Assumptions made in building electronic configuration of molecules

- Orbitals derived from hydrogen atom will work for all atoms and molecules

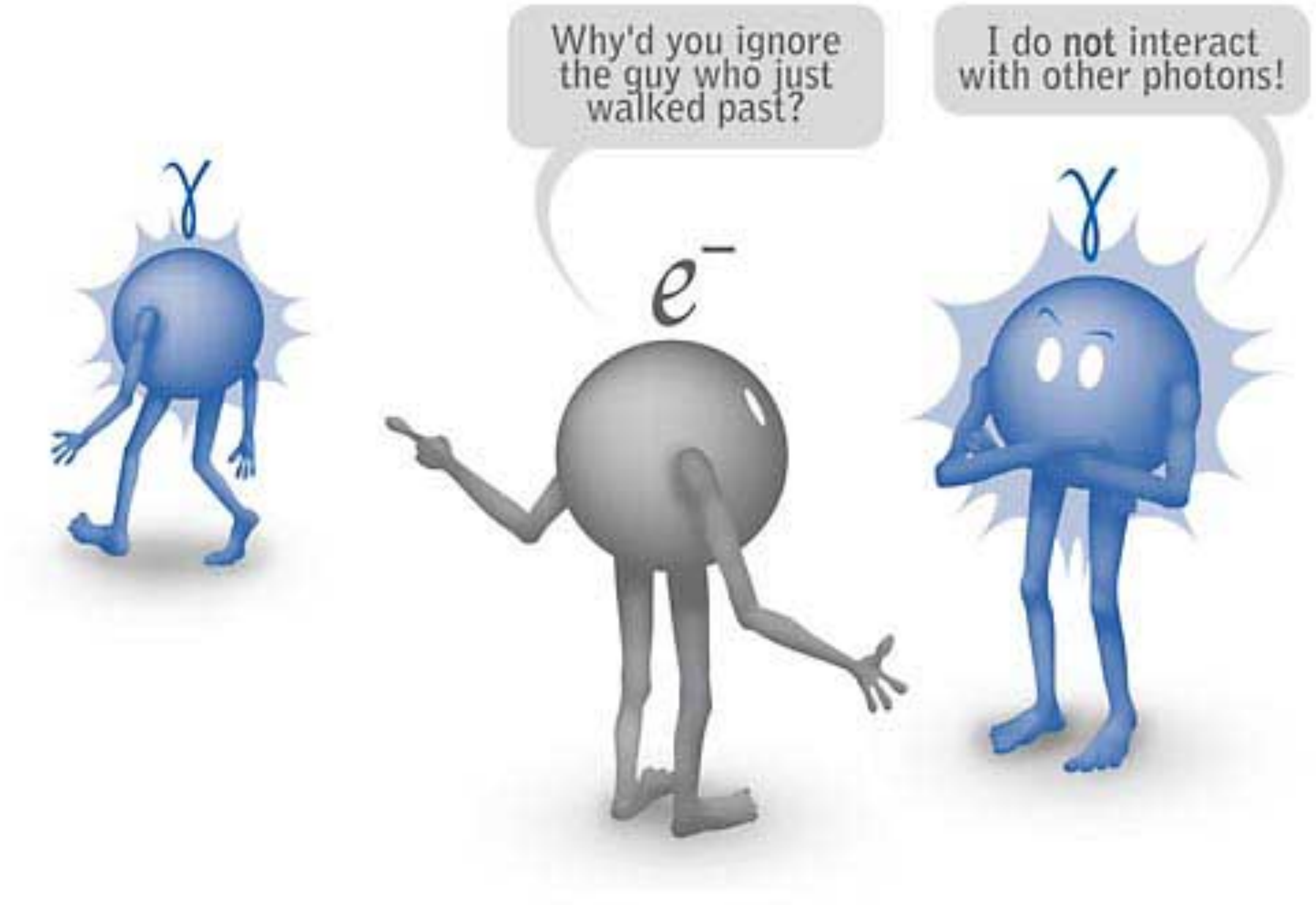
- All MOs could be built based on LCAO which is based on hydrogen atom orbitals

- To begin with e-e repulsion is ignored

- Molecule is stationary at its equilibrium geometry (Born-Oppenheimer approximation)

- The molecule could be built assuming there are no interactions between electronic, vibrational and spin motions of electrons and nuclei.

Interaction between a Photon and an Electron

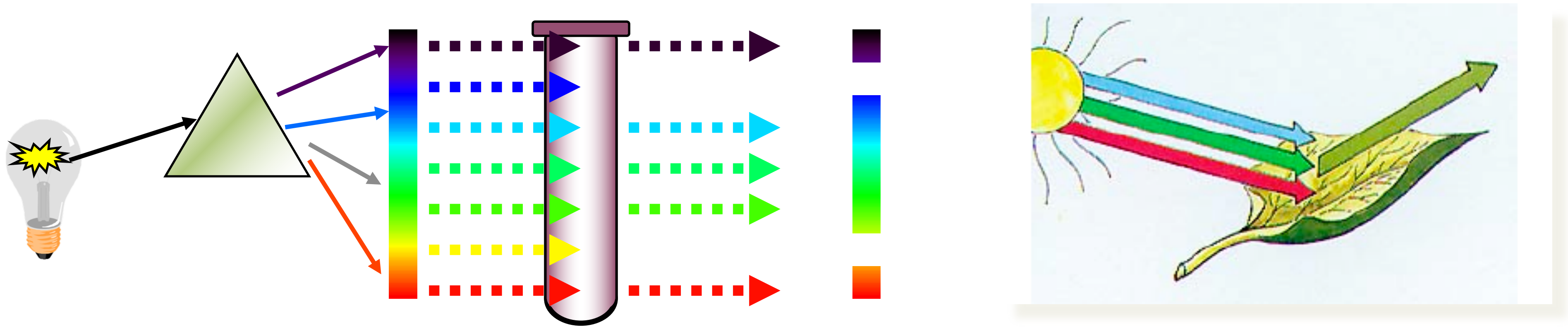


Manifestations of Light-Molecule (Material) Interaction

- Reflection
- Refraction
- Scatter
- **Absorption process**

Absorption and Emission: Chromophore and Lumophore

A chromophore ("color bearer") is defined as an atom or group of atoms that behave as a unit in light absorption.



A green object, such as a leaf, reflects only those wavelengths that create the visual effect of green. Other colors in the incident light are absorbed by the leaf. Leaf consists of chlorophylls and carotenoids. Red light is absorbed by the chlorophylls, blue light is absorbed mostly by the carotenoids. Green gets reflected and that is what we see.

The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: light must be absorbed for photochemistry to occur.

Grotthus

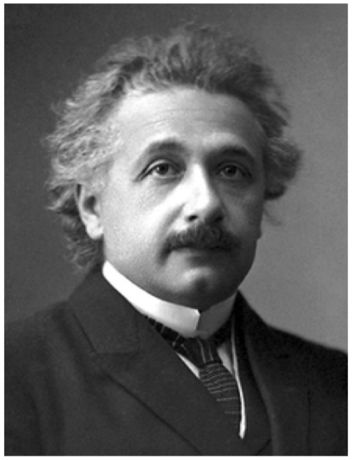
John William Draper (1811-1882)

Drapper

Stark-Einstein law

The Second Law of Photochemistry: for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

Stark

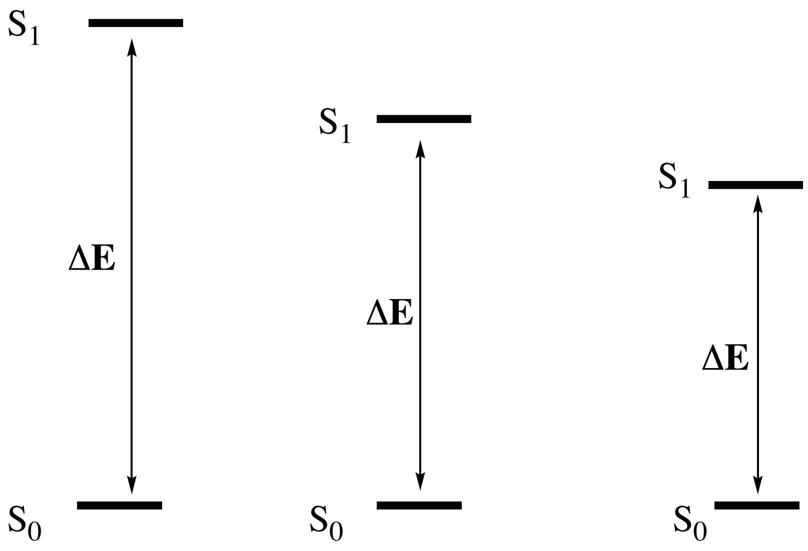


Einstein

Third law of photochemistry

Probability of light absorption is related to the energy gap and wavelength of light

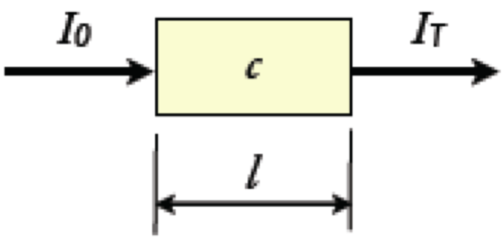
The *energy conservation rule* (Eq. 4.8): There must be an exact matching of the energy difference that corresponds to the energy required for the transition (ΔE) between orbitals and the energy of the photon ($h\nu$); that is, ΔE must exactly equal $h\nu$ (Eq. 4.8).



$$\Delta E\ (\text{kcal mol}^{-1}) = [2.86 \times 10^4\ \text{kcal mol}^{-1}\ \text{nm}]/\lambda\ \text{nm}$$

Absorption

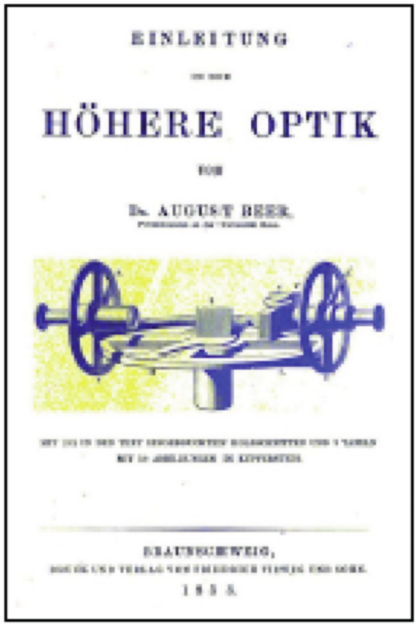
Beer-Lambert Law



$$A = -\log\frac{I_T}{I_0} = -\log T = \varepsilon \cdot c \cdot l \quad [-]$$

c molar concentration [mol l^{-1}]
l optical pathlength [cm]
ε molar decadic extinction coefficient

Example: $c = 10^{-3}$ M, $\varepsilon = 10^{4}$ mol$^{-1} \cdot$ l $\cdot$ cm^{-1}
⇒ $T = 0.01$, $A = 2$ ⇒ 99% of the light is absorbed within the first 2 mm of the solution



EINLEITUNG

HÖHERE OPTIK

VON

Dr. AUGUST BEER.

BRAUNSCHWEIG,

1853.

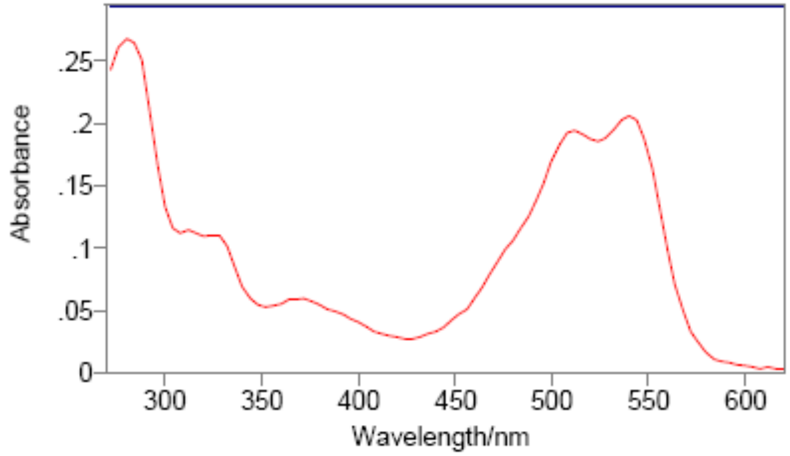
August Beer
(1825-1863)

OD ~ 2: 1% transmission
OD ~ 1: 10% transmission
OD ~ 0.01: 98% transmission

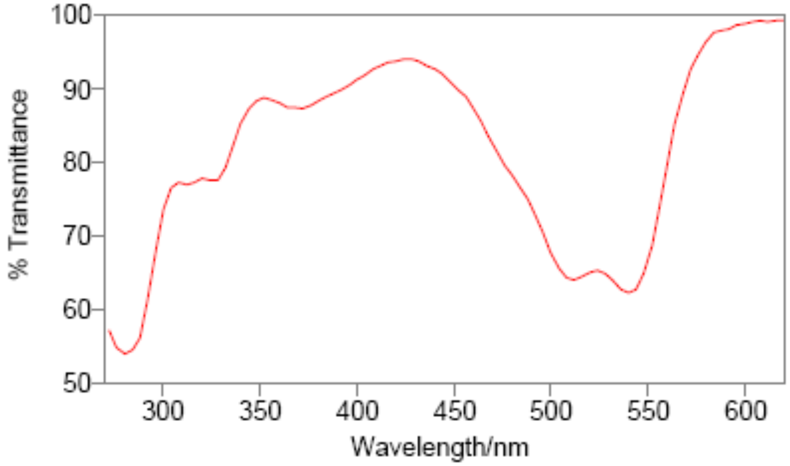
OD can be adjusted with concentration

ABSORPTION
&
TRANSMISSION
SPECTRA

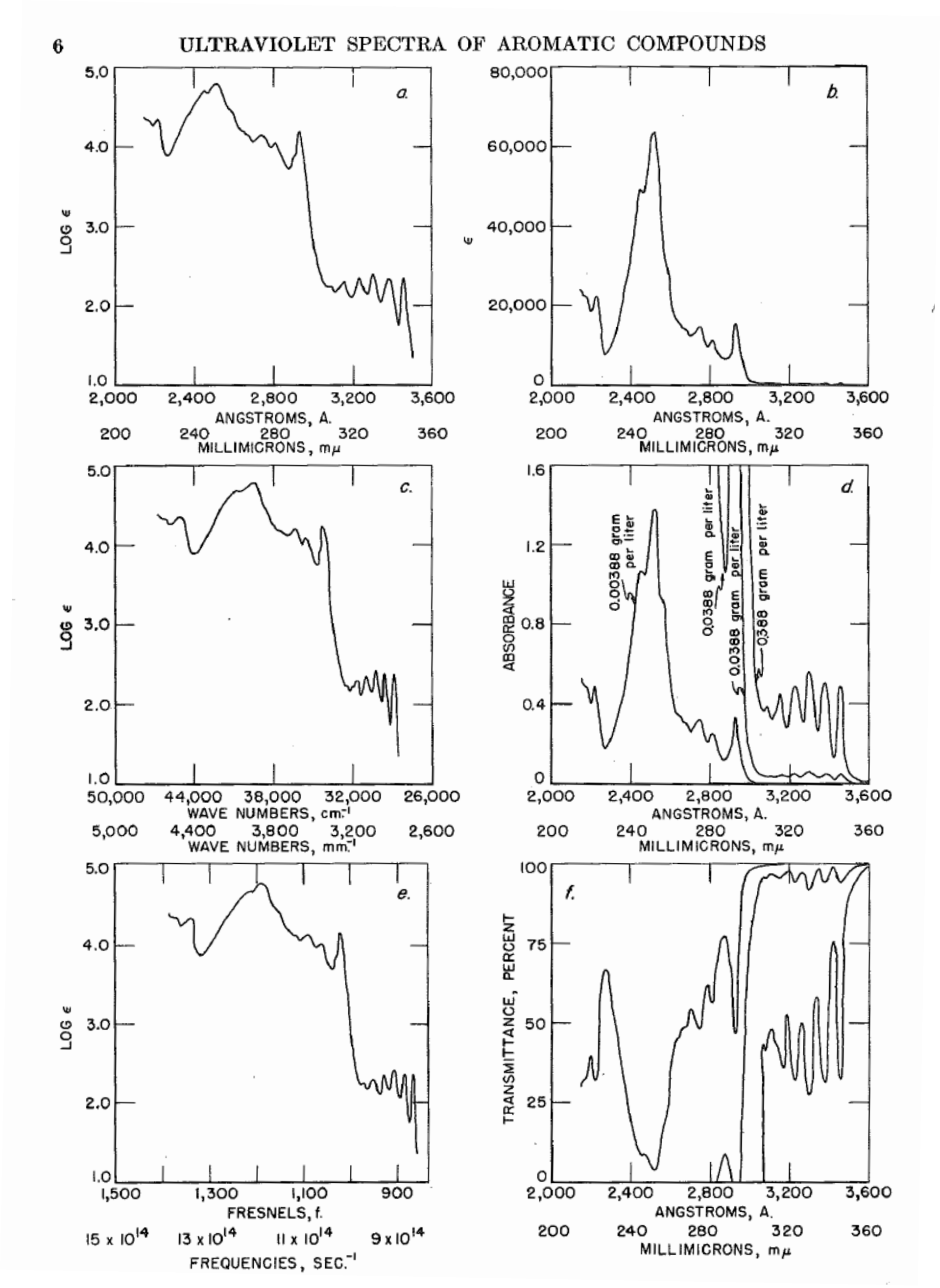
- Absorption spectrum of a red textile



- Transmission spectrum of the same



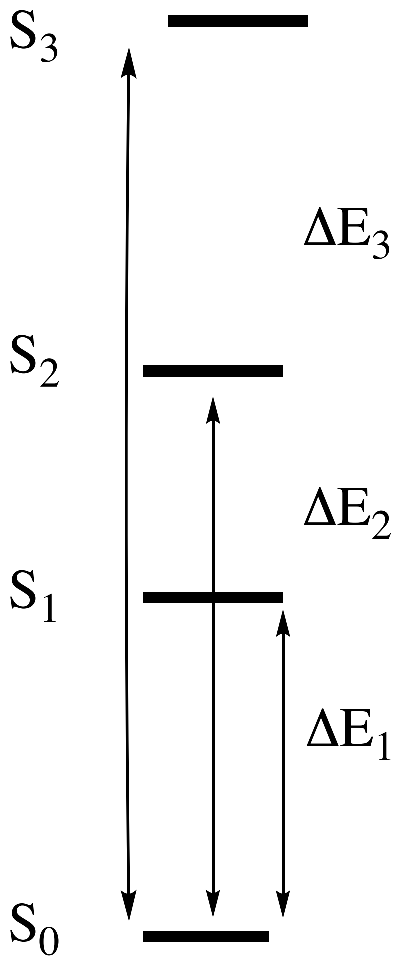
Be Watchful of the Units Used



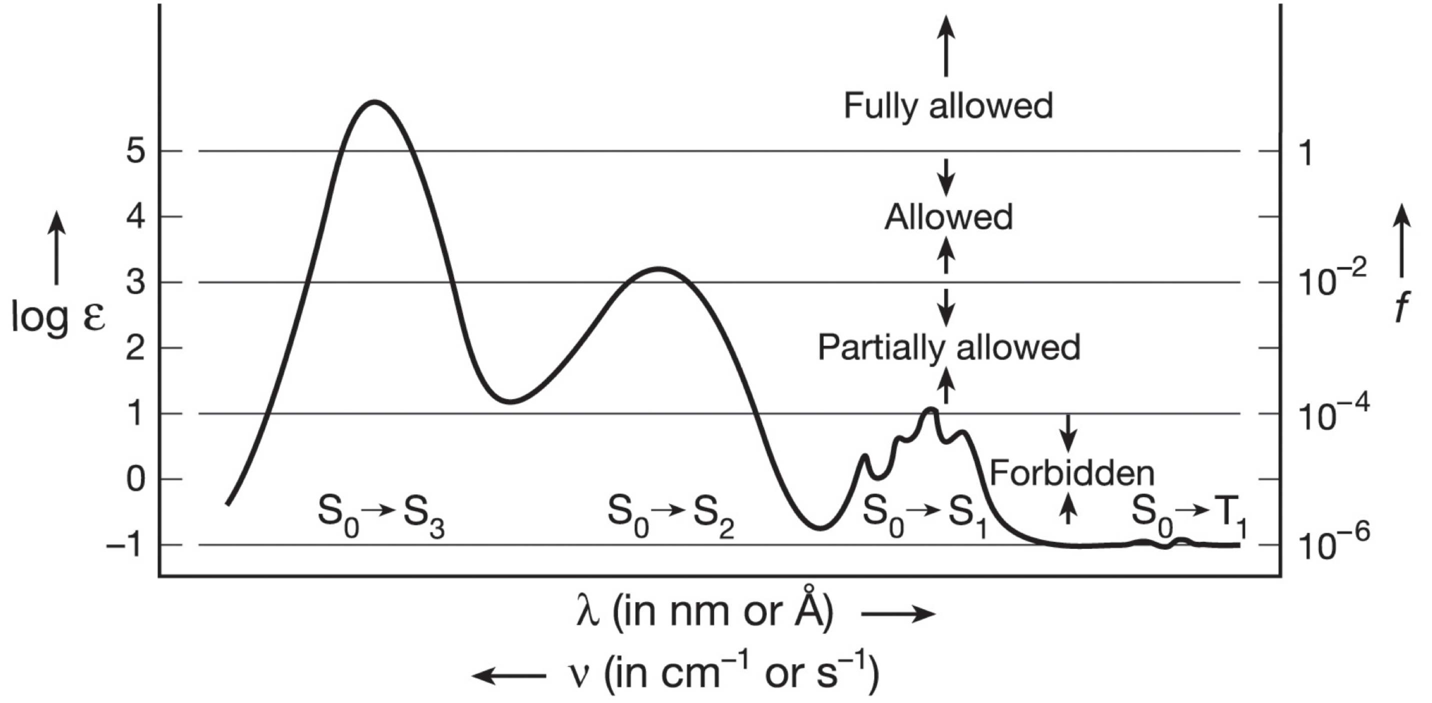
6 ULTRAVIOLET SPECTRA OF AROMATIC COMPOUNDS

Absorption Spectra

- What does it mean?
- Why so many bands?
- Why the intensities of the bands vary?



Electronic transitions



Long-Wavelength Absorption Bands (Corresponding to HO → LU Transitions) of Some Typical Organic Chromophores

Chromophore	λ_{max}(nm)	ε_{max}	Transition type
C-C	<180	1000	σ,σ*
C=C	180	10,000	π,π*
C=C-C=C	220	20,000	π,π*
C=C-C=C-C=C	260	40,000	π,π*
C=O	280	20	n,π*
C=C-C=O	350	30	n,π*
C=C-C=O	280	10,000	π,π*
Benzene	260	200	π,π*
Pyrene	350	510	π,π*
Anthracene	380	10,000	π,π*

Electronic structures for various states are generated assuming the molecule is stationary and it is in its lowest energy state

$\Phi_1 . \chi_1 . S_1$

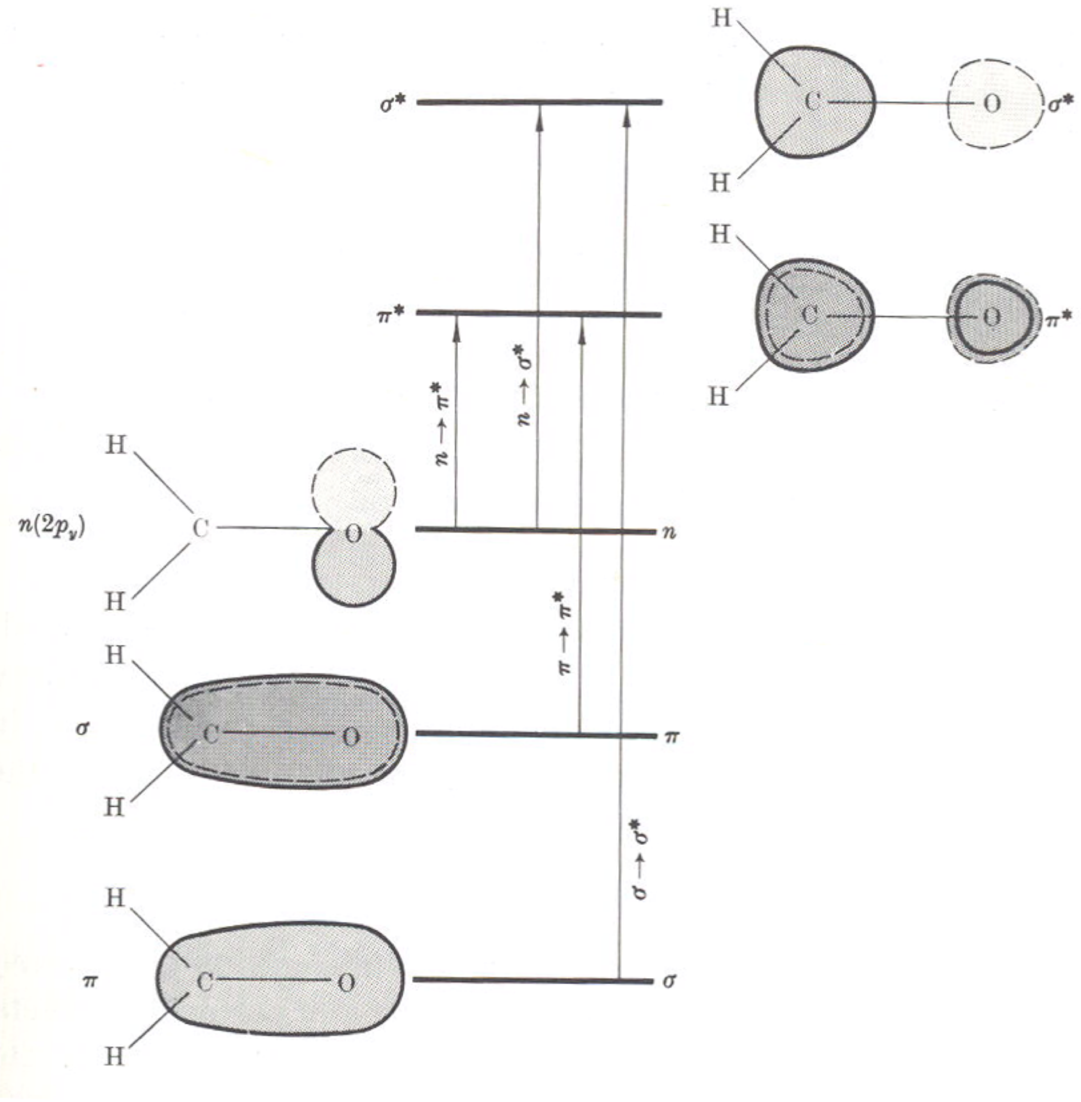
R Ψ_1

Electron jump between orbitals generally takes ~ 10^{-15} to 10^{-16} s

Nuclear vibrations take ~ 10^{-13} to 10^{-14} s

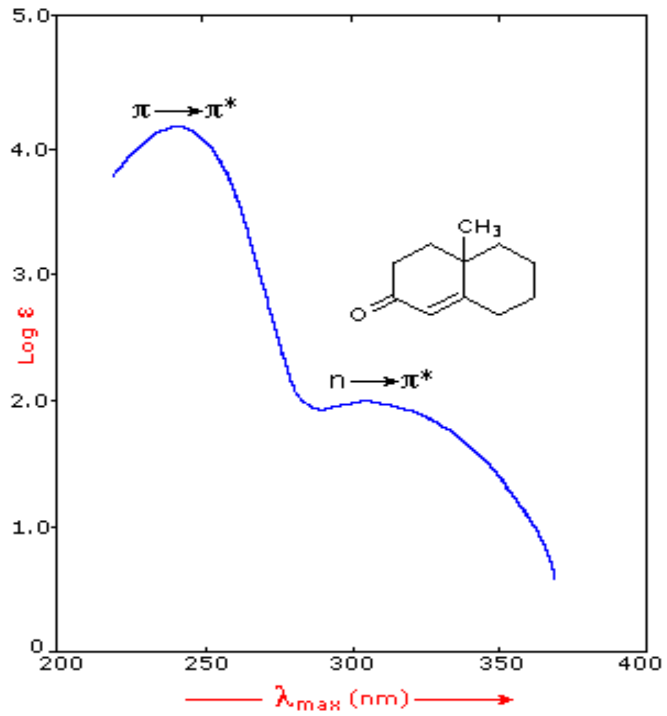
Spin change even at very high magnetic field occurs in ~ 10^{-12} s

Criteria for electronic transition: Orbital overlap

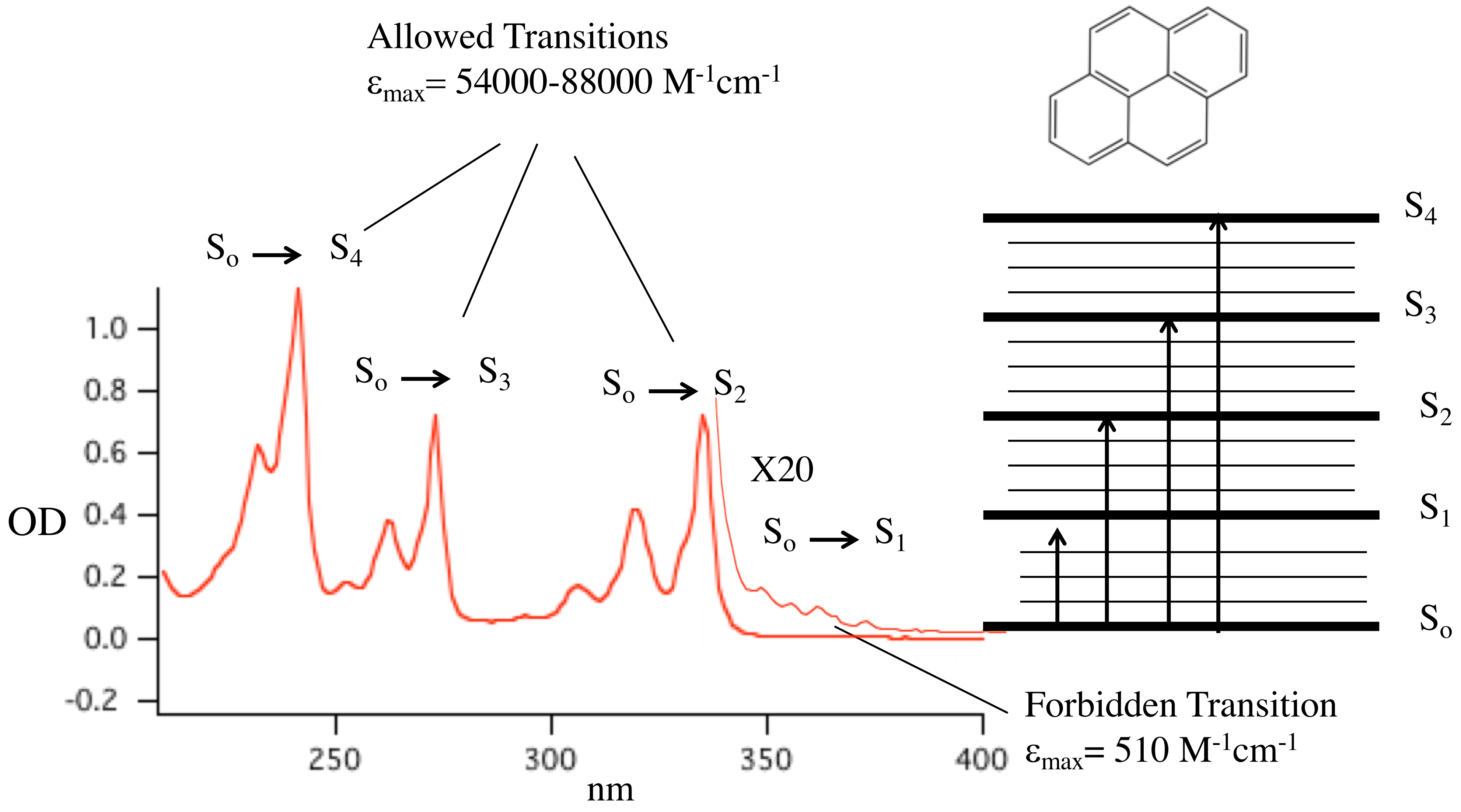


No orbital overlap n and π*

Orbital overlap π and π*



Criteria for electronic transitions: Symmetry of the involved orbitals

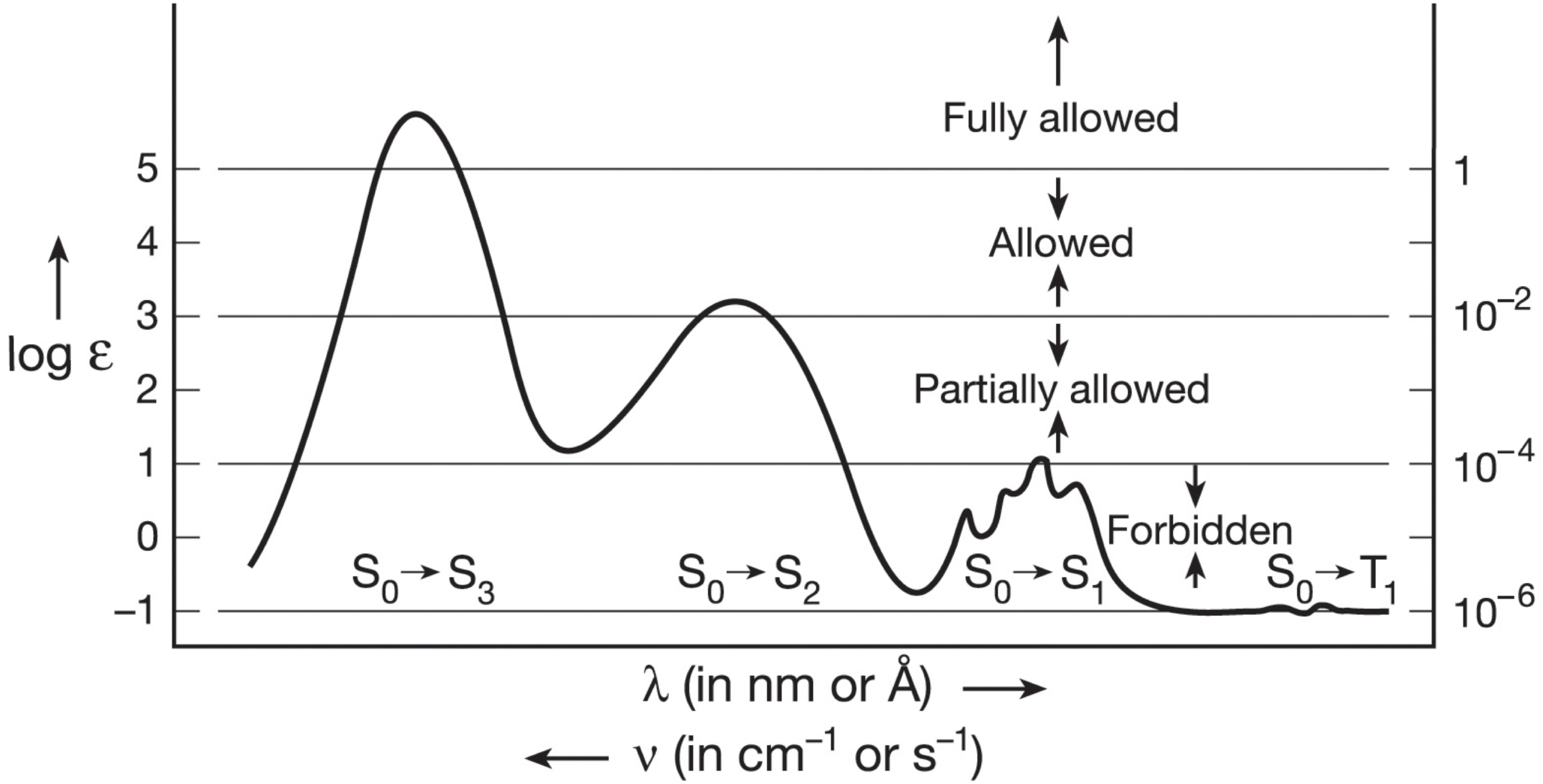


Allowed Transitions
ε_{max}= 54000-88000 $M^{-1}cm^{-1}$

Forbidden Transition
ε_{max}= 510 $M^{-1}cm^{-1}$

What controls the intensities of the bands?

Why the ε and *f* vary with the band?

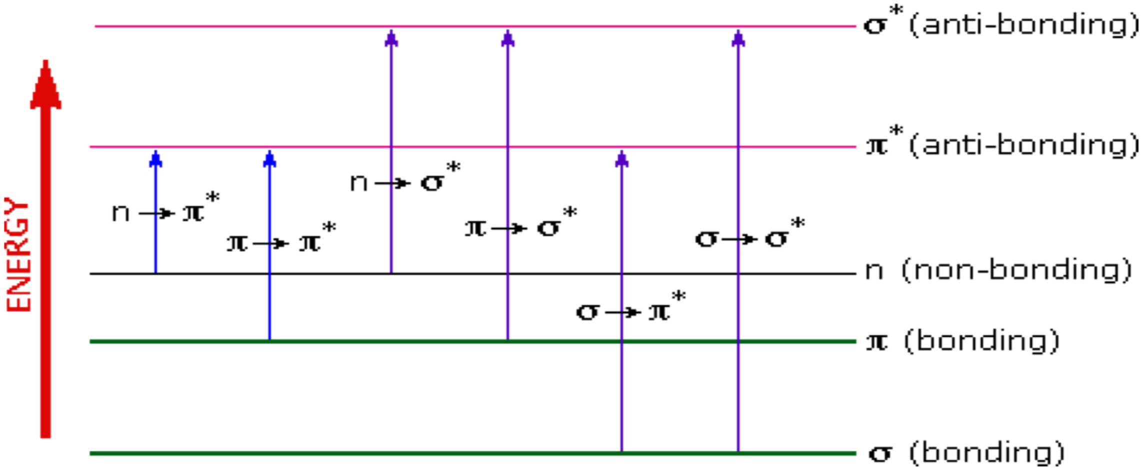


Electronic transitions: Orbital part

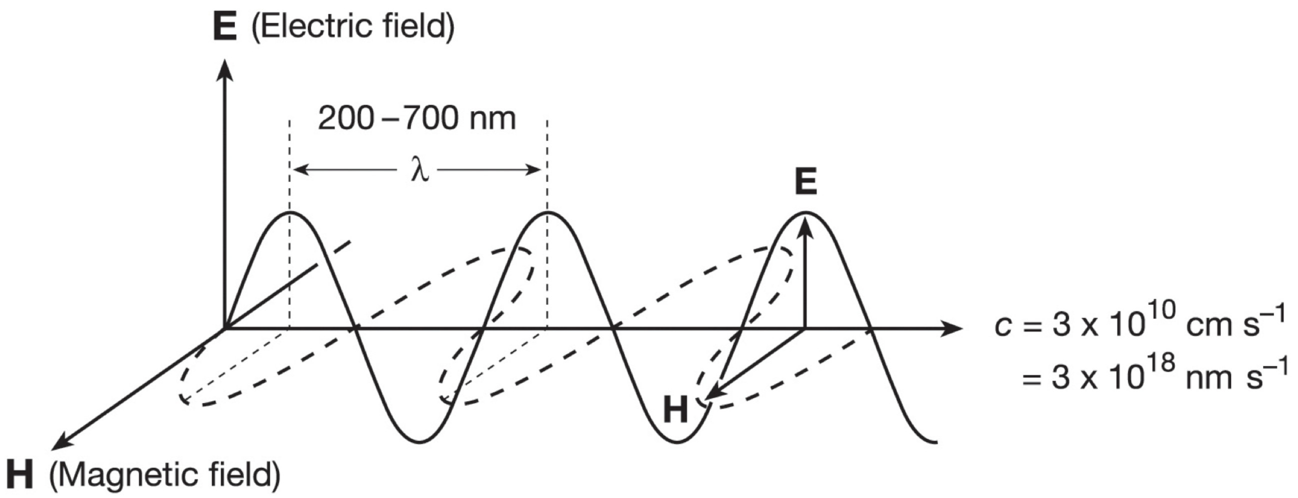
The electronic factor f_e may be subclassified in terms of different kinds of forbiddenness:

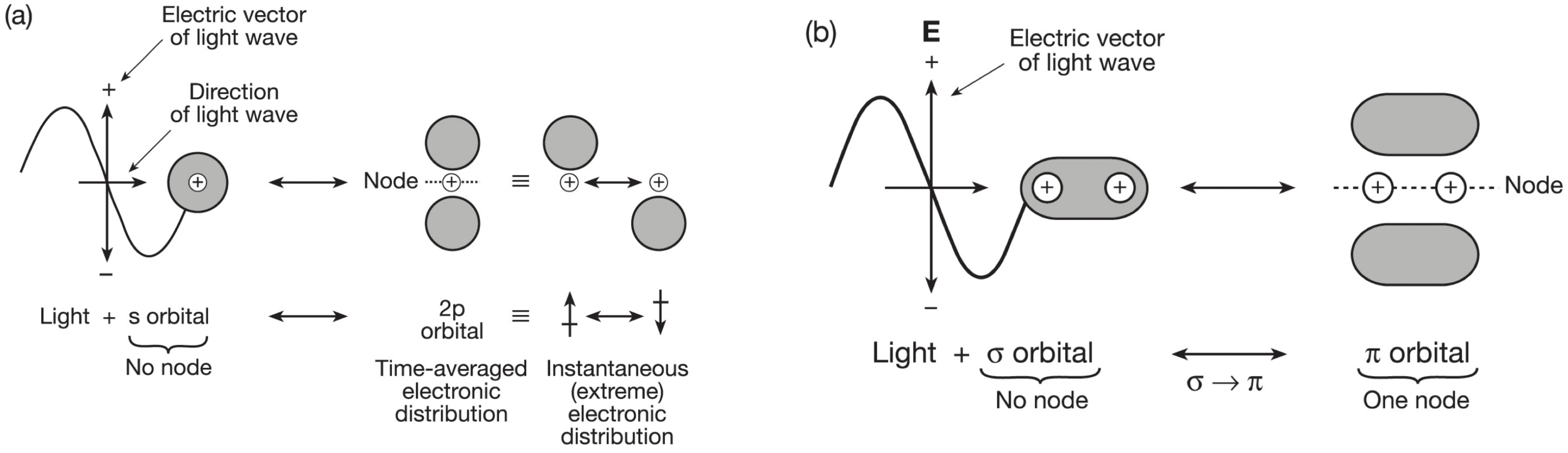
(1) ***Overlap* overlap forbiddenness**, which results from poor spatial overlap of the orbitals involved in the electronic transition, example, the n,π* transition in ketones, for which the HO and LU are orthogonal to one another and the overlap integral $<n|\pi^*>$ is close to zero.

(2) ***Orbital* smmetry forbiddenness,** which results from orbital wavefunctions (involved in the transition) that overlap in space but have their overlap integral canceled because of the symmetry of the wave functions. Examples transitions in benzene, naphthalene, and pyrene.

