}	π,π^*	1.0
Michler's ketone		61				1.0
Napthalene	92	61	10^{-7}	10^{-4}	π,π^*	0.7
2-Acetonaphthalene	78	59		10^{-4}	π,π^*	1.0
1-Acetonaphthalene	76	57		10^{-4}	π,π^*	1.0
Chrysene	79	57	5×10^{-8}		π,π^*	0.8
Biacetyl	~ 60	55	10^{-8}	10^{-3}	n,π^*	1.0
Benzil	~ 59	54	$\sim 10^{-8}$	10^{-4}	n,π^*	1.0
Camphorquinone	~ 55	50	$\sim 10^{-8}$		n,π^*	1.0
Pyrene	77	49	$\sim 10^{-6}$		π,π^*	0.3
Anthracene	76	47	$\sim 5 \times 10^{-9}$	10^{-4}	π,π^*	0.7
9,10-Dichloroanthracene	~ 74	40	$\sim 5 \times 10^{-9}$	10^{-4}	π,π^*	0.5
Perylene	66	~ 35	5×10^{-9}		π,π^*	0.005



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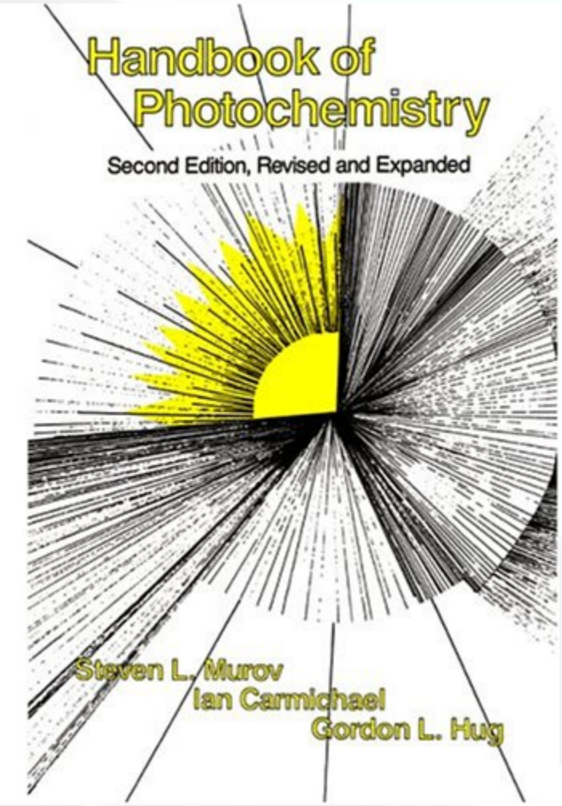

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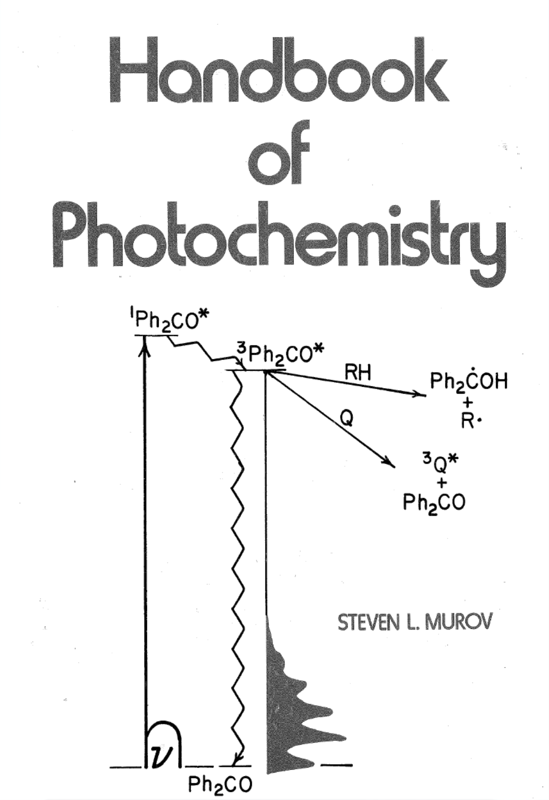

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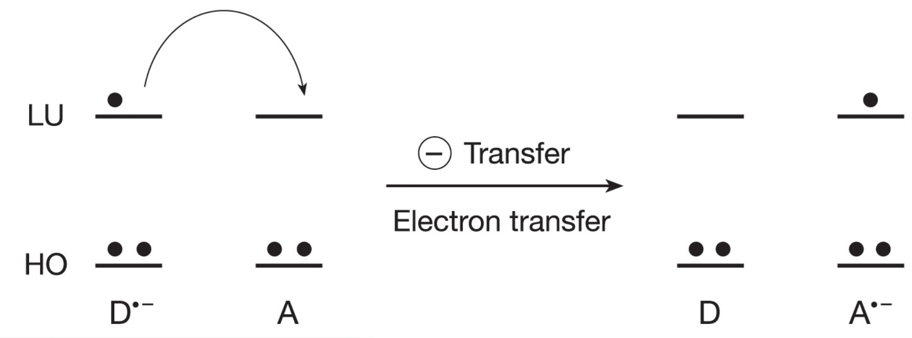
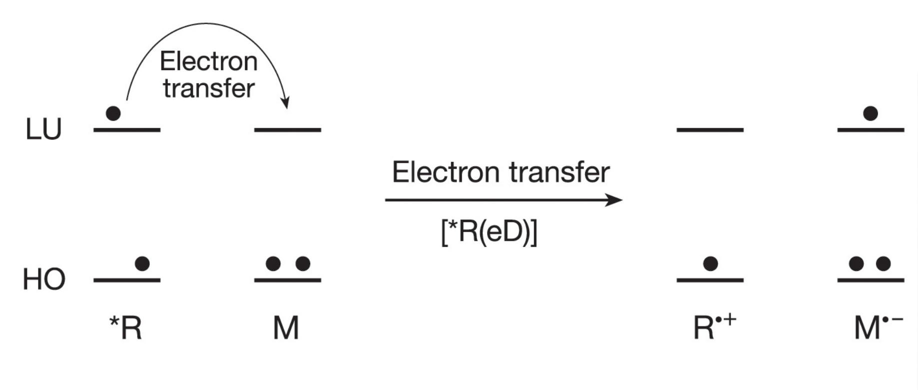
Electron Transfer

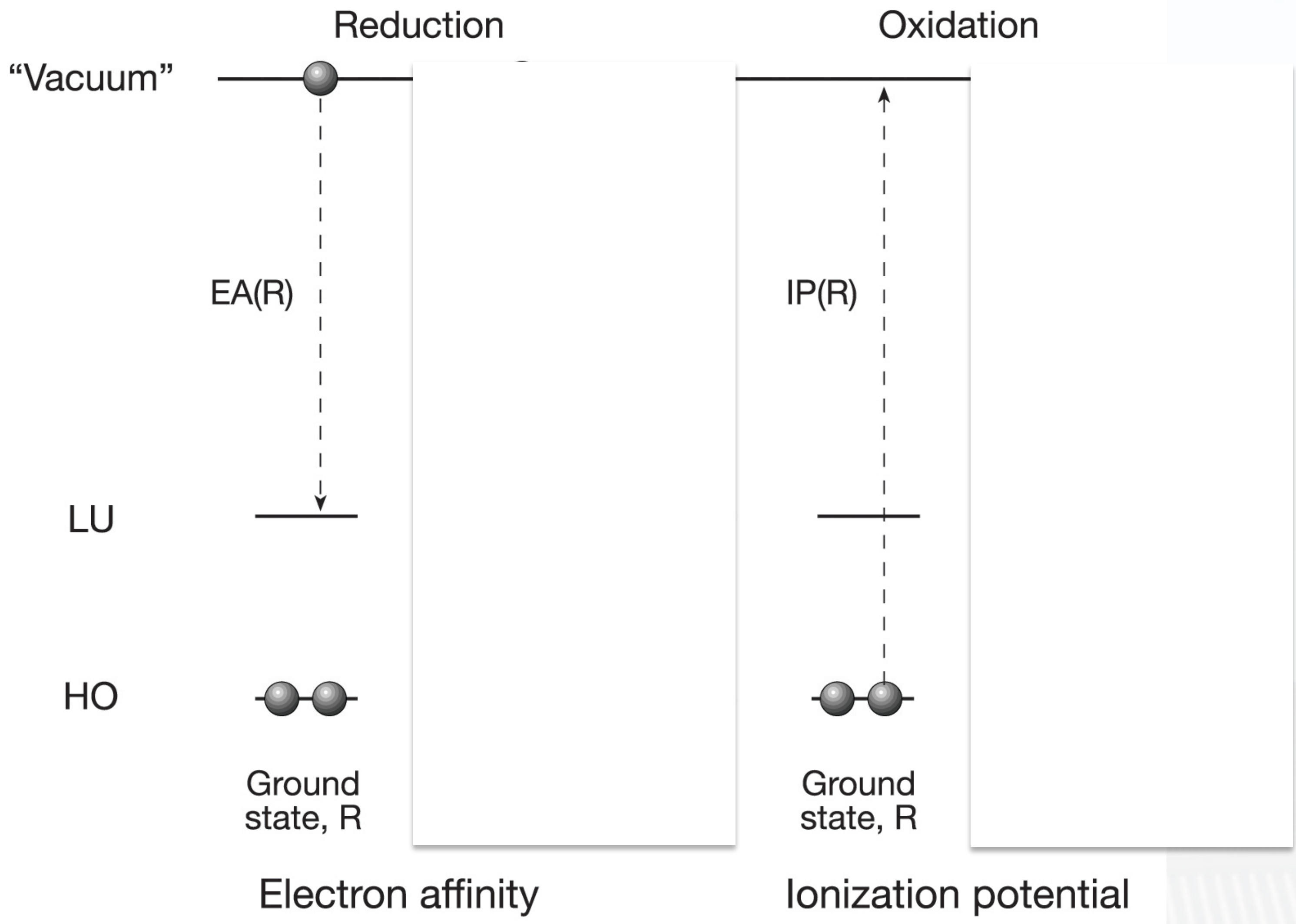
Charge Shift

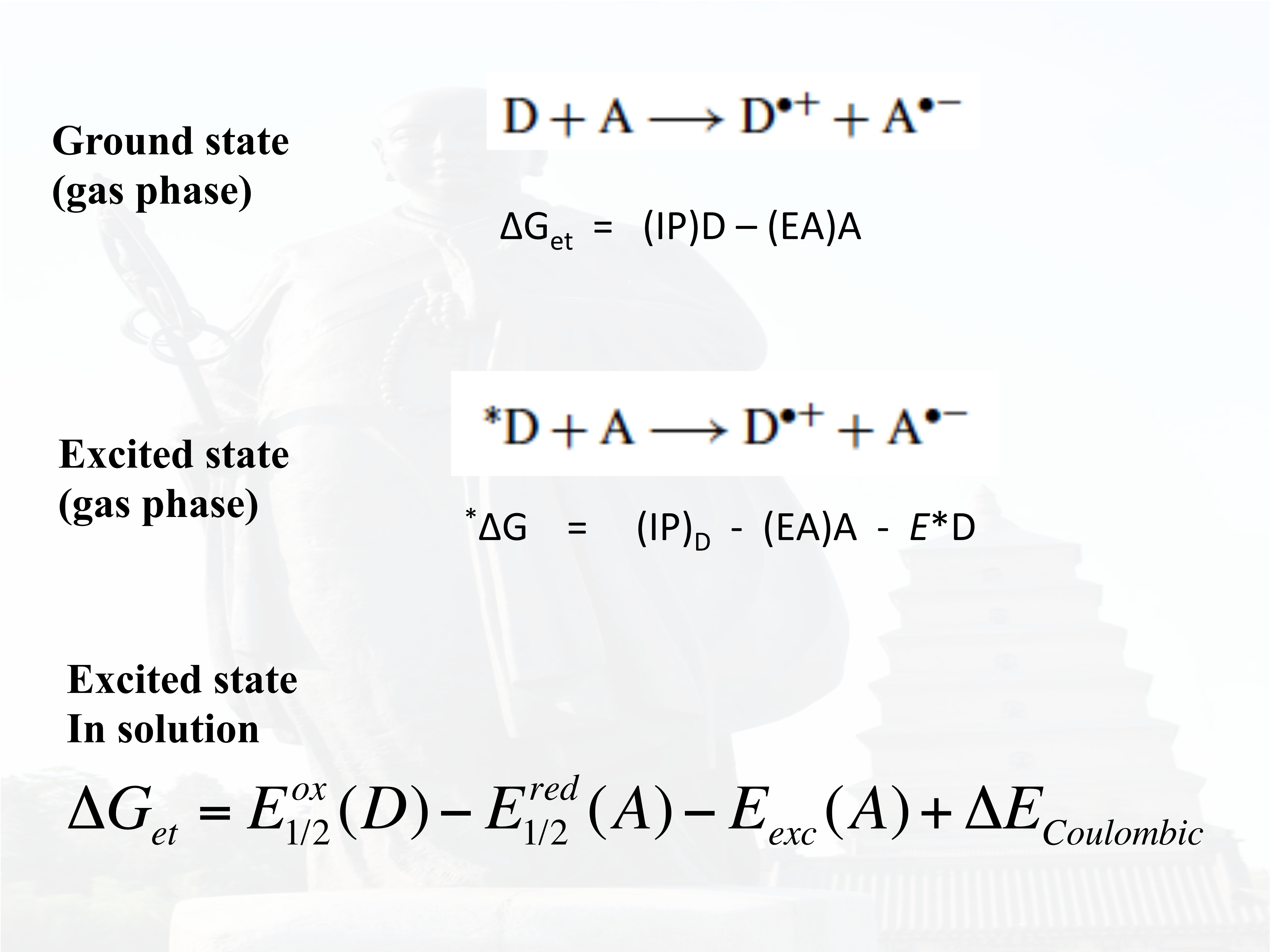


Photoinduced Electron Transfer Charge Separation



Electron Addition and Removal is Easier in the Excited State than in the Ground State





