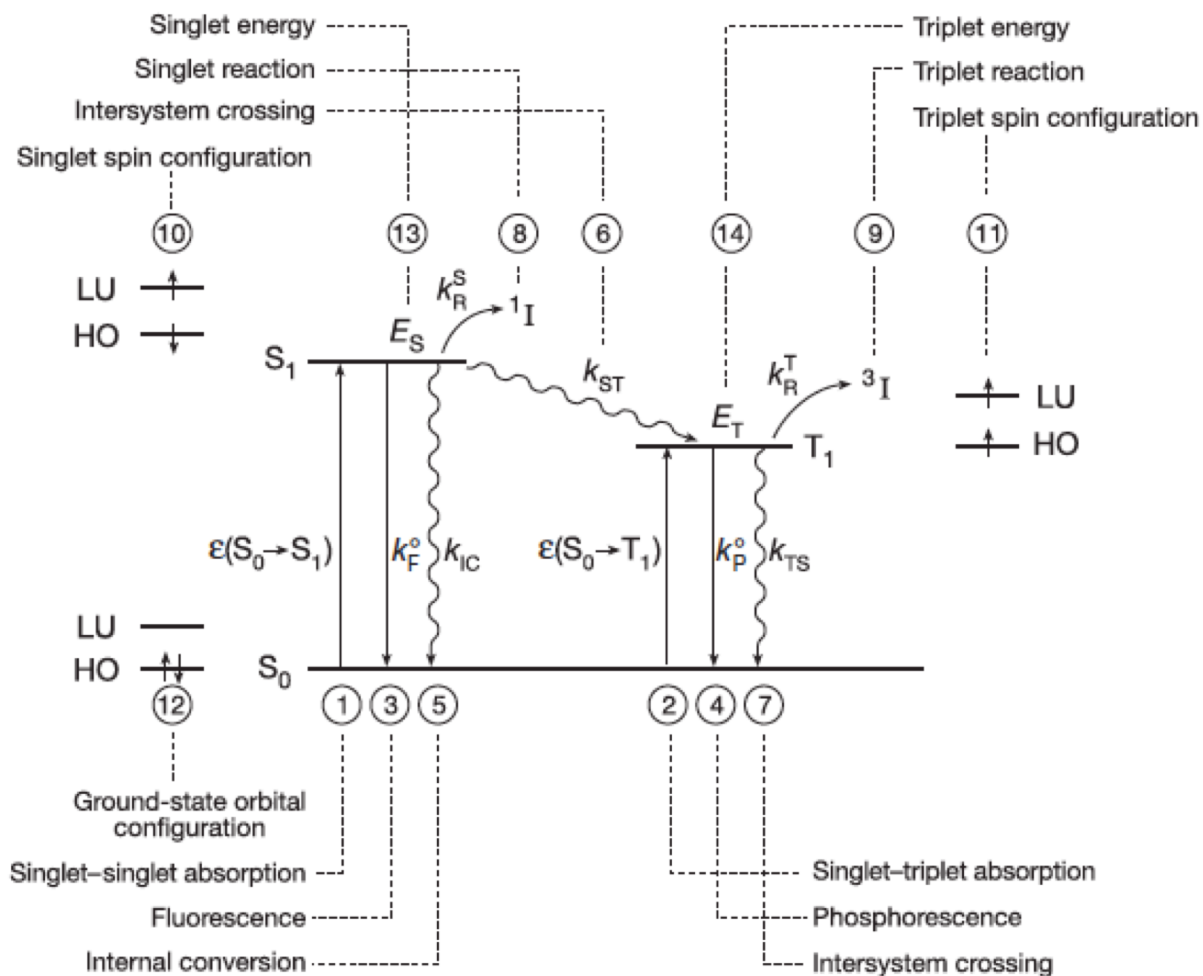


Energy Transfer

Jablonski Diagram



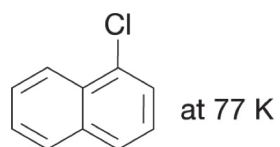
Alexander Jablonski
(1898-1980)



F. Perrin

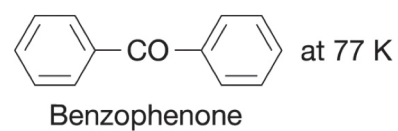
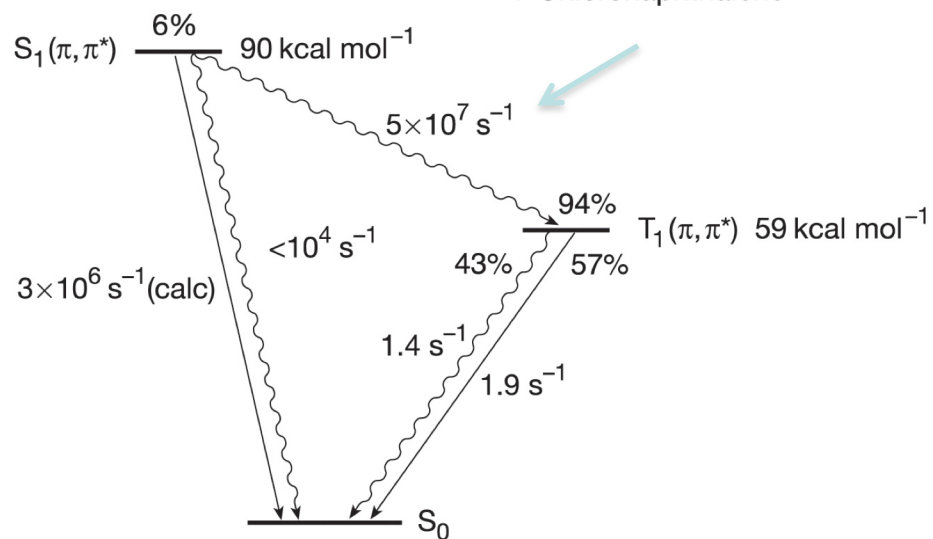


J. Perrin

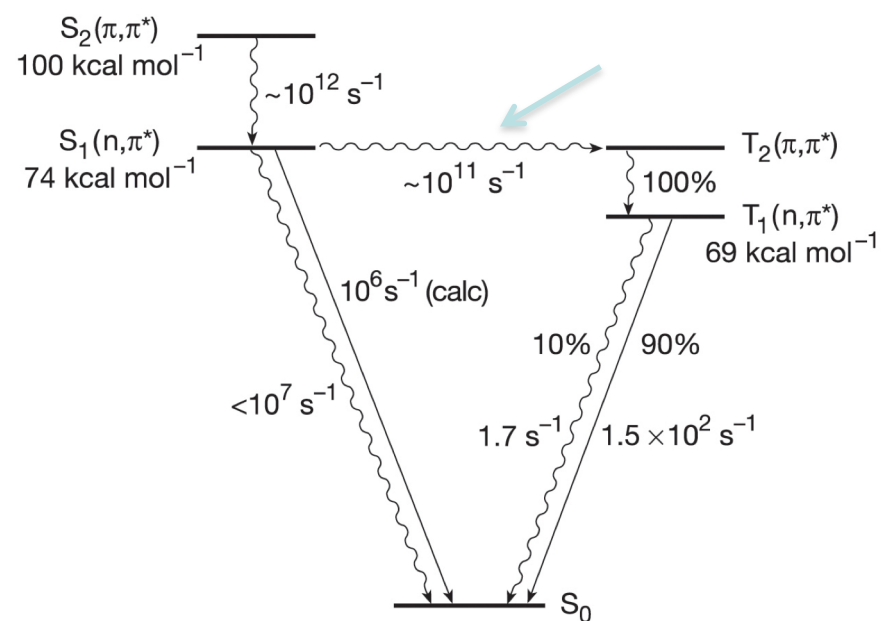


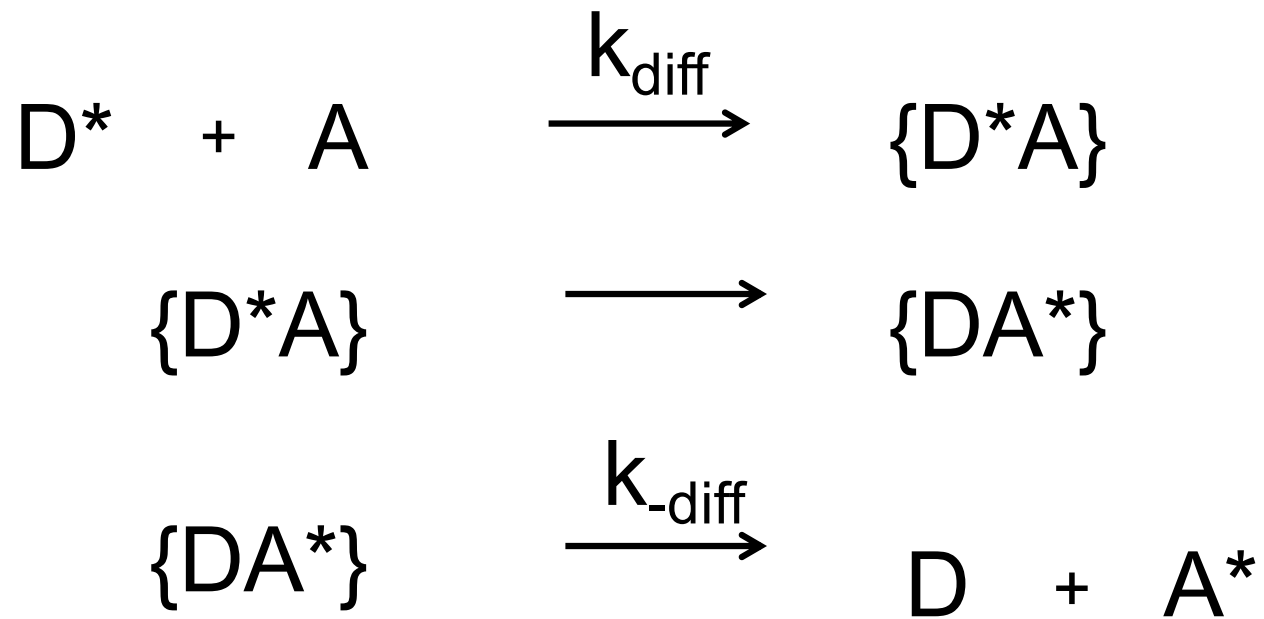
at 77 K

1-Chloronaphthalene



at 77 K





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

Diffusion

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

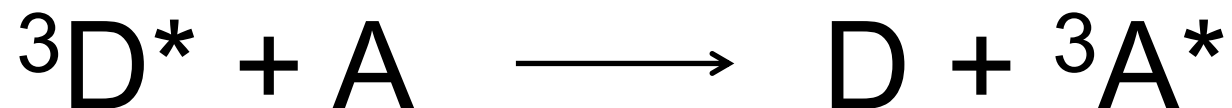
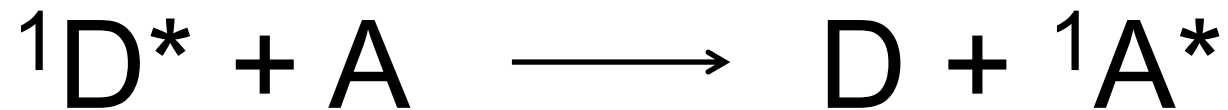
η is the viscosity of the solvent (in units of Poise, P)

R is the gas constant (8.31×10^7 erg/mol or 1.99 cal mol⁻¹ K⁻¹).

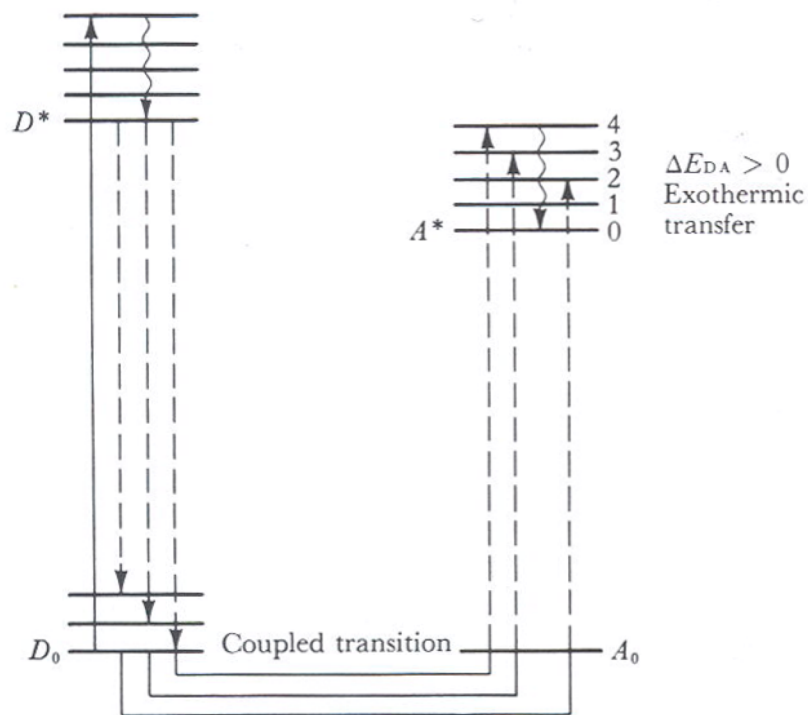
For typical non-viscous organic solvents (benzene, acetonitrile, hexane) at room temperature η is ~ 1 -10 cP

k_{DIF} has a value of around 10^9 - 10^{10} M⁻¹s⁻¹.

Possibilities



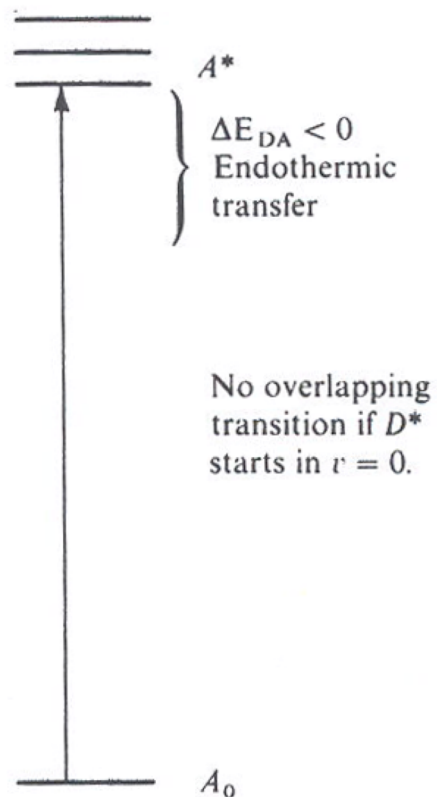
Energy Requirement



ENERGY TRANSFER

Allowed

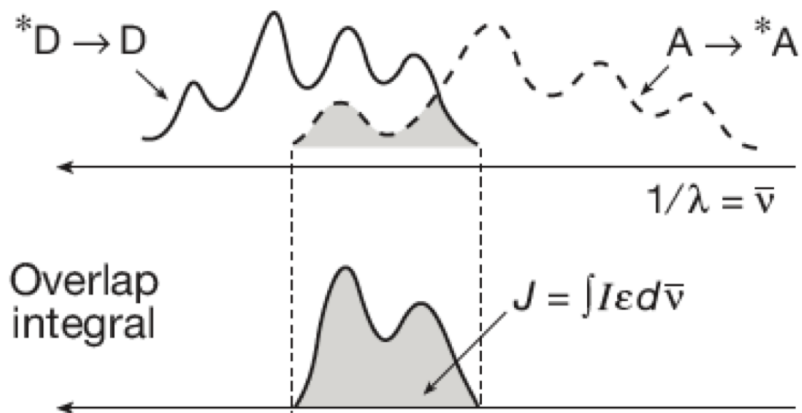
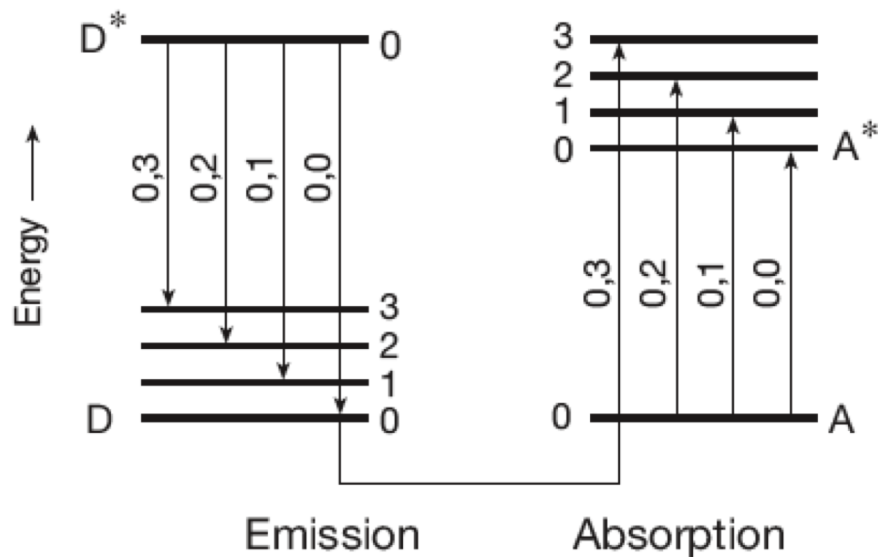
$$E_D > E_A$$



Forbidden

$$E_D < E_A$$

Criteria for Energy Transfer: Spectral Overlap



$$J = \int_0^{\infty} \underset{\substack{\uparrow \\ \text{emitted light intensity}}}{I_D(\bar{\nu})} \underset{\substack{\downarrow \\ \text{extinction coefficient of A}}}{\epsilon_A(\bar{\nu})} d\bar{\nu}$$

This overlap integral also can be used for energy transfer.

