

Energy Transfer from Excited Electronic States

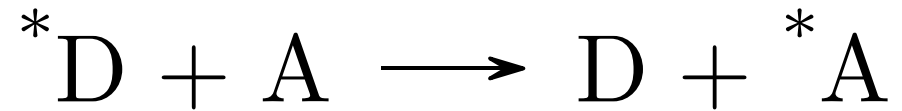
Molecular Photochemistry

CHEM 4801

Overview of Energy Transfer

Energy Transfer from Excited Electronic States

Applications of Energy Transfer

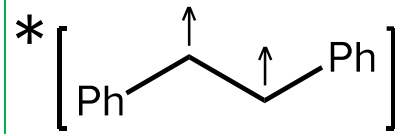


Energy harvesting

Photosynthesis

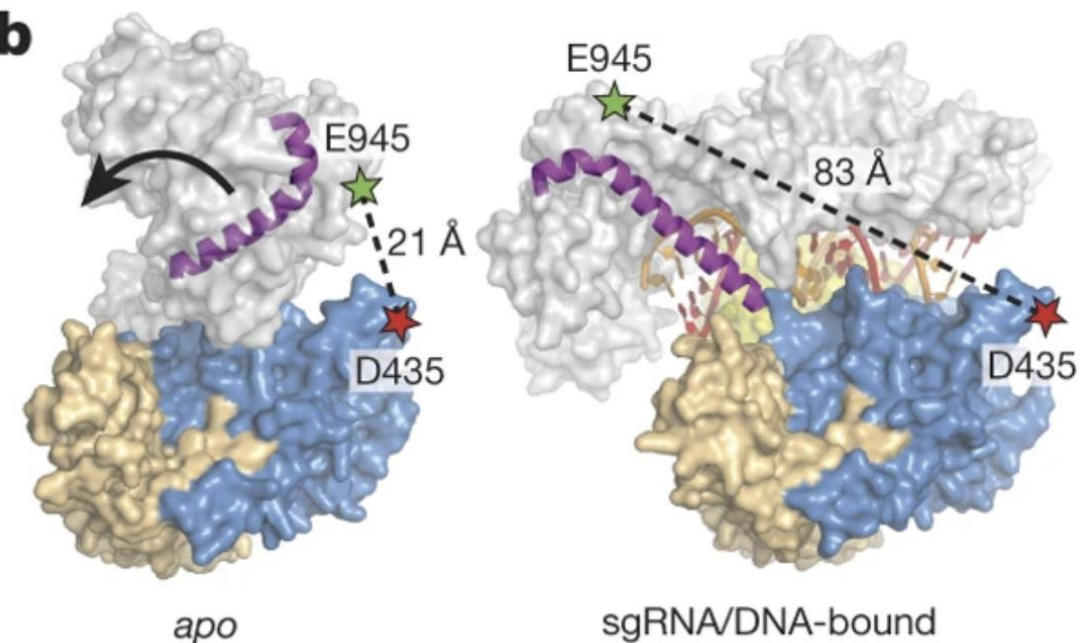
Photovoltaic cells

Unique reactivity



Measuring distances

b

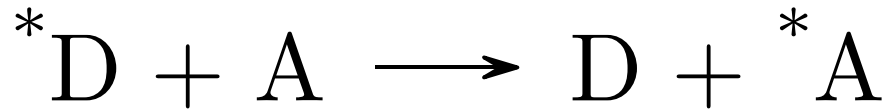


apo

sgRNA/DNA-bound

Thermodynamics and Spin

Energy transfer from an excited state must be thermodynamically favorable and consistent with quantum-mechanical selection rules (to zero order).



Energy donor

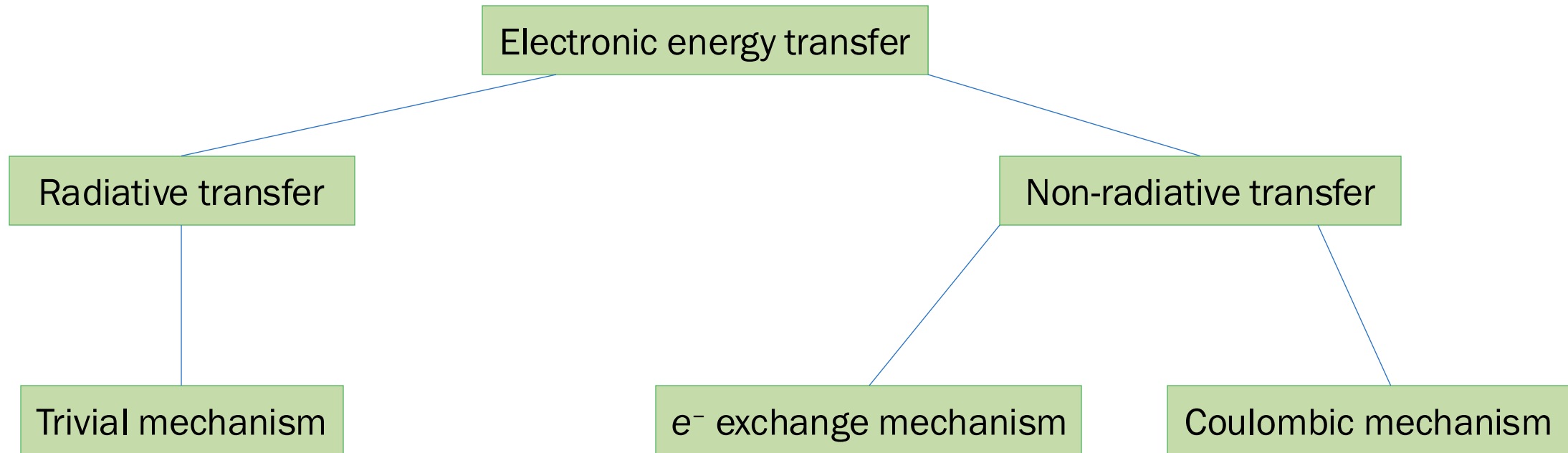
Energy acceptor

Thermodynamics: *A must be lower in energy (relative to A) than *D (relative to D).

Spin: No change in spin multiplicity unless coupling to a change in angular momentum is possible.

Types of Energy Transfer

Energy transfer may be radiative or non-radiative; non-radiative ET can be divided into exchange (Dexter) and Columbic (Förster or dipolar) mechanisms.