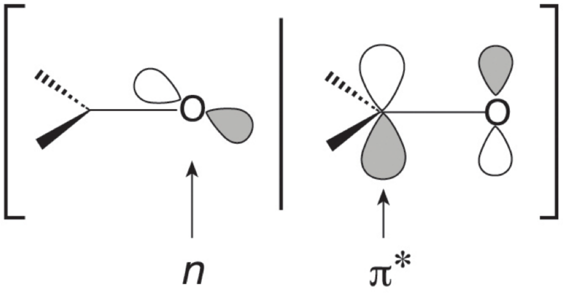


Light as electromagnetic wave



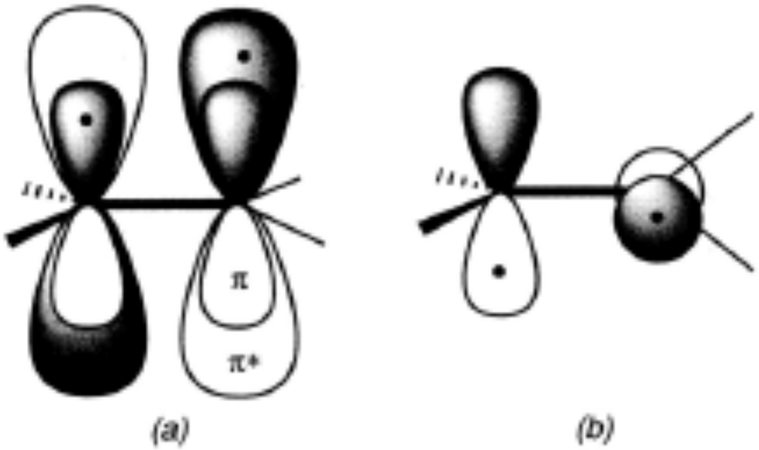


$J_{n,\pi^*} \longrightarrow$



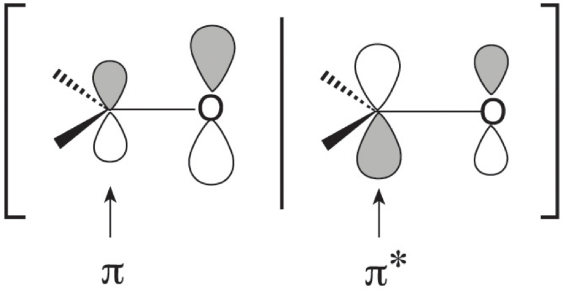
Small orbital overlap between *n* and π*

$\langle n | \pi^* \rangle$ Small



(a) (b)

$J_{\pi,\pi^*} \longrightarrow$



Large orbital overlap between π and π*

$\langle \pi | \pi^* \rangle$ Large

Electronic transitions

Electronic transition involves changes in

- Orbital
- Positions of nuclei
- Spin of the electron

If everything is perfect (favored) the transition is allowed, if not the transition is forbidden

A perfectly allowed transition has an oscillator strength of ONE and forbidden transition an oscillator strength of ZERO

Oscillator Strength-Absorption

$$\boxed{I_t(\lambda_x) = I_0(\lambda_x)\, e^{-\alpha L}}$$

Probability of light absorption is related to the oscillator strength ‘f’

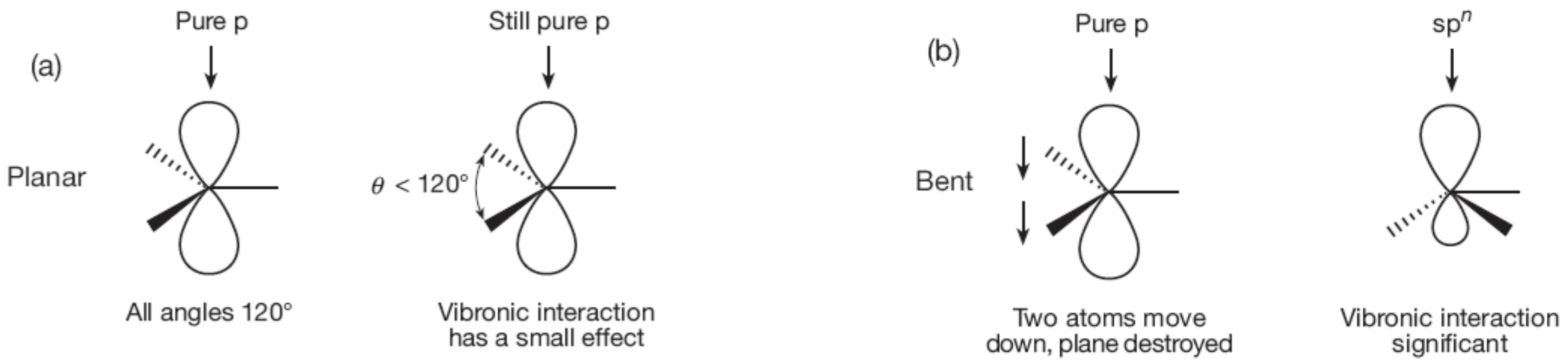
Electronic	**Orbital Symmetry**	f_e
	Orbital Overlap	f_e
Vibronic	**Nuclear position**	f_v
Spin	**Electron Spin**	f_s

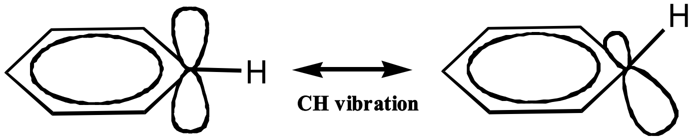
A perfectly allowed transition has $f = 1$

A non-allowed allowed transition may also occur with $f < 1$

Zero Order to First Order Through Vibronic Coupling

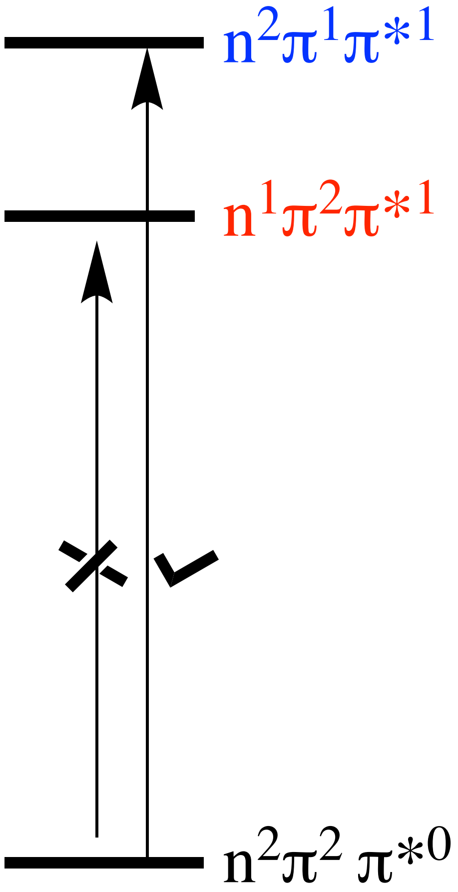
$$\langle n | H | \pi \rangle = 0 \quad \text{when n and } \pi \text{ are orthogonal}$$



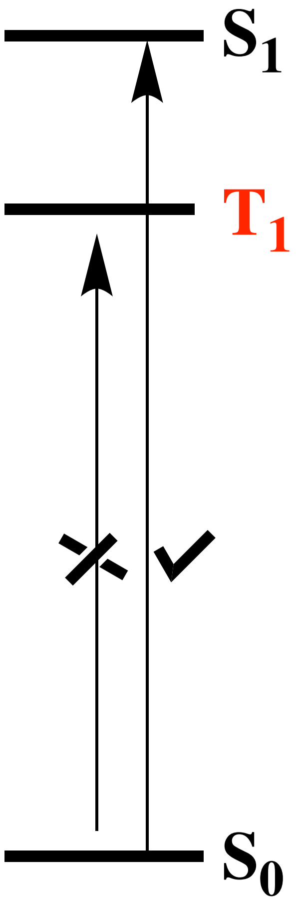


Vibrational mixing could change the shape of the zero order orbital and lead to slight overlap between ‘n’ and ‘π’ (and ‘π*’)

Forbidden Transitions

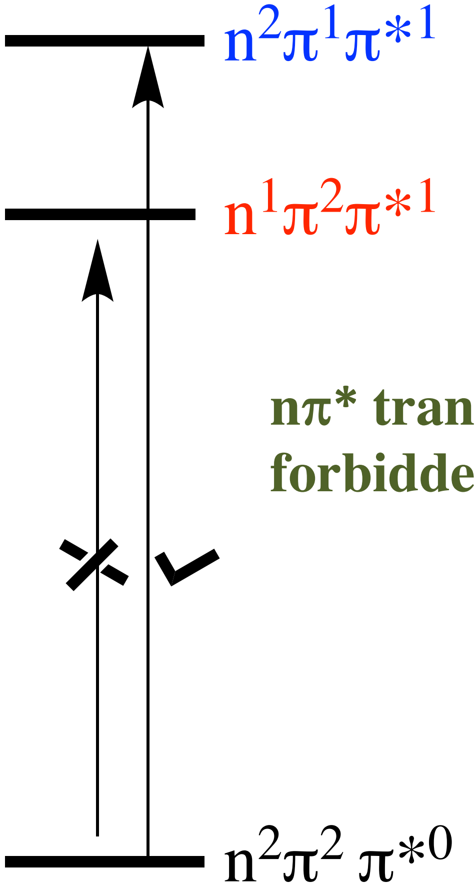


Orbital change



Spin change

Result of vibrational - electronic mixing

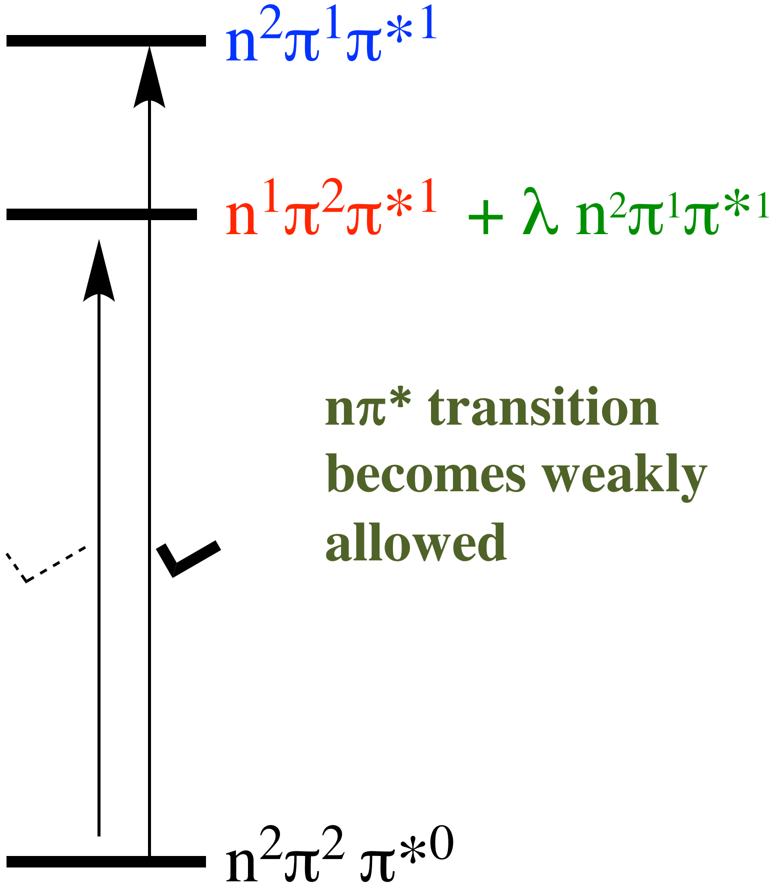


$n^2\pi^1\pi^{*1}$

$n^1\pi^2\pi^{*1}$

$n^2\pi^2\,\pi^{*0}$

nπ* transition forbidden



$n^2\pi^1\pi^{*1}$

$n^1\pi^2\pi^{*1} + \lambda\, n^2\pi^1\pi^{*1}$

$n^2\pi^2\,\pi^{*0}$

nπ* transition becomes weakly allowed

Vibration mixes the states,
no longer pure states

Orbital shape change could lead to state mixing

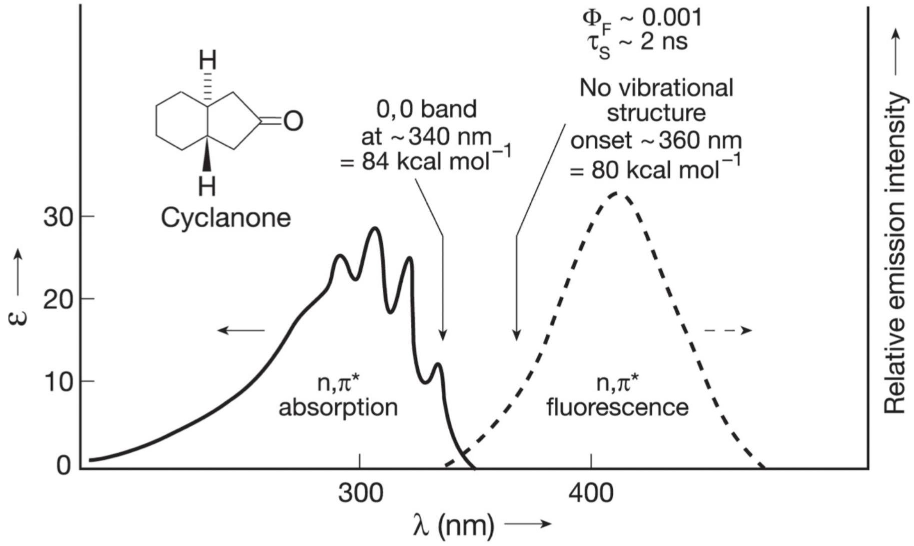
Due to vibration an n, π^* S_1 state is no longer pure but contains a finite amount of π, π^* character mixed in so the zero order wavefunction is not valid and the first order wavefunction may in fact be:

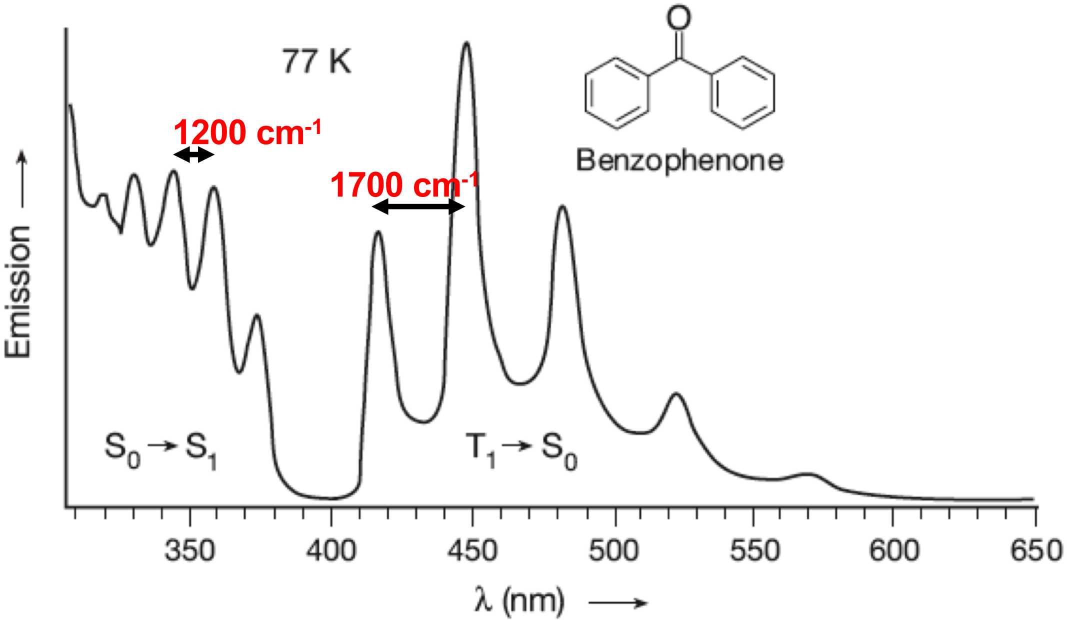
$$\substack{\text{first order}\\ n,\,\pi^*} \longrightarrow \psi(S_1) = \underset{\substack{\uparrow\\ \text{zero order}\\ n,\,\pi^*}}{\psi(n, \pi^*)} + \overset{\substack{\text{Mixing coefficient}\\ \swarrow}}{\lambda}\underset{\substack{\uparrow\\ \text{zero order}\\ \pi,\,\pi^*}}{\psi(\pi, \pi^*)}$$

$$\lambda = \left| \frac{\langle \psi_a | H | \psi_b \rangle}{E_a - E_b} \right|$$

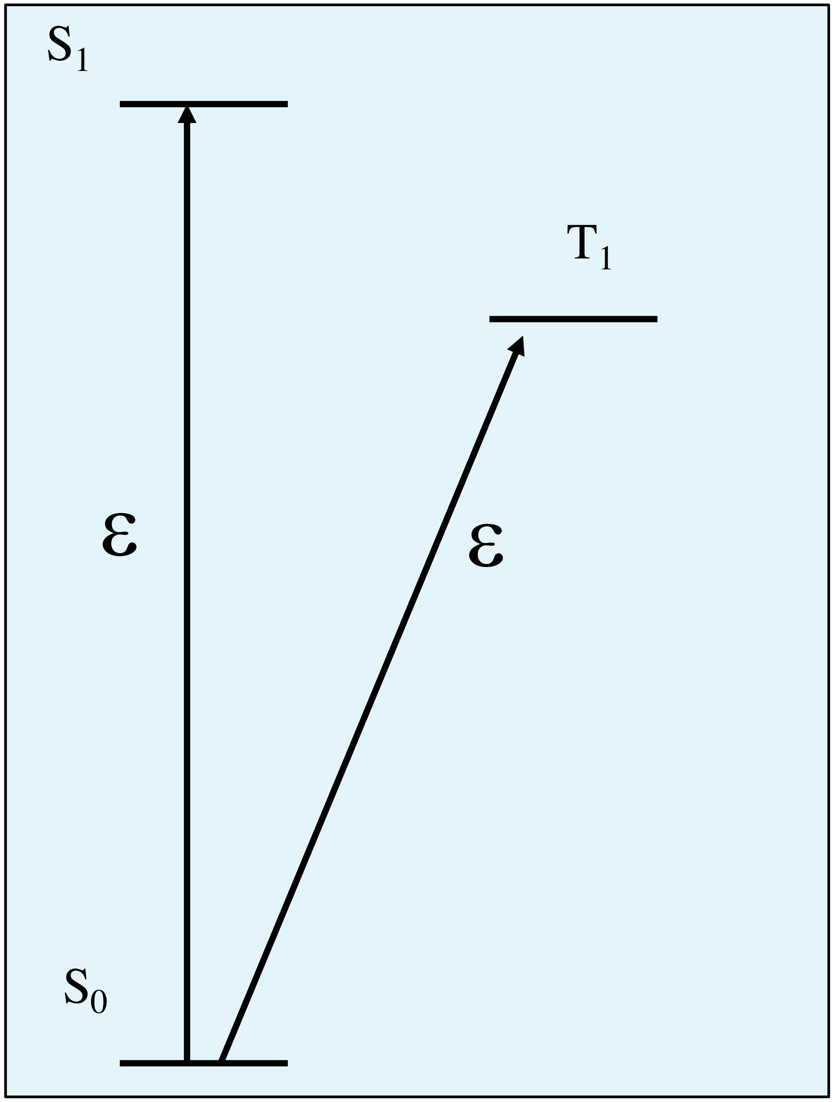
In general λ is the result of **vibrational mixing** (break down of Bonn-Oppenheimer approximation)

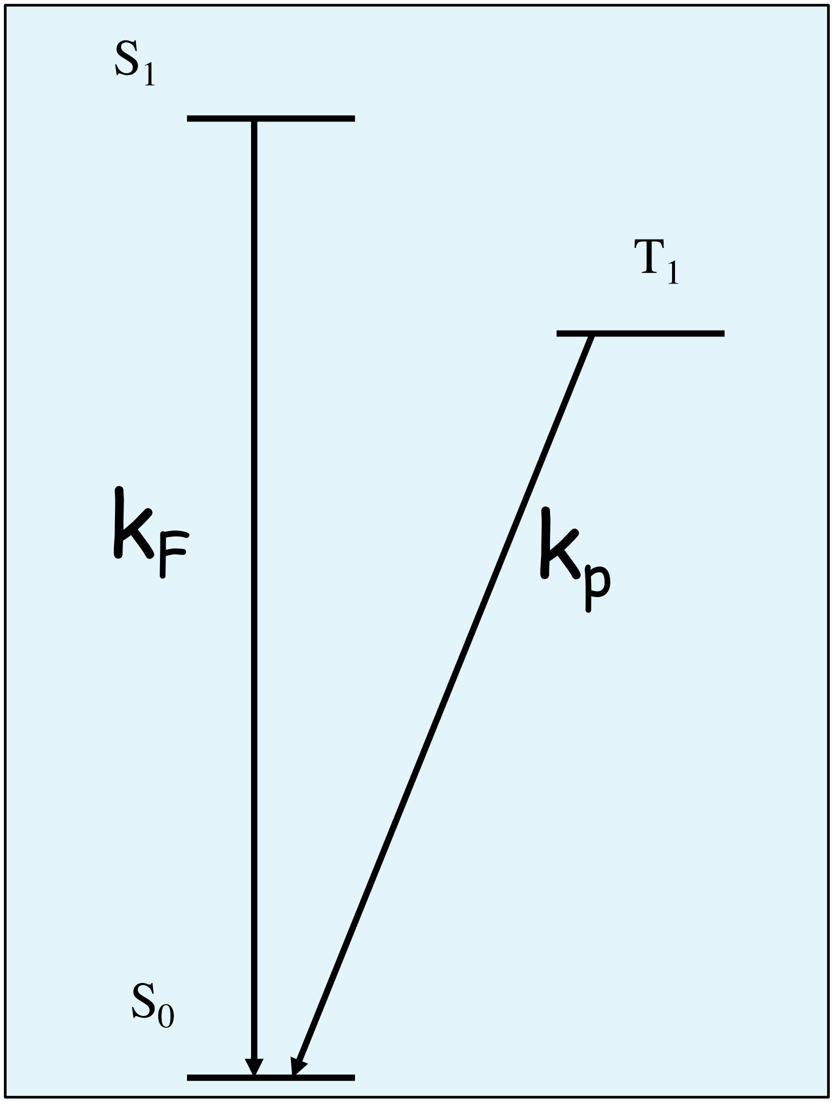
Absorption spectra
Vibrational structure due to vibrational mixing





Same Rules for Excitation & De-excitation





Probability of Absorption and Emission

Probability of light **absorption** is related to the oscillator strength f

Theoretical oscillator strength

$$f \sim 4.3\text{x}10^{-9} \int \varepsilon \, d\nu$$

Experimental absorption

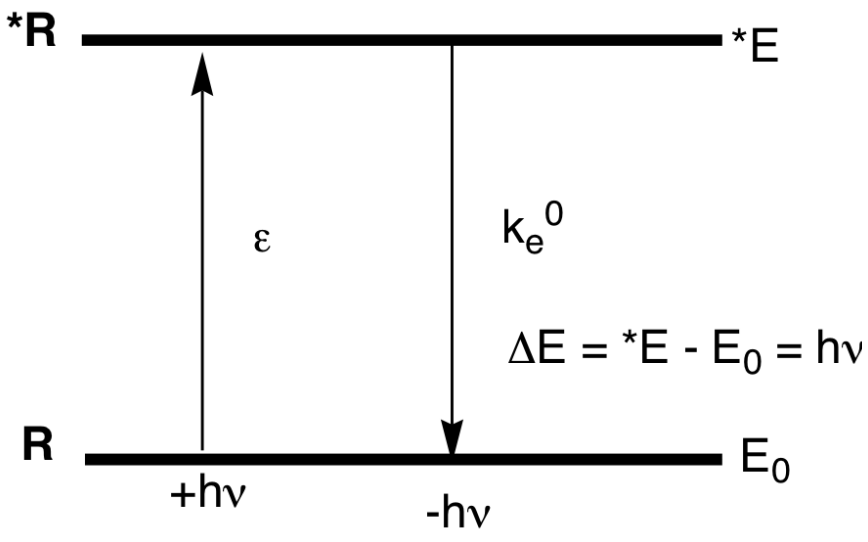
↓

Area under ε *vs.* wavenumber plot

Emission follows the same rules as absorption

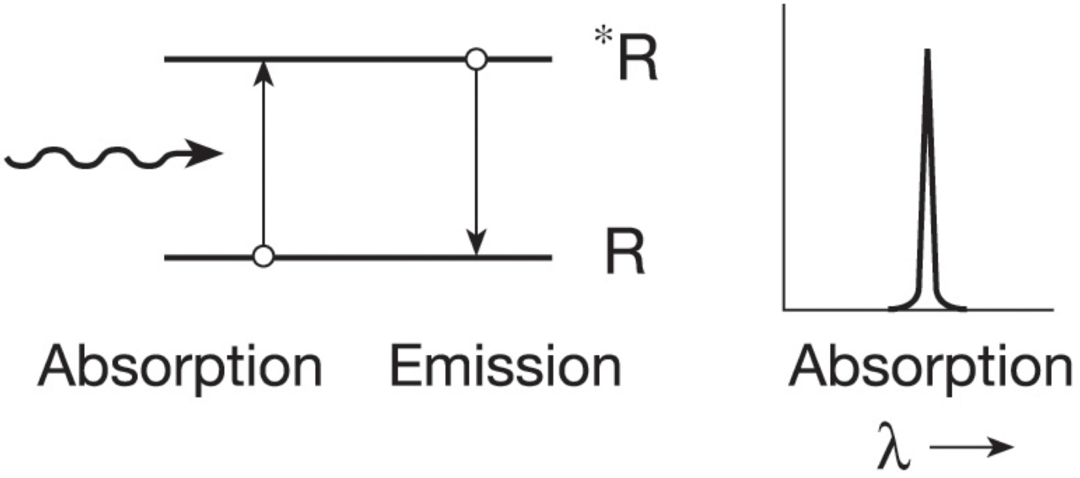
Rate constant for **emission** k^0_e is related to ε by:

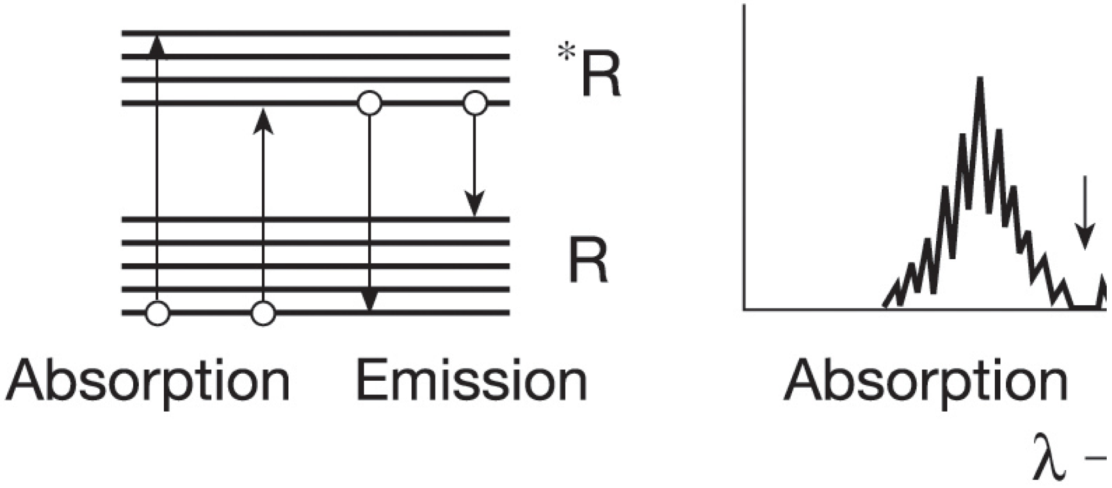
$$\boxed{k^0_e \sim 4.3\text{x}10^{-9} \, \nu^{-2}_0 \int \varepsilon \, d\nu \sim \nu^{-2}_0 f}$$



$k_e (s^{-1})$	Example	Transition type	ε_{max}	f
10^9	*p*-Terphenyl	$S_1(\pi,\pi^*) \rightarrow S_0$	3×10^4	1
10^8	Perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	4×10^4	10^{-1}
10^7	1,4-Dimethyl-benzene	$S_1(\pi,\pi^*) \rightarrow S_0$	7×10^2	10^{-2}
10^6	Pyrene	$S_1(\pi,\pi^*) \rightarrow S_0$	5×10^2	10^{-3}
10^5	Acetone	$S_1(n,\pi^*) \rightarrow S_0$	10	10^{-4}

Shapes of Absorption Spectra



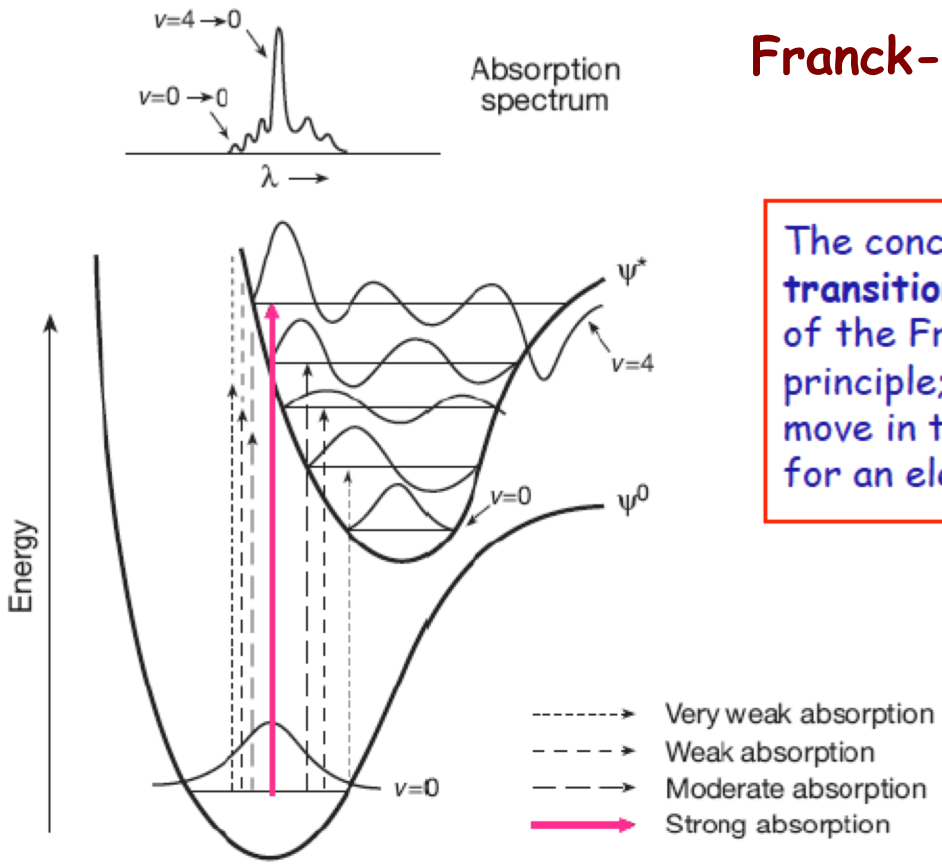


Vibrational Part Limits the Electronic Transition

Electron jump between orbitals generally takes ~ 10^{-15} to 10^{-16} s

Nuclear vibrations take ~ 10^{-13} to 10^{-14} s

In the time scale of electronic transition nuclei will remain stationary



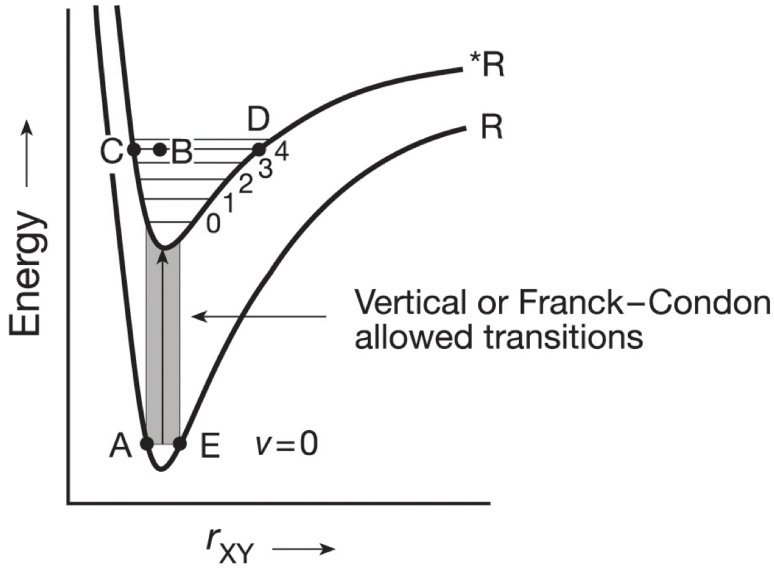
Franck-Condon Principle

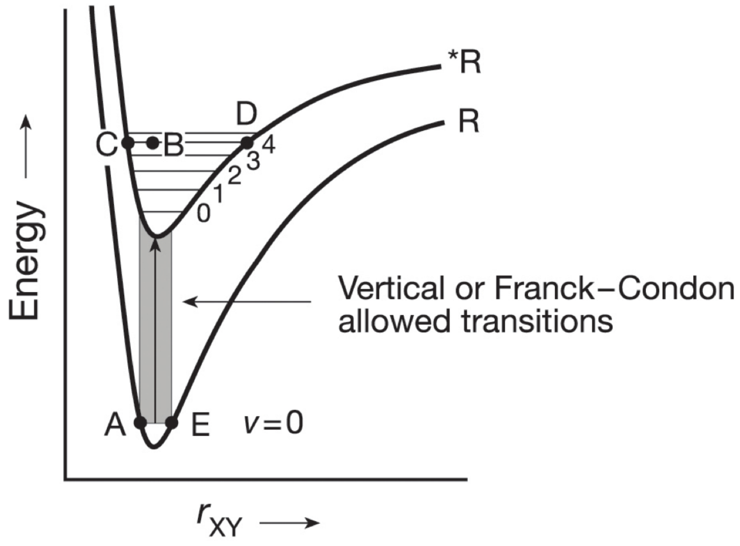
The concept of **vertical transitions** is a key aspect of the Frank-Condon principle; i.e., nuclei do not move in the time required for an electron transition.

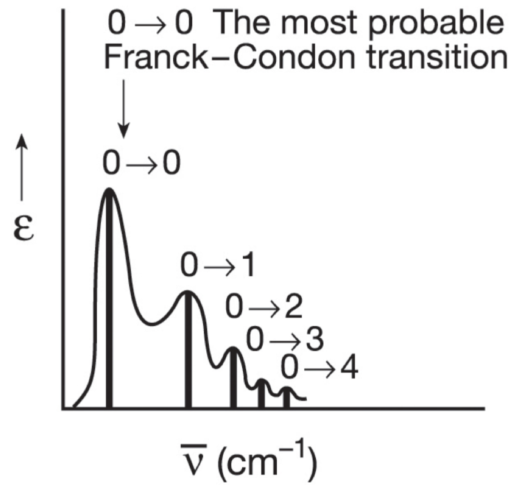
Franck

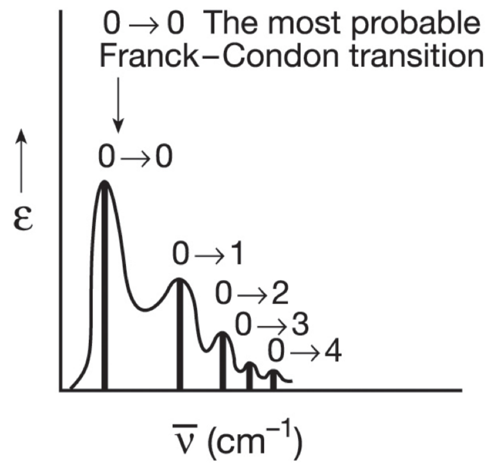
Condon

Franck-Condon Principle

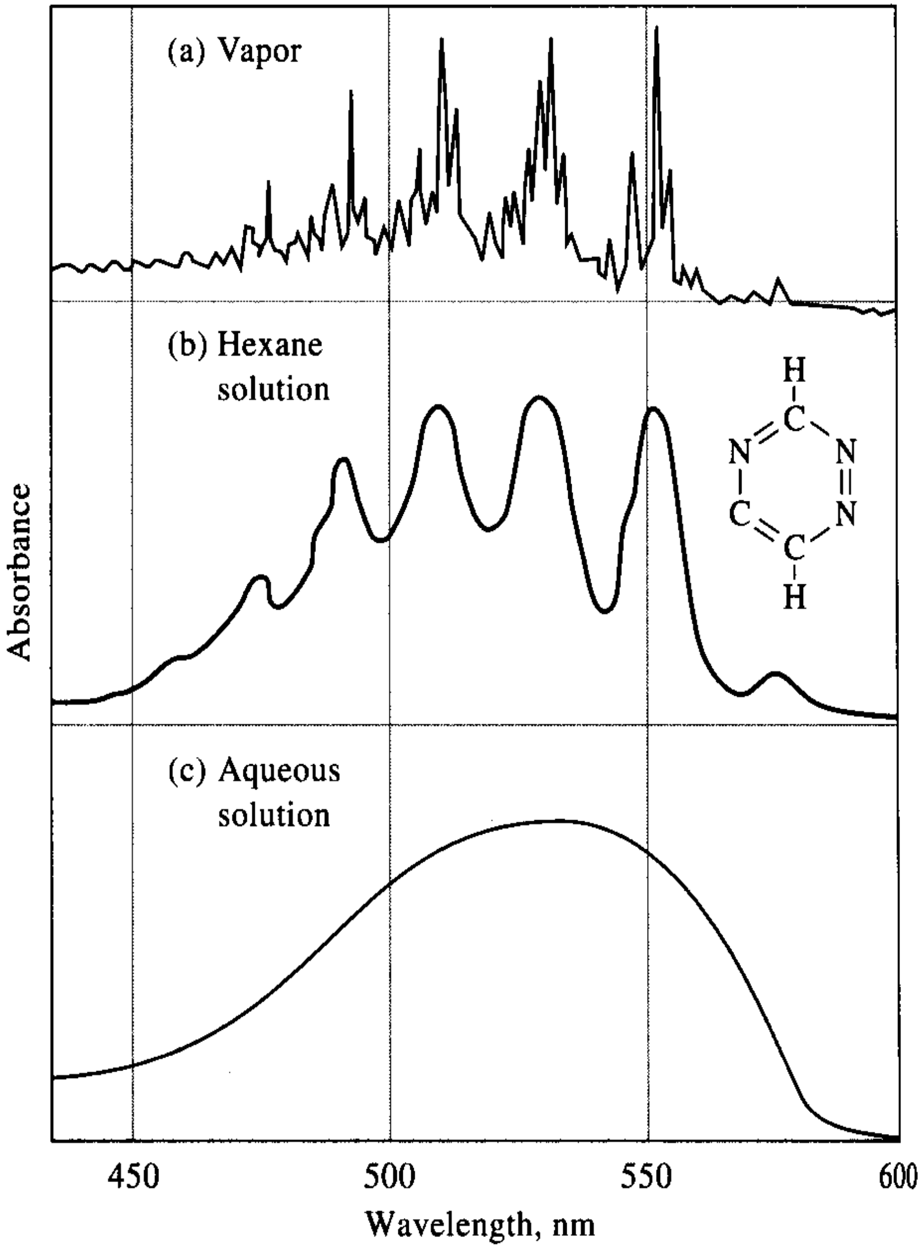




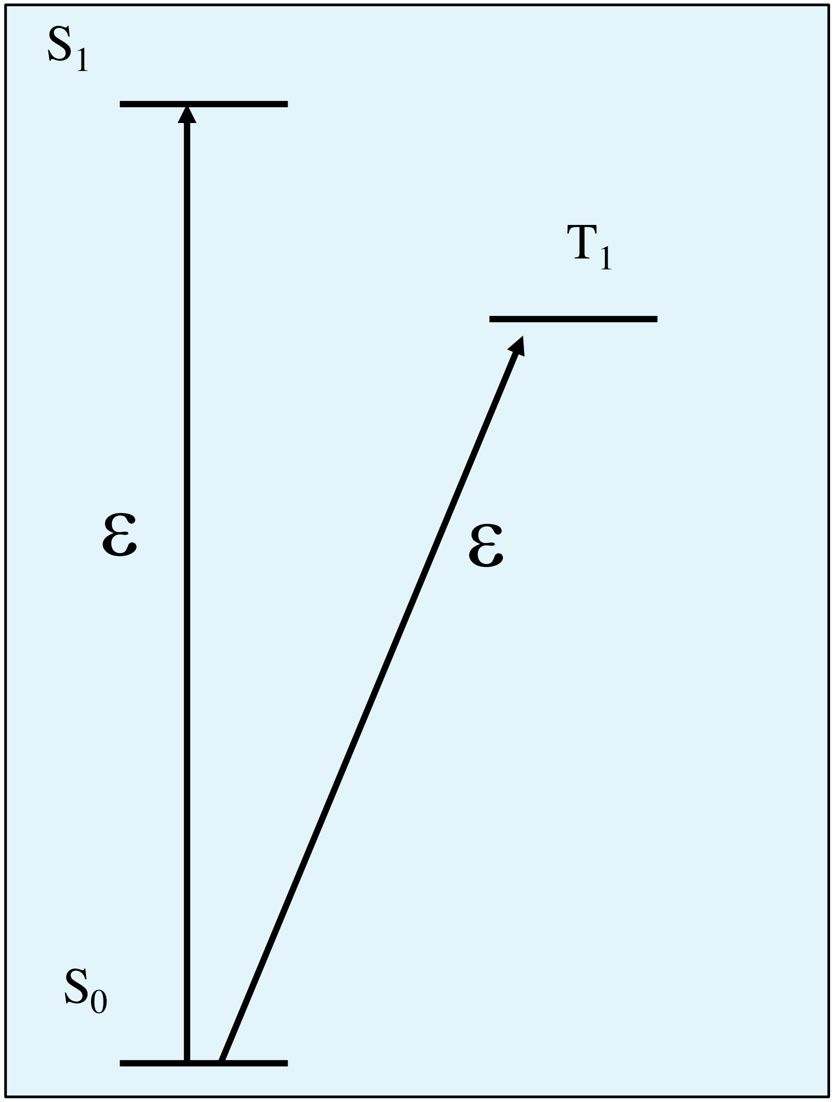


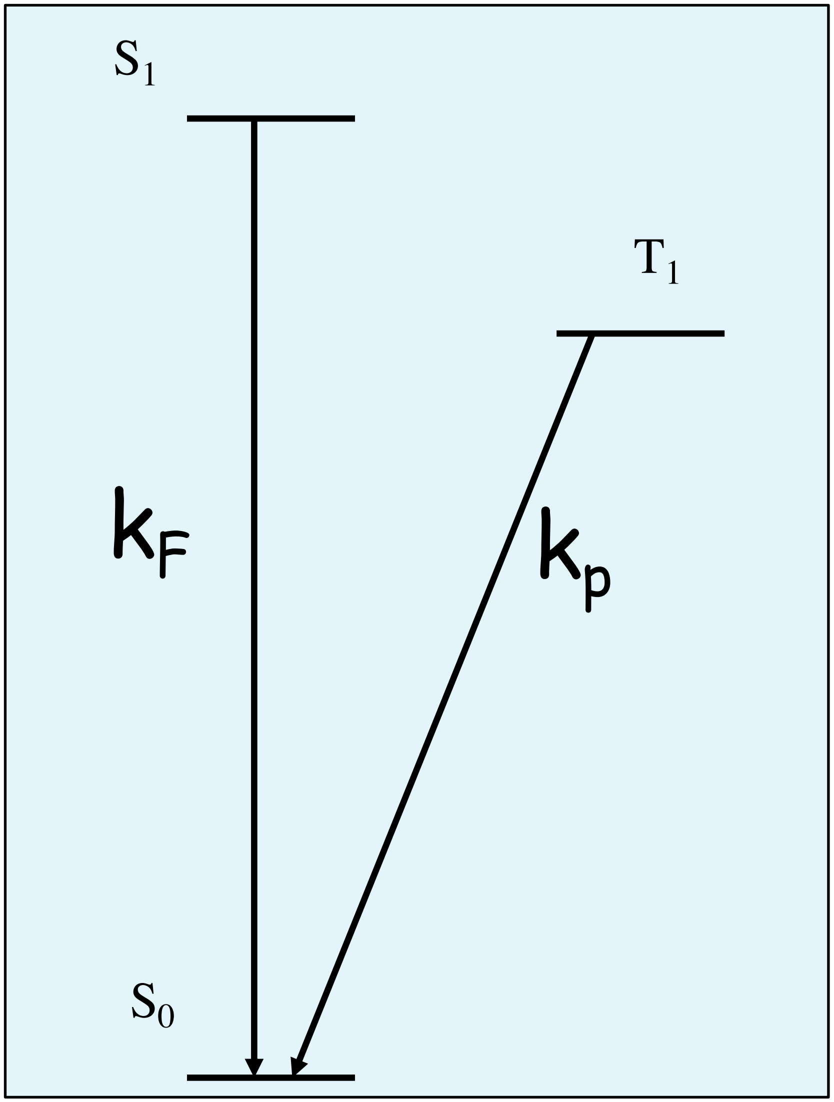


Shapes of Absorption Spectra: medium dependent



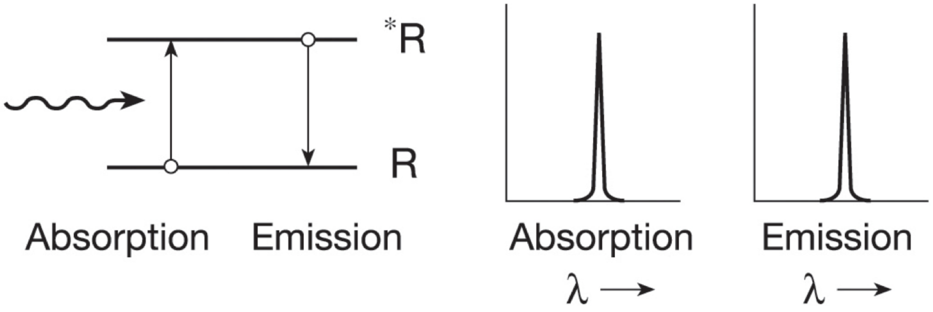
Same Rules for Excitation & De-excitation





