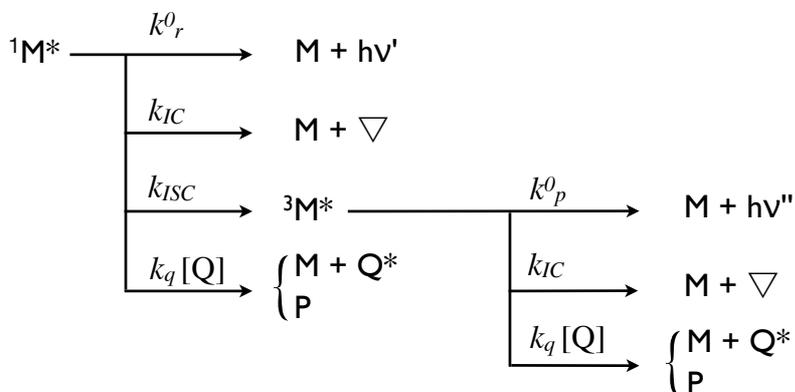


Kinetic competition of deactivation processes

Radiative deactivation process is not isolated but rather competes with other excited state's non-radiative deactivation and reaction (quenching) pathways.



Global deactivation rate:

$$k_f = \frac{1}{\tau_f} = \sum_i k_i = k_r^0 + k_{IC} + k_{ISC} + k_q \cdot [Q]$$

$k_f, k_r^0, k_{IC}, k_{ISC}$: 1st order rate const.
 k_q : 2nd order rate const.

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Kinetic competition of deactivation processes

Quantum yield of a process: $M + h\nu \rightarrow P$

$$\Phi = \frac{N(P)}{N(h\nu)_{\text{absorbed}}}$$

← number of molecules P produced (by unit of time, volume,...)
 ← number of light quanta absorbed (by unit of time, volume,...)

Fluorescence quantum yield: $M + h\nu \rightarrow M^* \rightarrow M + h\nu'$

$$\Phi = \frac{N(P)}{N(h\nu)_{\text{absorbed}}}$$

← number of photons $h\nu$ emitted (by unit of time, volume,...)
 ← number of photons $h\nu'$ absorbed (by unit of time, volume,...)

For any process i in competition with other parallel reaction pathways:

$$\Phi_i = \frac{k_i}{\sum_i k_i}$$

For fluorescence: $\Phi_f = \frac{k_r^0}{k_r^0 + k_{IC} + k_{ISC} + k_q \cdot [Q]} = \frac{\tau_f}{\tau_r^0}$

Vavilov's rule: $\Phi_f \neq f(\nu)$ independent of wavelength.

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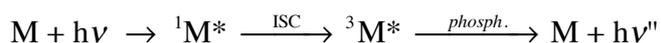
Kinetic competition of deactivation processes

$$\Phi_f = \frac{\tau_f}{\tau_r^0} \quad \tau_f \text{ is the excited state's lifetime or "fluorescence lifetime"}$$

M	τ_r^0 / ns	τ_f / ns	Φ_f
benzene	414	29	0.07
benzylic alcohol	362	29	0.08
toluene	200	34	0.17
ethyl-benzene	172	31	0.18
p-xylene	75	30	0.40
phenol	26	2.1	0.08
anthracene	13.8	4.9	0.36
9,10-dichloro anthracene	15.5	8.5	0.55
perylene	6.8	6.4	0.94

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Kinetic competition of deactivation processes



Phosphorescence quantum yield:

$$\Phi_p = \frac{k_{ISC}}{k_r^0 + k_{IC} + k_{ISC}} \cdot \frac{k_p^0}{\sum_j k_j} = \Phi_T \cdot \frac{\tau_p}{\tau_p^0}$$

↑
↑

deactivation of the singlet excited state
deactivation of the triplet state

M	Φ_T (298 K)	Φ_p (298 K)	Φ_p (77 K)	τ_p^0 / s
benzene	0.24	$< 10^{-4}$	0.20	10
benzophenone	1.00	0.1	0.08	10^{-2}
triphenylene	0.95	$< 10^{-4}$	0.50	10
naphtalene	0.67	$< 10^{-4}$	0.05	10