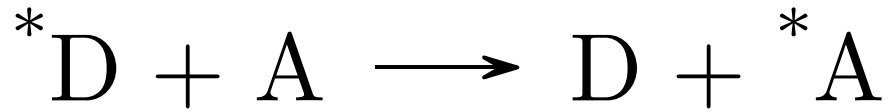


Sensitization: Introduction and Thermodynamics

Energy Transfer from Excited Electronic States

Sensitization: Definitions and Energetics

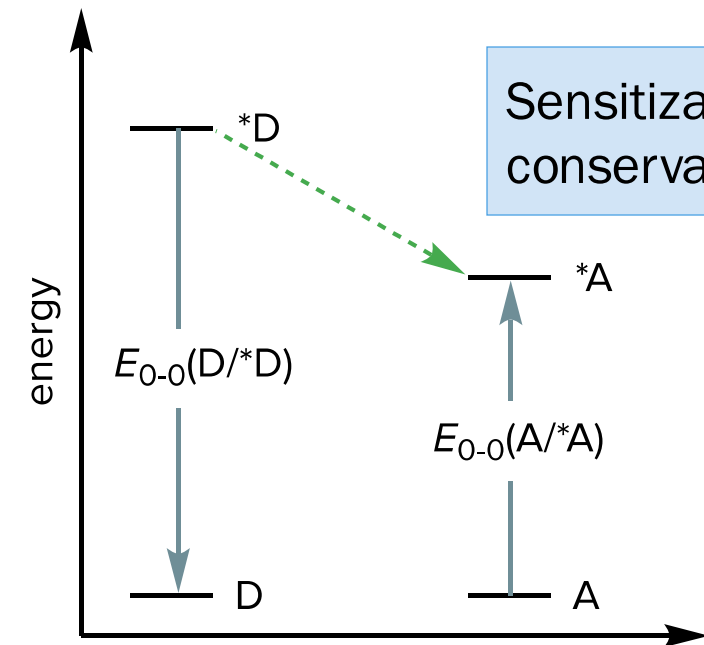
Photosensitizers transfer their excitation energy to acceptors. The energy donor is **quenched** when it transfers energy to the acceptor (**photosensitization**).



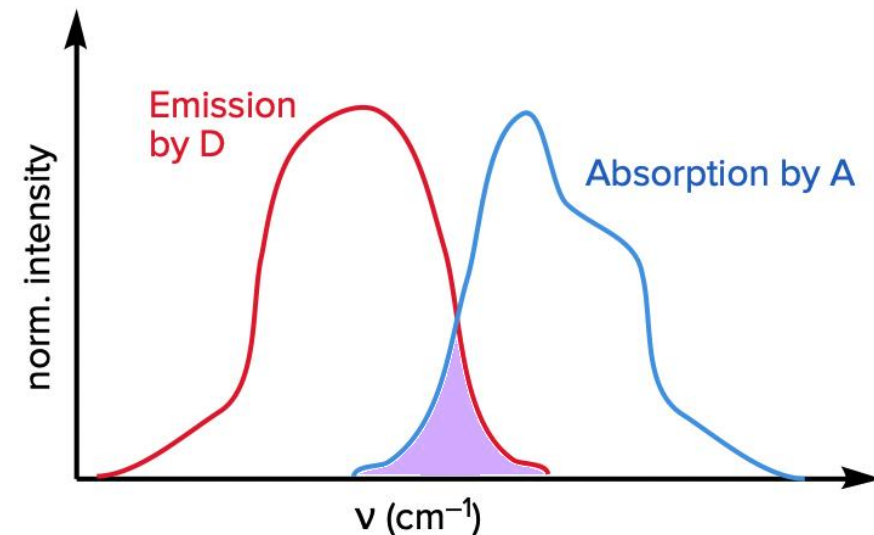
Sensitizer

Quencher

Sensitization must obey conservation of energy.



Emission spectrum of the donor and absorption spectrum of the acceptor must overlap.



Properties and Examples of Sensitizers

Compound	E_S	E_T	τ_S	τ_T	T_1	Φ_{ST}
	kcal/mol		s			
Benzene	110	84	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 ₃ -Acetophenone		71			n, π^*	1.0
Benzophenone	75	69	10^{-11}	10^{-4}	n, π^*	1.0
Triphenylene	83	67	5×10^{-8}	10^{-4}	π, π^*	0.9
Thioxanthone	78	65				
Anthraquinone		62			n, π^*	1.0
4-Ph-Benzoquinone	77	61		10^{-4}	π, π^*	1.0
Michler's ketone		61				1.0
Naphthalene	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	10^{-8}	10^{-4}	n, π^*	1.0
Camphorquinone	55	50	10^{-8}		n, π^*	1.0
Pyrene	77	49	10^{-6}		π, π^*	0.3
Anthracene	76	47	5×10^{-9}	10^{-4}	π, π^*	0.7
9,10-Dichloroanthracene	74	40	5×10^{-9}	10^{-4}	π, π^*	0.5
Perylene	66	35	5×10^{-9}		π, π^*	0.005

The ideal triplet sensitizer has:

- High triplet energy
- Short singlet lifetime
- Long triplet lifetime
- High quantum yield for ISC
- Minimal absorption overlap with the acceptor

Properties and Examples of Quenchers

Compound	E_S	E_T
	kcal/mol	
2-Butene	120	78
Phenylacetylene	100	72
Biphenyl	95	66
<i>ortho</i> -Terphenyl	90	62
1,3-Butadiene	90	60
2,4-Pentadiene	90	59
<i>para</i> -Terphenyl	105	58
Cyclopentadiene	90	58
<i>cis</i> -Stilbene	95	57
1,3-Cyclohexadiene	80	53
<i>trans</i> -Stilbene	90	50
Azulene	40	30
Tetracene	45	29
Oxygen (O ₂)		23

The ideal triplet quencher has:

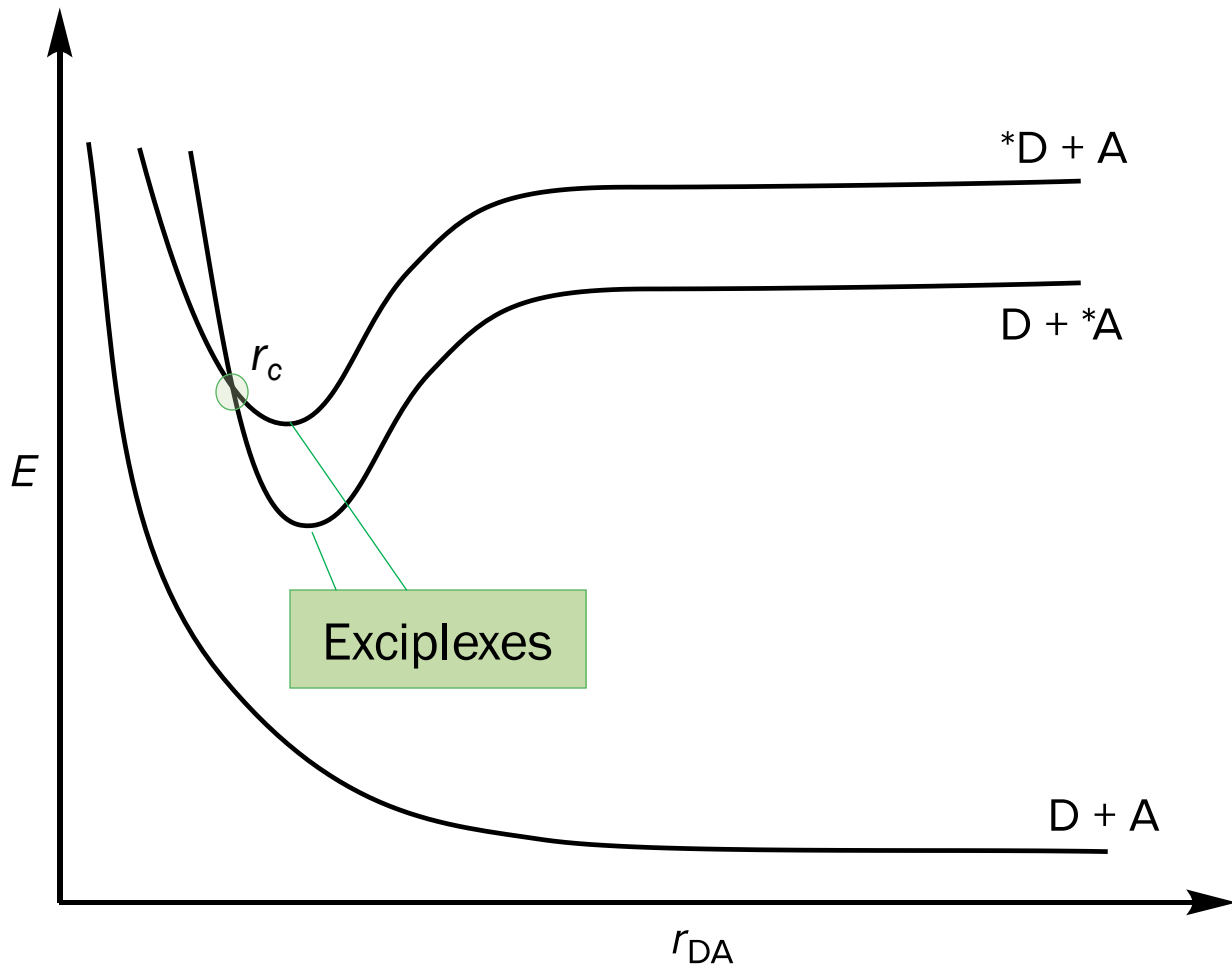
- Low triplet energy
- Short triplet lifetime (rapid decay to ground state)
- Minimal absorption overlap with the donor