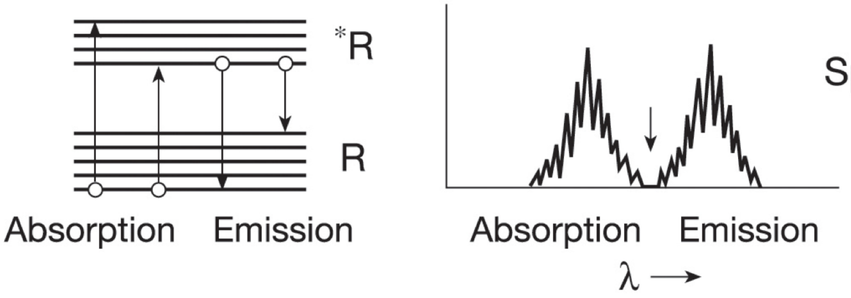
Shapes of Absorption and Emission Spectra

(a)
Atom



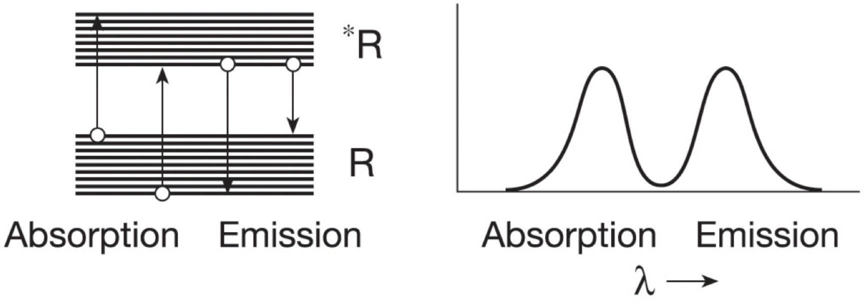
Sharp-line
spectrum

(b)
Molecule
with distinct
substates



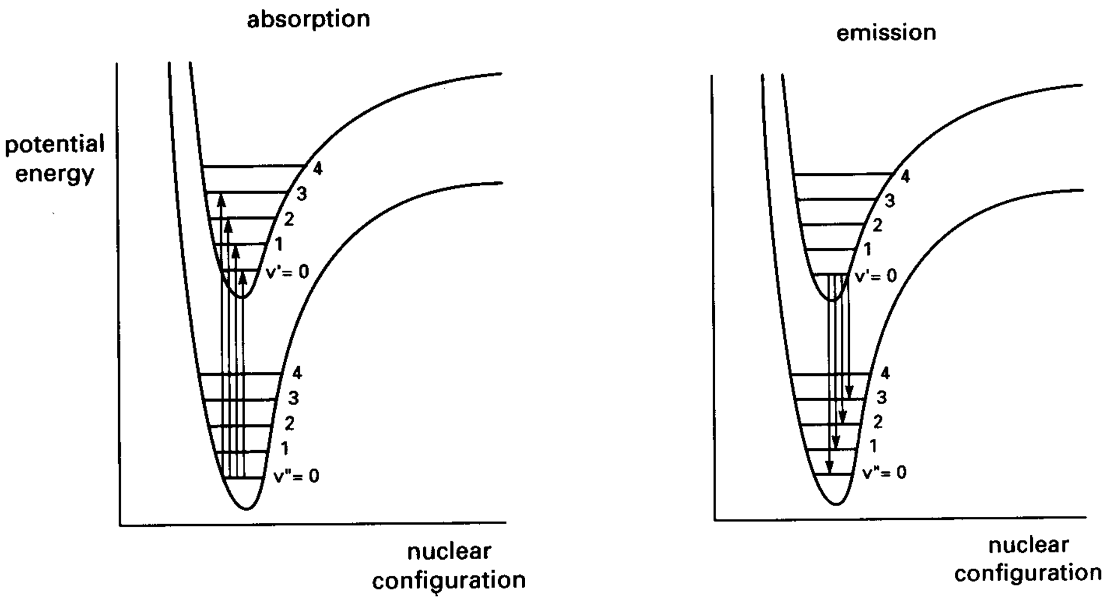
Spectrum with
vibrational
structure

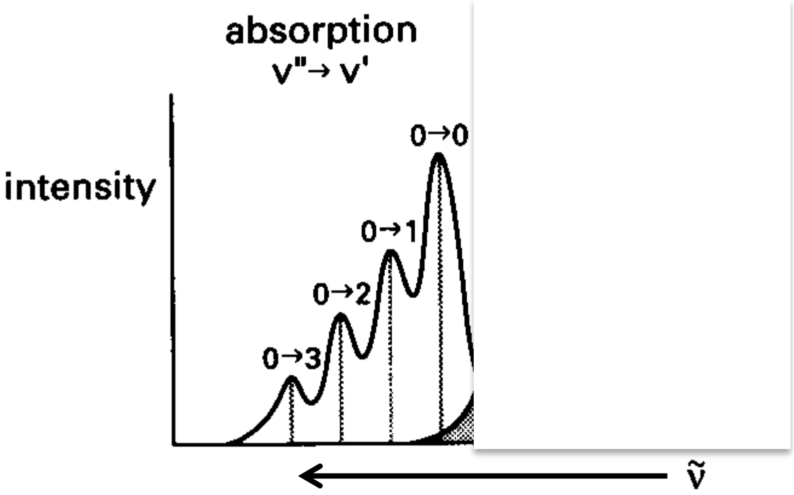
(c)
Molecule
with many
unresolved
substates



Broad-band
spectrum

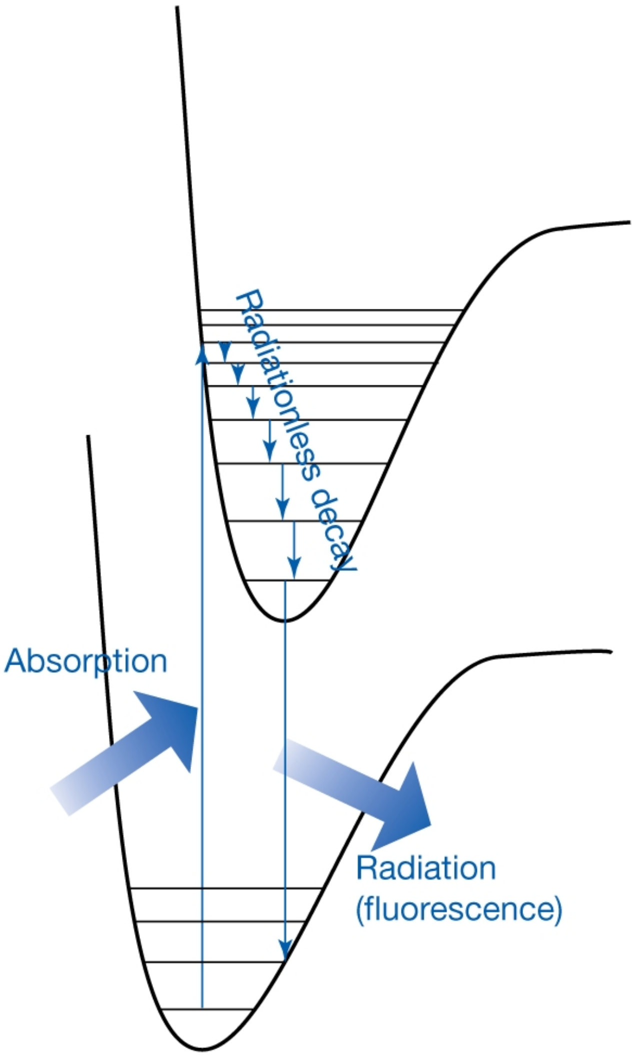
Mirror Image Rule and Stoke's Shift





G.G. Stokes (1819-1903)

Owing to a decrease in bonding of the molecule in its excited state compared to that of the ground state, the energy difference between S_0 and S_1 is lowered prior to fluorescence emission (in about 0.1 to 100 ps). This is called Stokes' shift.

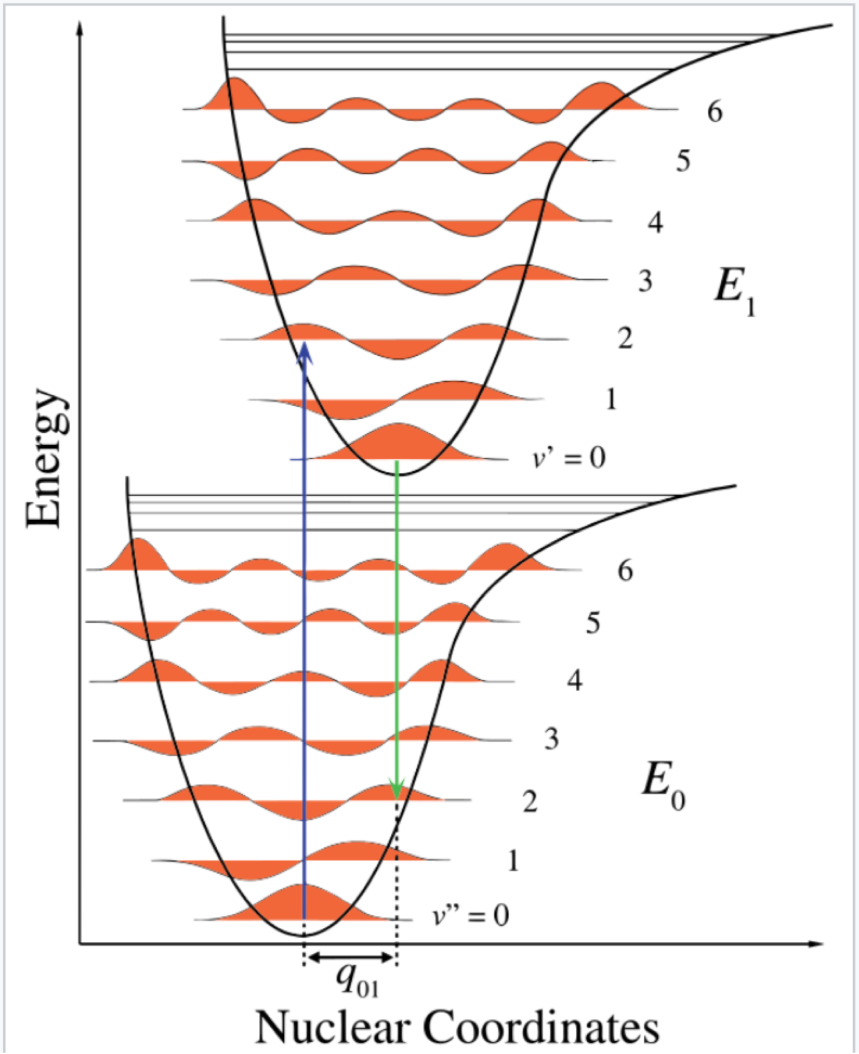


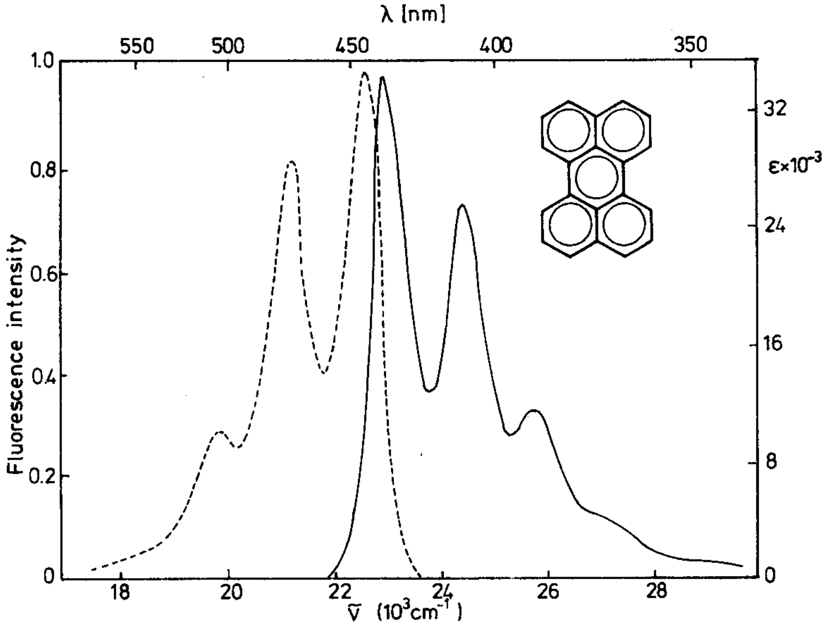
Absorption spectrum determined by (a) vibronic selection rules and (b) Franck-Condon overlap

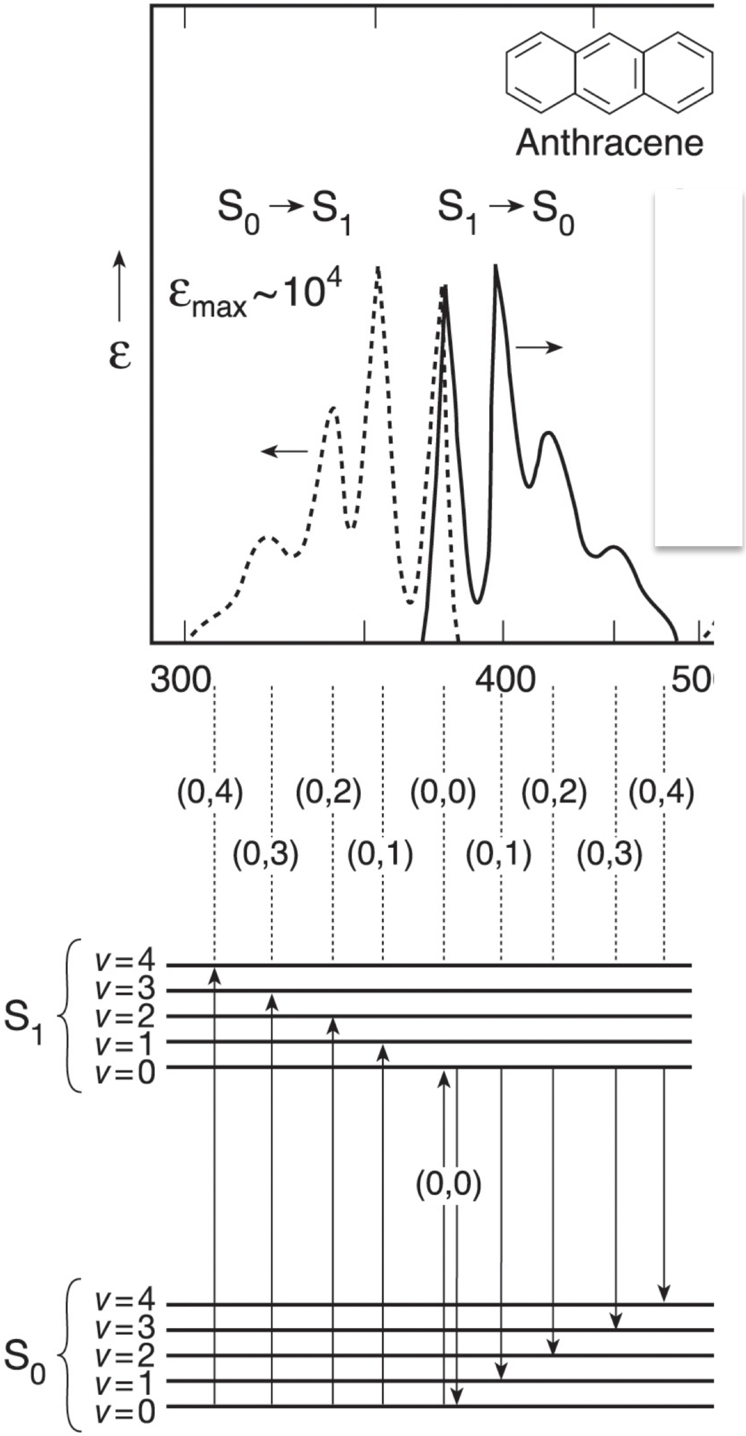
Emission (fluorescence) or other processes follow relaxation to lowest vibrational level of S_1

Shapes of Absorption and Emission Spectra

Mirror Image Rule, Franck-Condon Principle, and Stoke’s shift



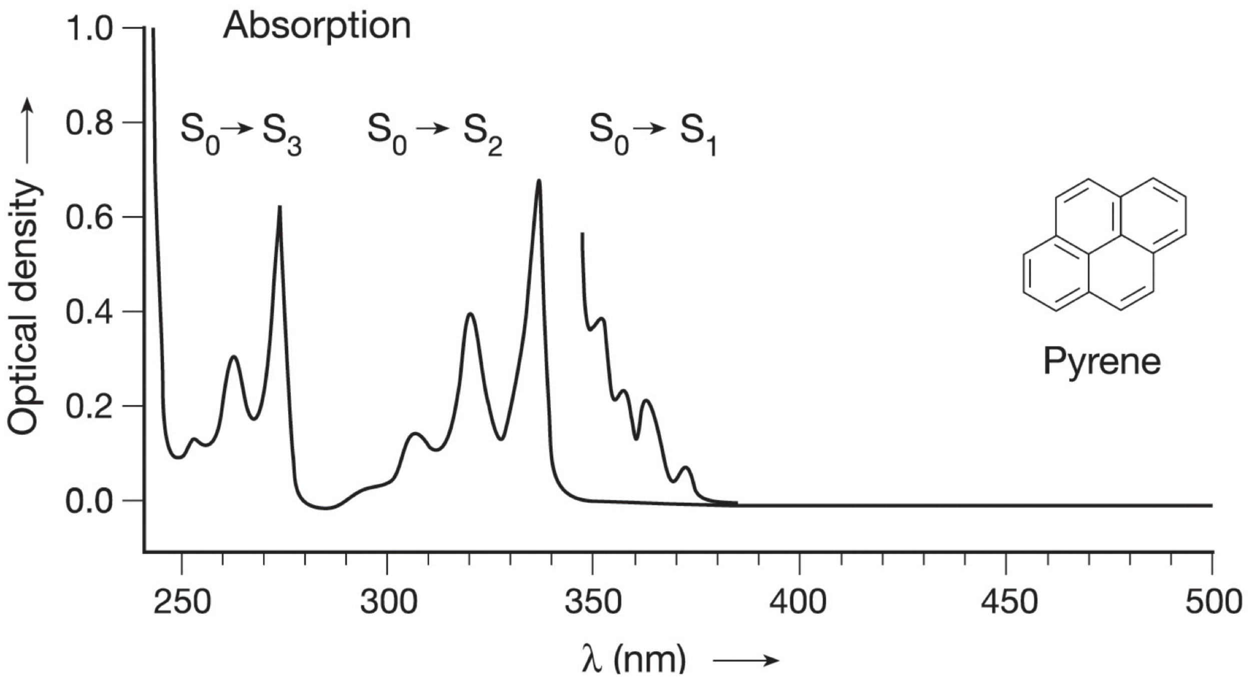


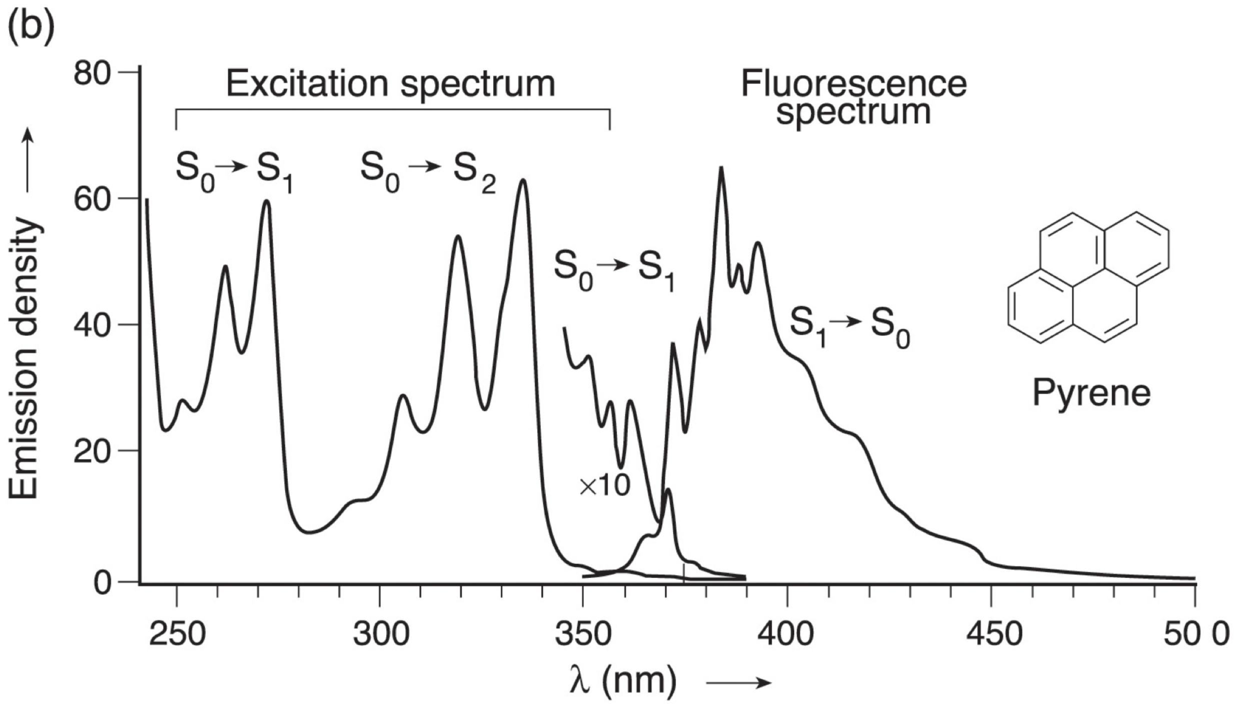

Anthracene
$S_0 \rightarrow S_1$
$S_1 \rightarrow S_0$
$\varepsilon_{max} \sim 10^4$
ε
300
400
(0,4)
(0,2)
(0,0)
(0,2)
(0,4)
(0,3)
(0,1)
(0,1)
(0,3)
S_1
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$
(0,0)
S_0
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$

Absorption

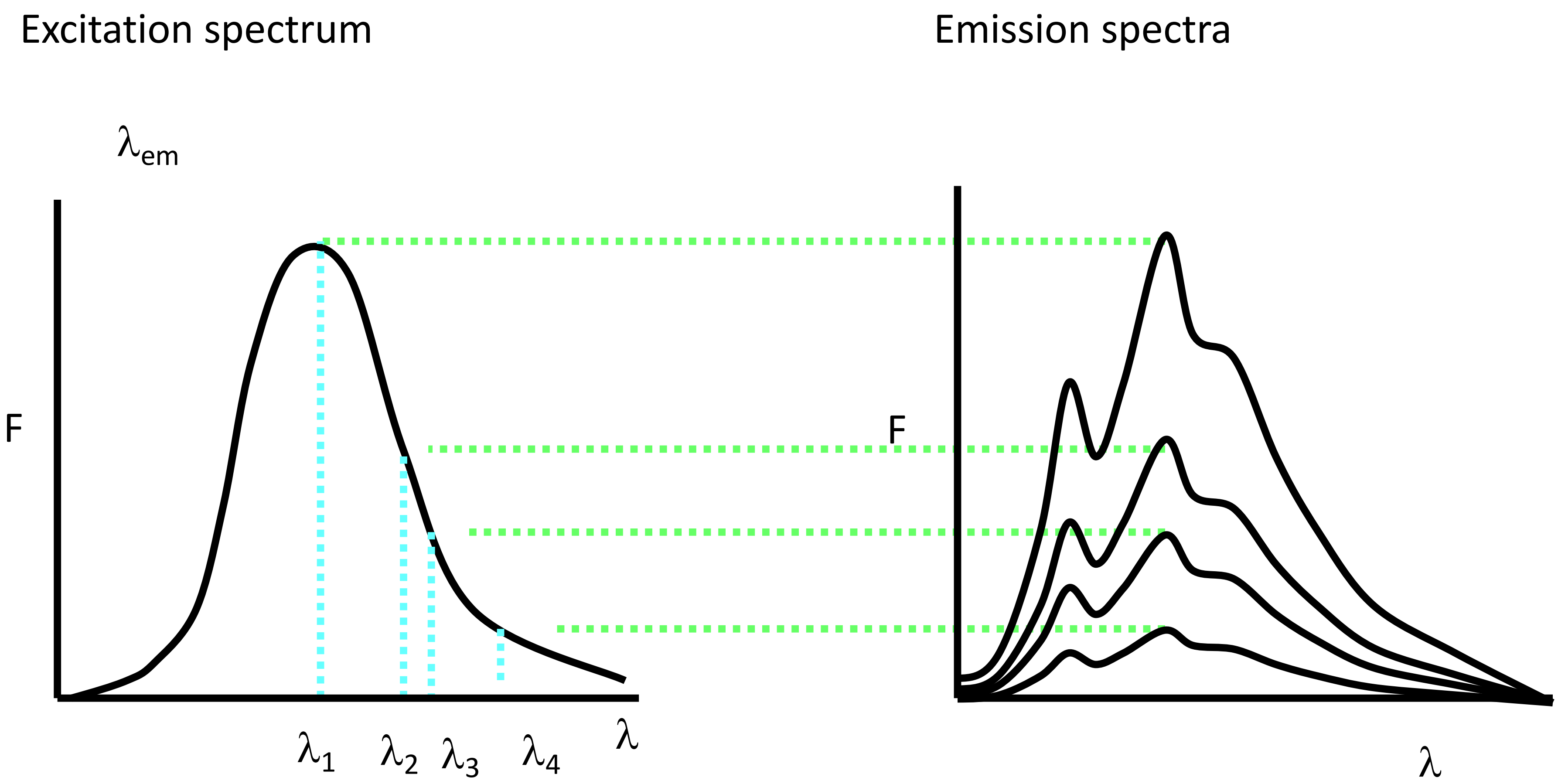
Emission

Excitation





Excitation and emission spectra

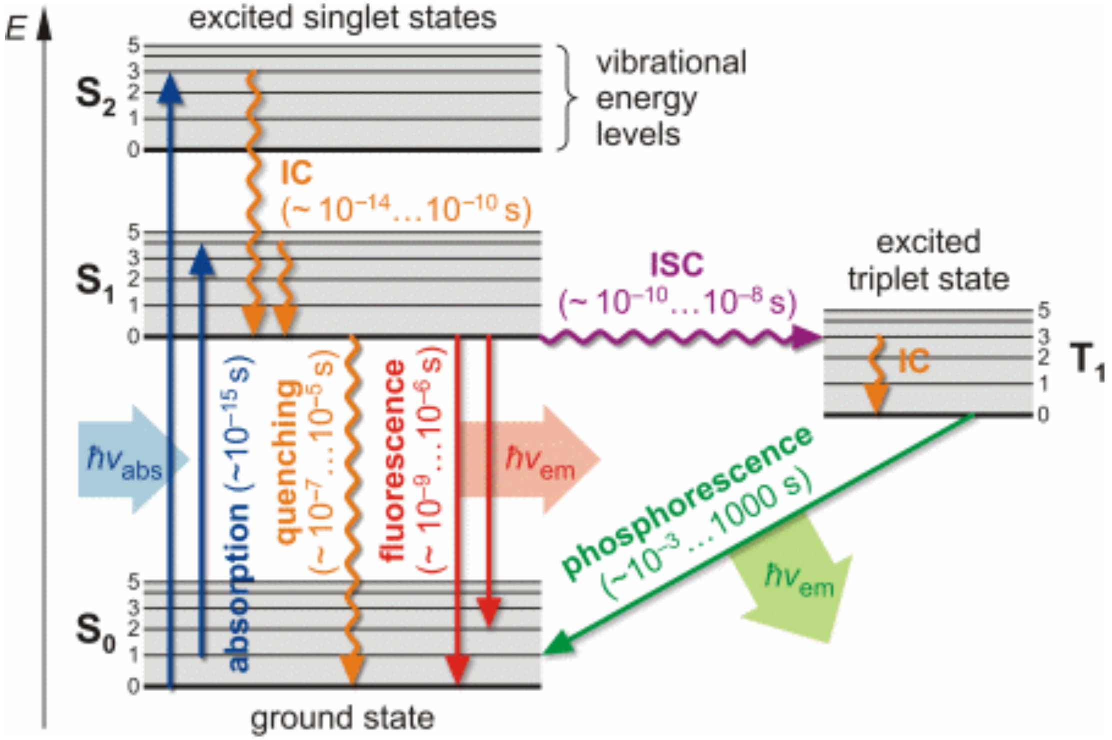


Excitation spectrum

Emission spectra

Vavilov's rule

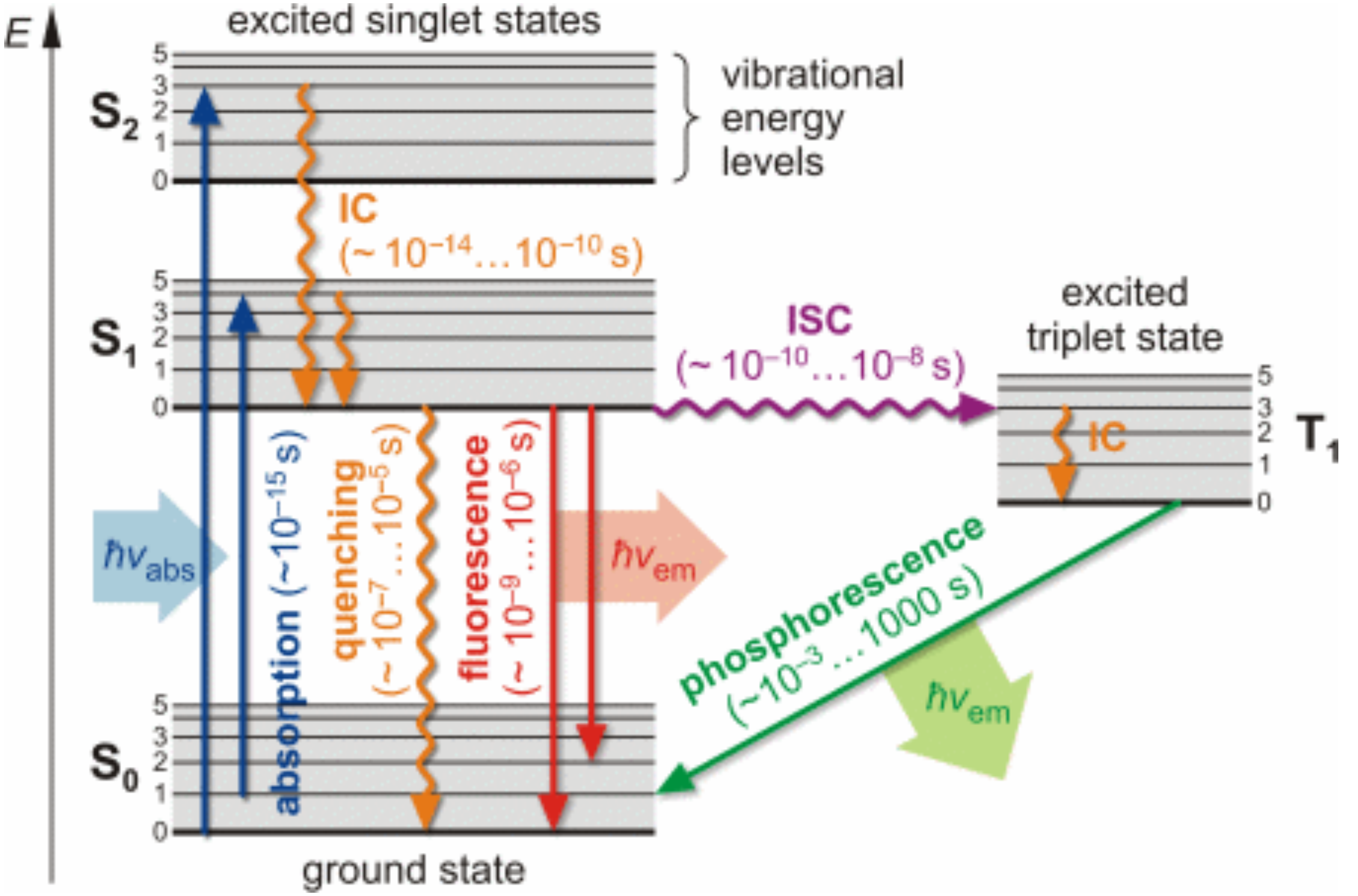
The quantum yield of fluorescence and the quantum yield of phosphorescence are independent of initial excitation energy.

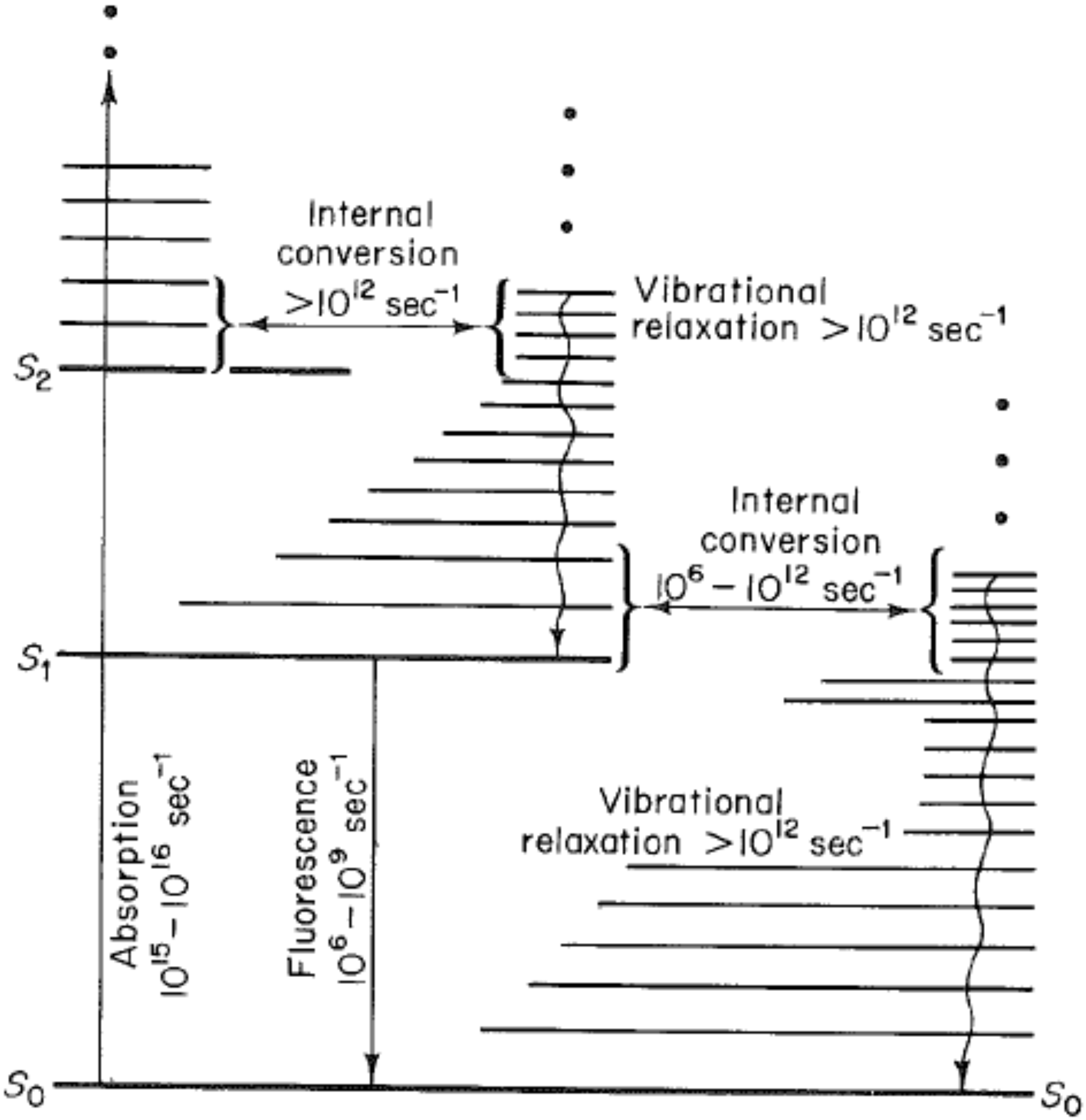


S. Vavilov

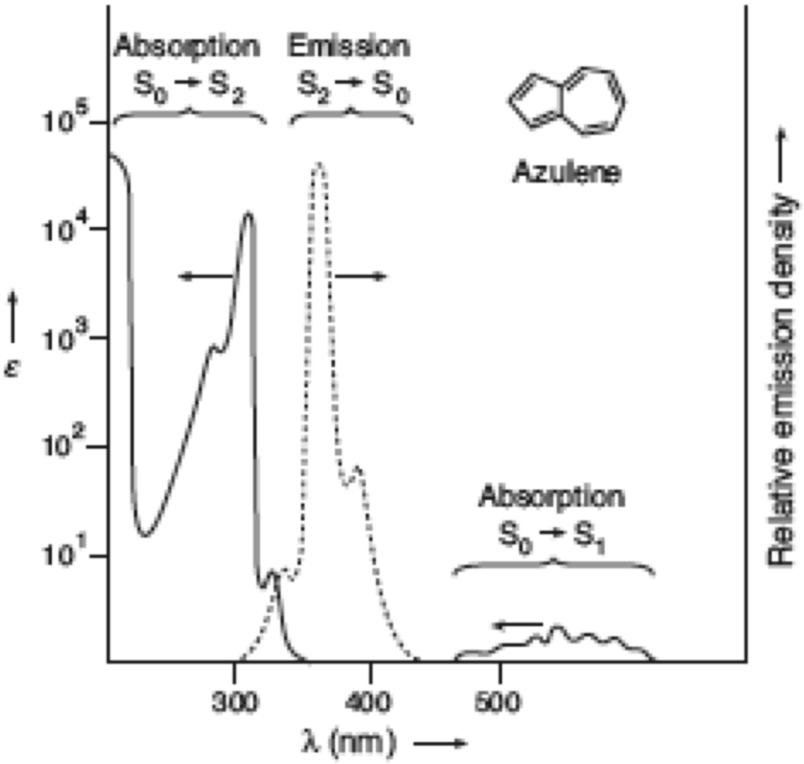
Kasha's rule

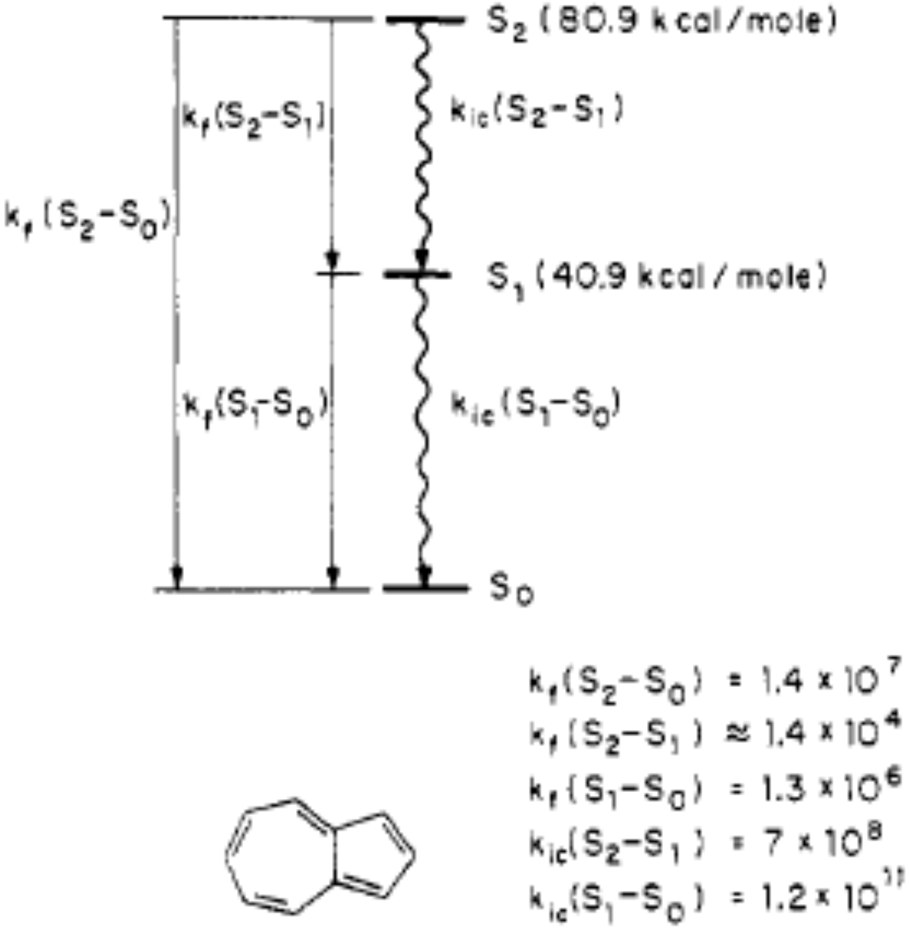
Fluorescence occurs only from S_1 to S_0; phosphorescence occurs only from T_1 to S_0; S_n and T_n emissions are extremely rare.