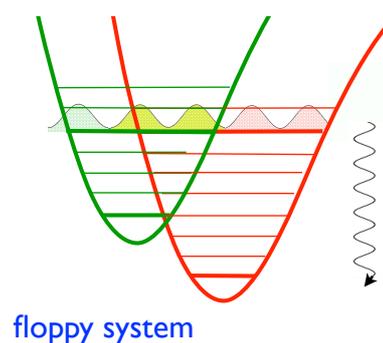
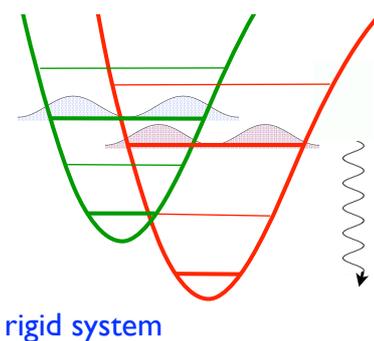
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Non-radiative deactivation pathways

Inter-system crossing (ISC) and internal conversion (IC) proceed primarily through a nuclear tunneling mechanism involving overlap of vibrational wave functions. In addition, fast vibrational relaxation of the product state must take place to hinder the reverse process.

Rigid molecules or molecules placed in a rigid environment (viscous solvent, solid matrix) are characterized by high-frequency modes and then by a large separation of vibrational energy levels. Overlap of vibrational wave functions and, therefore, IC and ISC processes are disfavored in this case.

Lowering the temperature participates in the rigidification of the system. It also decreases the rate of collisions with solvent molecules and the efficiency of energy dissipation.



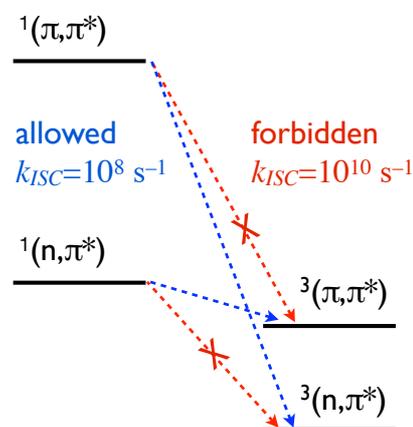
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Selection rules for non-radiative processes

In the case of $S_1 \rightarrow S_0$ internal conversion, the transition takes place into a region of high vibrational state density in S_0 , usually 1-2 eV above $v = 0$. A selection process still operates, since the final state wave functions must meet the requirement that they possess the same symmetry as the initial state.

Since the symmetries of the electronic wave functions are determined only by the symmetries of the spatial components and not the spin, $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states, for instance, have identical symmetries.

Now the mechanism of spin-orbit coupling gives the same symmetry properties as rotations about the three Cartesian axes. The resulting generalized selection rules for intersystem crossing are known as **El-Sayed's rules**: ISC transitions between $^1(n,\pi^*)$ and $^3(n,\pi^*)$ and between $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ states are forbidden, whereas transition from $^1(n,\pi^*)$ to $^3(\pi,\pi^*)$ and from $^1(\pi,\pi^*)$ to $^3(n,\pi^*)$ are allowed.



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Spin-orbit coupling

Heavy-atoms, as substituents of the same molecule, or present in the solvent / matrix surrounding the molecule, enhance spin-orbit coupling and therefore also enhance the rate of intersystem crossing k_{ISC} . The spin-orbit coupling constant is proportional to Z^4 , where Z is the atomic number. Delocalization of electrons in aromatic cycles also produce large spin-orbit interactions.

