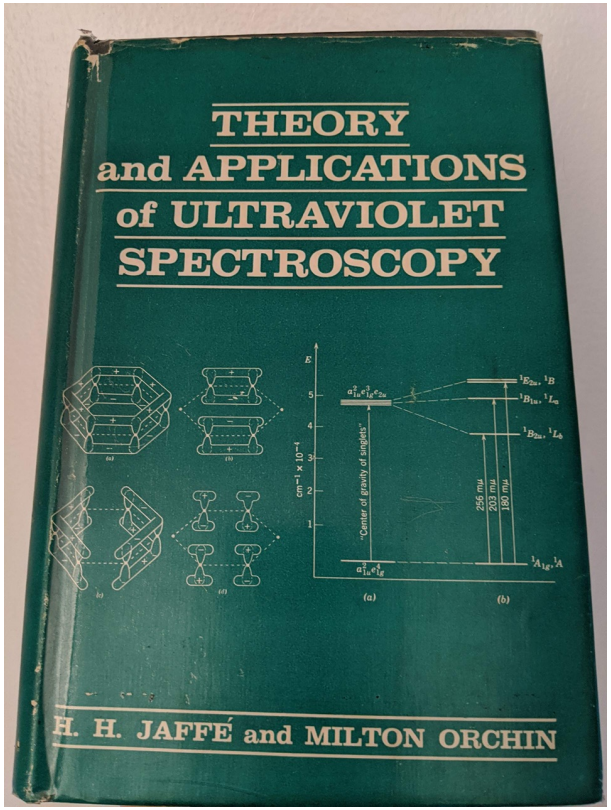
Manifestations of Light-Matter Interactions

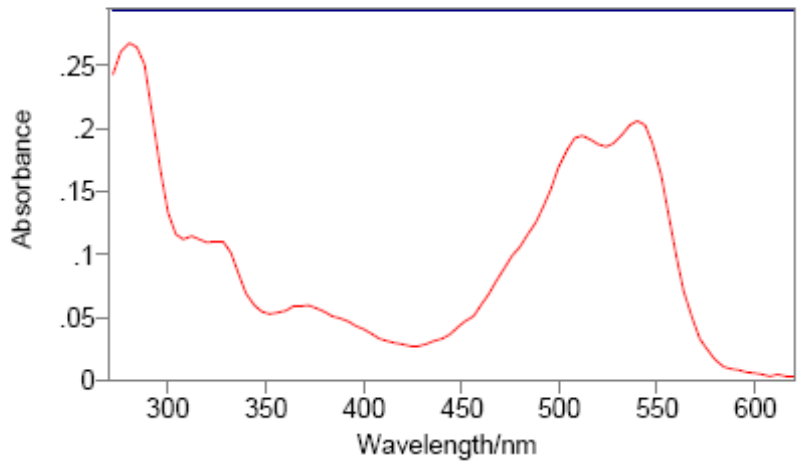
- Reflection
- Refraction
- Scattering
- **Absorption**

Absorption

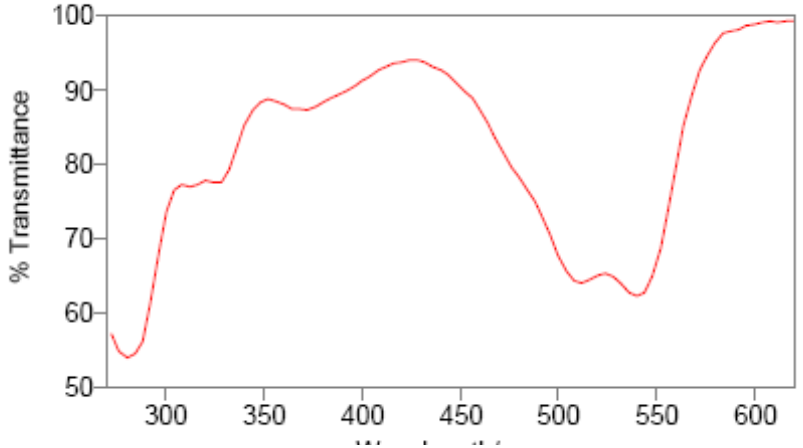


Theory and Applications of Ultraviolet Spectroscopy,
by H. H. Jaffe and M. Orchin

•**Absorption spectrum of a red textile d**

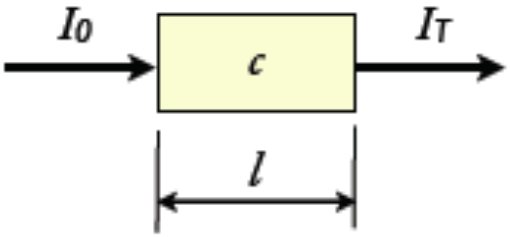


•**Transmission spectrum of the same**



Absorption

Beer-Lambert Law

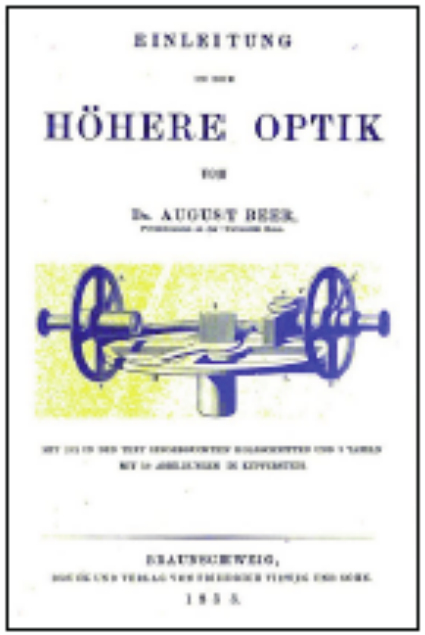


$$A = -\log\frac{I_T}{I_0} = -\log T = \varepsilon \cdot c \cdot l \quad [-]$$

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} · l · cm^{-1}

$\Rightarrow$ $T = 0.01$, $A = 2 \Rightarrow$ 99% of the light is absorbed within the first 2 mm of the solution


EINLEITUNG

HÖHERE OPTIK

Dr. AUGUST BEER

BRAUNSCHWEIG,

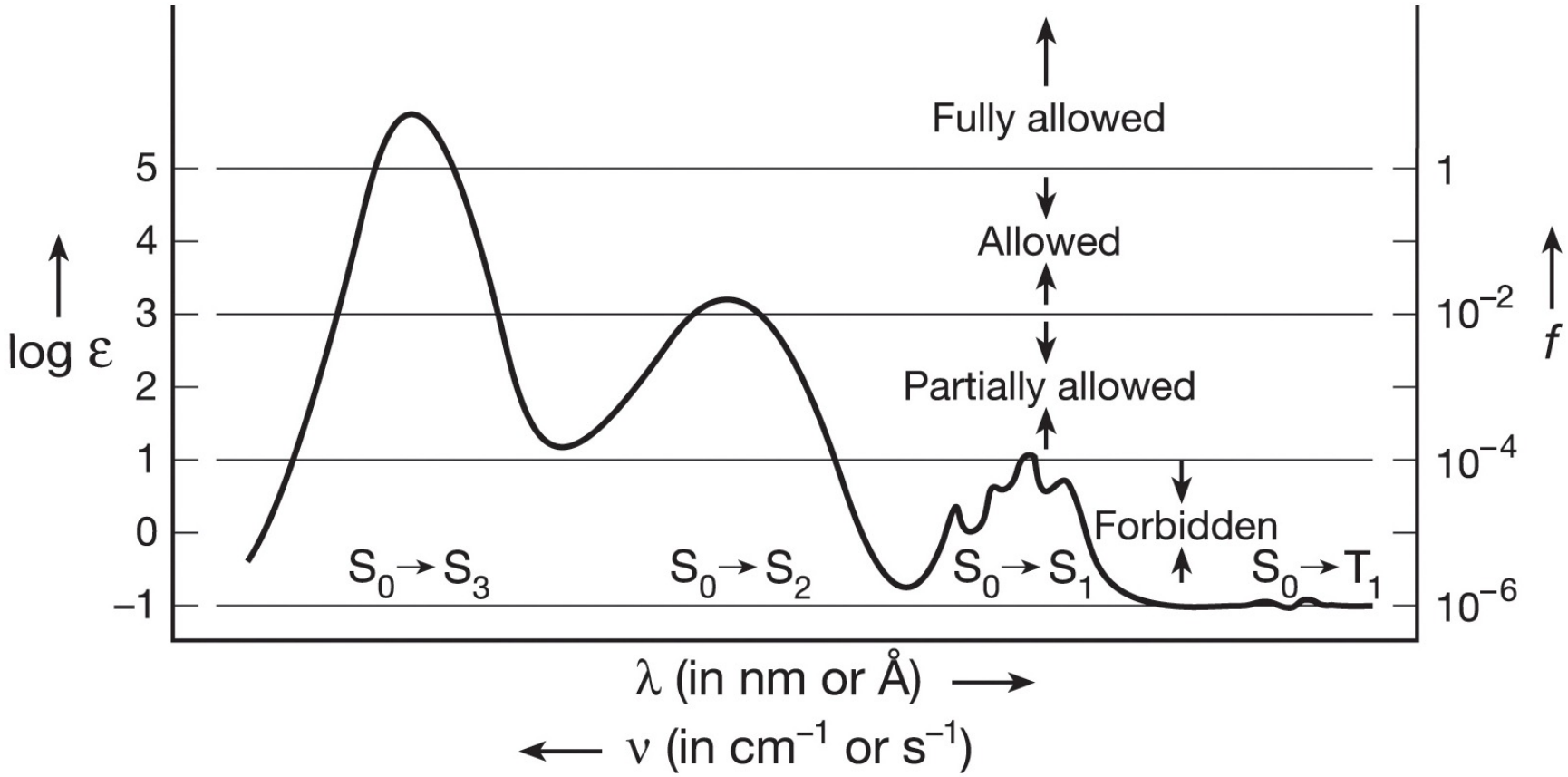
1853.

August Beer
(1825-1863)

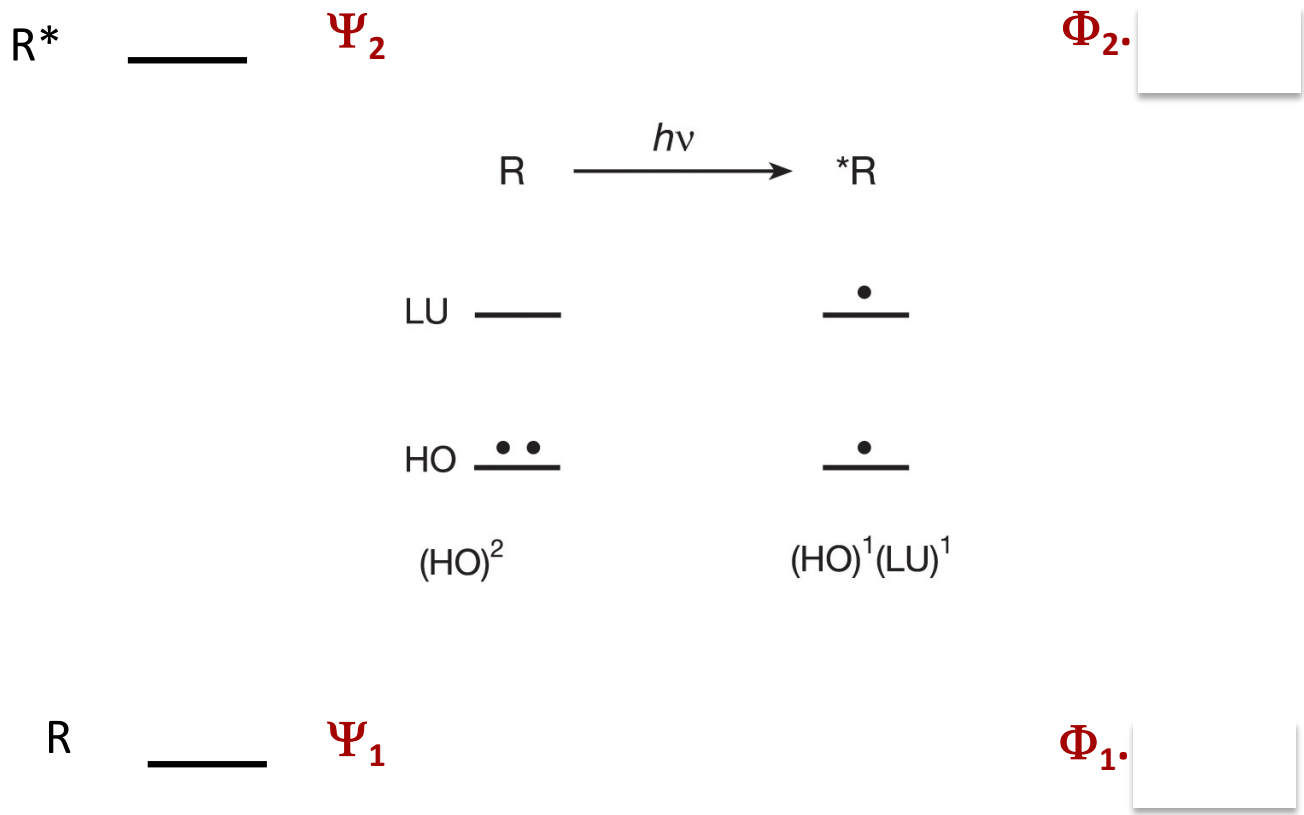
OD ~ 2: 1% transmission
OD ~ 1: 10% transmission
OD ~ 0.01: 98% transmission

OD can be adjusted with concentration

Absorption Spectra: Why the ε and *f* vary with the band?



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

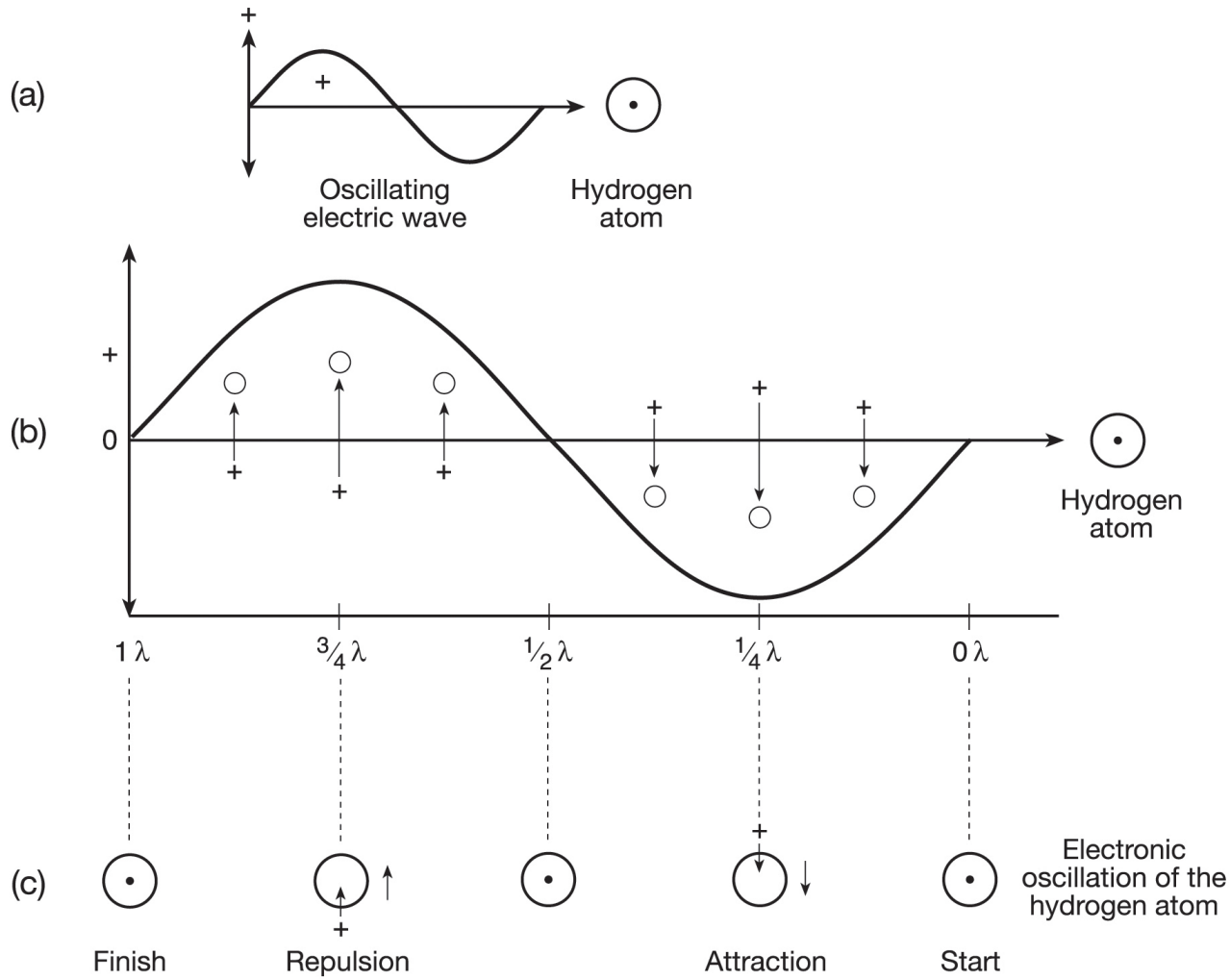


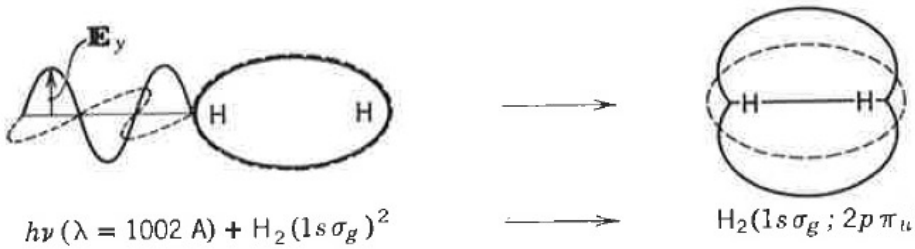
Electron jump between orbitals generally takes ~ 10^{-15} to 10^{-16} s

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

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

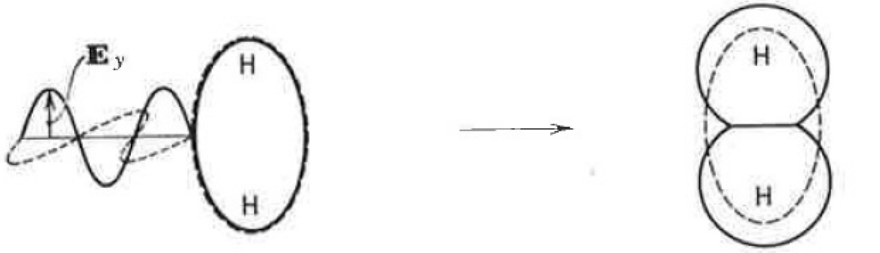
Light as an oscillating electric field





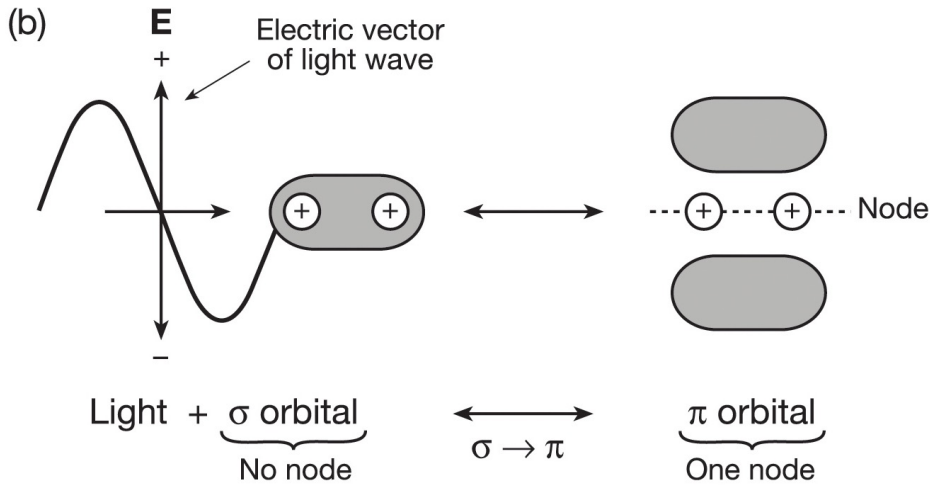
$h\nu\,(\lambda = 1002\ \text{A}) + H_2(1s\sigma_g)^2 \longrightarrow H_2(1s\sigma_g\,;\,2p\,\pi_u)$

$[h\nu + H_2(^1\Sigma_g^+) \rightarrow H_2(^1\Pi_u)]$



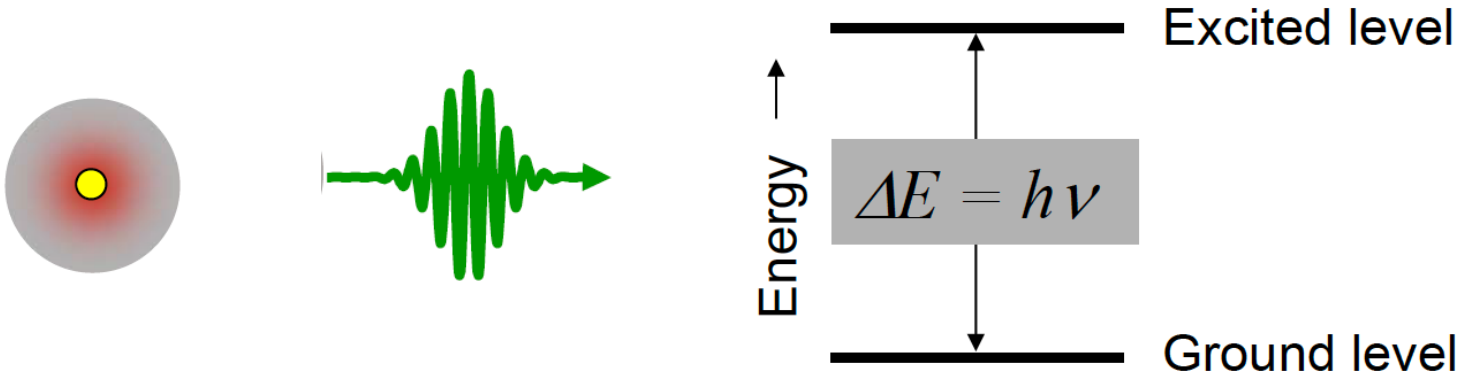
$h\nu\,(\lambda = 1109\ \text{A}) + H_2(1s\sigma_g)^2 \longrightarrow H_2(1s\sigma_g\,;\,2p\,\sigma_u^*)$

$[h\nu + H_2(^1\Sigma_g^+) \rightarrow H_2(^1\Sigma_u^+)]$

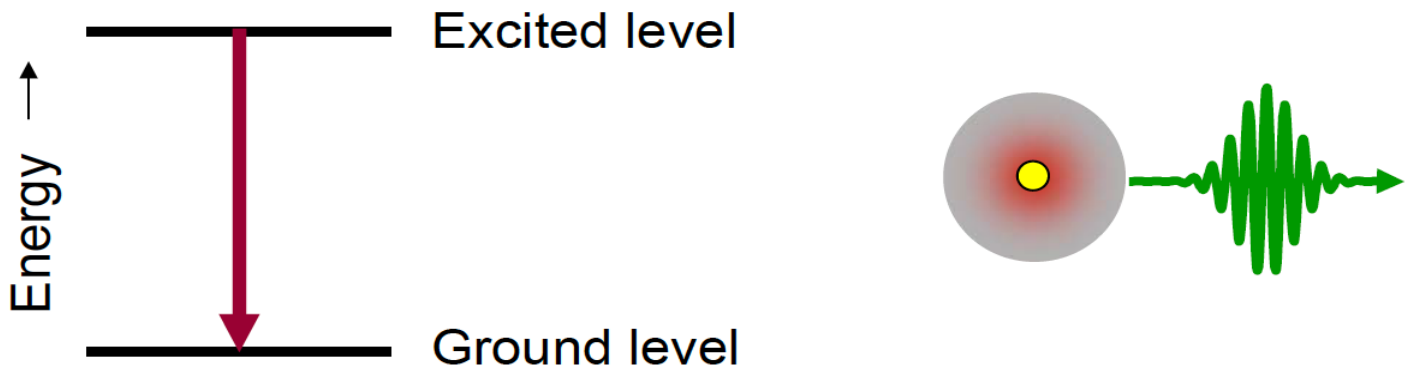


Rules for absorption and emission are the same

Absorption



Emission



Probability of light absorption and emission
Fermi's Golden Rule

$$\Psi_1 | P_{1\rightarrow 2} | \Psi_2 \qquad \Phi.\,\chi.\,S$$

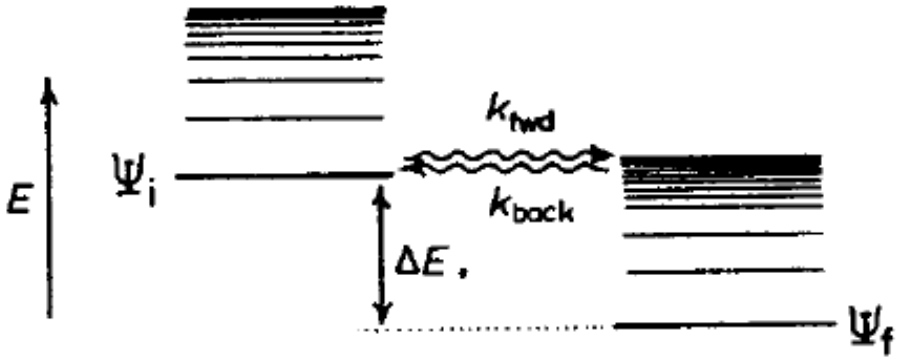
Enrico Fermi
Nobel Prize, 1938

$$k_{OBS} \sim P_{1\rightarrow 2} \qquad \rho \frac{2\pi}{\hbar} [<\Psi_1 | P_{1\rightarrow 2} | \Psi_2>]^2$$

$$R + h\nu \rightarrow {}^*R \qquad \rho \frac{2\pi}{\hbar} <\Psi_1(R) \,|\, P_{h\nu} \,|\, \Psi_2({}^*R)>^2$$

$$^*R \rightarrow R + h\nu$$

k_{OBS}	allowedness of absorption or emission
ρ	density of states
$P_{1\rightarrow 2}$	perturbing Hamiltonian



Oscillator Strength-Absorption

$\Psi_1 | P_{1\rightarrow 2} | \Psi_2$ $\quad\quad$ $\Phi . \chi . S$

Probability of light absorption and emission are related to the oscillator strength '*f*'

A perfectly allowed transition has $f = 1$

Electronic (Φ)	**Orbital Overlap**	f_e
	Orbital Symmetry	
Vibronic (χ)	**Nuclear position**	f_v
Spin (*S*)	**Electron Spin**	f_s

How probable $(\Phi . \chi . S)_2$ would 'look like' $(\Phi . \chi . S)_1$?