Internal conversion >10^12 sec^-1
Vibrational relaxation >10^12 sec^-1
S2
Internal conversion 10^6 – 10^12 sec^-1
S1
Absorption 10^15 – 10^16 sec^-1
Fluorescence 10^6 – 10^9 sec^-1
Vibrational relaxation >10^12 sec^-1
S0
S0

Exceptions





$k_f(S_2-S_0) = 1.4 \times 10^7$

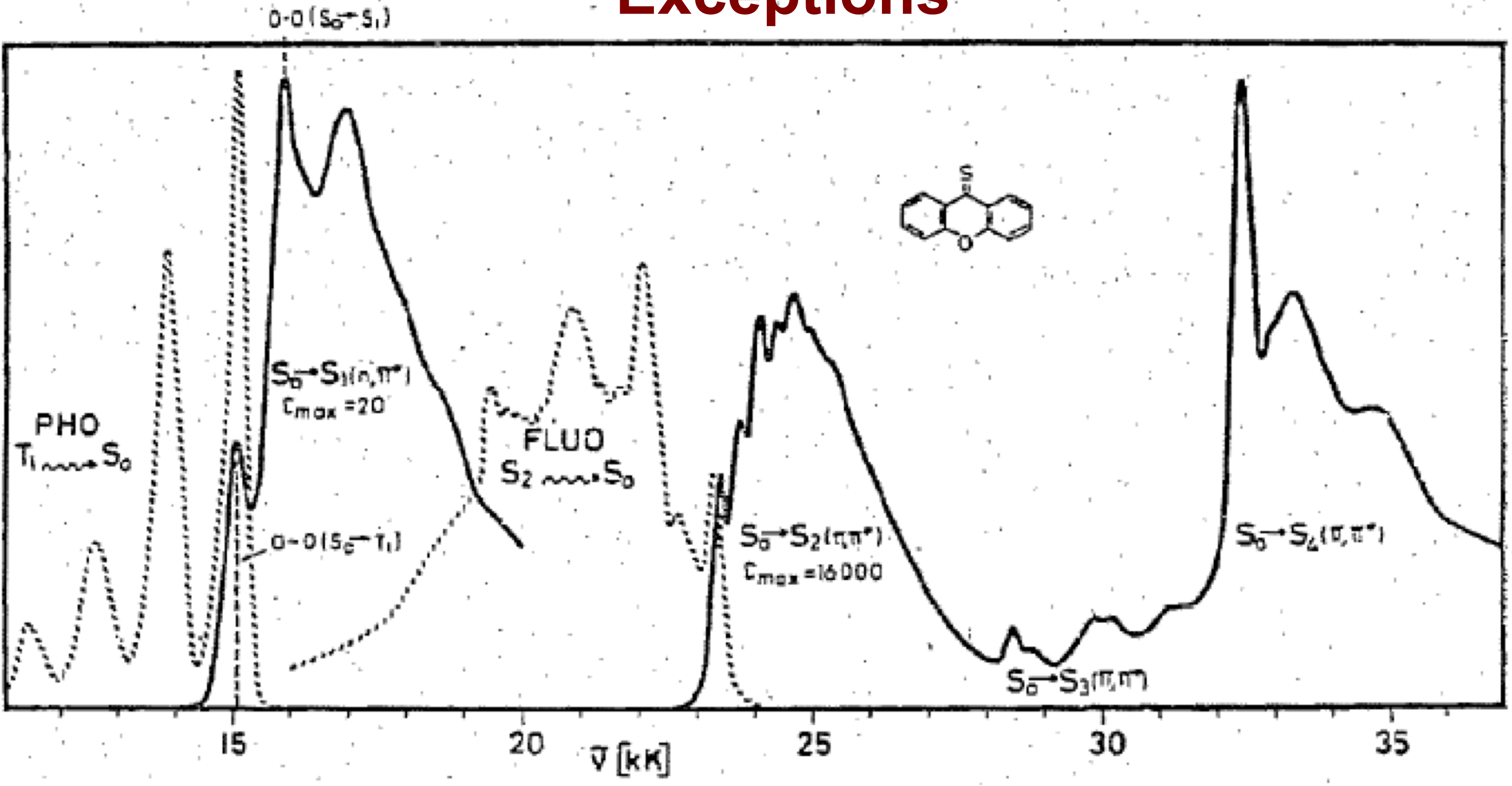
$k_f(S_2-S_1) \approx 1.4 \times 10^4$

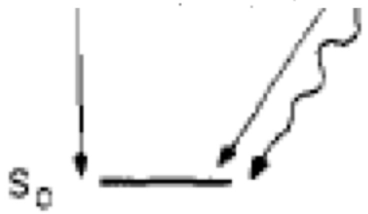
$k_f(S_1-S_0) = 1.3 \times 10^6$

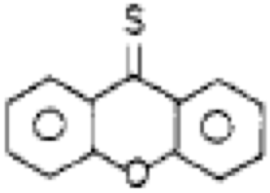
$k_{ic}(S_2-S_1) = 7 \times 10^8$

$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

Exceptions







$k_f(S_2-S_0) \approx 10^8$

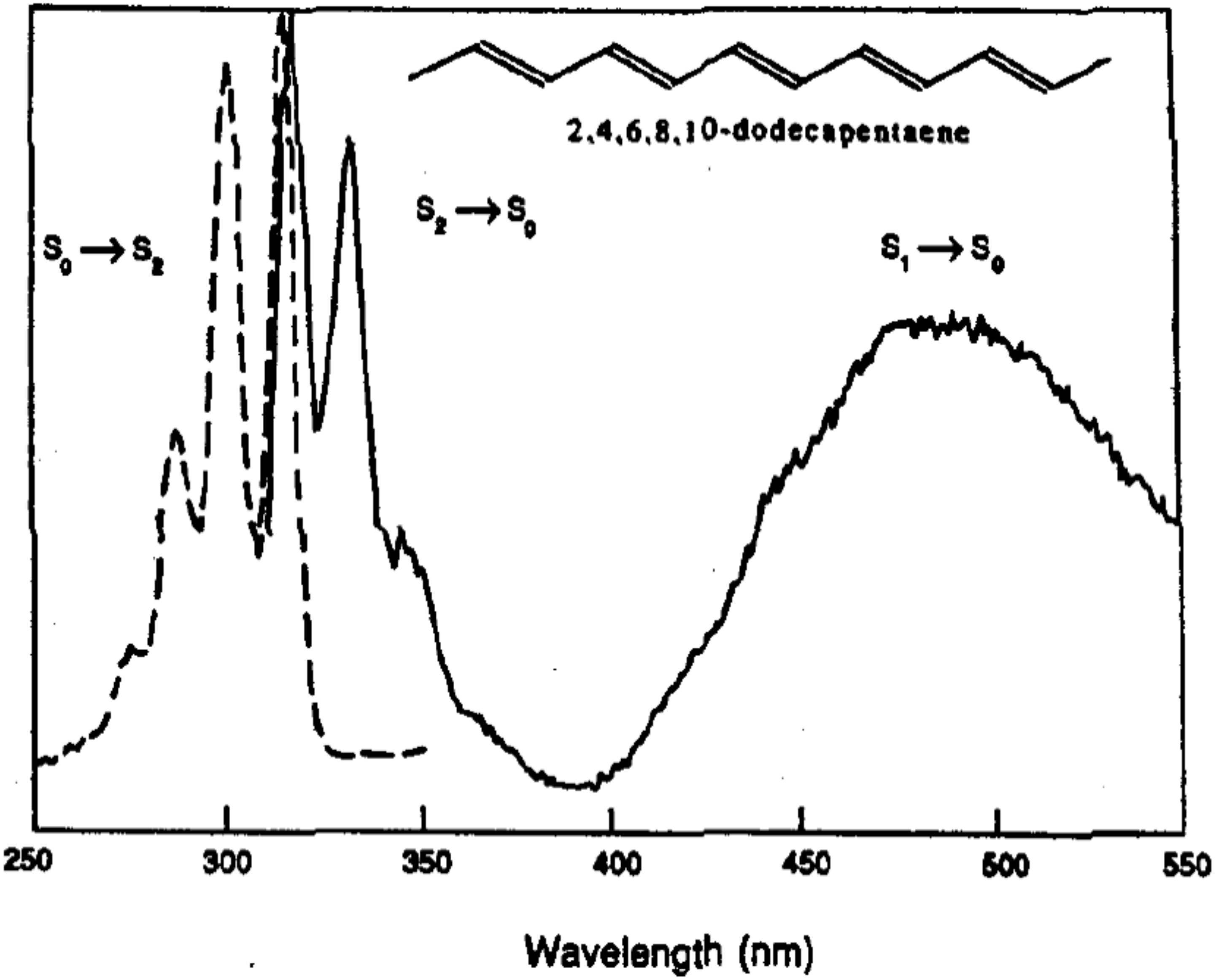
$k_{ic}(S_2-S_1) \approx 10^{10}$

$k_{isc}(S_1-T_1) > 10^{11}$

$k_{isc}(T_1-S_0) = 2 \times 10^4$

$k_p(T_1-S_0) = 7.5 \times 10^3$

Exceptions


2,4,6,8,10-dodecapentaene
$S_0 \rightarrow S_2$
$S_2 \rightarrow S_0$
$S_1 \rightarrow S_0$
250
300
350
400
450
500
550
Wavelength (nm)

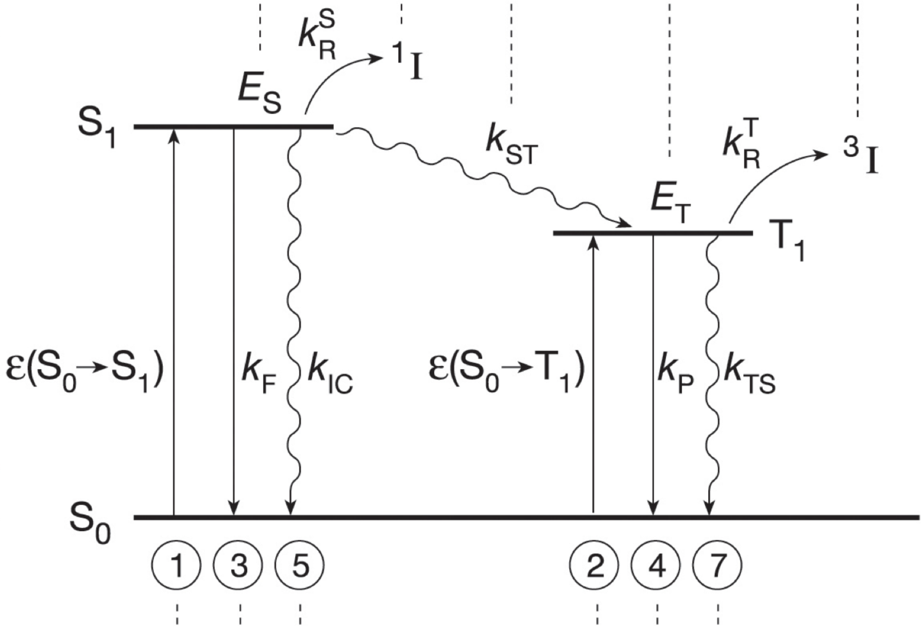
Competition with fluorescence

$$S_0 + h\nu \xrightarrow{I_{abs}} S_1$$

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

$$S_1 \xrightarrow{k_{isc}} T_1$$

$$S_1 \xrightarrow{k_{ic}} S_0$$



$$\phi_f = \frac{k_f[S_1]}{(k_f + k_{isc} + k_{ic} + \ldots)[S_1]}$$

$$\tau_f = \frac{1}{k_f + k_{isc} + k_{ic} + \ldots.}$$

Quantum Yields of Fluorescence

$$\Phi_F = k^0_e(k^0_e + \Sigma k_i)^{-1}$$

k_i is very sensitive to experimental conditions:

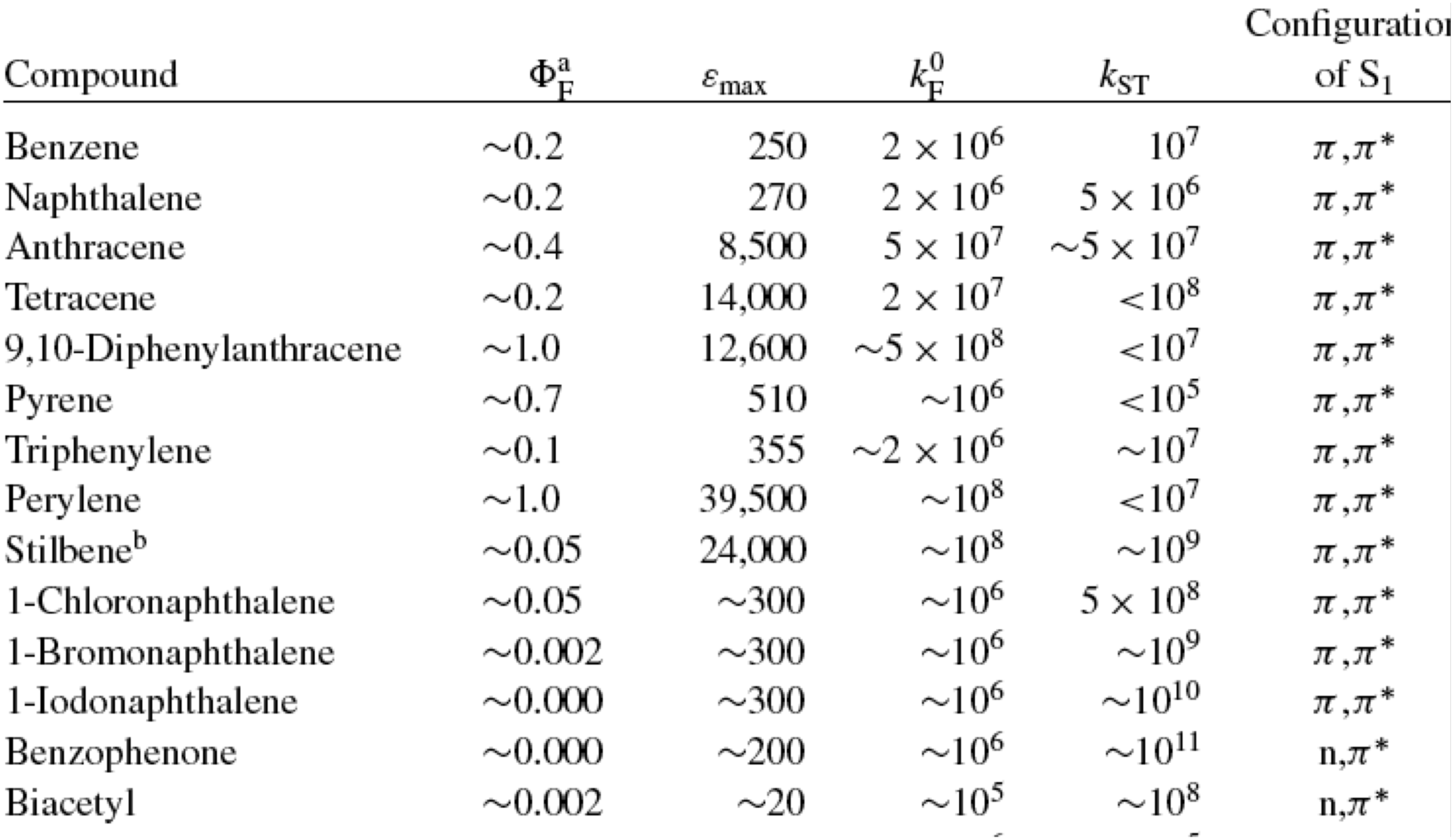
- Diffusional quenching and thermal chemical reactions may compete with radiative decay

- Certain molecular motions may also provide competitive decay pathways

- Measurements at low temperature (77K) cause k_i terms to become small relative to k^0_e

$$\Phi_F = k_F(k_F + k_{ST})^{-1} = k_F\,\tau$$

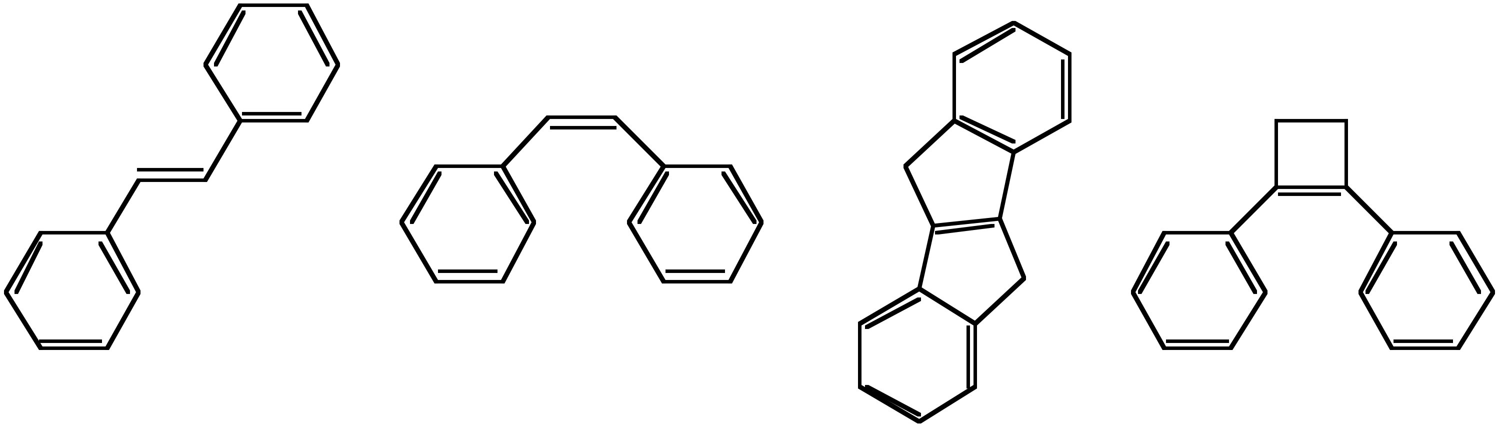
Variations in Quantum Yields of Fluorescence



Compound	Φ_F^a	ε_{max}	k_F^0	k_{ST}	Configuratio of S_1
Benzene	~0.2	250	2×10^6	10^7	π,π^*
Naphthalene	~0.2	270	2×10^6	5×10^6	π,π^*
Anthracene	~0.4	8,500	5×10^7	$\sim 5 \times 10^7$	π,π^*
Tetracene	~0.2	14,000	2×10^7	$< 10^8$	π,π^*
9,10-Diphenylanthracene	~1.0	12,600	$\sim 5 \times 10^8$	$< 10^7$	π,π^*
Pyrene	~0.7	510	$\sim 10^6$	$< 10^5$	π,π^*
Triphenylene	~0.1	355	$\sim 2 \times 10^6$	$\sim 10^7$	π,π^*
Perylene	~1.0	39,500	$\sim 10^8$	$< 10^7$	π,π^*
Stilbene[b]	~0.05	24,000	$\sim 10^8$	$\sim 10^9$	π,π^*
1-Chloronaphthalene	~0.05	~300	$\sim 10^6$	5×10^8	π,π^*
1-Bromonaphthalene	~0.002	~300	$\sim 10^6$	$\sim 10^9$	π,π^*
1-Iodonaphthalene	~0.000	~300	$\sim 10^6$	$\sim 10^{10}$	π,π^*
Benzophenone	~0.000	~200	$\sim 10^6$	$\sim 10^{11}$	n,π^*
Biacetyl	~0.002	~20	$\sim 10^5$	$\sim 10^8$	n,π^*

Factors Controlling Quantum Yield of Fluorescence

Rigid *vs* non-rigid molecules



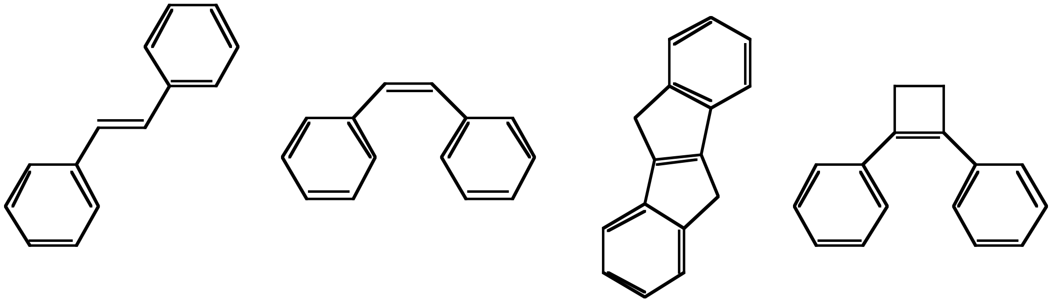
25°C	0.05	0.00	1.0	1.0
77 K	0.75	0.75	1.0	1.0

Molecular rigidity enhances Φ_F

Factors Controlling Quantum Yield of Fluorescence

Rigid *vs* non-rigid molecules

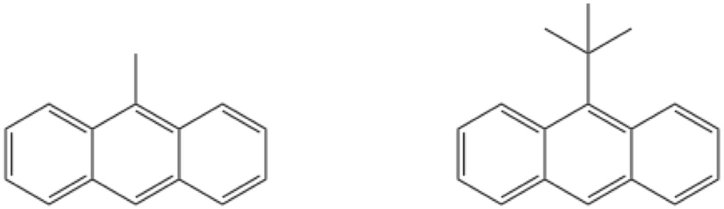
Bond rotation



25°C	0.05	0.00	1.0	1.0
77 K	0.75	0.75	1.0	1.0

Molecular rigidity enhances Φ_F

Loose Bolt



0.29 0.011

Quantum Yields of Fluorescence

$$\Phi_F = k^0_e(k^0_e + \Sigma k_i)^{-1}$$

k_i is very sensitive to experimental conditions:

- Diffusional quenching and thermal chemical reactions may compete with radiative decay
- Certain molecular motions may also provide competitive decay pathways
- Measurements at low temperature (77K) cause k_i terms to become small relative to k^0_e

Fluorescence generalizations

1. **Most rigid aromatic hydrocarbons (benzene, naphthalene, anthracene, pyrene, etc.) and their derivatives possess measurable, but variable, fluorescence quantum yields ($1 > \Phi_F > 0.01$), even at 77 K.**

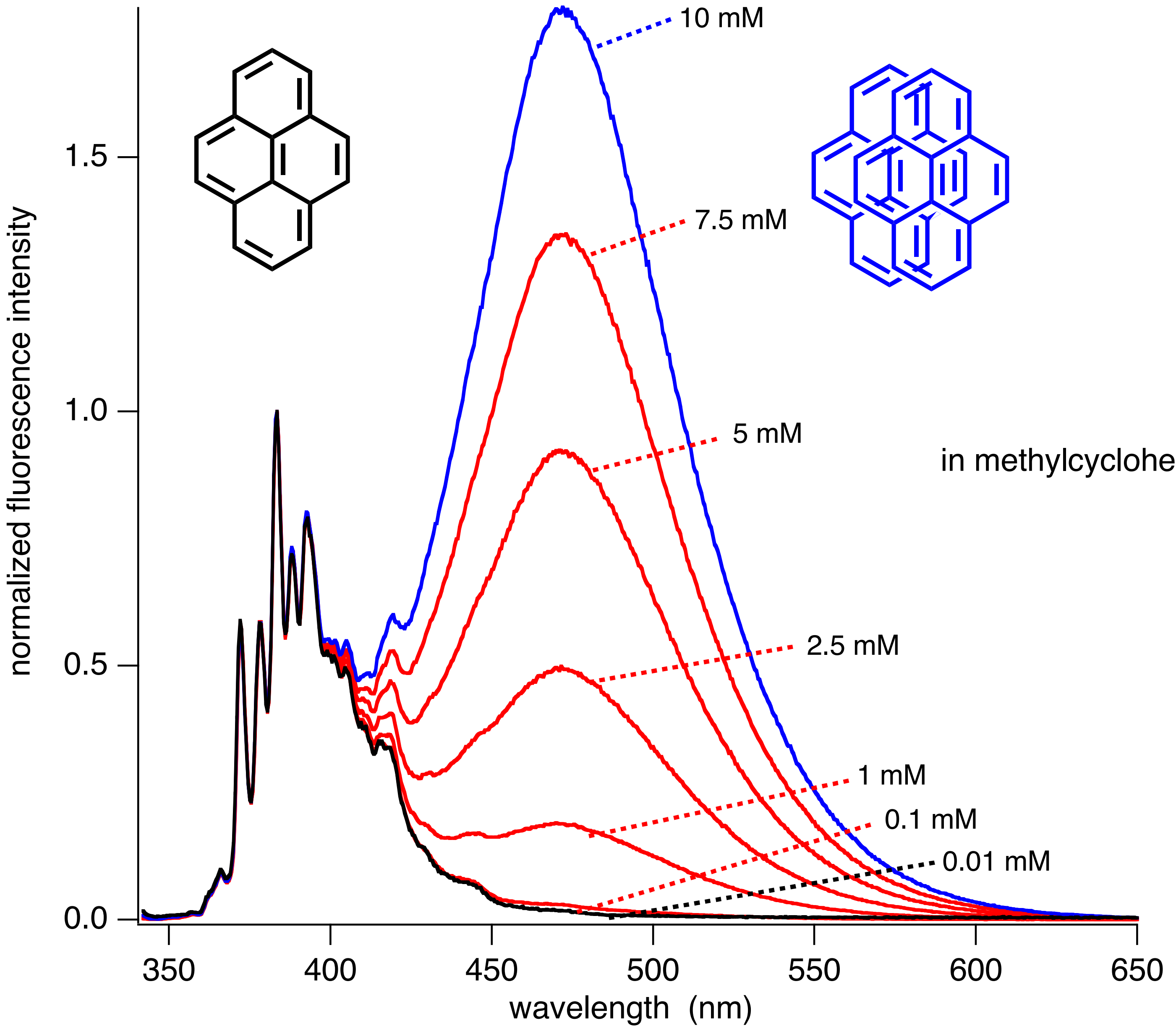
2. **Substitution of Cl, Br, or I, for H on an aromatic ring generally results in a decrease in Φ_F such that $\Phi_F^H > \Phi_F^{Cl} > \Phi_F^{Br} > \Phi_F^{I} >$ (eg. naphthalene vs. halonaphthalene)**

3. **Substitution of C=O for H on an aromatic ring generally results in a substantial decrease in Φ_F (cf. benzene with benzophenone).**

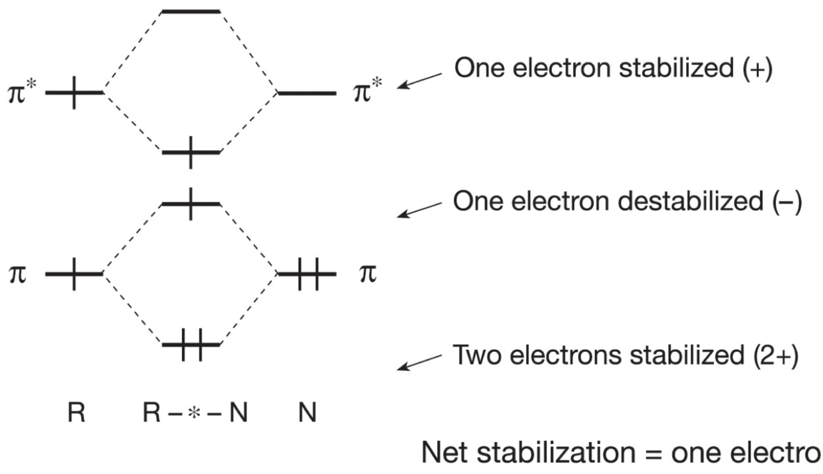
4. **Molecular rigidity (due to structural or environmental constraints) enhances Φ_F (compare. rigid and flexible with stilbenes).**

5. **Low values of Φ_F for nonrigid aromatic hydrocarbons are common and usually the result of competing internal conversion ($S_1 \rightarrow S_0$) or intersystem crossing ($S_1 \rightarrow T_1$) triggered by molecular motion.**

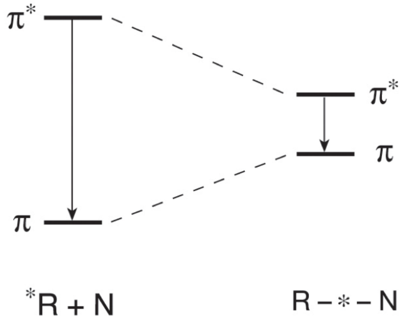
Bimolecular absorption and emission: Excited state complexes



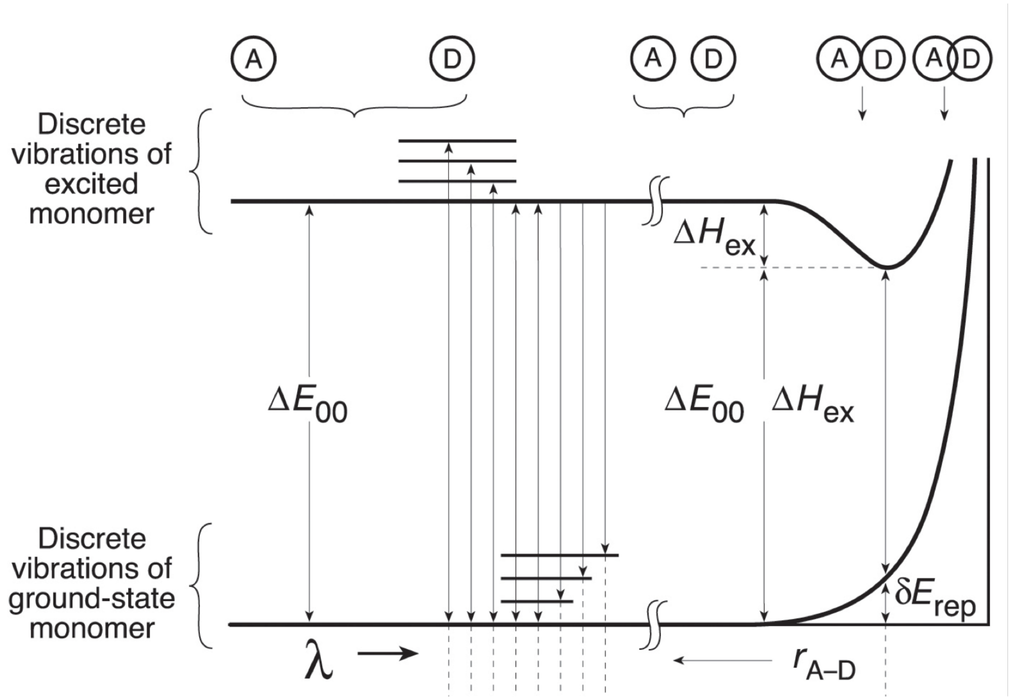
in methylcyclohexane solution



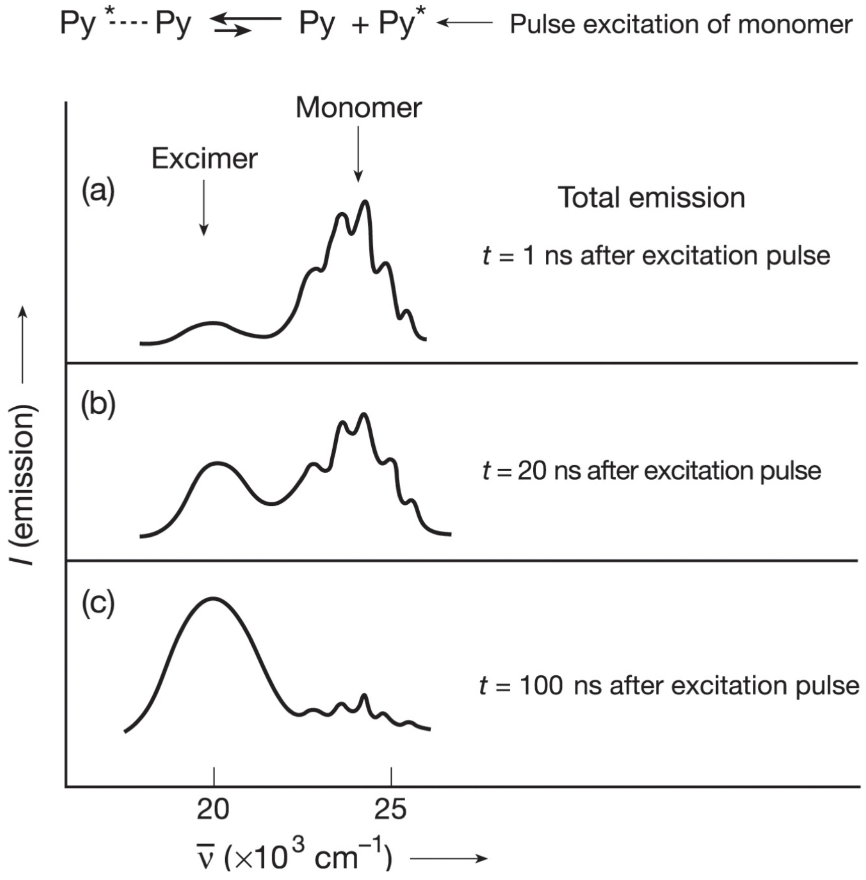
π*
π*
One electron stabilized (+)
One electron destabilized (–)
π
π
Two electrons stabilized (2+)
R
R – * – N
N
Net stabilization = one electron



π*
π*
π
π
*R + N
R – * – N

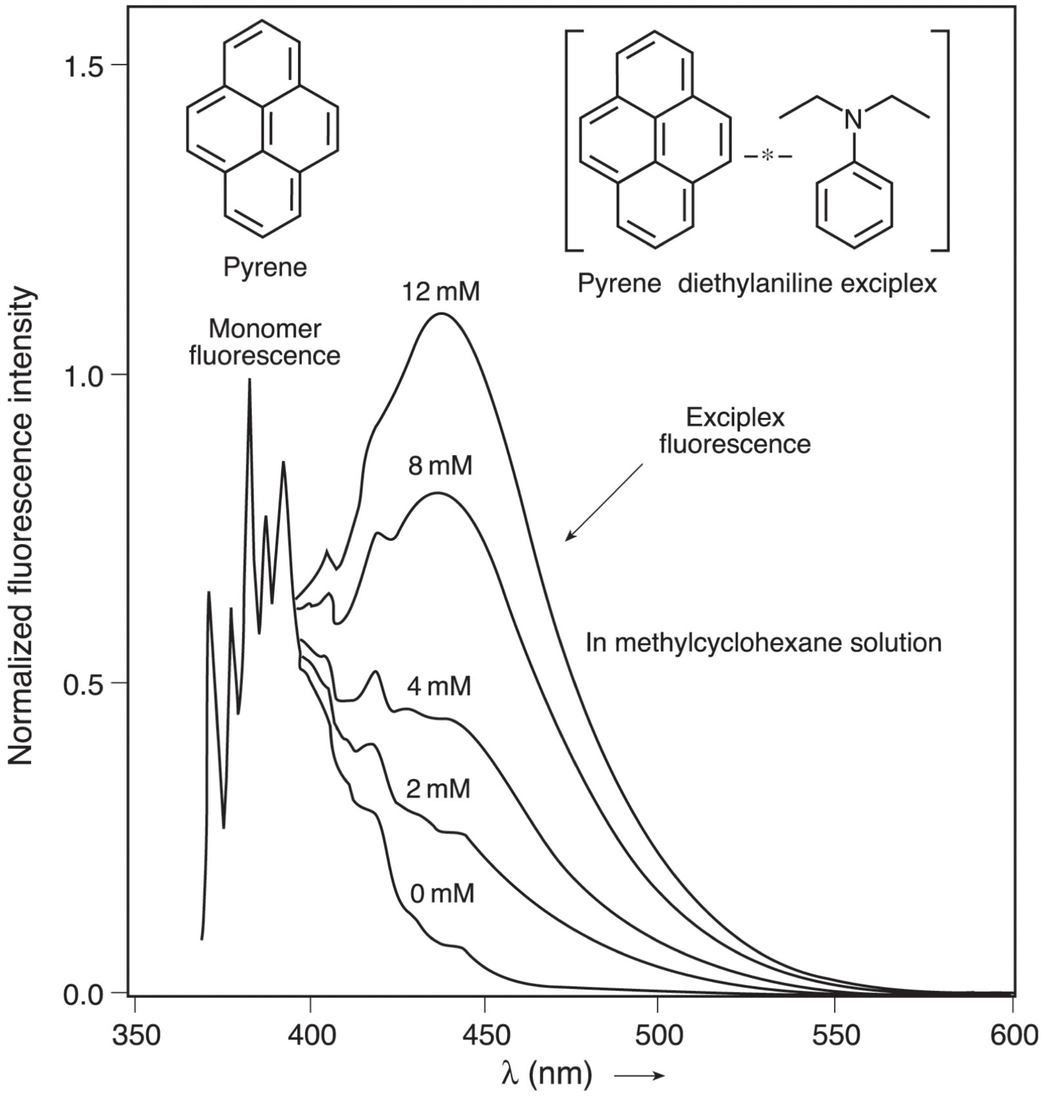


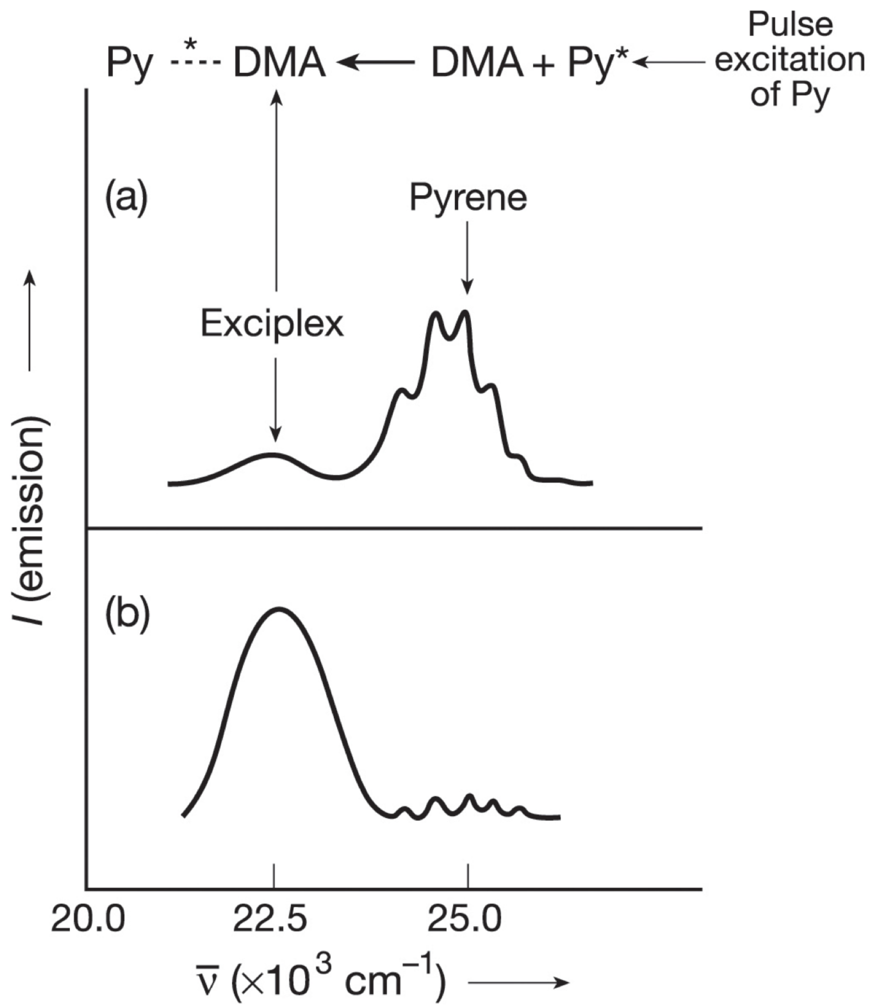
A
D
A
D
A
D
A
D
Discrete vibrations of excited monomer
Discrete vibrations of ground-state monomer
ΔE00
ΔH ex
ΔE00
ΔH ex
δE rep
λ
r A–D



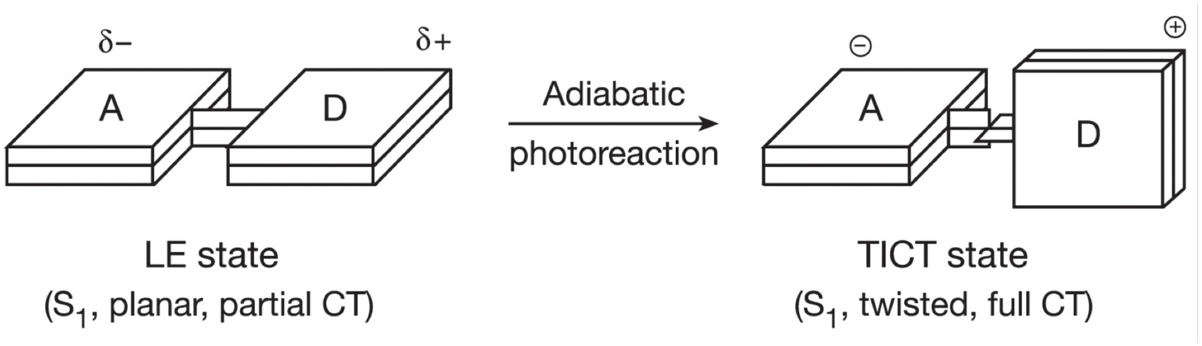
Py *---- Py ⇌ Py + Py* ← Pulse excitation of monomer
Monomer
Excimer
(a)
Total emission
t = 1 ns after excitation pulse
(b)
t = 20 ns after excitation pulse
(c)
t = 100 ns after excitation pulse
I (emission)
20
25
ν̄ (×10³ cm⁻¹)

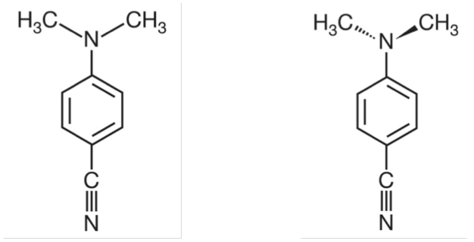
Bimolecular absorption and emission: Excited state complexes

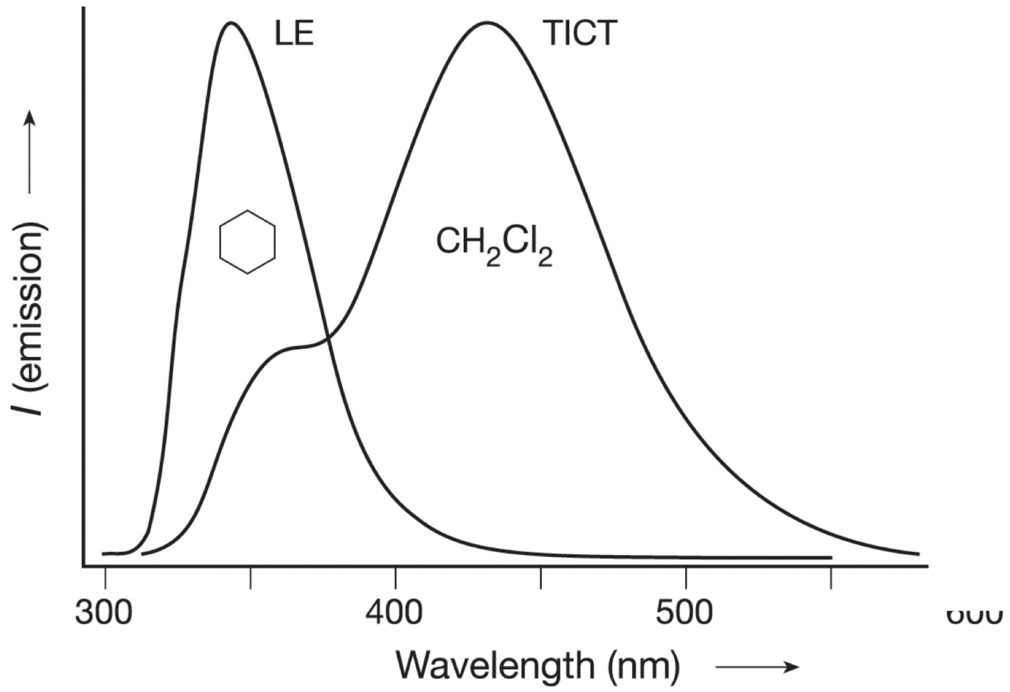


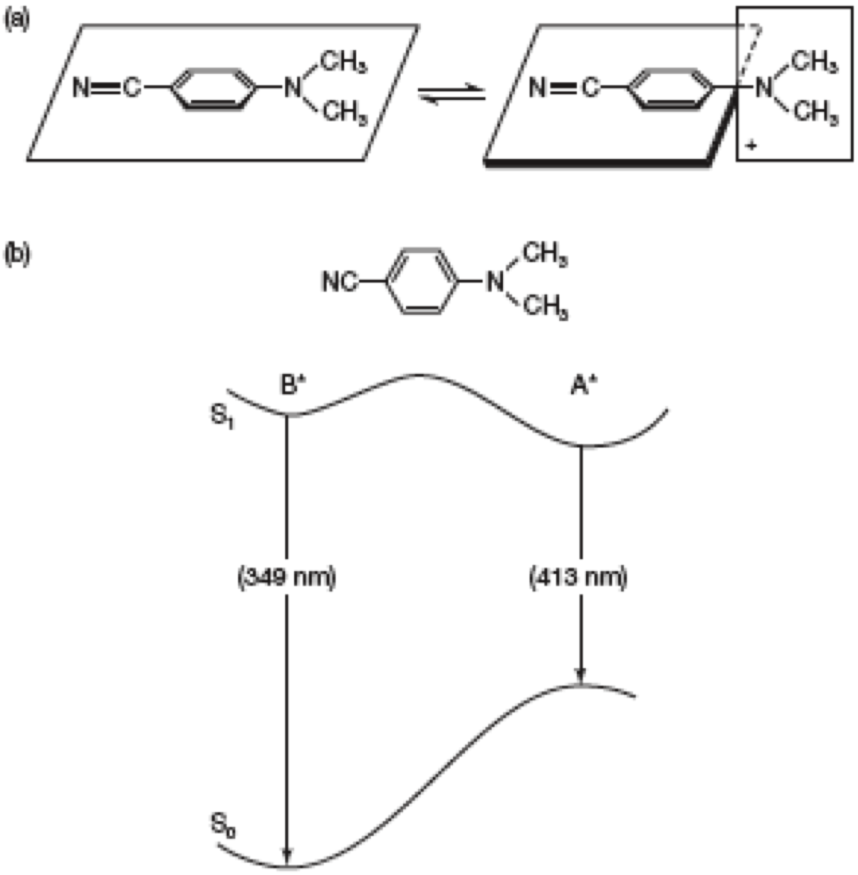


TICT Emission









Delayed Fluorescence

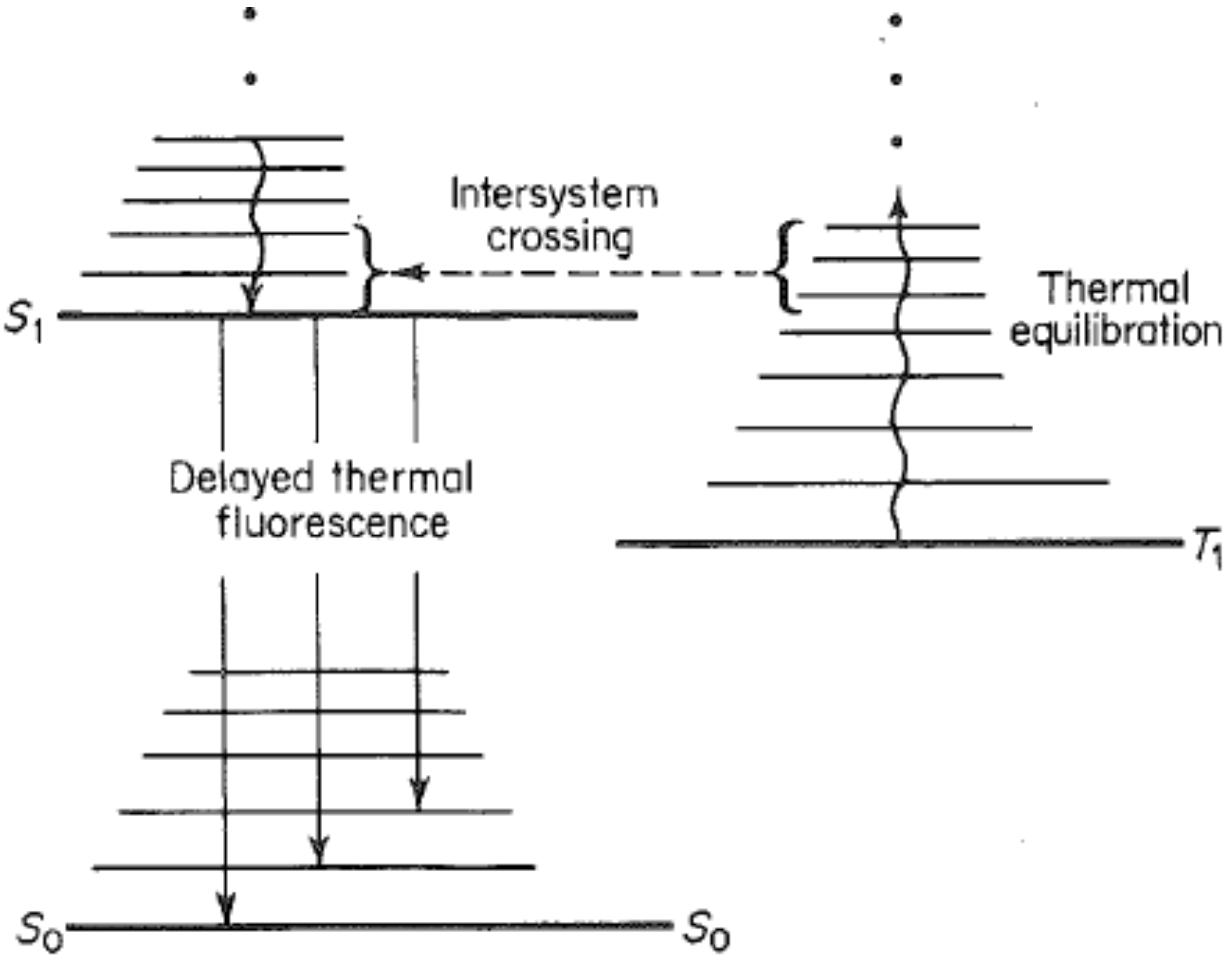
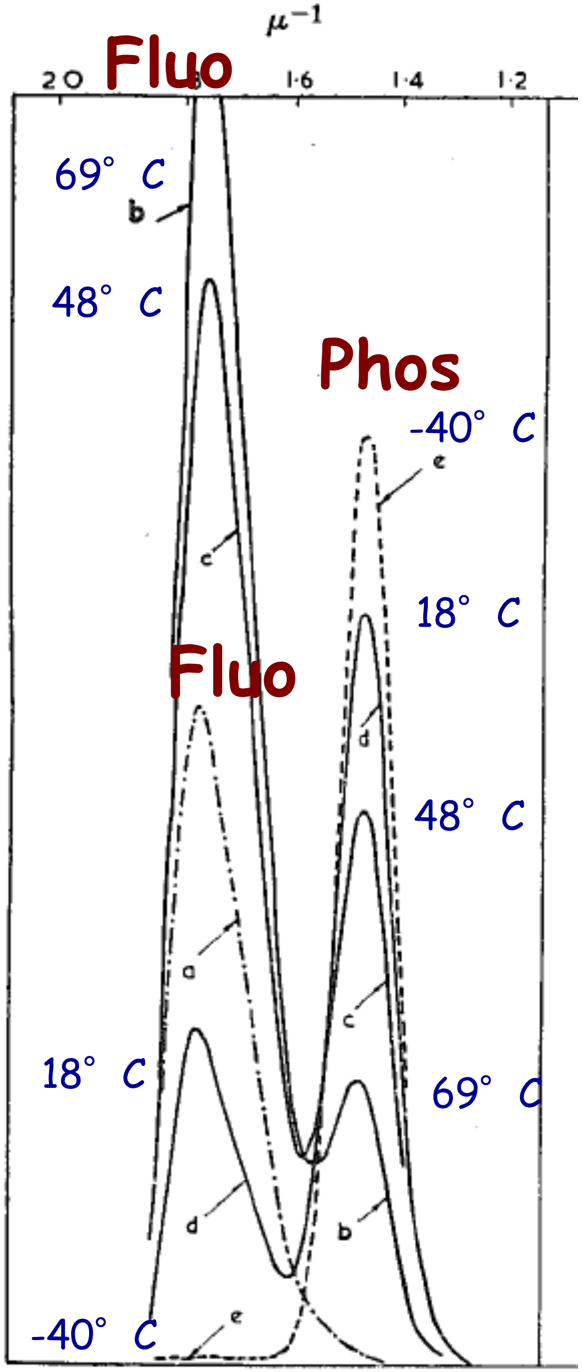
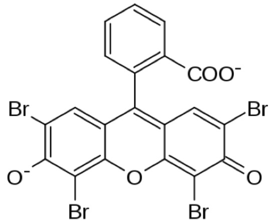


Fig. 1.11 Illustrating production of delayed thermal fluorescence (DTF).