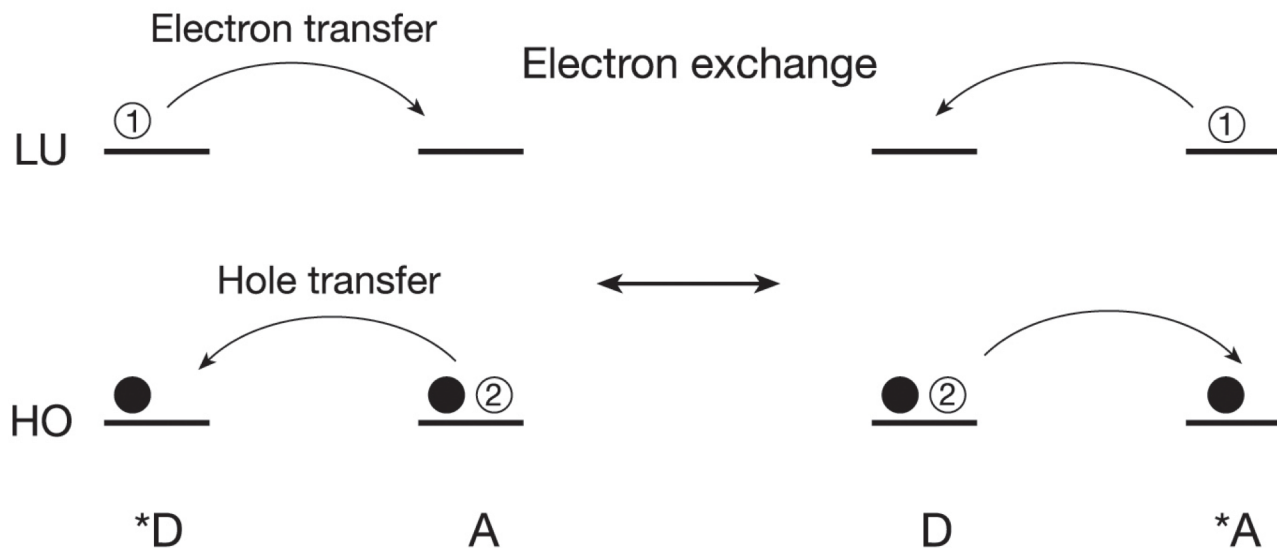
- Non-Radiative Energy Transfer
 - Resonance ET
 - Exchange ET

Non-Radiative Energy Transfer

Exchange Energy Transfer

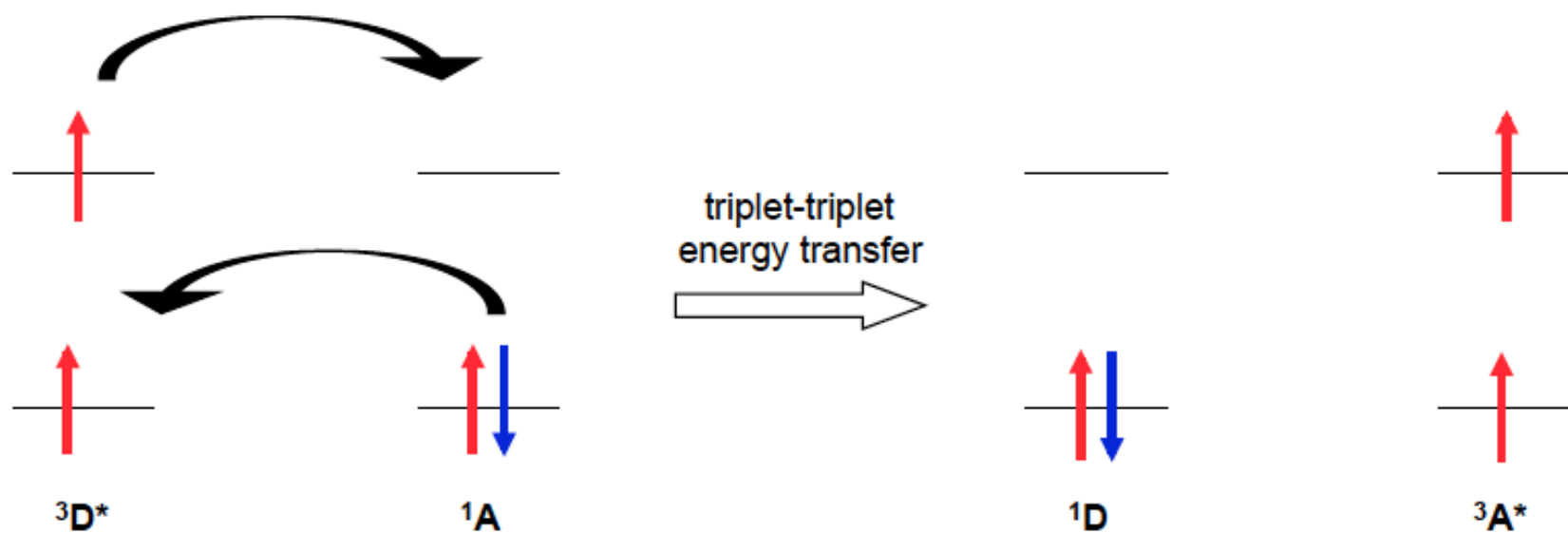
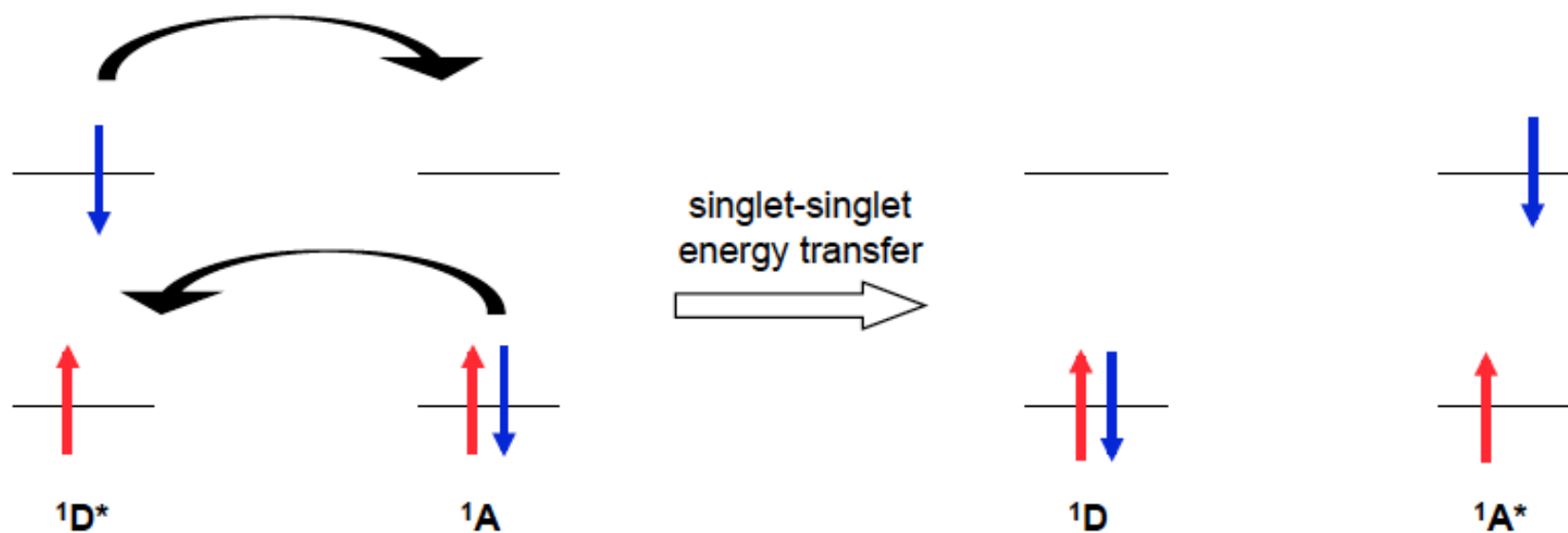
Dexter Energy Transfer

Collisional Energy Transfer



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

Exchange Energy Transfer



Exchange Energy Transfer

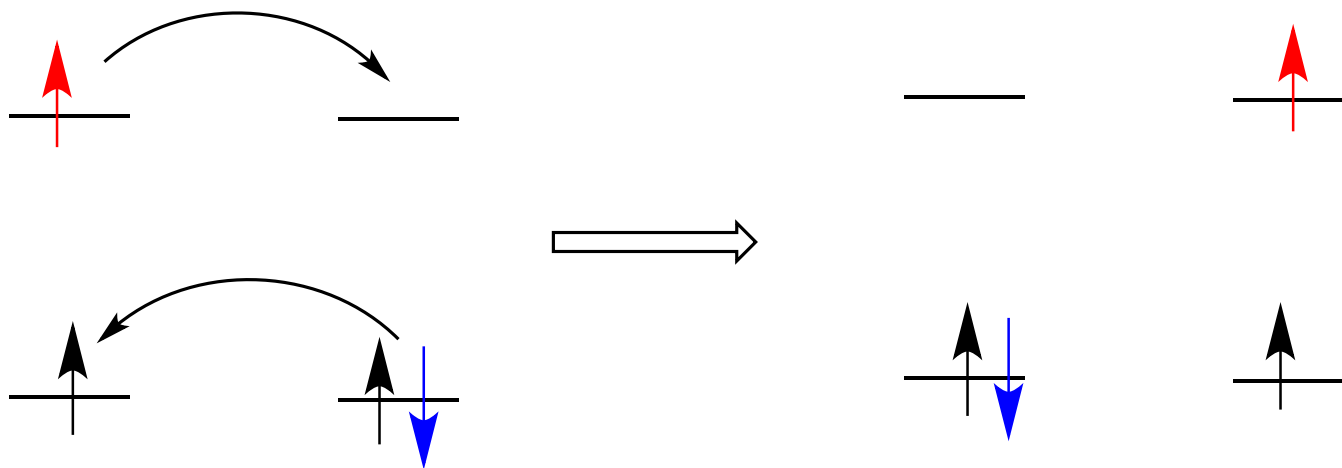
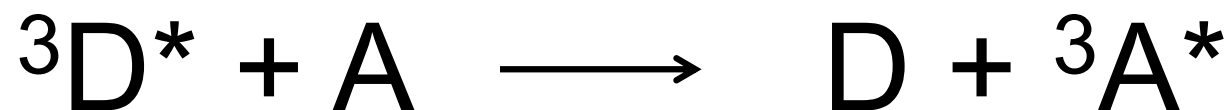
$$k_{\text{ET}} (\text{exchange}) = KJ \exp(-2r_{\text{DA}}/L)$$

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

Triplet-Triplet Energy Transfer



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

Sensitized Phosphorescence at 77 ° K

A. Terenin and V. Ermolaev, *Doklady, Acad. Sc., U.S.S.R.*, 85, 547, **1952**; *Trans. Faraday Soc.*, 52, 1042, **1956**

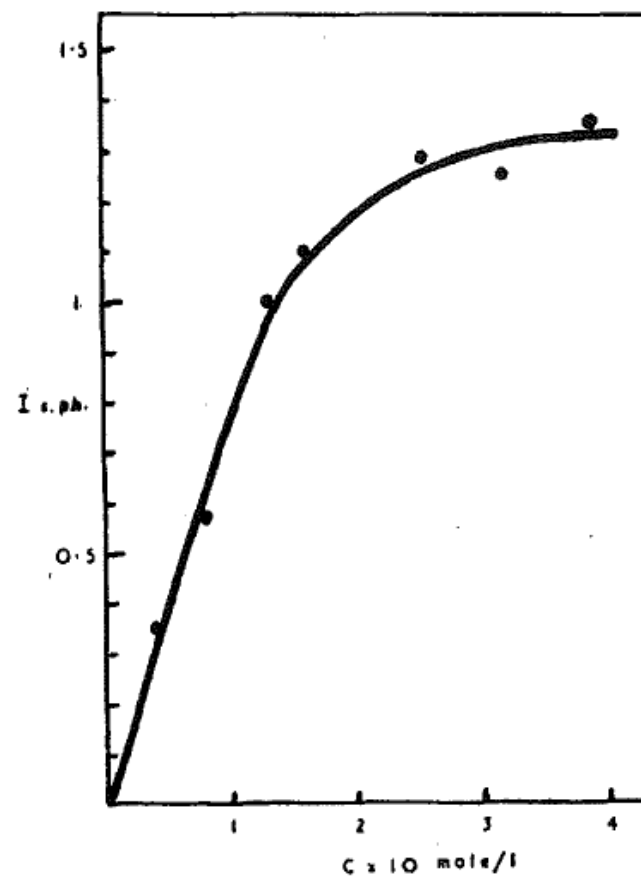
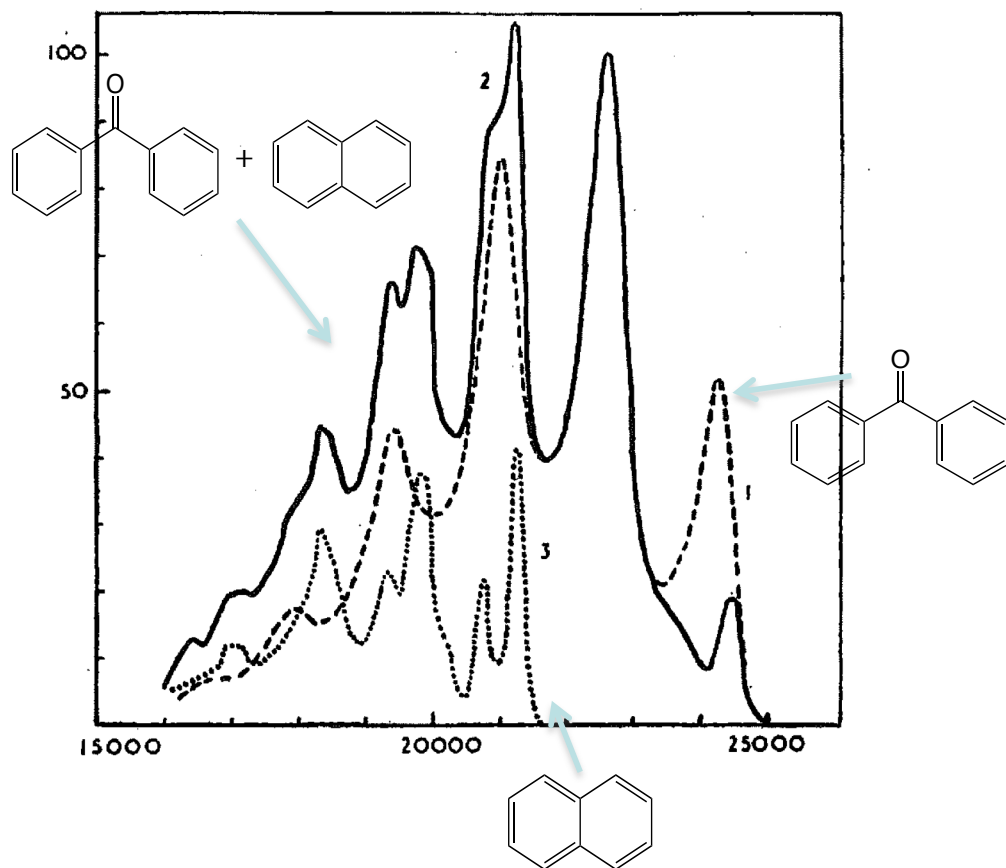
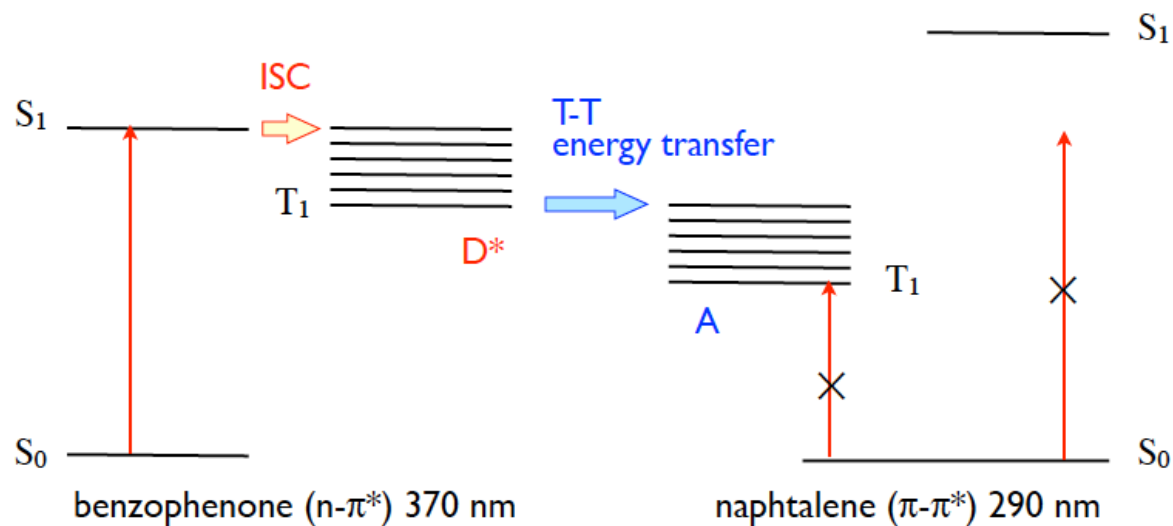


FIG. 3.—Phosphorescence intensity of naphthalene, sensitized by benzophenone against naphthalene concentration.