Ground state (gas phase)

$$D + A \longrightarrow D^{\bullet +} + A^{\bullet -}$$

$$\Delta G_{et} = (IP)D - (EA)A$$

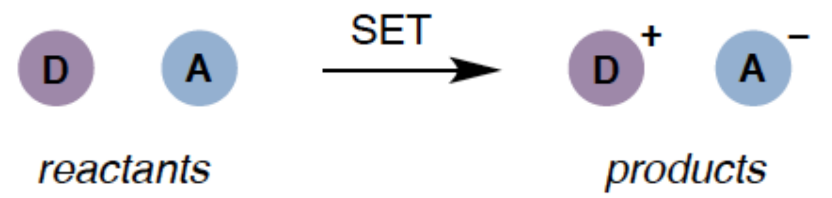
Excited state (gas phase)

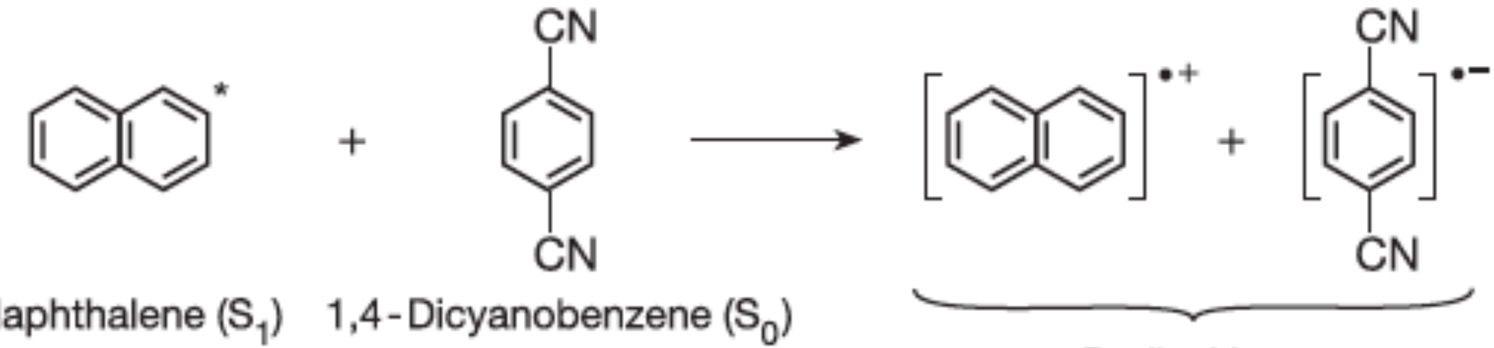
$$^{*}D + A \longrightarrow D^{\bullet +} + A^{\bullet -}$$

$$^{*}\Delta G = (IP)_{D} - (EA)A - E^{*}D$$

Excited state In solution

$$\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_{exc}(A) + \Delta E_{Coulombic}$$





Naphthalene (S_1)   1,4-Dicyanobenzene (S_0)

Radical ions

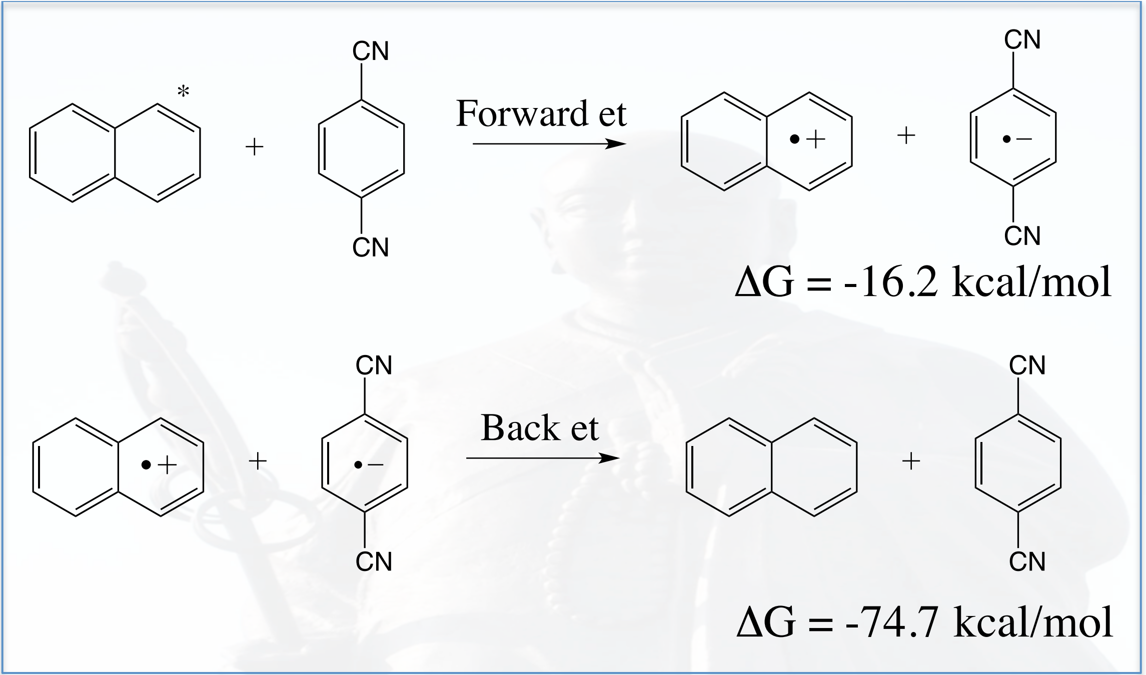
$E^0_{D^+/D} = +1.60$ V $E^0_{A/A^-} = -1.64$ V

$$\boxed{E(S_1) = 3.94 \text{ eV} = 90.9 \text{ kcal mol}^{-1}}$$

$$\Delta G^\circ = \mathcal{F}E^0_{D^+/D} - \mathcal{F}E^0_{A/A^-} - E^*_D - 0.2$$

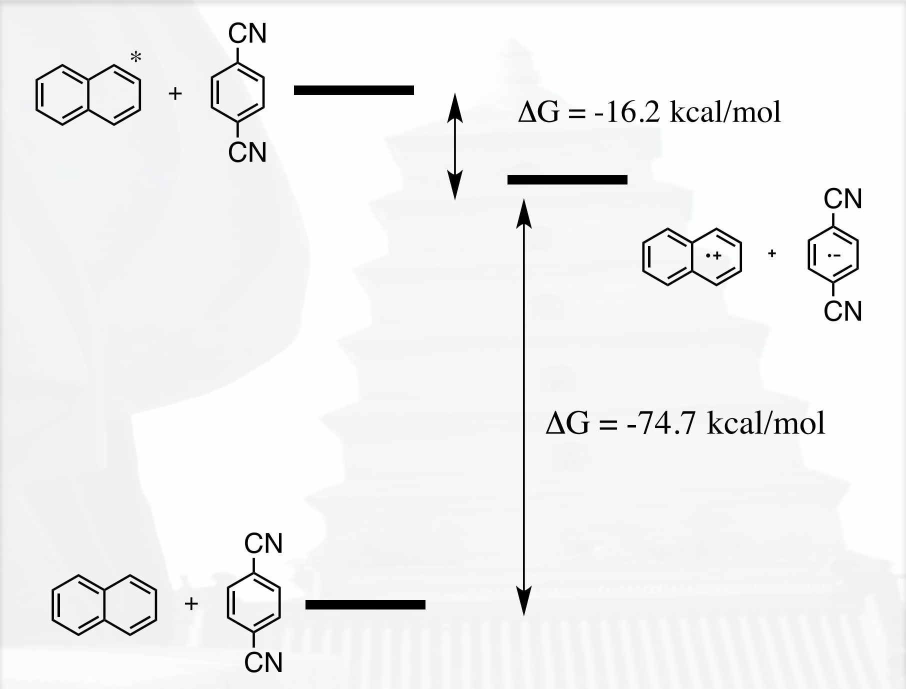
$$\Delta G^\circ = 36.9 - (-37.8) - 90.9 - 0.2 = -16.4 \text{ kcal mol}^{-1}$$

$$k \text{ (electron transfer)} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$



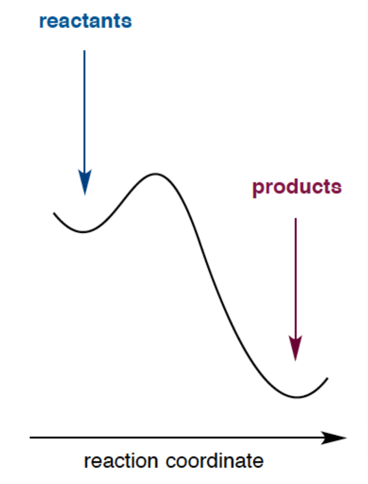
ΔG = -16.2 kcal/mol

ΔG = -74.7 kcal/mol



Free energy of activation expressed in terms of the free energy of reaction (ΔG) and free energy of activation (ΔG#)

$$k_{\mathrm{et}} = k_0 \exp\left(-\frac{\Delta G_{\mathrm{et}}^{\ddagger}}{RT}\right)$$

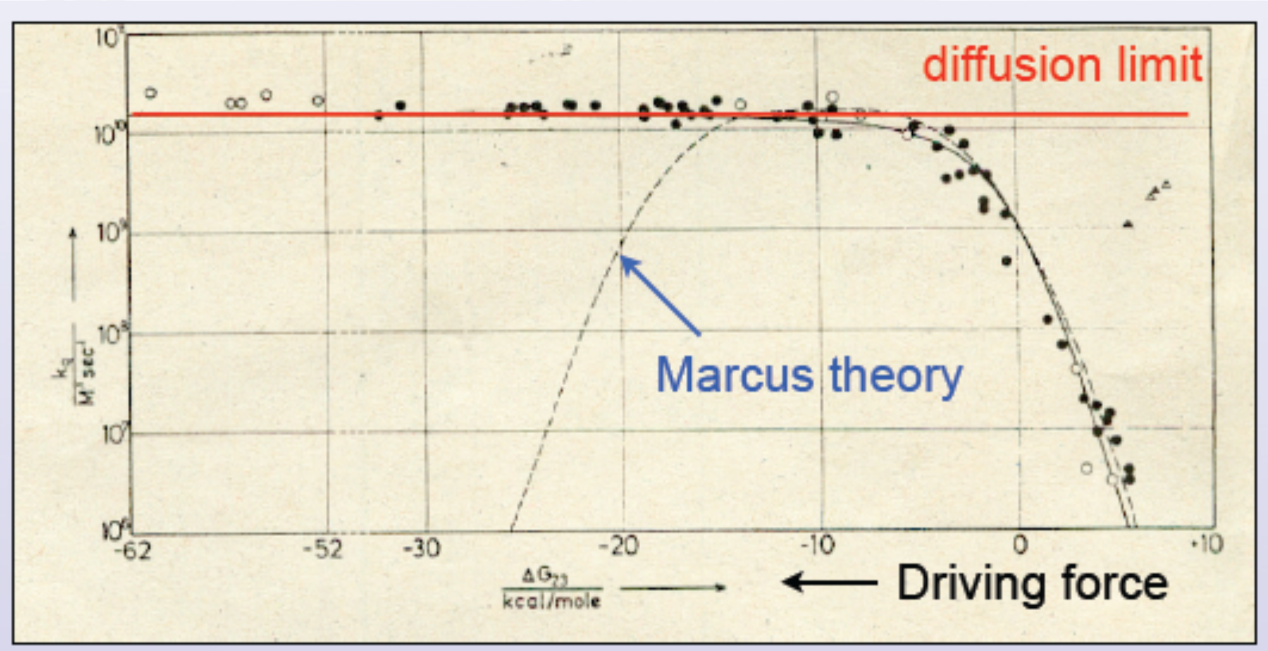


$$\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_{*}(D) + \Delta E_{Coulombic}$$

Rehm-Weller Equation

Dependence of the electron transfer rate on the driving force ΔG^0 and the free energy of activation $\Delta G^‡$

D. Rehm and A. Weller, *Isr. J. Chem., 8*, 259, **1970**



A. Weller

Rehm-Weller Plot

The value of k_{et} reaches a plateau value of ~ 2 x 10^{10} $M^{-1}s^{-1}$ after an exothermicity of ~ -10 kcal mol^{-1} and the value of k_{et} remains the diffusion controlled value to the highest negative values of achievable.