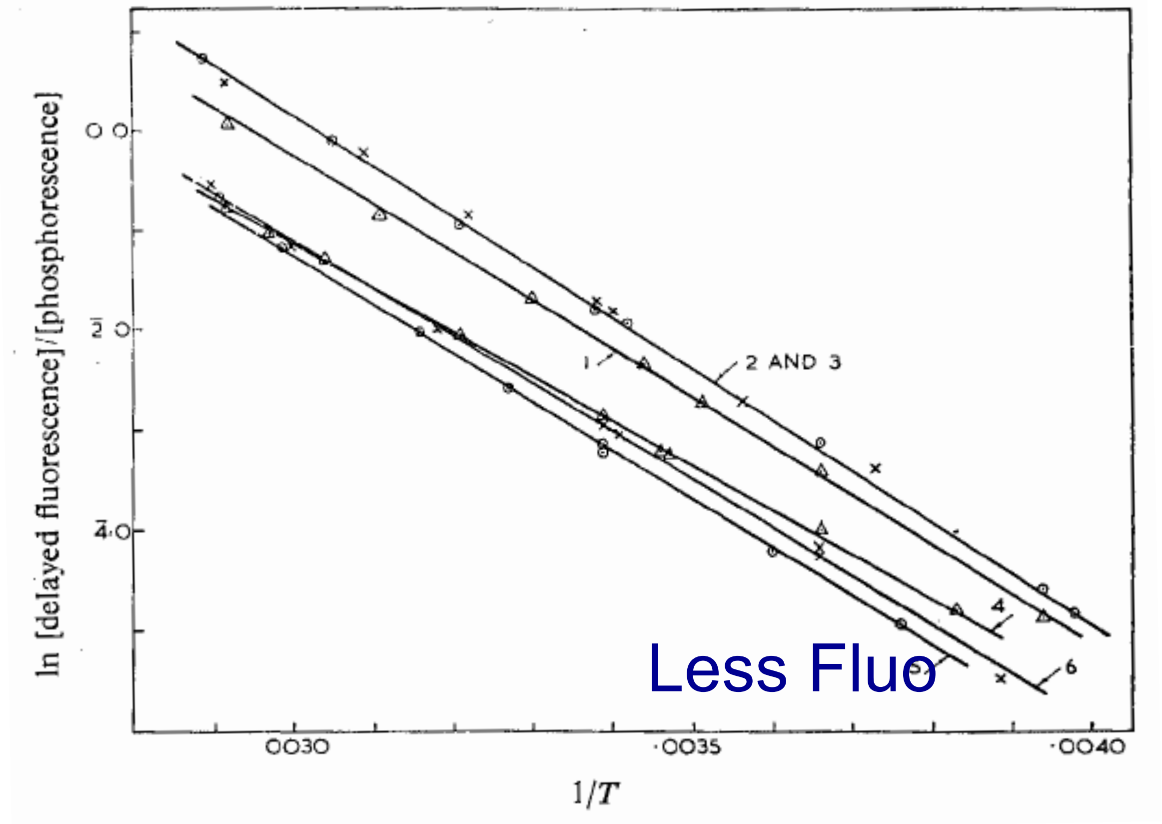
Delayed Fluorescence





Eosin Y

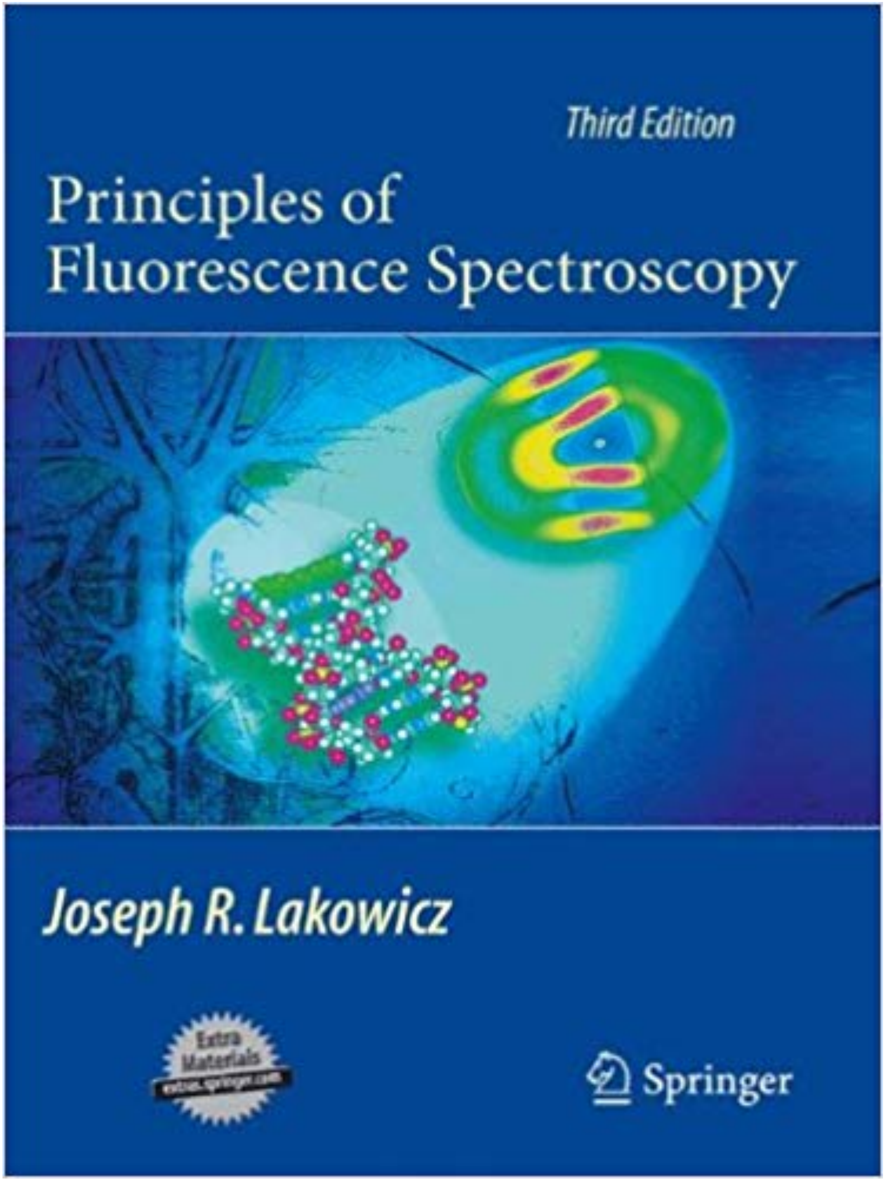
More Fluo



Less Fluo

High Temp

Low Temp



Third Edition

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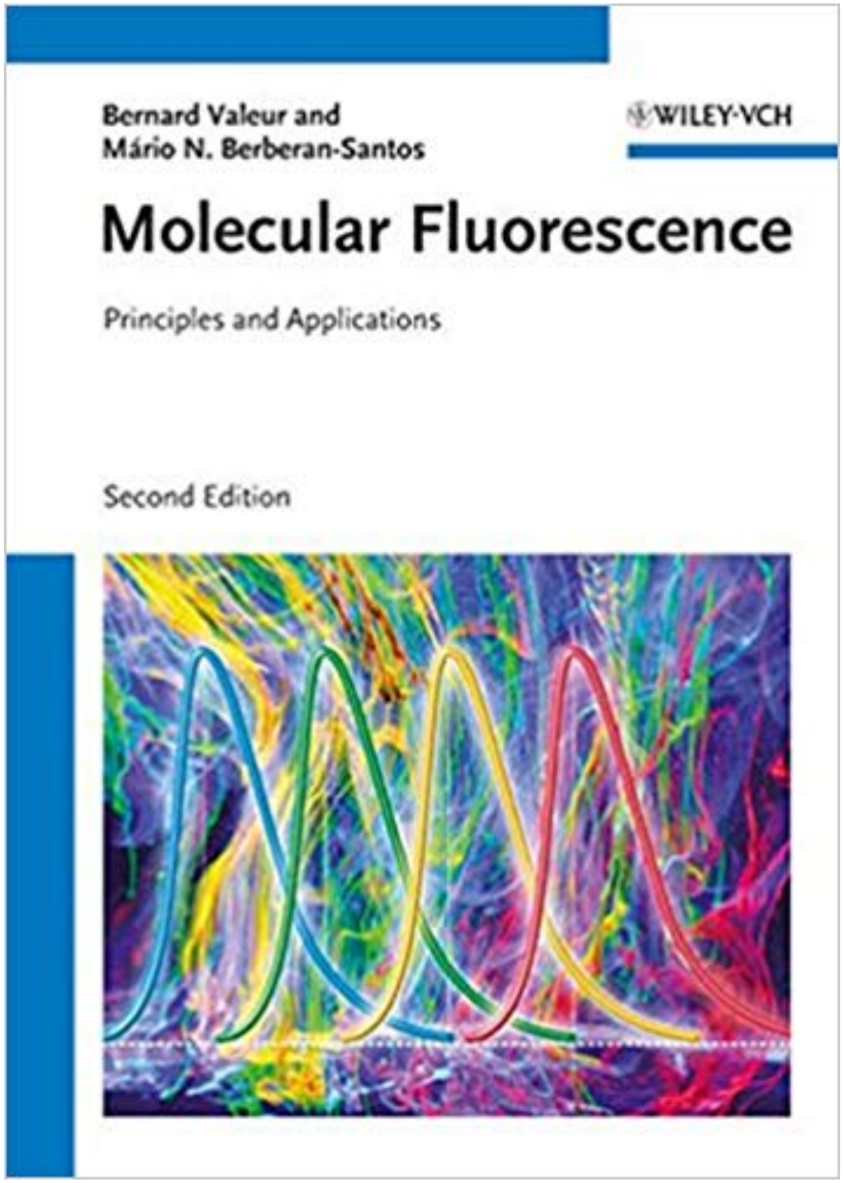

Bernard Valeur and
Mário N. Berberan-Santos

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Molecular Fluorescence

Principles and Applications

Second Edition

Intrinsic fluorophore and extrinsic fluorophore

- Intrinsic fluorophores are those which occur naturally
- Extrinsic fluorophores, fluorescence probes

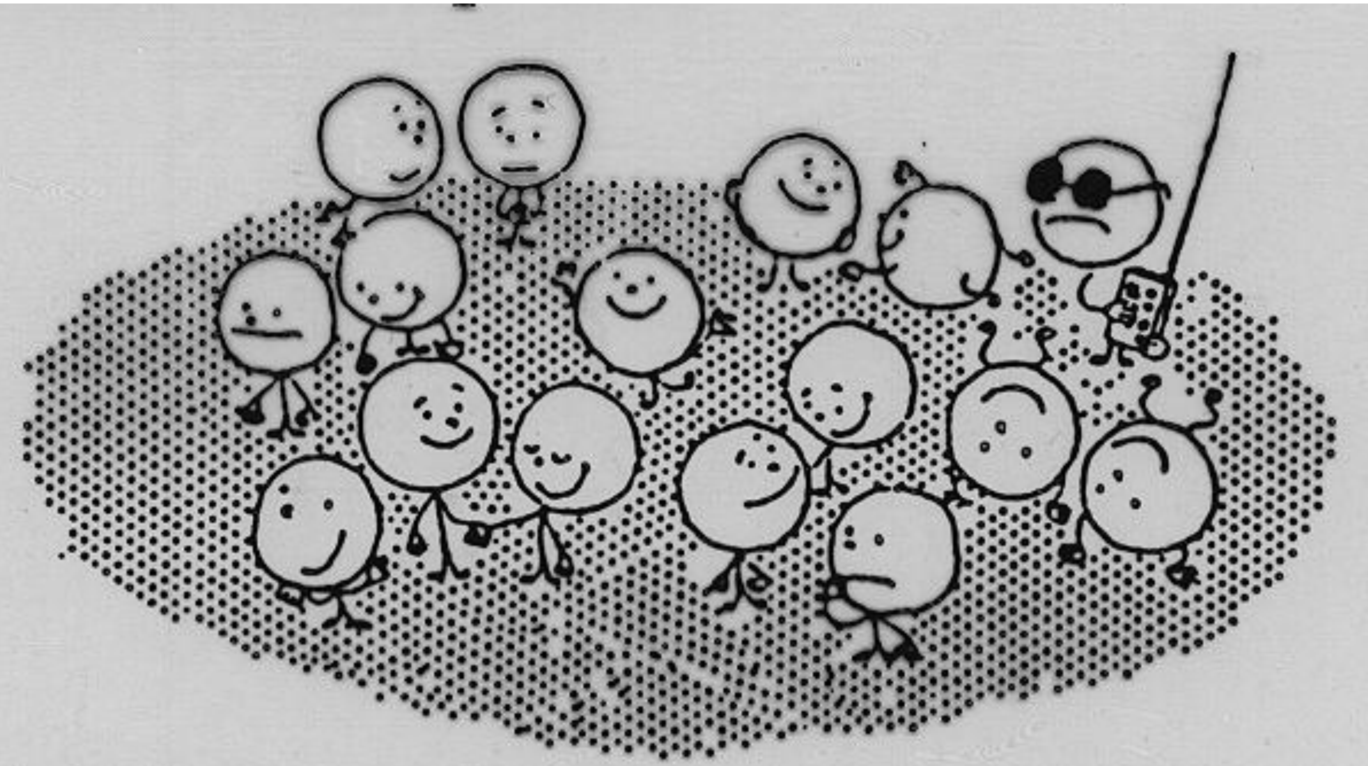
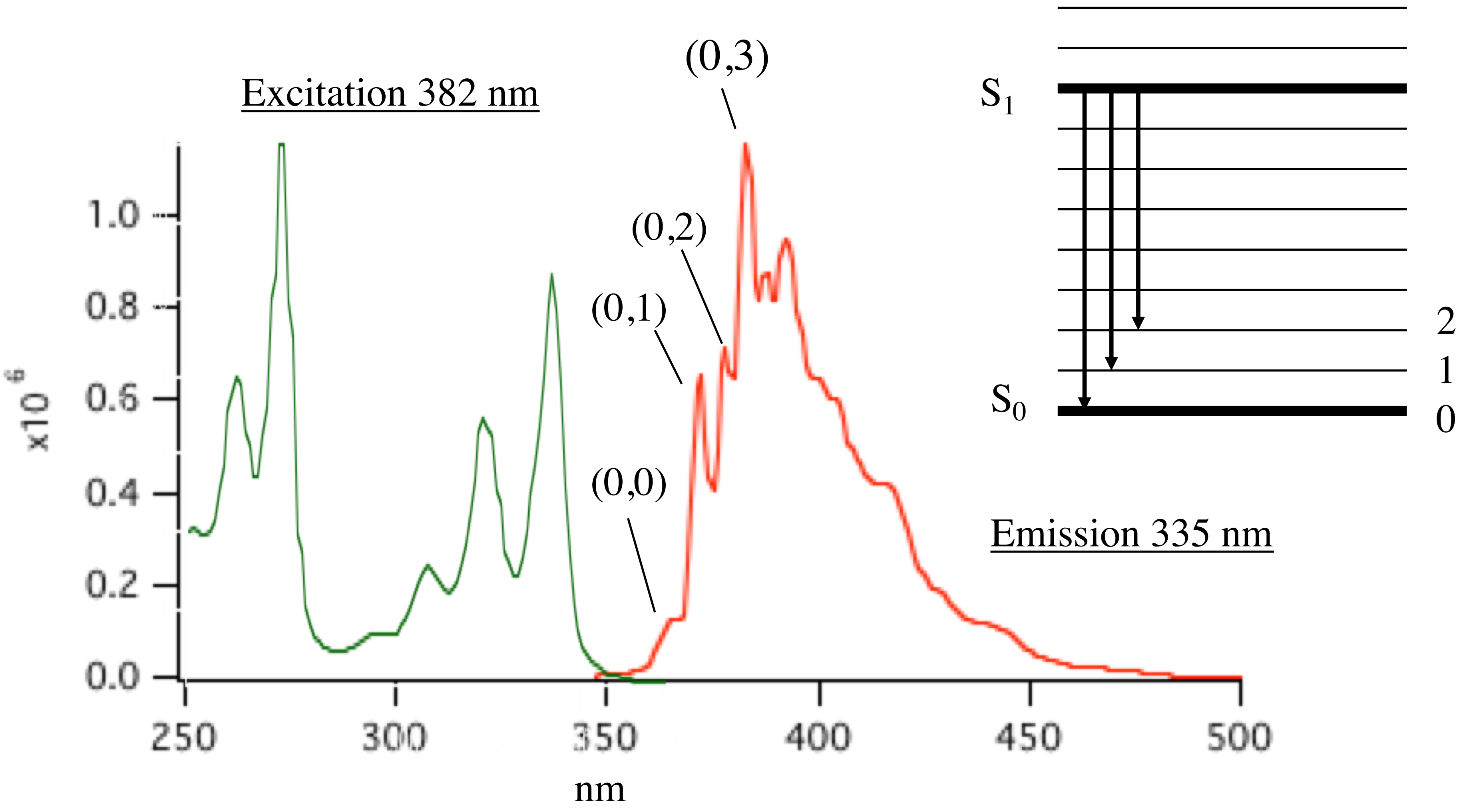
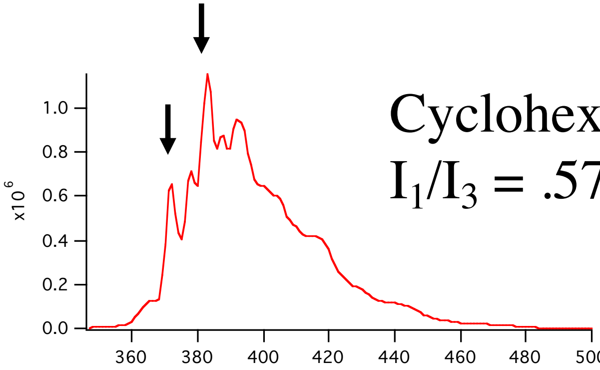


Fig.1. Fluorescent probe represents a molecular reporter in the biological sample.

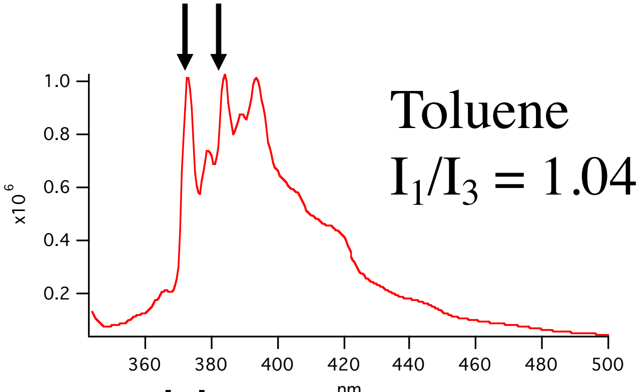
Pyrene Emission at Room Temperature Vibrational Pattern



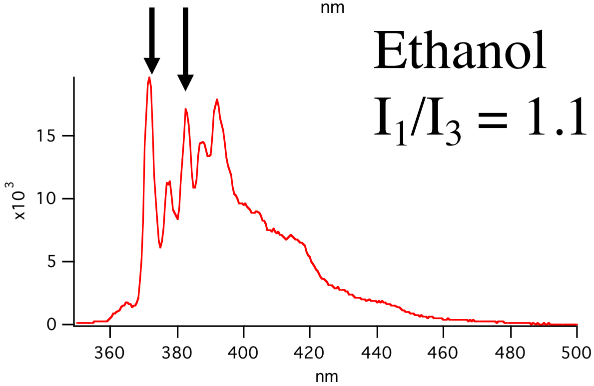
Comparison of Pyrene Emission in Different Solvents: I_1/I_3 as Polarity Probe



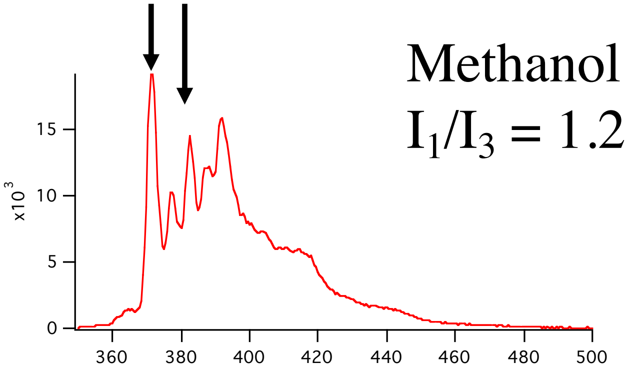
Cyclohexane
$I_1/I_3 = .57$



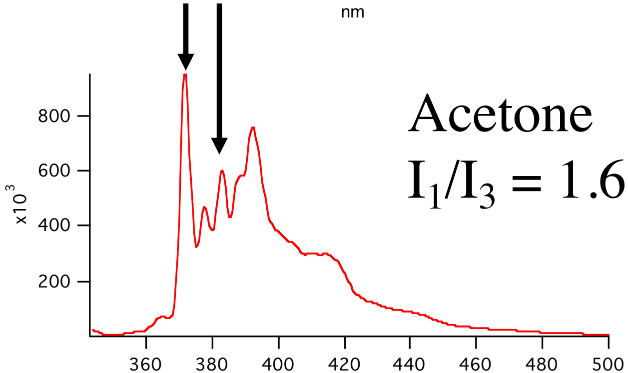
Toluene
$I_1/I_3 = 1.04$



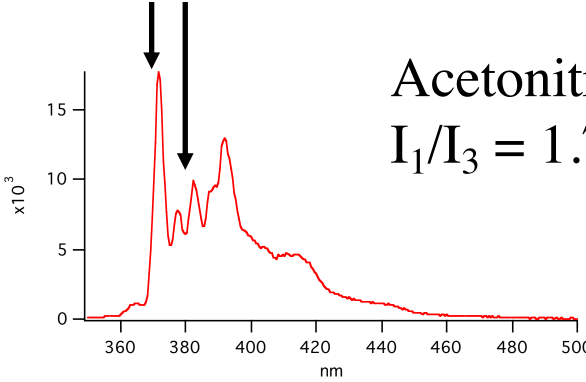
Ethanol
$I_1/I_3 = 1.15$



Methanol
$I_1/I_3 = 1.28$



Acetone
$I_1/I_3 = 1.65$



Acetonitrile
$I_1/I_3 = 1.79$

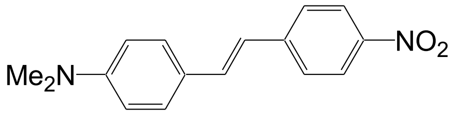
94 Solvents have been tested, showing ratios from 0.41 to 1.95. *Can. J. Chem. Vol.* 62 **1984**

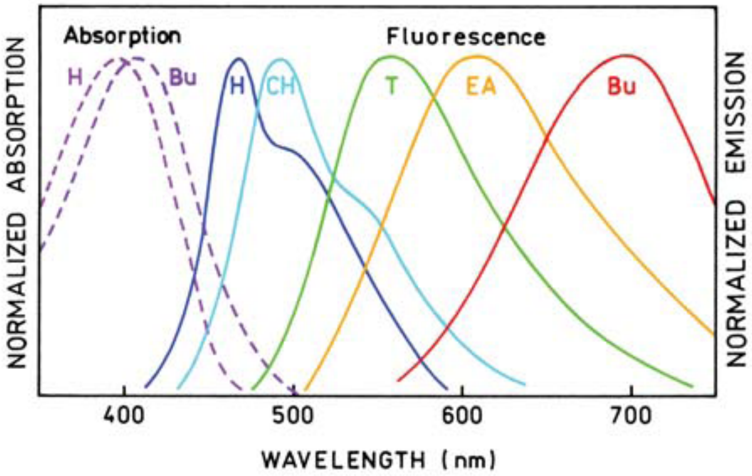
Polarity Probe

Dipole Moment = The dipole moment of a molecule in S_1 is generally greater than that that of the same molecule in S_0

Solvent Polarity = The energy of S_1 after solvent reorganization generally decrease with solvent polarity

Emission Wavelength = The emission wavelength generally increases with solvent polarity





H = Hexane

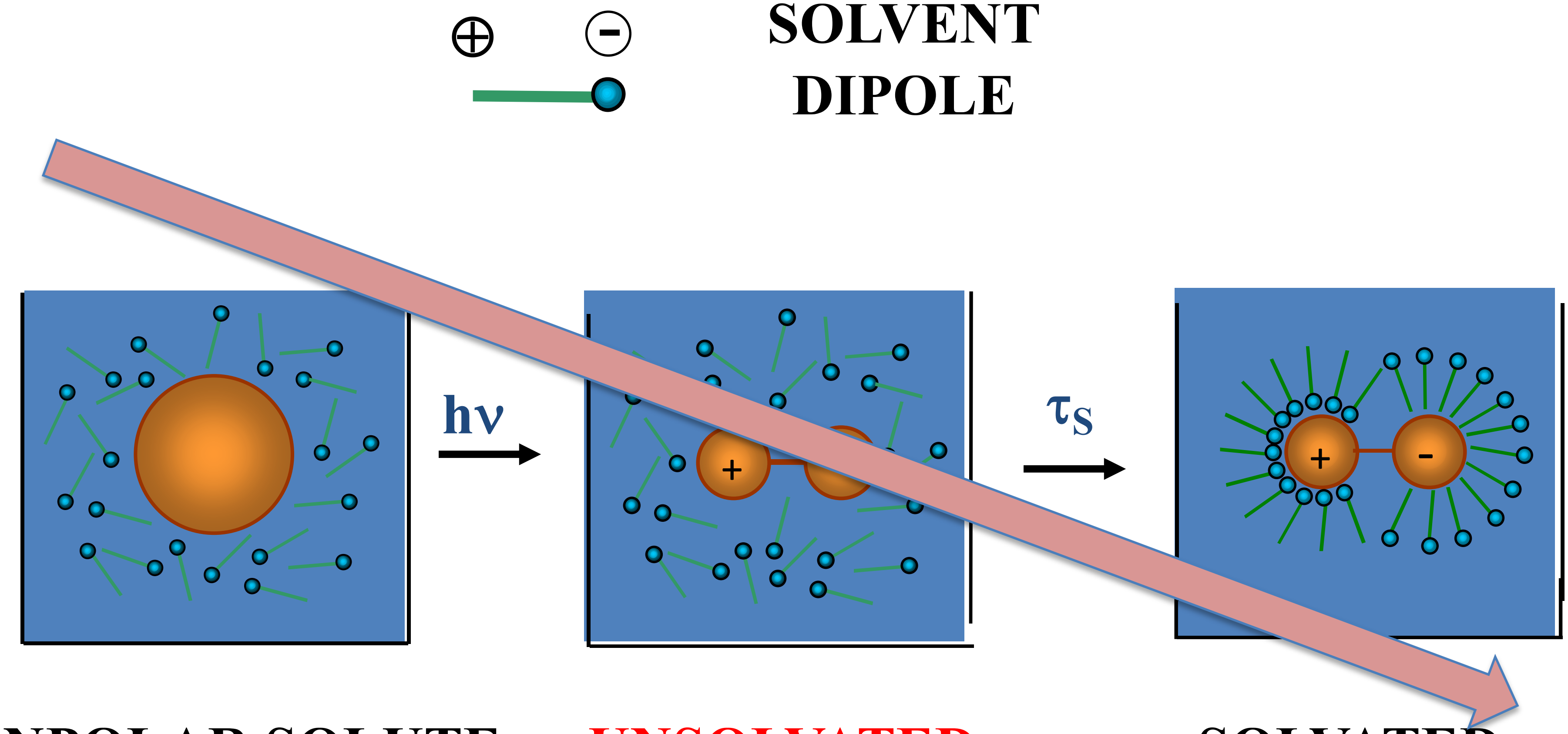
CH = Cyclohexane

T = Toluene

EA = Ethyl acetate

Bu = Butanol

Solvation Dynamics



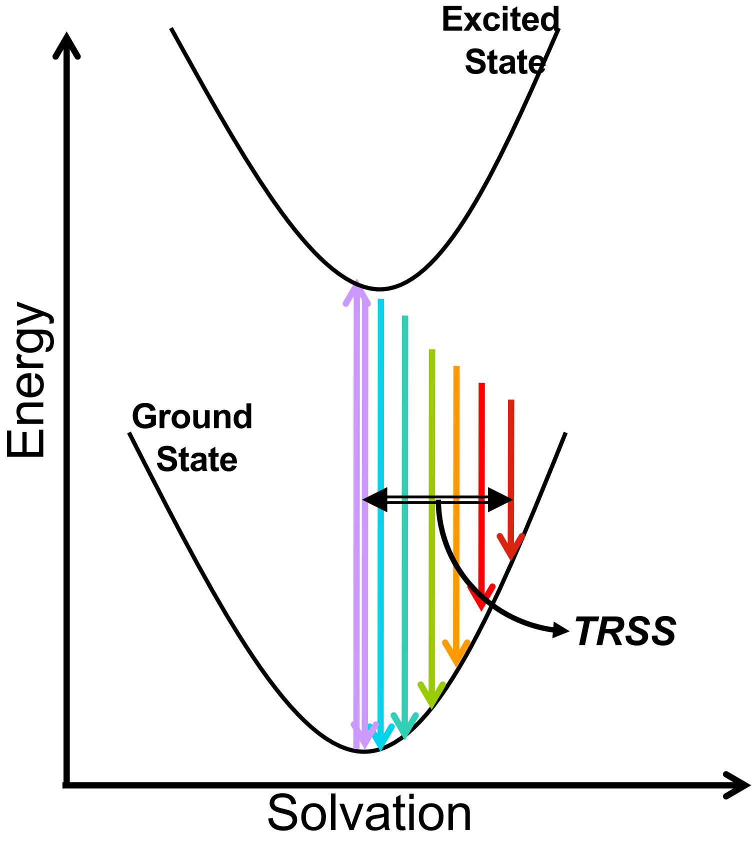
SOLVENT
DIPOLE

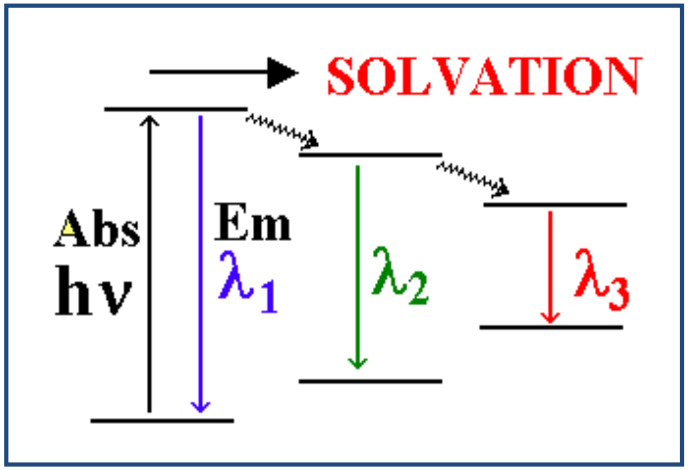
NONPOLAR SOLUTE
RANDOM SOLVENT

UNSOLVATED
HIGH ENERGY

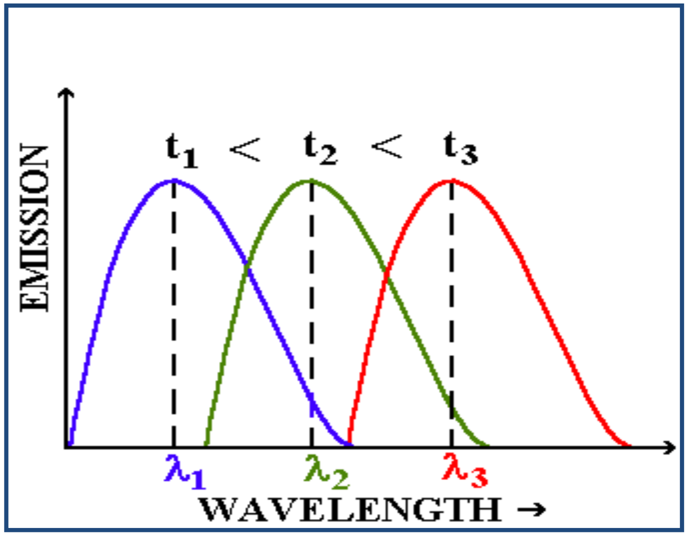
SOLVATED
LOW ENERGY

Solvation Dynamics

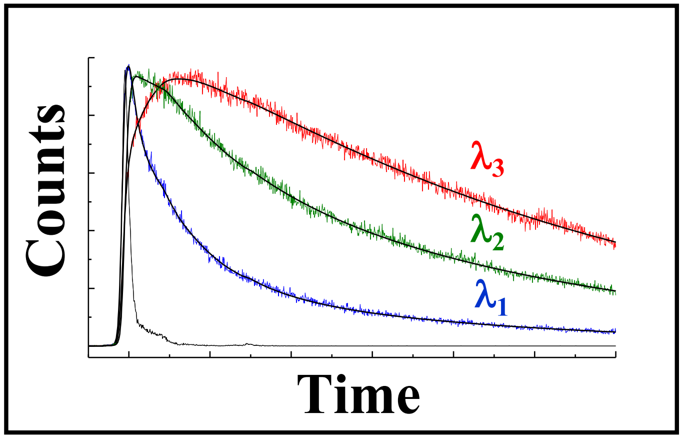




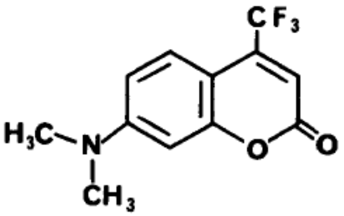
DECREASE OF ENERGY OF EXCITED DIPOLE



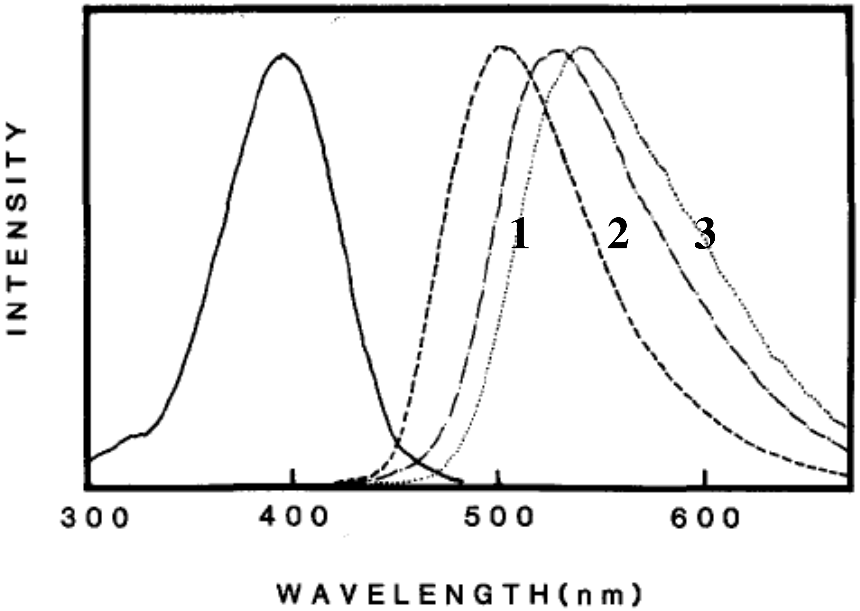
TIME DEPENDENT FLUORESCENCE STOKES SHIFT



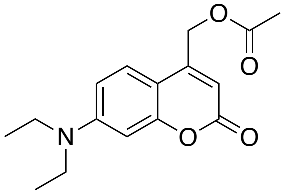
EM. WAVELENGTH DEPENDENT FL. DECAYS

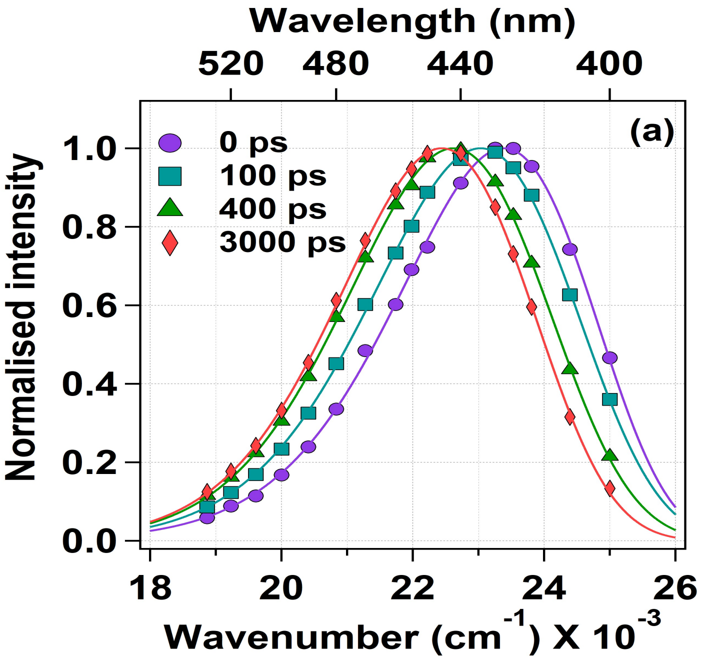


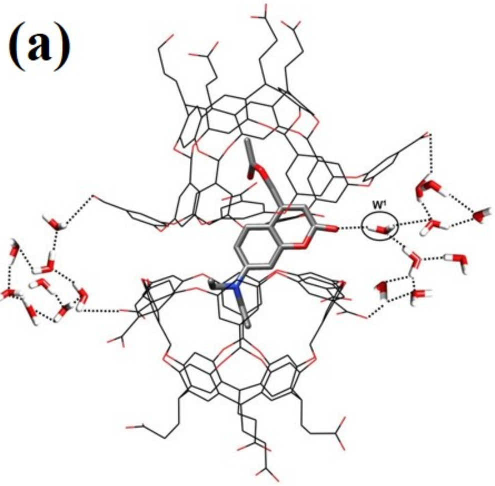
Coumarin 152



1: ethyl acetate; 2: propylene carbonate
3: methanol

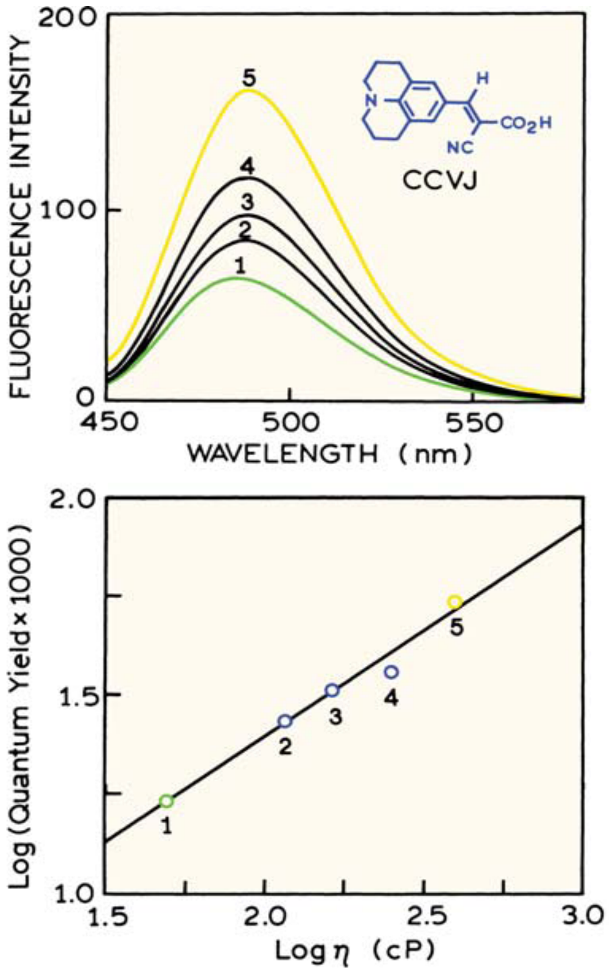




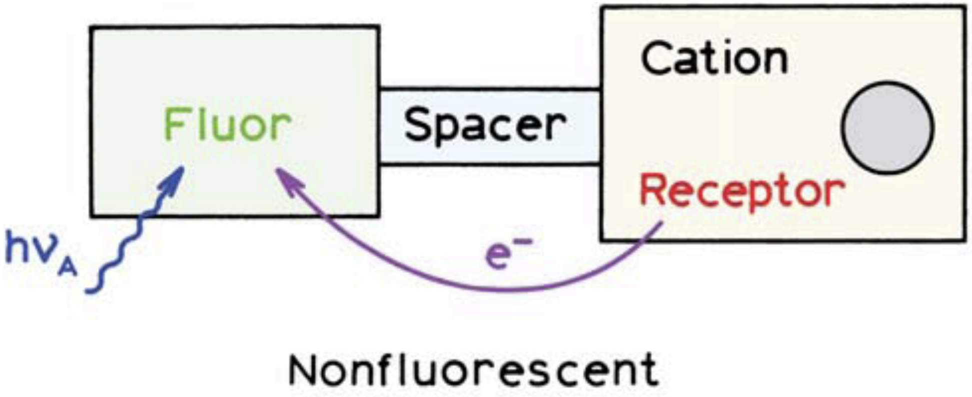


Viscosity Probes

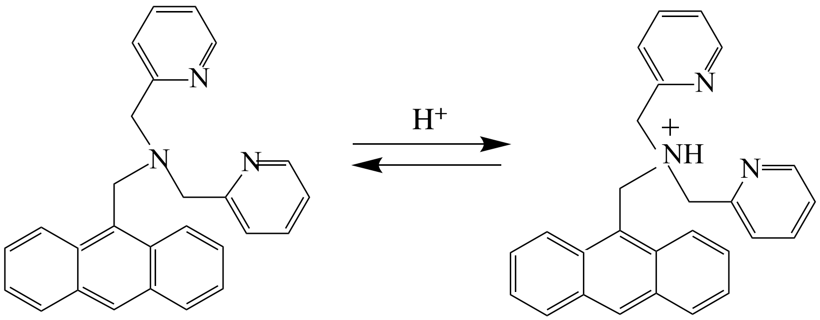
Viscosity Probes = An increase in the viscosity of the medium surrounding a fluorophore can restrict conformational freedom and alter the quantum yield