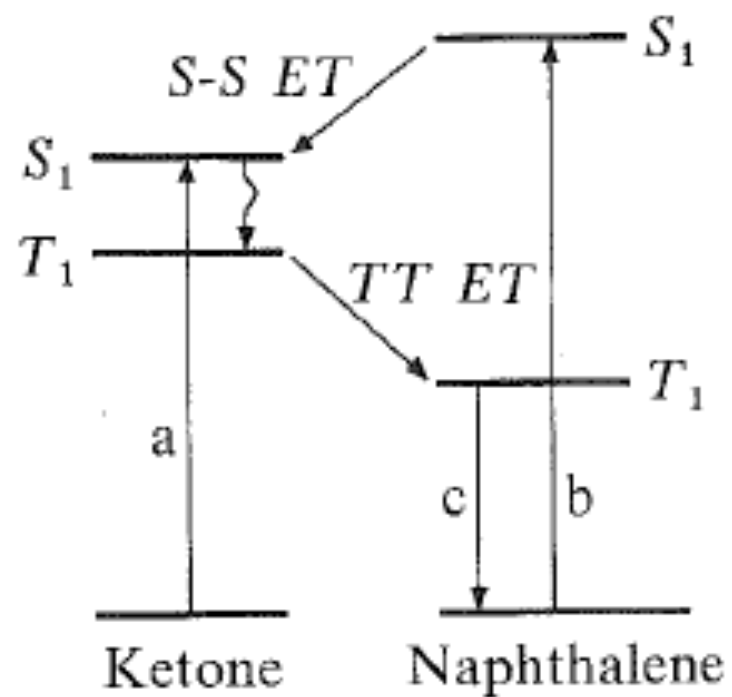
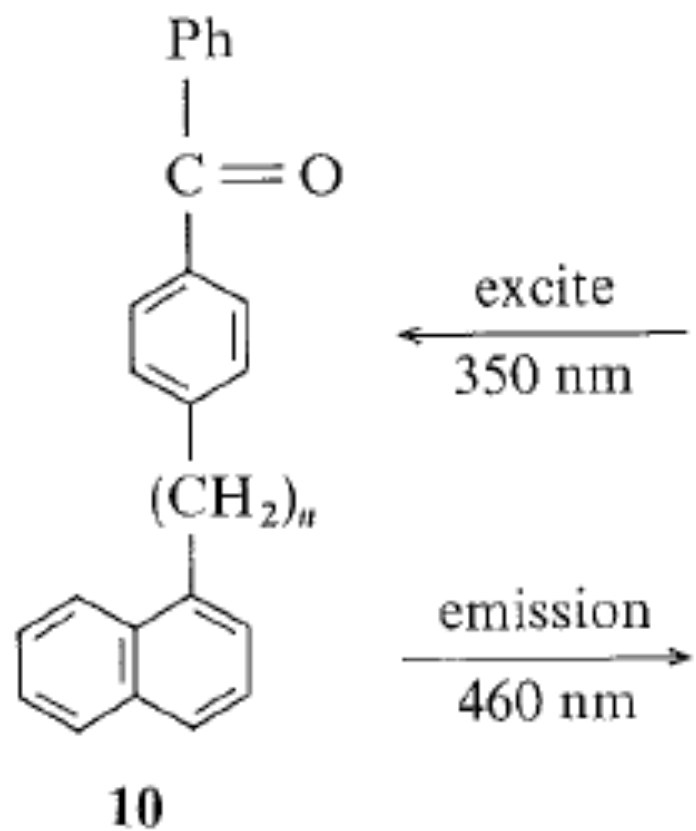
Sensitized Phosphorescence at 77 ° K



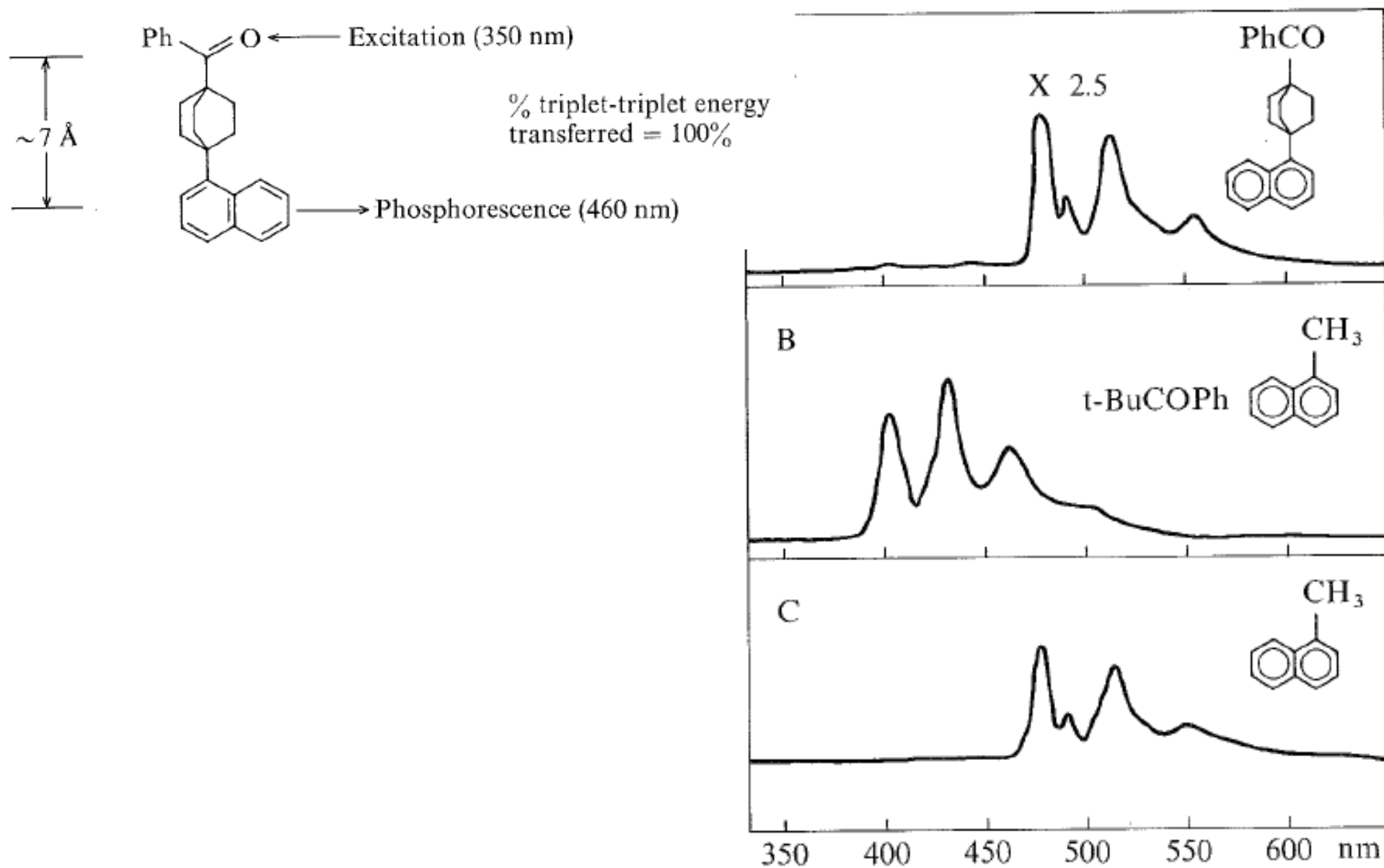
Sensitized Phosphorescence in Rigid Solution at 77°K

Donor	Acceptor	$R_c(\text{\AA})$
Benzaldehyde	Naphthalene	12
	1-Chloronaphthalene	12
	1-Bromonaphthalene	12
Benzophenone	Naphthalene	13
	1-Chloronaphthalene	13
	1-Bromonaphthalene	13
	1-Iodonaphthalene	13
	Naphthalene	11
<i>m</i> -Iodobenzaldehyde	1-Bromonaphthalene	11
	Naphthalene	13
Triphenylamine	Naphthalene	15
Carbazole	Naphthalene	13
Phenanthrene	1-Chloronaphthalene	14
	1-Bromonaphthalene	14
	Naphthalene	13

Sensitized Phosphorescence at 77 ° K

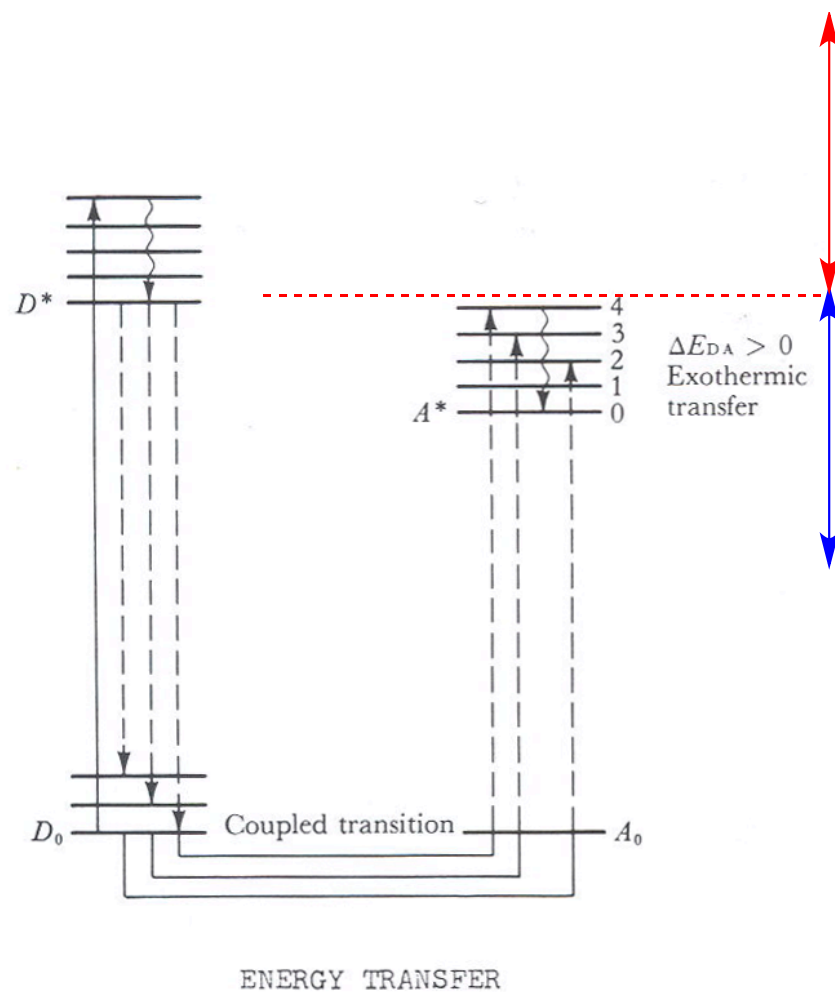
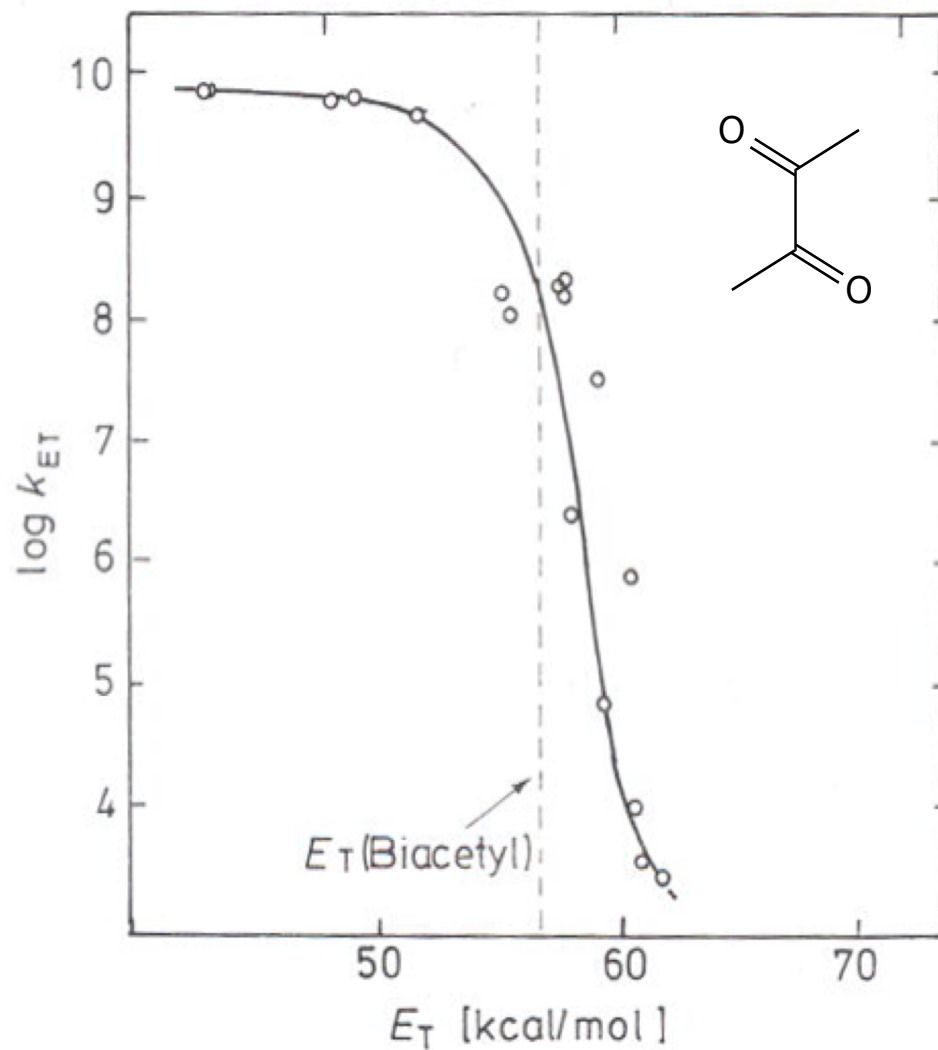


Sensitized Phosphorescence at 77 ° K



Triplet-Triplet ET in Solution

H. L. J. Backstrom and K. Sandros, *Acta Chemica Scand.* 12, 823 (1958)



Triplet-Triplet ET in Solution: Correlation of rate with triplet energy gap

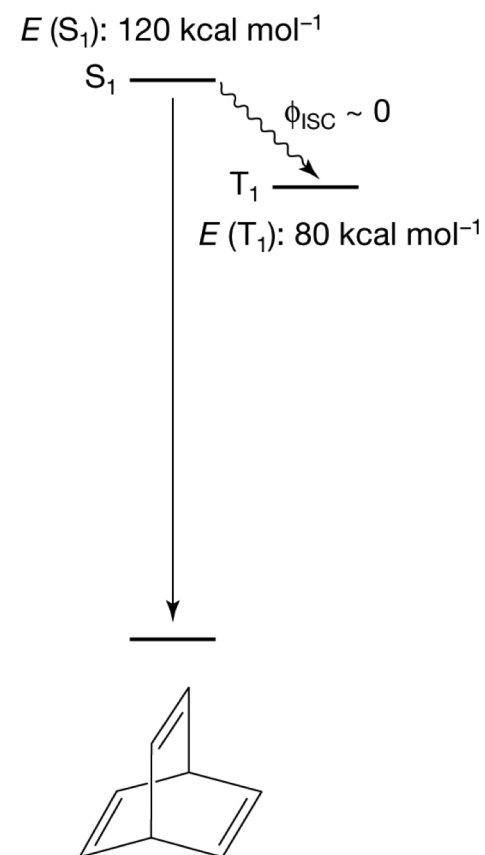
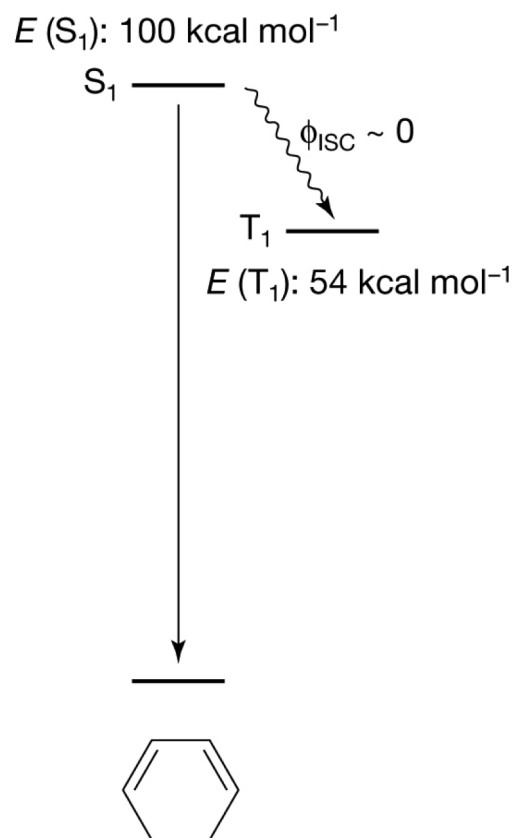
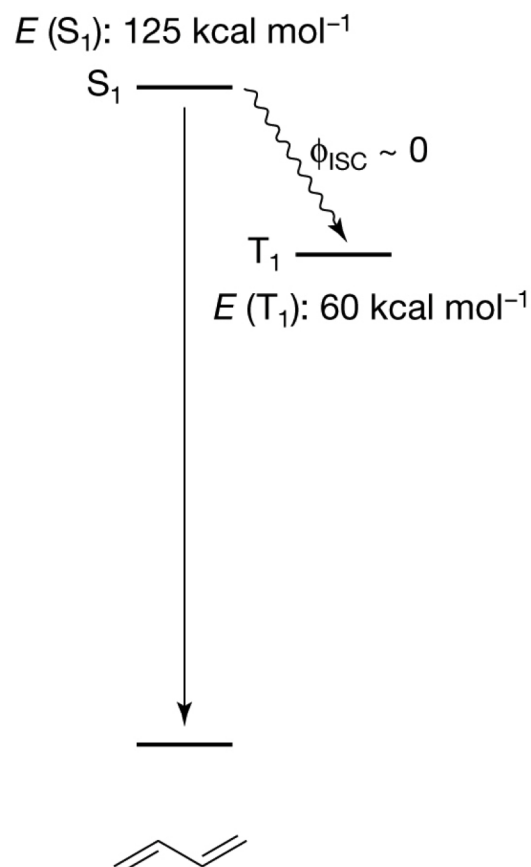
G. Porter and F. Wilkinson, *Proc. Royal Soc. A*, 264, 1 (1961)