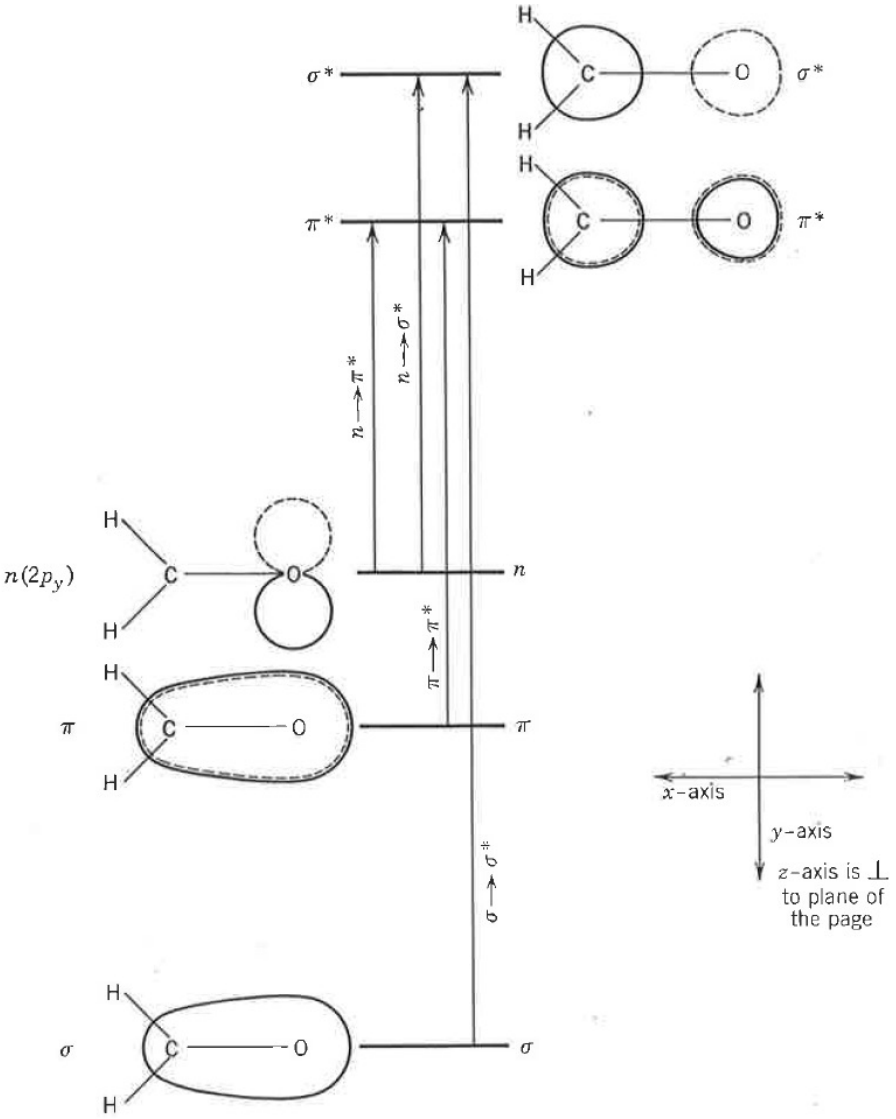
Electronic transitions: Overlap and symmetry of orbitals involved

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

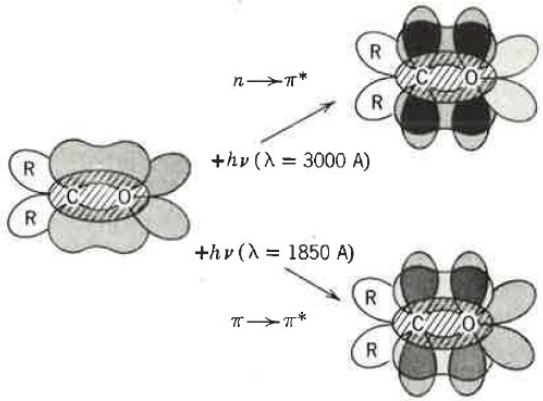
(1) *Orbital* ***overlap*** forbiddenness, which results from poor spatial overlap of the orbitals involved in the electronic transition, example, the n,π* transition in ketones, for which the HO and LU are orthogonal to one another and the overlap integral $\langle n | \pi^* \rangle$ is close to zero.

(2) *Orbital* **symmetry** 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.

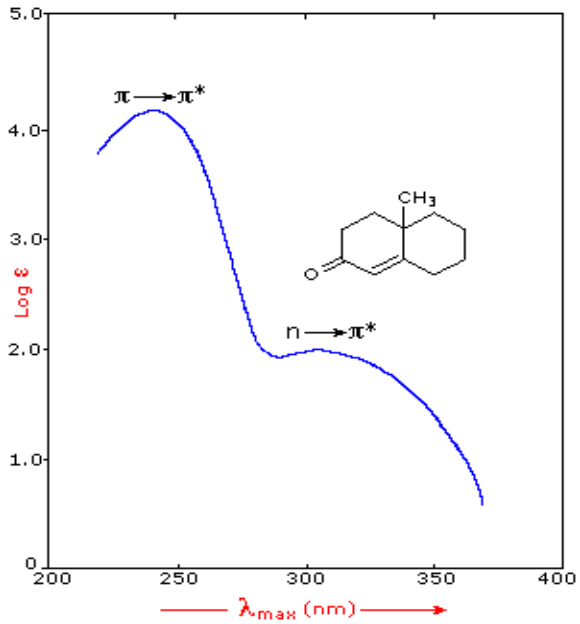
Electronic factor - Orbital overlap



No orbital overlap n and π*



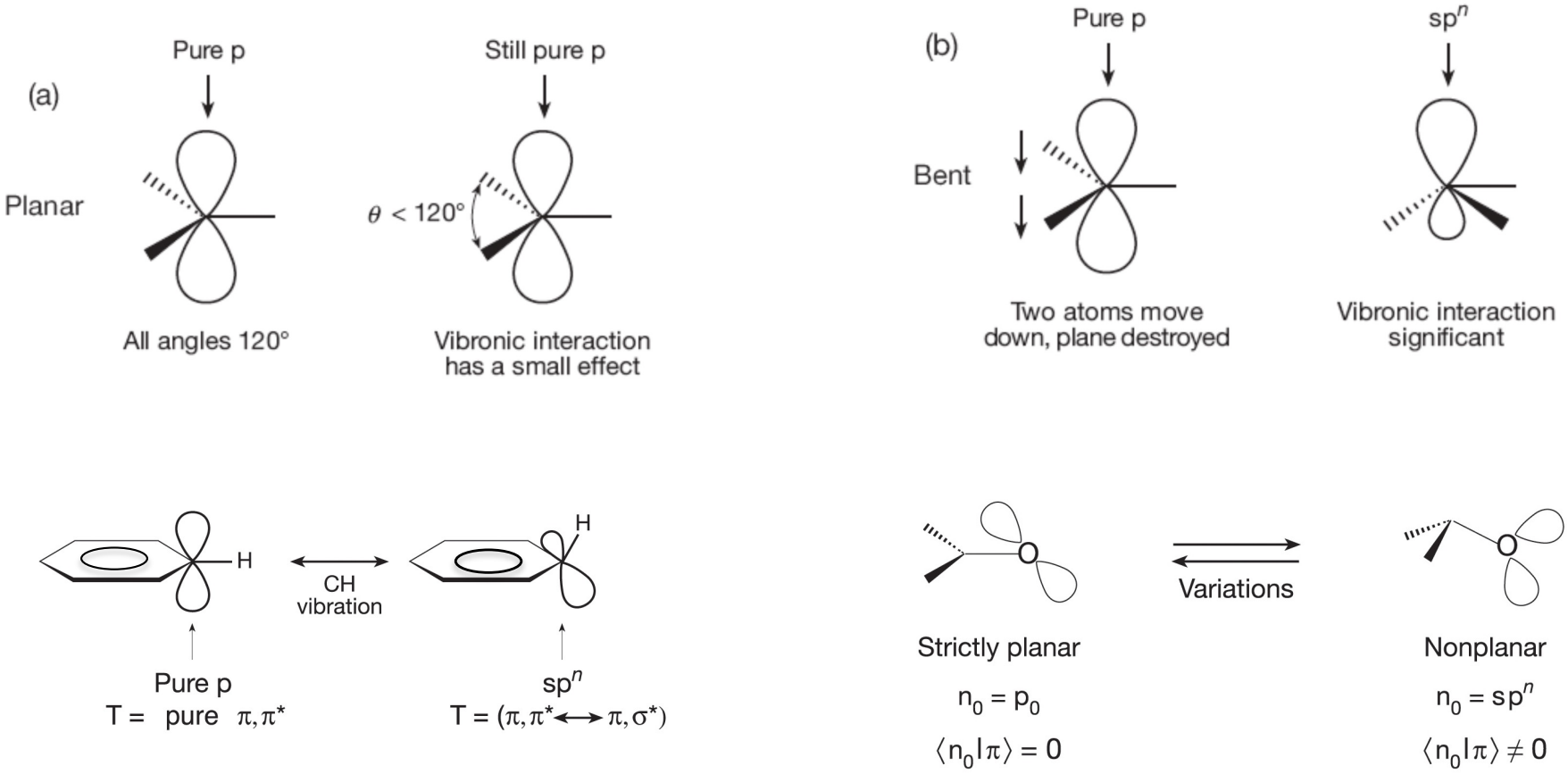
Orbital overlap π and π*



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*

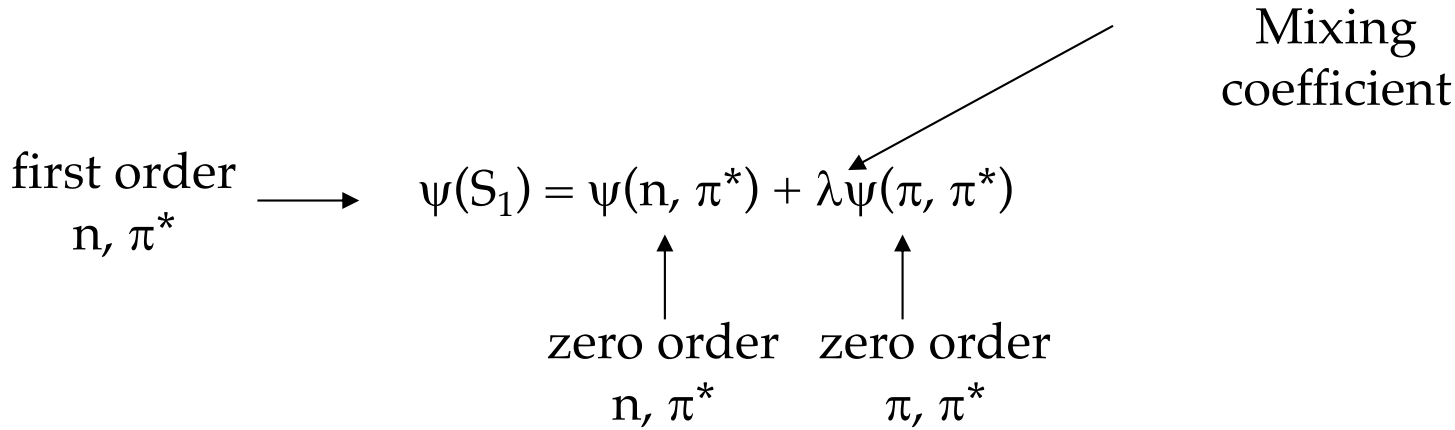
Zero Order to First Order Through Vibronic Coupling



Vibrational mixing could change the shape of the zero-order orbital and lead to slight overlap between perpendicular orbitals (e.g., 'n', σ and 'π' and 'π*')

Vibronic mixing results in state mixing

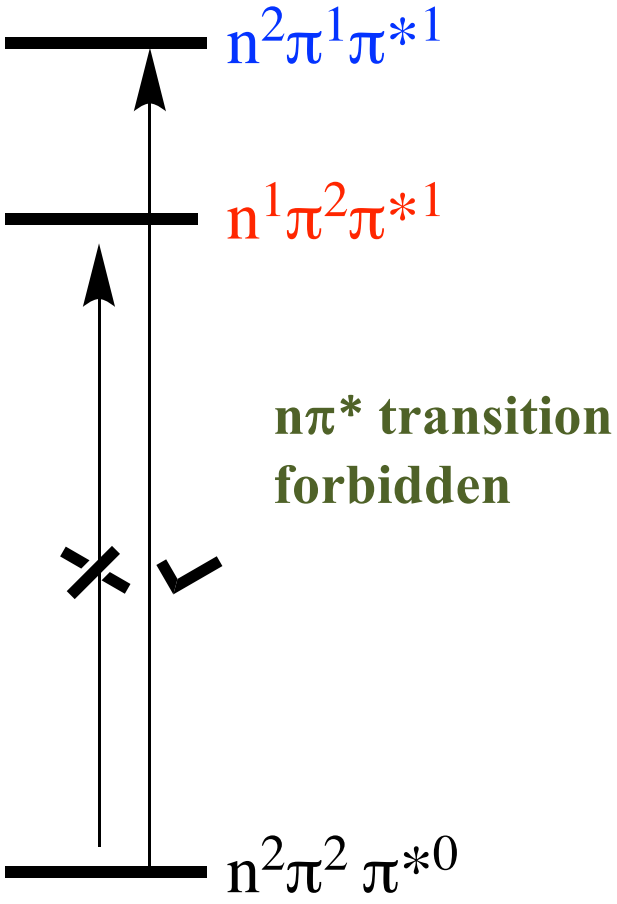
Due to vibration an n, π^* S_1 state is no longer pure but contains a finite amount of π, π^* character mixed in so the zero order wavefunction is not valid and the first order wavefunction may in fact be:



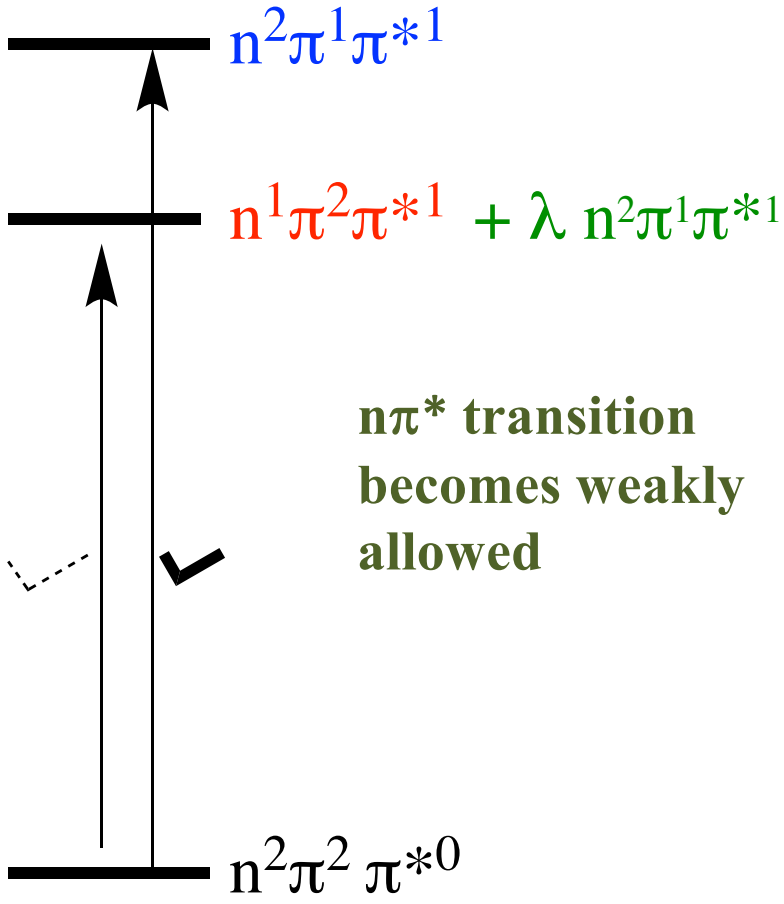
$$\lambda = \left| \frac{\langle \psi_a | H | \psi_b \rangle}{E_a - E_b} \right|$$

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

Result of vibrational – electronic mixing (vibronic coupling)

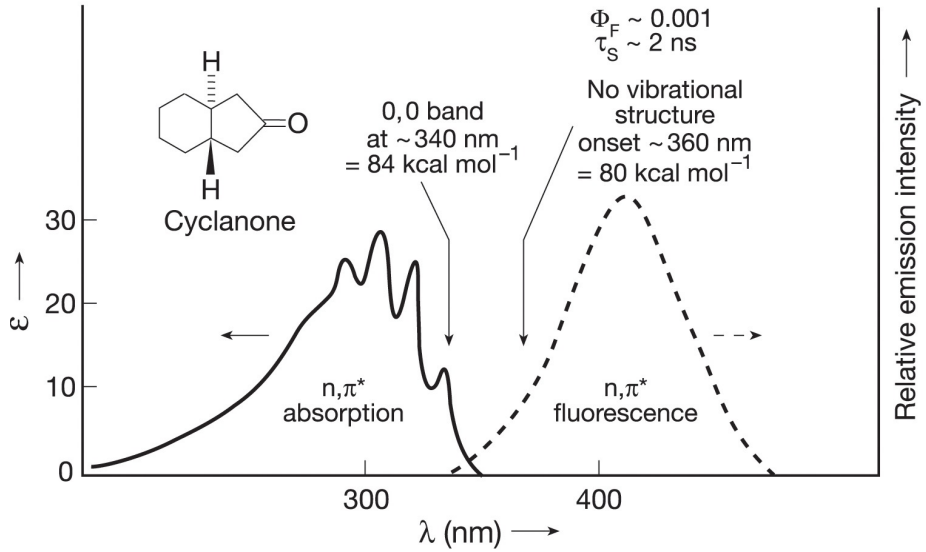


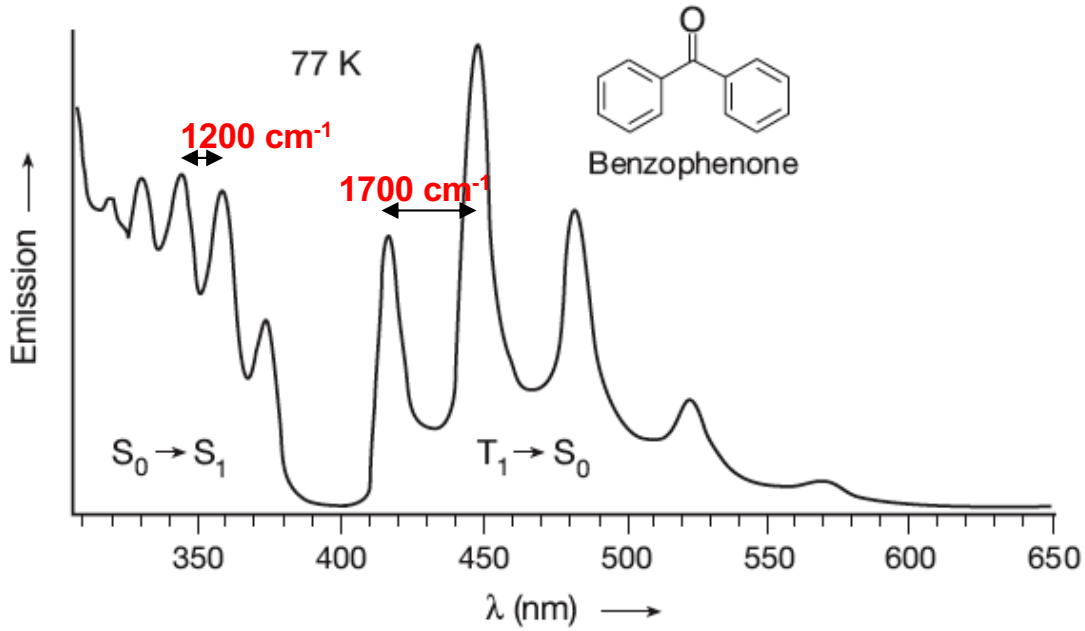
As per Bonn-Oppenheimer approximation



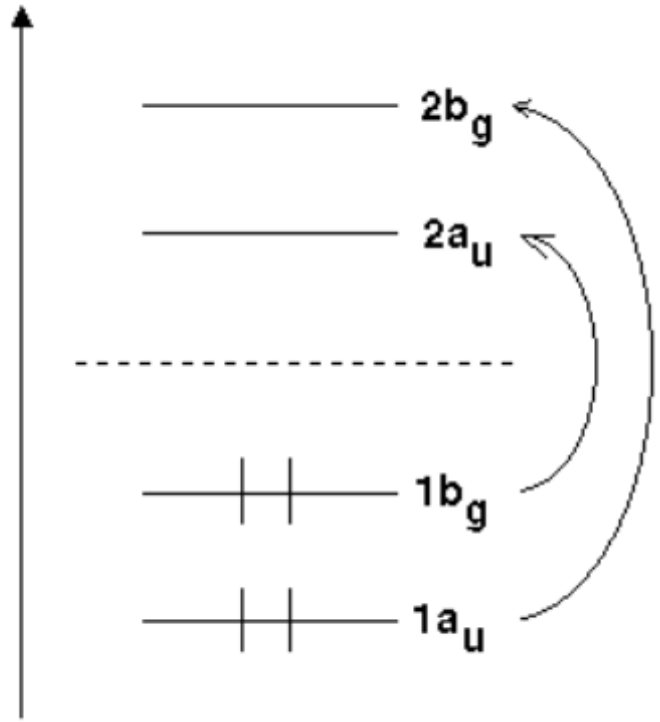
Vibration mixes the states, no longer pure states