Dexter (Exchange) Energy Transfer and Trivial Energy Transfer

Energy Transfer from Excited Electronic States

PES for Exchange Energy Transfer

Exchange energy transfer requires a collision between the donor and acceptor. Delocalization results in energy lowering as *D and A approach; at r_c an interaction causes a shift to the lower surface.



Initial state: $\psi(^*D)\psi(A)$

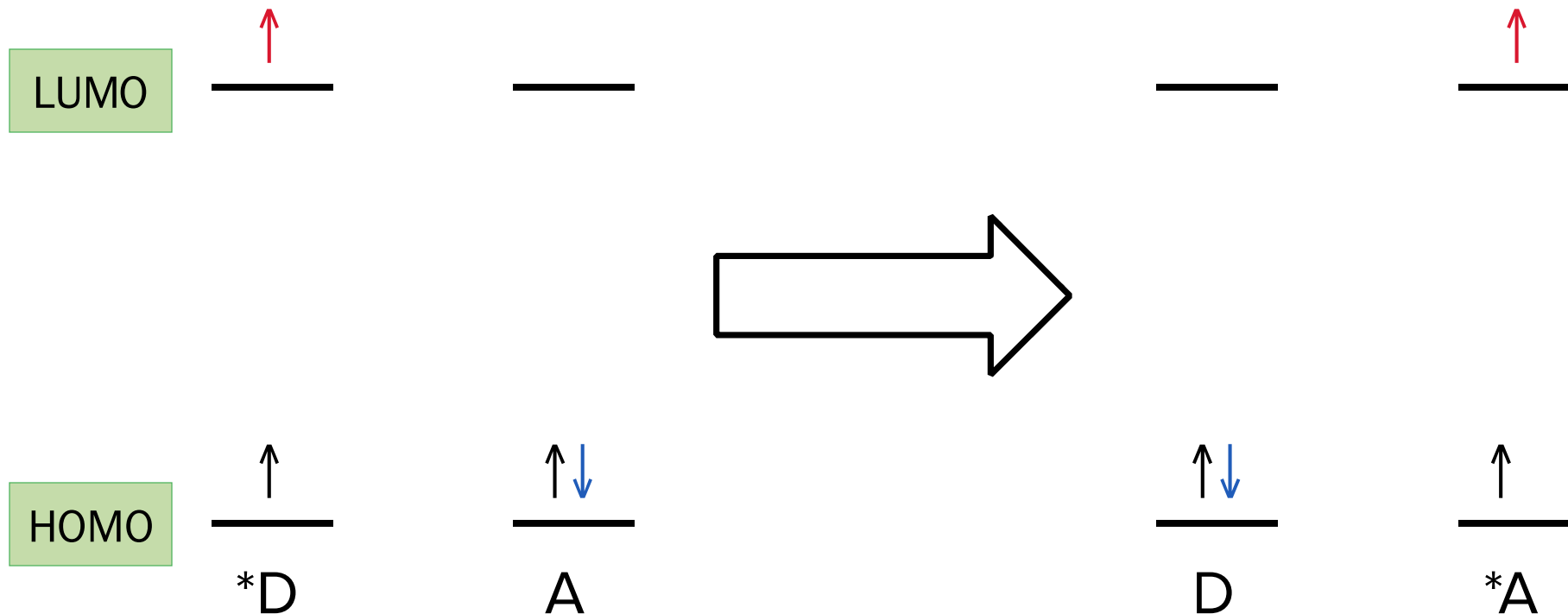
Final state: $\psi(D)\psi(^*A)$

$k \propto \langle \psi(D)\psi(^*A) | H_e | \psi(^*D)\psi(A) \rangle^2$
based on Fermi's golden rule.

Electron Exchange Interaction

Collisional energy transfer involves double electron transfer to and from the donor and acceptor. As a result, *D returns to the ground state and A ends up in an excited state.