Supramolecular Sensors: Proton



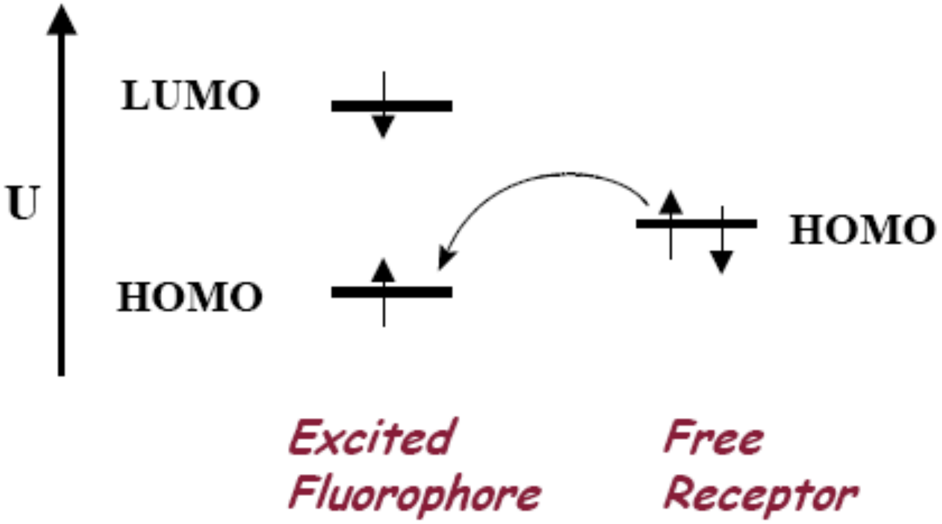
Nonfluorescent

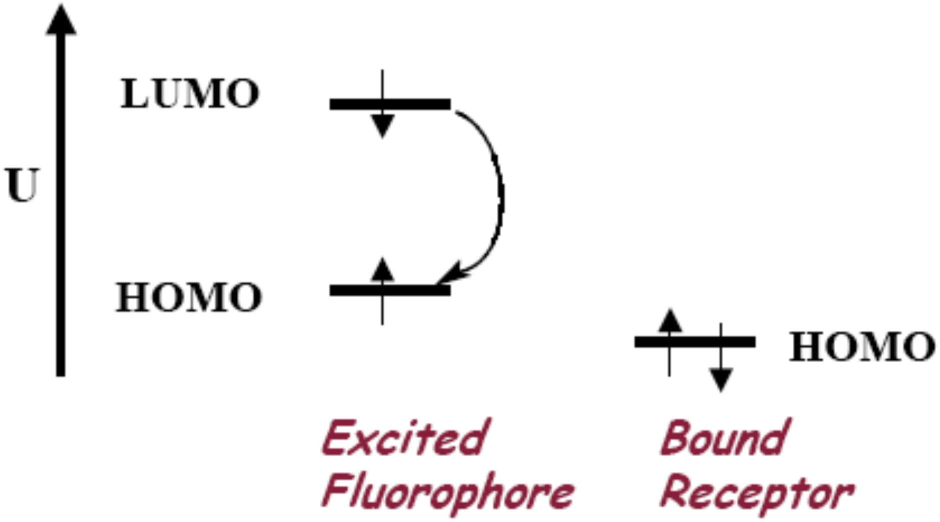


Non Fluorescent

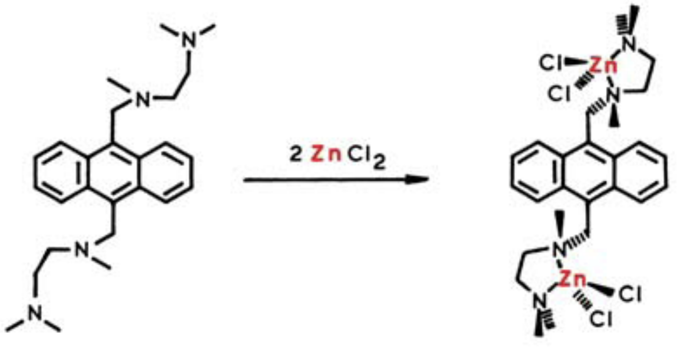
Fluorescent

Mechanism of PET Signaling





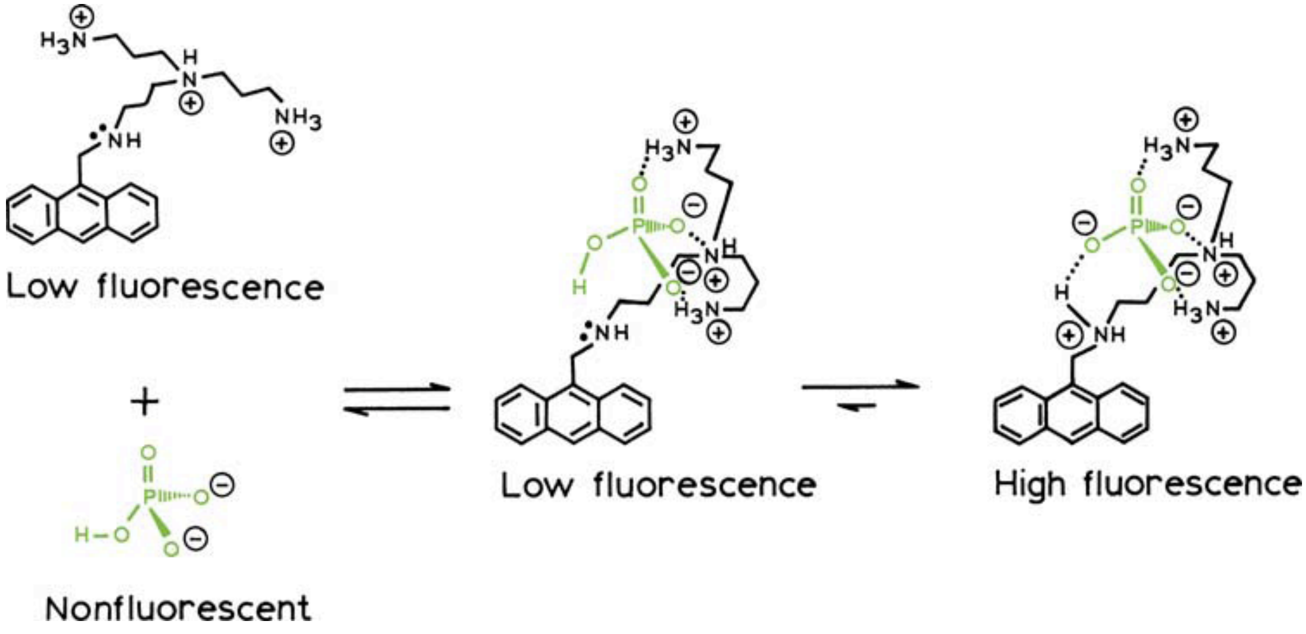
Metal ion sensing



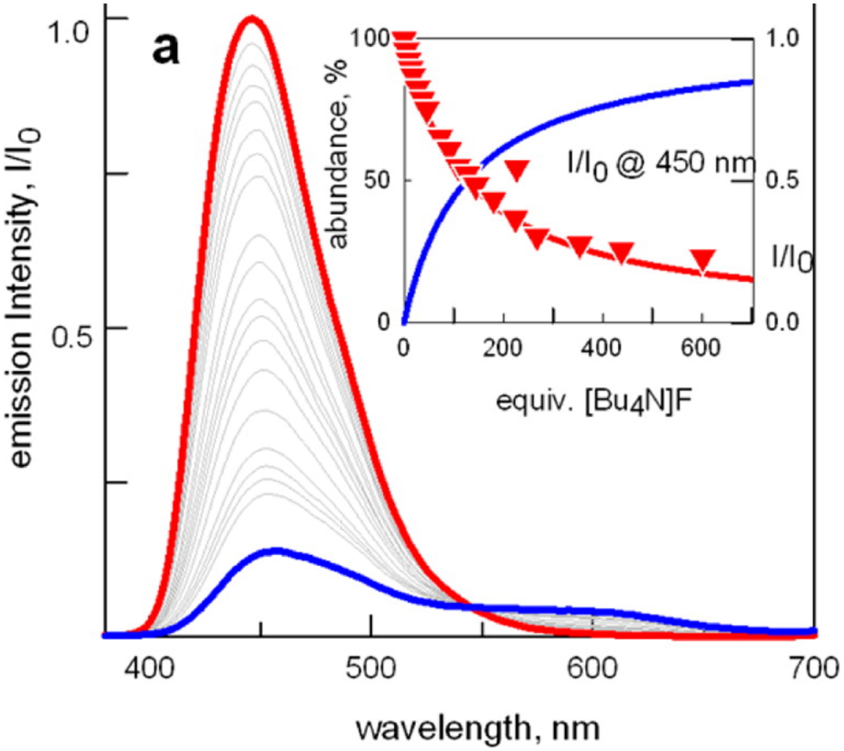
Non-fluorescent

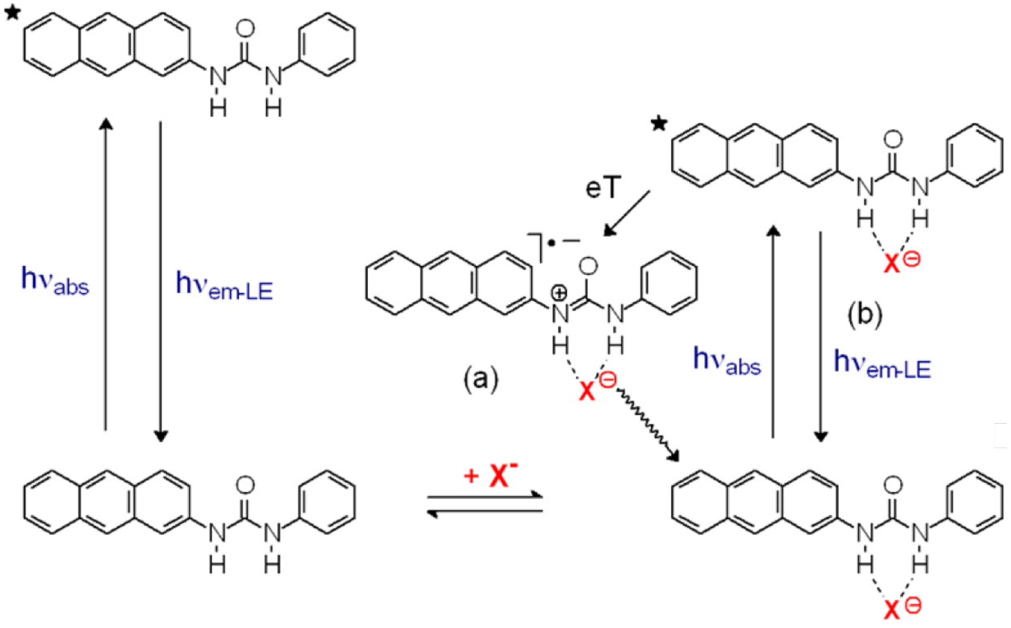
Fluorescent

Anion sensing

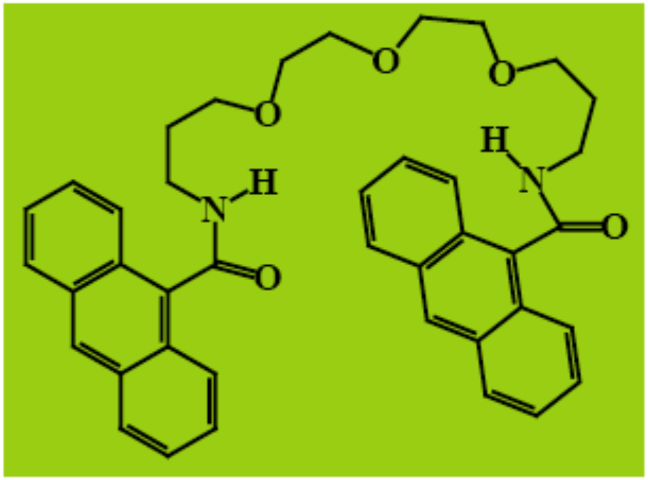


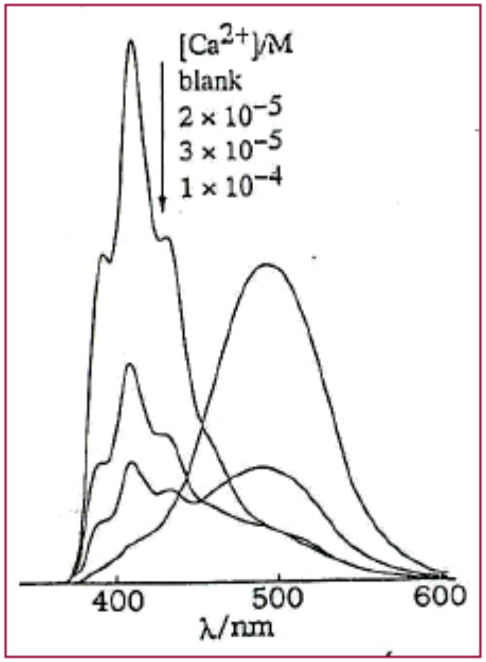
Fluoride ion sensing





Use of Excimer Emission in Ca^{2+} Sensing



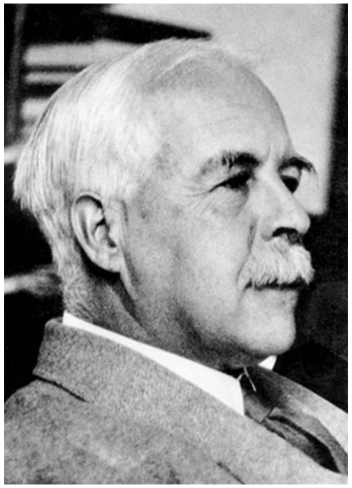


Nakamura *et al. J. Phys. Chem. B*, **2001**, *105*, **2923**

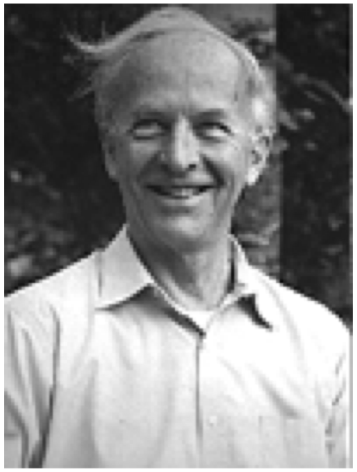
- ***A fluorescent host with anthracene moiety at each end of a linear polyether chain***

- ***Upon addition of Ca^{2+} fluorescence spectrum changes from monomer emission to excimer emission***

Triplet State and Phosphorescence

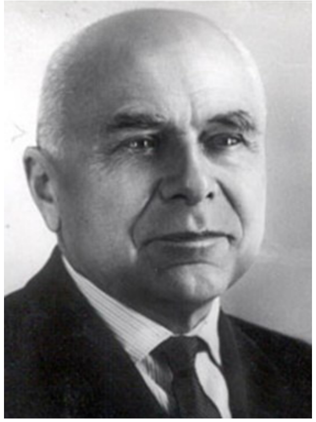


G. N. Lewis



Kasha

S. Vavilov



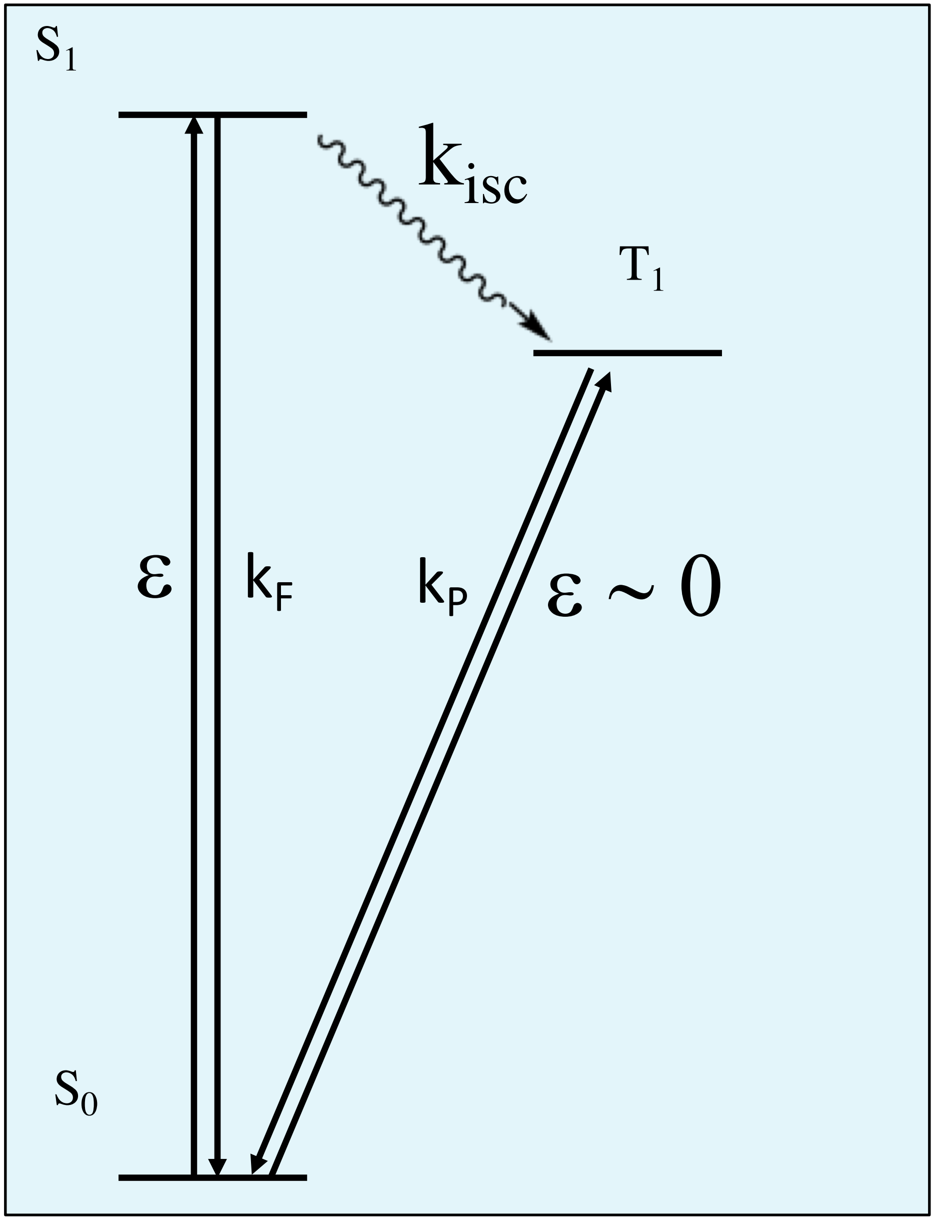
A. Terenin

Porter

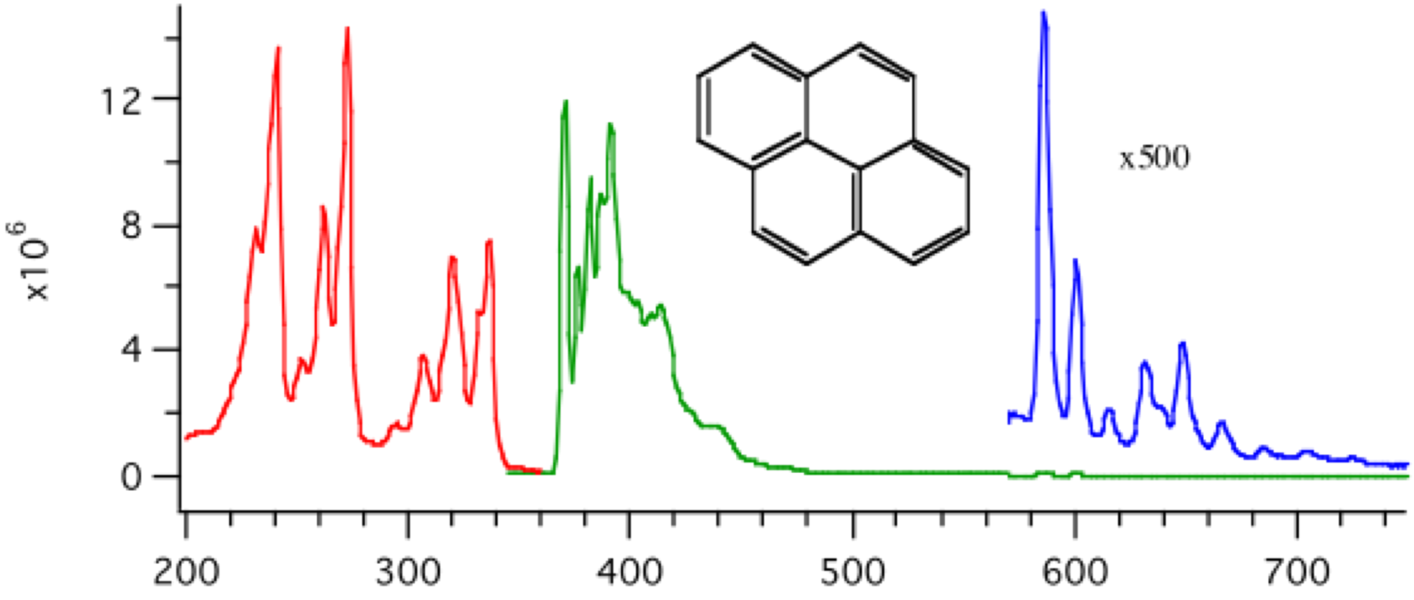
Triplet State

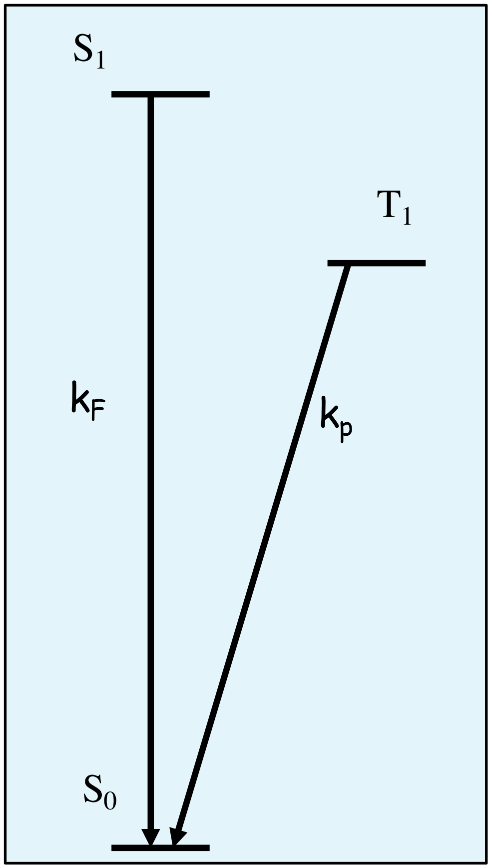
- Two electrons with the same spin
- Always lower in energy than the corresponding singlet state with the same electronic configuration
- The gap between S_1 and T_1 depends on the electronic configuration
- Emits (phosphorescence) at a longer wavelength than from S_1 (fluorescence)
- Has a longer lifetime than S_1
- Is paramagnetic, shows EPR signals

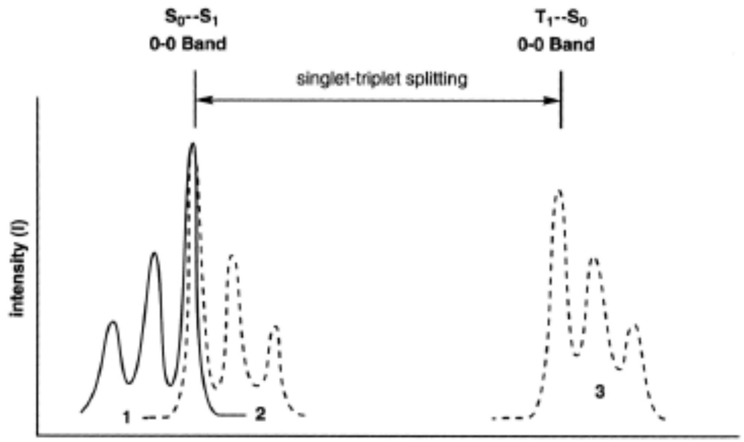
Fluorescene and Phosphorescence

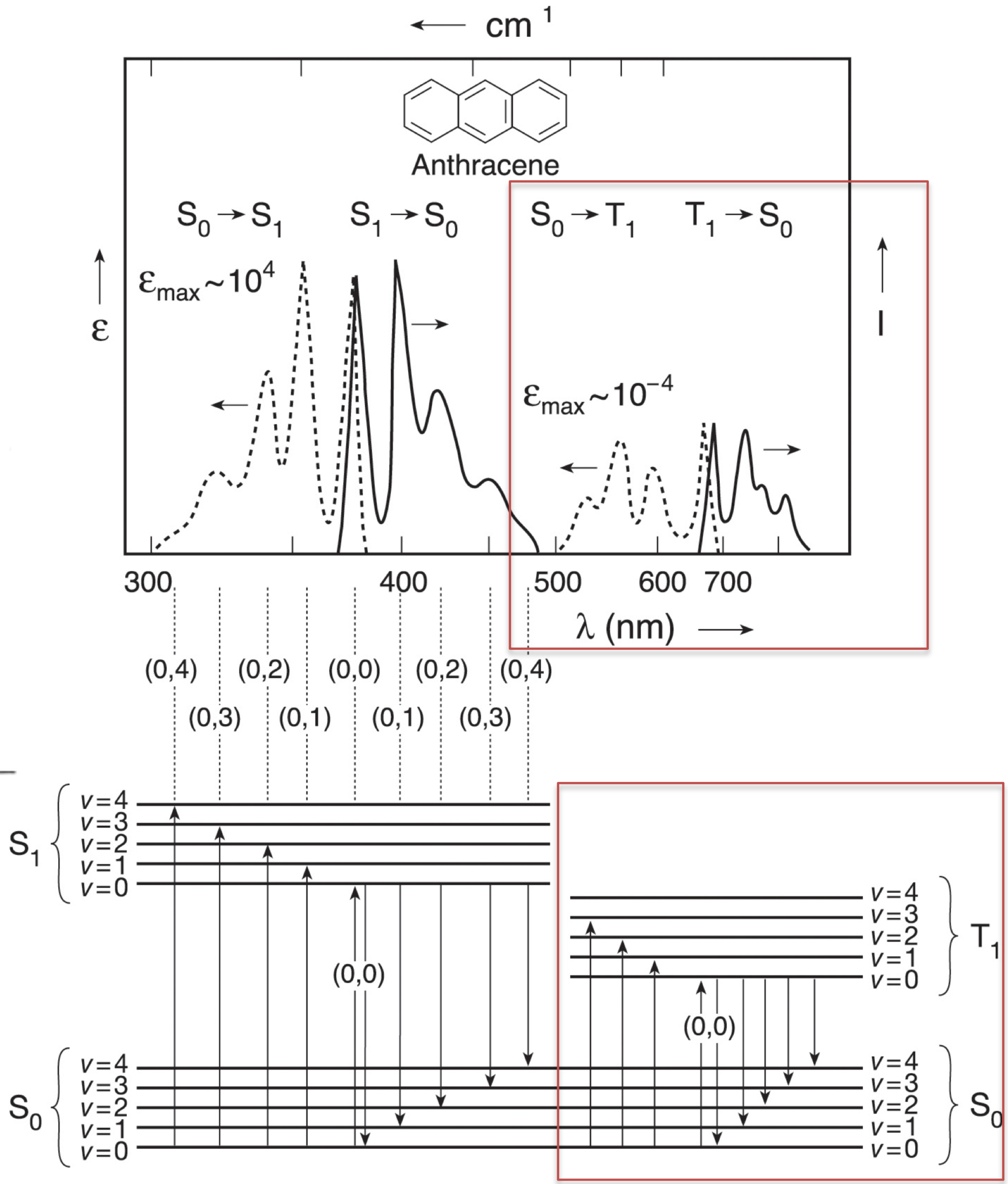


Fluorescence and Phosphorescence

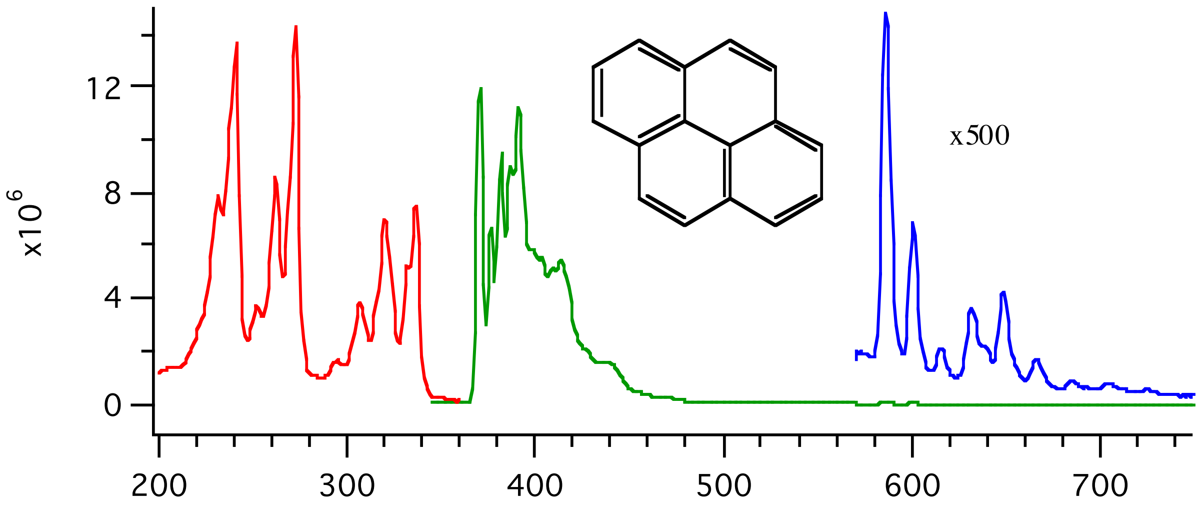


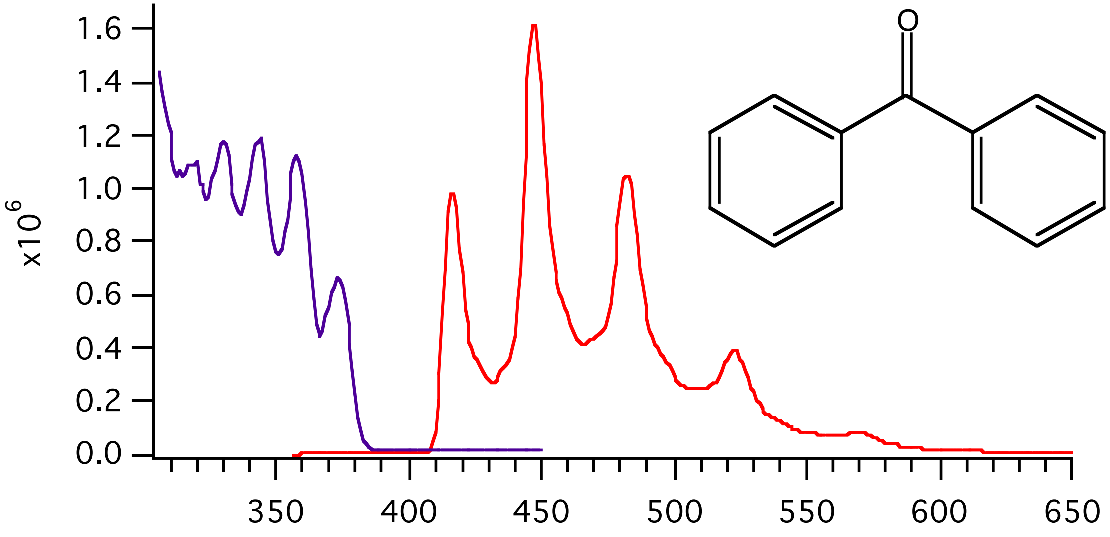


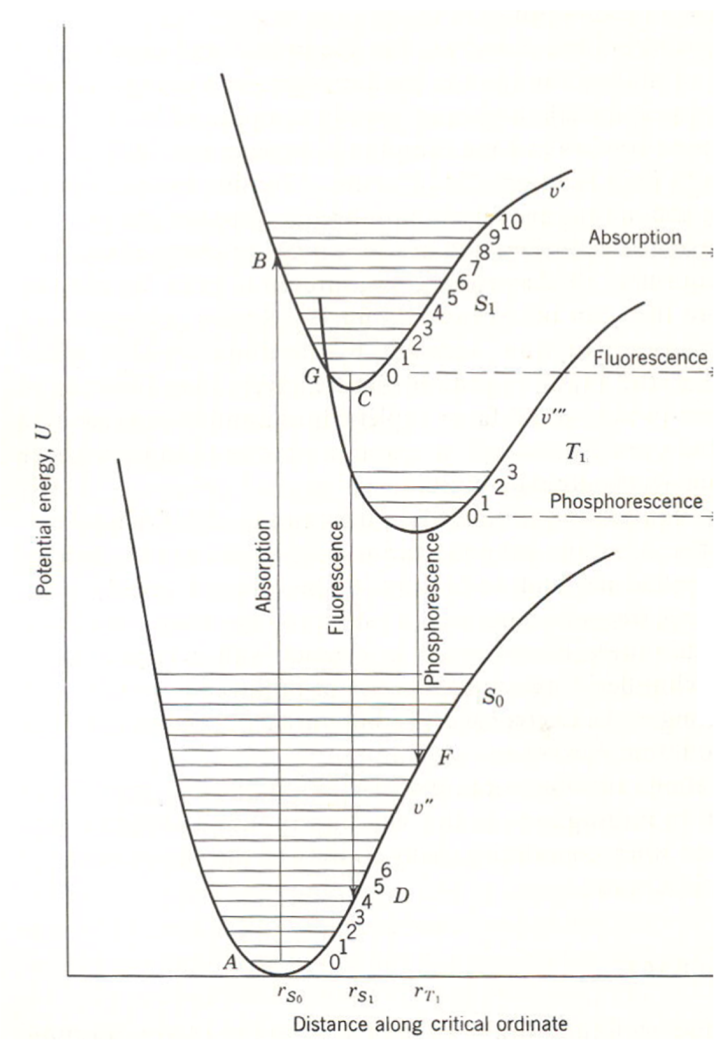

S0--S1
0-0 Band
T1--S0
0-0 Band
singlet-triplet splitting
intensity (I)
1
2
3


← cm⁻¹
Anthracene
S0 → S1
S1 → S0
S0 → T1
T1 → S0
εmax ~ 10^4
ε
I
εmax ~ 10^-4
300
400
500
600
700
λ (nm) →
(0,4)
(0,3)
(0,2)
(0,1)
(0,0)
(0,1)
(0,2)
(0,3)
(0,4)
S1
v=4
v=3
v=2
v=1
v=0
(0,0)
S0
v=4
v=3
v=2
v=1
v=0
T1
v=4
v=3
v=2
v=1
v=0
(0,0)
S0
v=4
v=3
v=2
v=1
v=0

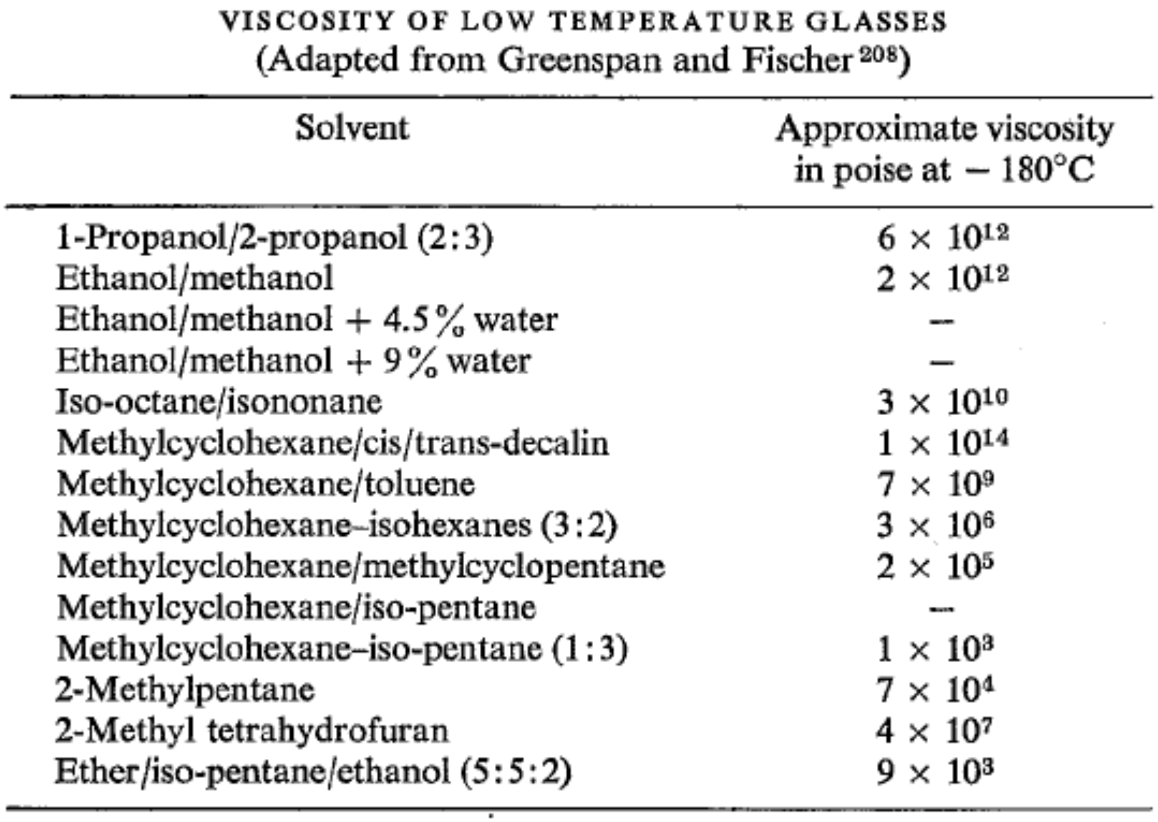
Fluorescence and Phosphorescence







Organic Glass for Phosphorescence



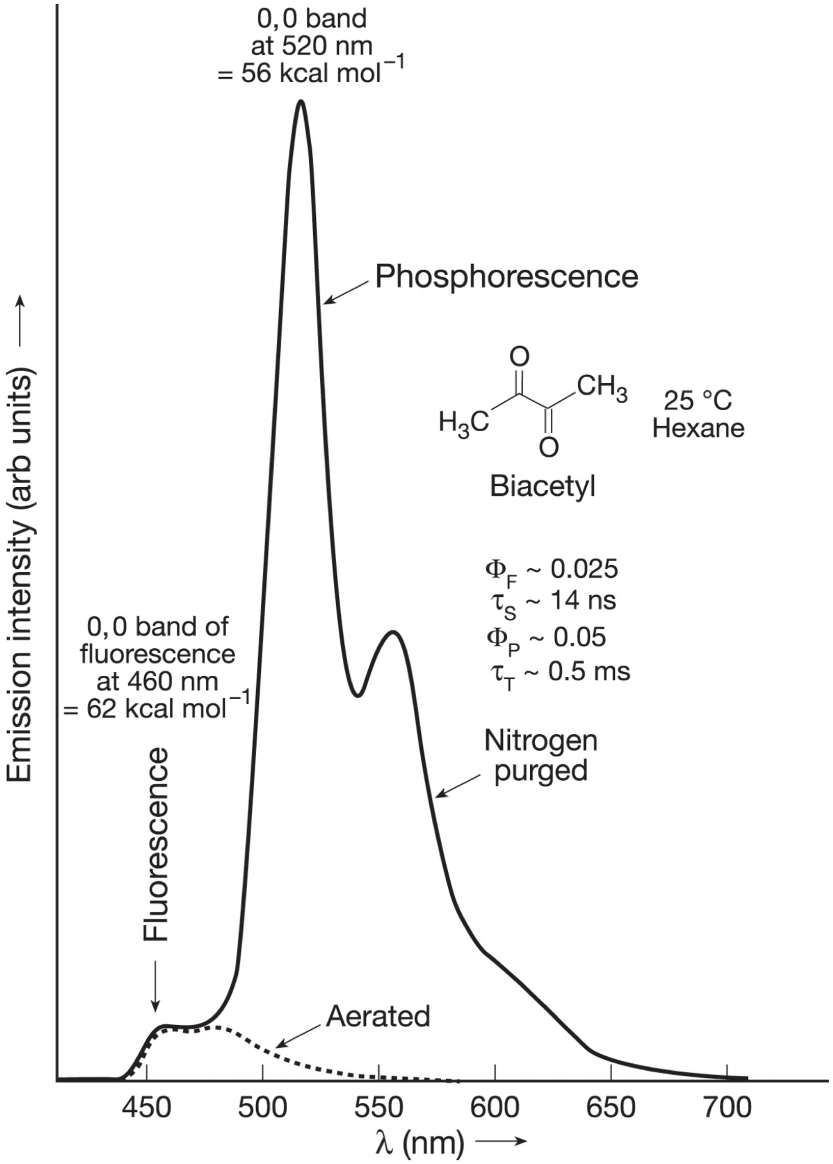
VISCOSITY OF LOW TEMPERATURE GLASSES

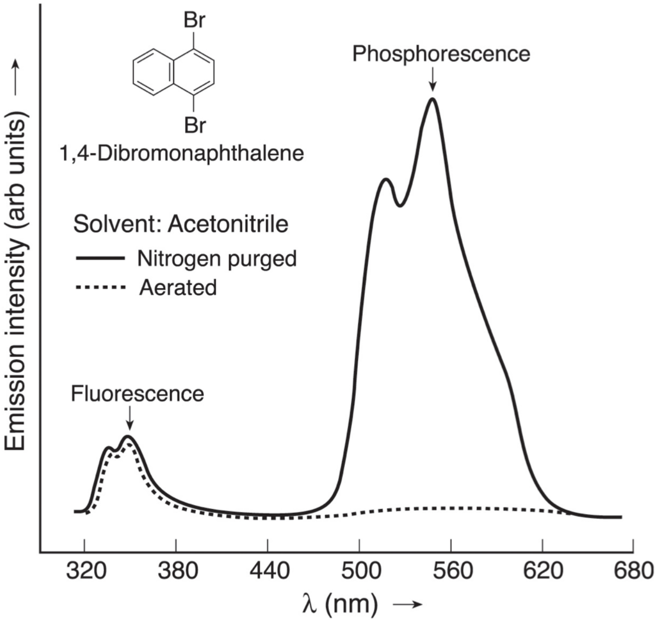
(Adapted from Greenspan and Fischer[208])