Acceptor	Solvent	$\Delta E_T(\text{kcal/mole})$	k_q , liter mole ⁻¹ sec ⁻¹
1,2-Benzanthracene	Benzene	9.15	3.0×10^9
Naphthalene	Benzene	8.85	2.0×10^9
	Hexane	6.30	1.3×10^9
1-Iodonaphthalene	Hexane	3.15	7.0×10^9
	Ethylene glycol	3.15	2.1×10^9
	Ethylene glycol	2.30	2.8×10^9
1-Bromonaphthalene	Hexane	2.60	1.5×10^9
	Ethylene glycol	2.60	1.5×10^7
1-Iodonaphthalene	Ethylene glycol	0.55	8.0×10^8
Naphthalene	Hexane	0.85	2.9×10^6
	Ethylene glycol	0.85	2.3×10^6

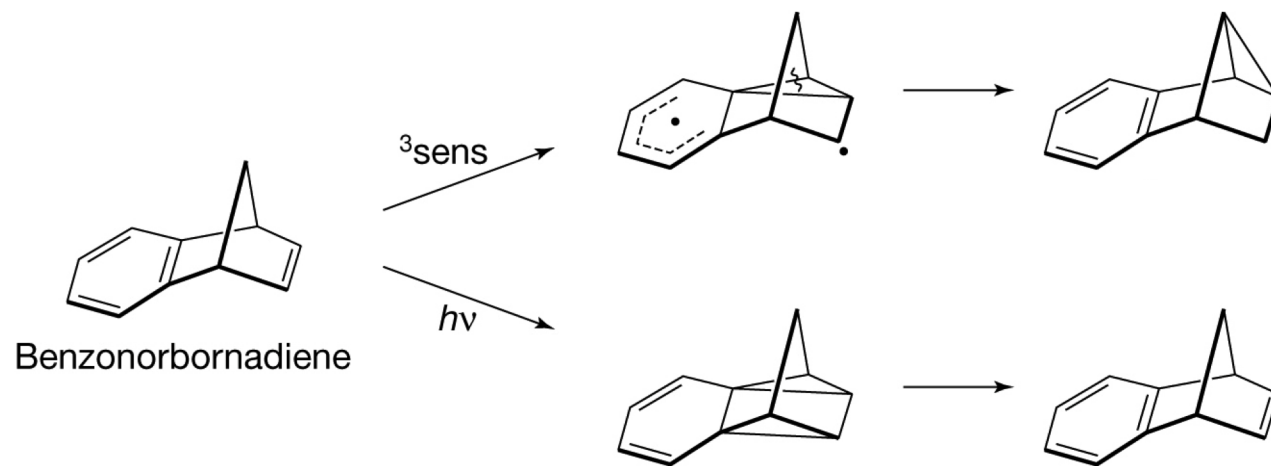
Upper limits for the quenching rate could be established for the following systems:

Phenanthrene	Hexane	-0.85	2×10^4
	Ethylene glycol	-0.85	1×10^5
	Ethylene glycol	-2.60	5×10^4
Triphenylene	Hexane	-6.30	5×10^4
Benzophenone	Benzene	-8.85	1×10^4
Biacetyl	Benzene	-9.15	5×10^4
1-Iodonaphthalene	Ethylene glycol	-16.60	2×10^4
Naphthalene	Hexane	-18.85	4×10^4
1-Iodonaphthalene	Ethylene glycol	-19.70	5×10^3

Need for Triplet Sensitization



Triplet Sensitization



Sensitizers

- Should be able to excite the sensitizer alone even in presence of acceptor.
- Sensitizer should have high intersystem crossing efficiency (S_1 to T_1).
- Sensitizer should have triplet energy higher than the acceptor.
- Sensitizer should be photostable.

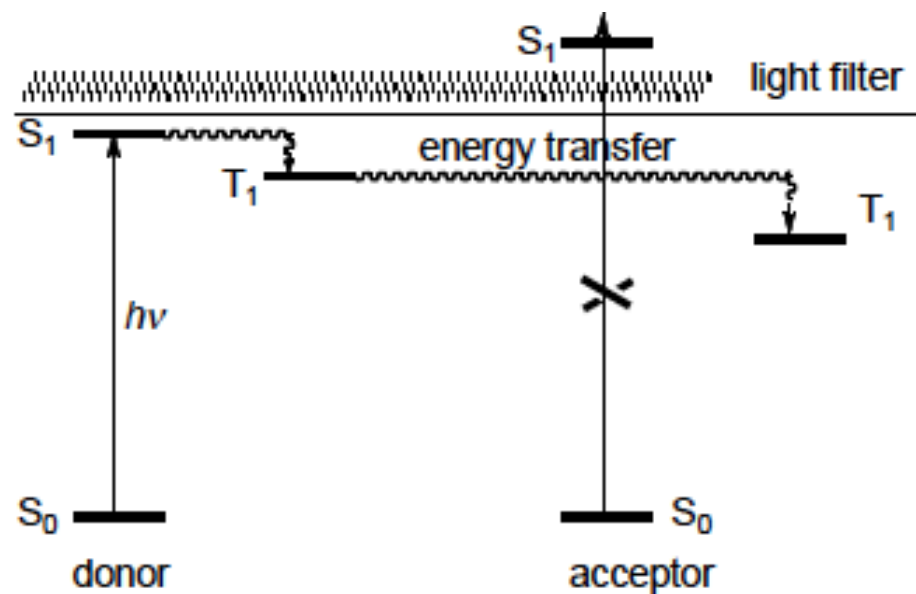
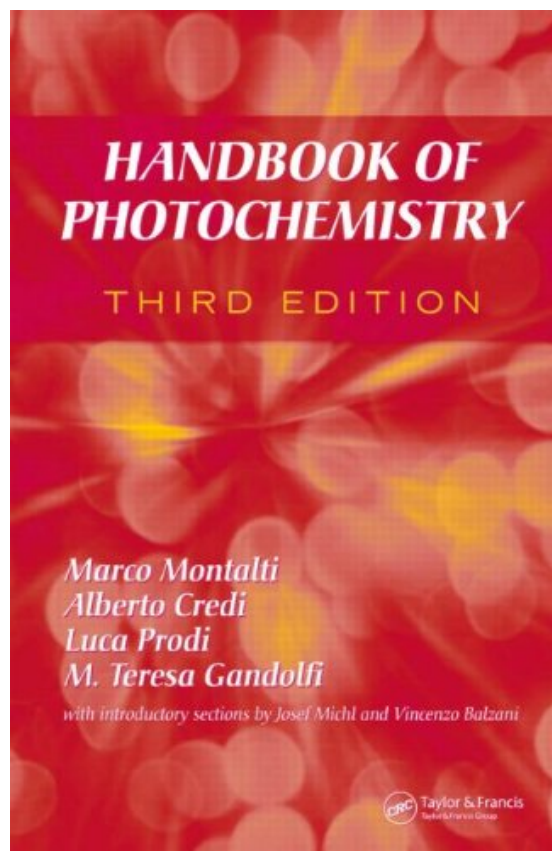
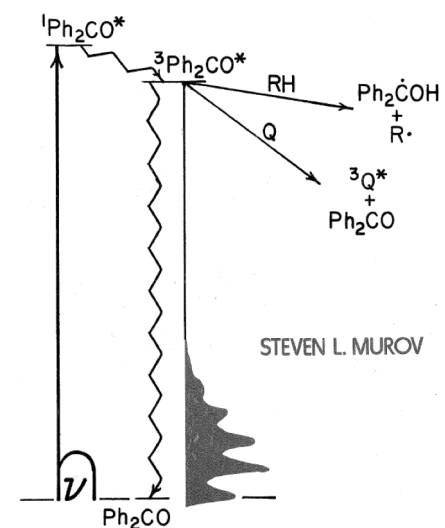


Table 10.3 Important Parameters for Triplet Photosensitizers

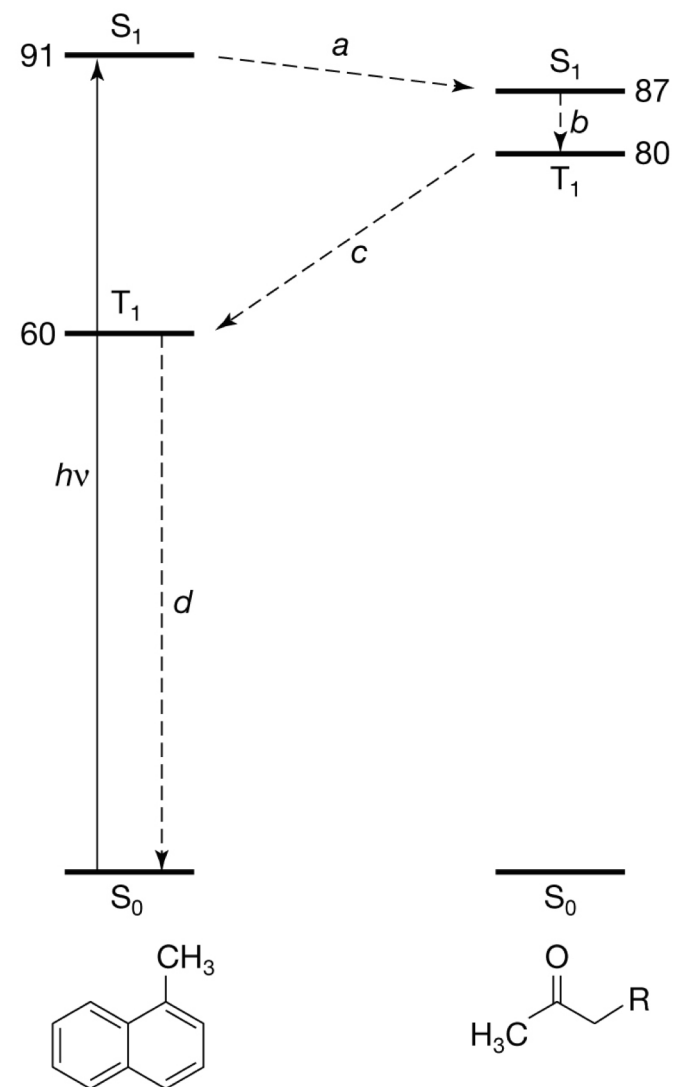
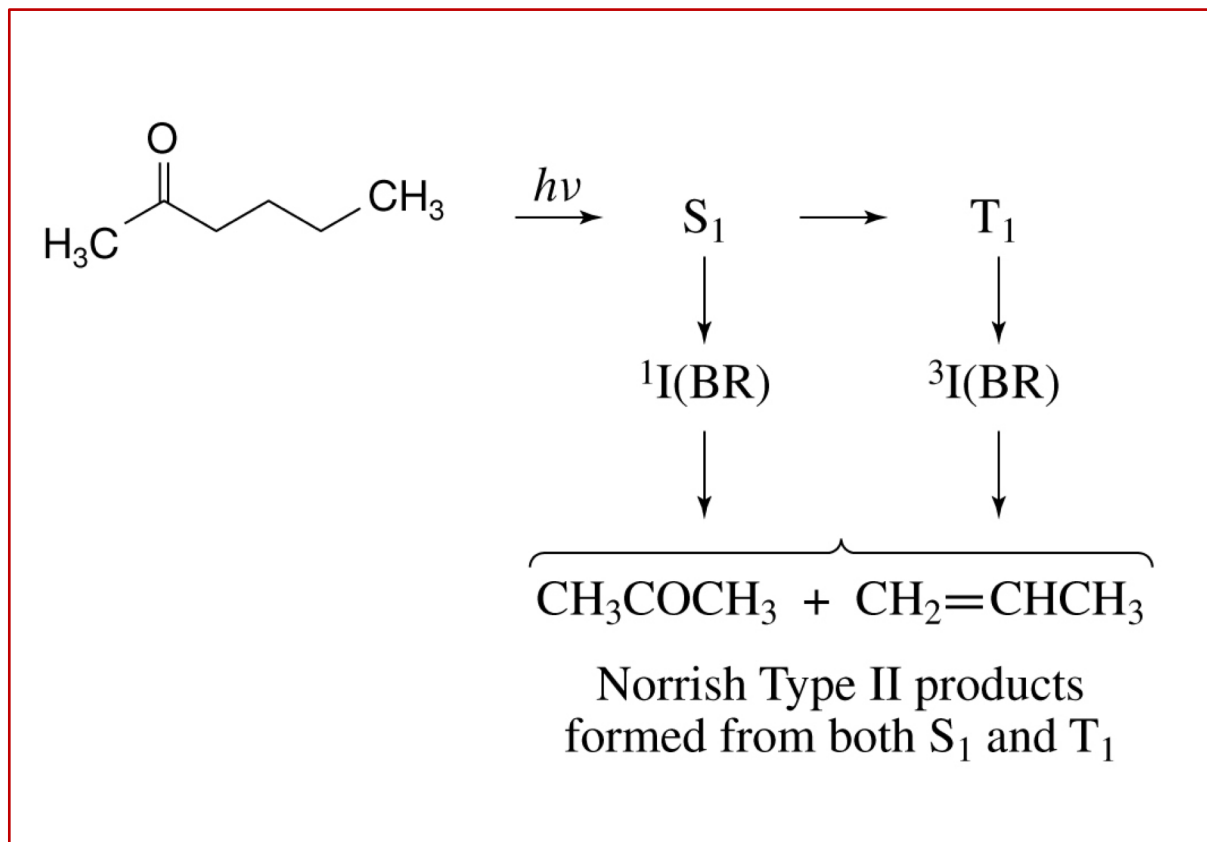
Compound	E_S (kcal mol ⁻¹)	E_T	τ_S (s)	τ_T	Conf. T_1	Φ_{ST}
Benzene	110	84	$\sim 10^{-7}$	10^{-6}	π, π^*	0.2
Acetone	~ 85	~ 78	10^{-9}	10^{-5}	n, π^*	1.0
Xanthone		74			π, π^*	1.0
Acetophenone	~ 79	74	10^{-10}	10^{-4}	n, π^*	1.0
4-CF ₃ Acetophenone		71			n, π^*	1.0
Benzophenone	~ 75	69	10^{-11}	10^{-4}	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



Handbook of Photochemistry

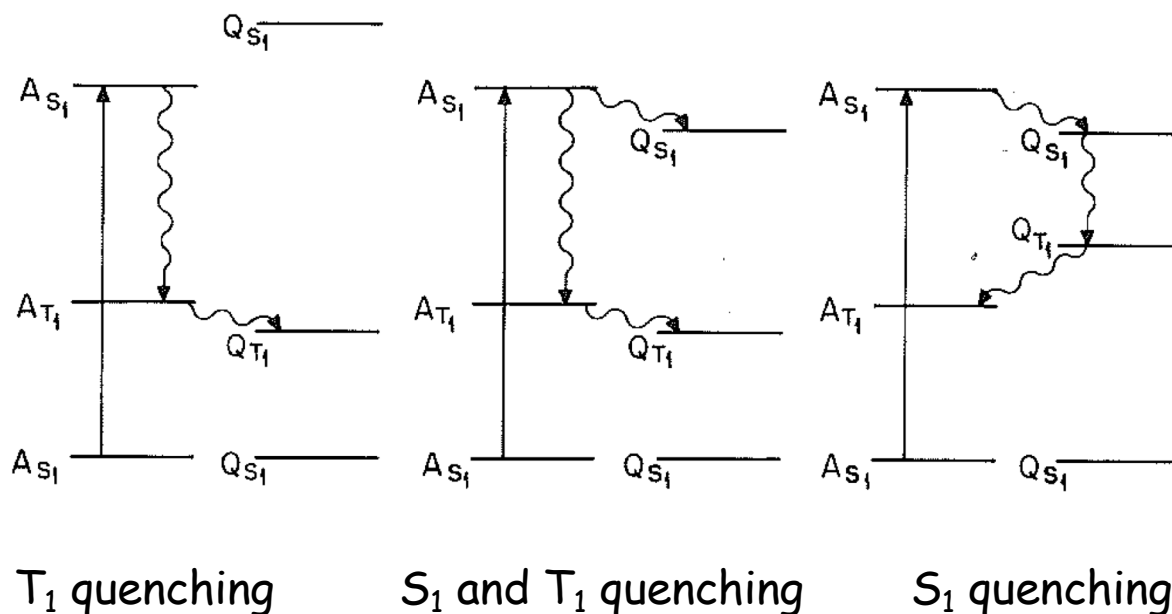


Reaction from S_1 and T_1 : Selective Triplet Quenching



Quenchers

- ❖ Quencher should have absorption away from that of the reactant (donor).
- ❖ Quencher should have the triplet energy lower and the singlet energy higher than the reactant.
- ❖ Quencher should quench the reactant only by TT transfer, not by any other process.
- Quencher should be photostable.