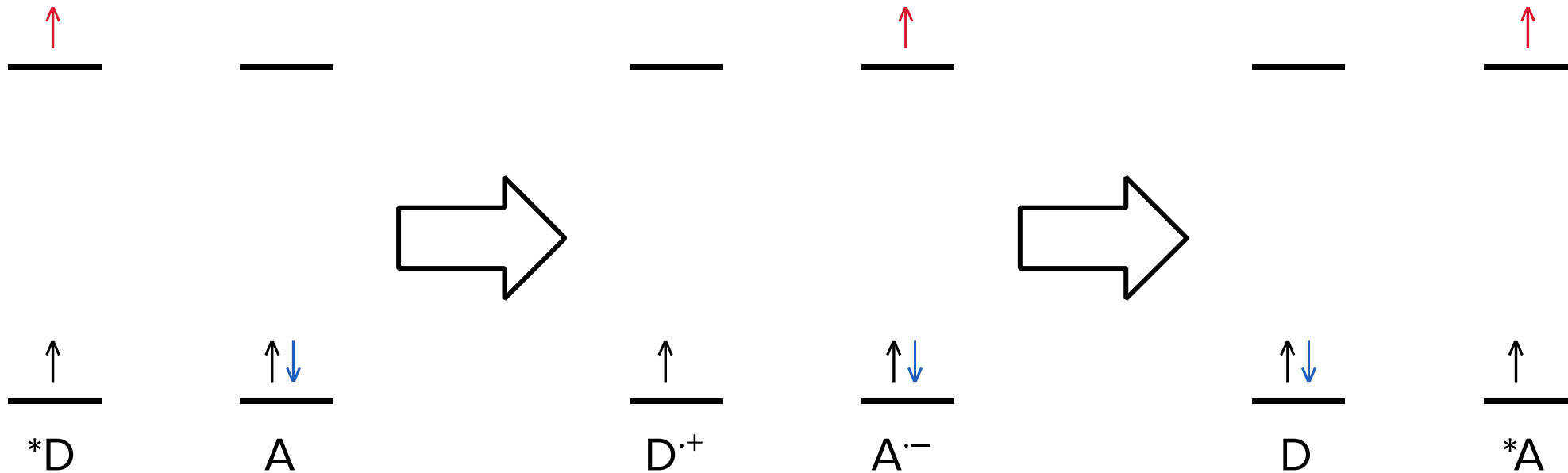
Concerted mechanism



Electron Exchange Interaction

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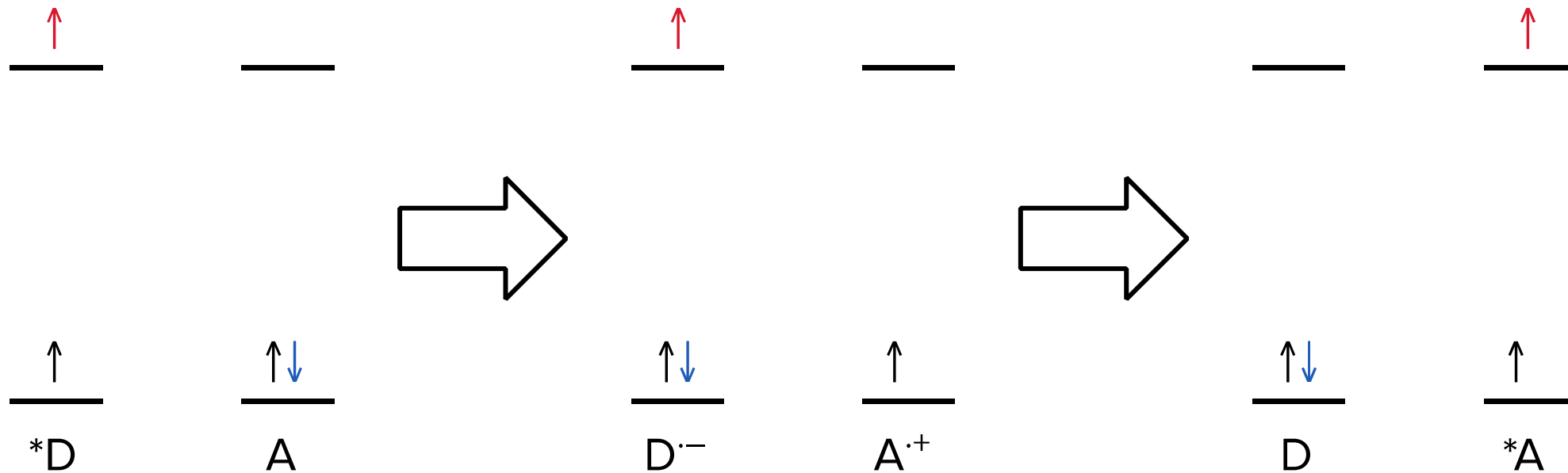
Oxidative mechanism



Electron Exchange Interaction

Collisional energy transfer involves double electron transfer to and from the donor and acceptor. As a result, *D returns to the ground state and A ends up in an excited state.

Reductive mechanism



Distance and Spectral Dependence

Dexter proposed that $k_{\text{ET}}(\text{exchange})$ was directly proportional to the *spectral overlap integral* J and exhibited an inverse exponential dependence on r_{DA} .

$$k_{\text{ET}}(\text{exchange}) = K J \exp[-2r_{\text{DA}}/(r_{\text{D}} + r_{\text{A}})]$$

Spectral overlap integral
normalized for ϵ_{A}

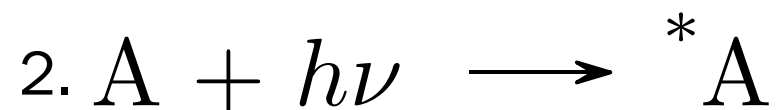
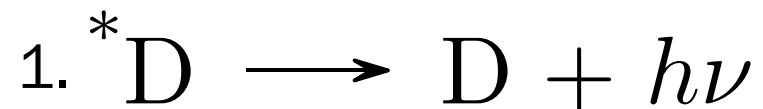
Orbitals exhibit exponential
decay with distance

Rate is independent of absorption characteristics of A

Collision is *required* as k becomes negligible for $r_{\text{DA}} > r_{\text{D}} + r_{\text{A}}$

Trivial Energy Transfer

Emission of a photon by *D followed by absorption by A is called *trivial energy transfer*.

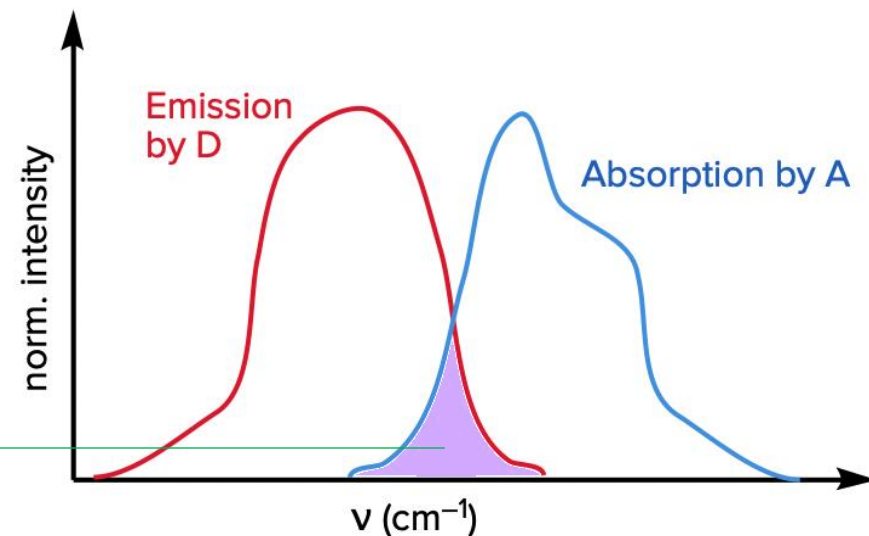


The rate of trivial energy transfer depends on:

1. Quantum yield of emission by *D (Φ_e)
2. Concentration of A
3. Absorptivity of A (ϵ_A)
4. Spectral overlap of D emission and A absorption