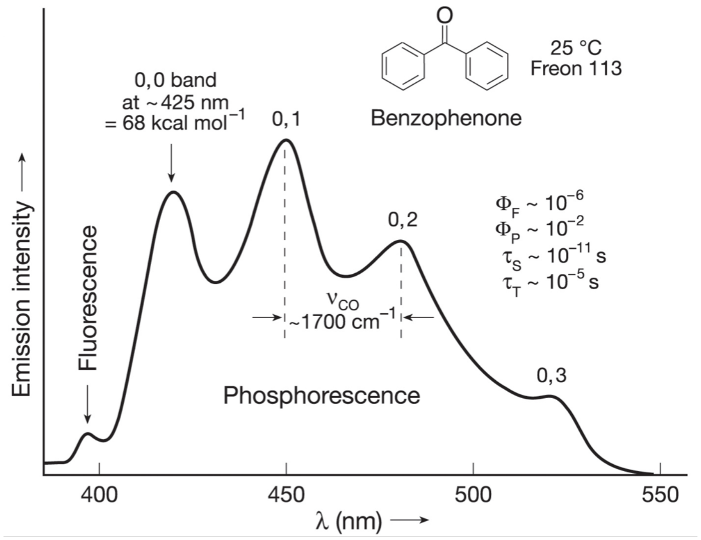
Solvent	Approximate viscosity in poise at − 180°C
1-Propanol/2-propanol (2:3)	6×10^{12}
Ethanol/methanol	2×10^{12}
Ethanol/methanol + 4.5% water	–
Ethanol/methanol + 9% water	–
Iso-octane/isononane	3×10^{10}
Methylcyclohexane/cis/trans-decalin	1×10^{14}
Methylcyclohexane/toluene	7×10^{9}
Methylcyclohexane–isohexanes (3:2)	3×10^{6}
Methylcyclohexane/methylcyclopentane	2×10^{5}
Methylcyclohexane/iso-pentane	–
Methylcyclohexane–iso-pentane (1:3)	1×10^{3}
2-Methylpentane	7×10^{4}
2-Methyl tetrahydrofuran	4×10^{7}
Ether/iso-pentane/ethanol (5:5:2)	9×10^{3}

- Be chemically inert
- Have no absorption in the region of optical pumping
- Have a large solubility for the studied material
- Be stable (don't crack) to the action of light
- Have a good optical quality

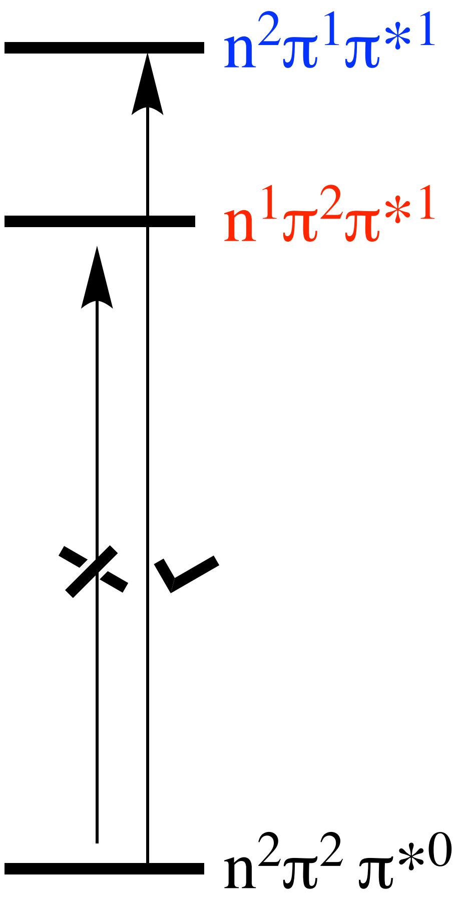
Phosphorescence at RT in a solvent: Role of oxygen



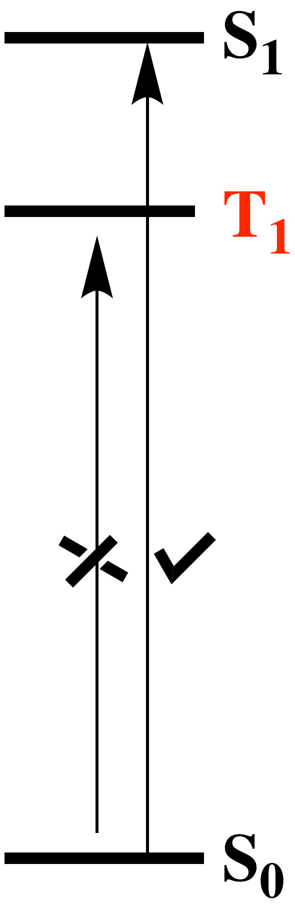




Forbidden Transitions

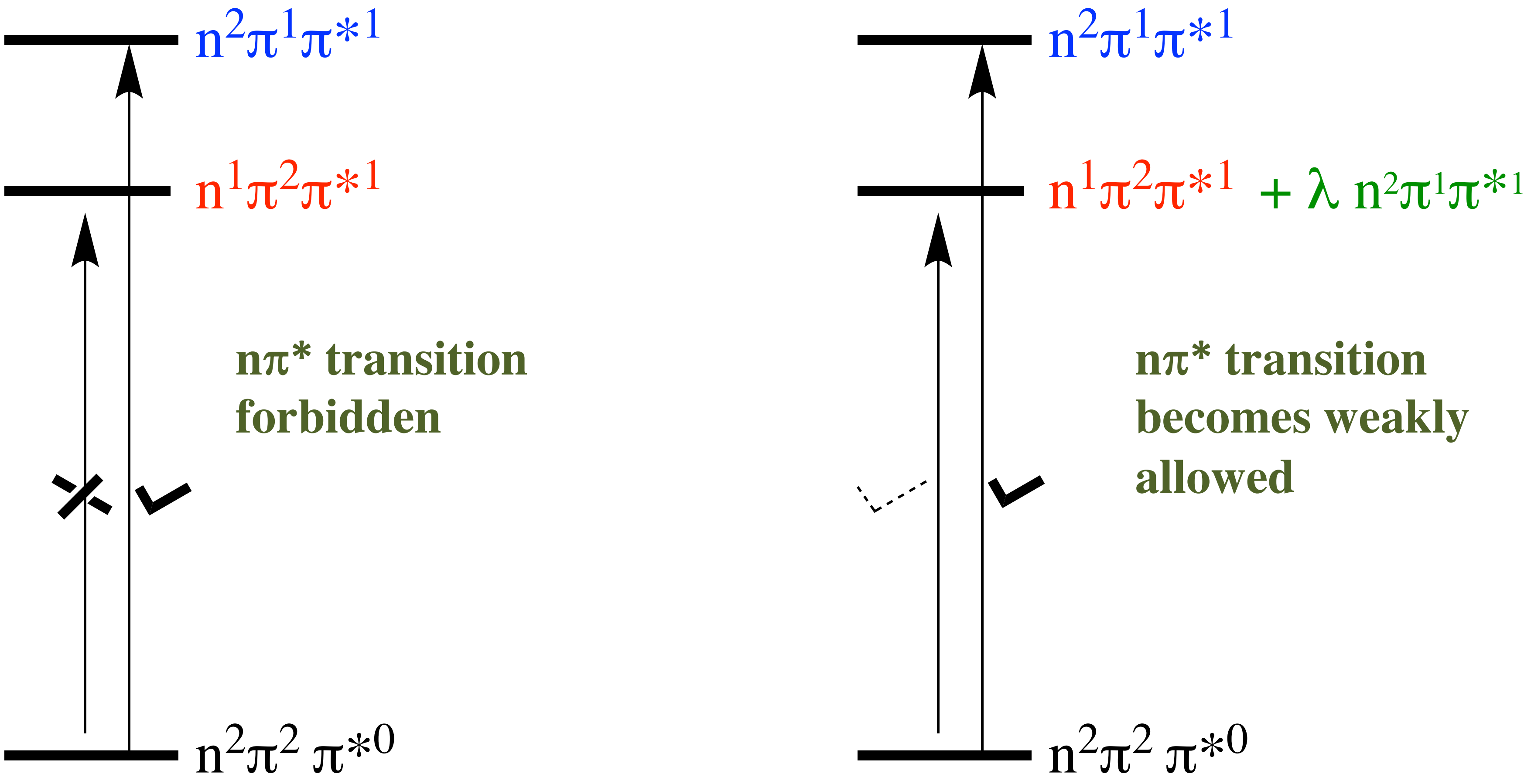


Orbital change



Spin change

Result of vibrational – electronic mixing



$n^2\pi^1\pi^{*1}$

$n^1\pi^2\pi^{*1}$

nπ* transition forbidden

$n^2\pi^2\,\pi^{*0}$

$n^2\pi^1\pi^{*1}$

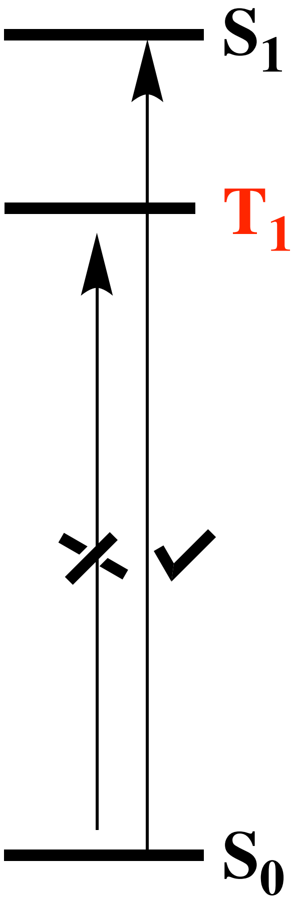
$n^1\pi^2\pi^{*1} + \lambda\, n^2\pi^1\pi^{*1}$

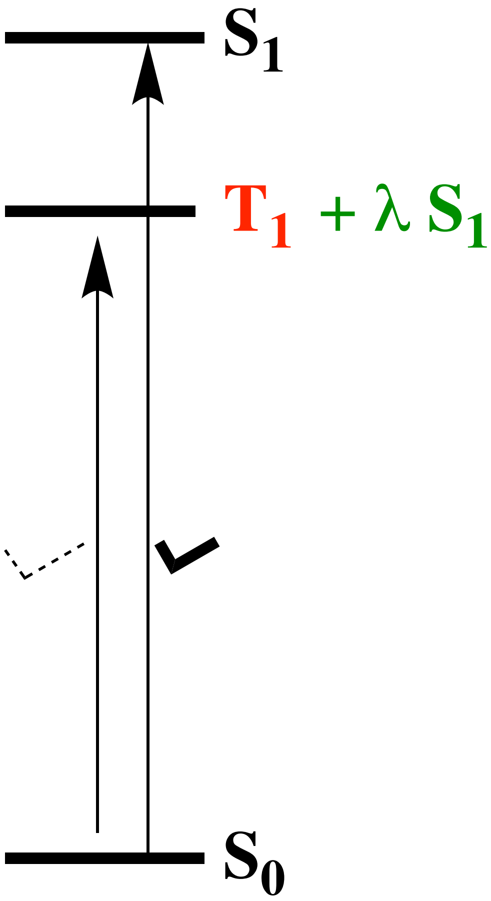
nπ* transition becomes weakly allowed

$n^2\pi^2\,\pi^{*0}$

Vibration mixes the states,
no longer pure states

Singlet-Triplet Transitions: Role of Spin-Orbit Coupling





Spin-Orbit coupling mixes the states,
no longer pure states

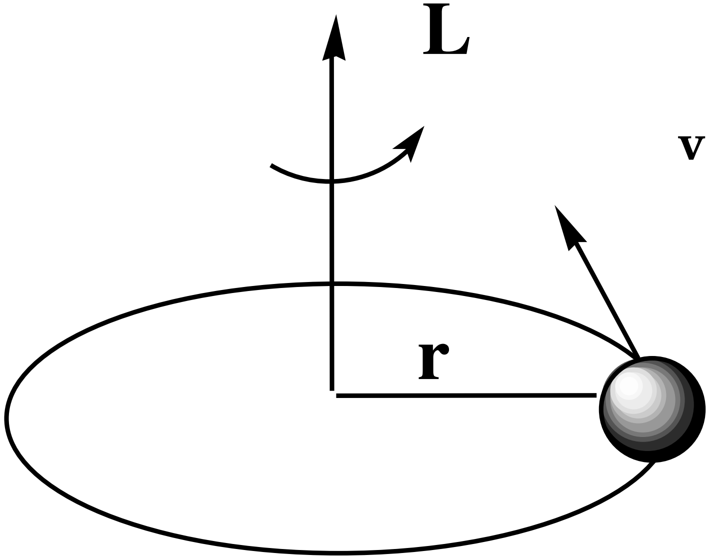
Spin Quantum Number (m_s)

Electron spin ⇒ +½ or -½

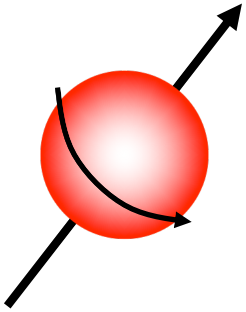
An orbital can hold 2 electrons that spin in opposite directions.

Electron spin and orbital angular momenta

orbitral angular momentum vector, **L**



spin angular momentum vector, **S**

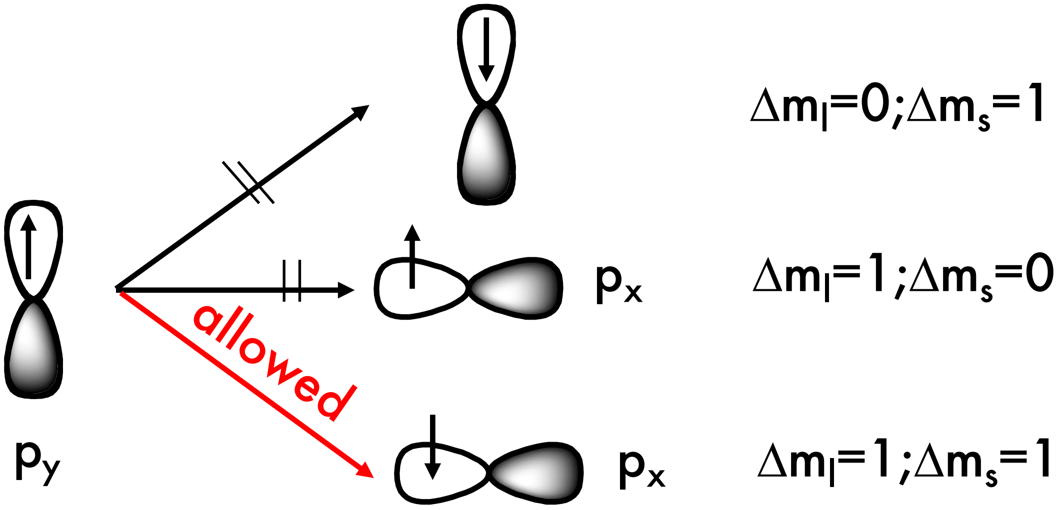


Selection rules for spin change in organic molecule

Conservation of angular momentum

- The electron spin must either remain unchanged or *change by one unit of angular momentum*, *ħ* (say, +1/2 *ħ* → -1/2 *ħ*).

- A spin change is exactly compensated by an equal and opposite change of angular momentum which occurs from some other (coupled) interaction with another source of angular momentum.

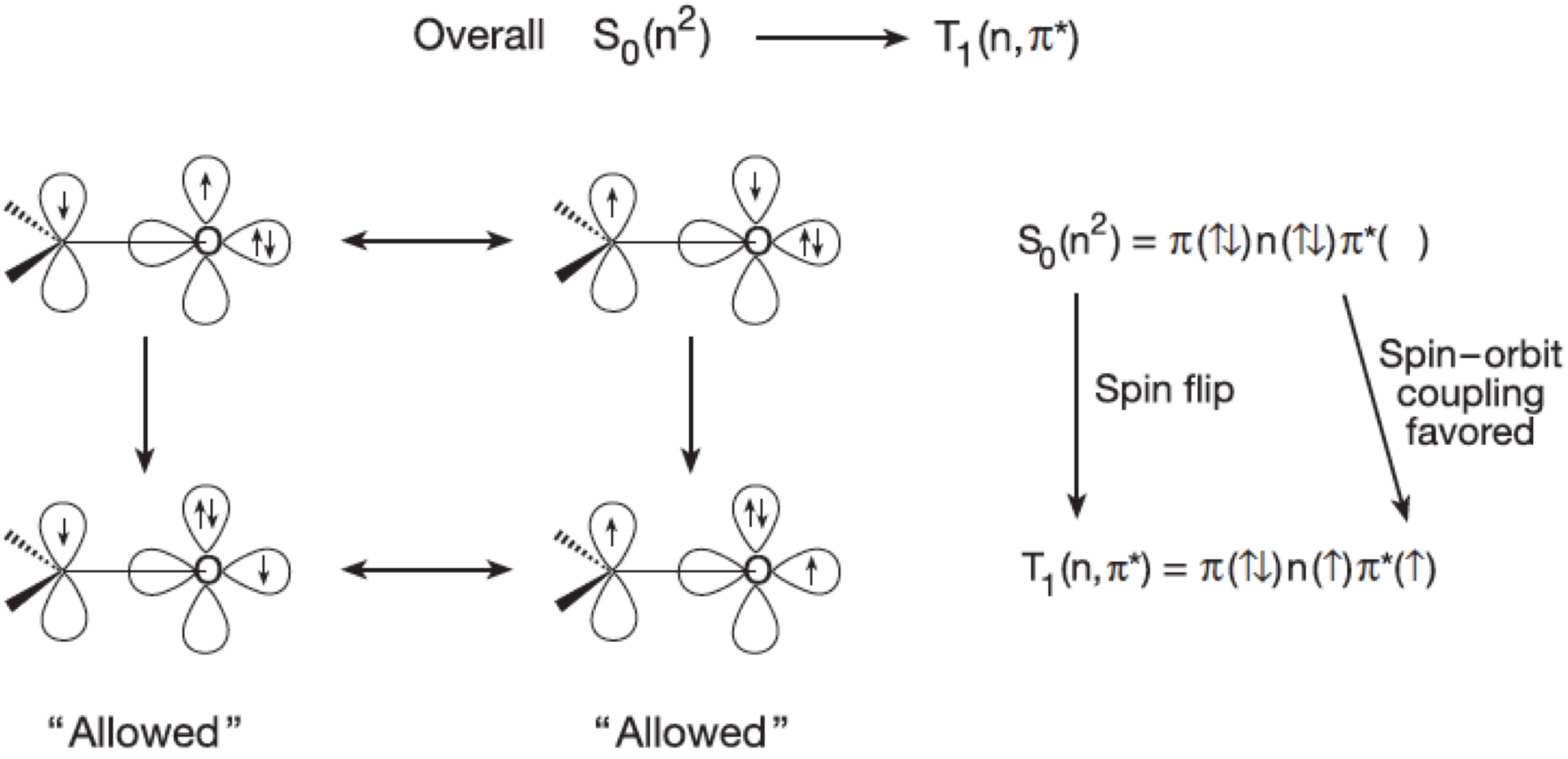


$\Delta m_l=0;\Delta m_s=1$

$\Delta m_l=1;\Delta m_s=0$

$\Delta m_l=1;\Delta m_s=1$

Spin-forbidden nπ* transition becomes allowed due to spin-orbit coupling



$$\text{Overall} \quad S_0(n^2) \longrightarrow T_1(n,\pi^*)$$

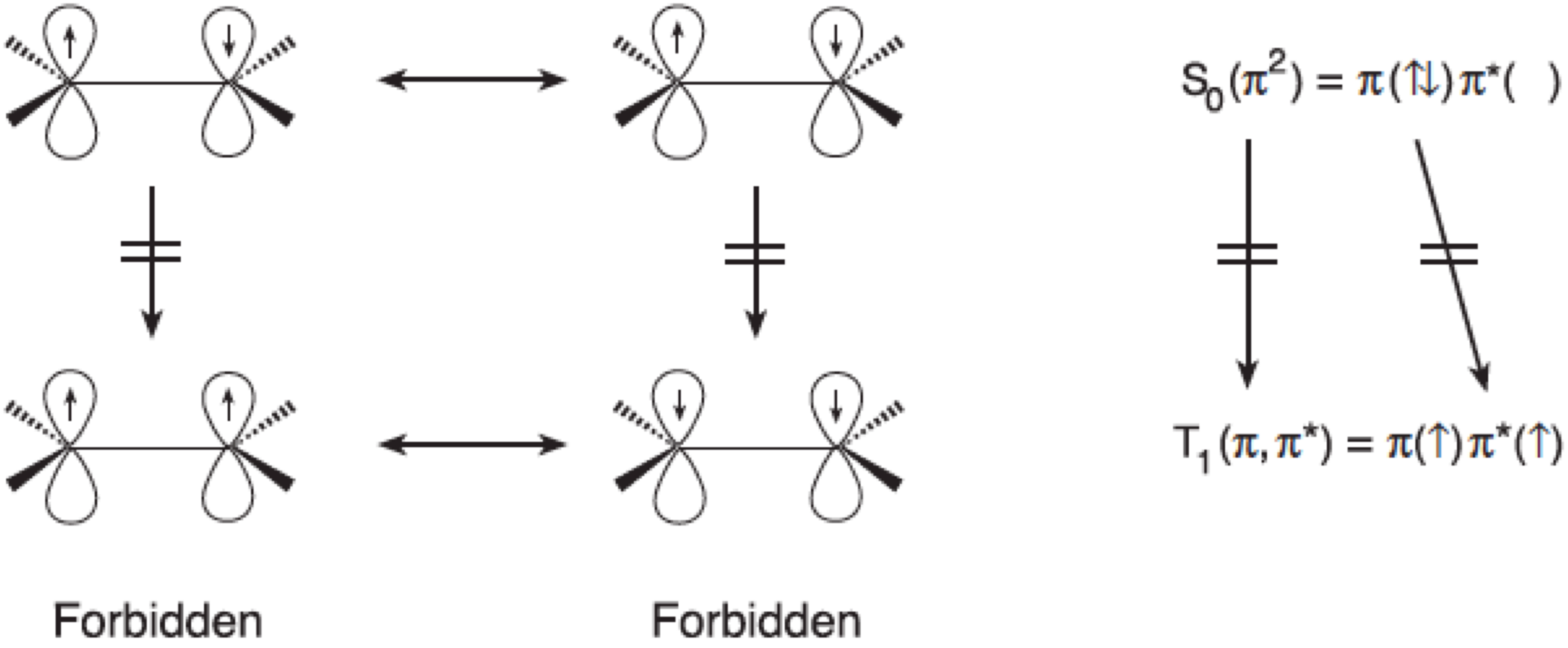
$$S_0(n^2) = \pi(\uparrow\downarrow)n(\uparrow\downarrow)\pi^*(\ \ )$$

$$T_1(n,\pi^*) = \pi(\uparrow\downarrow)n(\uparrow)\pi^*(\uparrow)$$

Figure 4.21 Orbital description of the spin–orbit selection rules for a radiative transition involving a spin flip. The $n^2 \rightarrow n,\pi^*$ transition involves an orbital angular momentum change that can be coupled with a spin momentum change on a single (oxygen) atom and is therefore spin–orbit “allowed.”

Spin-forbidden ππ* transition

Overall $S_0(\pi^2) \longrightarrow T_1(\pi,\pi^*)$



$S_0(\pi^2) = \pi(\uparrow\downarrow)\pi^*(\ )$

$T_1(\pi,\pi^*) = \pi(\uparrow)\pi^*(\uparrow)$

Figure 4.22 Orbital description of the spin–orbit selection rules for a radiative transition involving a spin flip. The $\pi^2 \rightarrow \pi,\pi^*$ transition does not involve an orbital angular momentum change and is spin–orbit "forbidden."

Triplet State: Singlet ⟷ Triplet Interconversion

ε_{max} (S_0 to T_1) and k^0_p (T_1 to S_0) values – depend on the orbital configuration of T_1 ($\pi\pi^*$, $n\pi^*$)

Molecules possessing pure π, π^* configurations

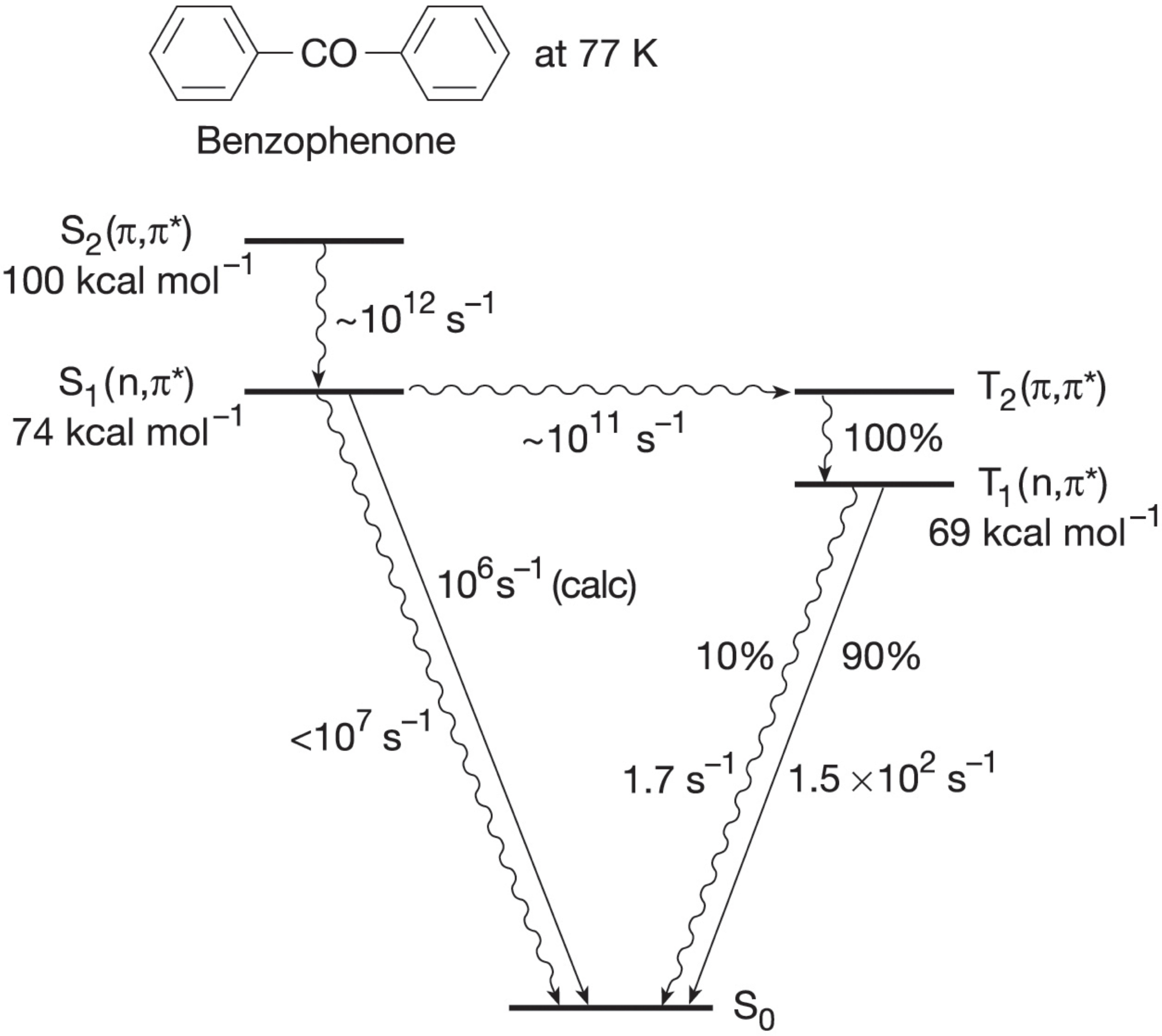
the value of ε max is ~10^{-5} to 10^{-6}

k^0_p is ~ 10^1 to 10^{-1} s^{-1}

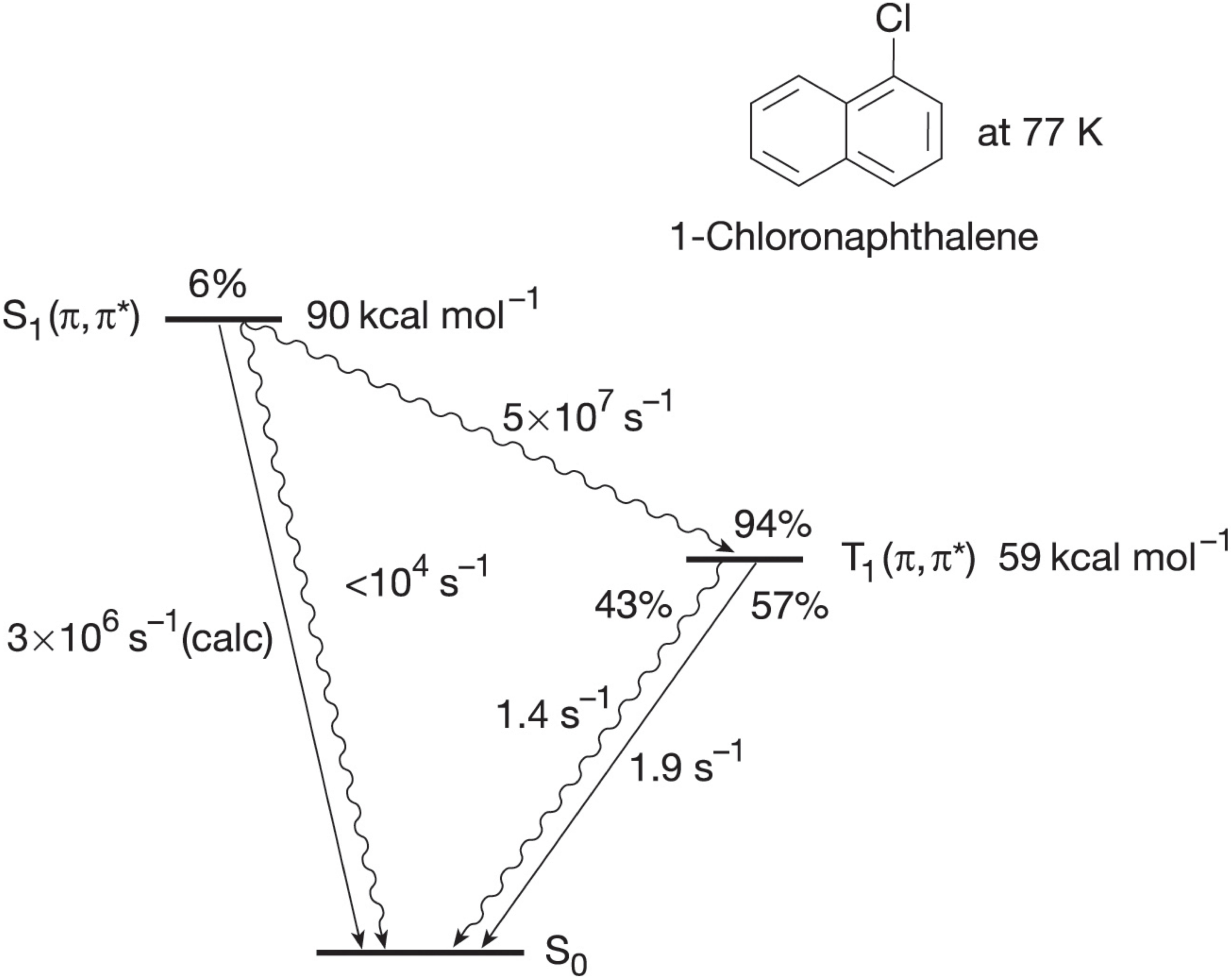
Molecules possessing pure n, π^* configurations

the value of ε max is ~10^{-1} to 10^{-2}

k^0_p is ~ 10^3 to 10^2 s^{-1}



CO
at 77 K
Benzophenone
S2(π,π*)
100 kcal mol−1
~10^12 s−1
S1(n,π*)
74 kcal mol−1
~10^11 s−1
T2(π,π*)
100%
T1(n,π*)
69 kcal mol−1
10^6 s−1 (calc)
10%
90%
<10^7 s−1
1.7 s−1
1.5 ×10^2 s−1
S0


Cl
at 77 K
1-Chloronaphthalene
6%
$S_1(\pi,\pi^*)$
90 kcal mol^{-1}
5×10^7 s^{-1}
94%
$T_1(\pi,\pi^*)$
59 kcal mol^{-1}
<10^4 s^{-1}
43%
57%
3×10^6 s^{-1}(calc)
1.4 s^{-1}
1.9 s^{-1}
S_0

Strength of coupling of an electron spin with internal magnetic fields

If L is coupled to S, they both precess around their resultant. If they are strongly coupled they precess rapidly, if they are weakly coupled they precess slowly.

Strength of L-S coupling is defined by

$$\hat{H}_{SO} = \zeta l \cdot s$$

$$\zeta_{n,l} \propto \frac{Z^4}{n^3 l(l+1/2)(l+1)}$$

the magnitude of the spin orbital coupling operator (H_{SO}) depends on ξ

the spin-orbit coupling parameter ξ increases with the nuclear magnetic field seen by the electron (with the nuclear charge)

⇓

ξ increases with the atomic number Z

Spin-orbit coupling energies for selected atoms

Table 4.7 Spin–Orbit Coupling in Atoms[a,b]

Atom	Atomic number	ζ (kcal mol^{-1})	Atom	Atomic number	ζ (kcal mol^{-1})
C[c]	6	0.1	I	53	14.0
N[c]	7	0.2	Kr	36	15
O[c]	8	0.4	Xe	54	28
F[c]	9	0.7	Pb	82	21
Si[c]	14	0.4	Hg	80	18
P[c]	15	0.7	Na	11	0.1
S[c]	16	1.0	K	19	0.2
Cl[c]	17	1.7	Rb	37	1.0
Br	35	7.0	Cs	55	2.4

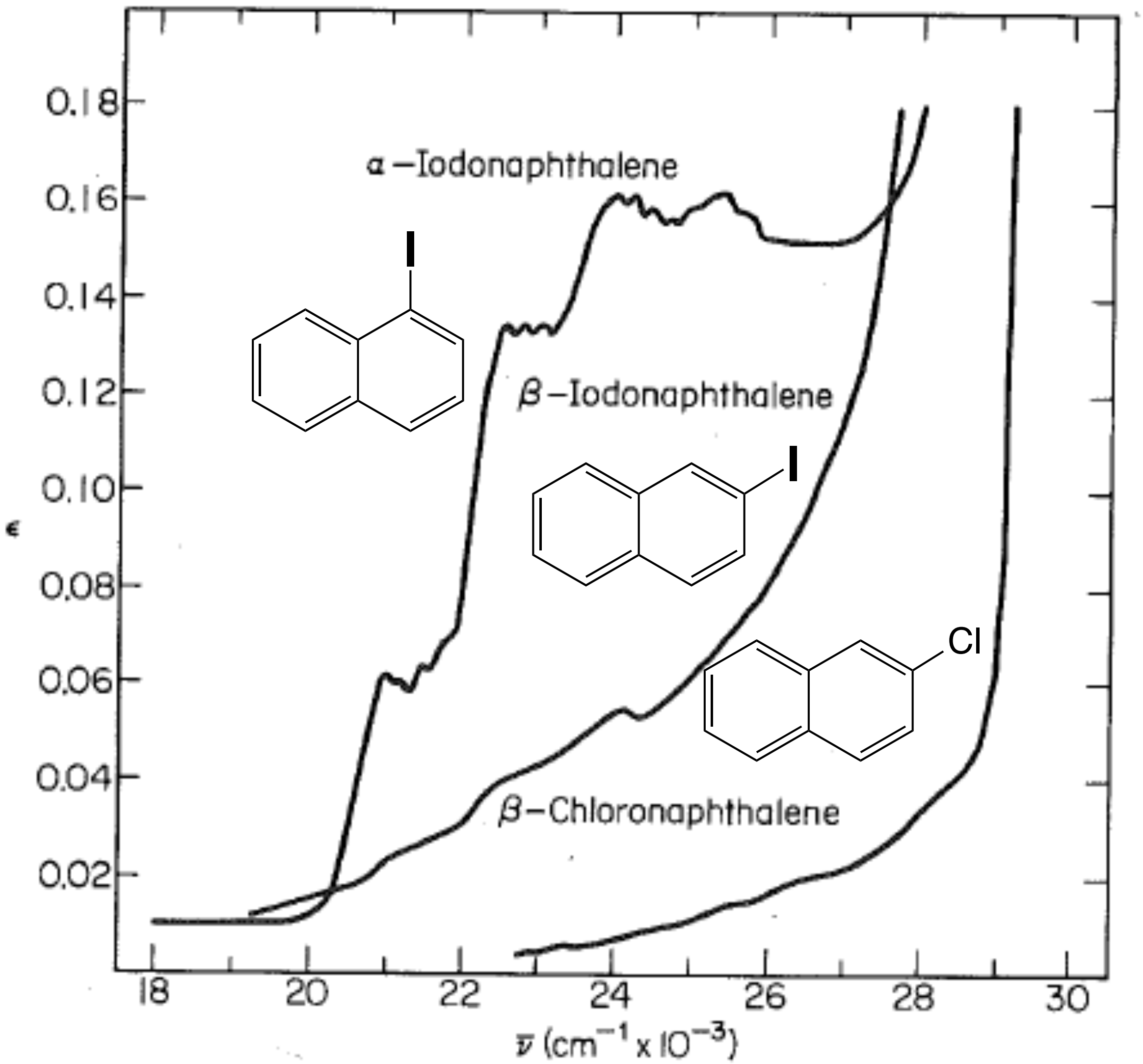
The heavy atom effect on spin transitions

The “heavy atom” effect is an “atomic number” effect that is related to the coupling of the electron spin and electron orbital motions (spin-orbit coupling, SOC).

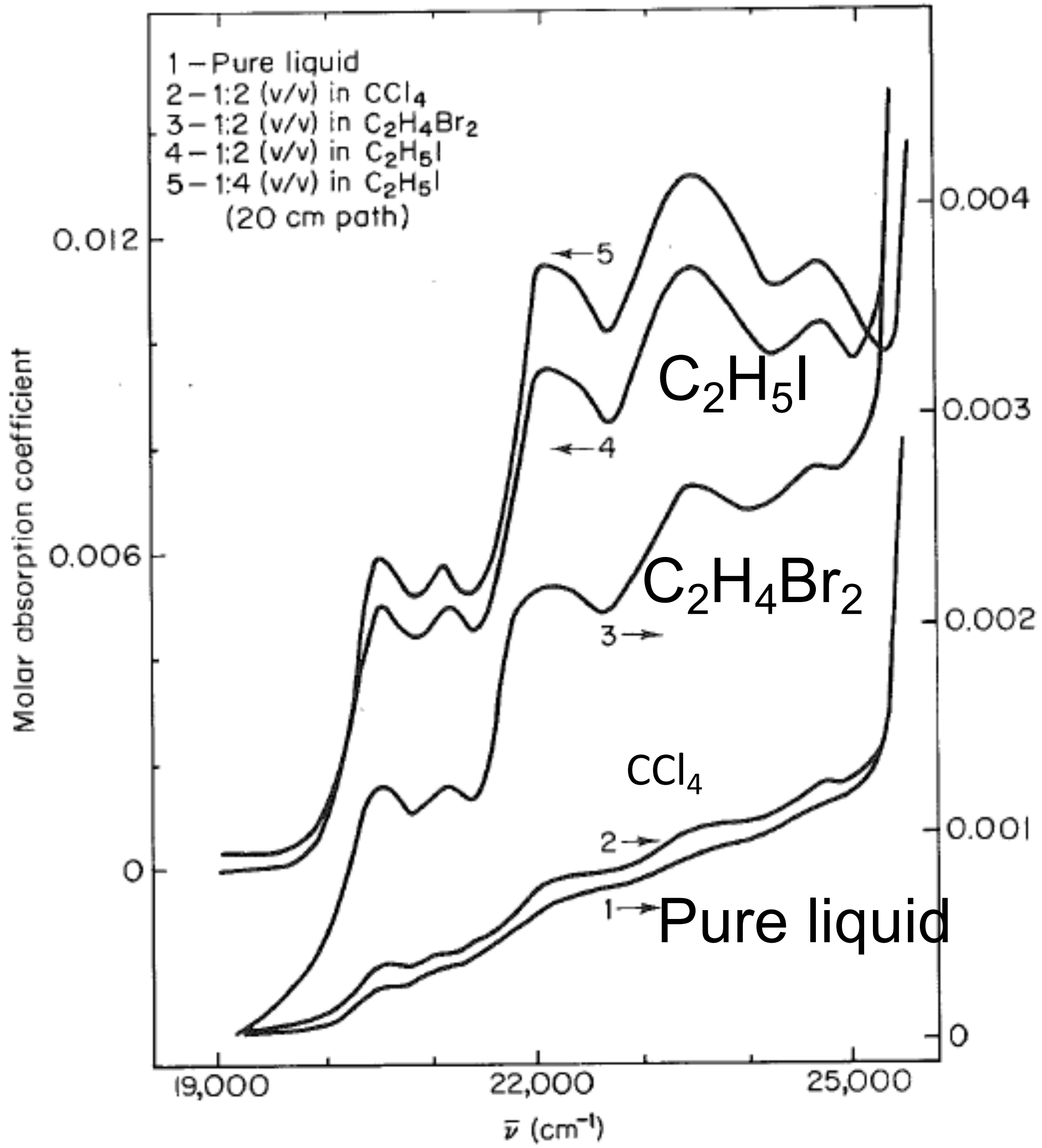
Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z.