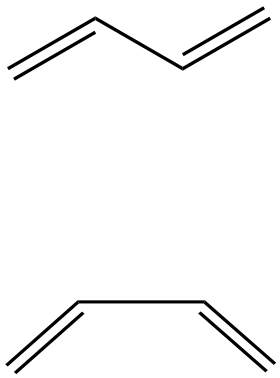
Absorption and emission spectra
Vibrational structure due to vibrational mixing

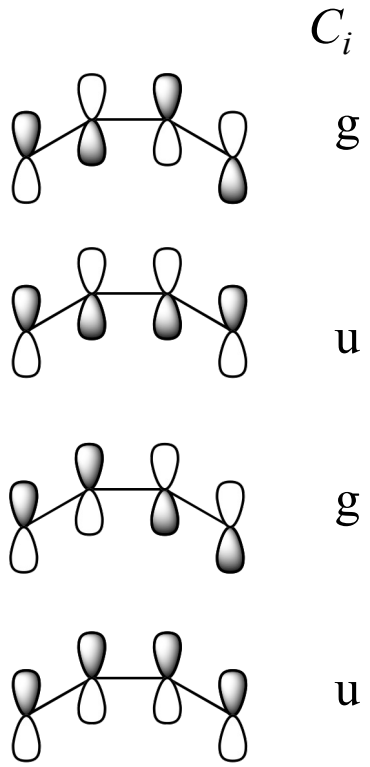




Symmetry based selection rules







The absorption spectra of conjugated dienes in the vacuum ultra-violet (1)

By W. C. Price and A. D. Walsh
Physical Chemistry Laboratory, Cambridge

(*Communicated by R. G. W. Norrish, F.R.S.—Received* 14 *August* 1939)

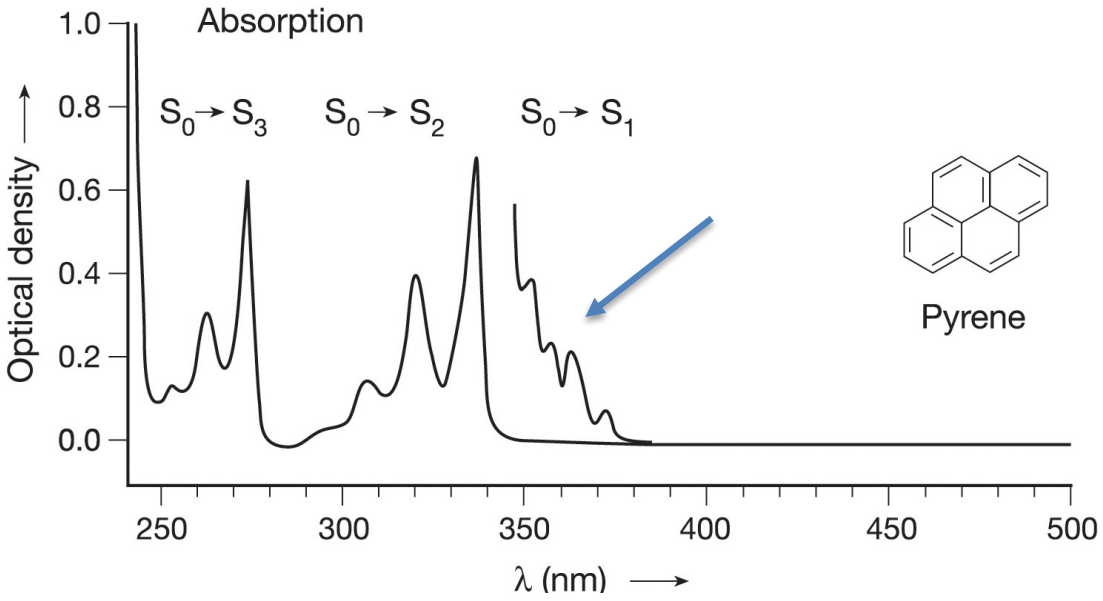
Intensities of Electronic Transitions in Molecular Spectra

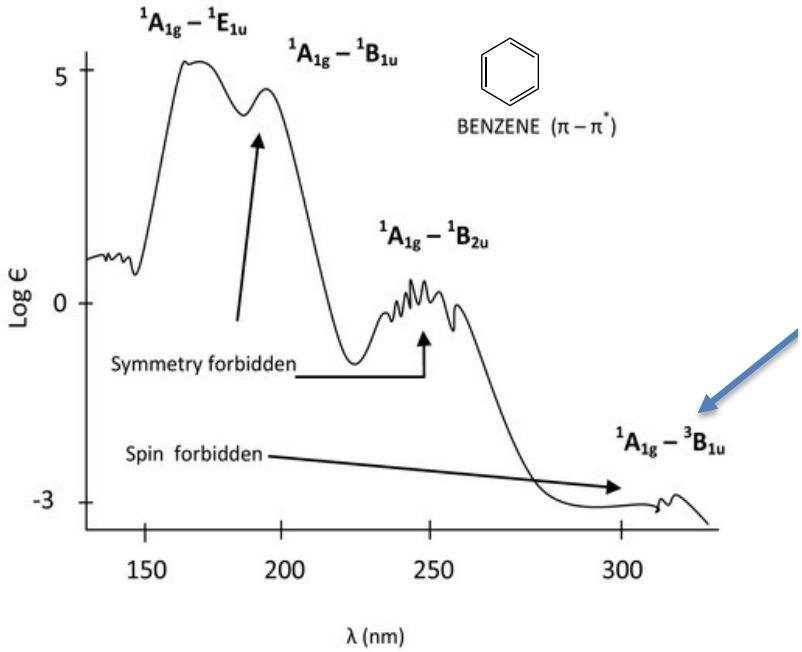
III. Organic Molecules with Double Bonds. Conjugated Dienes

Robert S. Mulliken
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

(Received December 9, 1938)

Selection Rules (Electronic part)





Orbital Symmetry ($\pi\pi^*$, e.g., benzene, pyrene**)**

The two orbitals involved in the transition can't have the same symmetry, i.e., ***g*** to ***g*** or ***u*** to ***u*** *transition is forbidden*

Symmetry can be destroyed by vibration and these symmetry forbidden transitions can become weakly allowed due to vibrational mixing.

Probability of Absorption and Emission

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

Theoretical oscillator strength

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

Experimental absorption

↓

Area under ε *vs*. wavenumber plot

Emission follows the same rules as absorption

Relationship between absorption intensity (and fluorescence lifetime)

Strickler and Berg "Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules" *J. Chem. Phys*. **1962**, 37, 814.

Strickler-Berg relation

The relation of the radiative lifetime of the molecule and the absorption coefficient over the spectrum

$$k_r = \frac{1}{\tau_n} = \frac{\tilde{\nu}_{max}^2 \cdot n^2}{3.42 \cdot 10^8} \int \varepsilon(\tilde{\nu}) d\tilde{\nu}$$

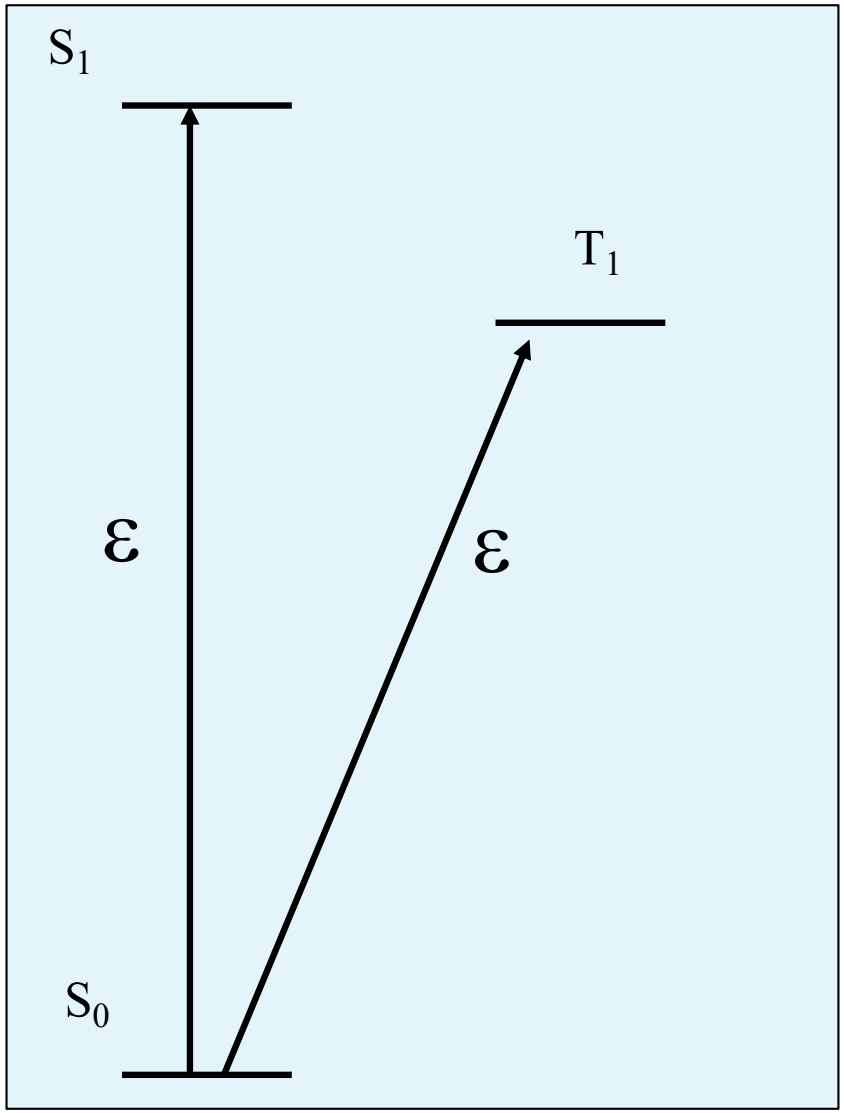
n: refractive index of medium

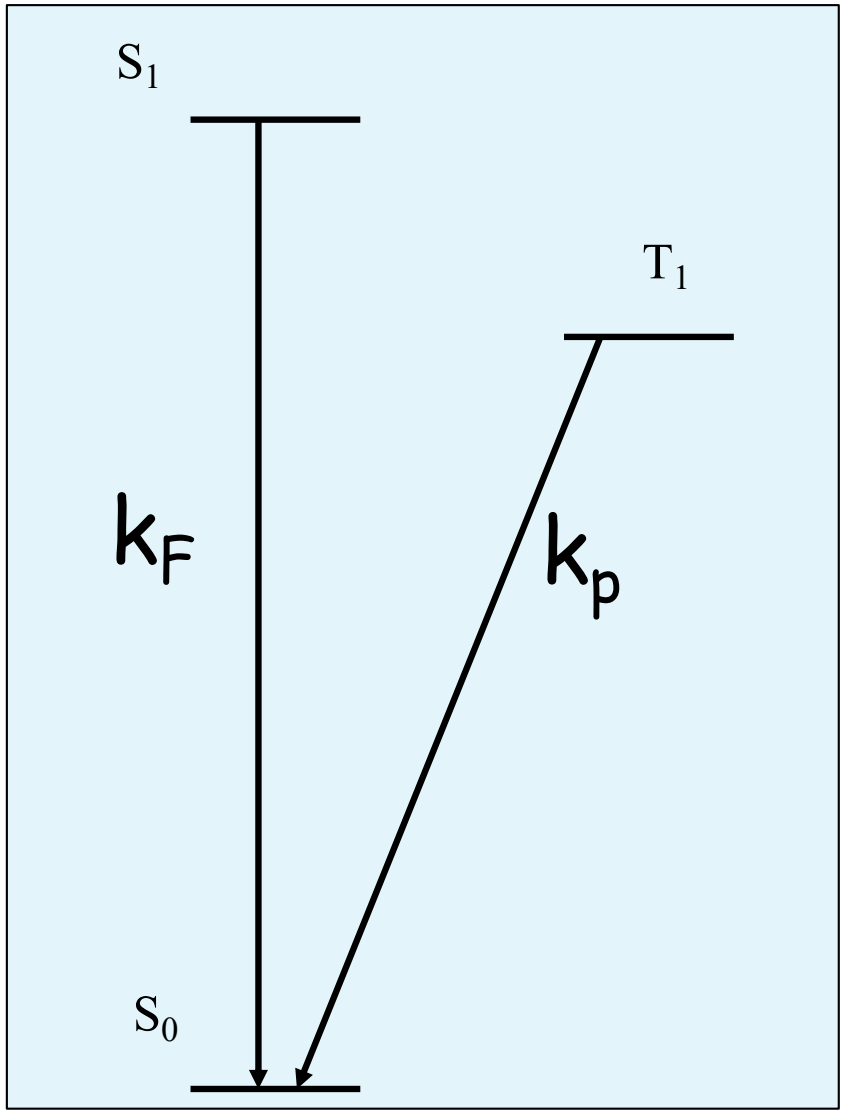
ν: position of the absorption maxima in wavenumbers [cm^{-1}]

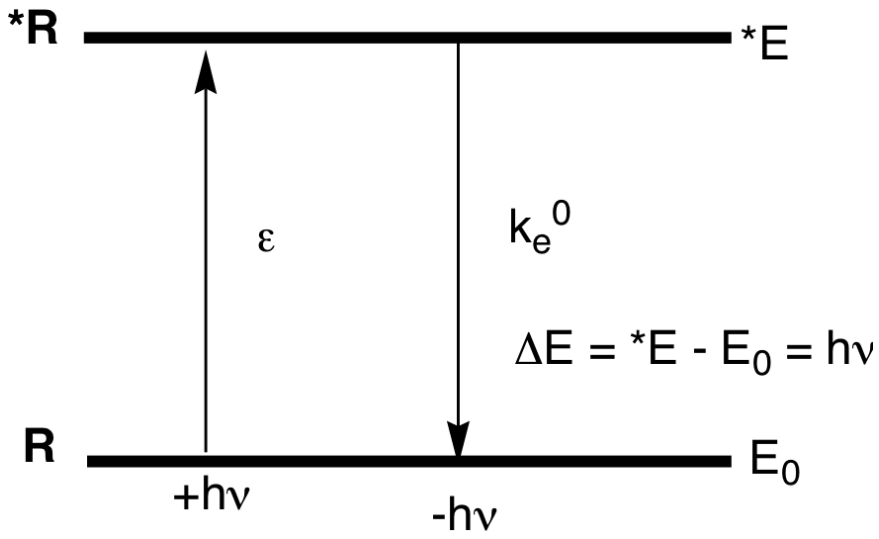
ε : absorption coefficient

τ_n : radiative lifetime

Same Rules for Excitation & De-excitation







$k_e(s^{-1})$	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}

Radiative rate constant

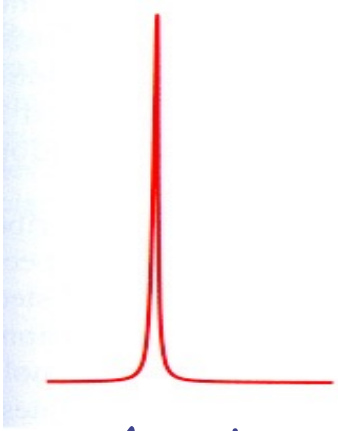
$$k_e^0 = 3 \times 10^{-9} \overline{\nu}_0^2 \int \varepsilon d\overline{\nu} \cong \overline{\nu}_0^2 f$$

$$1/\tau^0 = k_e{}^0 \sim \varepsilon_{max} \Delta\nu^2 \sim 10^4 \varepsilon_{max}$$

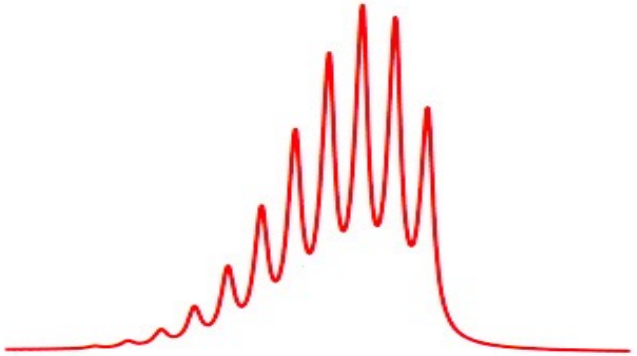
Experimental and Calculated Radiative Lifetimes for Singlet-Singlet Transitions

Compound	τ^0 (x 10^9)	τ (x 10^9)
Anthracene	13.5	16.7
Perylene[c]	4.1	4.6
9,10-Diphenylanthracene	8.9	8.8
Acridone	14.9	14.1
Fluorescein	4.7	4.0
9-Aminoacridine	14.6	14.3
Rhodamine B	6.0	6.0
Acetone	10,000	1,000
Perfluoroacetone	10,000	5,000
Benzene	140	600