$$J = \int_0^\infty I_D \epsilon_A d\bar{\nu}$$

Spectral overlap integral J

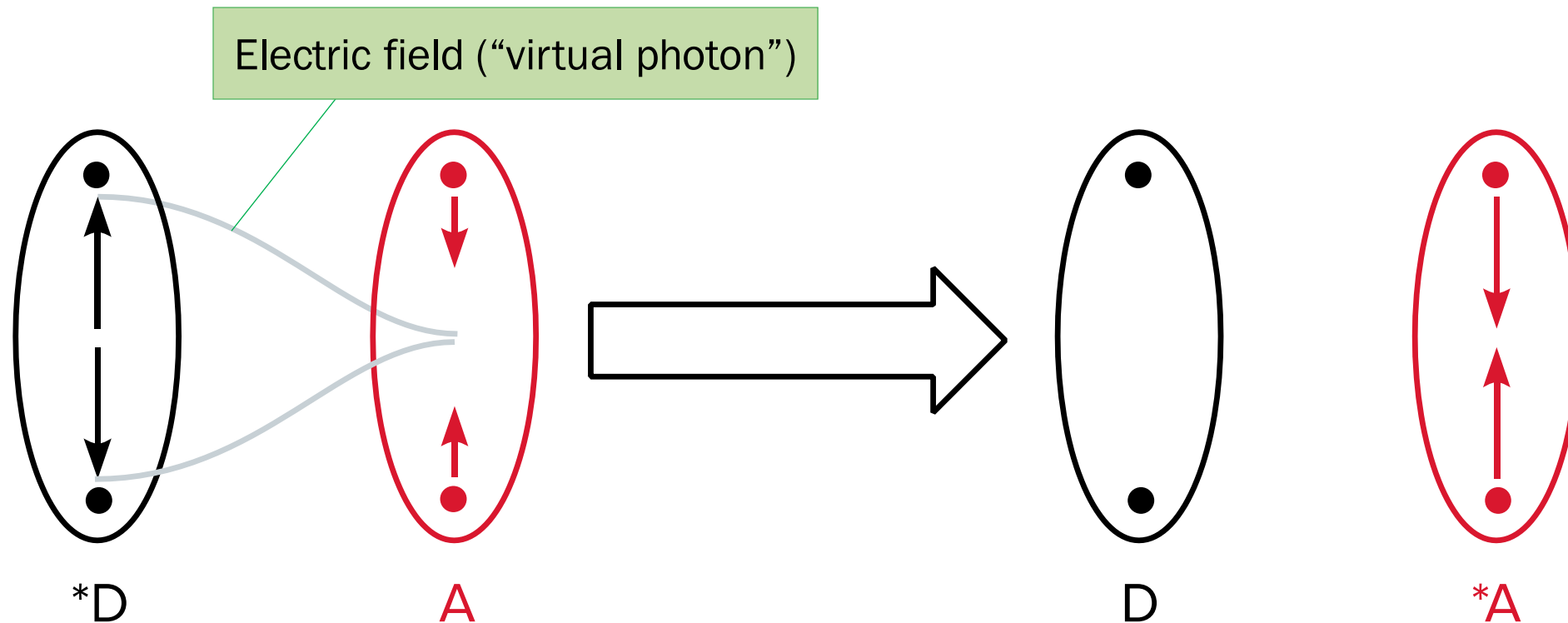


Förster Resonance Energy Transfer (FRET)

Energy Transfer from Excited Electronic States

Interaction of Transition Dipoles

Coulombic or *Förster resonance energy transfer (FRET)* involves the electrostatic interaction of equal-energy transition dipoles in *D and A.



The oscillating dipole in *D induces an oscillating dipole in A. Conservation of energy requires $\Delta E(^*D \rightarrow D) = \Delta E(A \rightarrow ^*A)$.

Förster Theory

Combining classical theory of interacting dipoles with the transition dipole moments μ_A and μ_D reveals the dependence of k_{ET} (Coulombic) on distance and spectral parameters.

$$k_{ET}(\text{Coulombic}) \sim \frac{\mu_D^2 \mu_A^2}{r_{DA}^6}$$

From relations between μ , radiative rate k_D^0 , and integrated absorptivity $\int \epsilon_A dv$,

$$k_{ET}(\text{Coulombic}) \sim \frac{k_D^0 \int \epsilon_A}{r_{DA}^6}$$

Incorporating the requirement for spectral overlap,

$$k_{ET}(\text{Coulombic}) = \alpha \frac{\kappa^2 k_D^0}{r_{DA}^6} J(\epsilon_A)$$

Dipole orientation factor

Spectral overlap integral
without ϵ_A normalized

Förster Theory

Förster theory points to conditions for rapid Coulombic energy transfer (FRET). The **critical separation** r_0 is a convenient distance when measuring FRET efficiency.

$$k_{\text{ET}}(\text{Coulombic}) = \alpha \frac{\kappa^2 k_D^0}{r_{\text{DA}}^6} J(\epsilon_A)$$

The rate of FRET is greatest when:

1. The $*D \rightarrow D$ and $A \rightarrow *A$ processes have large overlap integral J
2. The radiative rate of D (k_D^0) is large
3. The absorptivity of A (ϵ_A) is large
4. $*D$ and A are close in space (r_{DA} small)

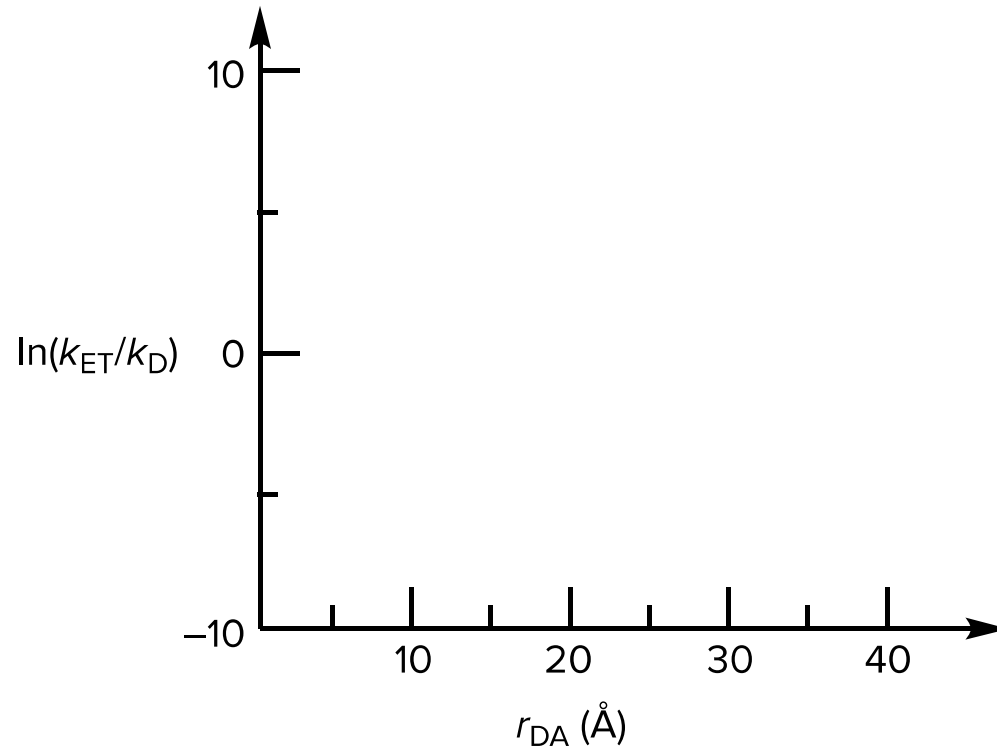
Critical separation r_0 is defined as the distance at which FRET is 50% efficient; i.e., the distance at which the rate of de-excitation of $*D$ is equal to the rate of FRET to A.

$$k_{\text{ET}} \propto k_D \left(\frac{r_0}{r} \right)^6 = \left(\frac{1}{\tau_D} \right) \left(\frac{r_0}{r} \right)^6$$

Comparing Exchange ET and FRET

Coulombic and exchange energy transfer differ profoundly in the effects of distance and oscillator strengths. However, both mechanisms depend on spectral overlap.

$k(\text{Coulombic})$ decreases as r^{-6} while $k(\text{exchange})$ decreases as $\exp(-2r)$.



$k(\text{Coulombic})$ depends on the oscillator strengths of $^*D \rightarrow D$ and $A \rightarrow ^*A$, especially the latter. $k(\text{exchange})$ does not.