Triplet Quenching

Stern-Volmer equation

Derivation of Stern-Volmer equation:

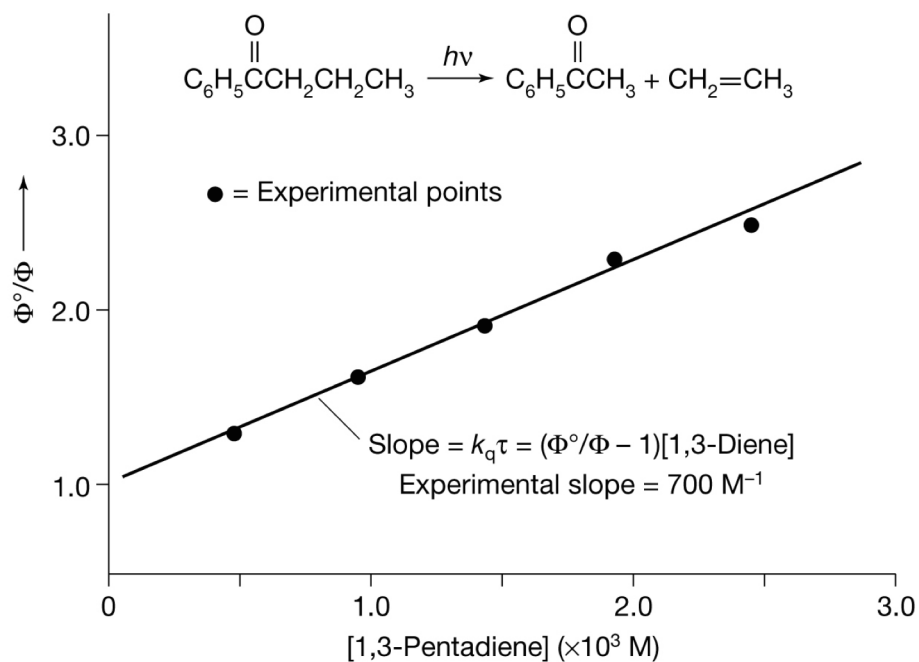
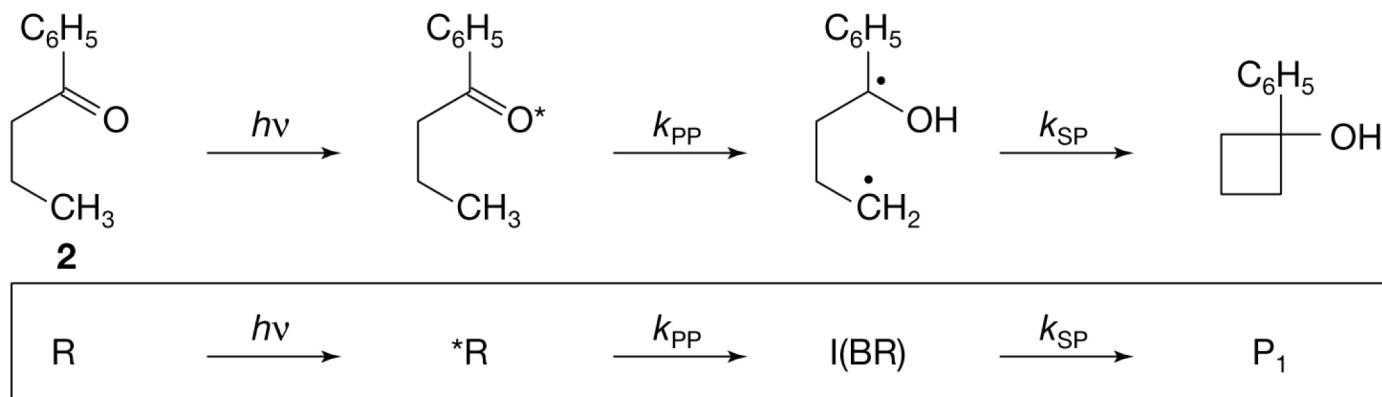
$$\tau_0 = \frac{1}{k_f + k_{nr}} \quad \tau = \frac{1}{k_f + k_{nr} + k_q[Q]}$$

Presence of quencher – opens up an additional nonradiative deexcitation channel

$$\tau_0/\tau = 1 + k_q\tau_0[Q]$$

$$I_0/I = 1 + K_{SV}[Q]$$

Triplet Quenchers Helps Resolve the Reactive State Stern-Volmer Plot



Non-Radiative Energy Transfer

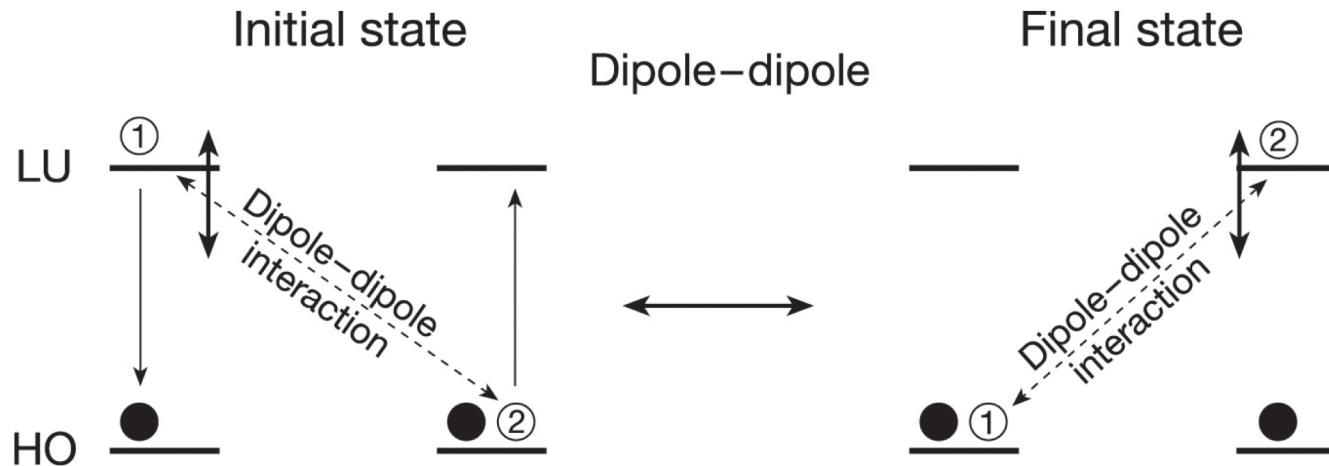
Dipole-Dipole Energy Transfer

Coulombic Energy Transfer

Resonance Energy Transfer

Förster Energy Transfer

Förster Resonance Energy Transfer (FRET)



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

FRET - Fluorescence (Förster) Resonance Energy Transfer

Milestones in the Theory of Resonance Energy Transfer

1918 J. Perrin proposed the mechanism of resonance energy transfer

1922 G. Cario and J. Franck demonstrate that excitation of a mixture of mercury and thallium atomic vapors with 254nm (the mercury resonance line) also displayed thallium (sensitized) emission at 535nm.

1924 E. Gaviola and P. Pringsham observed that an increase in the concentration of fluorescein in viscous solvent was accompanied by a progressive depolarization of the emission.

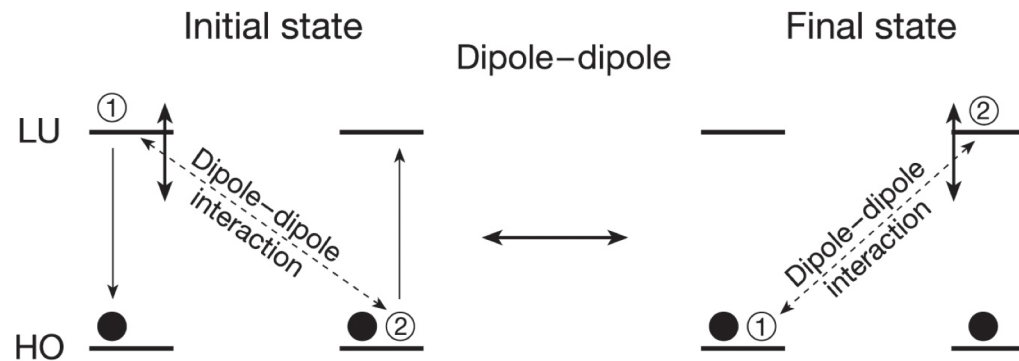
1928 H. Kallmann and F. London developed the quantum theory of resonance energy transfer between various atoms in the gas phase. The dipole-dipole interaction and the parameter R_0 are used for the first time.

1932 F. Perrin published a quantum mechanical theory of energy transfer between molecules of the same specie in solution. Qualitative discussion of the effect of the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.

1946-1949 T. Förster developed the first quantitative theory of molecular resonance energy transfer.

Förster Resonance Energy Transfer (FRET)

A Transmitter-Antenna Receiver-Antenna Mechanism



$$\Delta E (*D \rightarrow D) = \Delta E (A \rightarrow *A)$$

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

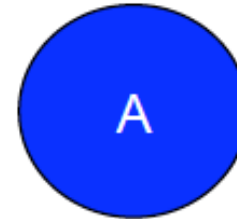
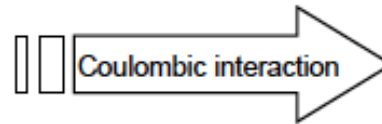
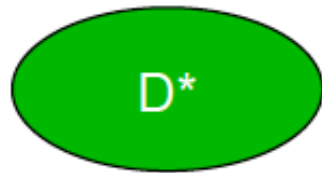
$$k_{ET}(\text{dipole - dipole}) \rightarrow \frac{k_D^0 \int \epsilon_A}{R_{DA}^6}$$

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

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



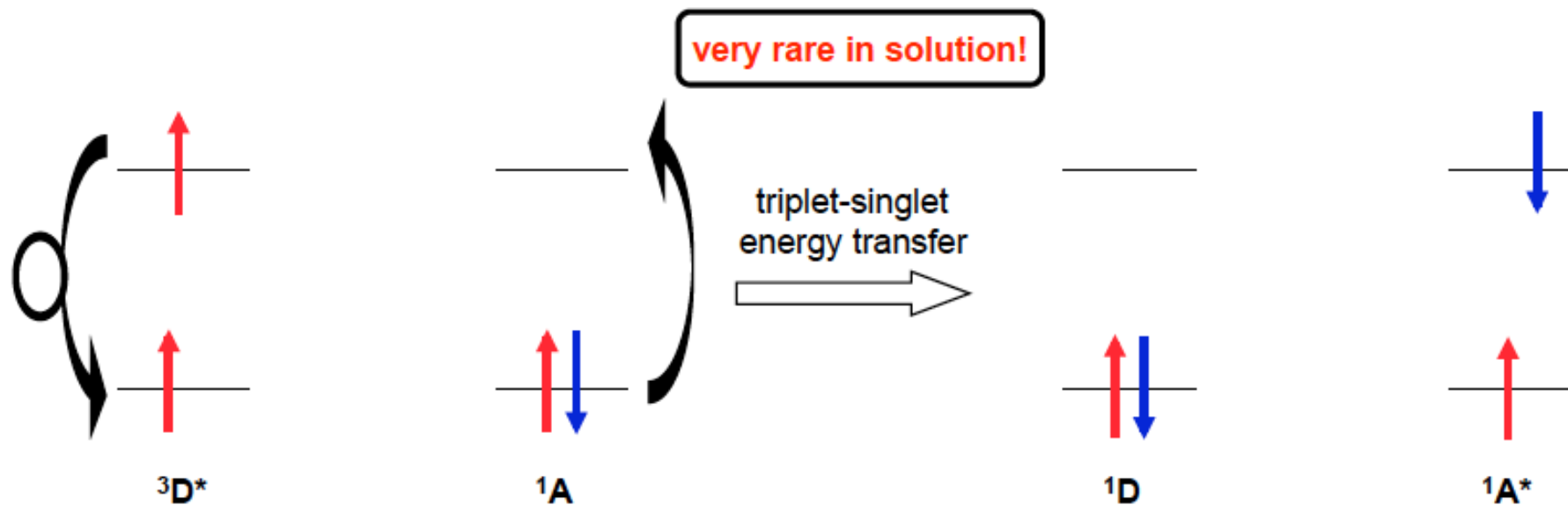
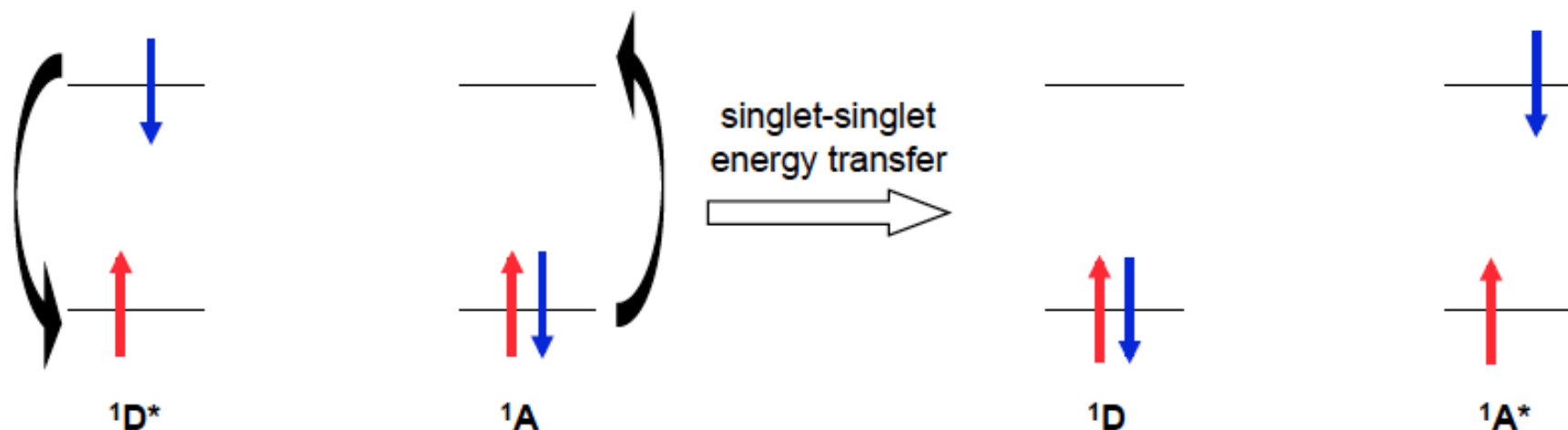
the electrons in
the ground state
of A are assumed
not to be
oscillating at all

- 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 the oscillating electric field of the light wave