More Rehm-Weller Plots

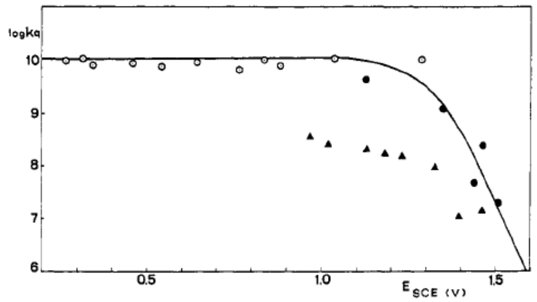


Figure 2. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of $Cr(bpy)_3{}^{3+}$ by aromatic amines (⊙), methoxybenzenes (●), and aliphatic amines (▲).

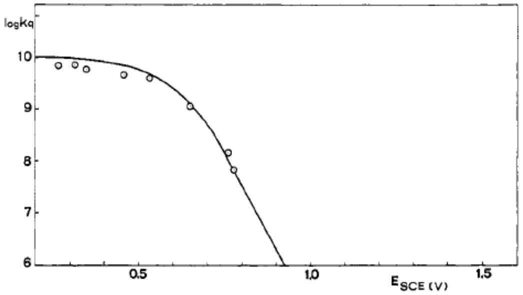


Figure 3. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of $Ru(bpy)_3{}^{2+}$ by aromatic amines.

V. Balzani, et. al., *JACS*, *100*, 7219, **1978**

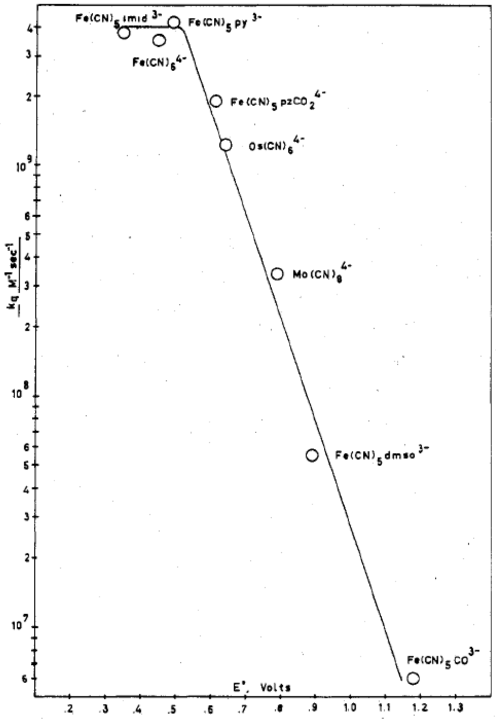


Figure 4. Dependence of quenching rate constant on quencher redox potential for several metallocyanide complexes.

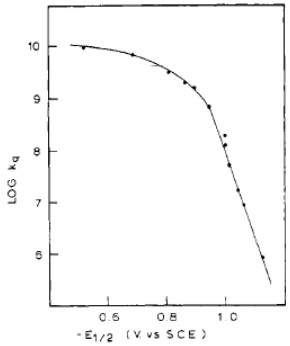


Figure 1. Plot of log $k_q{}^{obsd}$ vs. quencher reduction potential, $E_{1/2}[Q/Q^-]$.

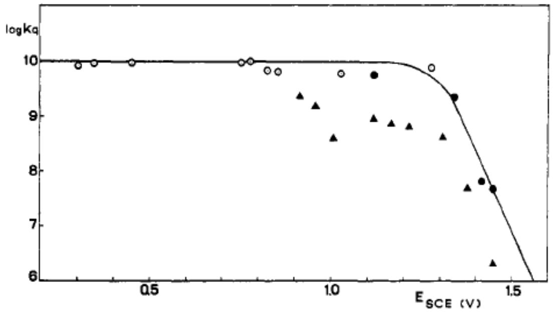


Figure 4. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of $Ir(Me_2phen)_2Cl_2{}^+$ by aromatic amines (⊙), methoxybenzenes (●), and aliphatic amines (▲).

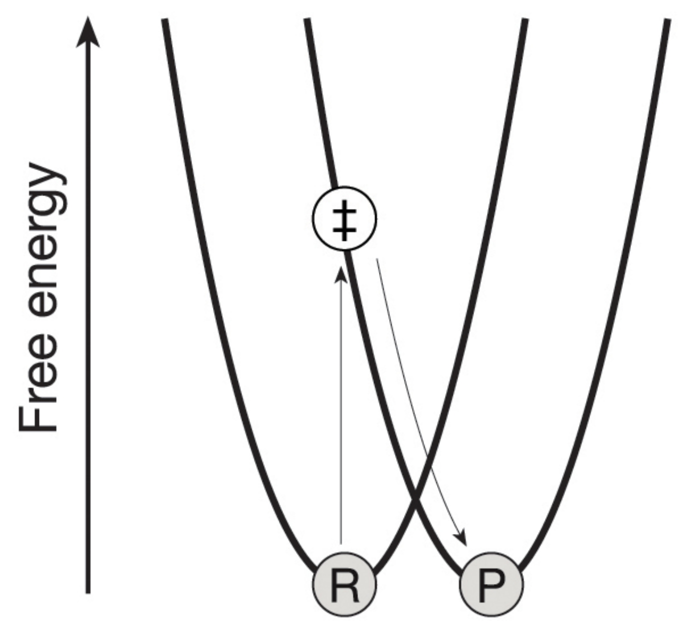
C. R. Brock, T. J. Myers and D. G. Whitten, et. al.,
JACS, *97*, 2909, **1975**

H. Toma and C. Creutz ,
Inorganic Chemistry,
16, 545, **1977**

Libby Model

W. F. Libby, *J. Phys. Chem.*, *56*, 863, **1952**; *J. Chem. Phys.*, *38*, 420, **1963**;

Willard F. Libby

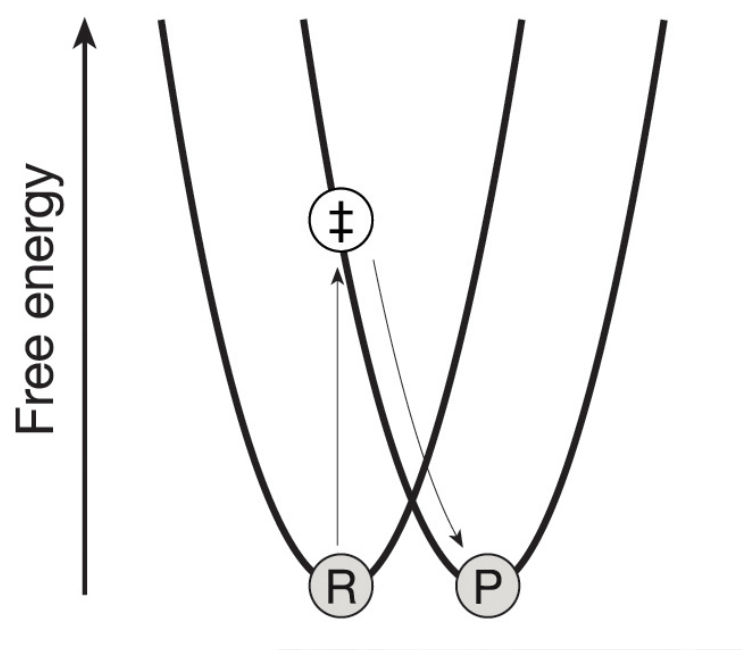


The Nobel Prize in Chemistry 1960 was awarded to Willard F. Libby "for his method to use carbon-14 for age determination in archaeology, geology, geophysics, and other branches of science".

Libby Model

$$R^{\bullet+}(\text{solvated}) + R(\text{solvated}) \rightarrow R(\text{solvated}) + R^{\bullet+}(\text{solvated})$$

$$[{}^{*}Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [{}^{*}Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$



The electron jump from R* to $R^{\bullet+}$ is analogous to the electron jump from a HO to a LU that leads to formation of an electronically excited state.

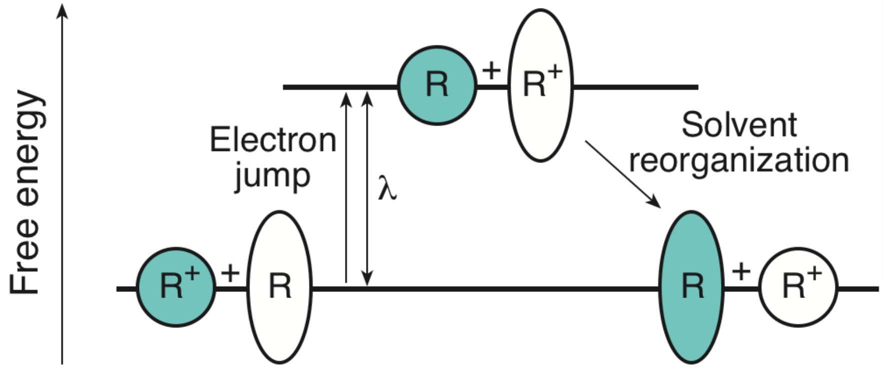
The electron jump is expected to occur "vertically" and to follow the Franck-Condon principle; the geometry of the products formed by an electron transfer would be the same as the geometry of the reactants.

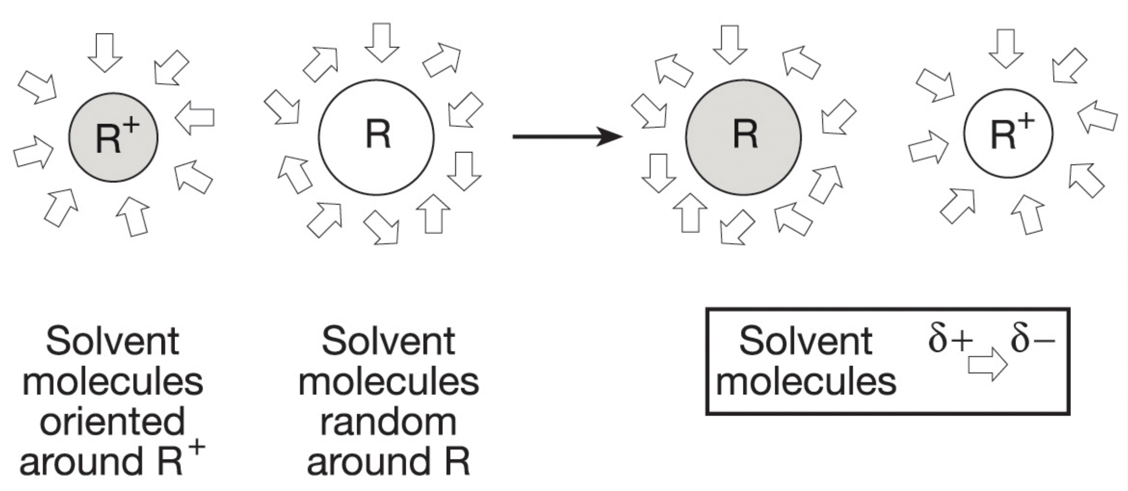
Two types of reorganization occur after the et: (1) an electronic and vibrational reorganization, termed *internal molecular reorganization*; and (2) a solvent reorganization associated with the solvent reorientation to accommodate the new electronic structures termed *external solvent reorganization*.