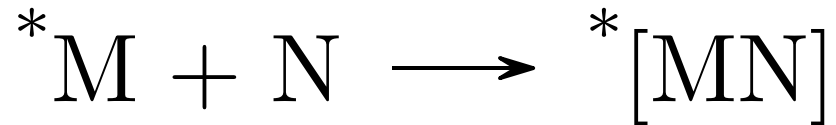


Excimers and Exciplexes

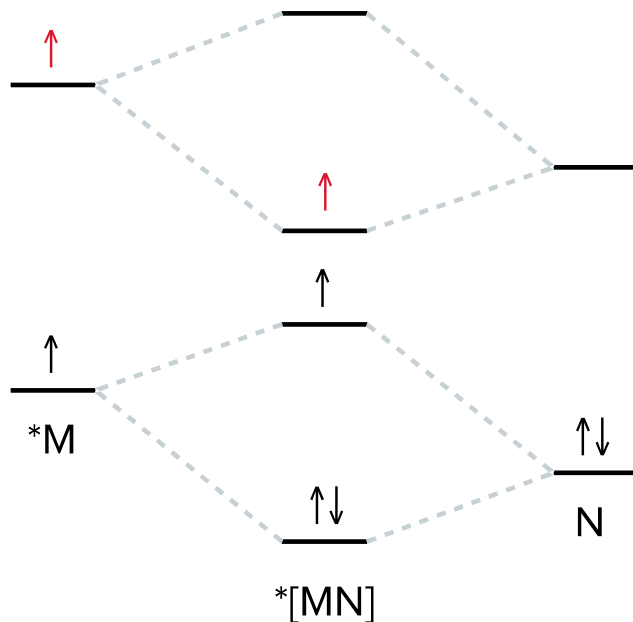
Energy Transfer from Excited Electronic States

Excimers and Exciplexes

When an excited molecule *M coordinates with a ground-state molecule N , the result is an **excimer** ($M = N$) or **exciplex** ($M \neq N$). Excimer formation is common because *M is often stabilized via orbital interactions with N .



Orbital interactions in exciplexes



Example: pyrene excimer

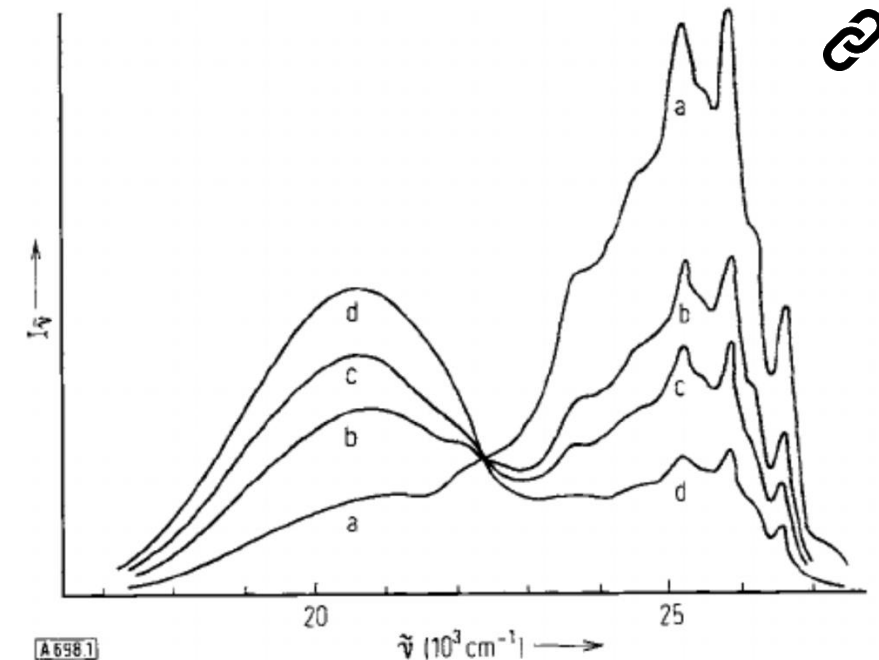
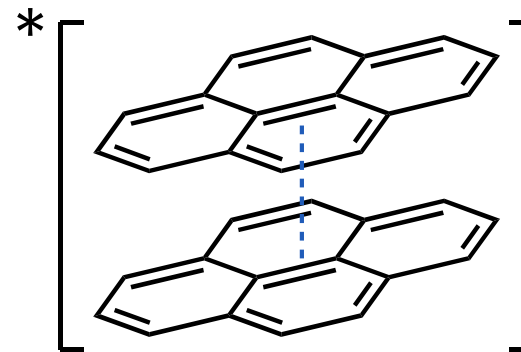
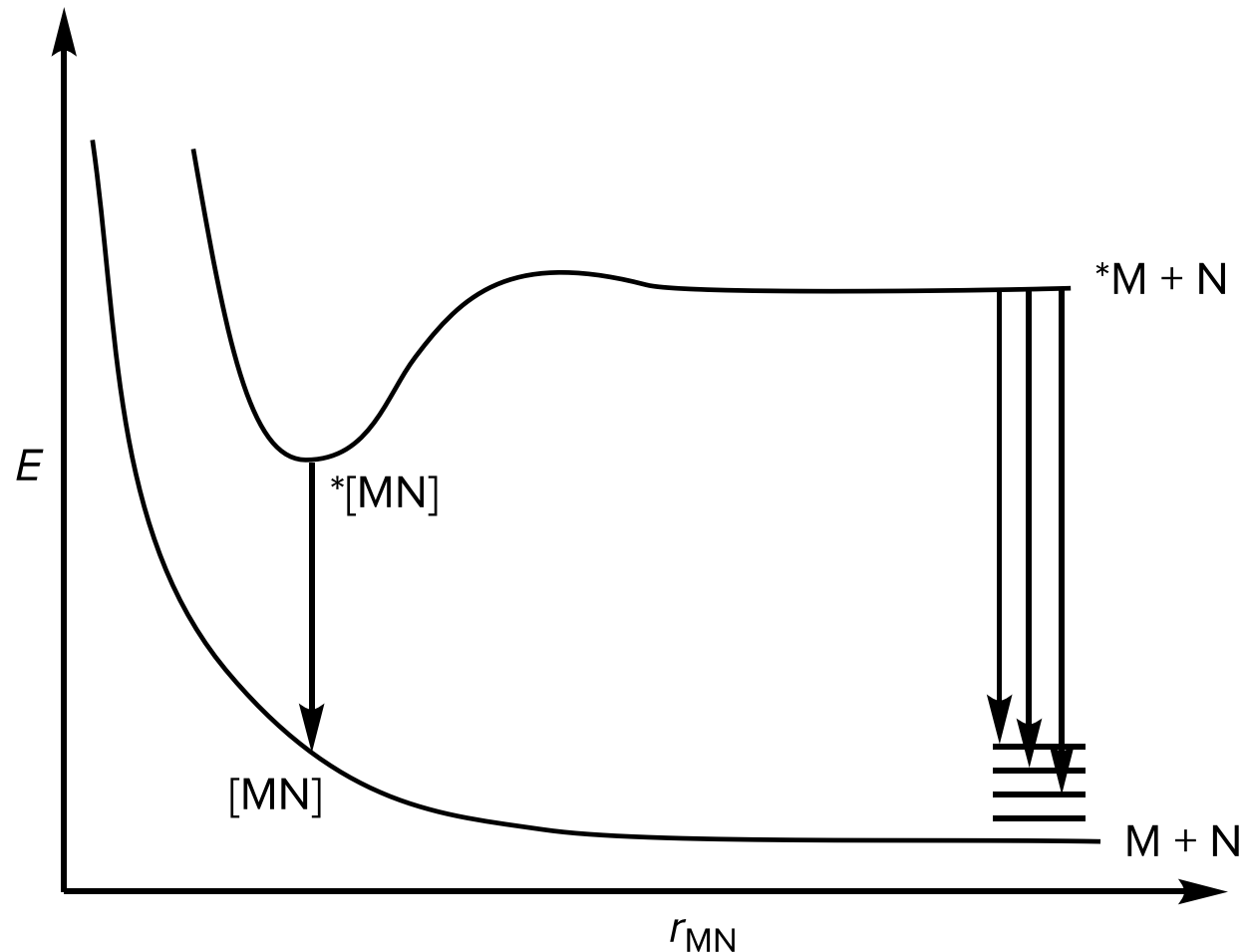