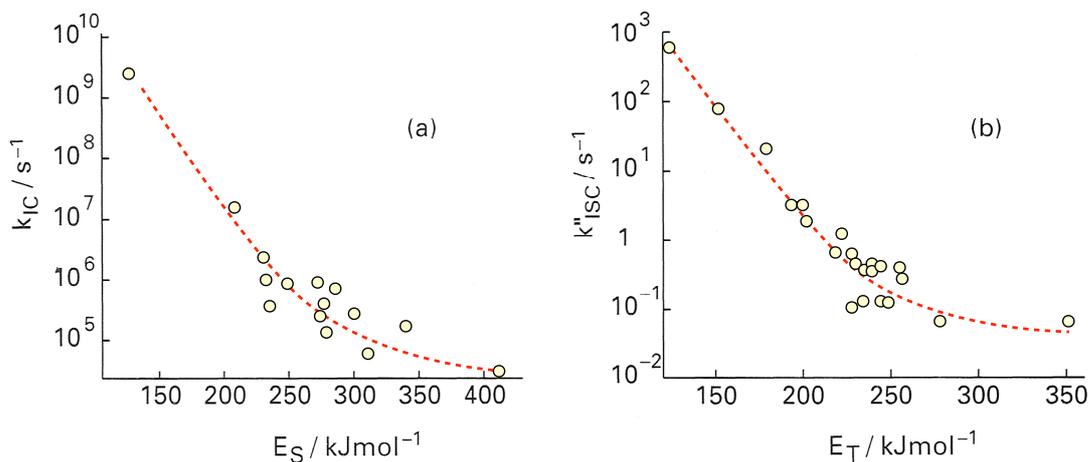
M	$k_{ISC}(S \rightarrow T) / 10^6 \text{ s}^{-1}$	$k''_{ISC}(T \rightarrow S) / \text{s}^{-1}$	Φ_p	τ_p^0 / s
naphtalene	1.6	0.39	0.05	2.1
1-methyl naphtalene	0.5	0.34	0.04	7
1-fluoro naphtalene	0.6	0.44	0.06	4
1-chloro naphatalene	49	2.35	0.30	0.9
1-bromo naphtalene	1850	36	0.27	0.07
1-iodo naphtalene	> 6000	310	0.38	0.005

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Energy-gap law

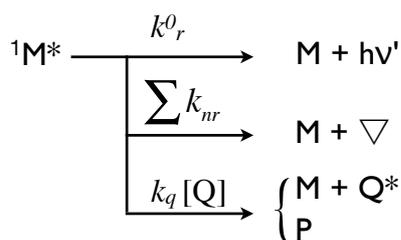
Siebrand's theory and later the work by Englman and Jortner (1970) reached the conclusion that the non-radiative decay rate of an excited state increases exponentially as the energy-gap (excitation energy) decreases.

An example of this "Energy-gap law" is provided here below. a) shows the variation of the rate constant for internal conversion ($S_1 \rightarrow S_0$) for a series of aromatic hydrocarbons vs. the singlet excitation energy. b) displays the variation of the rate constant of intersystem crossing ($T_1 \rightarrow S_0$) vs. the triplet state energy.



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Quenching of the emission - Stern-Volmer relation



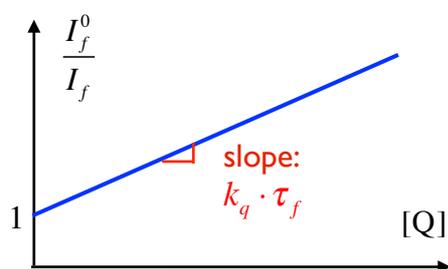
$$\frac{-d}{dt} [M^*] = k_q \cdot [M^*] \cdot [Q] \quad \text{second order kinetics}$$

$$\frac{-d}{dt} [M^*] = k_q' \cdot [M^*] \quad \text{pseudo-first order kinetics}$$

with $k_q' = k_q \cdot [Q]$

In the presence of a quencher Q:

$$\Phi_f = \frac{k_r^0}{\sum k_i + k_q \cdot [Q]}$$



In the absence of a quencher:

$$\Phi_f^0 = \frac{k_r^0}{\sum k_i}$$

$$\frac{\Phi_f^0}{\Phi_f} = \frac{k_r^0 \cdot \sum k_i + k_q \cdot [Q]}{\sum k_i \cdot k_r^0} = 1 + \frac{k_q \cdot [Q]}{\sum k_i}$$