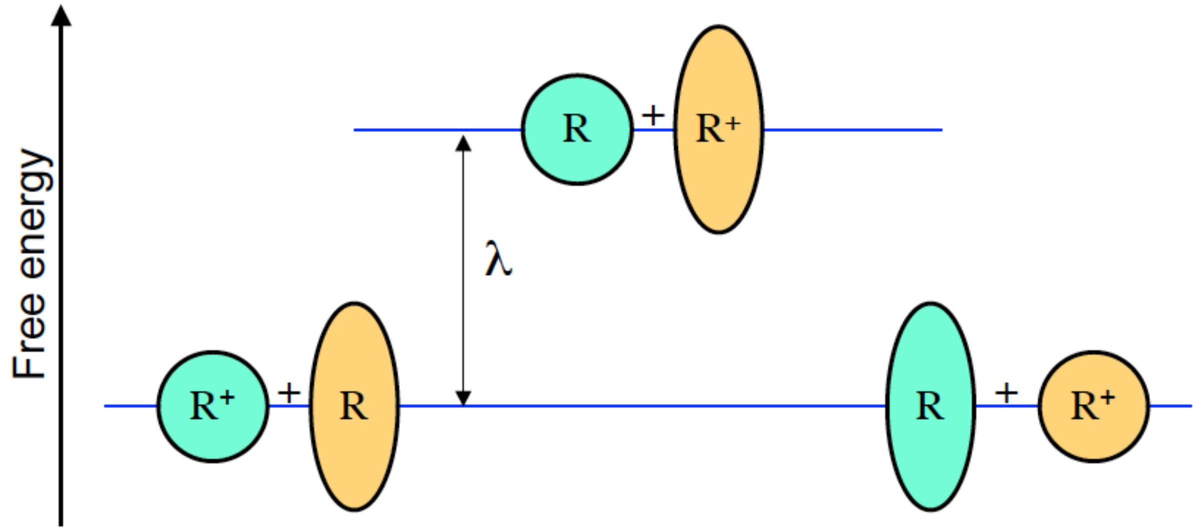
Libby Model

$$\mathrm{R^{\bullet +}(solvated) + R(solvated) \rightarrow R(solvated) + R^{\bullet +}(solvated)}$$

$$[{}^{*}\mathrm{Fe(H_2O)_6}]^{2+} + [\mathrm{Fe(H_2O)_6}]^{3+} \rightarrow [{}^{*}\mathrm{Fe(H_2O)_6}]^{3+} + [\mathrm{Fe(H_2O)_6}]^{2+}$$







Libby Model

Electron transfer is a two step process:

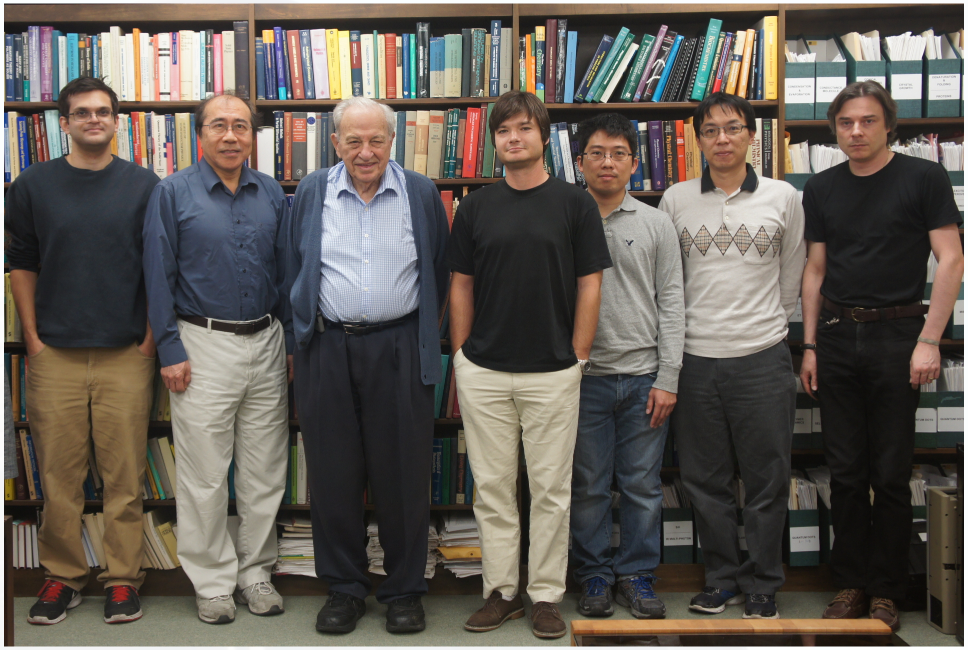
(a) Electron transfer first with no change of nuclear positions (Franck-Condon principle)

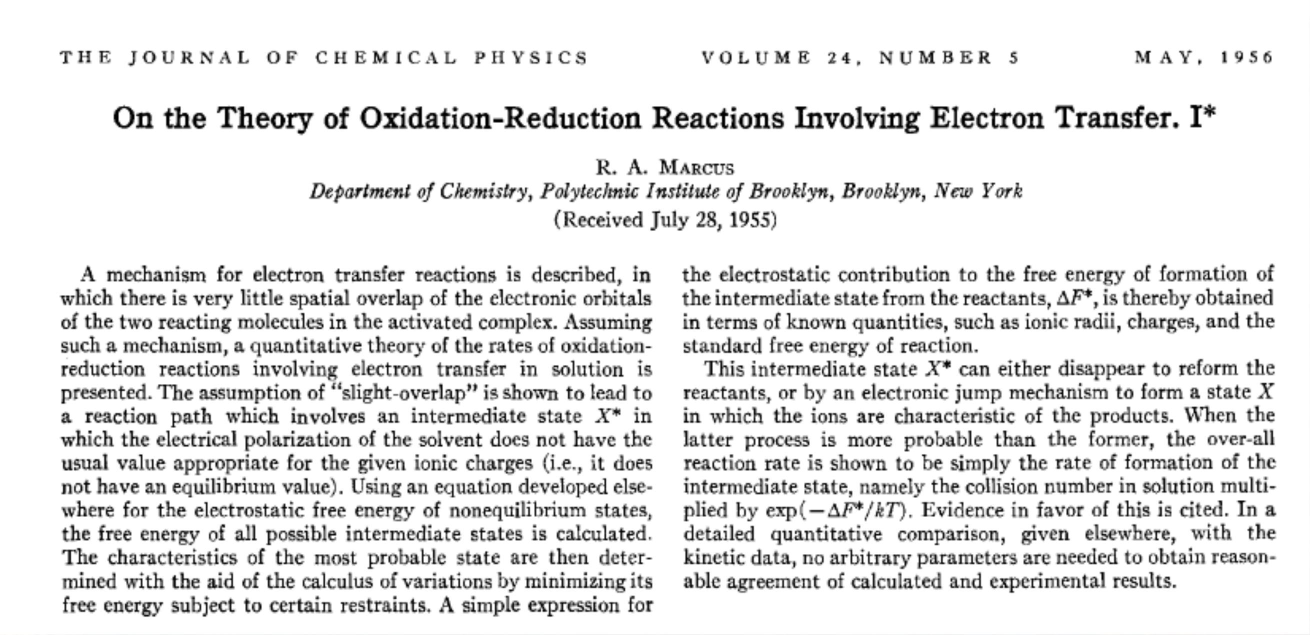
(b) Solvent reorganization

Marcus Model

The above two step model violates thermodynamic principle conservation of energy.

Marcus Theory





THE JOURNAL OF CHEMICAL PHYSICS VOLUME 24, NUMBER 5 MAY, 1956

On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I*

R. A. Marcus
Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York

(Received July 28, 1955)

A mechanism for electron transfer reactions is described, in which there is very little spatial overlap of the electronic orbitals of the two reacting molecules in the activated complex. Assuming such a mechanism, a quantitative theory of the rates of oxidation-reduction reactions involving electron transfer in solution is presented. The assumption of "slight-overlap" is shown to lead to a reaction path which involves an intermediate state X^* in which the electrical polarization of the solvent does not have the usual value appropriate for the given ionic charges (i.e., it does not have an equilibrium value). Using an equation developed elsewhere for the electrostatic free energy of nonequilibrium states, the free energy of all possible intermediate states is calculated. The characteristics of the most probable state are then determined with the aid of the calculus of variations by minimizing its free energy subject to certain restraints. A simple expression for the electrostatic contribution to the free energy of formation of the intermediate state from the reactants, ΔF^*, is thereby obtained in terms of known quantities, such as ionic radii, charges, and the standard free energy of reaction.

This intermediate state X^* can either disappear to reform the reactants, or by an electronic jump mechanism to form a state X in which the ions are characteristic of the products. When the latter process is more probable than the former, the over-all reaction rate is shown to be simply the rate of formation of the intermediate state, namely the collision number in solution multiplied by $\exp(-\Delta F^*/kT)$. Evidence in favor of this is cited. In a detailed quantitative comparison, given elsewhere, with the kinetic data, no arbitrary parameters are needed to obtain reasonable agreement of calculated and experimental results.

R. A. Marcus, *J. Chem. Phys.*, *24*, 966, **1956**.

R. A. Marcus and N. Sutin, *Biochemica et Biophysica Acta*, *811*, 265, **1985**.

R. A. Marcus, *Electron transfer Reactions in Chemistry: Theory and Experiment*, (Nobel Lecture) *Angew. Chem. Int. Ed.*,*32*, 1111, **1993**.

R. A. Marcus

Rates are expected:

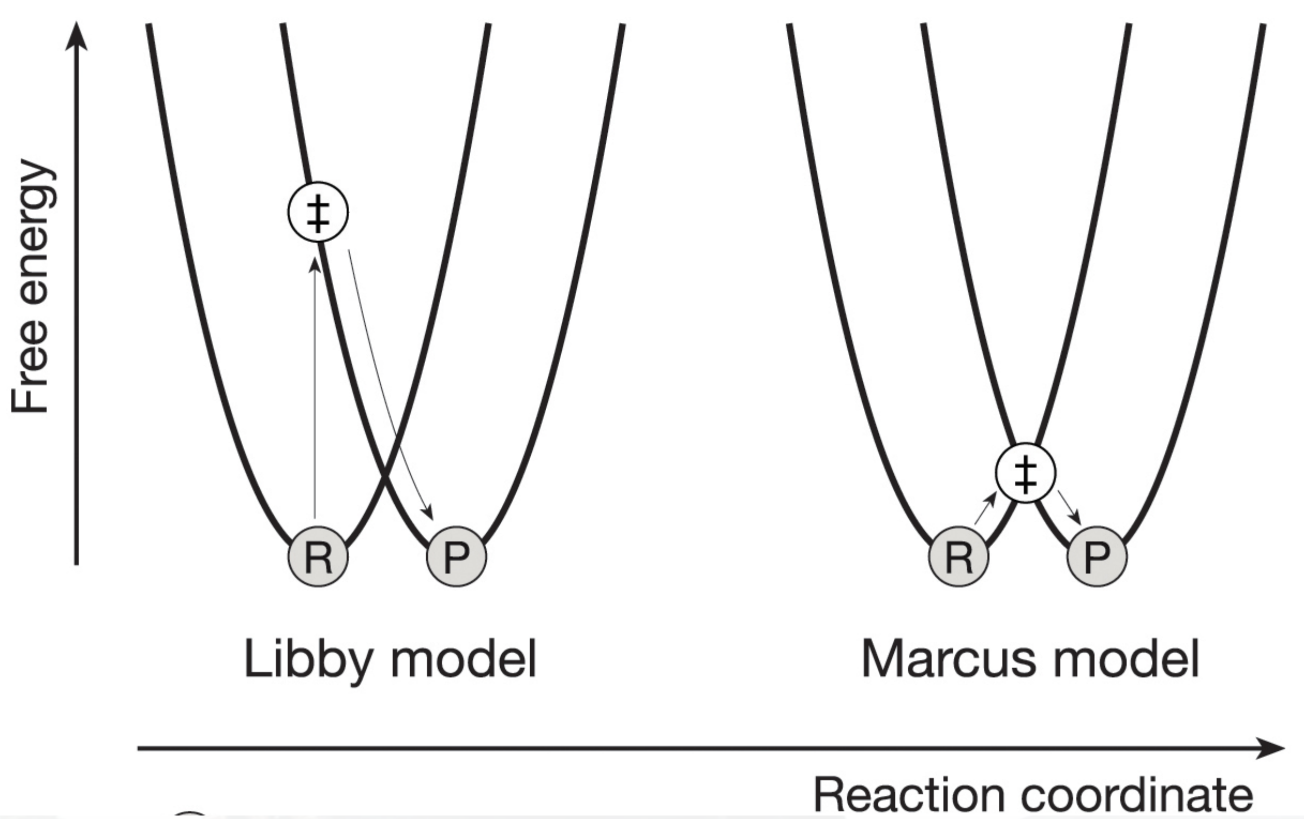
✧ to be slow for weakly exothermic reactions,

✧ to increase to a maximum for moderately exothermic reactions, and then

✧ **to decrease with increasing exothermicity for highly exothermic et reactions.**