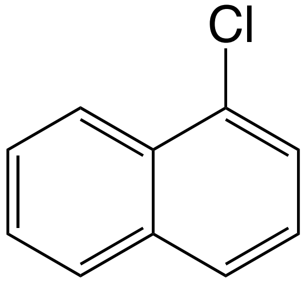
The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

Internal Heavy Atom Effect

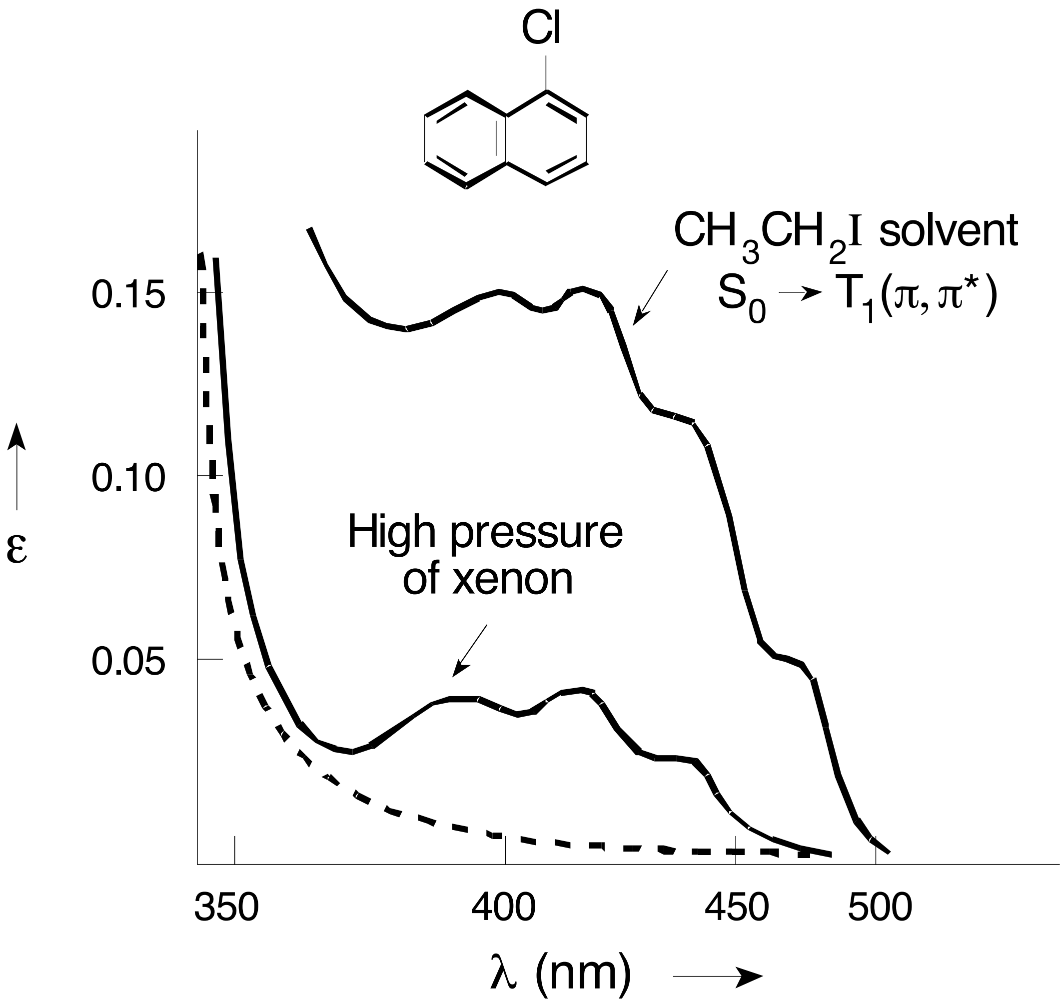


External Heavy Atom Effect

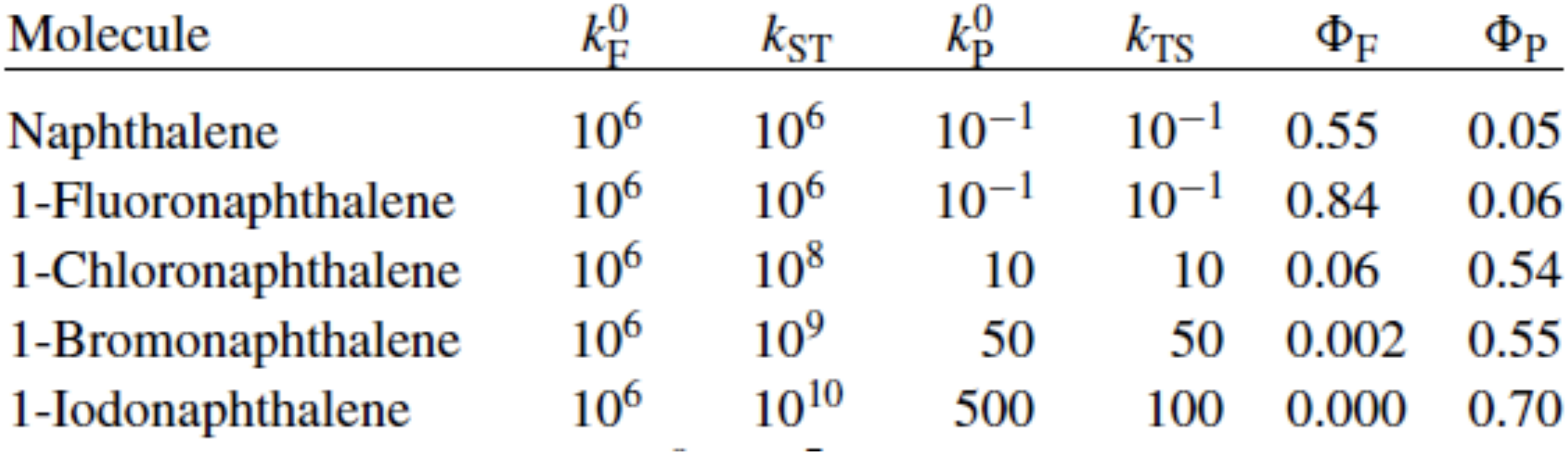




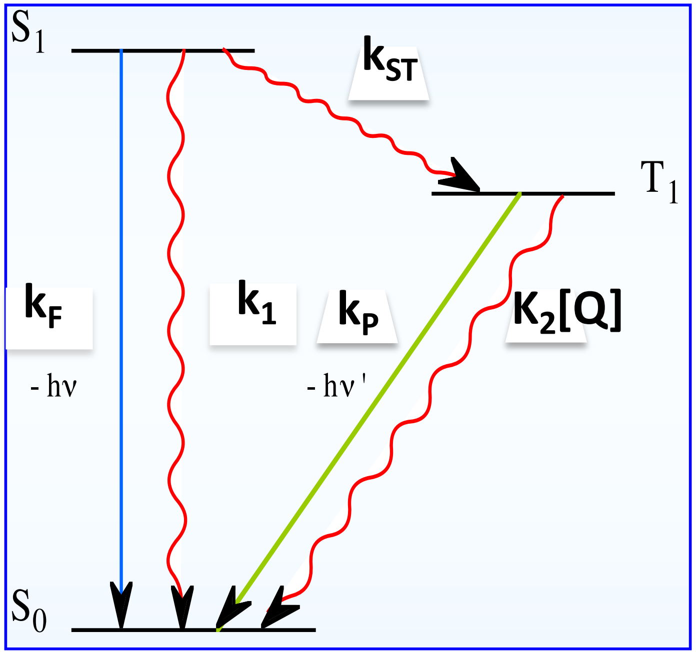
External Heavy Atom Effect



Examples of internal heavy atom effect



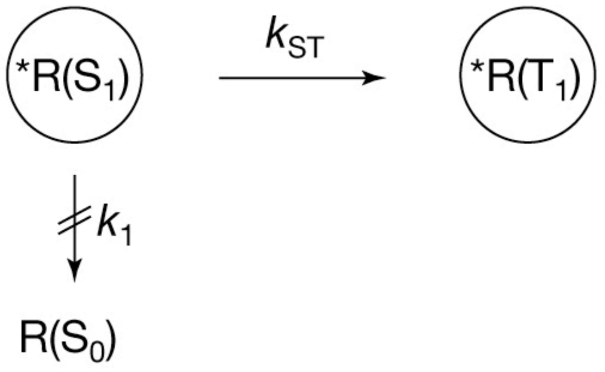
Molecule	k_F^0	k_{ST}	k_P^0	k_{TS}	Φ_F	Φ_P
Naphthalene	10^6	10^6	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^6	10^6	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10^6	10^8	10	10	0.06	0.54
1-Bromonaphthalene	10^6	10^9	50	50	0.002	0.55
1-Iodonaphthalene	10^6	10^{10}	500	100	0.000	0.70



$$\begin{tikzcd}
{}^*\mathrm{R}(\mathrm{S}_1) \arrow[r, "k_{\mathrm{ST}}"] \arrow[d, "k_1"] & {}^*\mathrm{R}(\mathrm{T}_1) \arrow[r, "k_{\mathrm{P}}"] \arrow[d, "k_2\,[\mathrm{Q}]"] & \mathrm{S}_0 + h\nu_{\mathrm{P}} \\
\text{not } {}^*\mathrm{R}(\mathrm{T}_1) & \text{not } h\nu_{\mathrm{P}} &
\end{tikzcd}$$

Strategy to record phosphorescence at room temperature through supramolecular approach

Stage 1

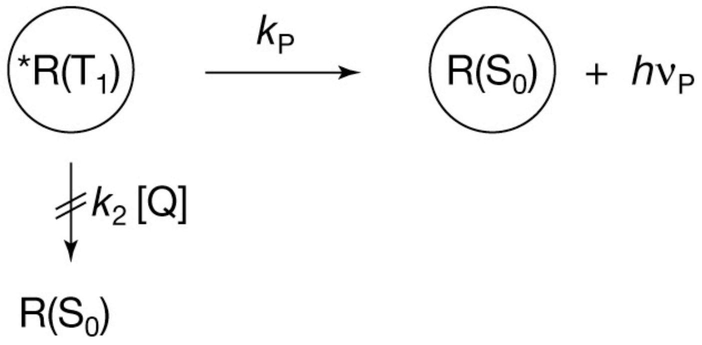


$$\begin{tikzcd} {}^*R(S_1) \arrow[r, "k_{ST}"] \arrow[d, "/" marking, "k_1"] & {}^*R(T_1) \\ R(S_0) \end{tikzcd}$$

Heavy atom effect mainly on k_{ST} so that $k_{ST} > k_1$

Make more triplets through the heavy atom effect

Stage 2

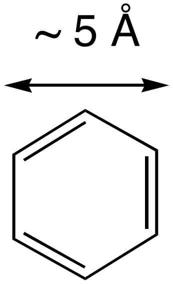


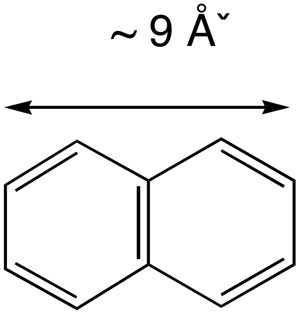
$$\begin{tikzcd} {}^*R(T_1) \arrow[r, "k_P"] \arrow[d, "/" marking, "k_2\,[Q]"] & R(S_0) + h\nu_P \\ R(S_0) \end{tikzcd}$$

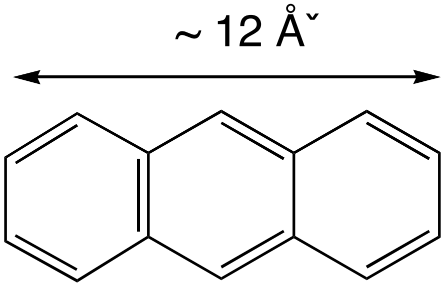
Heavy atom effect mainly on k_P so that $k_P > k_2\,[Q]$

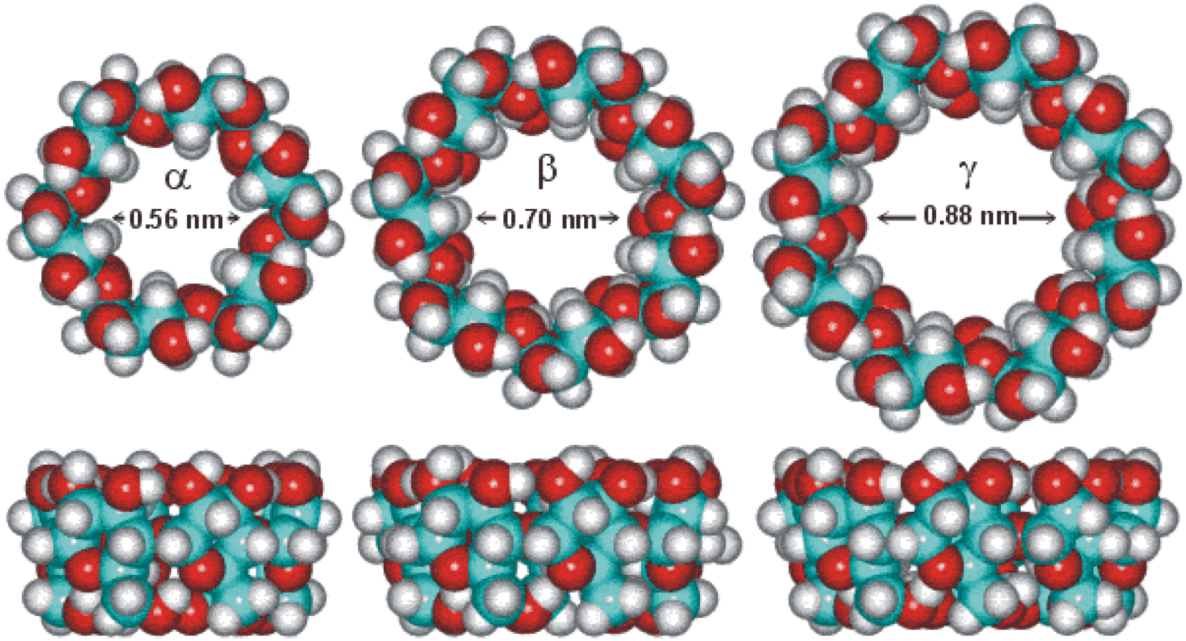
Make triplets emit faster in competition with quenching processes

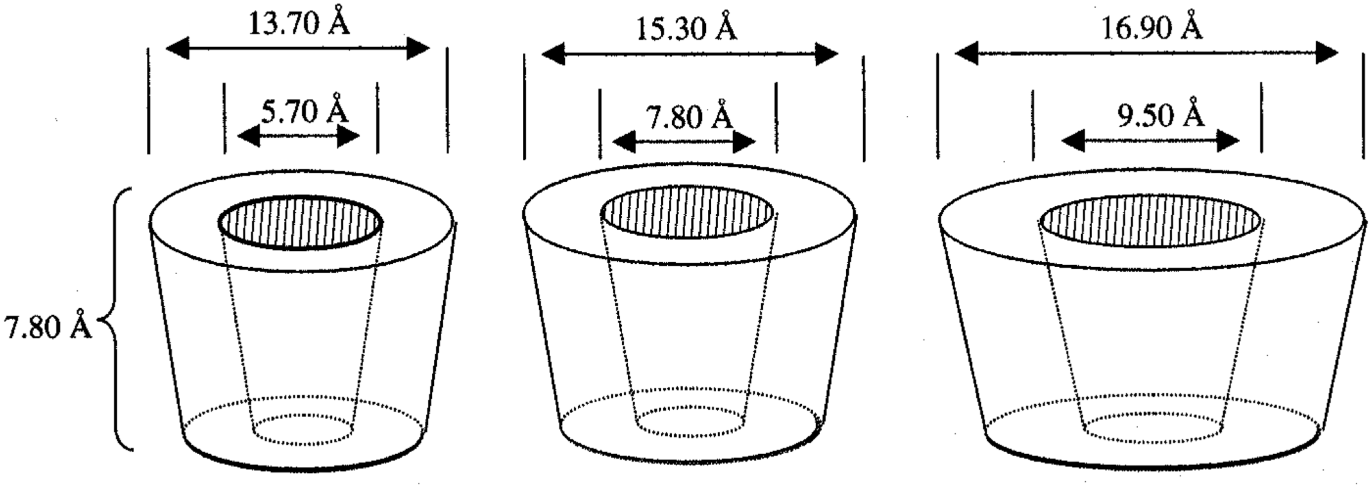
Water soluble organic hosts: Cyclodextrins







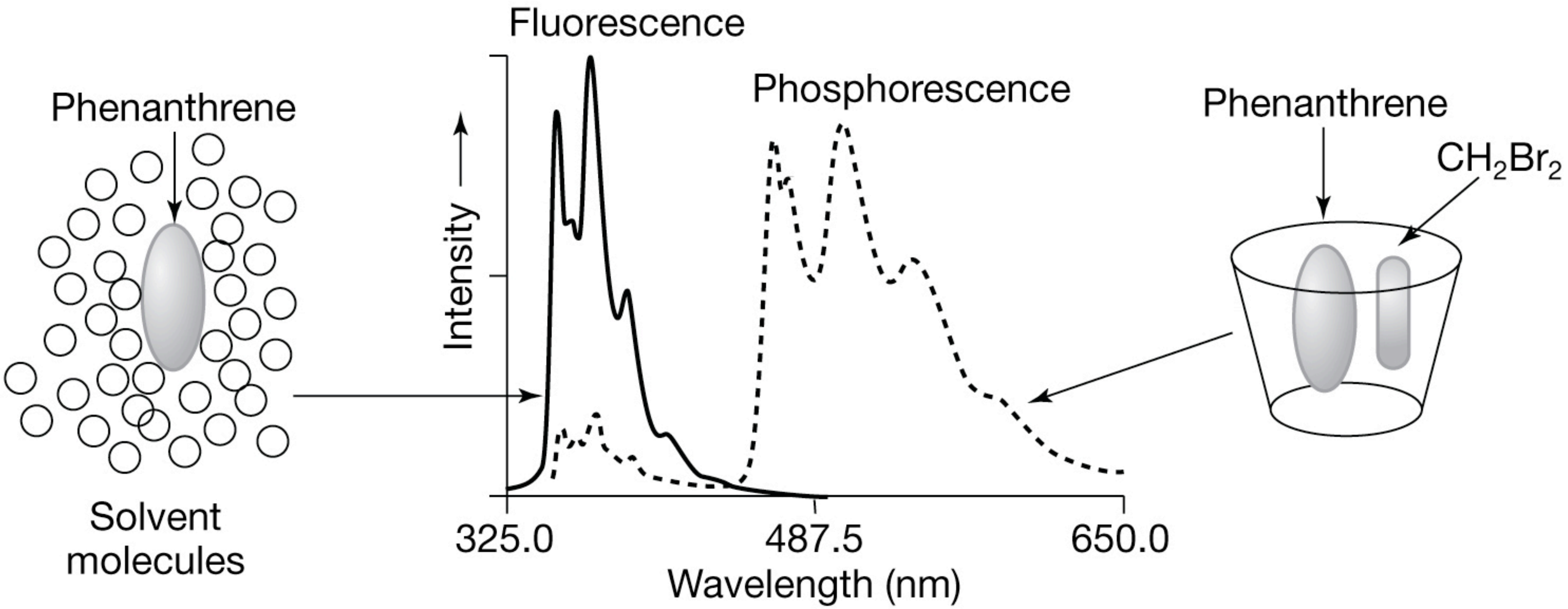




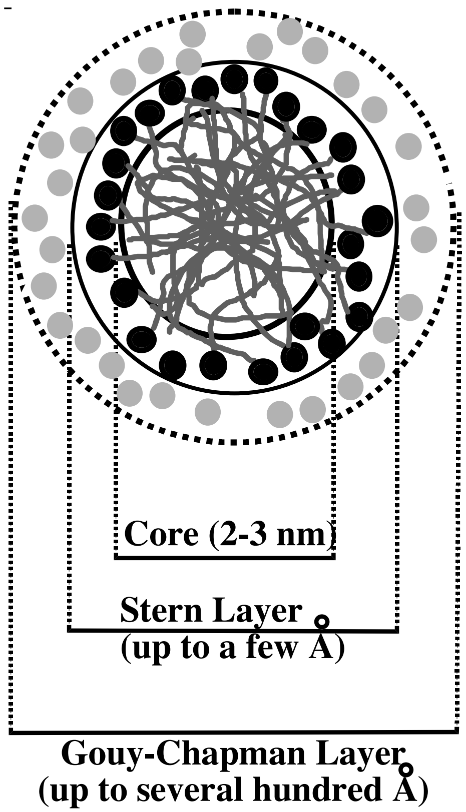
α-CD β-CD γ-CD

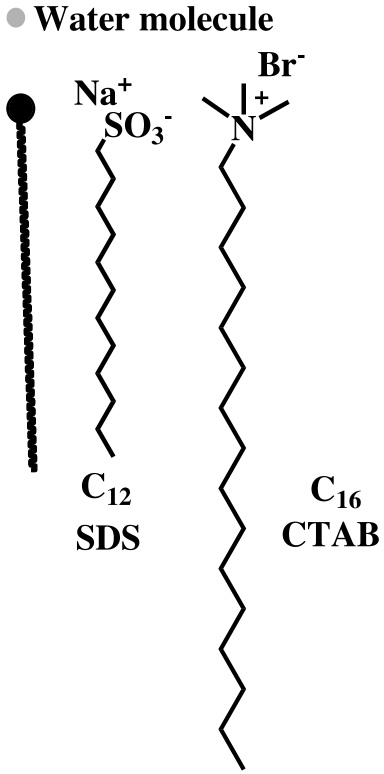
Cyclodextrins as hosts

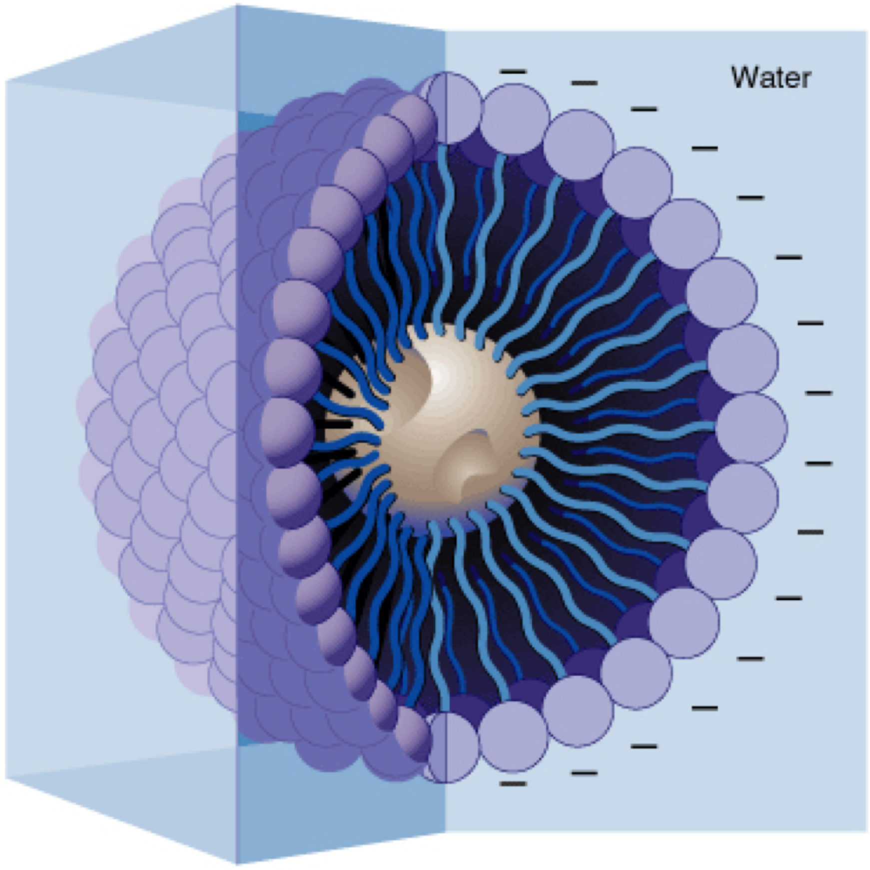
Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest



Micelles


Core (2-3 nm)
Stern Layer (up to a few Å)
Gouy-Chapman Layer (up to several hundred Å)


● Water molecule
Na$^+$
SO$_3^-$
Br$^-$
+
N
C$_{12}$
SDS
C$_{16}$
CTAB

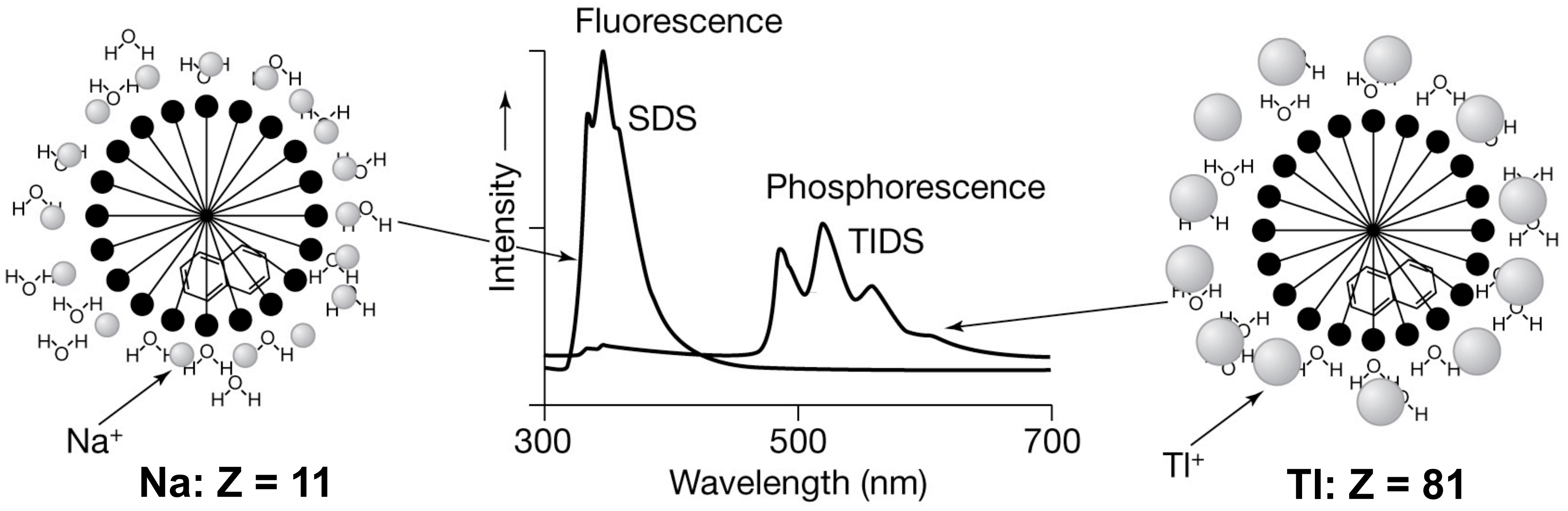

Water

Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom pertuber

Atom	Ionic Radius of the Cation (Å)	Spin-Orbit Coupling ζ cm^{-1}
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

Micelles as hosts

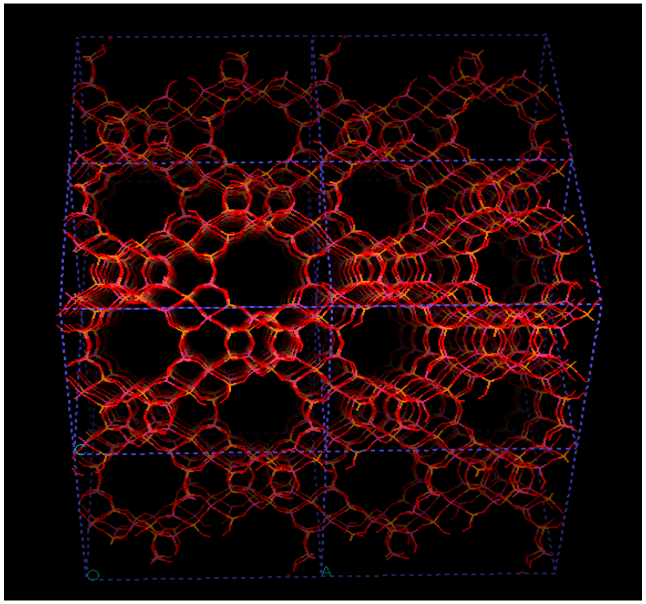
Naphthalene@SDS micelle: effect of heavy atom counterions

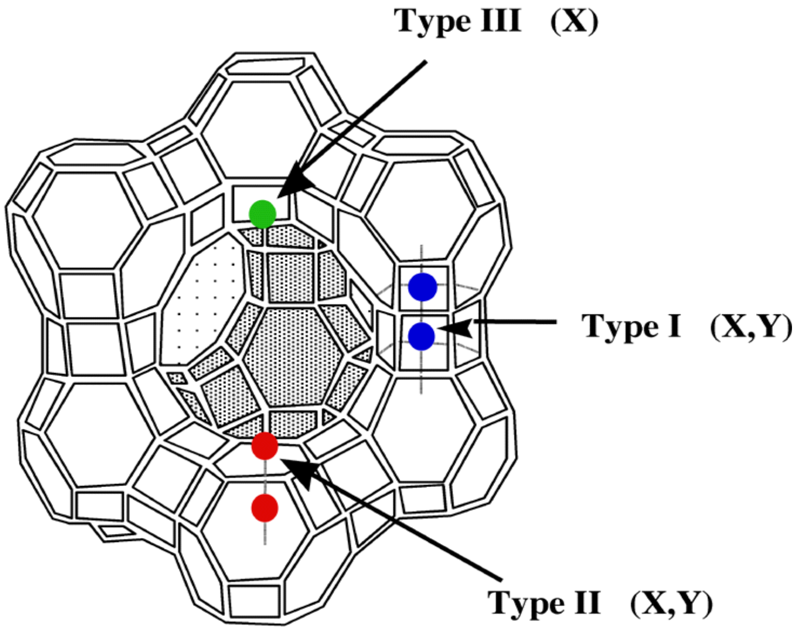


Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

Characteristics of Faujasites (Zeolites)

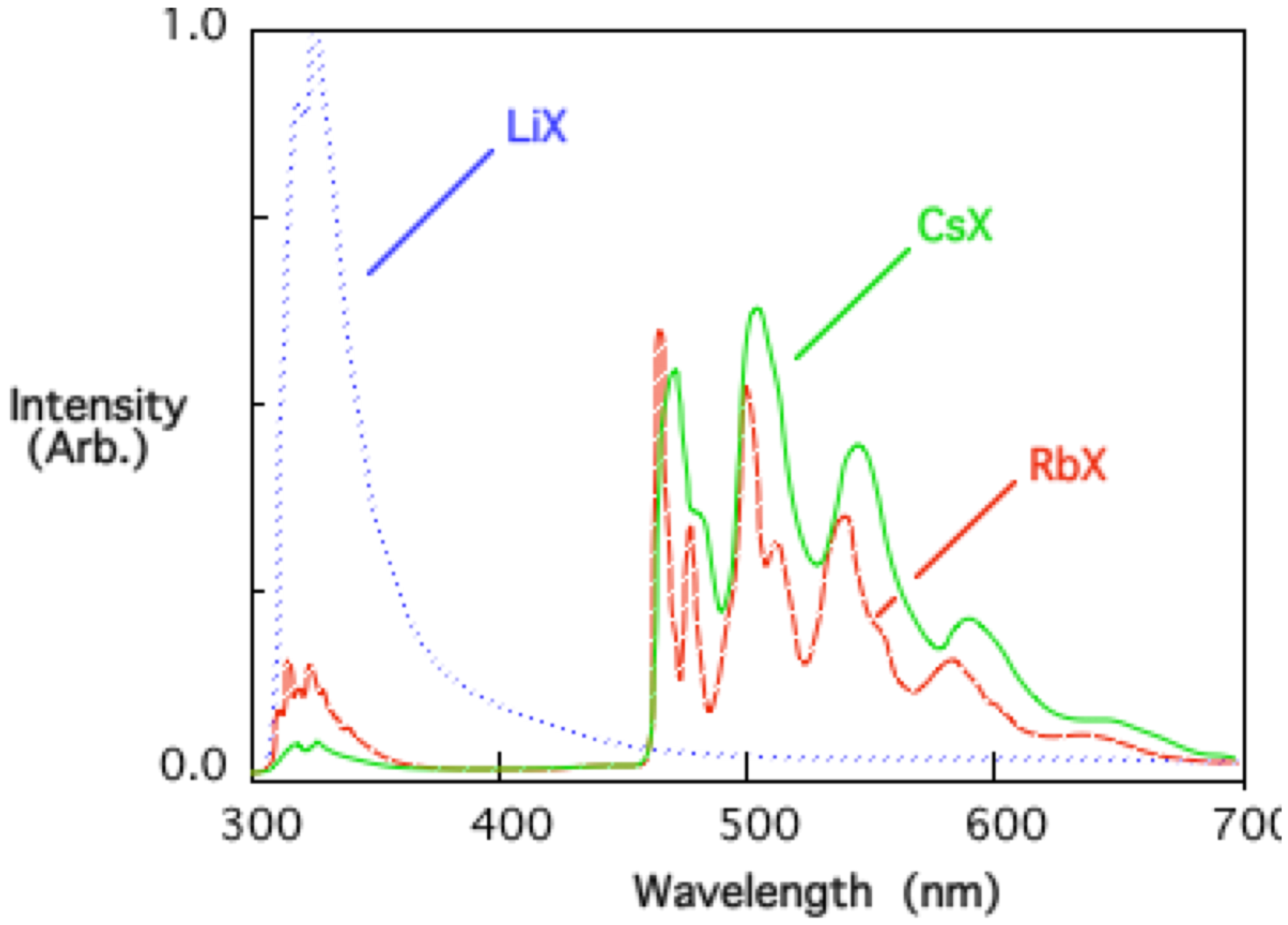
$M_x(AlO_2)_x\ (SiO_2)_y.ZH_2O$

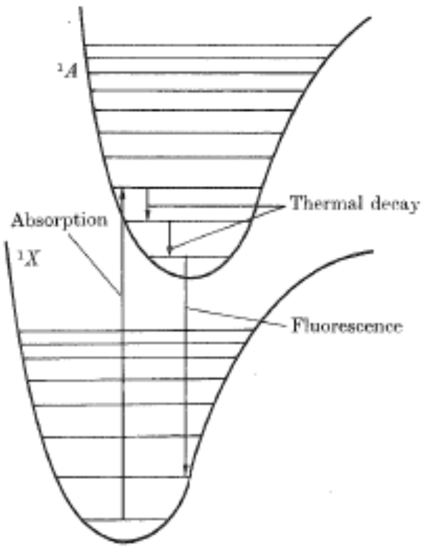


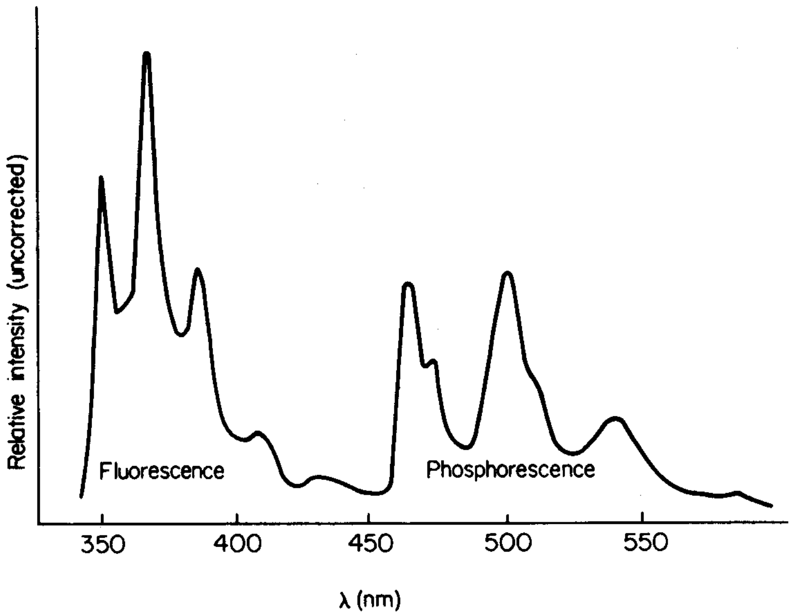


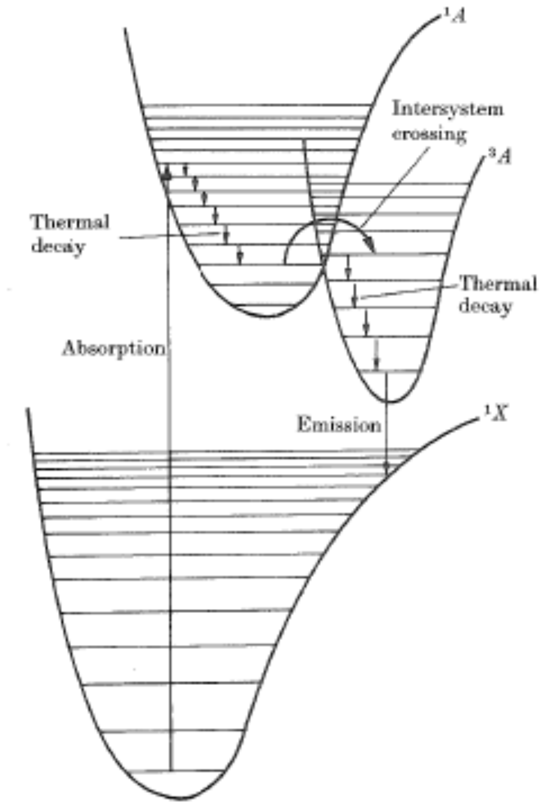
- **Microporous solid**
- **Large surface area**
- **Well defined channels/cages**
- **Si/Al ratio = 2.4**
- **Type I - 4 cations /supercage**
- **Type II- 4 cations /supercage**

Emission Spectra of Naphthalene Included in MY Zeolites







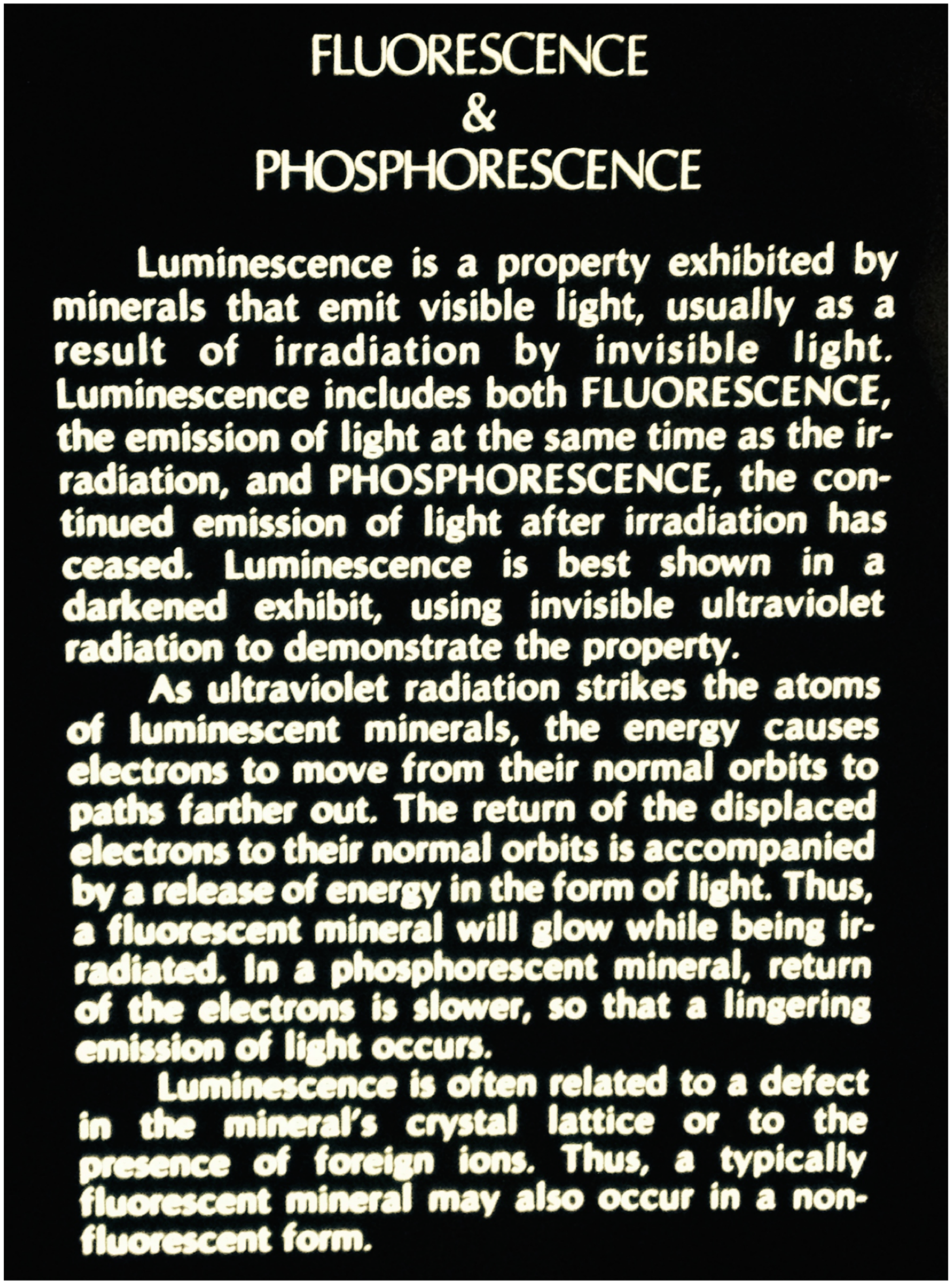


Fluorescence:

- High radiative rate constant, 10^{-10} to
- Precursor state (S_1) has short lifetime
- Generally not susceptible to quenching

Phosphorescence:

- Low radiative rate constant, 10^{-6} to $10\ s^{-1}$
- Precursor state (T_1) has long lifetime
- Very much susceptible to quenching
- Emission quantum yield depends on S_1 to T_1 crossing

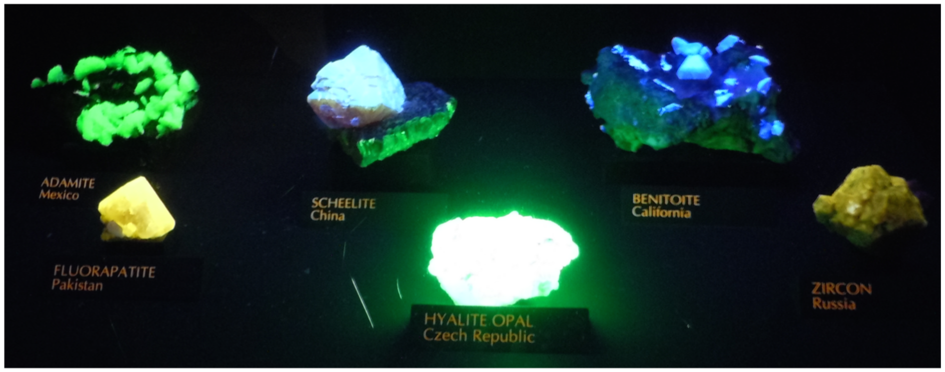


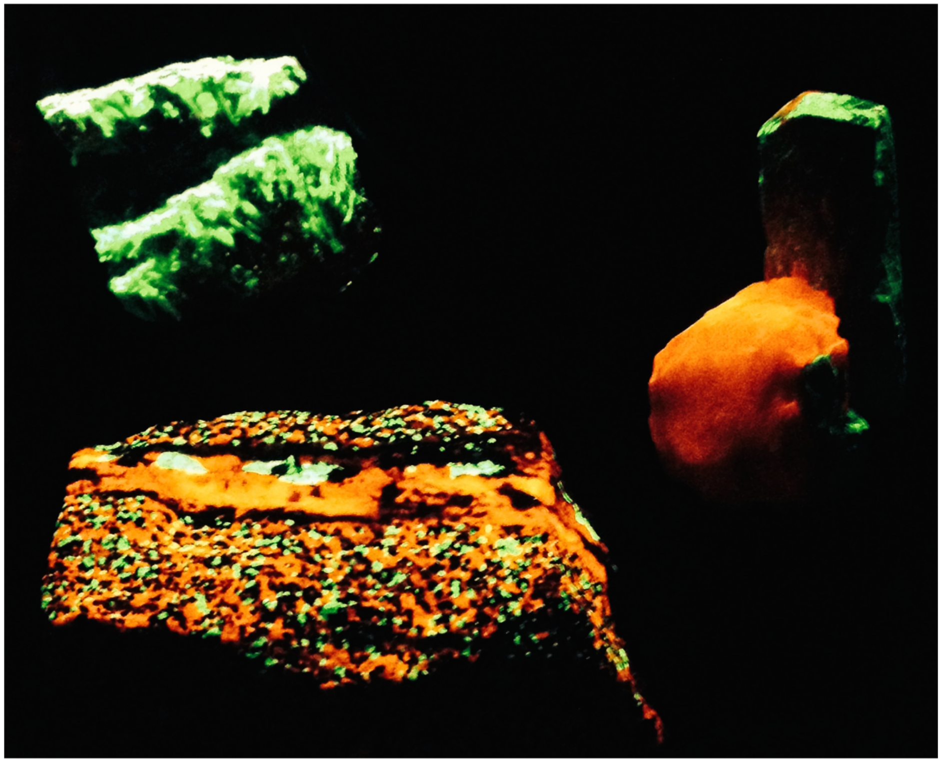
FLUORESCENCE & PHOSPHORESCENCE

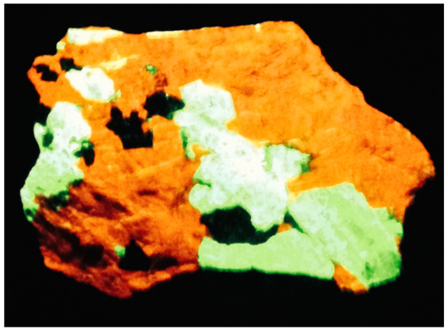
Luminescence is a property exhibited by minerals that emit visible light, usually as a result of irradiation by invisible light. Luminescence includes both FLUORESCENCE, the emission of light at the same time as the irradiation, and PHOSPHORESCENCE, the continued emission of light after irradiation has ceased. Luminescence is best shown in a darkened exhibit, using invisible ultraviolet radiation to demonstrate the property.

As ultraviolet radiation strikes the atoms of luminescent minerals, the energy causes electrons to move from their normal orbits to paths farther out. The return of the displaced electrons to their normal orbits is accompanied by a release of energy in the form of light. Thus, a fluorescent mineral will glow while being irradiated. In a phosphorescent mineral, return of the electrons is slower, so that a lingering emission of light occurs.

Luminescence is often related to a defect in the mineral's crystal lattice or to the presence of foreign ions. Thus, a typically fluorescent mineral may also occur in a non-fluorescent form.







Types of emissions

- Fluorescence
- Phosphorescence
- Emission from upper excited states
- Excimer emission
- Exciplex emission
- TICT emission
- Delayed emission

Points to Remember

- Electronic Configuration of States, nπ*; ππ*
- Spin Configuration of States (S and T)
- Singlet-Triplet Gap, ΔE (S-T)
- Rules of Intersystem Crossing (El-Sayed's Rule)
- Heavy Atom Effect
- Absorption and Emission
- Fluorescence and Phosphorescence
- Radiative and Radiationless Transitions
- Kasha's Rule