Fig. 1. Fluorescence spectra of pyrene in *n*-heptane.
 $t = 20^\circ\text{C}$, c (mole/l): 5×10^{-5} (a), 1.8×10^{-4} (b), 3.1×10^{-4} (c), 7.0×10^{-4} (d).

Potential Energy Surfaces

The ground-state complex MN is typically unstable, so excimer emission appears as a broad, featureless peak at lower energy than emission of the monomer *M .



$\Delta H < 0$ but $\Delta S < 0$ for excimer formation.

Time-resolved experiments show that excimer formation is rate-limited by diffusion.

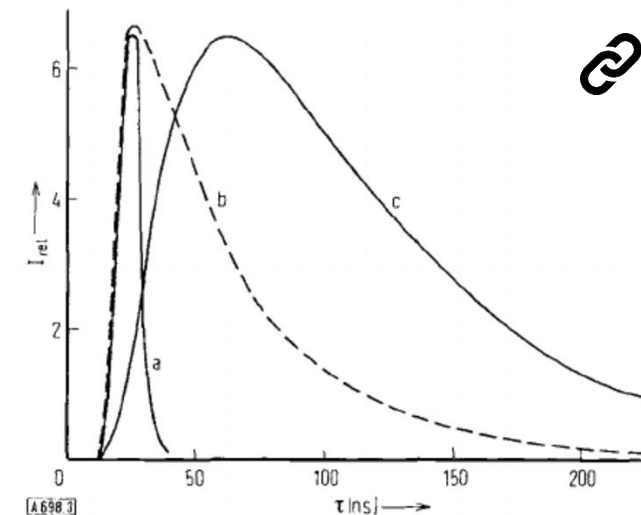


Fig. 3. Time dependence of excitation (a), monomer component (b), and excimer component (c) of pyrene in cyclohexane. $c = 5 \times 10^{-3}$ mole/l [8].

Classifying Exciplexes by Structure

A given exciplex $^*(MQ)$ can be represented as a quantum-mechanical superposition of four basis states that capture the “essential ingredients” of the exciplex.

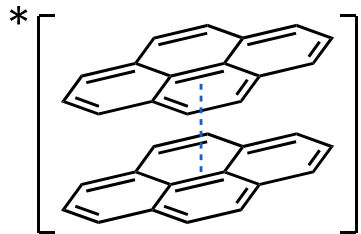
$$\psi^*_{(MQ)} = a\psi_{(^*MQ)} + b\psi_{(M^*Q)} + c\psi_{(M^-Q^+)} + d\psi_{(M^+Q^-)}$$

Local excitation on M

Electron transfer to M

Local excitation on Q

Electron transfer to Q



In excimers, $a = -b$ and $c = -d$ because M and Q are identical.

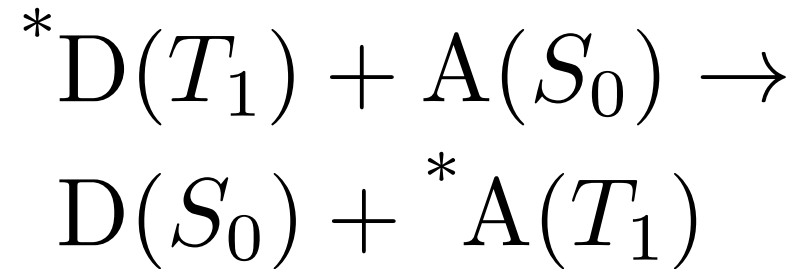
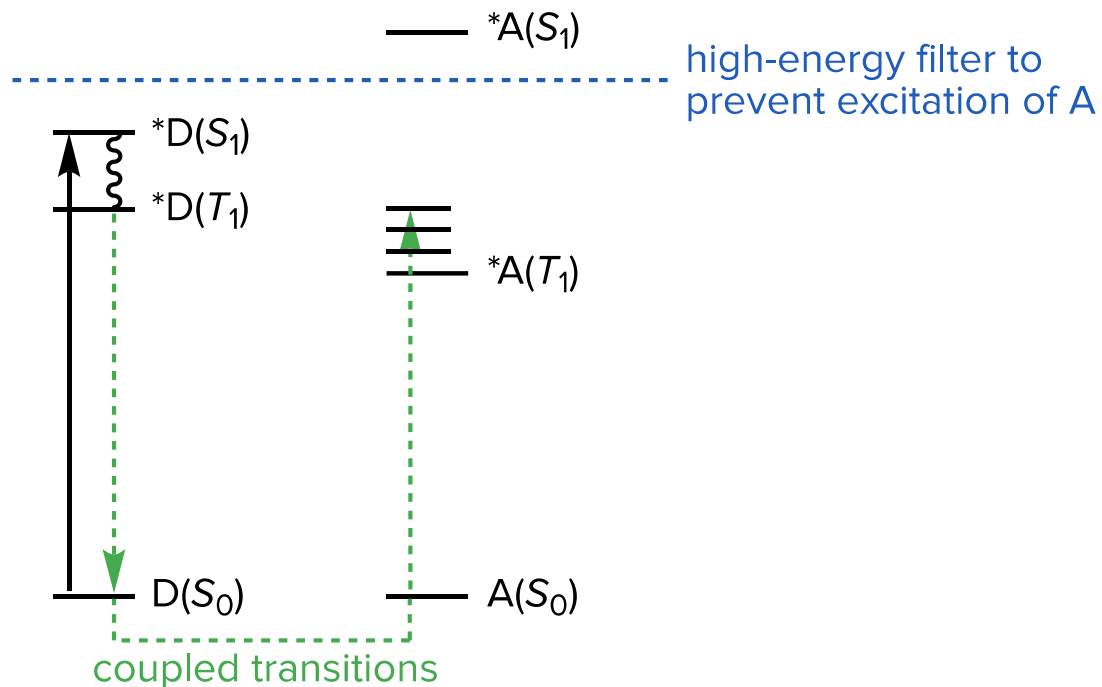


Triplet Energy Transfer

Energy Transfer from Excited Electronic States

Triplet Energy Transfer

Triplet-triplet energy transfer (TET) is the most common and important energy transfer process in organic photochemistry.