Electronic spectra of larger molecules

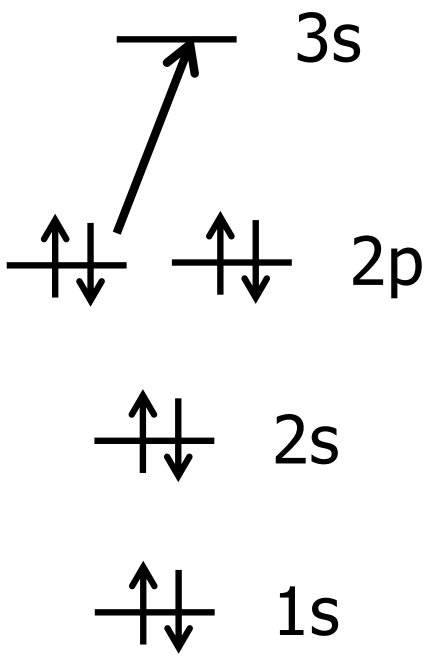


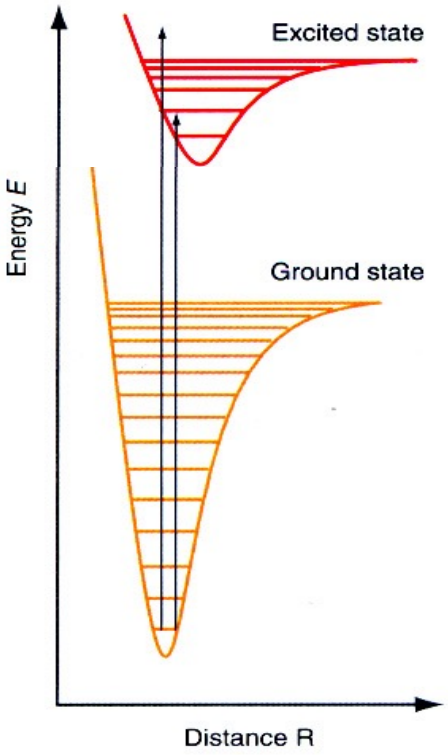
An atom

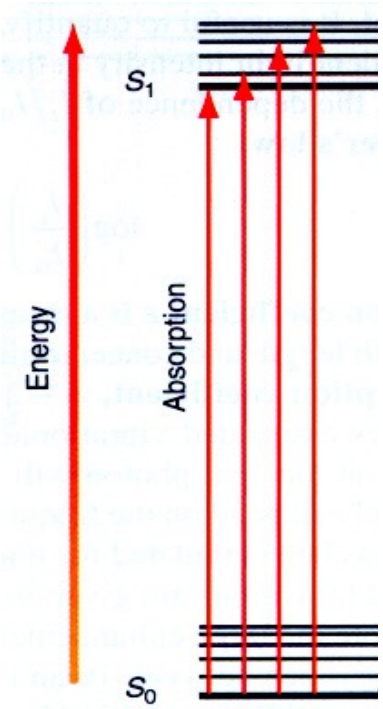


A diatomic (or other small) molecule

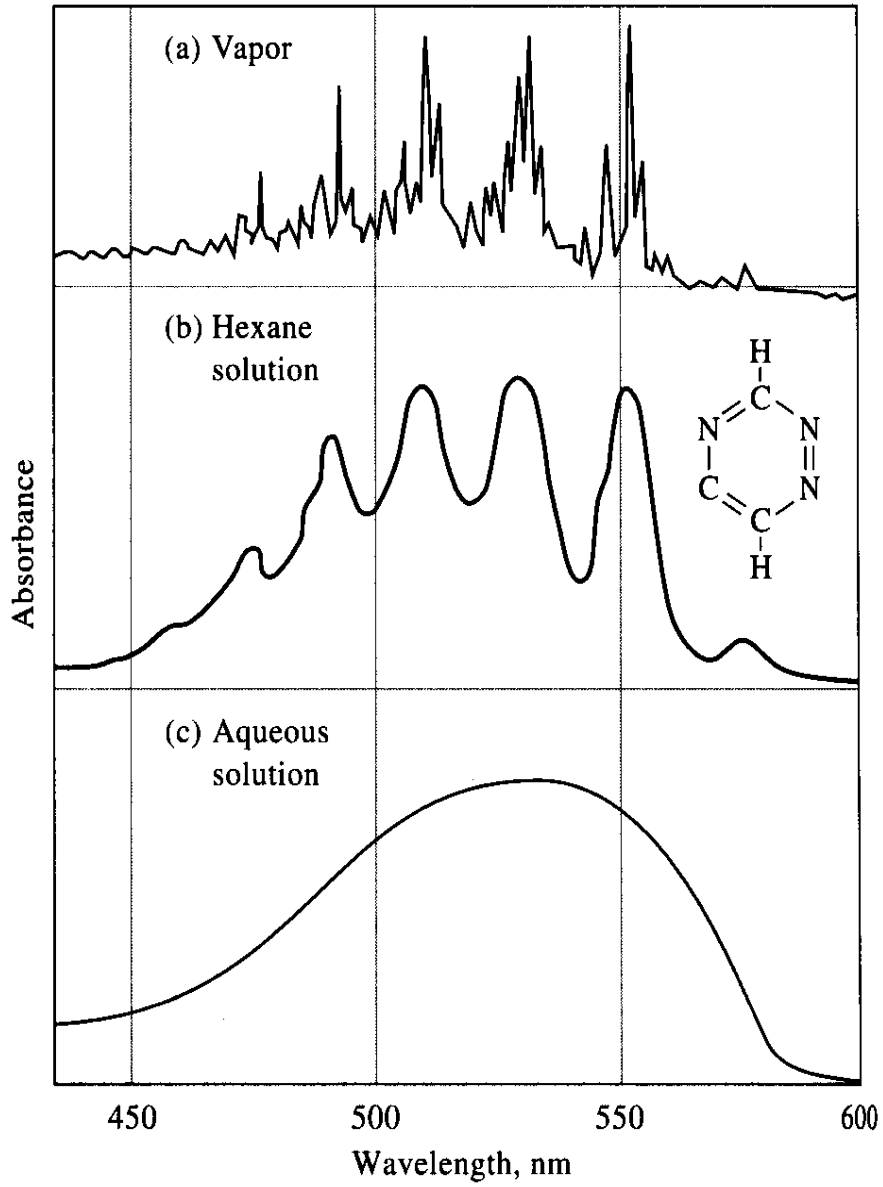
A large molecule

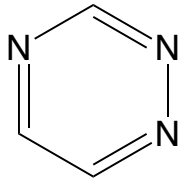




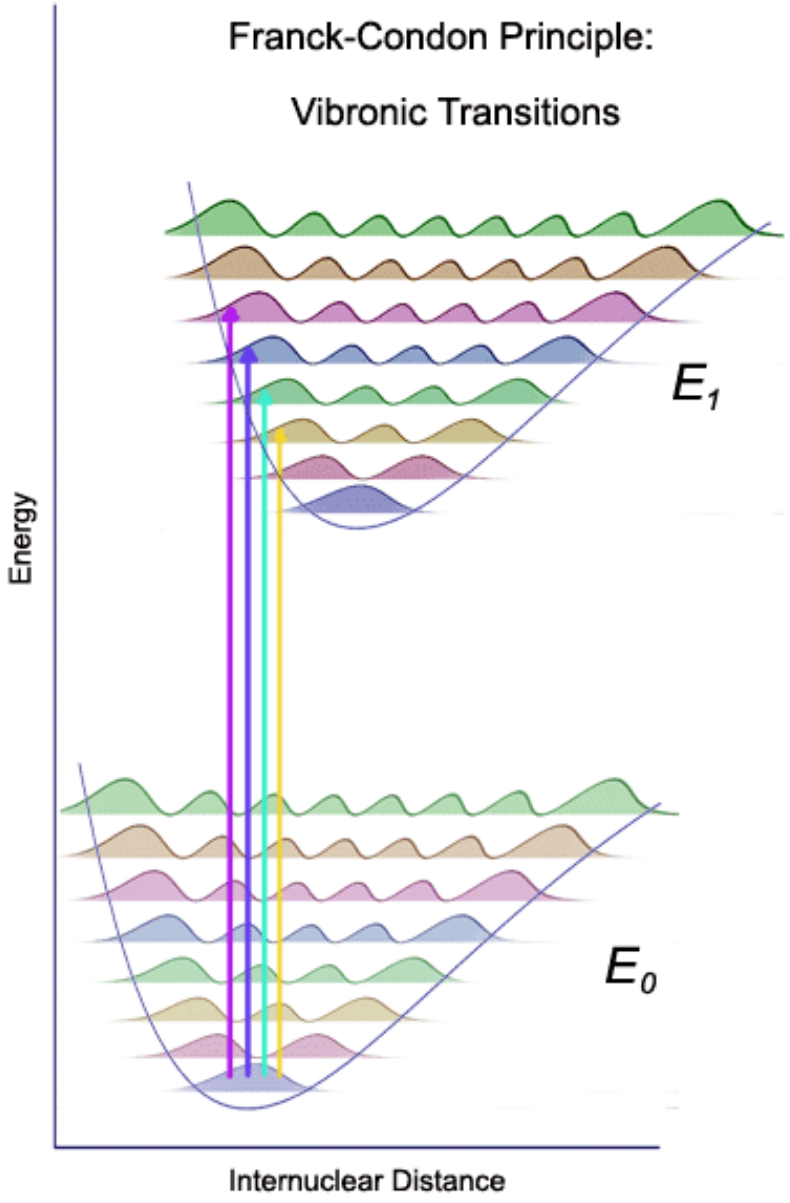


Shapes of Absorption Spectra: medium dependent





Franck-Condon principle and vertical transitions



J. Franck
1882-1964
Nobel Prize, 1925

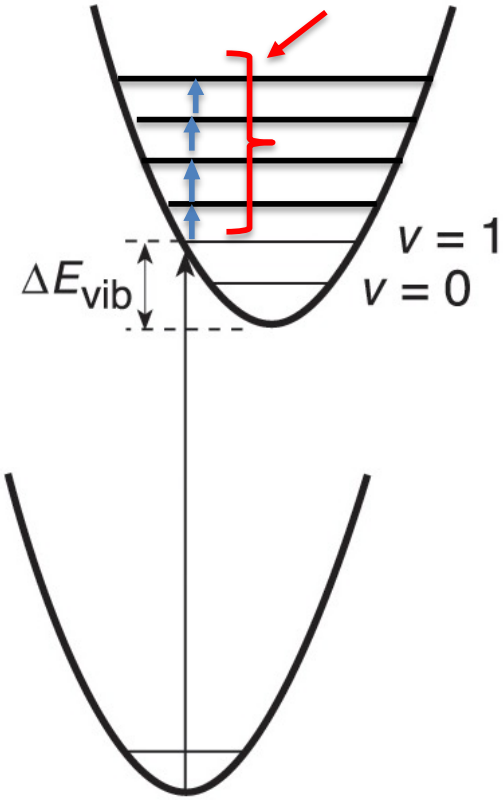
E. Condon
1902-1974

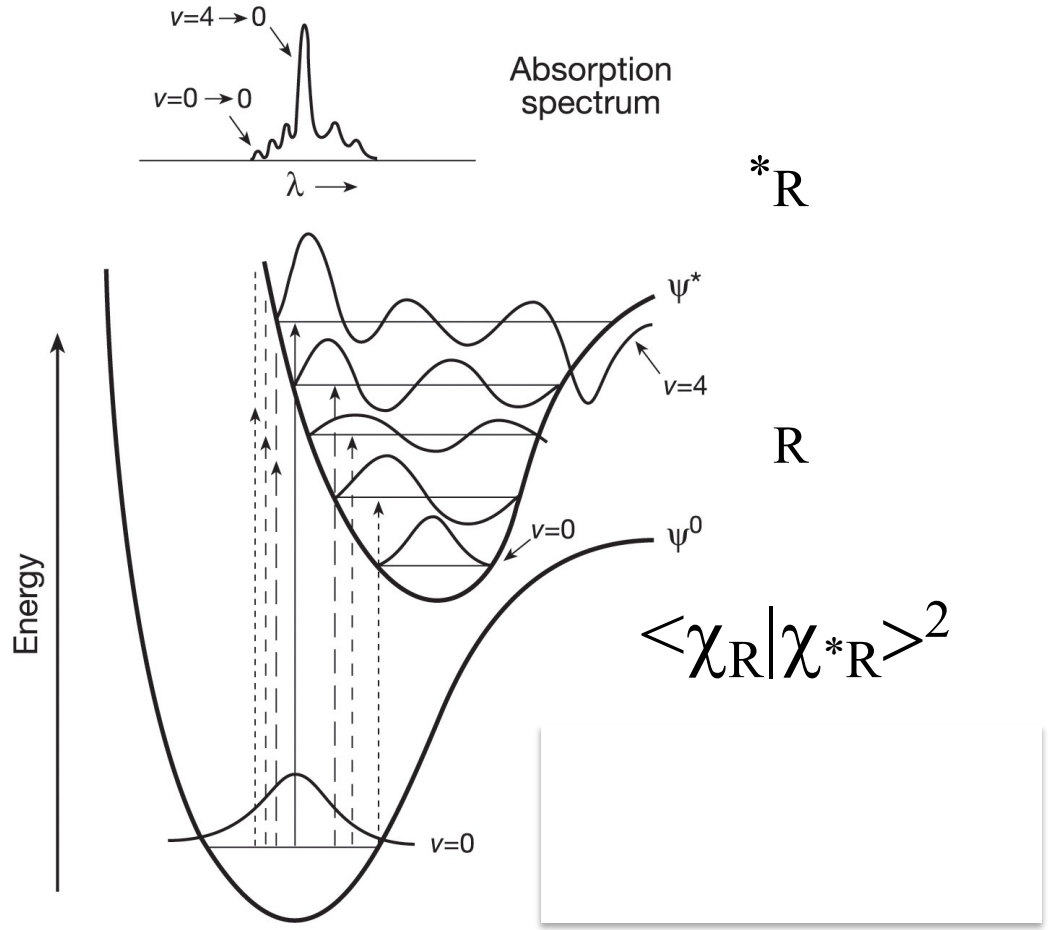
The ground state (E_0) supports a large number of vibrational energy levels. At room temperature, only the lowest vibrational level is populated, and electronic transitions originate from the v=0 vibrational level.

Franck-Condon principle is based on the fact that electrons move faster than nuclei that are heavier.

Franck-Condon principle

An electronic transition occurs without changes in the positions of the nuclei in the molecules and its environment



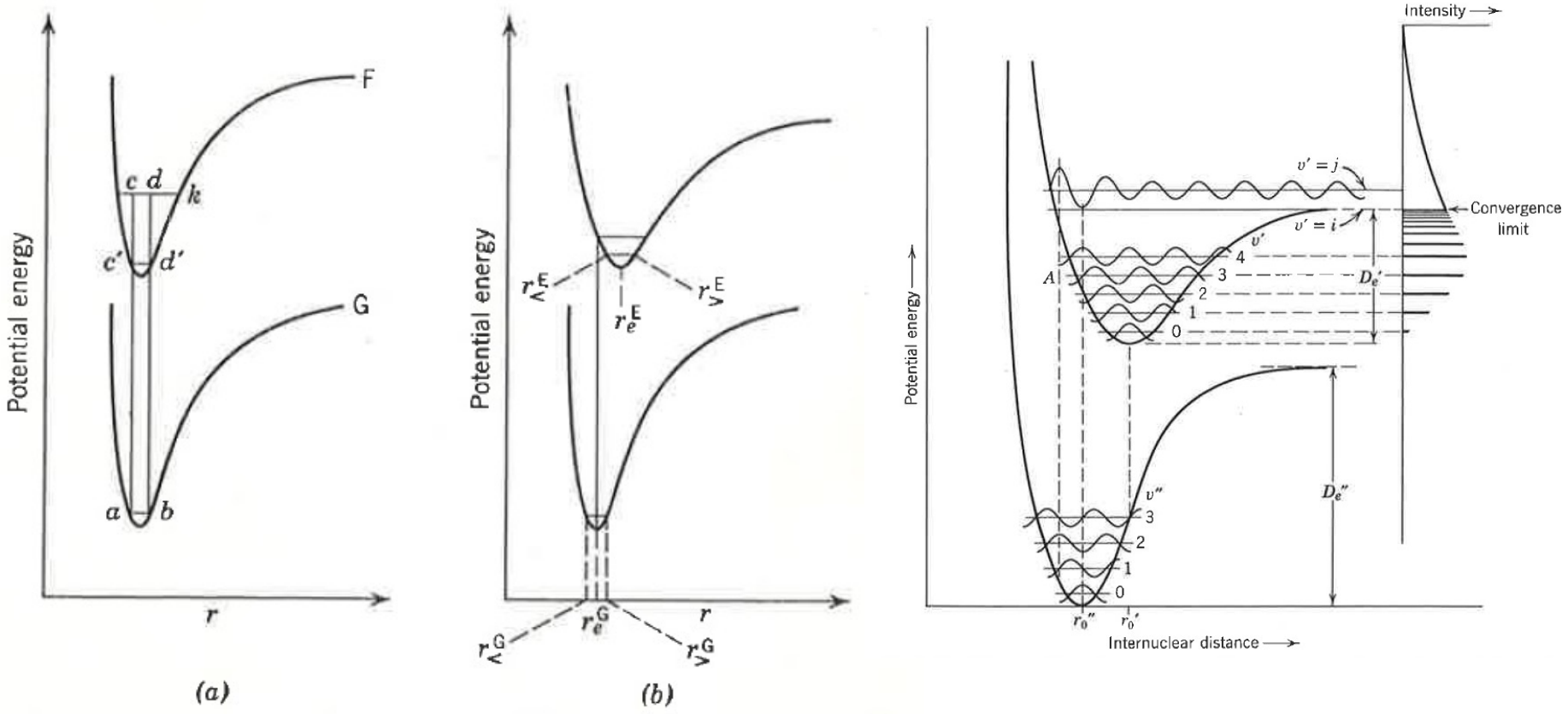


QM harmonic oscillator

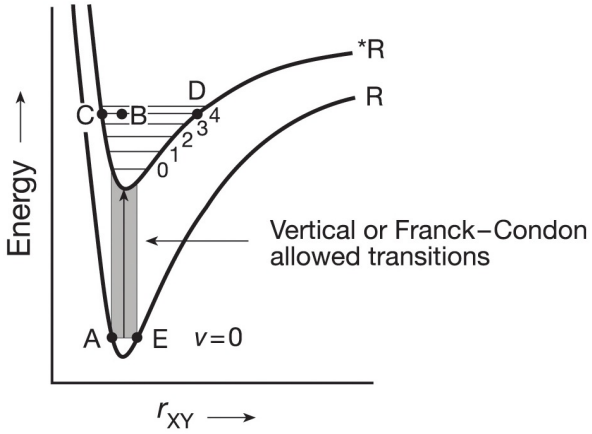
QM anharmonic oscillator

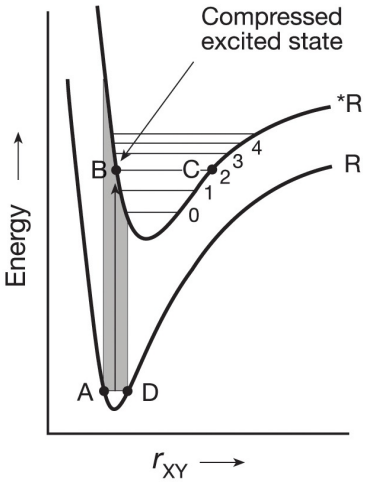
Vibrational overlap integral decides the intensity of absorption

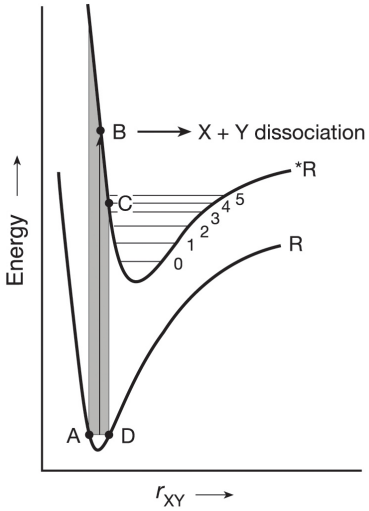
Relative position of energy surfaces and **Franck-Condon principle** control the shape of the absorption and emission spectra

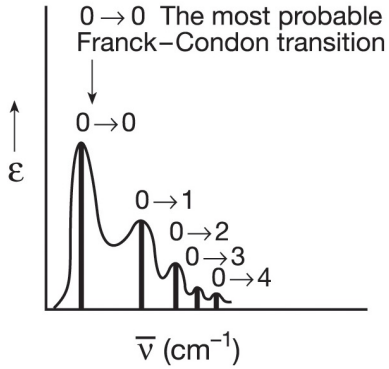


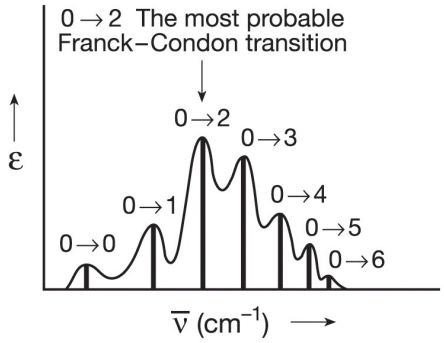
Relative position of energy surfaces and **Franck-Condon principle** control the shape of the absorption and emission spectra

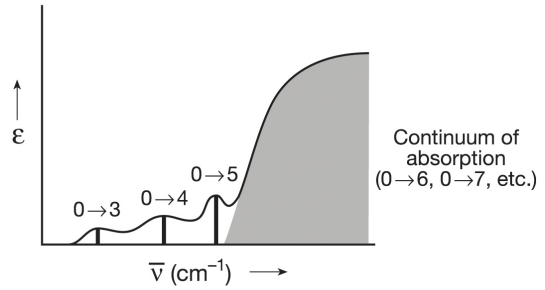


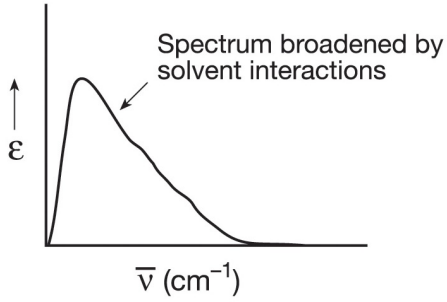


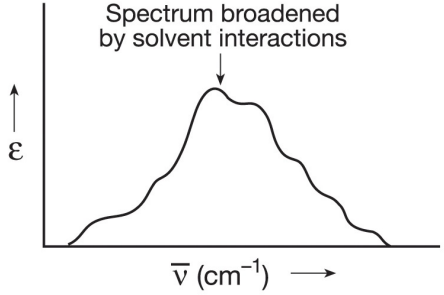








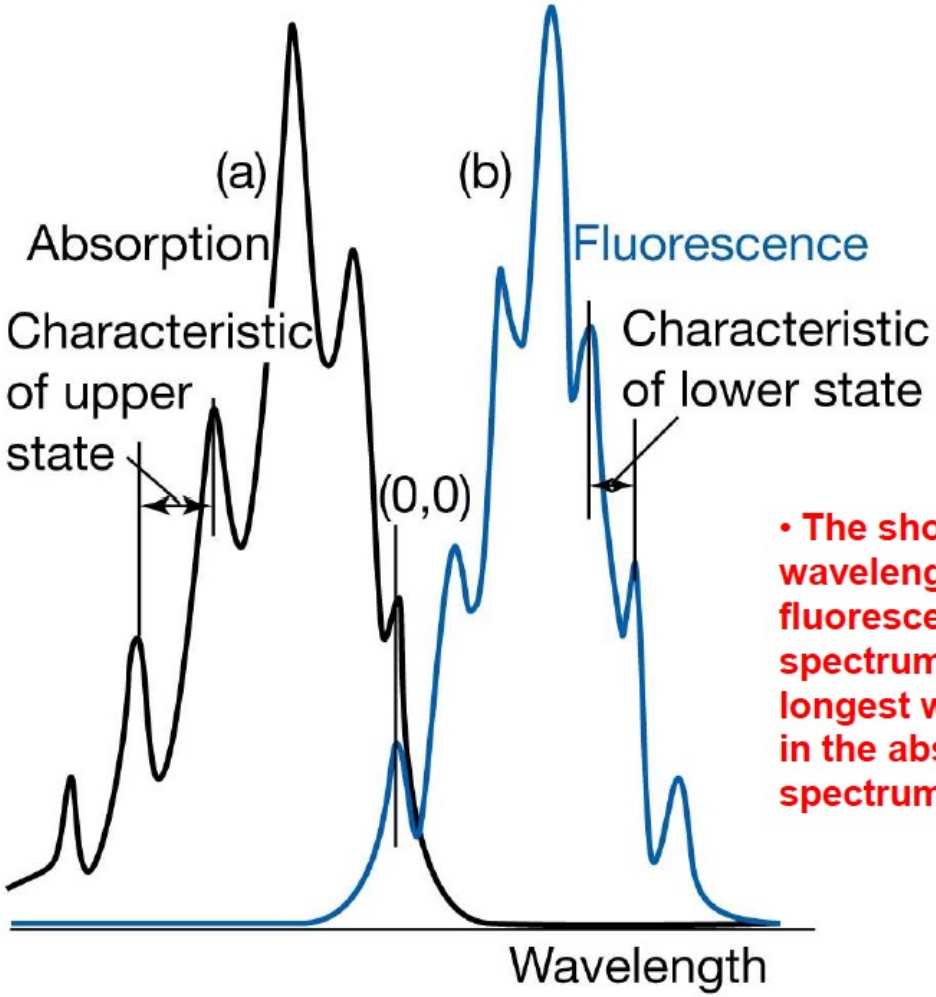




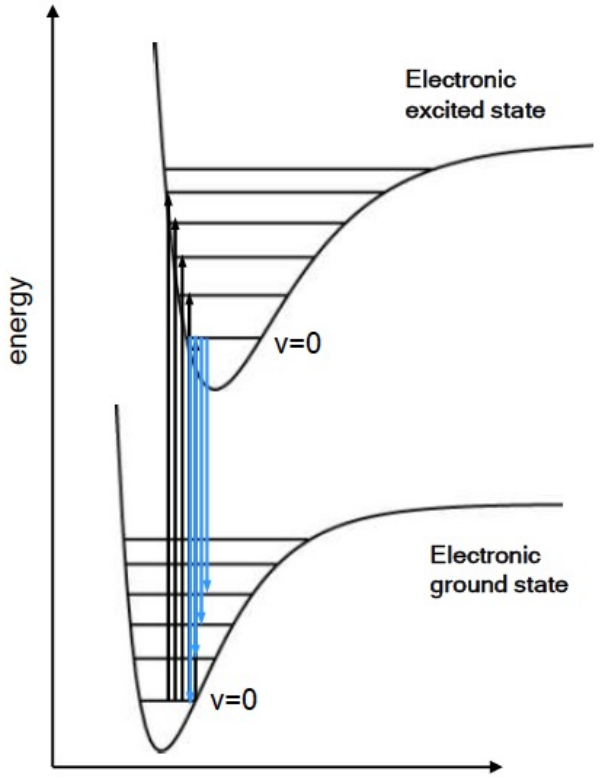
Photoablation & Lasik use this part of the spectrum

Stoke's shift: Absorption and Emission Spectra

G.G. Stokes (1819-1903)



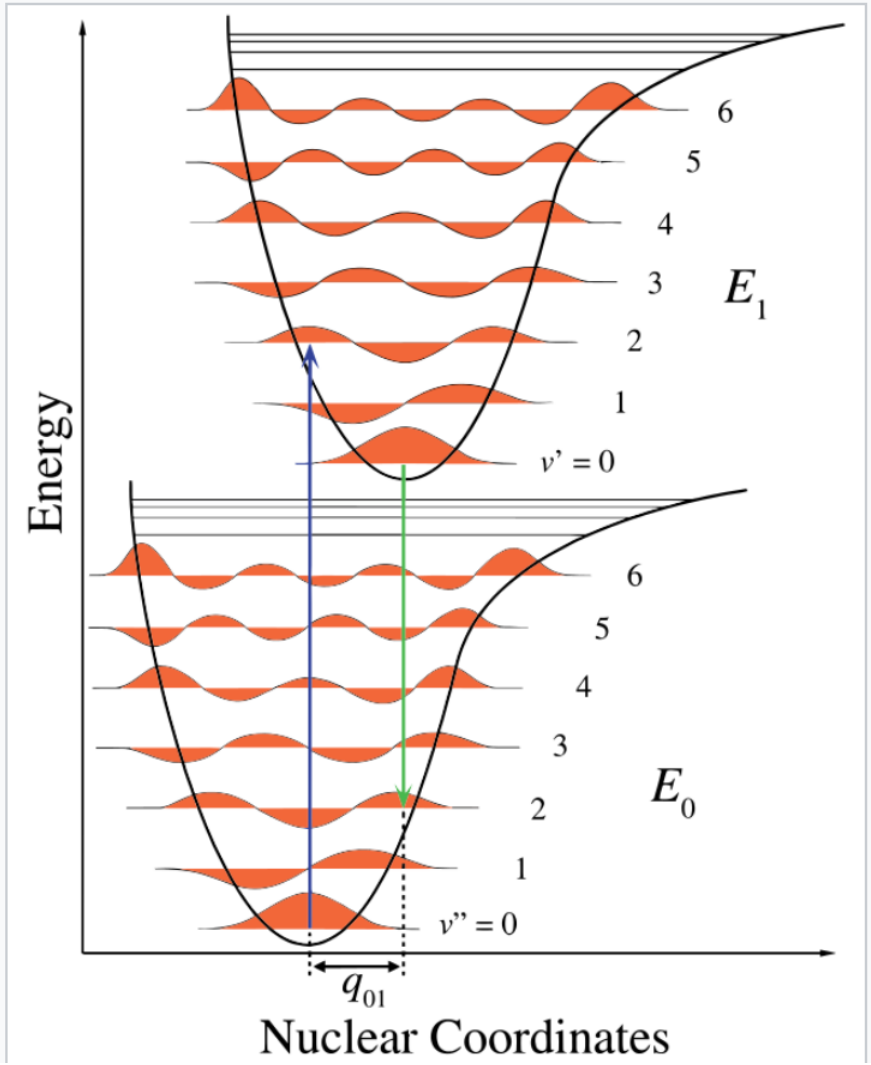
- The shortest wavelength in the fluorescence spectrum is the longest wavelength in the absorption spectrum

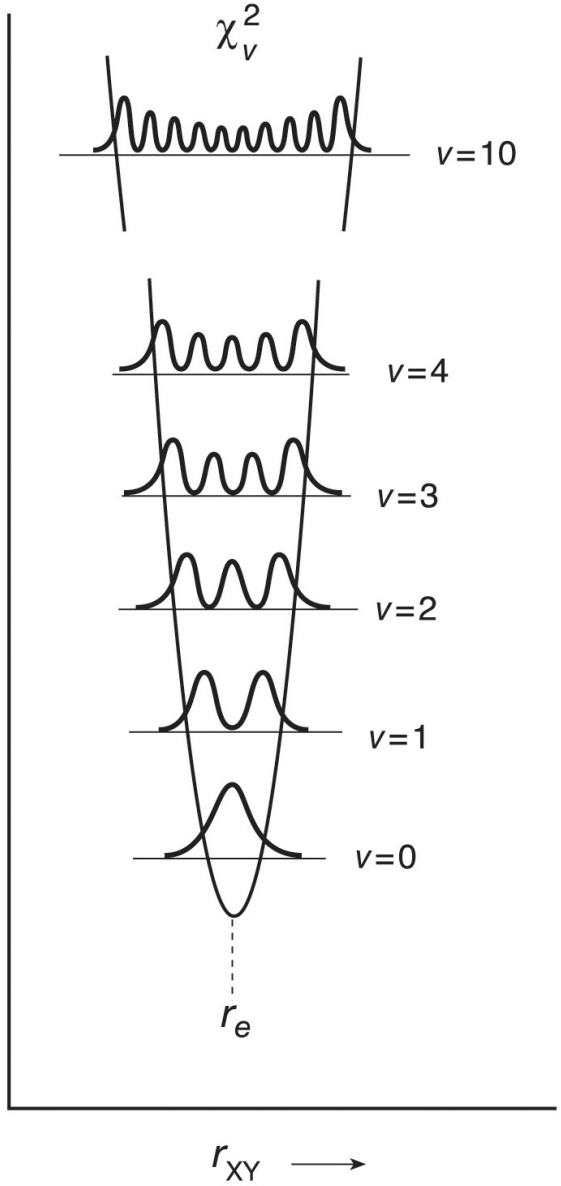


Owing to a decrease in bonding of the molecule in its excited state compared to that of the ground state, the energy difference between S_0 and S_1 is lowered prior to fluorescence emission. This is known as Stoke's shift.