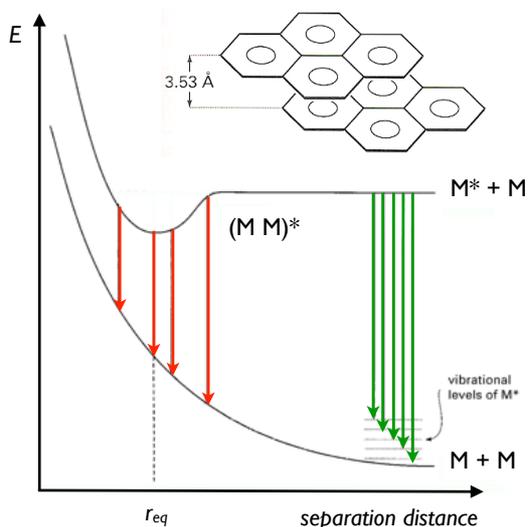
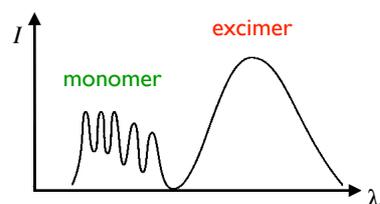
$$\frac{I_f^0}{I_f} = 1 + k_q \cdot [Q] \cdot \tau_f$$

Stern-Volmer

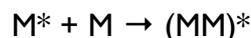
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2.3 Intermolecular energy transfer

Excimers and exciplexes



For most aromatic hydrocarbons, electronically excited molecules M^* tend to form dimers with ground state molecules M :



Such a dimer species $(MM)^*$ is stable only in an electronically excited state and is called an **excimer**.

Similarly, a complex $(MQ)^*$ formed between an excited state M^* and a ground state molecule Q of a different nature is called an **exciplex**.

The intermolecular potential energy curve scheme shows that fluorescence of excimers (or exciplexes):



is red-shifted compared to that of monomers and is characterized by a broad, featureless emission spectrum.

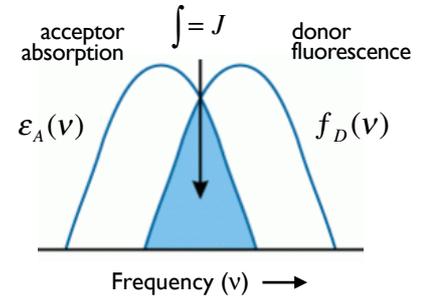
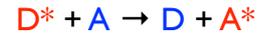
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Intermolecular electronic energy transfer

The electronic excitation energy of a molecule D (energy donor) can be transferred to another molecule A (energy acceptor) through radiative and non-radiative mechanisms.

Energy transfer can obviously occur only if the energy conservation principle is satisfied. This condition is verified if the overlap integral between the donor fluorescence and the acceptor absorption spectra is non-zero: $J \neq 0$.

Radiative energy transfer implies the radiative deactivation of a donor molecule (fluorescence) and subsequent reabsorption of the emitted radiation by an acceptor molecule. The probability of energy transfer (rate constant) is given by: $k_{ET} \propto [A] \cdot l \cdot J$, where J is the spectral overlap integral, $[A]$ is the concentration of the acceptor, and l is the sample thickness.



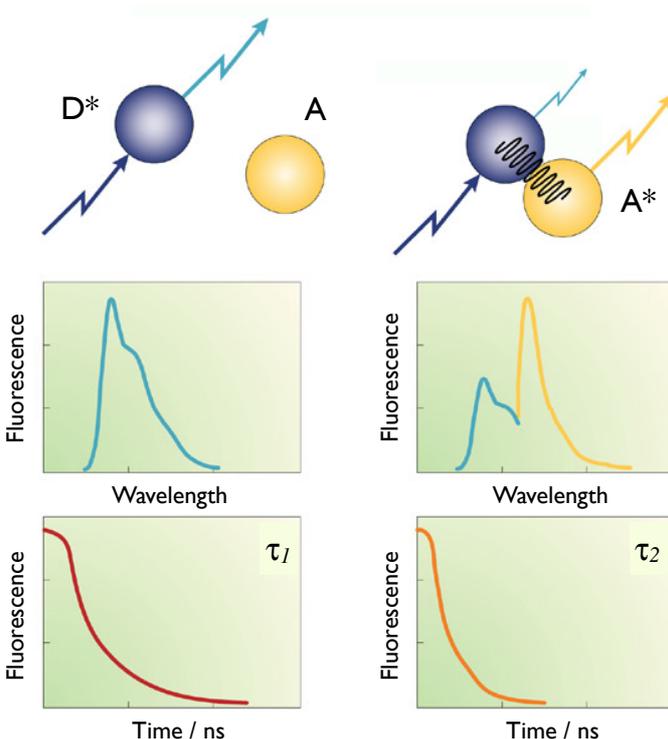
$$J = \int_0^{\infty} f_D(\nu) \cdot \epsilon_A(\nu) d\nu$$