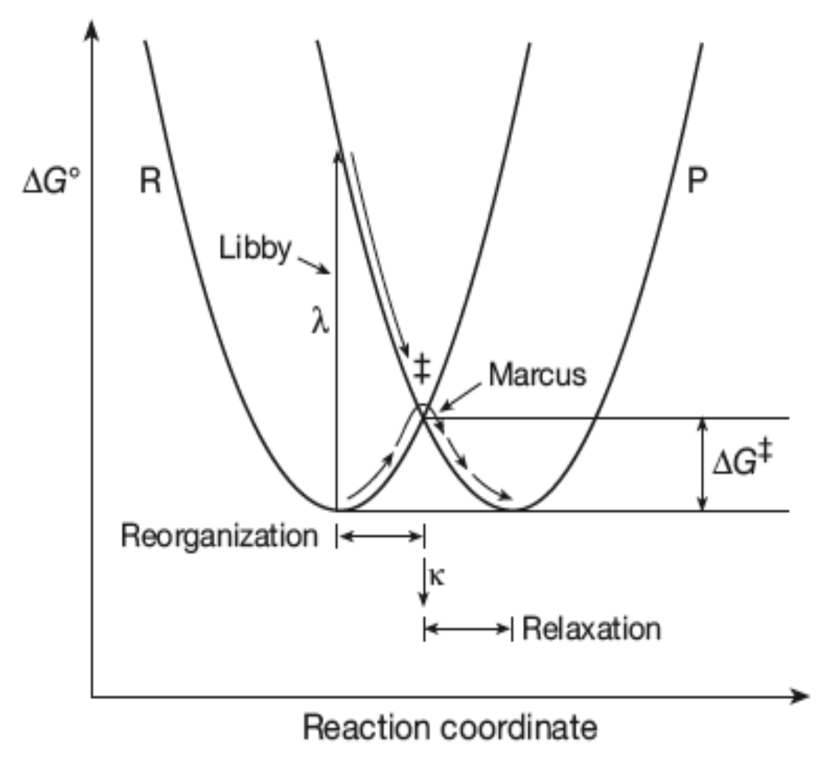
Evolution of Marcus model

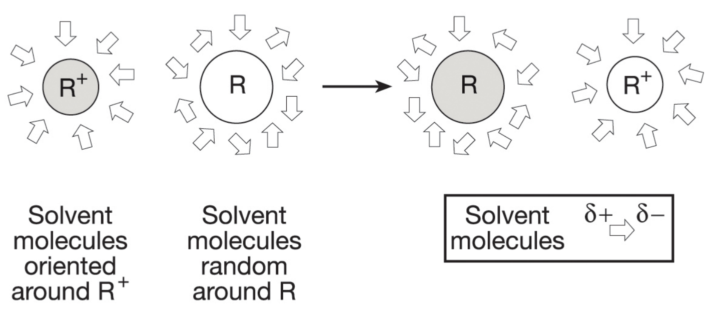
R. A. Marcus, *J. Chem. Phys.*, *24*, 966, **1956**.



$$k_{et} = A\ \exp^{-(\Delta G‡/RT)}$$

The Marcus model





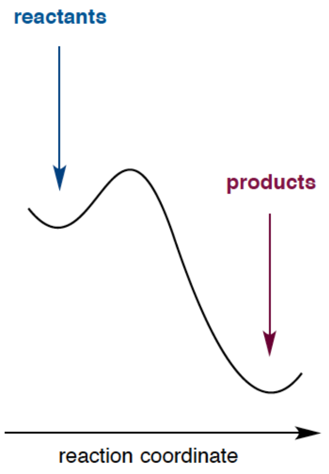
$$k_{\mathrm{et}} = k_0 \exp\left(-\frac{\Delta G^{\ddagger}_{\mathrm{et}}}{RT}\right)$$

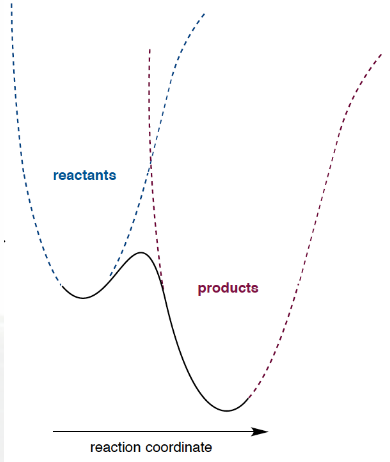
$$\Delta G_{et} = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) - E_{*}(A) + \Delta E_{Coulombic}$$

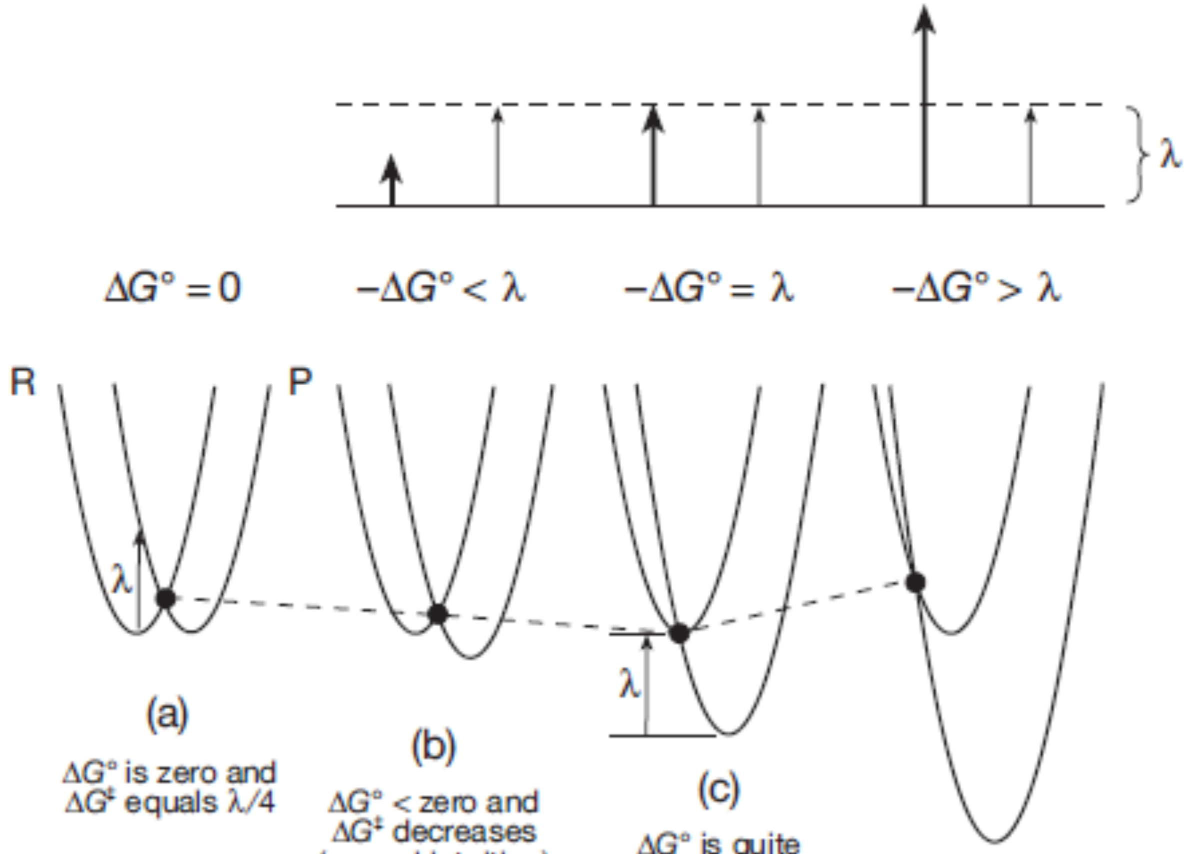
$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{\mathrm{o}})^2}{4\lambda}$$

$$k_{ET} = \kappa \frac{k_B T}{h} \exp\left(\frac{-(\lambda + \Delta G^{\mathrm{o}})^2}{4\lambda \mathrm{RT}}\right)$$

The re-emergence of the activation barrier ($\Delta G^{\ddagger}$) at large negative ΔG^0 values







(a)

ΔG° is zero and $\Delta G^{\ddagger}$ equals $\lambda/4$

(b)

ΔG° < zero and $\Delta G^{\ddagger}$ decreases (normal intuition)

(c)

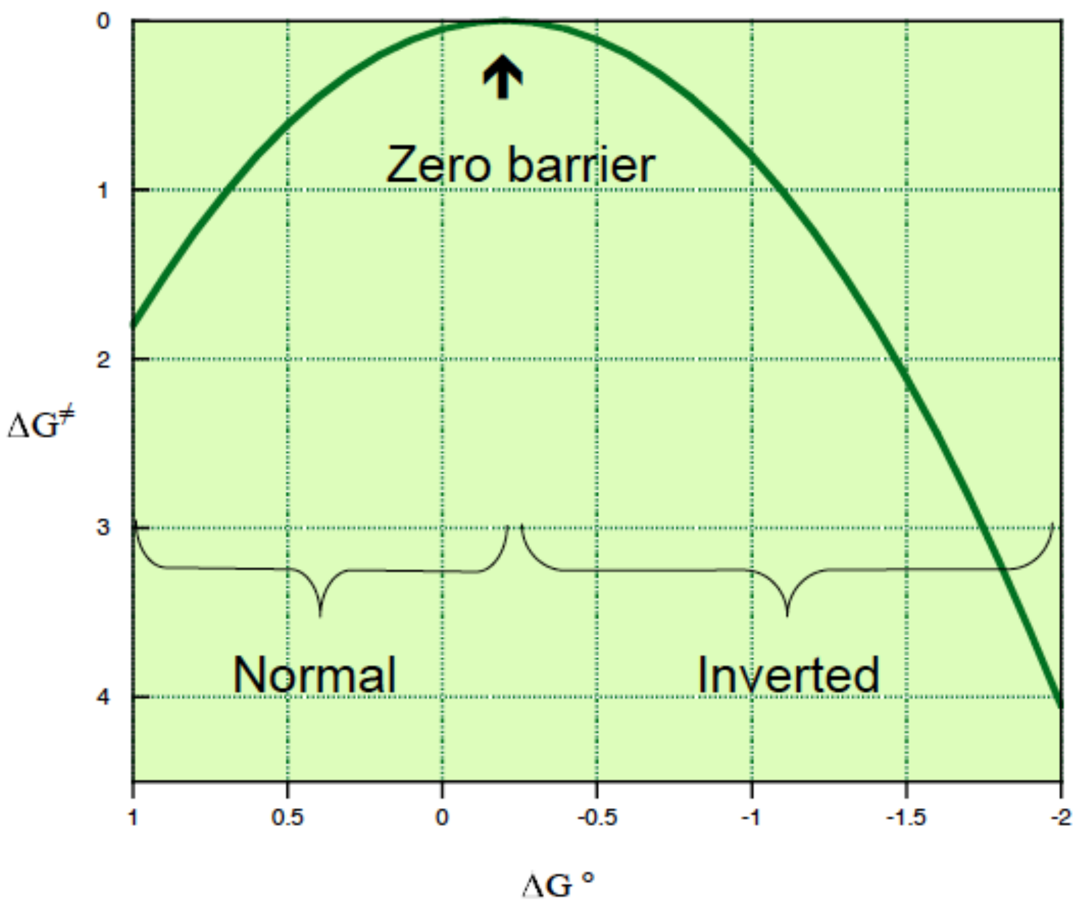
ΔG° is quite negative and $\Delta G^{\ddagger}$ becomes zero

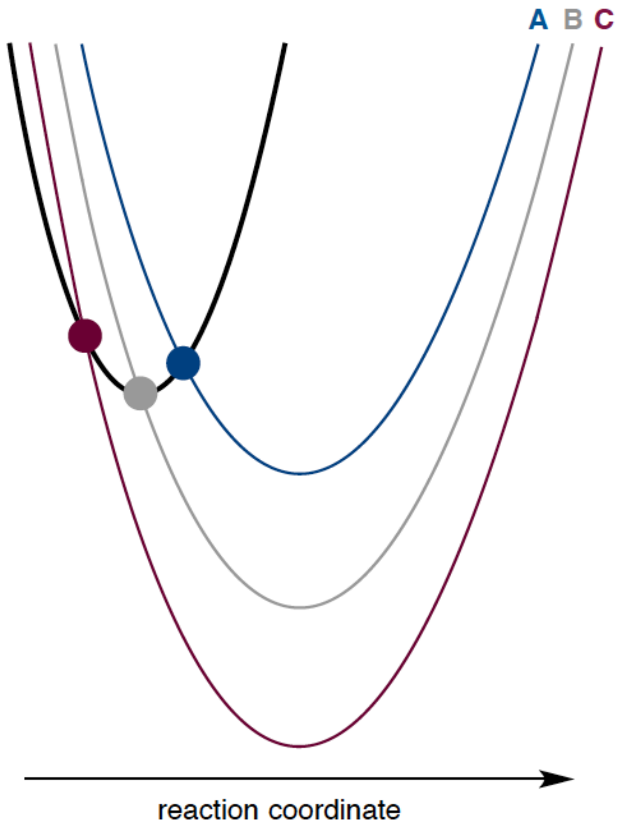
(d)

ΔG° is even more negative and $\Delta G^{\ddagger}$ becomes positive again (!)