Absorption and Emission Spectra

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



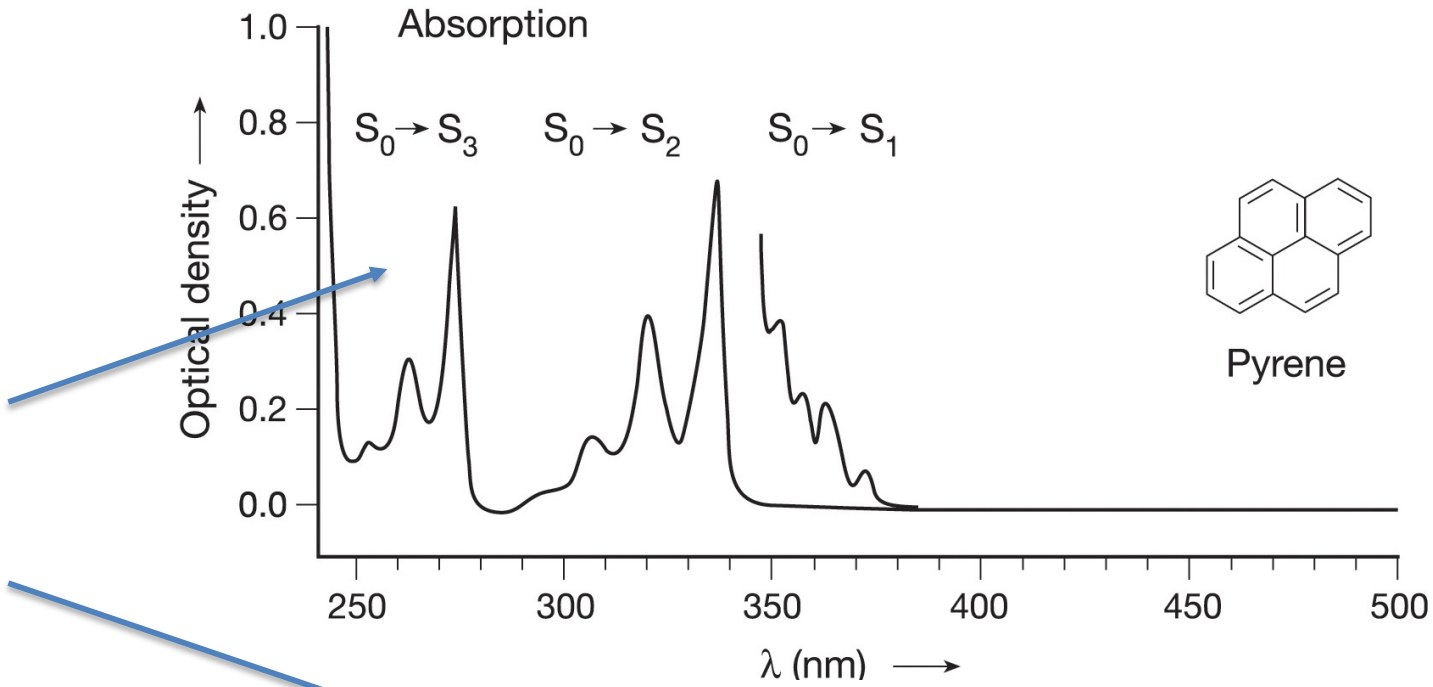


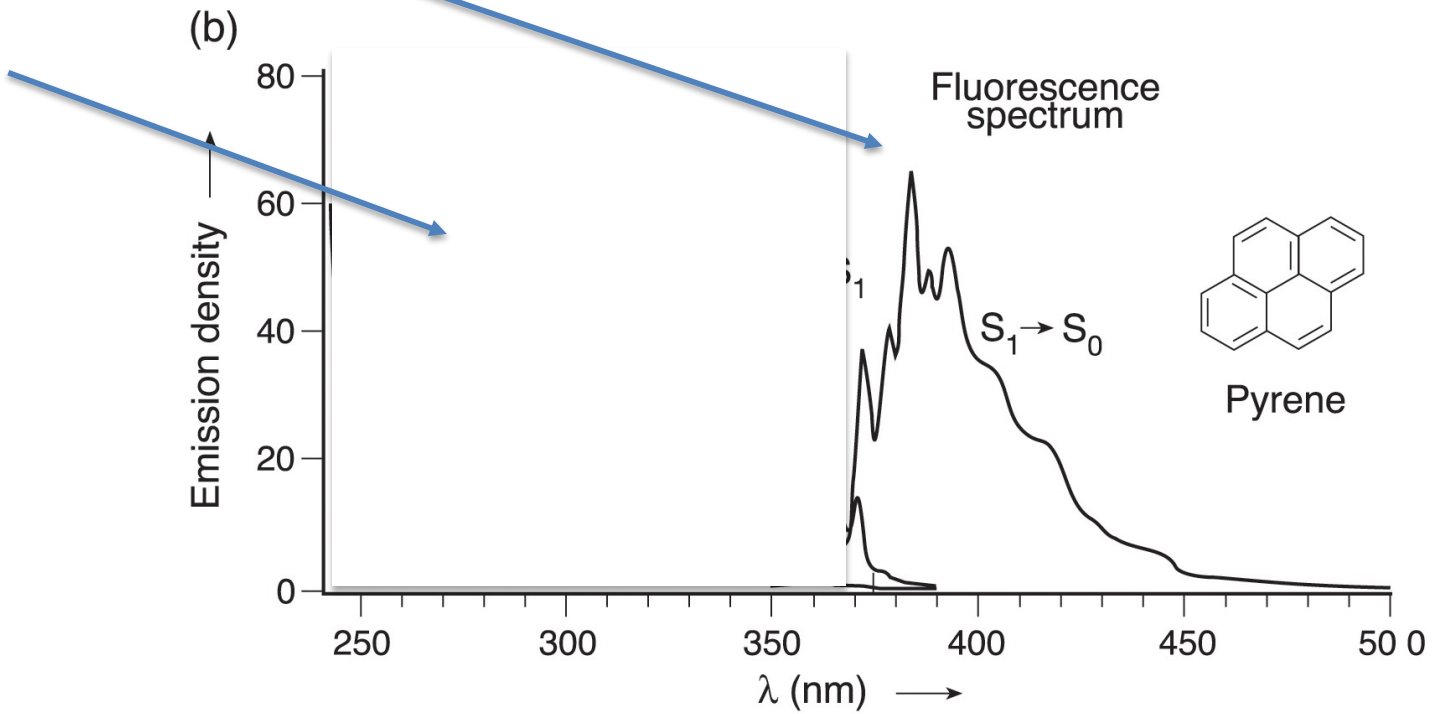
https://www.youtube.com/watch?v=ULCTTxeHI6o&t=0s

Absorption

Emission

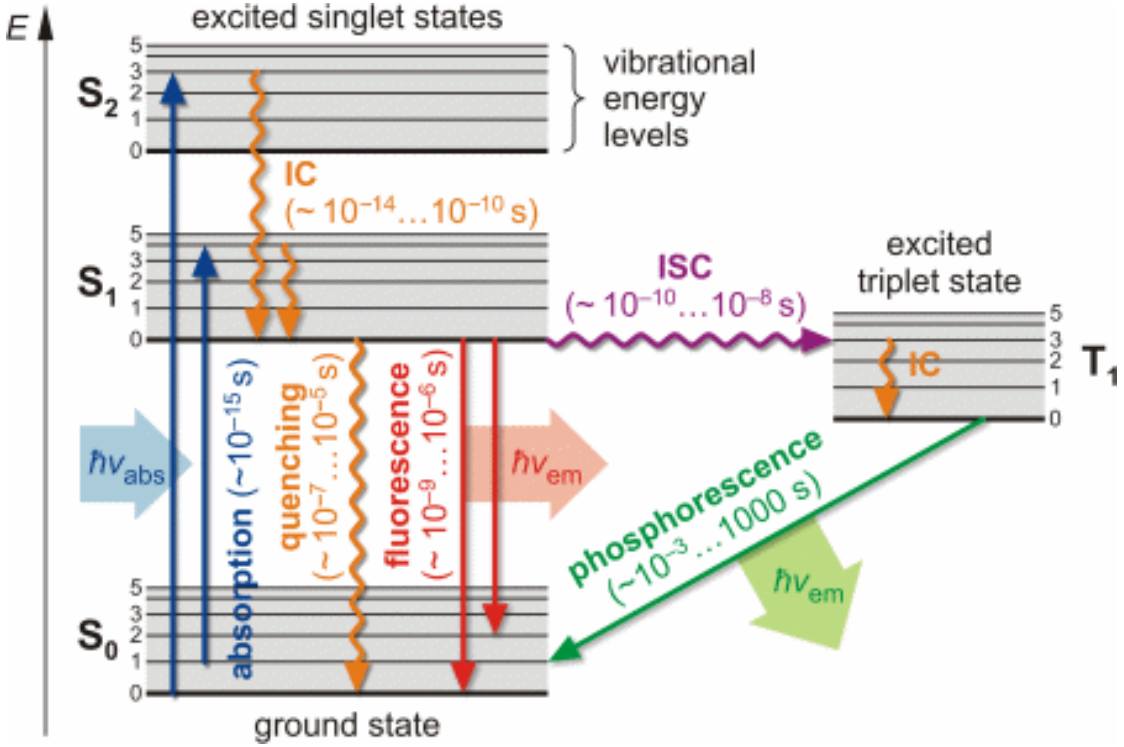
Excitation





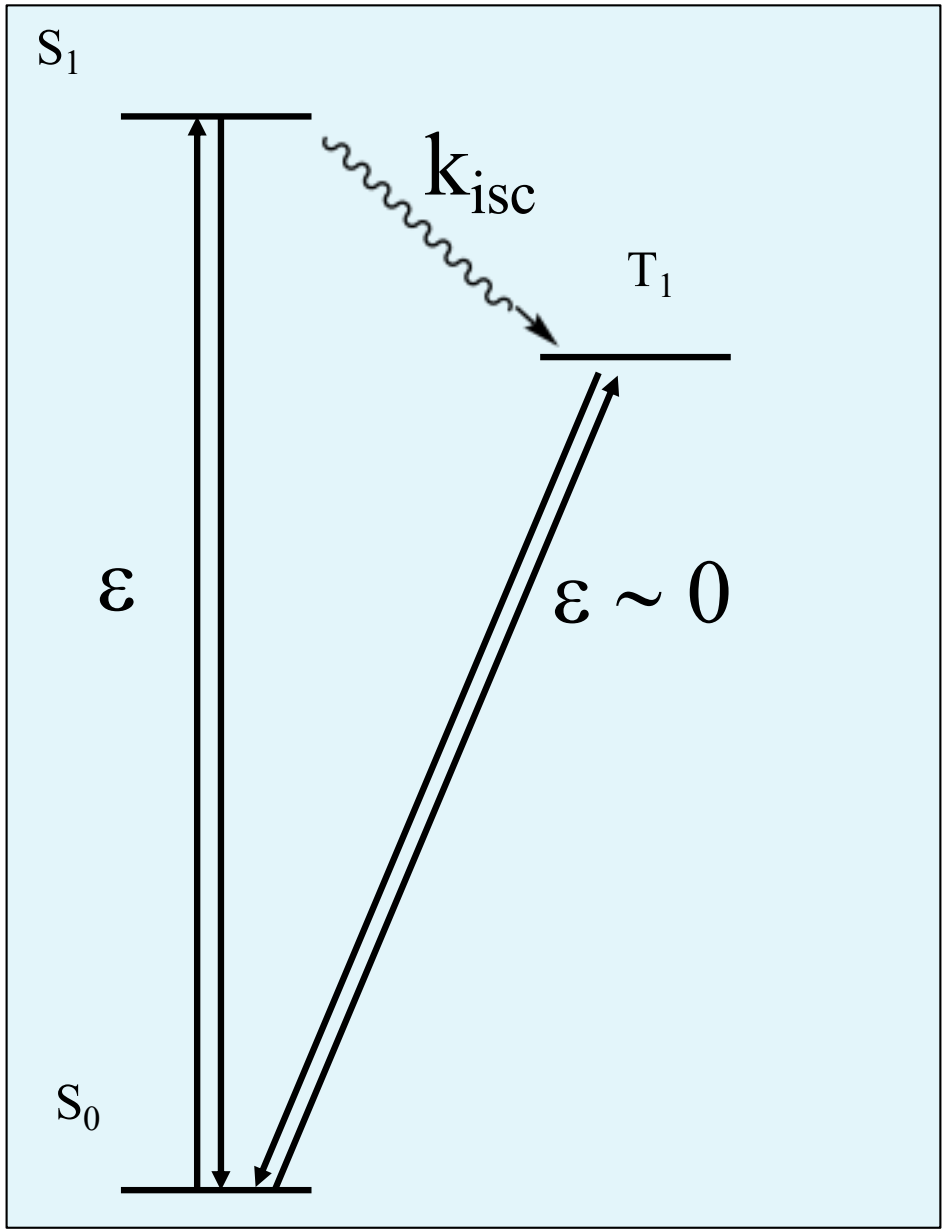
Vavilov's rule

The quantum yield of fluorescence (and the quantum yield of phosphorescence) are independent of initial excitation energy. Emission originates from the lowest vibrational level.

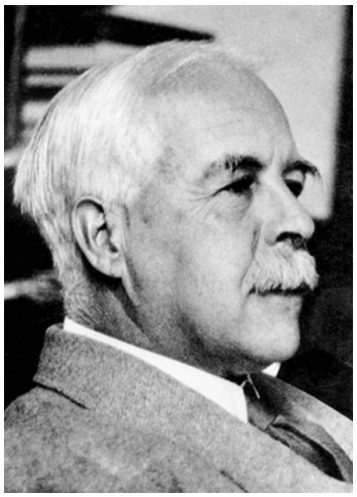


S. Vavilov

Singlet-Triplet Crossing and Phosphorescence



Triplet State and Phosphorescence



G. N. Lewis

Kasha

S. Vavilov

A. Terenin

Porter

Pioneering Publications

[Contribution from the Chemical Laboratory of the University of California]

Reversible Photochemical Processes in Rigid Media. A Study of the Phosphorescent State

By Gilbert N. Lewis, David Lipkin and Theodore T. Magel

[Contribution from the Chemical Laboratory of the University of California]

Phosphorescence and the Triplet State

By Gilbert N. Lewis and M. Kasha

[Contribution from the Chemical Laboratory of the University of California]

Phosphorescence in Fluid Media and the Reverse Process of Singlet–Triplet Absorption

By Gilbert N. Lewis and M. Kasha

Photomagnetism. Determination of the Paramagnetic Susceptibility of a Dye in Its Phosphorescent State*

G. N. Lewis, M. Calvin, and M. Kasha†
Department of Chemistry, University of California, Berkeley, California
(Received December 16, 1948)

PHOTOMAGNETISM OF TRIPLET STATES OF ORGANIC MOLECULES

By Dr. D. F. EVANS
Physical Chemistry Laboratory, Oxford

PARAMAGNETISM OF THE PHOSPHORESCENT STATE

Chemical Laboratories of the
University of California
Berkeley, California
Gilbert N. Lewis
M. Calvin
Received June 16, 1945

Paramagnetic Resonance Absorption in Naphthalene in Its Phosphorescent State*

Clyde A. Hutchison, Jr., and Billy W. Mangum†
Enrico Fermi Institute for Nuclear Studies and Department of Chemistry, University of Chicago, Chicago, Illinois
(Received August 8, 1958)

Triplet States in Solution

George Porter and Maurice W. Windsor
Department of Physical Chemistry, University of Cambridge, Cambridge, England
(Received August 19, 1953)

SENSITIZED PHOSPHORESCENCE IN ORGANIC SOLUTIONS AT LOW TEMPERATURE

ENERGY TRANSFER BETWEEN TRIPLET STATES

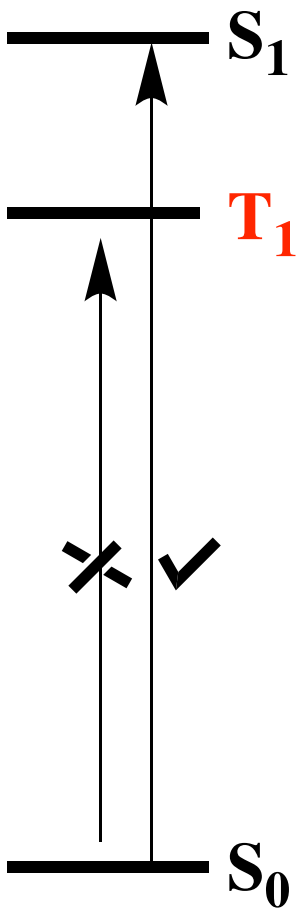
By A. Terenin and V. Ermolaev
Photochemical Laboratory, Section of Chemical Sciences, Academy of Science of U.S.S.R.
Received 21st March, 1956

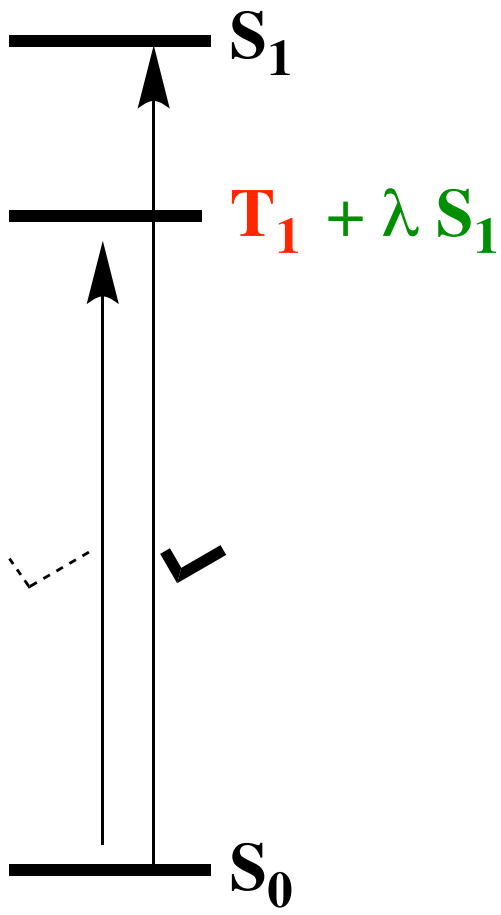
CLASSIC REFERENCES ON TRIPLET STATE AND HEAVY ATOM EFFECT

1. JACS., **63**, 3005, (1941).
2. JACS., **64**, 1916, (1942).
3. JACS., **66**, 2100, (1944).
4. JACS., **66**, 1579, (1944).
5. JACS., **67**, 994, (1945).
6. JACS., **67**, 1232, (1945).
7. Chem. Rev., **47**, 401 (1947)
8. J. Chem. Phys., **17**, 905 (1949)
9. J. Chem. Phys., **17**, 1182 (1949)
10. J. Chem. Phys., **17**, 804 (1949)
11. J. Chem. Phys., **20**, 71 (1952)
12. Nature, **176**, 777, (1955).
13. J. Chem. Soc., 1351, (1957).