Radiative energy transfer:

$$k_{ET} \propto [A] \cdot l \cdot J$$

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Intermolecular electronic energy transfer



Two mechanisms of **non-radiative energy transfer** can be distinguished a) Short distance (Dexter) electron exchange mechanism taking place in exciplexes; b) Förster resonance energy transfer (FRET) mechanism occurring through a transition dipole-dipole interaction.

Both non-radiative mechanisms result in the quenching of the donor excited state's fluorescence. The acceptor molecule can thus be seen as a *physical quencher*.

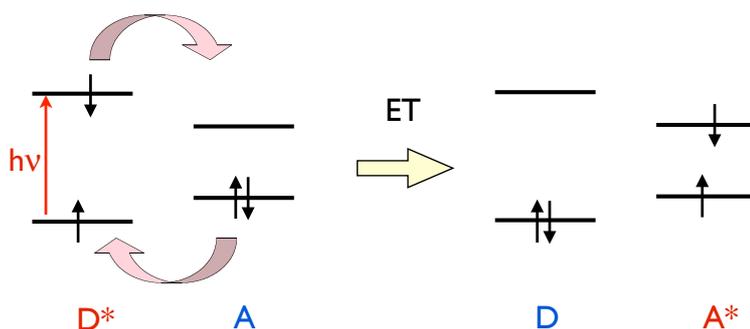
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Intermolecular electronic energy transfer

Excitation energy transfer can occur as a result of an **electron exchange mechanism (Dexter)**. It requires an overlap of the orbitals of the energy donor (D) and the energy acceptor (A), generally interacting within an excimer (DA)*. It is the dominant mechanism in triplet-triplet ET. The transfer rate constant k_{ET} , is given by:

$$k_{ET} \propto \frac{h}{2\pi} \cdot P^2 J \cdot \exp\left(\frac{-2r}{L}\right)$$

where r is the D-A distance, L and P are constants, and J is the spectral overlap integral. For this mechanism the spin conservation rules are obeyed.



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Intermolecular electronic energy transfer

Förster (dipole-dipole) resonance energy transfer (FRET) mechanism occurs between molecules separated by distances considerably exceeding the sum of their van der Waals radii. It is described in terms of an interaction between the transition dipole moments. The transfer rate constant k_{ET} is given by:

$$k_{ET} = \frac{K^2 \cdot J \cdot 8.8 \times 10^{-28} \text{ mol}}{n^4 \cdot \tau_r^0 \cdot r^6}$$

where K is an orientation factor, n the refractive index of the medium, τ_r^0 the radiative lifetime of the donor, r the distance [cm] between donor (D) and acceptor (A), and J the spectral overlap (in coherent units $\text{cm}^6 \cdot \text{mol}^{-1}$) between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor. The critical quenching radius r_0 is the distance at which $k_{ET} = k_r^0 = 1 / \tau_r^0$.

D	A	k_{ET} [$10^{10} \text{ M}^{-1} \text{ s}^{-1}$]	r_0 [nm]
anthracene	perylene	12	5.4
anthracene	rubrene	3.7	3.9
perylene	rubrene	13	6.5

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Spectral sensitization

Intermolecular excitation energy transfer allows for the preparation of an excited state A^* that cannot be produced directly by absorption of light, either because the energetics or selection rules are not satisfied. A is said to be **sensitized** through energy transfer from D^* .



Example: triplet-triplet energy transfer