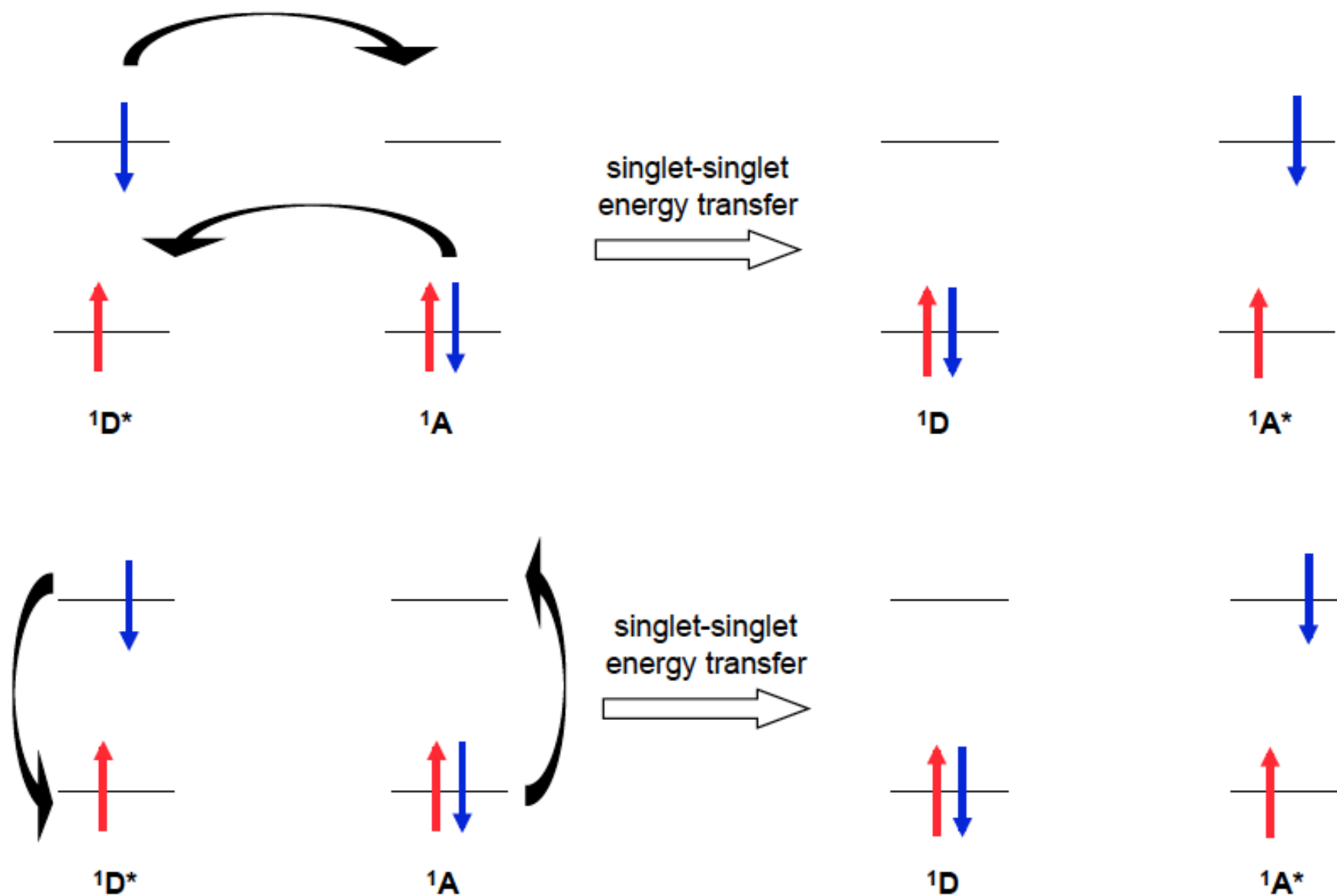
$$\mu = \mu_0 \cos(2\pi\nu t)$$

transition dipole μ induced dipole μ_0 time t oscillation frequency ν

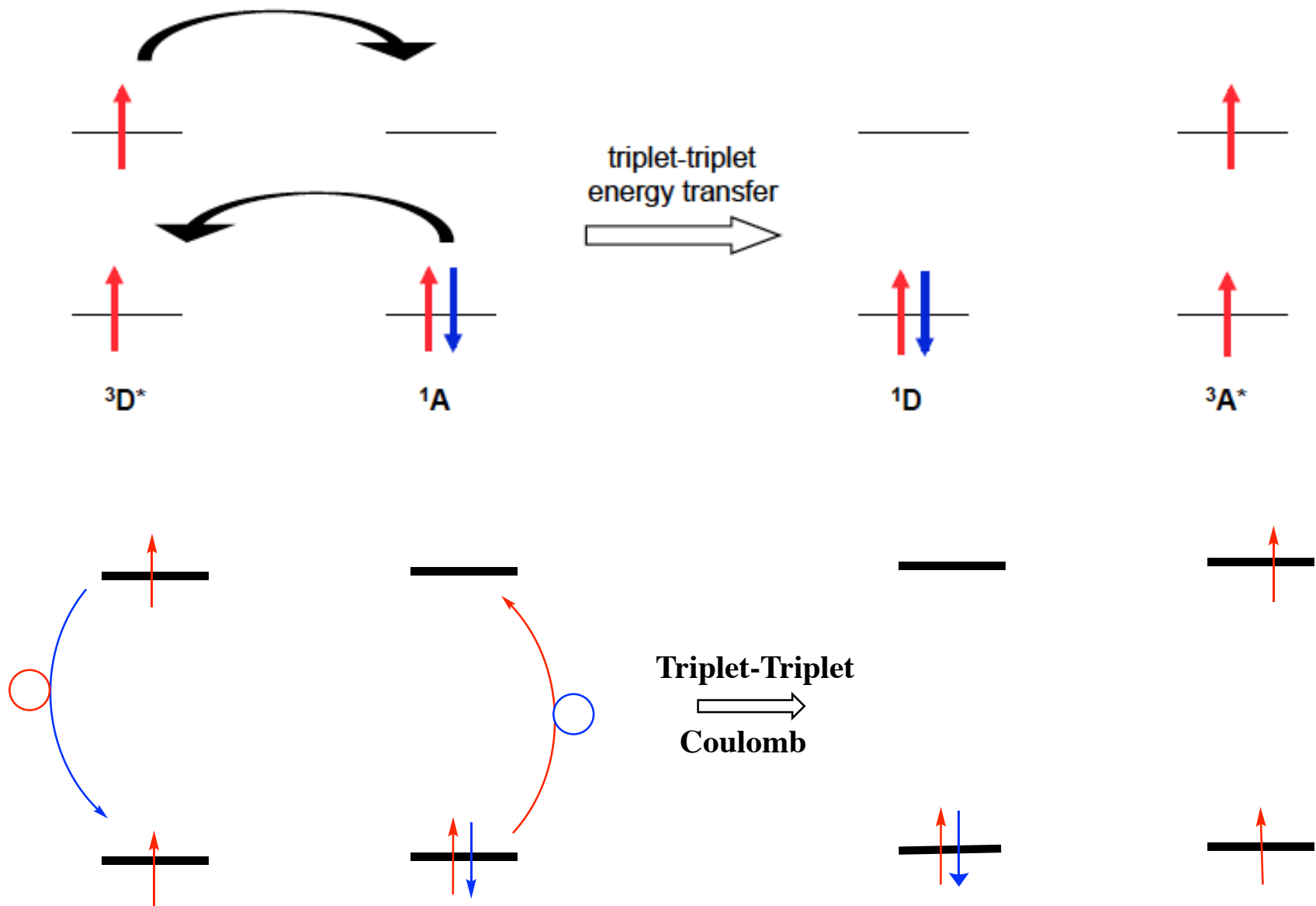
Resonance Energy Transfer



Exchange vs Coulomb (Singlet-Singlet)



Exchange vs Coulomb (Triplet-Triplet)



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

K^2 mutual orientation of the dipoles in space

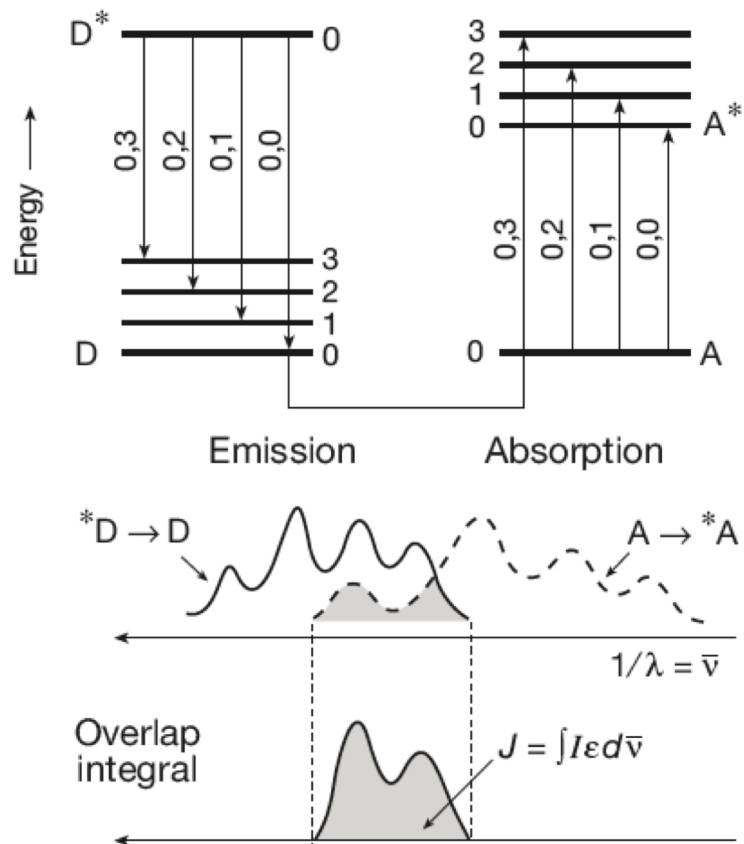
ϕ_D = quantum yield of donor emission

n = refractive index of the solvent

τ_D = actual donor lifetime

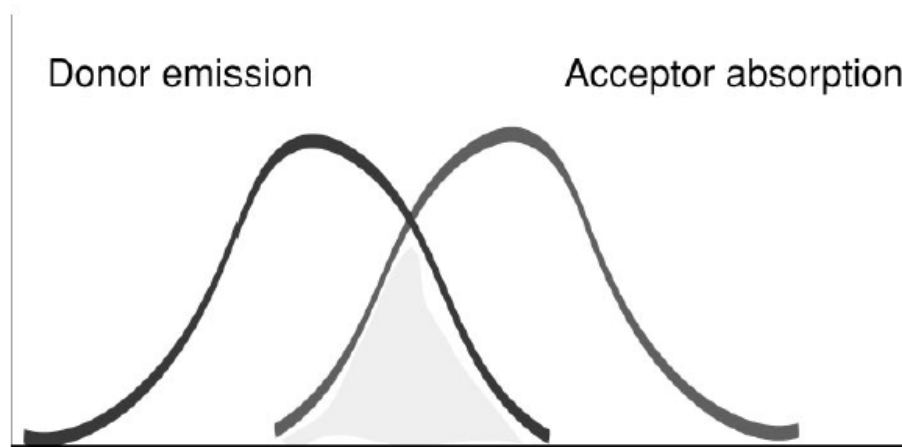
R = distance between donor and acceptor

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



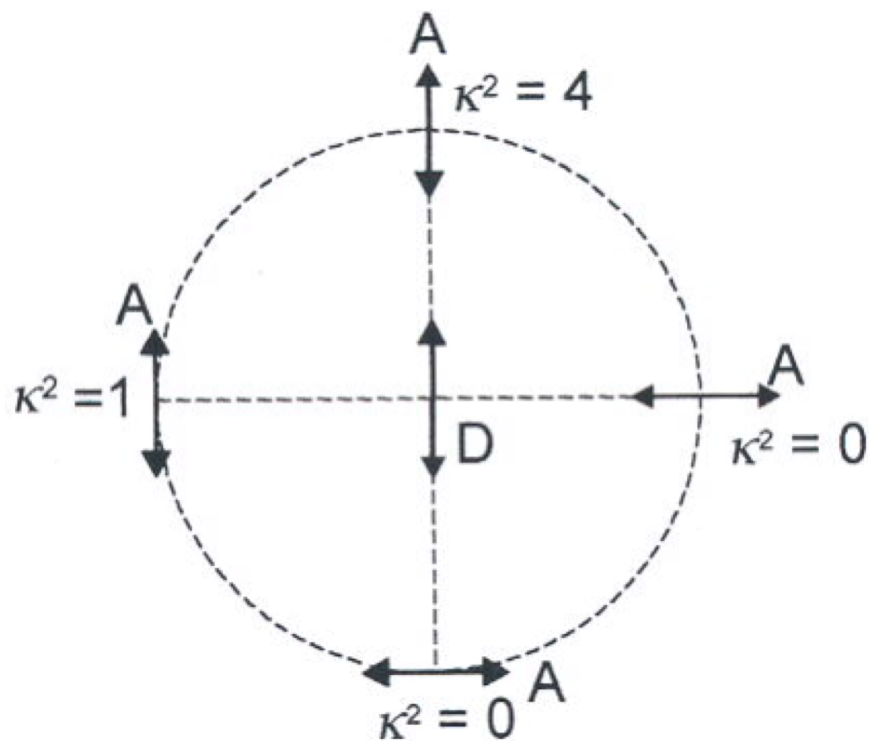
$$\int_0^{\infty} F_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$

= spectral overlap integral



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

$$k_{\text{ET}} \text{ (dipole - dipole)} = \alpha \frac{\kappa^2 k_D^o}{R_{\text{DA}}^6} J(\epsilon_A)$$



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 μ_{D} , corresponding to the $^*\text{D} \rightarrow \text{D}$ transition.
- The square of the transition dipole moment μ_{A} corresponding to the $\text{A} \rightarrow ^*\text{A}$ transition.
- The inverse sixth power of the separation between $^*\text{D}$ and A (i.e. $1/R_{\text{DA}}^6$).

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

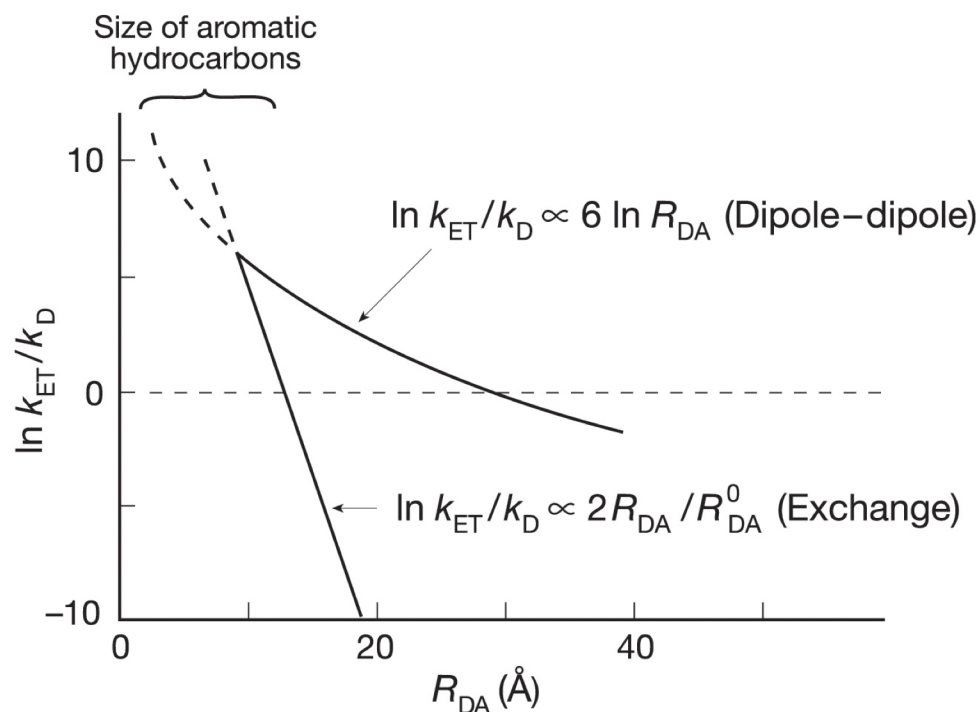
- The $^*D \rightarrow D$ and $A \rightarrow ^*A$ processes correspond to a large (spectral) overlap integral, J .
- The radiative rate constant, k_D° , is as large as possible.
- The magnitude of ϵ_A is as large as possible.
- There is a small spatial separation between *D and A .
- There will be a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



$$k_{\text{ET}} (\text{total}) \propto \left[\alpha \underbrace{\left\langle \Psi(\mathbf{D}^*) \Psi(\mathbf{A}) \middle| H_{\text{e}} \middle| \Psi(\mathbf{D}) \Psi(\mathbf{A}^*) \right\rangle^2}_{\text{Electron exchange}} + \beta \underbrace{\left\langle \Psi(\mathbf{D}^*) \Psi(\mathbf{A}) \middle| H_{\text{e}} \middle| \Psi(\mathbf{D}) \Psi(\mathbf{A}^*) \right\rangle^2}_{\text{Electron dipole-dipole interactions}} \right]$$

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

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



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 $\mathbf{R}_{\text{DA}}$

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

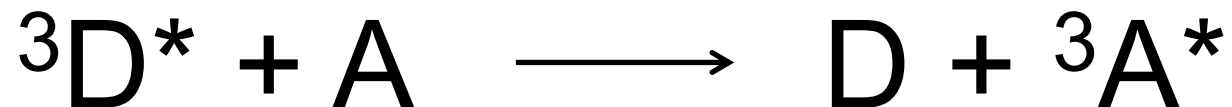
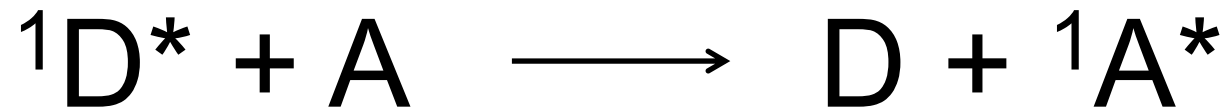
- The rate of dipole-induced energy transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as $\exp(-(2r/L))$. Quantitatively, this means that $k_{ET}(\text{exchange})$ drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) 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 $^*D \rightarrow D$ and $A \rightarrow ^*A$ radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the $^*D \rightarrow D$ and $A \rightarrow ^*A$ transitions



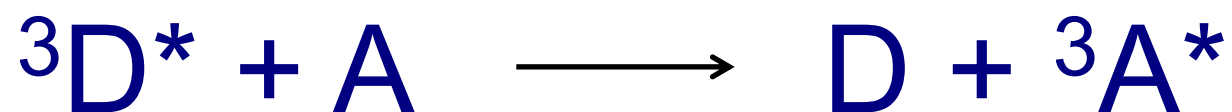
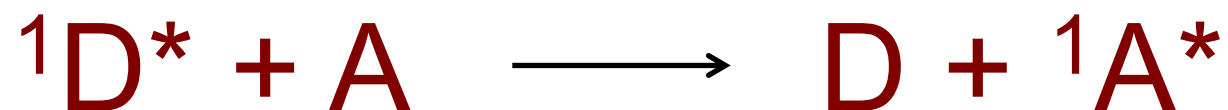
A Theory of Sensitized Luminescence in Solids, D. L. Dexter,
J. Chem. Phys. 21, 836 (1953)

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

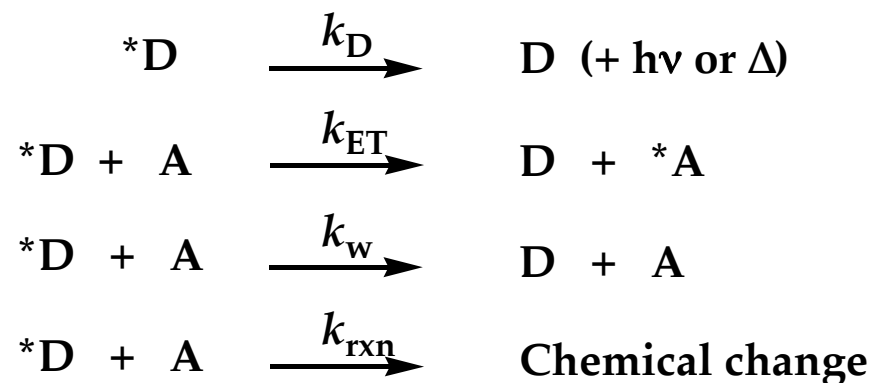
Spin in Energy Transfer



Spin Allowed Energy Transfer Processes



Energy Transfer Efficiency



$$k_Q = k_{ET} + k_w + k_{rxn}$$

$$\phi_{ET} = \frac{k_{ET} [A]}{k_D + k_Q [A]} = \frac{k_{ET} [A]}{k_D + (k_{ET} + k_w + k_{rxn}) [A]}$$