1. J. Chem. Phys., **29**, 952 (1958)
2. JACS., **82**, 5966 (1960)
3. J. Chem. Phys., **32**, 1261 (1960)
4. J. Mol. Spectroscopy, **6**, 58 (1961)
5. J. Phys. Chem., **66**, 2499 (1962)
6. J. Chem. Phys., **39**, 675 (1963)
7. J. Chem. Phys., **40**, 507 (1964)
8. Photochem. Photobiology, **3**, 269 (1964)
9. J. Chim. Phys., **61**, 1147 (1964)
10. Trans. Faraday Soc., **62**, 3393 (1966)
11. Chem. Rev., **66**, 199 (1966)
12. J. Chem. Ed., **46**, 2 (1969)
13. JACS, **114**, 3883 (1992)

Singlet-Triplet Transitions
Role of Spin-Orbit Coupling





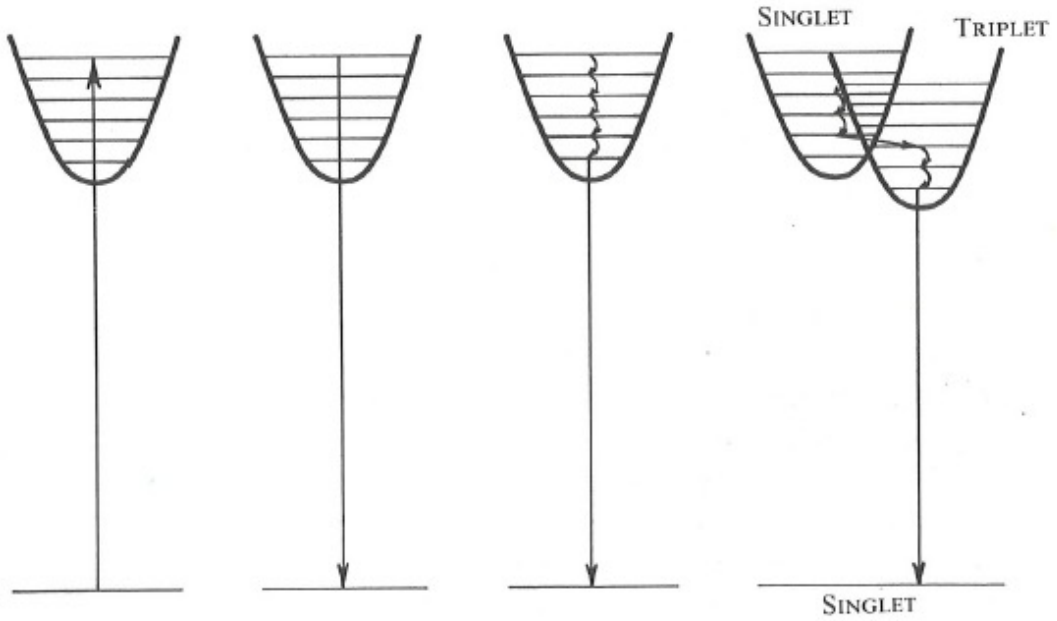
Spin-Orbit coupling mixes the states,
no longer pure states

Observed Rate Constant | Zero-point Motion-Limited Rate Constant | "Fully Allowed Rate"

$$\underbrace{k_{obs}}_{\text{Prohibition to maximal caused by "selection rules"}} = k^0_{max} \times \underbrace{f_e \times f_v \times f_S}_{\text{Prohibition factors due to changes in electronic, nuclear, or spin configuration}} \tag{3.7}$$

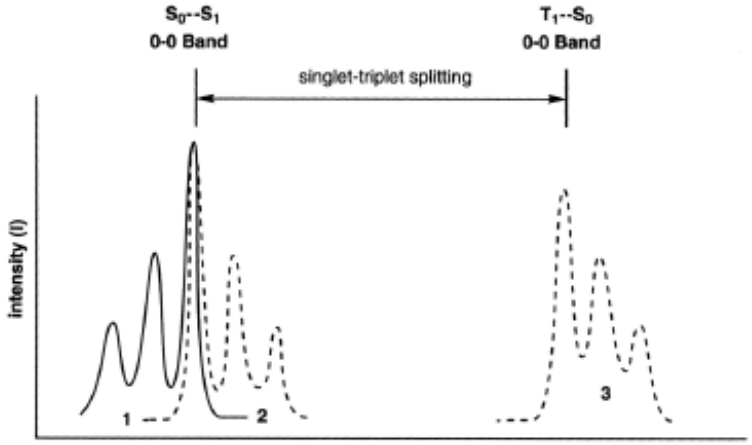
$$k_{obs} = \underbrace{\left[\frac{k^0_{max} < \psi_1 | P_{vib} | \psi_2 >^2}{\Delta E^2_{12}}\right]}_{\text{Vibrational coupling}} \times \underbrace{\left[\frac{< \psi_1 | P_{so} | \psi_2 >^2}{\Delta E^2_{12}}\right]}_{\text{Spin–orbital coupling}} \times \underbrace{\left[< \chi_1 | \chi_2 >^2\right]}_{\text{Vibrational overlap Franck-Condon factors}}$$

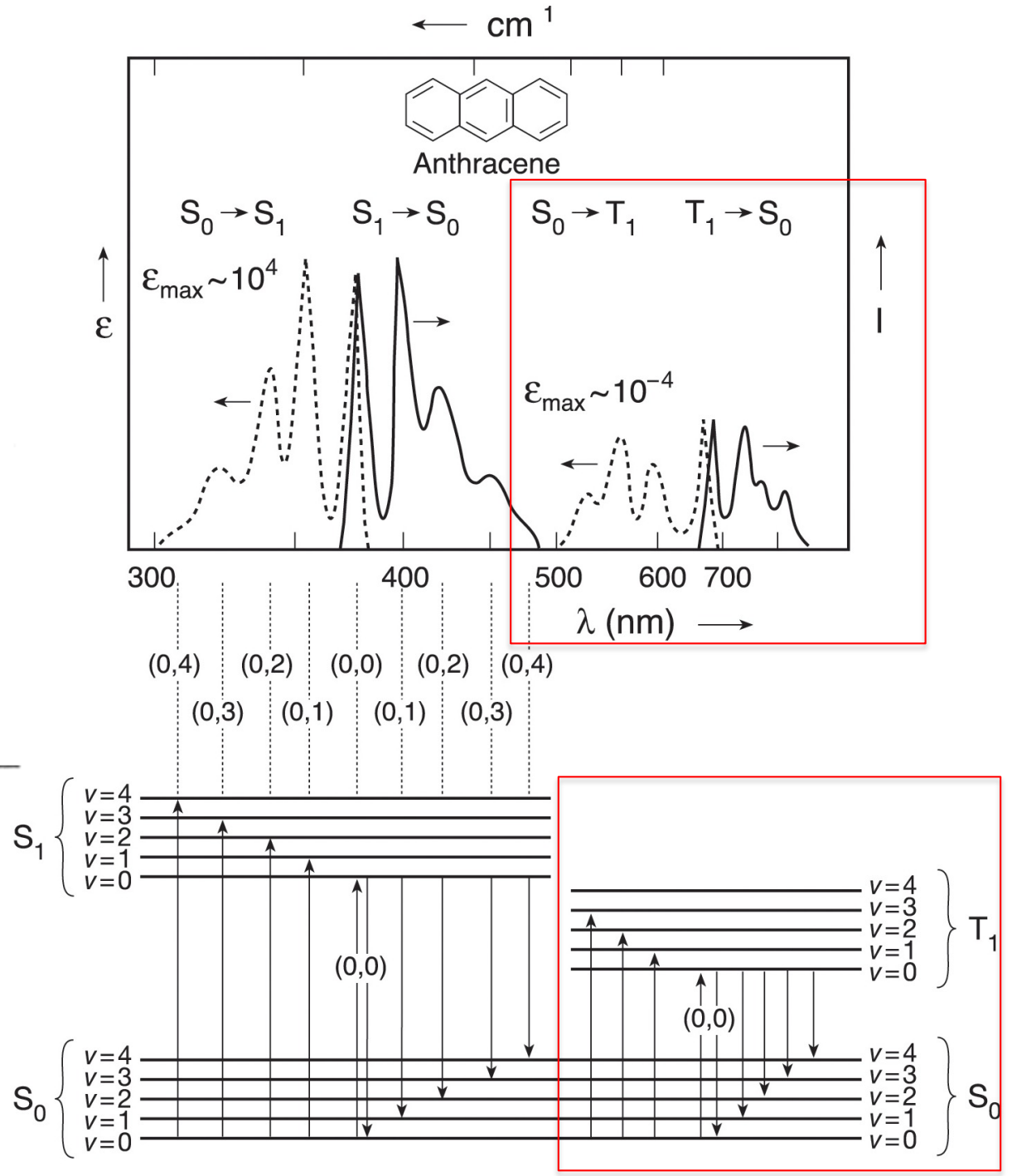
Absorption and Emission

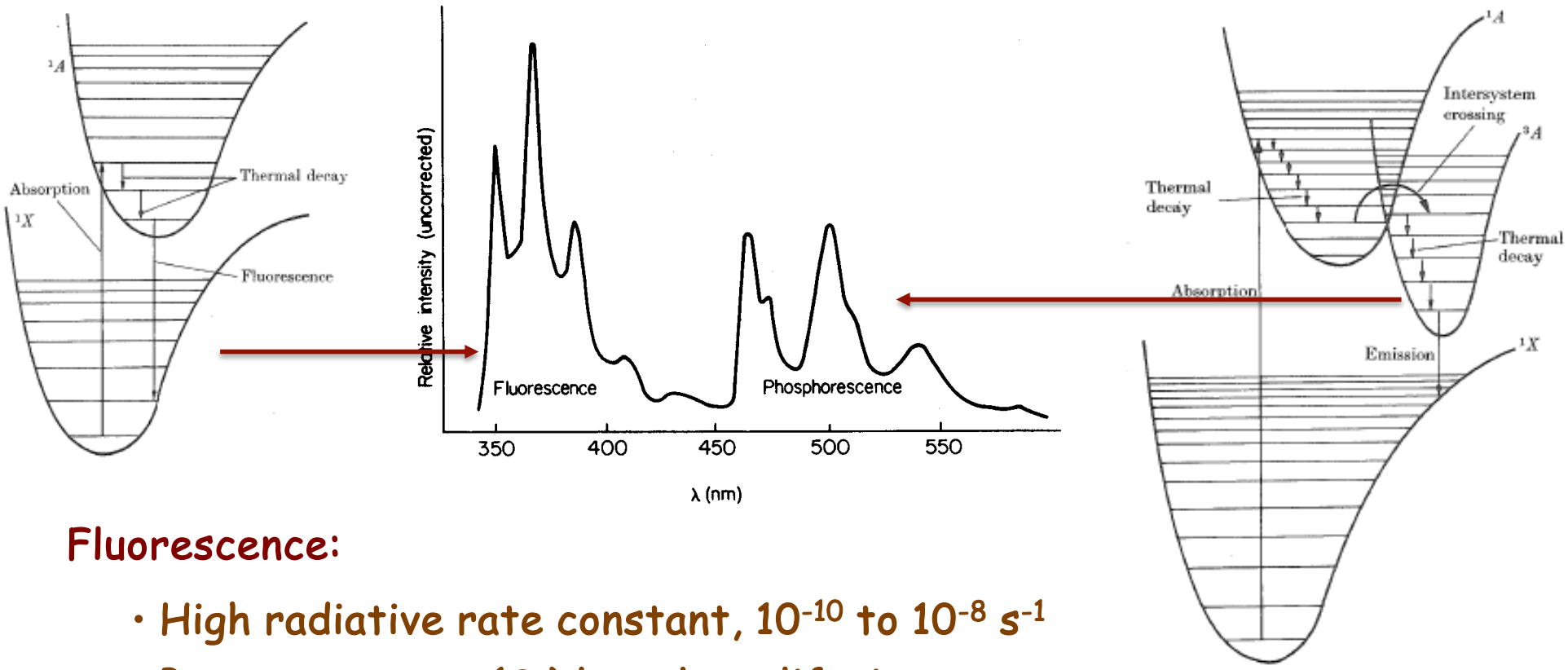


(*a*) Absorption (*b*) Re-emission (*c*) Fluorescence (*d*) Phosphorescence

Phosphorescence







Fluorescence:

- High radiative rate constant, 10^{-10} to 10^{-8} s^{-1}
- 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

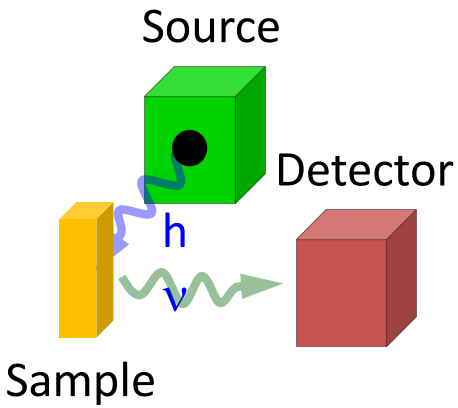
Organic Glass for Phosphorescence

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}

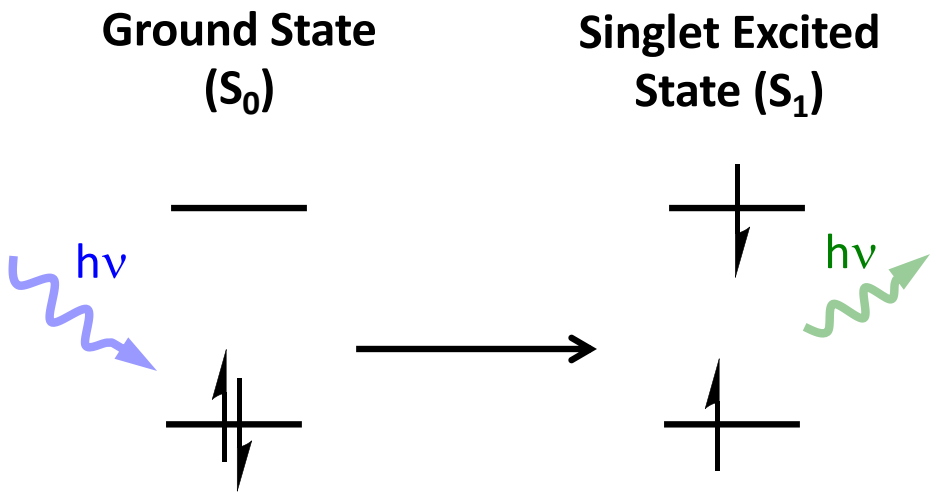
- Be chemically inert
- Have no absorption in the region of optical pumping
- Have a large solubility for the studied material
- Be stable (don't crack) to the action of light
- Have a good optical quality

Emission Quantum Yield



Emission Quantum Yield (Φ)

$$\Phi = \frac{\text{\# of photons emitted}}{\text{\# of photons absorbed}}$$



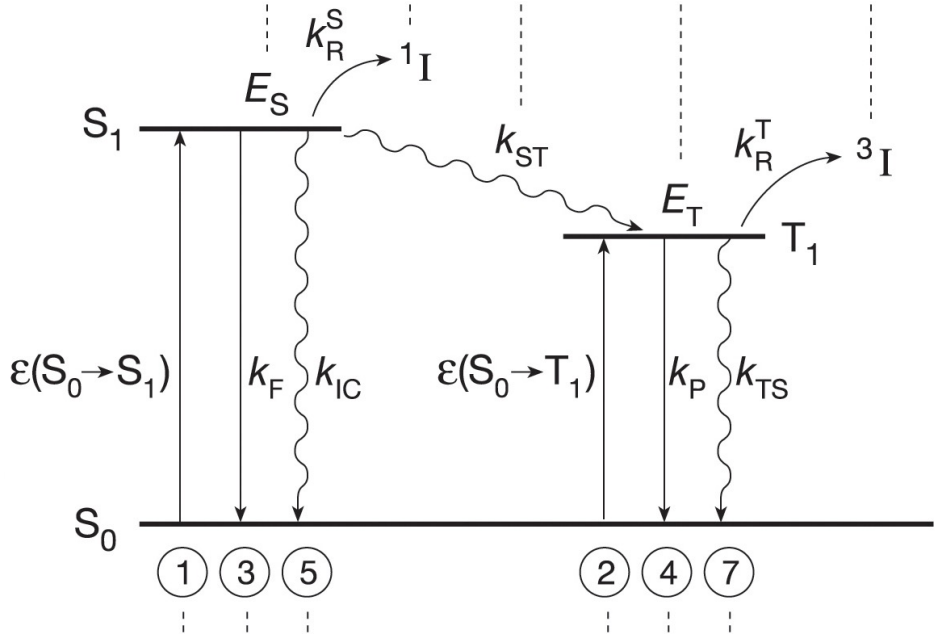
Competition with fluorescence

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

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

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

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



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

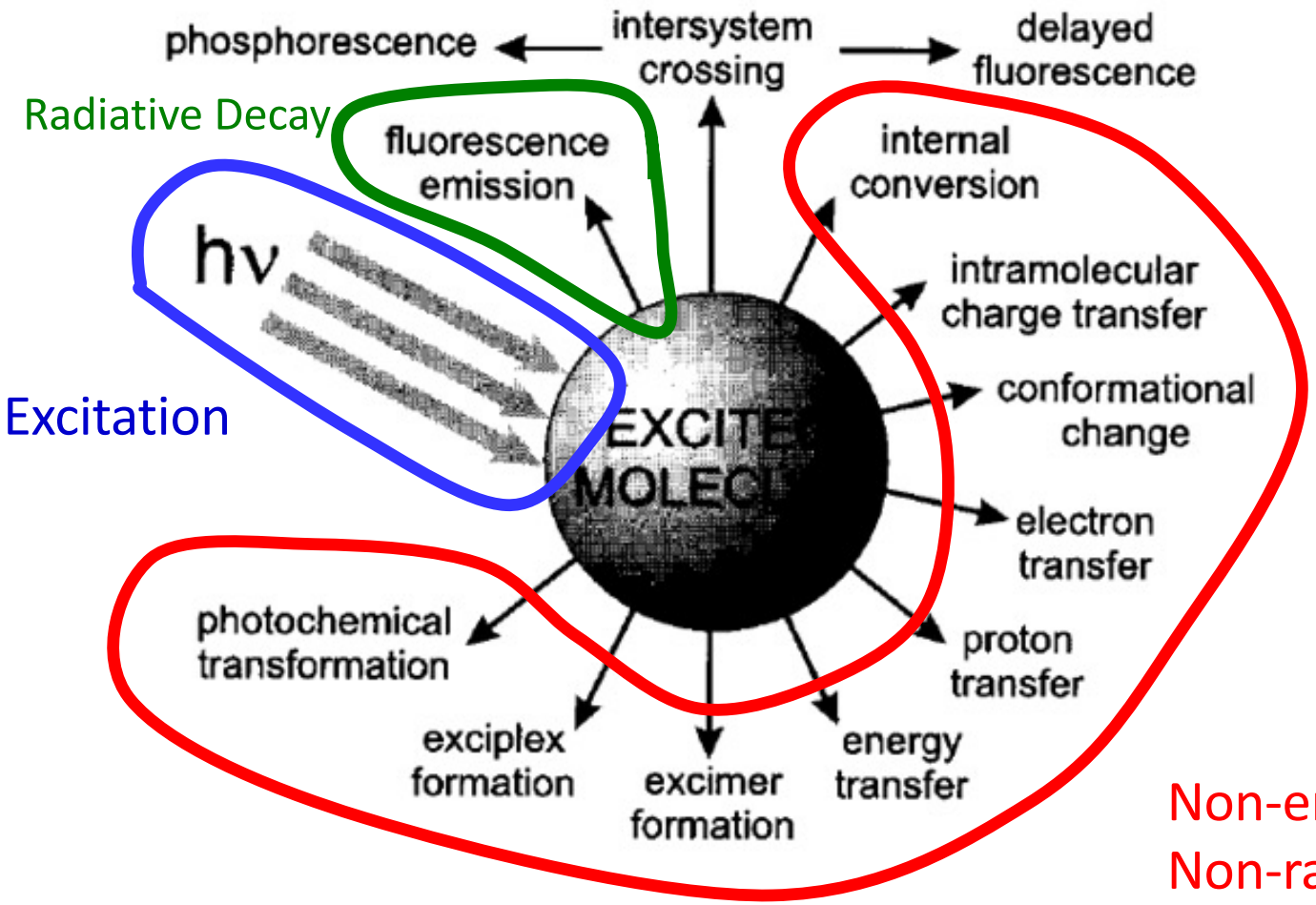
$$\tau_f = \frac{1}{k_f + k_{isc} + k_{ic} + \ldots.}$$

Lifetime

$$1/\tau^0 = k_e{}^0 \sim \varepsilon_{max}\Delta\nu^2 \sim 10^4\varepsilon_{max}$$

Radiative lifetime

Excited State Decay

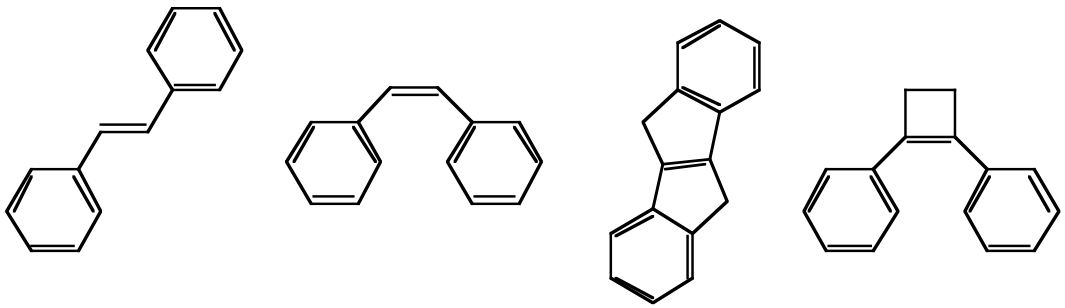


$$\Phi = \frac{\text{\# of photons emitted}}{\text{\# of photons absorbed}}$$

Factors Controlling Quantum Yield of Fluorescence

Rigid *vs* non-rigid molecules

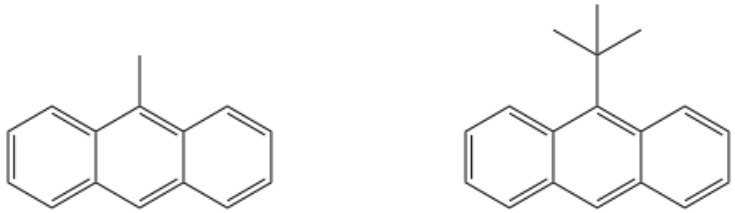
Bond rotation



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

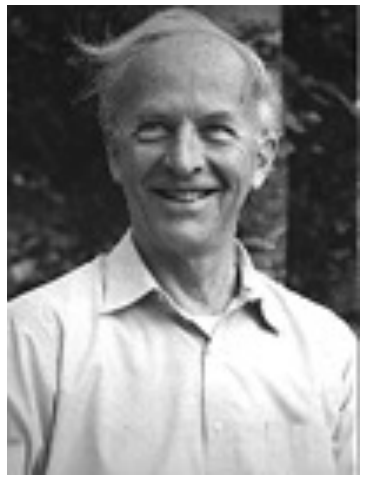


0.29 0.011

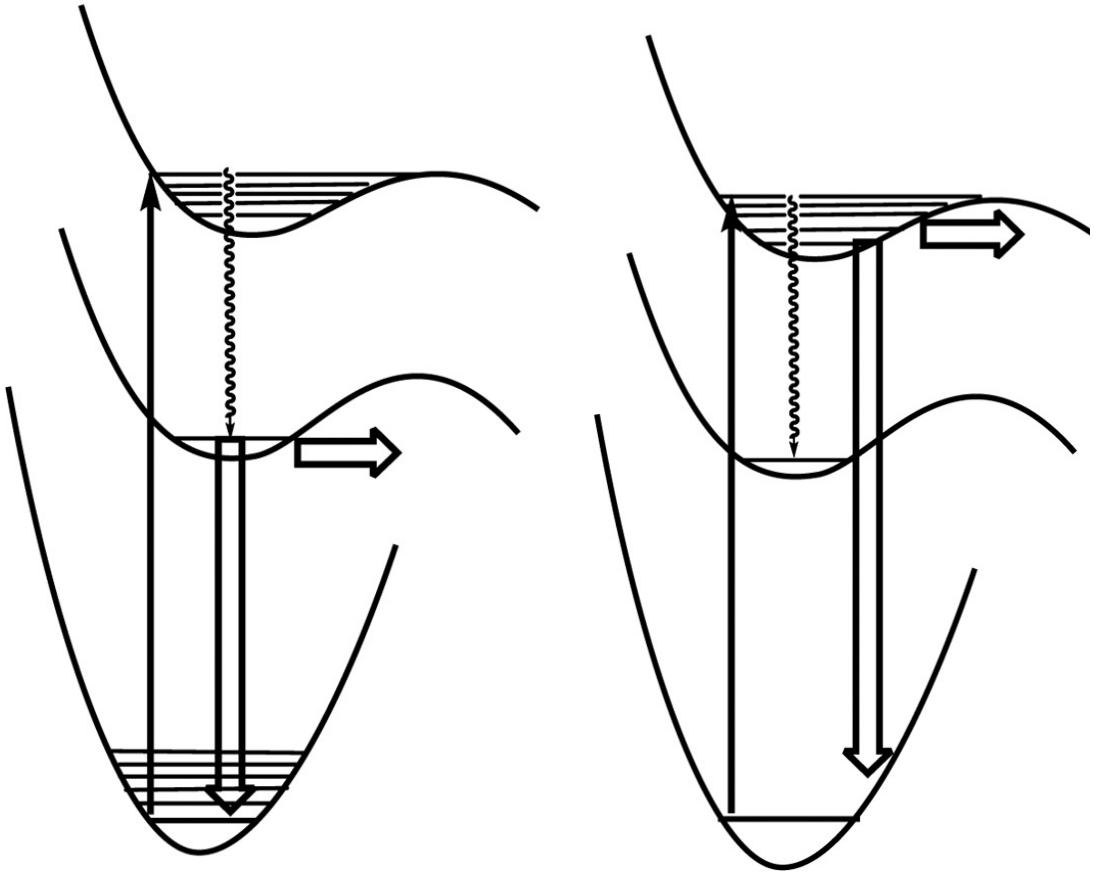
Kasha's rule

"The emitting level of a given multiplicity is the lowest excited level of that multiplicity"

Kasha, Characterization of Electronic Transitions in Complex Molecules, *Faraday Soc. Discussion* **9**, 14-19 (1950)



Michael Kasha (1920 – 2013).



Fluorescence occurs only from S_1 to S_0;

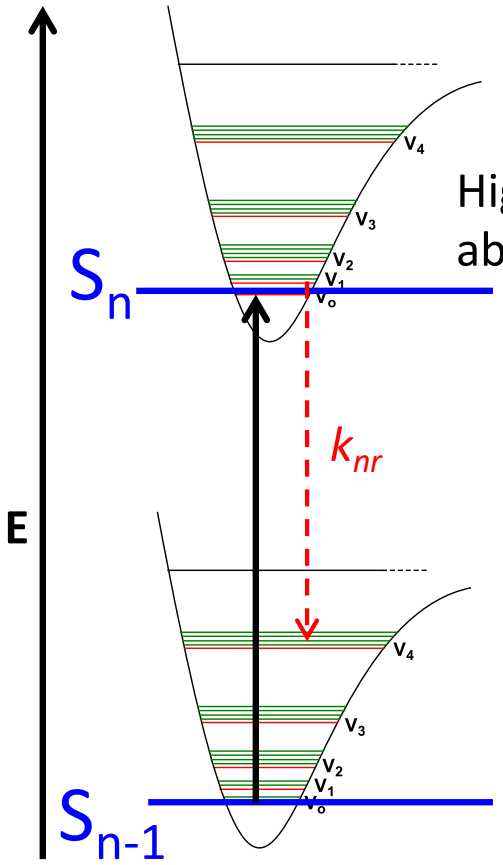
Phosphorescence occurs only from T_1 to S_0;

S_n and T_n emissions are extremely rare.