● The dot traces the energy of the transition state as ΔG° becomes more negative

Marcus Prediction

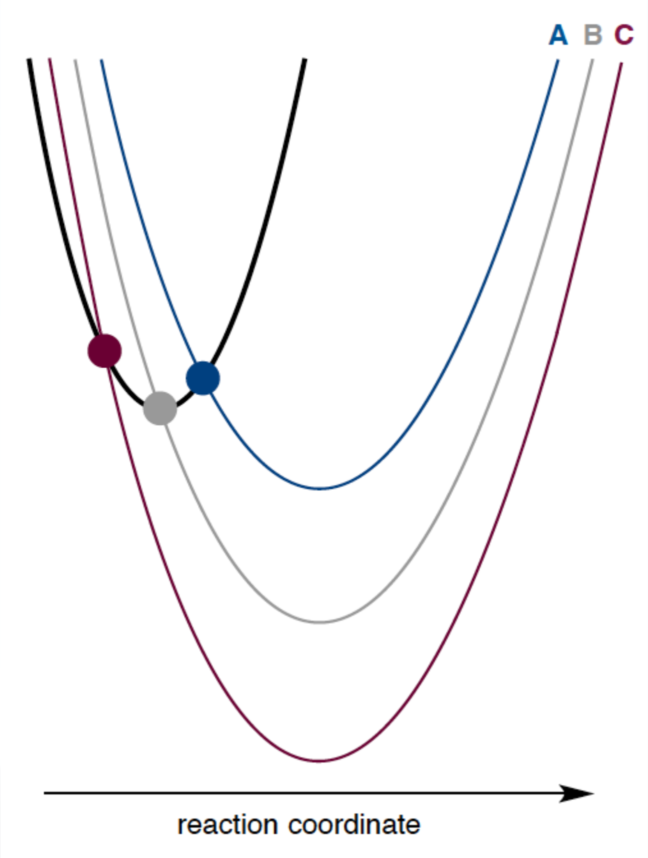




The '***normal*'** region exists for values of $-\Delta G^0 < \lambda$. In this region the rate of electron transfer will *continuously increase* as the exothermicity increases as long as $-\Delta G^0 < \lambda$ because the value of $\Delta G^{\ddagger}$ *continuously decreases* in this "normal" region of reaction exothermicity.

The '**barrierless**' region ($\Delta G^{\ddagger} = 0$) at which $-\Delta G^0 = \lambda$. This corresponds to the maximum rate of electron transfer.

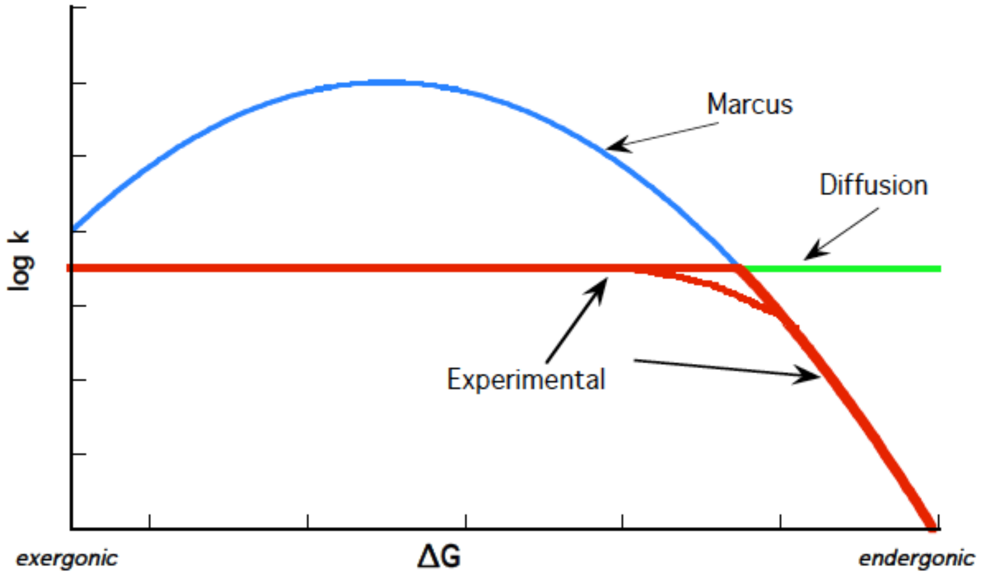
The '**inverted**' region where $-\Delta G^0 > \lambda$. The rate of electron transfer begins to decrease when $-\Delta G^0 > \lambda$.



$$k_{et} = A\ \exp^{-(\Delta G\ddagger/RT)}$$

$$\Delta G^{\ddagger} = (\Delta G^0 + \lambda)^2/4\lambda$$

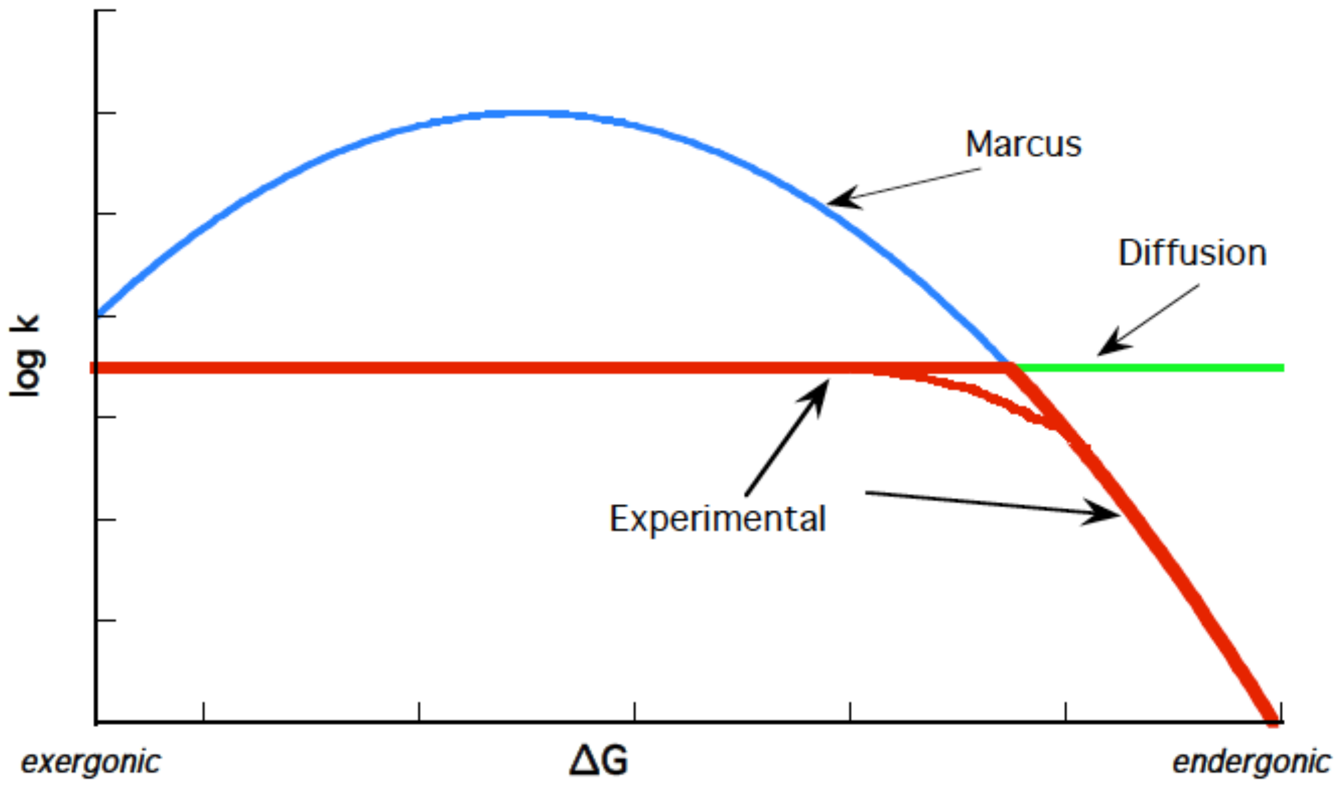
Electron Transfer Involves Two Steps



$$D^*+A \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} D^*\cdot A \underset{k_{-CS}}{\overset{k_{CS}}{\rightleftarrows}} D^{+}\cdot A^{-}$$

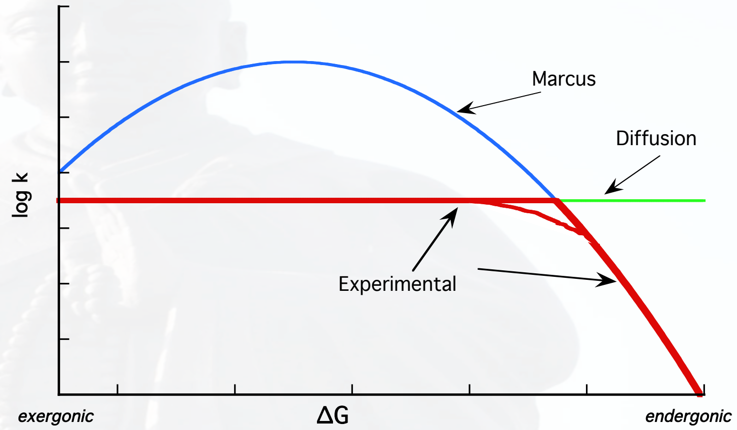
The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.

Marcus prediction vs Weller's experiments



The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.

Experimental conditions to observe the Marcus “inverted region”?

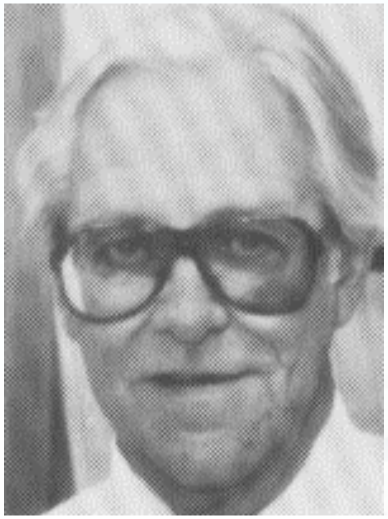


For most donor-acceptor (DA) systems the inverted region is obscured by the diffusion limit.

This can be circumvented by:

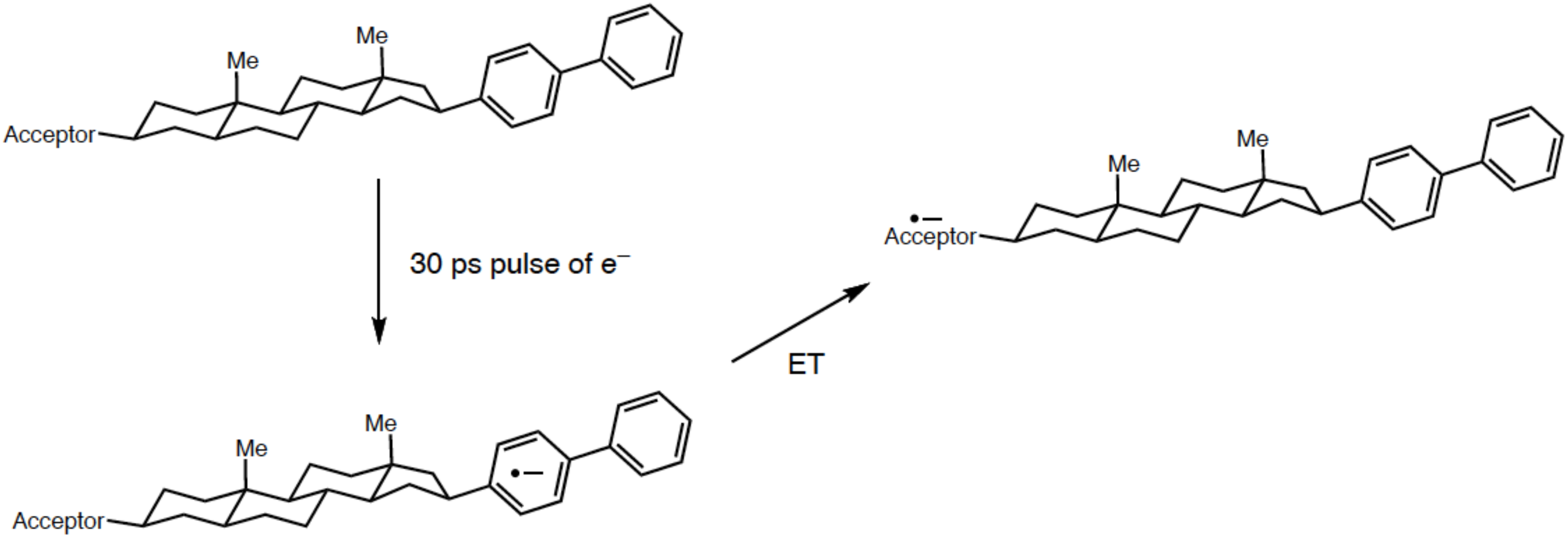
- freezing the donor-acceptor distribution (glassy medium)
- covalently linking the donor and the acceptor
- lowering the donor-acceptor interaction (electronic coupling V) so that the maximum rate for $-\Delta G^0 = \lambda$ is **lower** than the diffusion limit.