Efficiency of Resonance Energy Transfer Depends on the Distance

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

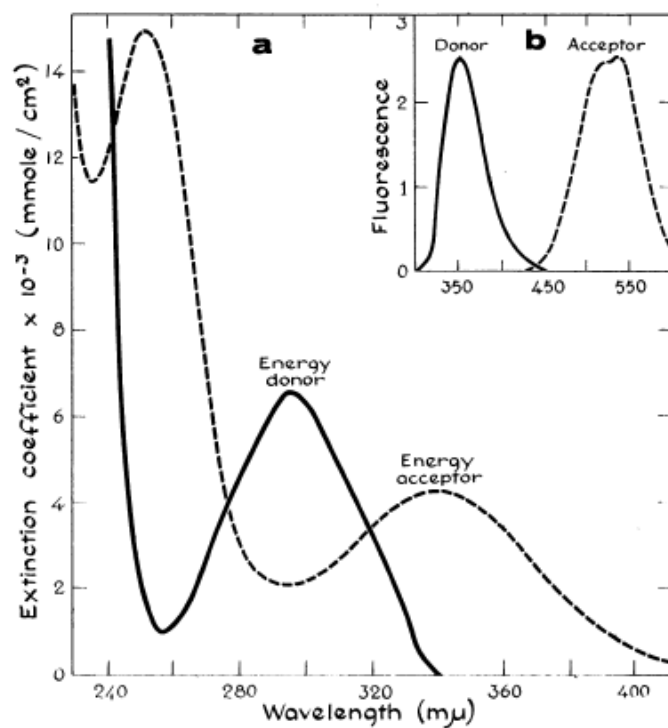
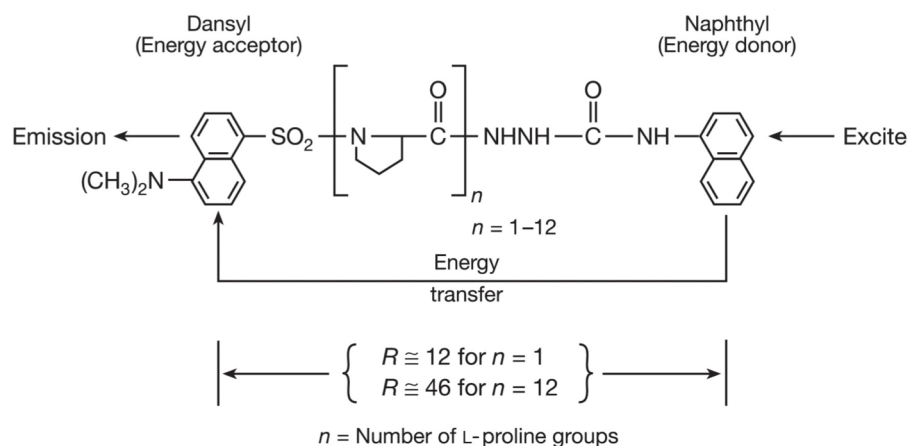
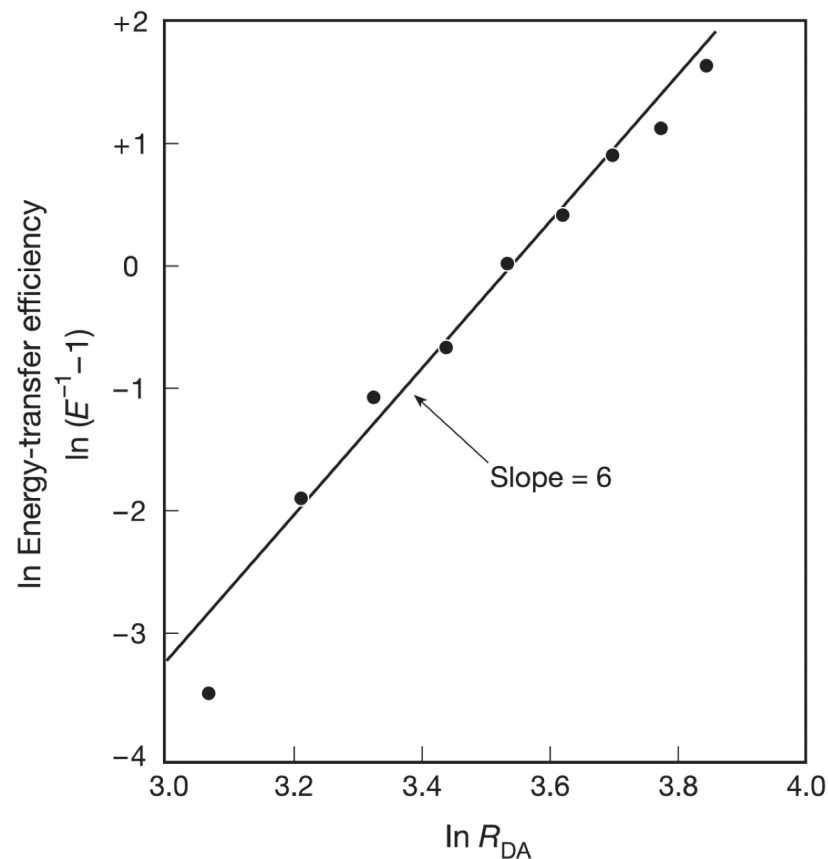
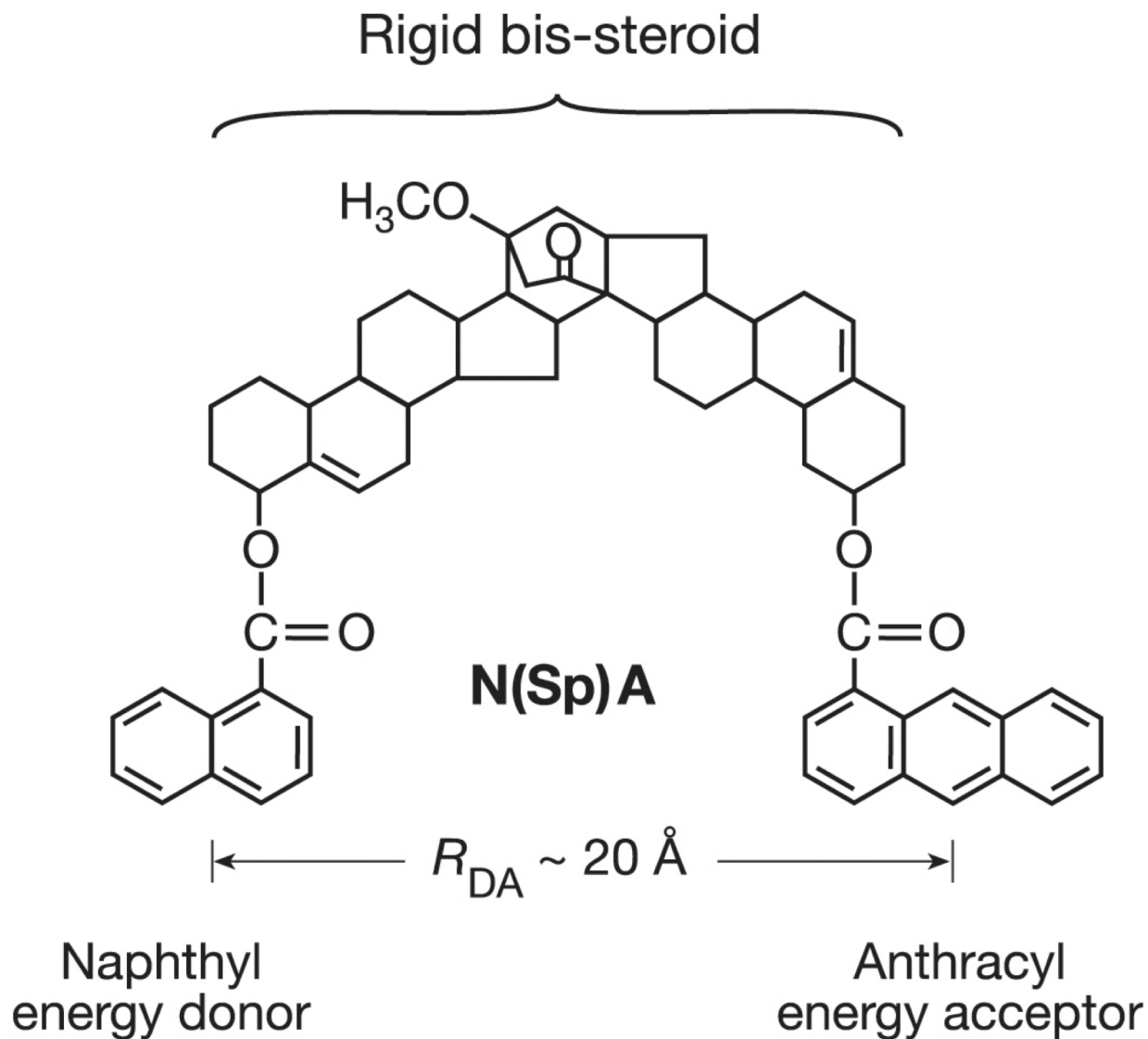


FIG. 2.—(a) Absorption spectrum of the energy donor (1-acetyl-4-(1-naphthyl) semicarbazide, —) and the energy acceptor (dansyl-L-prolyl-hydrazide, ----) in ethanol; (b) emission spectrum of the energy donor (—) and the energy acceptor (----) in ethanol.

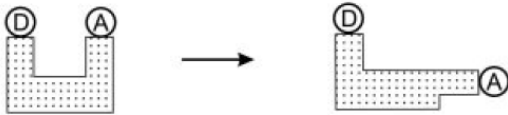


Resonance Energy Transfer Occurs at Longer Distance: A Proof

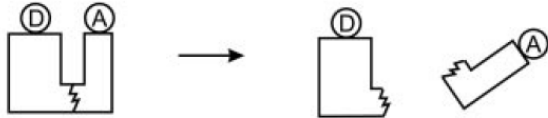


Making Use of Förster Resonance Energy Transfer

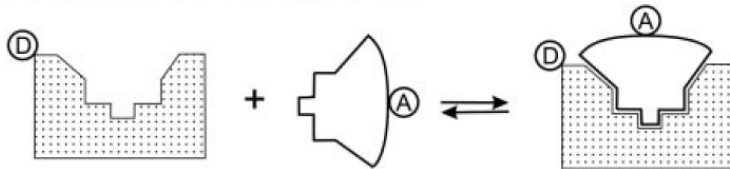
- CONFORMATIONAL CHANGES



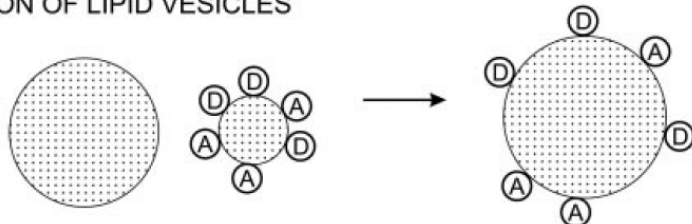
- HYDROLYSIS OF A SUBSTRATE



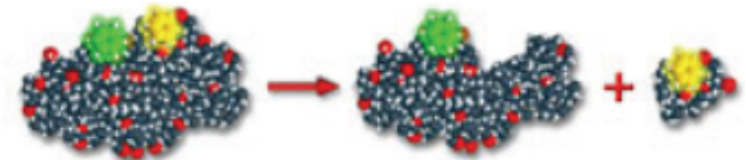
- INTERACTION LIGAND-RECEPTOR



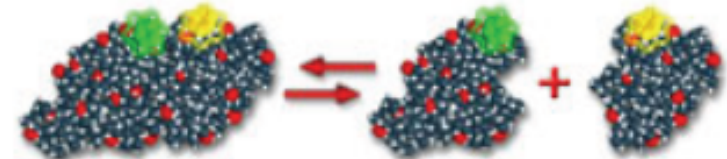
- FUSION OF LIPID VESICLES



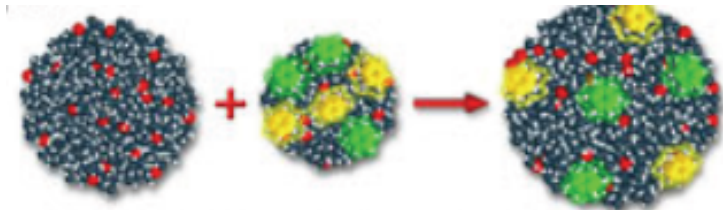
Conformational Changes



Protein Hydrolysis



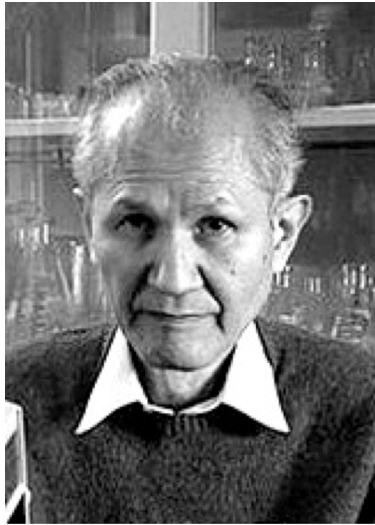
Ligand-Receptor Interactions



Fusion of Lipid Vesicles

The Nobel Prize in Chemistry 2008

"for the discovery and development of the green fluorescent protein, GFP"