Energy Gap Law

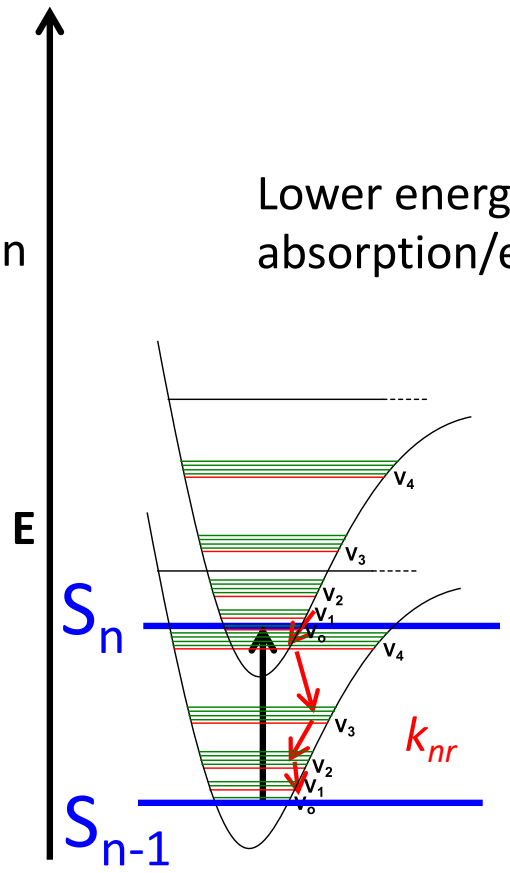
$$\Phi = \frac{k_r}{k_r + k_{nr}}$$

Large Gap



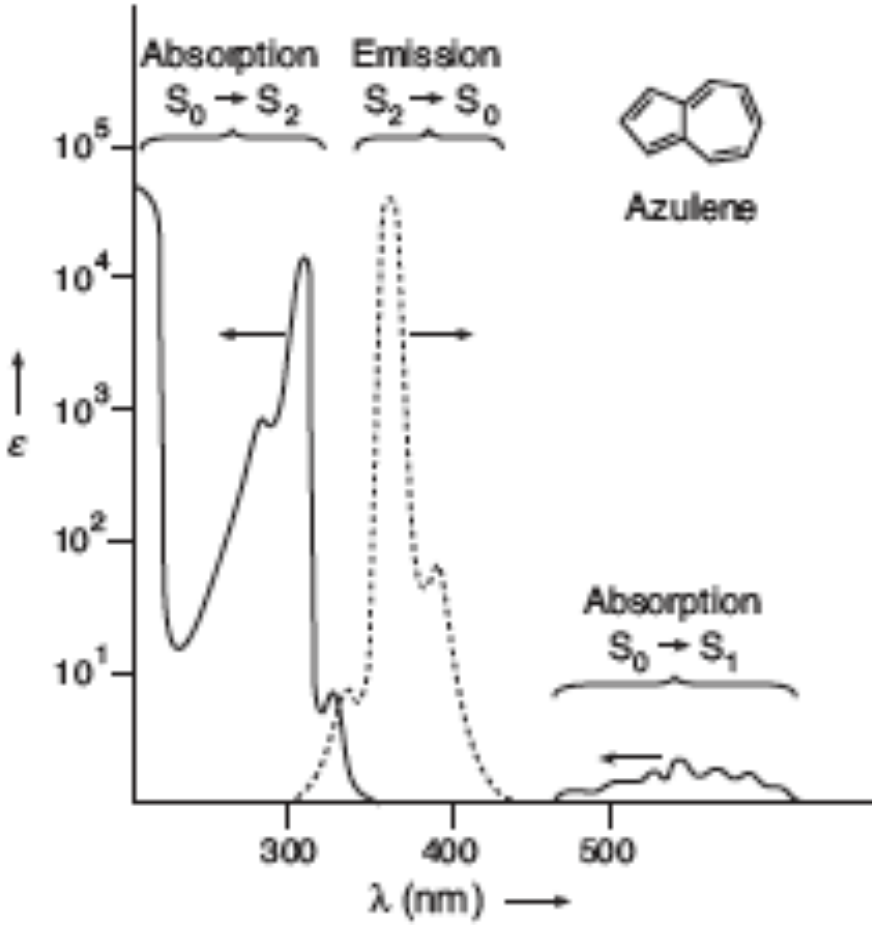
Higher energy absorption/emission

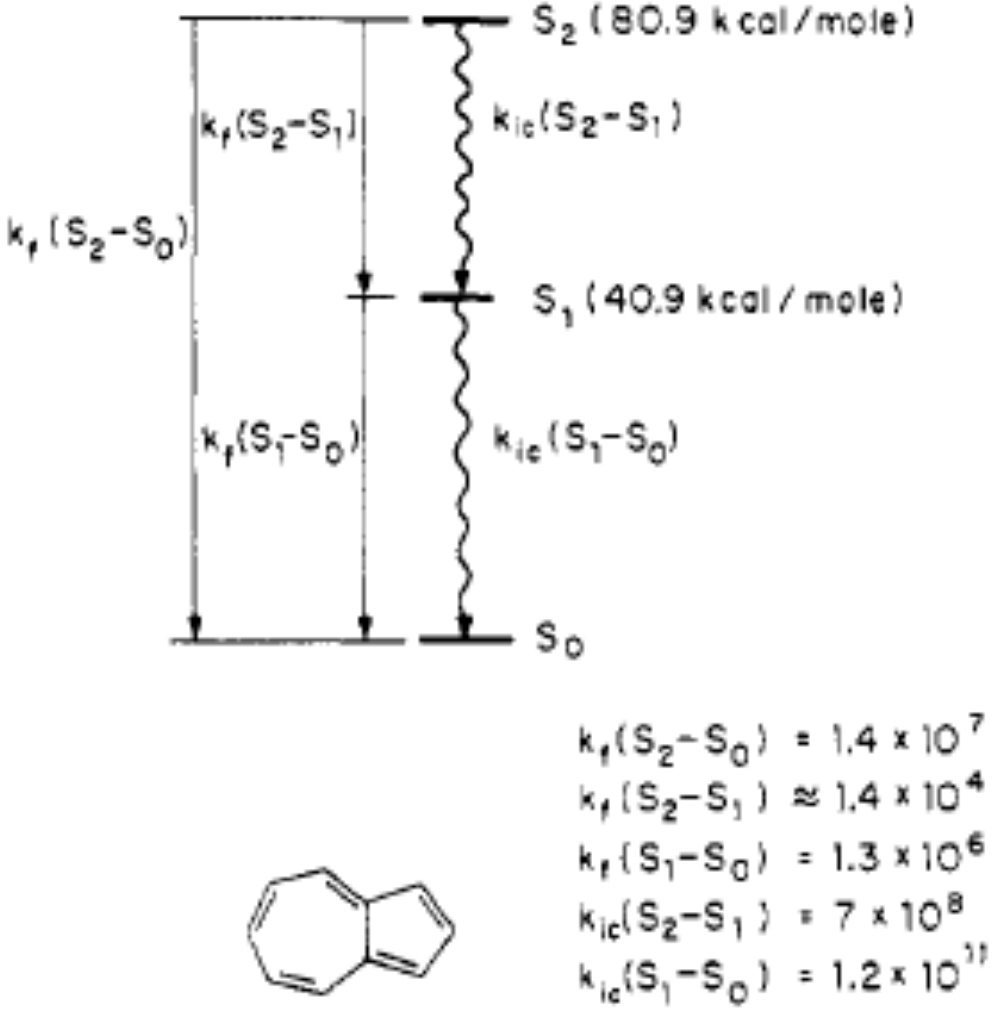
Small Gap



Lower energy absorption/emission

Exceptions

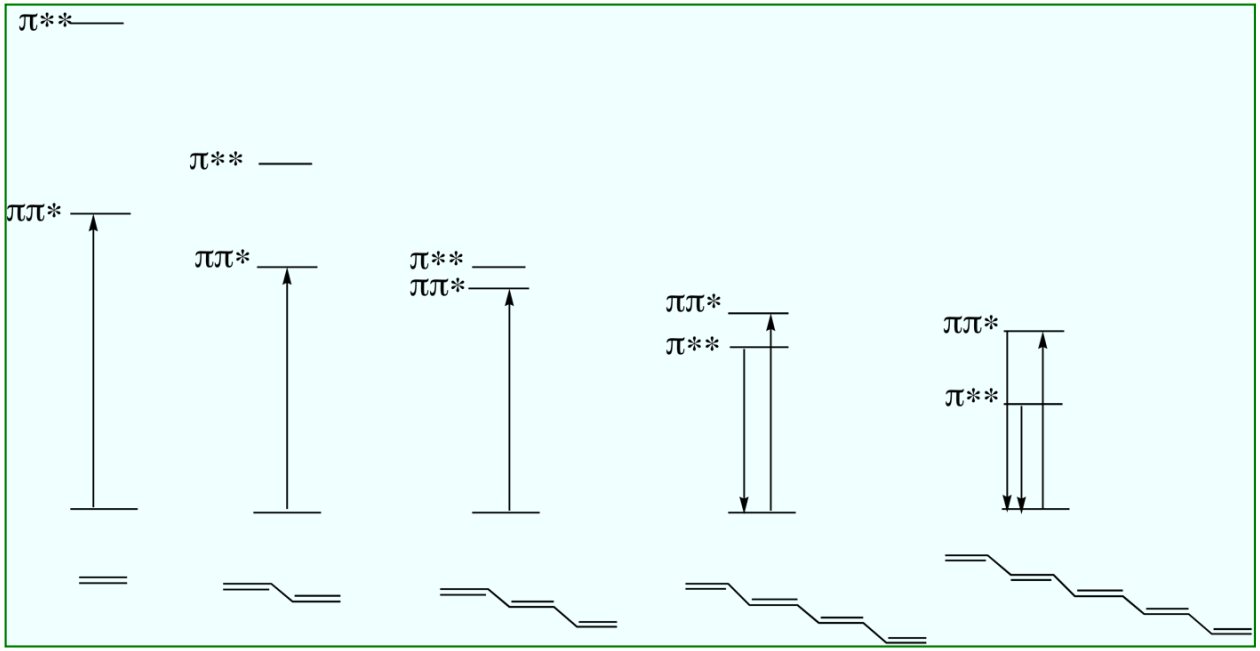


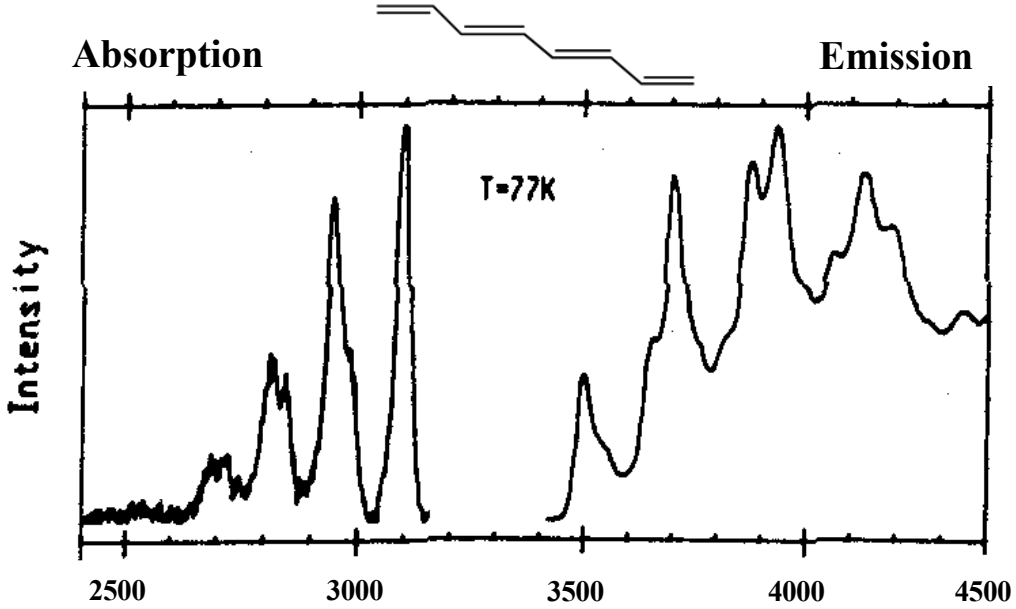


$k_f(S_2-S_0) = 1.4 \times 10^7$
$k_f(S_2-S_1) \approx 1.4 \times 10^4$
$k_f(S_1-S_0) = 1.3 \times 10^6$
$k_{ic}(S_2-S_1) = 7 \times 10^8$
$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

M. Kasha; G. Viswanath, Confirmation of the anomalous fluorescence of azulene. *J. Chem. Phys*. **1956**, *24*, 574.

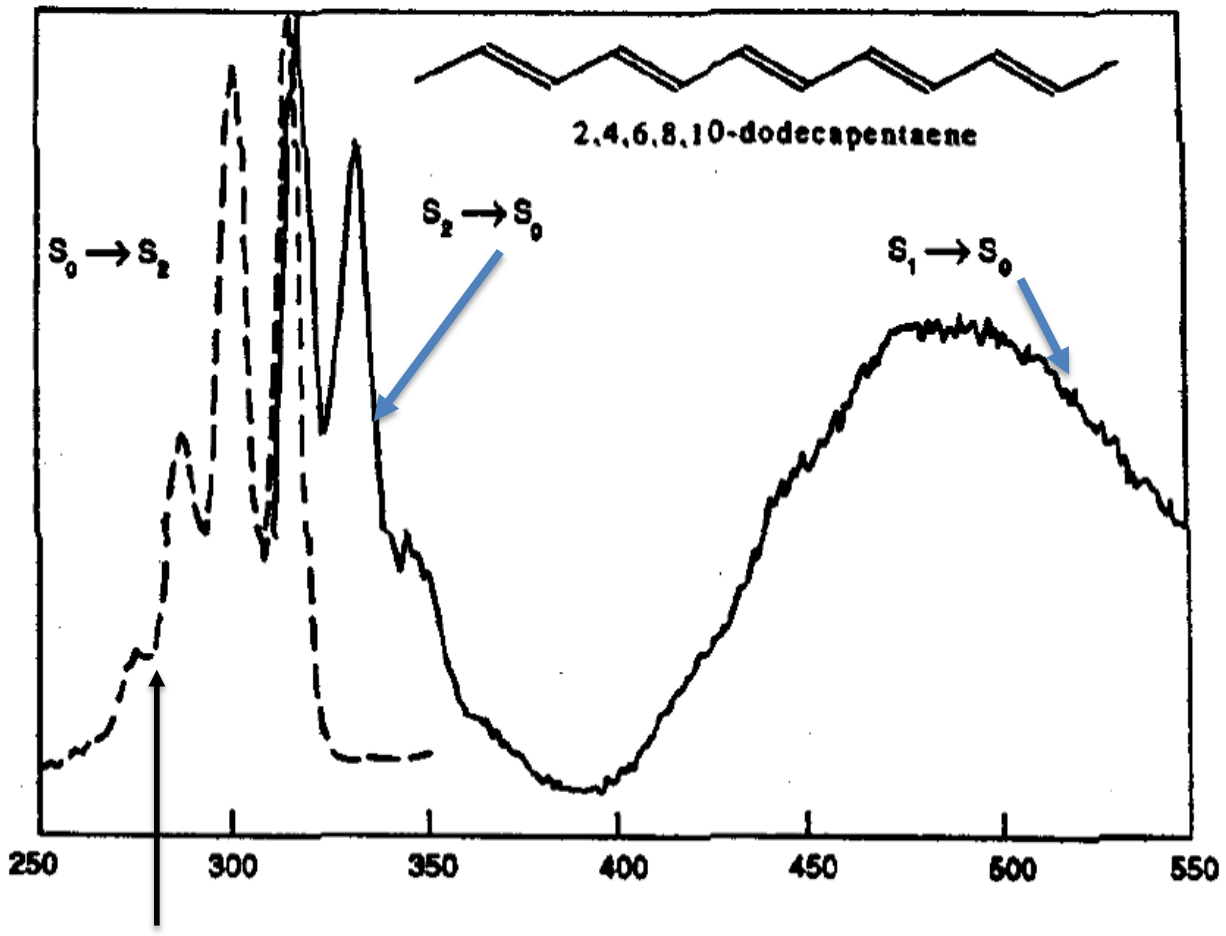
Ordering of excited states depends on chain length



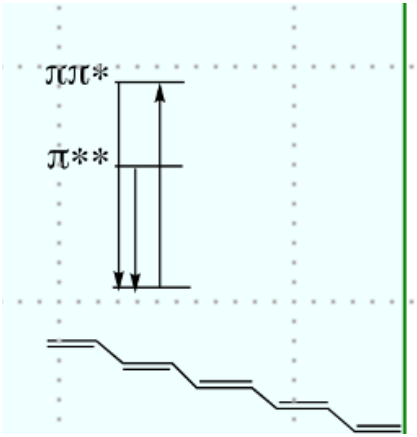


R. L. Christensen et. al., J. Phys. Chem. 1990, 94, 7429

Exceptions



Broken line absorption



R. L. Christensen et. al., *J. Phys. Chem*. **1990**, *94*, 7429
T. Gilbro, R. S. H. Liu, et. al., *J. Luminescence*, **1992**, *51*, 11

RETURN TO ISSUE | < PREV ARTICLE NEXT >

The effect of wavelength on organic photoreactions in solution. Reactions from upper excited states

N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth

Cite this: *Chem. Rev.* 1978, 78, 2, 125–145
Publication Date: April 1, 1978
https://doi.org/10.1021/cr60312a003
RIGHTS & PERMISSIONS Subscribed

Article Views 877 | Altmetric - | Citations 186
LEARN ABOUT THESE METRICS

Share Add to Export RIS

ACS Legacy Archives

Fluorescence and Phosphorescence from Higher Excited States of Organic Molecules

Takao Itoh

View Author Information

Cite this: *Chem. Rev.* 2012, 112, 8, 4541–4568
Publication Date: May 16, 2012
https://doi.org/10.1021/cr200166m
Copyright © 2012 American Chemical Society
RIGHTS & PERMISSIONS Subscribed

Article Views 11919 | Altmetric - | Citations 206
LEARN ABOUT THESE METRICS

CHEMICAL REVIEWS

Review

Cite This: *Chem. Rev.* 2017, 117, 13353-13381

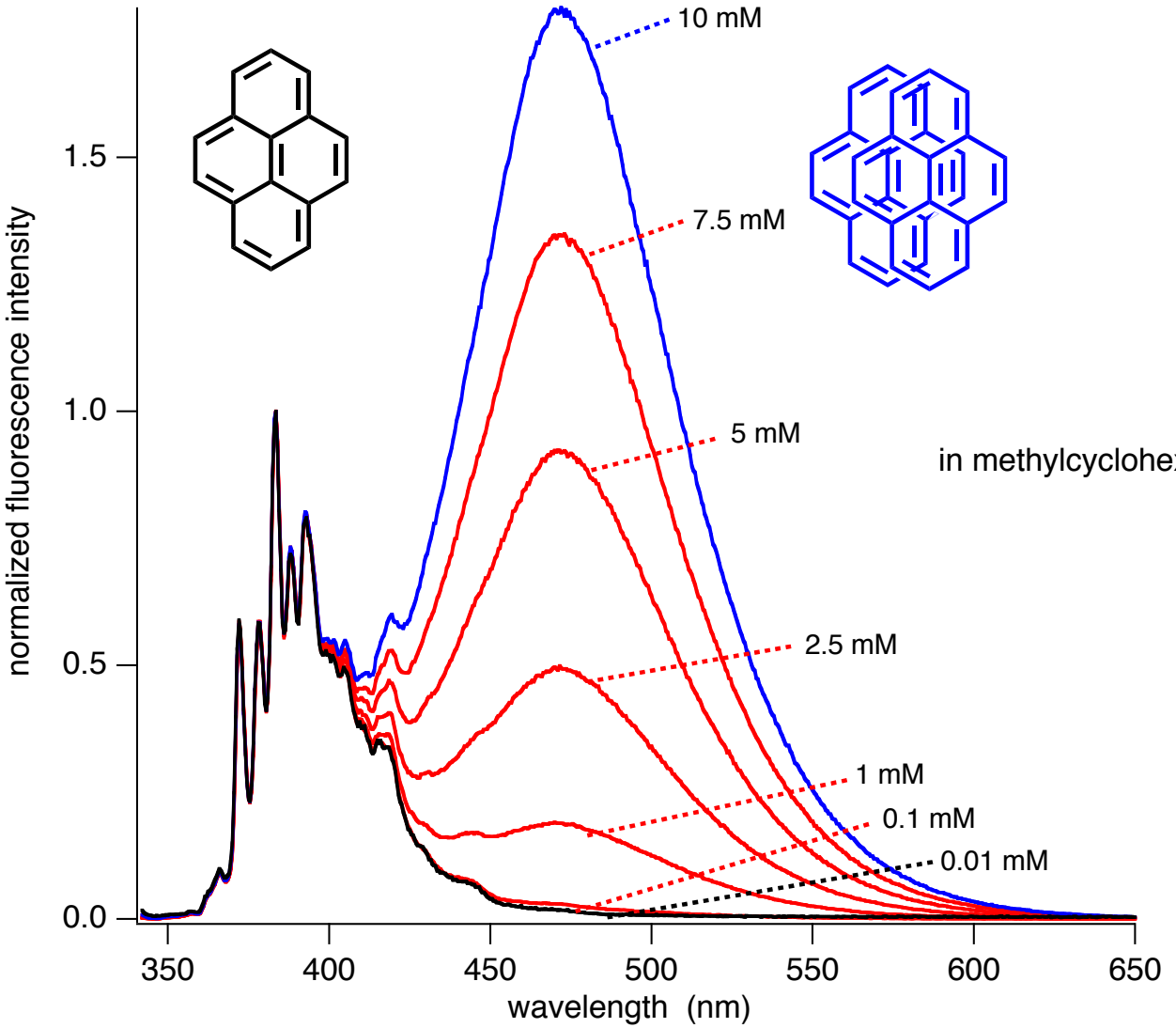
pubs.acs.org/CR

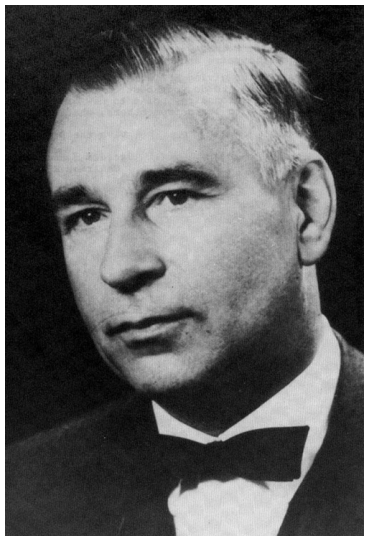
Breaking the Kasha Rule for More Efficient Photochemistry

Alexander P. Demchenko,[†] Vladimir I. Tomin,[‡] and Pi-Tai Chou*[,§]

[†]Palladin Institute of Biochemistry, National Academy of Sciences of Ukraine, 9 Leontovicha Street, Kyiv 01030, Ukraine
[‡]Institute of Physics, Pomeranian University in Słupsk, ul. Arciszewskiego, 22b, Słupsk 76-200, Poland
[§]Department of Chemistry, National Taiwan University, 1 Roosevelt Road Section 4, Taipei 106, Taiwan