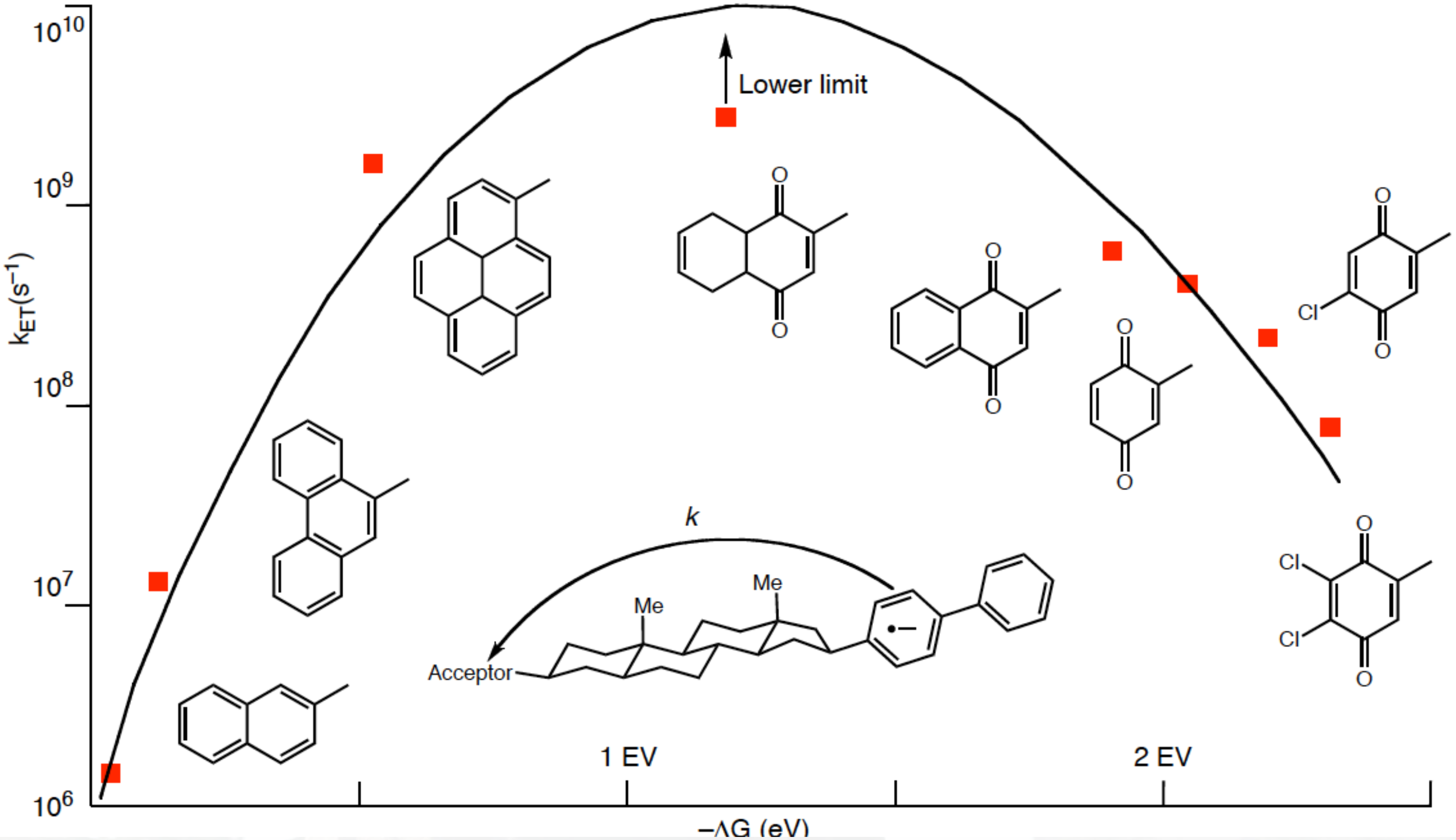
■ Pioneering 1984 Study by Miller and Closs Definitively Proved the Existence of the Inverse Region



G. Closs

J. R. Miller




10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
$k_{ET}(s^{-1})$
Lower limit
k
Me
Me
Acceptor
O
O
Cl
Cl
Cl
1 EV
2 EV
$-\Delta G$ (eV)

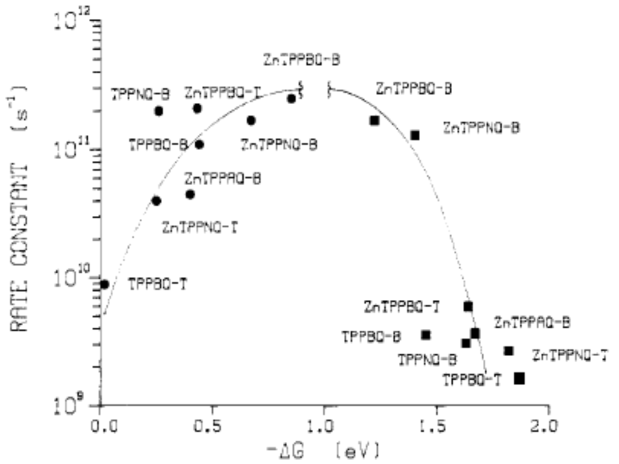
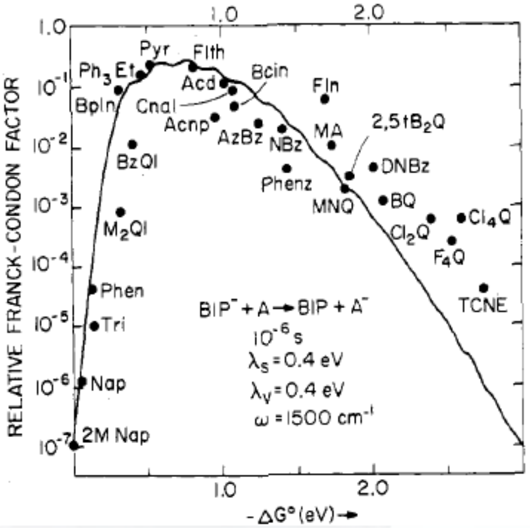
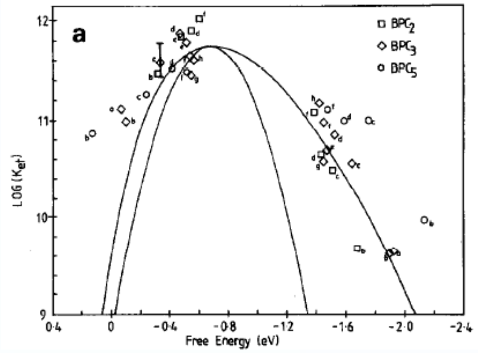
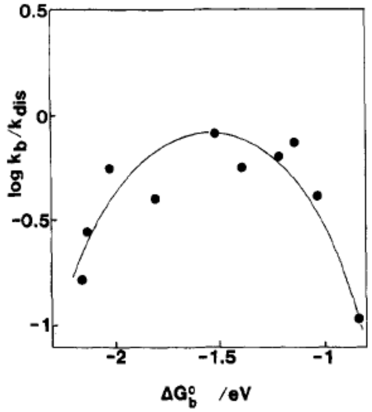


Figure 2. Plot of rate constant vs. exothermicity for the reaction $^{1*}P-Q \rightarrow P^+-Q^-$ and for $P^+-Q^- \rightarrow P-Q$, where P = porphyrin and Q = quinone. The B and T after the name of the compounds indicate data obtained in butyronitrile or in toluene, respectively. The maximum uncertainty in any given rate constant is ±20%.







e 8. ΔG° dependence of k_b/k_{dis} for backward ET between Ru- $_3^+$ and the cation radicals of the aromatic donors. The line is drawn isy viewing.

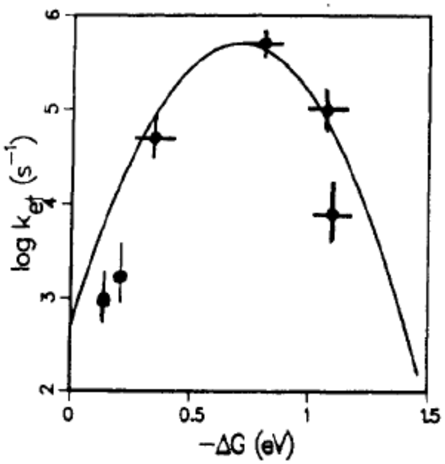
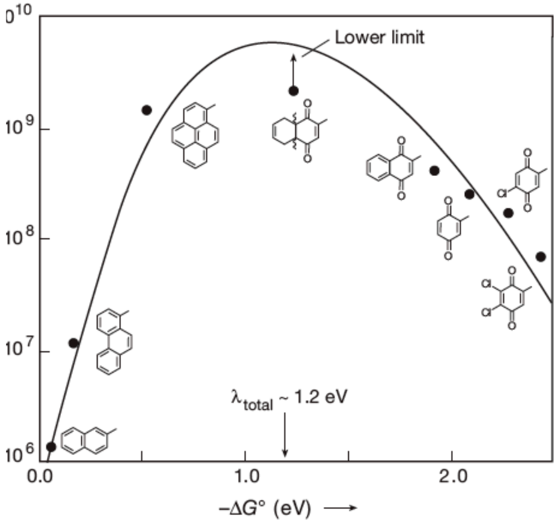


Figure 8. Plot of intracomplex electron-transfer rate between cyt *c* and cyt b_5 as a function of free energy. Solid line is fit to Marcus' theory, λ = 0.8*v*.



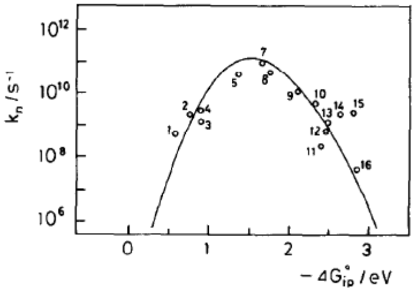
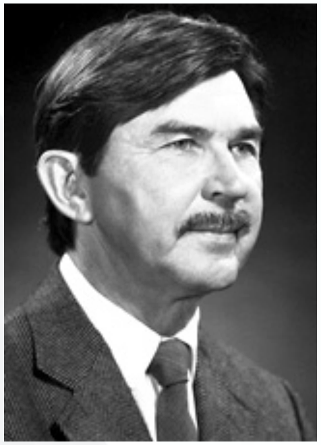


Fig. 10. The dependence of the CR rate constant k_n of geminate ion pairs produced by fluorescence quenching reaction on the free energy gap $-\Delta G_{ip}^0$ in acetonitrile solution.