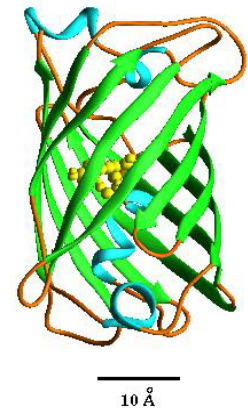
Osamu Shimomura



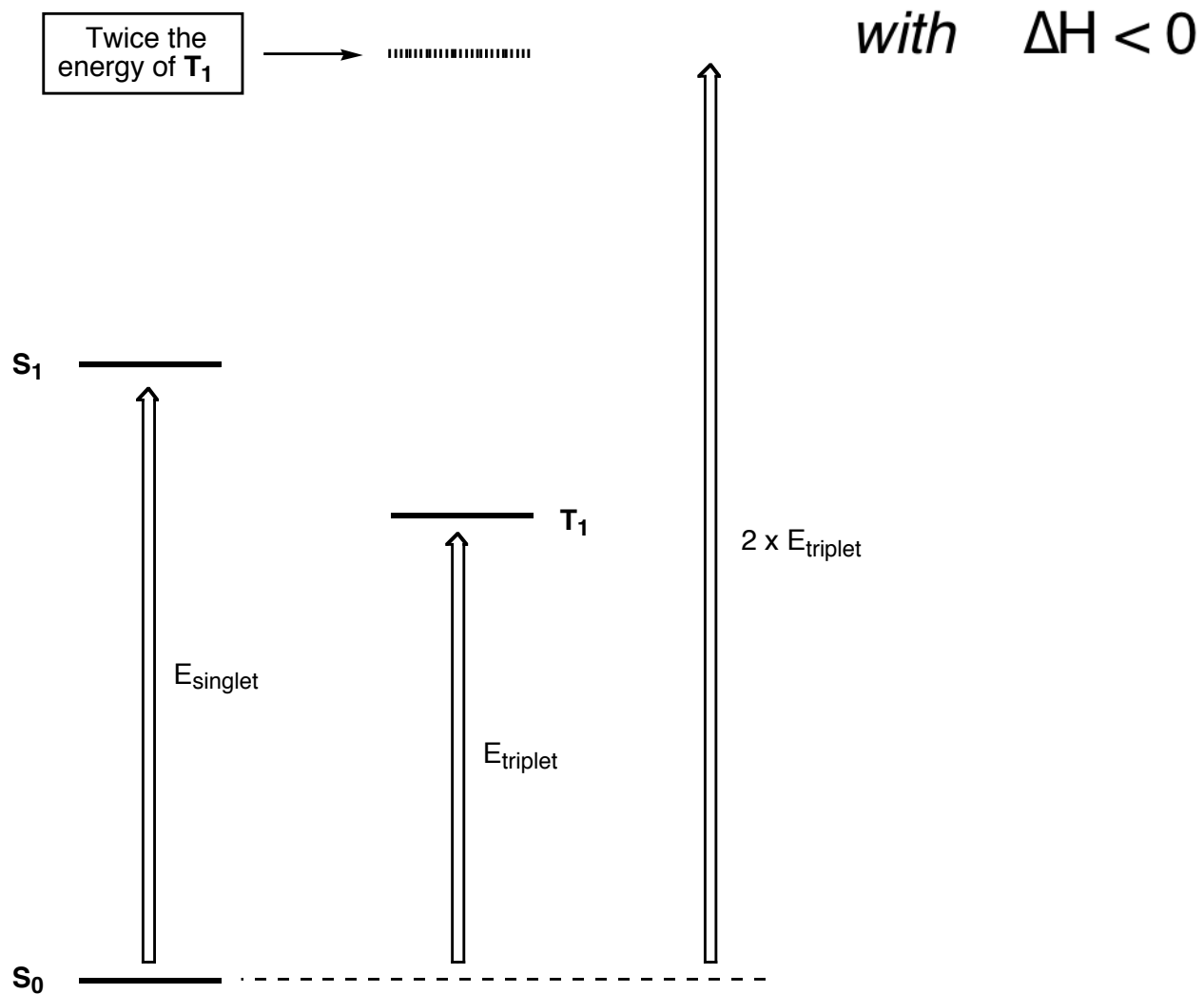
Martin Chalfie



Roger Y. Tsien



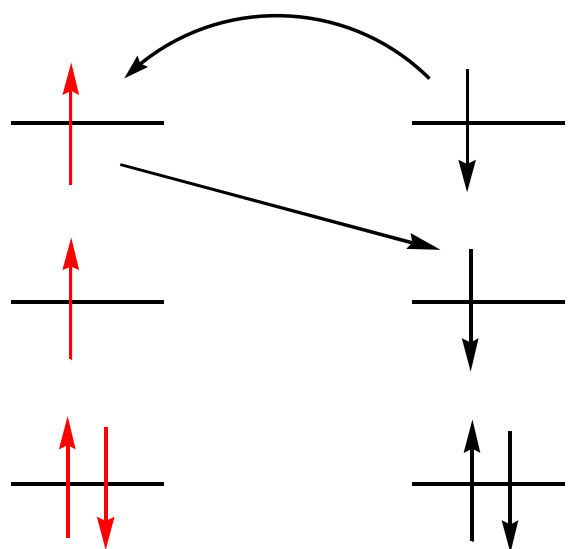
Triplet-Triplet Annihilation





with $\Delta H < 0$

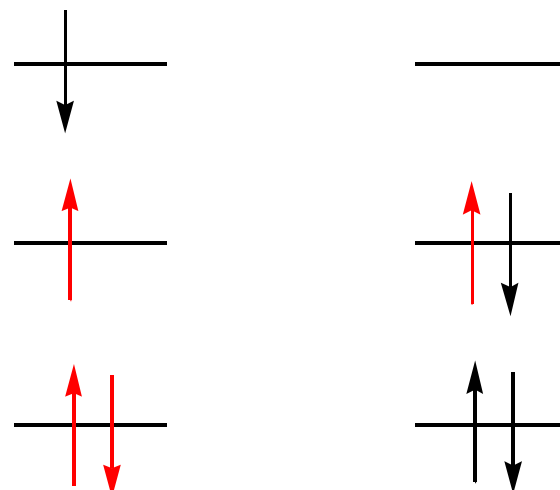
Initial states



$^*D(T_1)$

$^*D(T_1)$

Final states



$^*D(S_1)$

$^*D(S_0)$

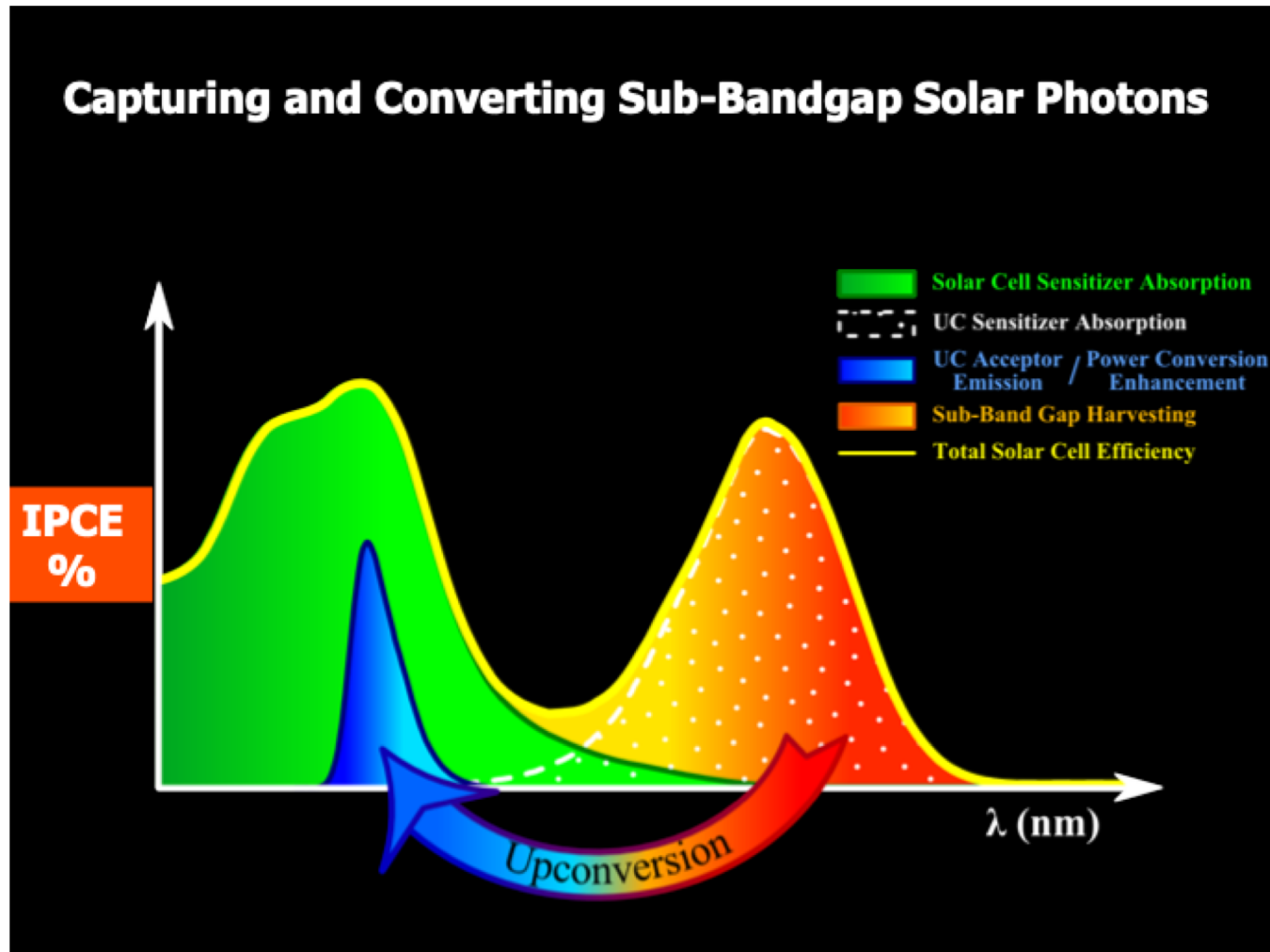
Properties of TTA in Solution

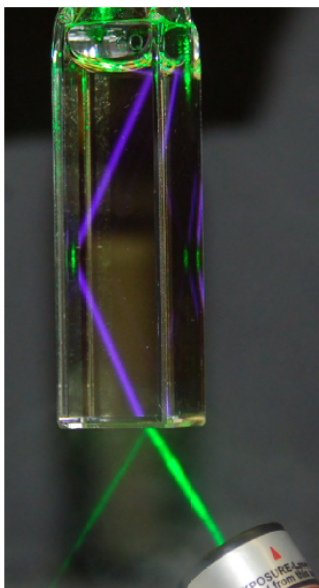
- The rate constants for TTA, k_{TTA} , are generally very large.
- With laser light excitation, triplet state concentrations in excess of 10^{-5} M can be readily achieved. Thus, any triplet with lifetime of a few microseconds (a common situation) will undergo at least some TTA in fluid solution.
- The high sensitivity with which fluorescence can be detected makes TTA an easily observable process even when it is not the major mechanism for triplet decay.

Table 7.2 Representative Rate Constants for TTA in Solution.^{20,21,22}

Substrate	Reference	Solvent	T , (K)	k_{TTA} ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Anthracene	20	Toluene	258	2.74
Anthracene	20	Toluene	298	4.10
1,2-Benzanthracene	21	<i>n</i> -Hexane	296	20.3
Pyrene	22	Cyclohexane	Room T	7 ± 2
Pyrene	22	Dodecane	Room T	5 ± 1
Pyrene	22	Hexadecane	Room T	1.9 ± 0.2

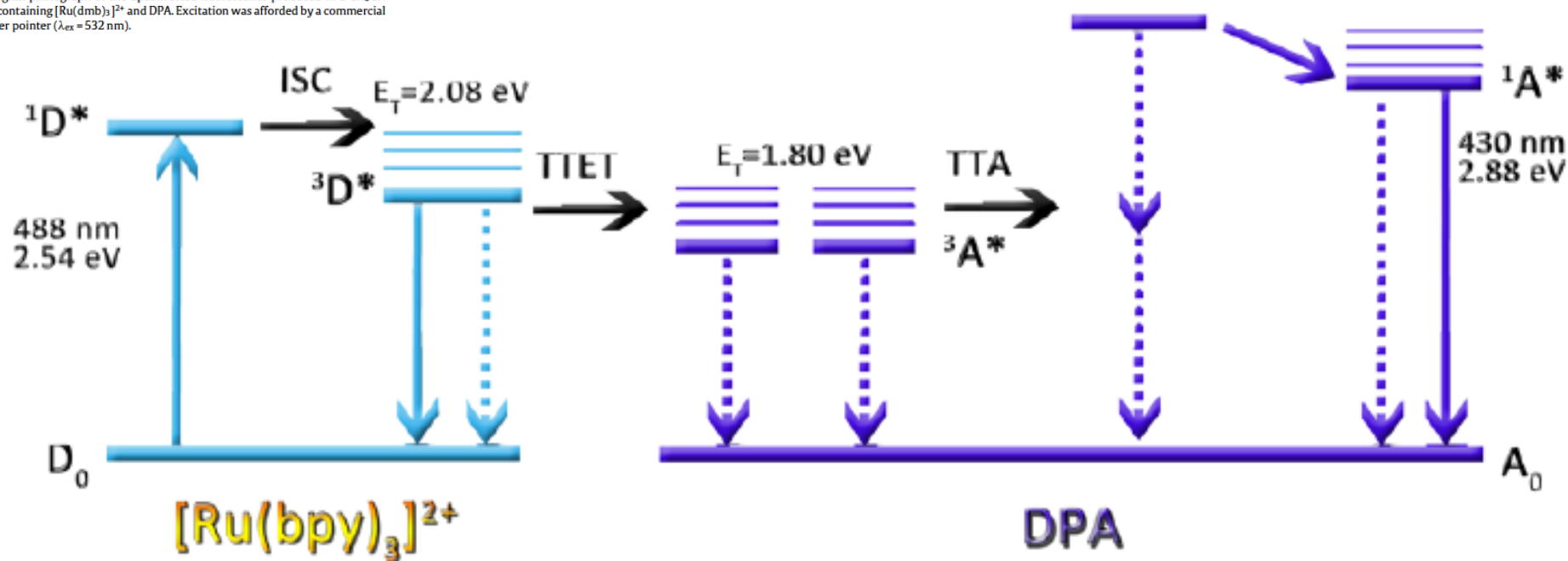
Photochemical Upconversion: Sensitized TTA (or Sensitized Triplet Fusion)





Upconversion Through Triplet-Triplet Annihilation

Fig. 1. Digital photograph of the upconverted fluorescence produced in a CH_3CN solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ and DPA. Excitation was afforded by a commercial green laser pointer ($\lambda_{\text{ex}} = 532 \text{ nm}$).

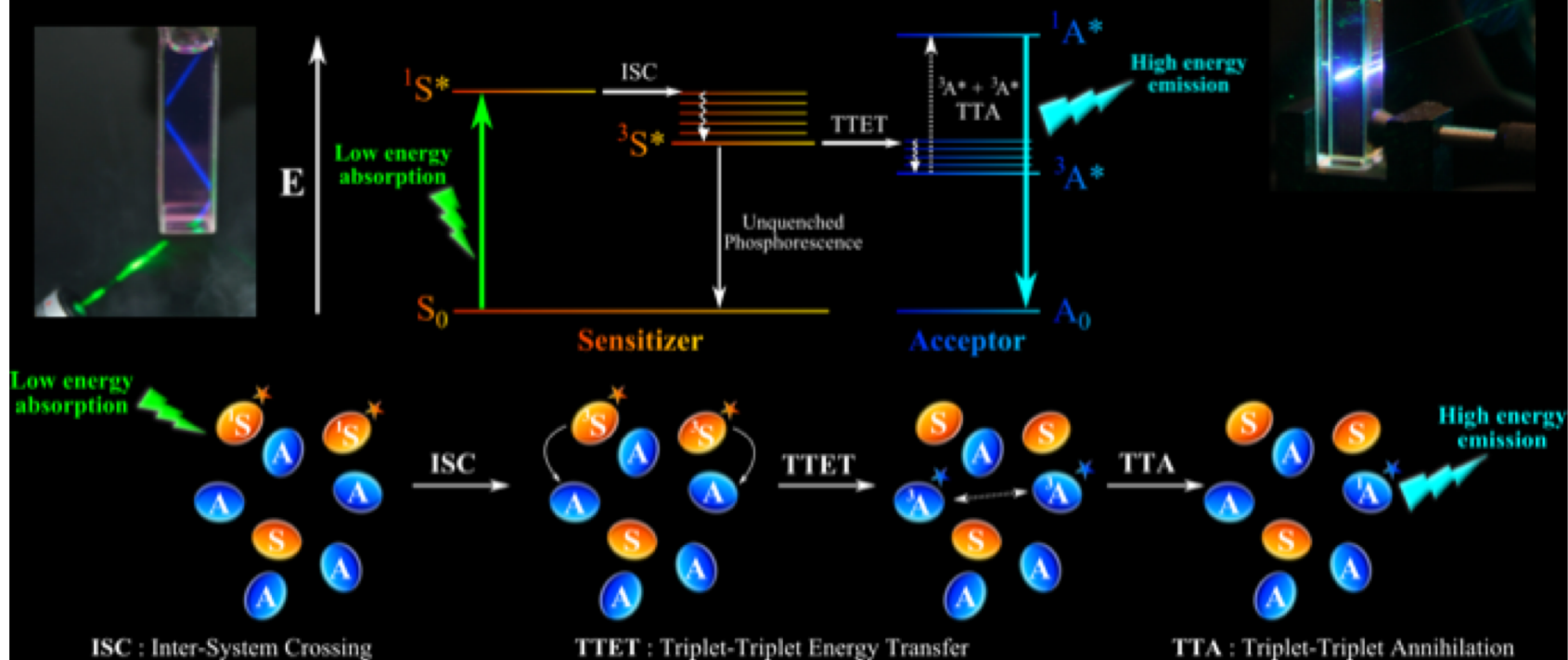
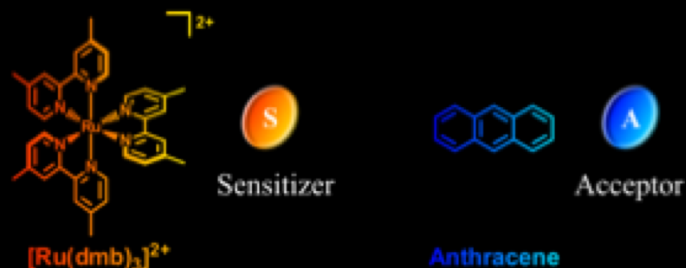


Scheme 2: Jablonski diagram outlining the processes occurring during photon upconversion between $[\text{Ru}(\text{bpy})_3]^{2+}$ and DPA.

MLCT Sensitized Upconversion

Photochemical Upconversion: A Wavelength-Shifting Technology

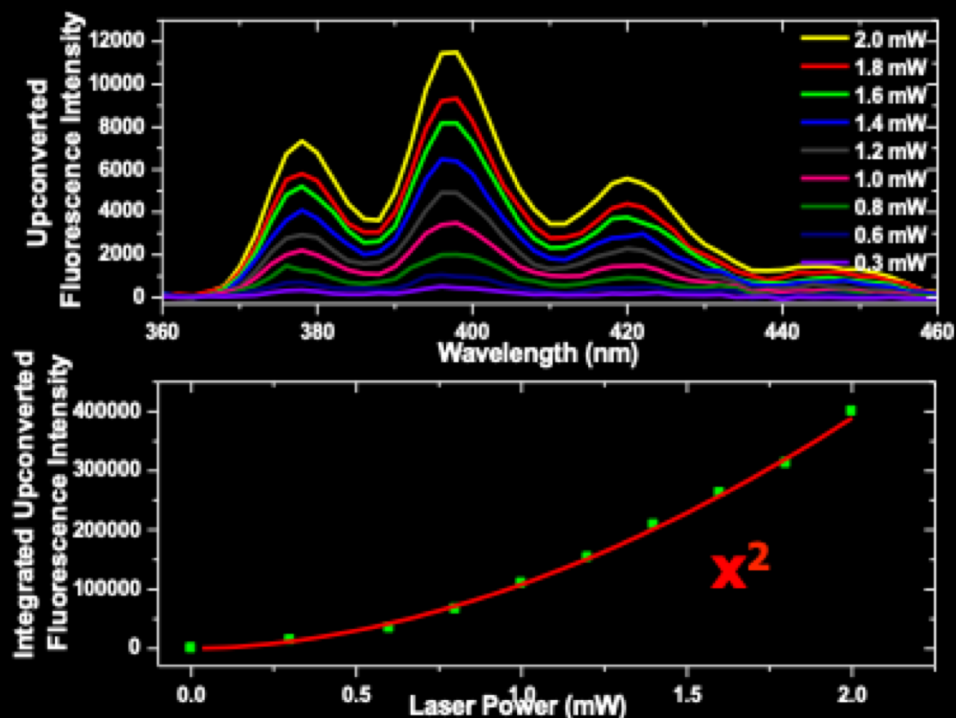
Original Bimolecular Prototype:



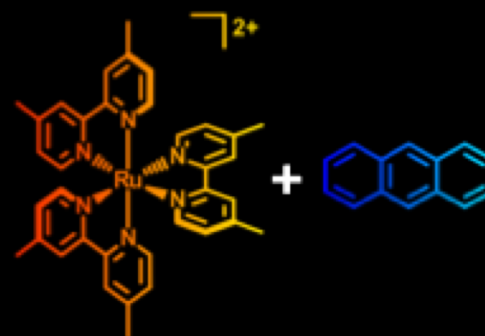
"Sandwiched" state model original report: Parker and Hatchard *Proc. Chem. Soc.* **1962**, 386-387.

MLCT Sensitized Upconversion

Low Power CW Photon Upconversion using $[\text{Ru}(\text{dmb})_3]^{2+}$ / Anthracene



$\lambda_{\text{ex}} = 514.5 \text{ nm}$
 $[\text{Ru}(\text{dmb})_3]^{2+}$ @ $3.0 \times 10^{-5} \text{ M}$
Anthracene @ $1.3 \times 10^{-4} \text{ M}$
 CH_3CN



Chem. Commun. 2004, 2860-2861.