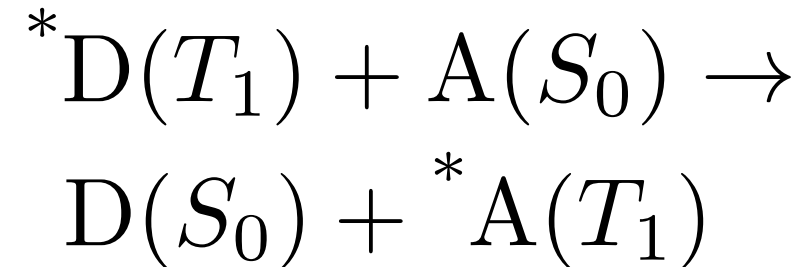


TET by the Columbic mechanism is forbidden due to very small ϵ_A .

Compounds with small ΔE_{ST} are ideal triplet sensitizers.

Thermodynamics and Rate

Endothermic TET is negligibly slow for ΔE greater than a few kcal/mol. In contrast, exothermic TET is typically rate limited by diffusion.



Donor	Acceptor	Solvent	$k_{\text{dif}} (\text{s}^{-1})$	$k_{\text{ET}} (\text{s}^{-1})$	$k_{-\text{ET}} (\text{s}^{-1})$	$\Delta E(\text{D}-\text{A})$
triphenylene	naphthalene	<i>n</i> -hexane	10^{10}	2×10^9	—	−6
naphthalene	triphenylene	<i>n</i> -hexane	10^{10}	—	$<10^4$	+6
naphthalene	biacetyl	benzene	10^{10}	9×10^9	—	−5
biacetyl	naphthalene	benzene	10^{10}	—	2×10^6	+5
acetone	biacetyl	acetonitrile	10^{10}	5×10^9	—	−23
naphthalene	benzophenone	benzene	10^{10}	—	$<10^4$	+8

For exothermic TET, rate appears unaffected by ΔE (no “energy gap law”). However, sterics can affect the rate of TET; see *JACS* 97, 4864.



Stern-Volmer Analysis

Energy Transfer from Excited Electronic States

Kinetic Scheme for Quenching

Stern-Volmer analysis involves measurement of the concentration-dependent quenching of fluorescence or phosphorescence. It is based on a simple mechanistic scheme for quenching.

Reaction	Description	Rate	
$M + h\nu \rightarrow {}^*M$	absorption	$k_{abs}[M][h\nu]$	Generation of *M
${}^*M \rightarrow M + h\nu$	fluorescence	$k_{em}[{}^*M]$	Consumption of *M
${}^*M \rightarrow M$	other decay pathways	$\sum k_i[{}^*M]$	
${}^*M + Q \rightarrow M + {}^*Q$	quenching	$k_q[{}^*M][Q]$	

Stern-Volmer Relation

The quantum yield of emission Φ_{em} depends on the concentration of quencher. Considering kinetics and quantum yields allows us to derive the **Stern-Volmer relation**.

$$k_d = k_{em} + \sum_{i \neq em} k_i$$

$$\Phi_{em} = \frac{k_{em}}{k_d + k_q[Q]}$$

$$\frac{\Phi_{em}^0}{\Phi_{em}} = \frac{k_d + k_q[Q]}{k_d} = 1 + \left(\frac{k_q}{k_d} \right) [Q]$$

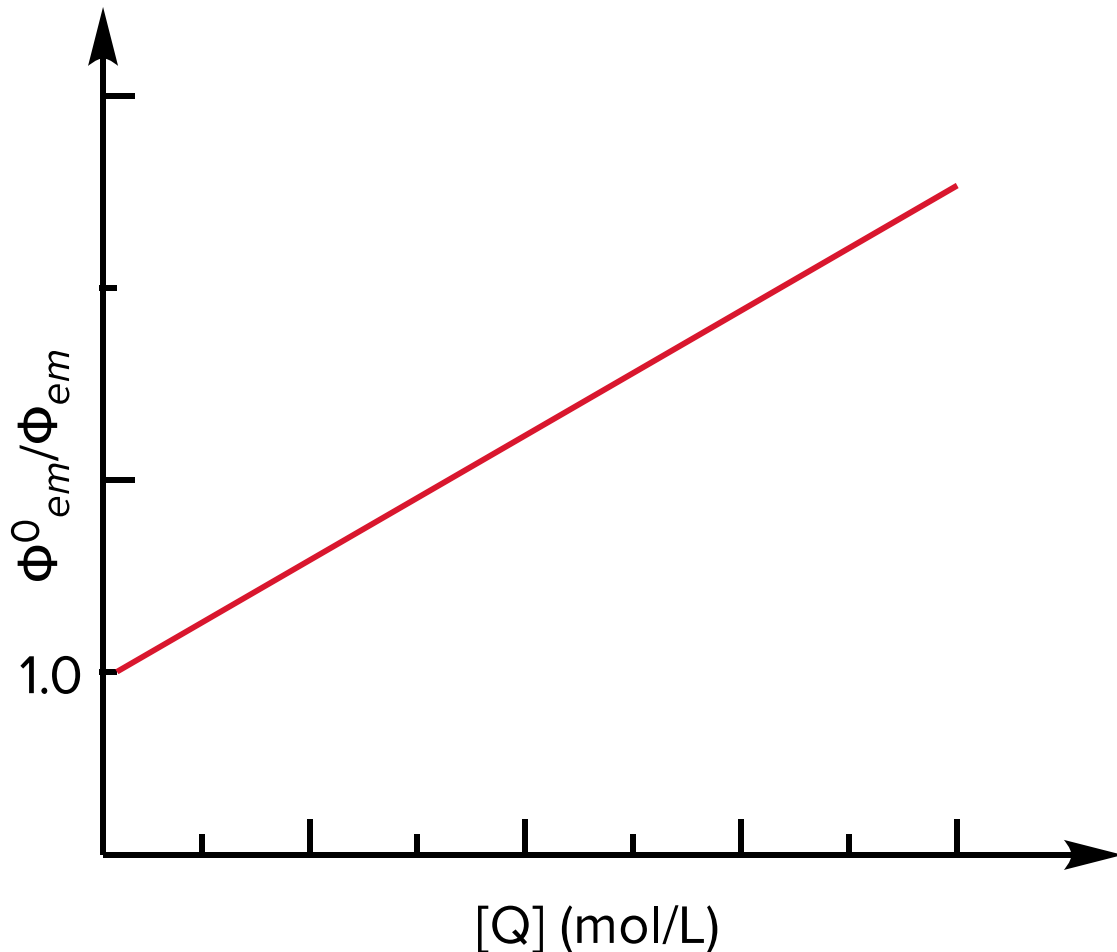
$$\frac{\Phi_{em}^0}{\Phi_{em}} = 1 + k_q \tau_M^* [Q]$$

$$\frac{I_0}{I} = 1 + k_q \tau_M^* [Q]$$

This equation holds for *any* quenching mechanism: energy transfer, electron transfer, and even reaction of Q with *M !

Stern-Volmer Plot

Assuming our mechanistic scheme holds, a plot of Φ_{em}^0/Φ_{em} (or I_0/I) against $[Q]$ should result in a line with an intercept of 1.0 and a slope of $k_q/k_d = k_q\tau_{*M}$.



$$\frac{\Phi_{em}^0}{\Phi_{em}} = 1 + k_q\tau_{*M}[Q]$$

Evidence for interaction between $*M$ and Q

Rate constants for quenching or reaction

Nonlinear plots suggest interesting mechanisms...



Try it yourself!