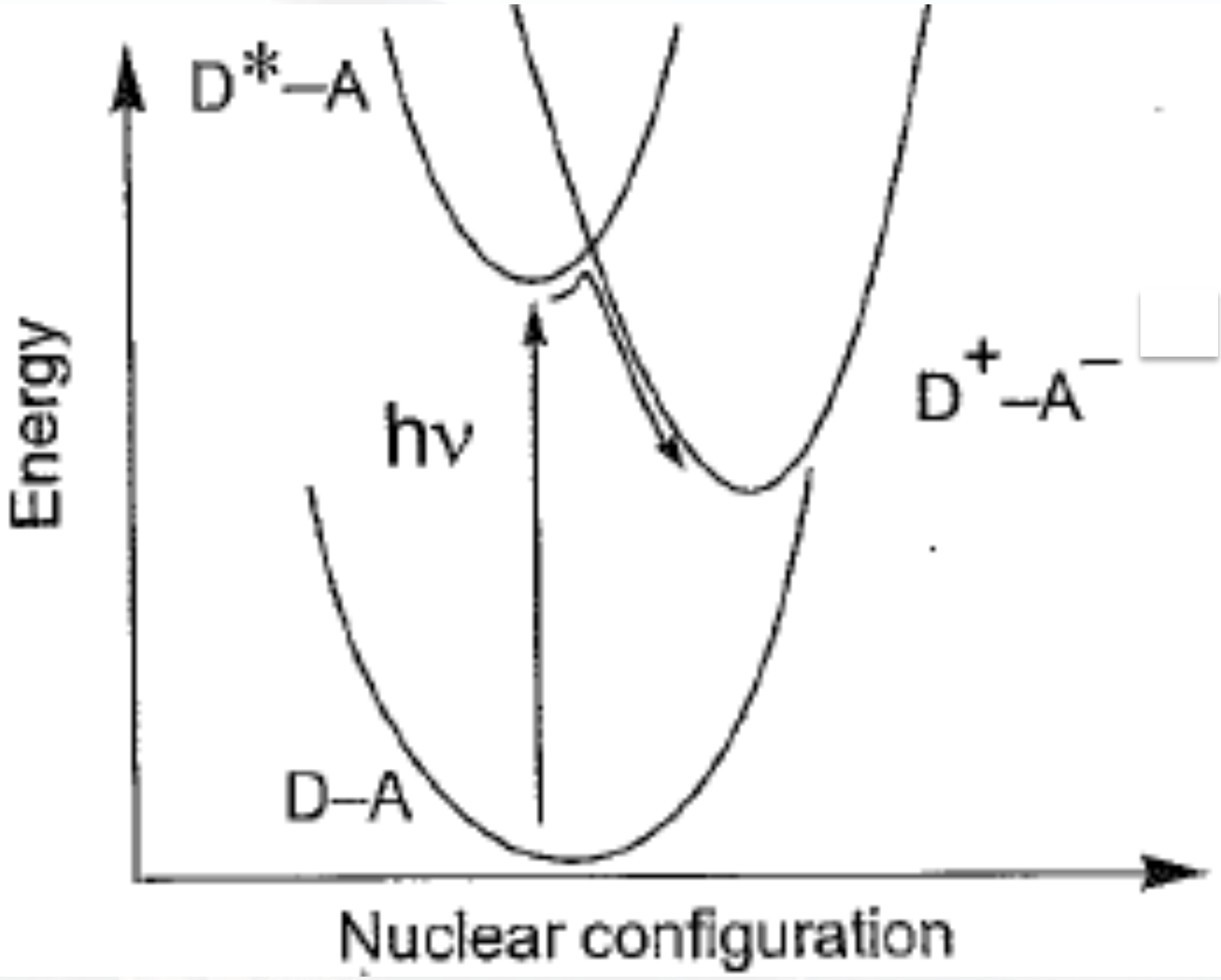
The Nobel Prize in Chemistry 1992



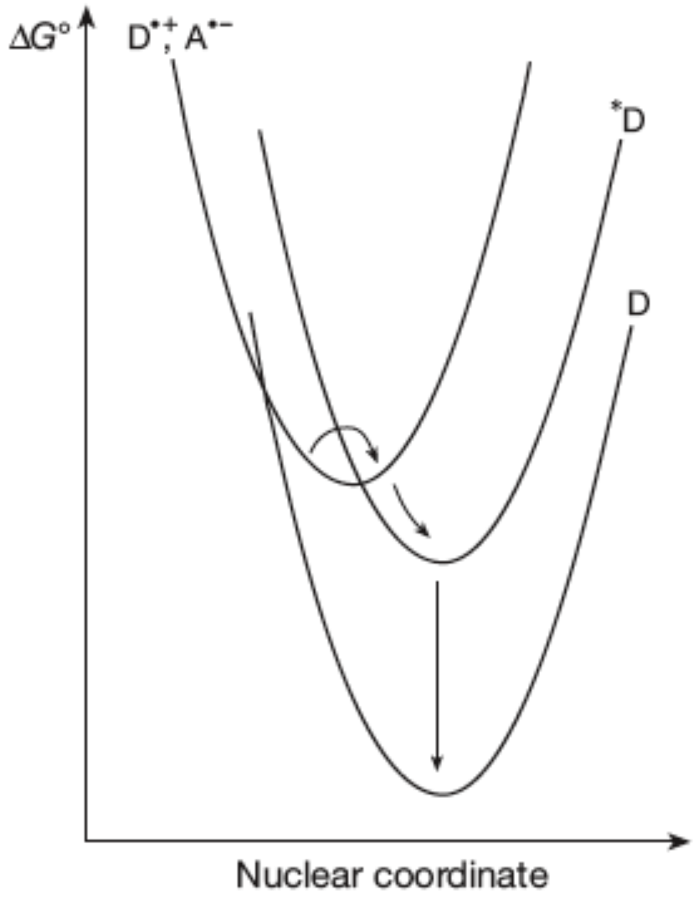
The Nobel Prize in Chemistry 1983 was awarded to Henry Taube "for his work on the mechanisms of electron transfer reactions, especially in metal complexes".

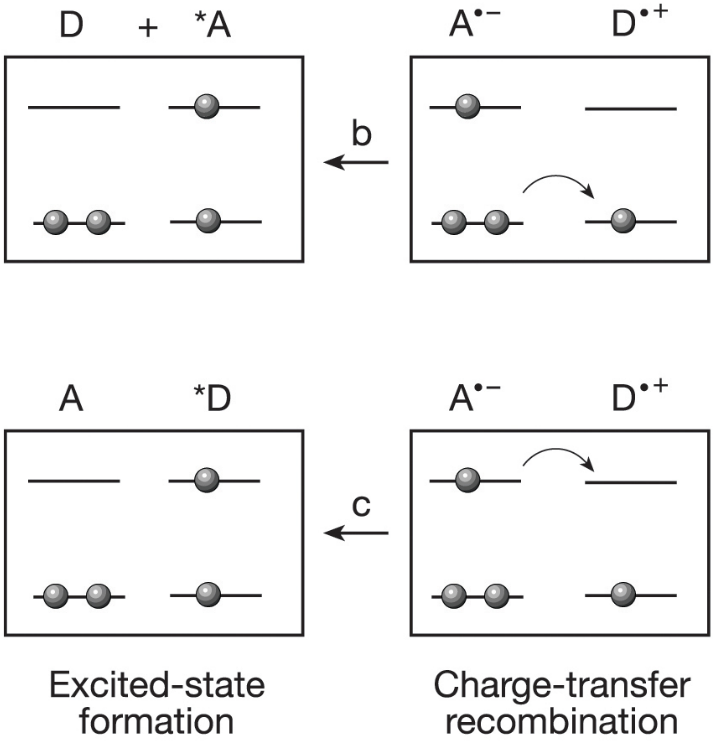
The Nobel Prize in Chemistry 1992 was awarded to Rudolph A. Marcus "for his contributions to the theory of electron transfer reactions in chemical systems".

Photoinduced electron transfer

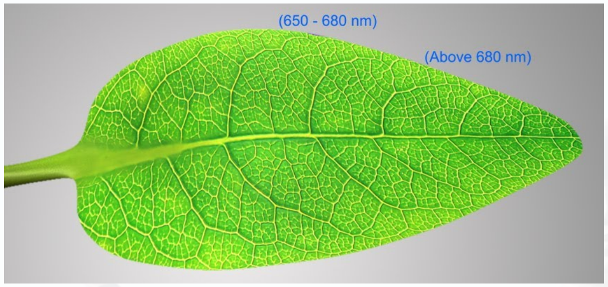


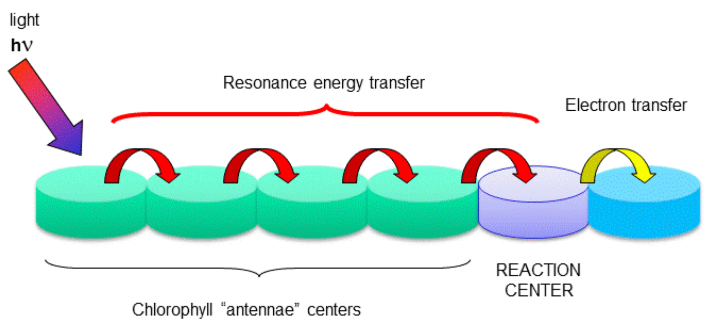
Excited state production through back electron transfer

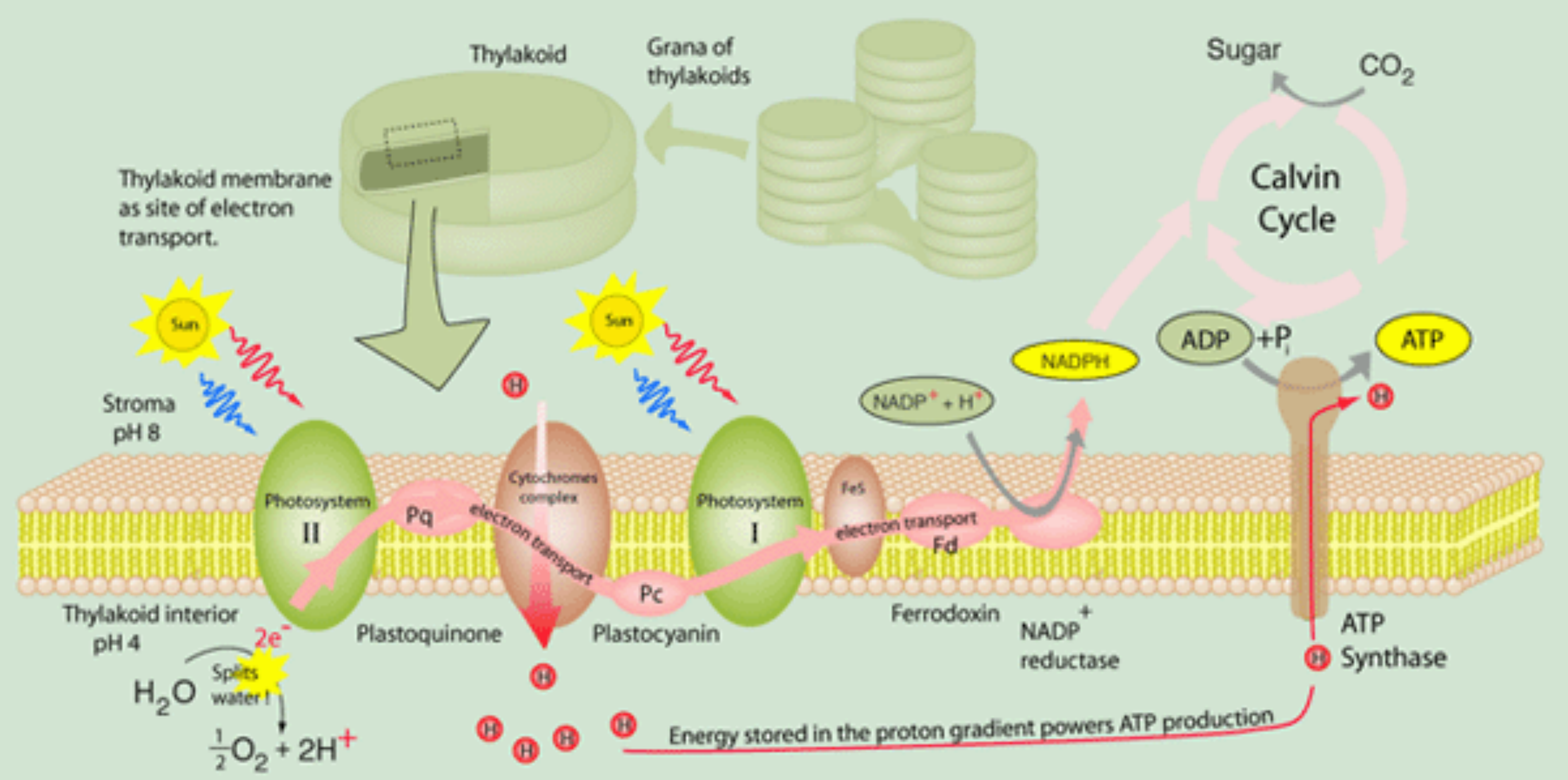




Bioapplications, Light emitting diodes (TV, Computerr, Cell phone screens)


(650 - 680 nm)
(Above 680 nm)


light
hν
Resonance energy transfer
Electron transfer
REACTION CENTER
Chlorophyll "antennae" centers


Thylakoid
Grana of thylakoids
Sugar
CO_2
Calvin Cycle
Thylakoid membrane as site of electron transport.
Sun
Sun
Stroma pH 8
H
NADPH
ADP
$+P_i$
ATP
$NADP^+ + H^+$
H
Photosystem II
Pq
Cytochromes complex
electron transport
Photosystem I
FeS
electron transport
Fd
Pc
Thylakoid interior pH 4
$2e^-$
Plastoquinone
Plastocyanin
Ferrodoxin
$NADP^+$ reductase
ATP Synthase
H
H_2O
Splits water!
$\frac{1}{2}O_2 + 2H^+$
H
H
H
H
H
Energy stored in the proton gradient powers ATP production