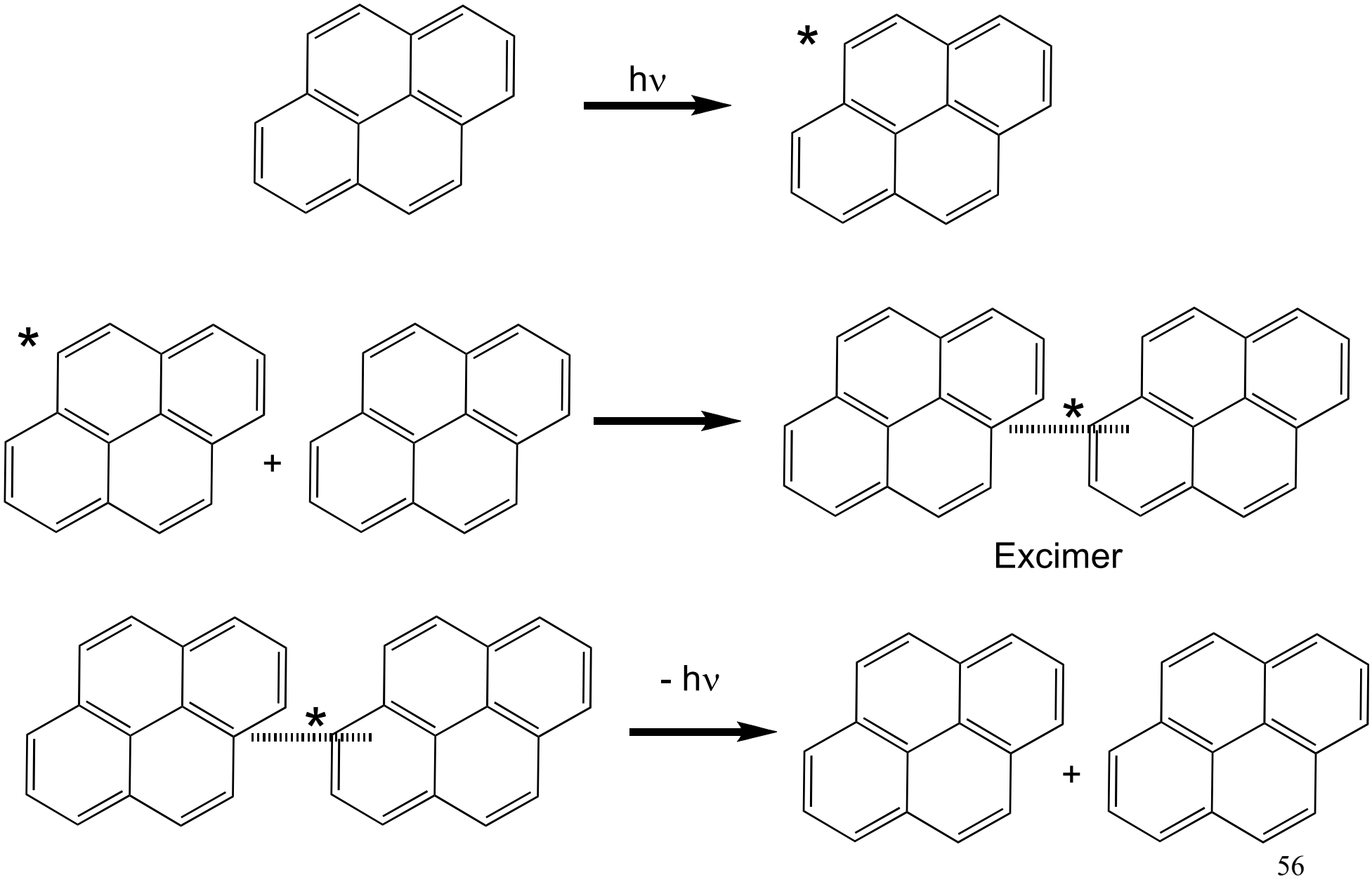
Excimers



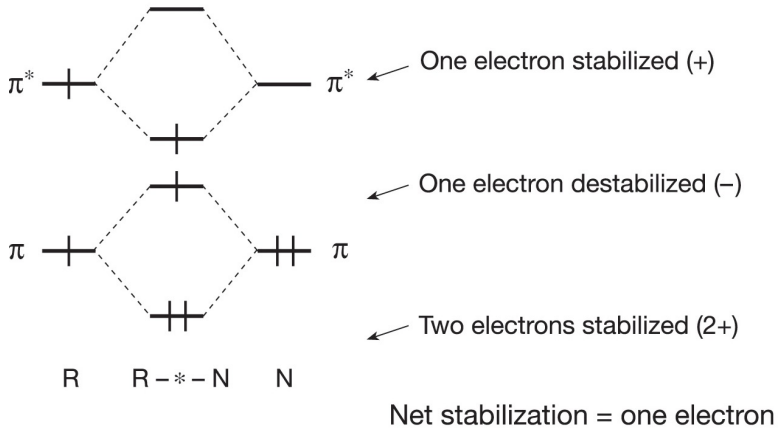


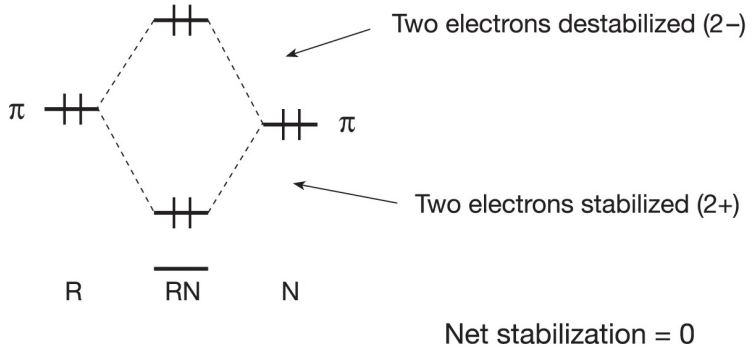
Th. Förster

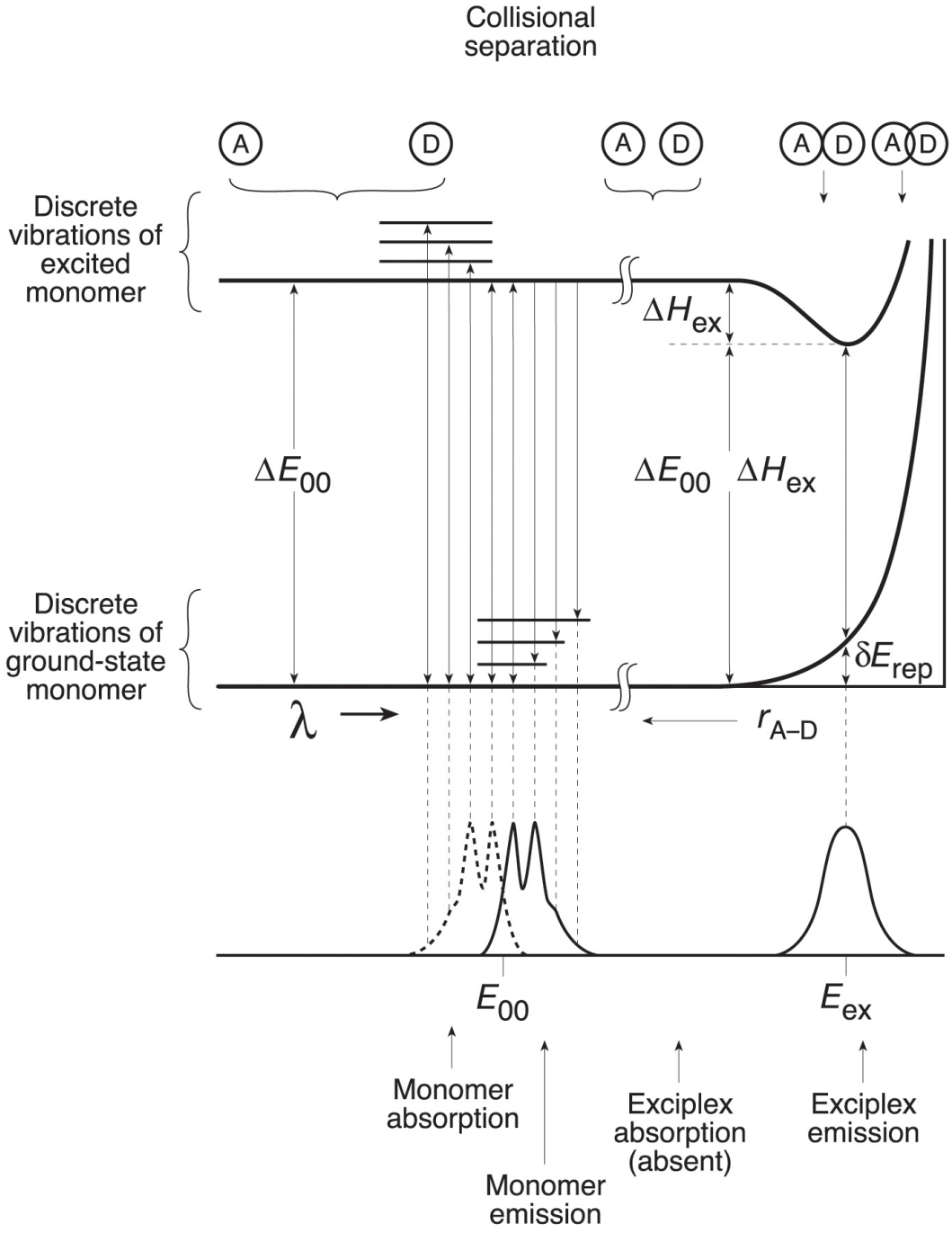
Pyrene as an exemplar of excimer formation



Why excited state complexes are more stable?

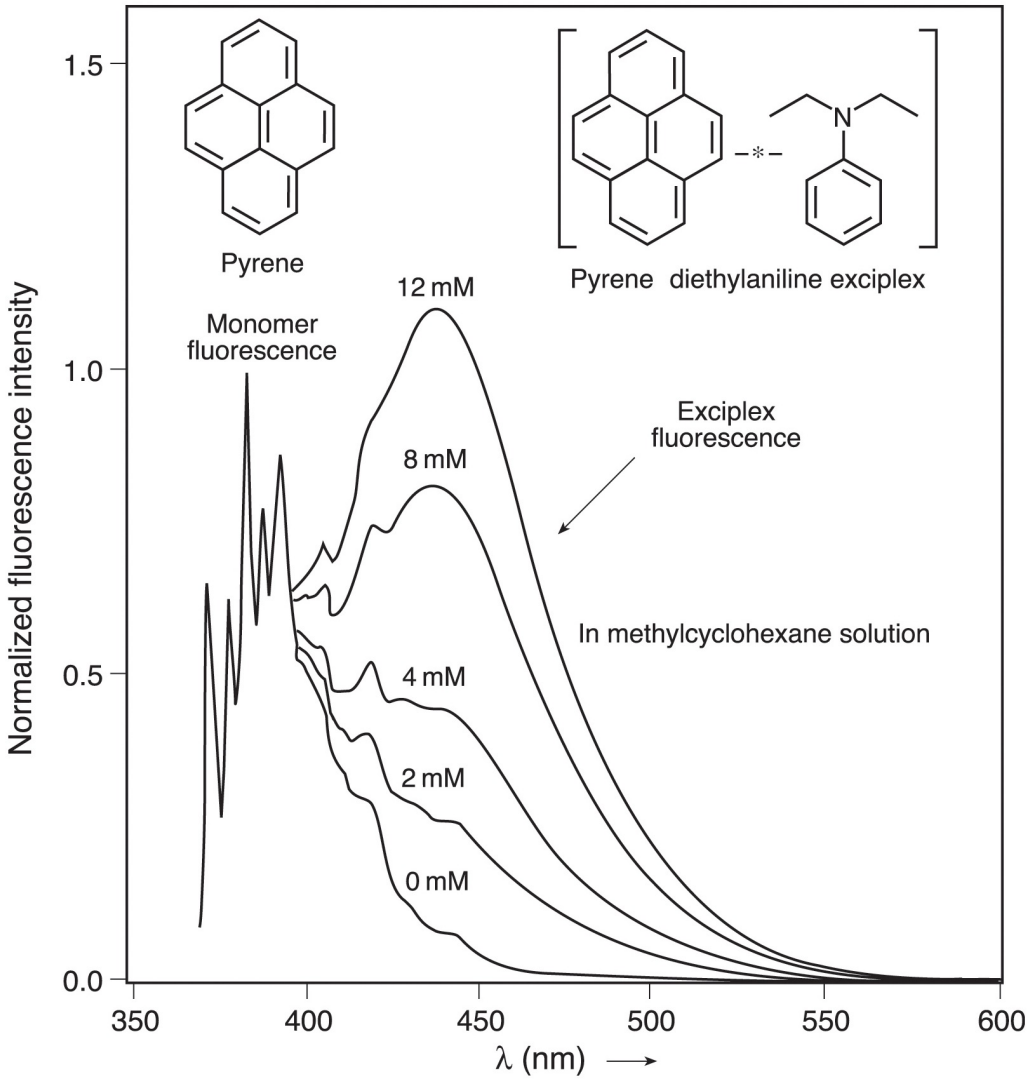


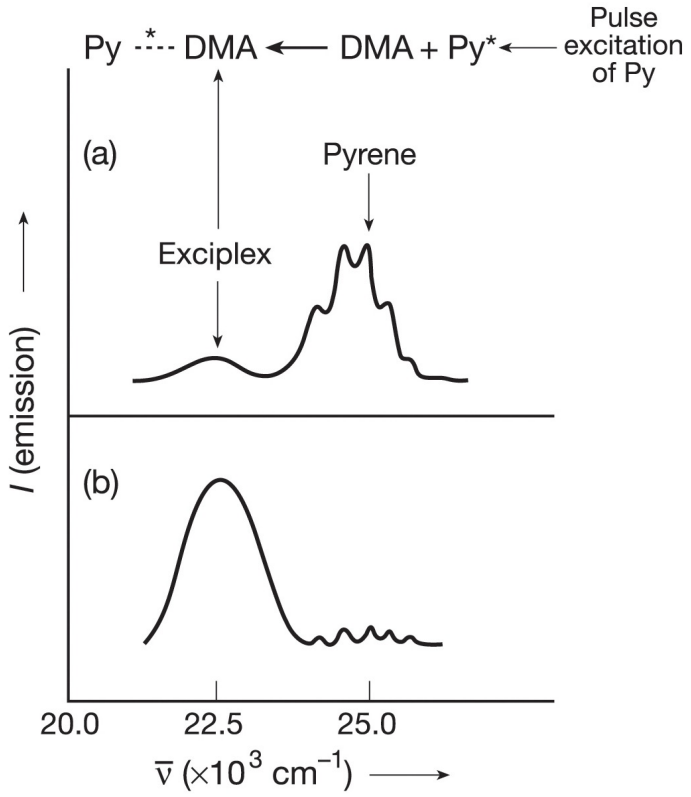




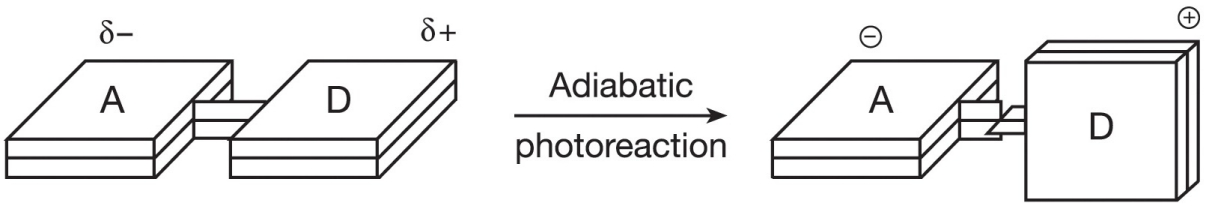
Excited state complexes: Exciplexes

Albert F. Weller



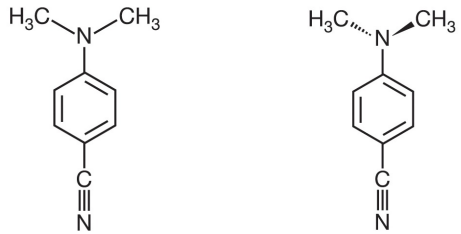


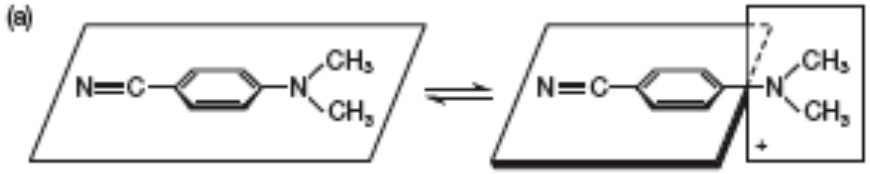
TICT Emission

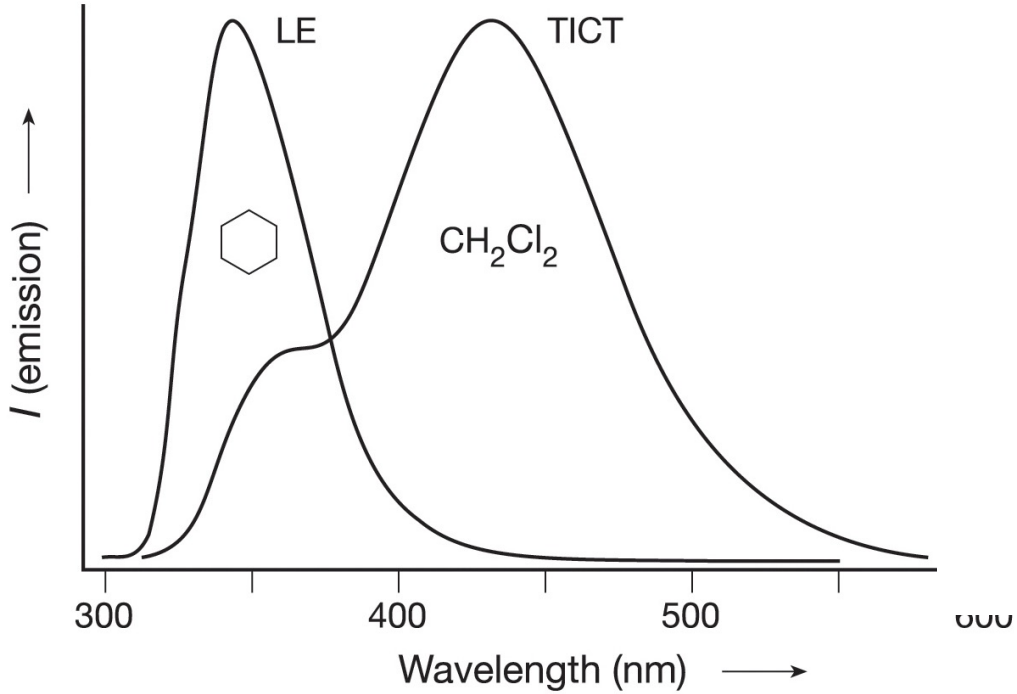


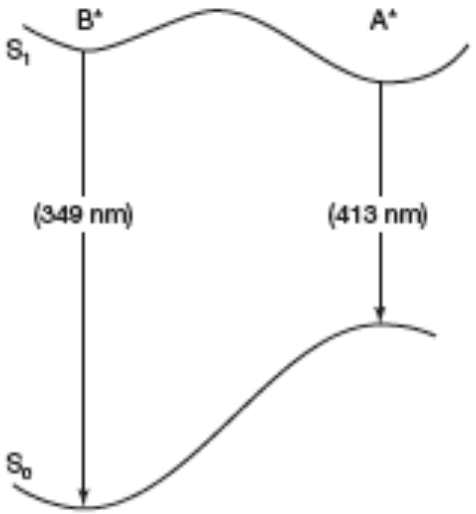
LE state
(S_1, planar, partial CT)

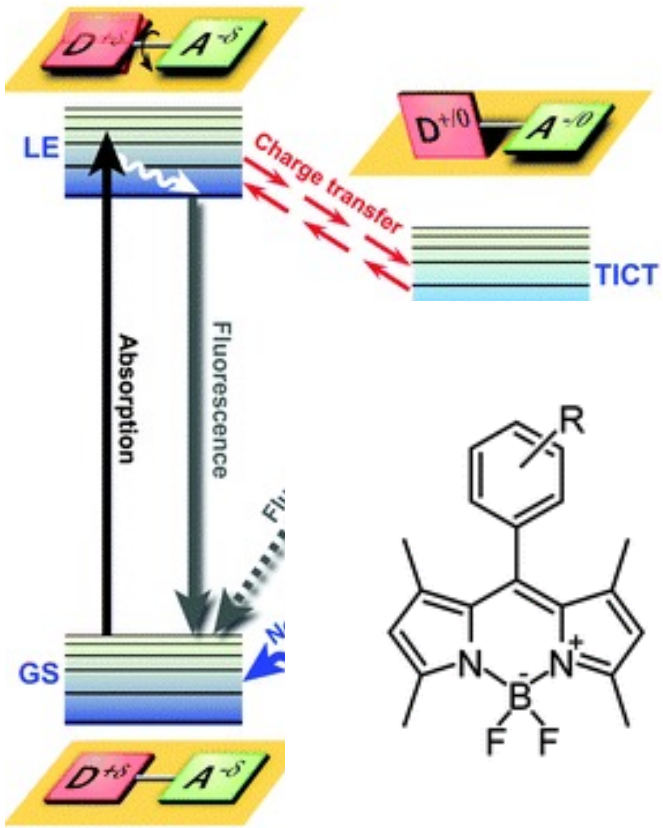
TICT state
(S_1, twisted, full CT)







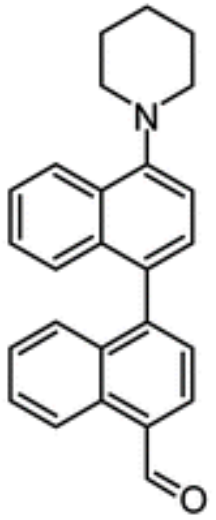



LE
Charge transfer
TICT
Absorption
Fluorescence
GS

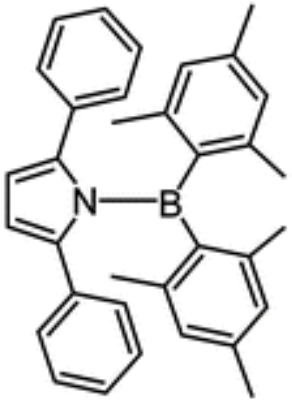
(1)


Planarity⟶Bright fluorescence
Twisting⟶Intense solvatochromism

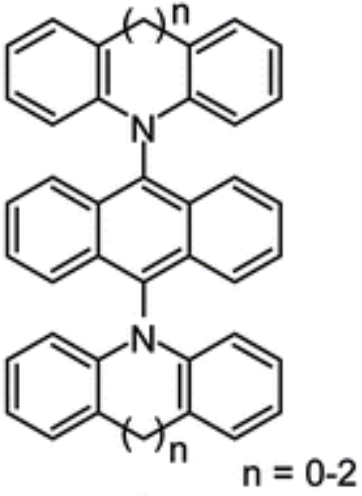
(2)



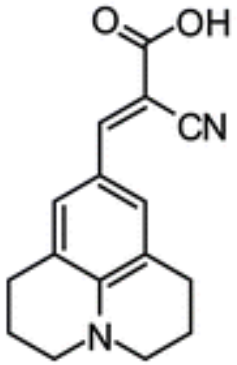
(3)



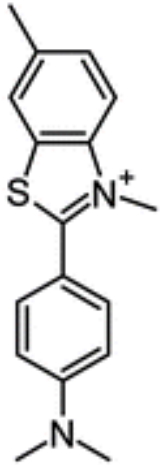
(4)


n = 0-2

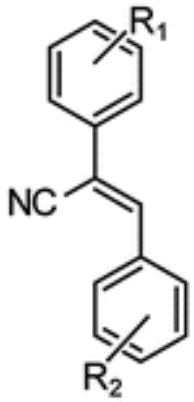
(5)



(6)



(7)



(8)

Delayed Fluorescence

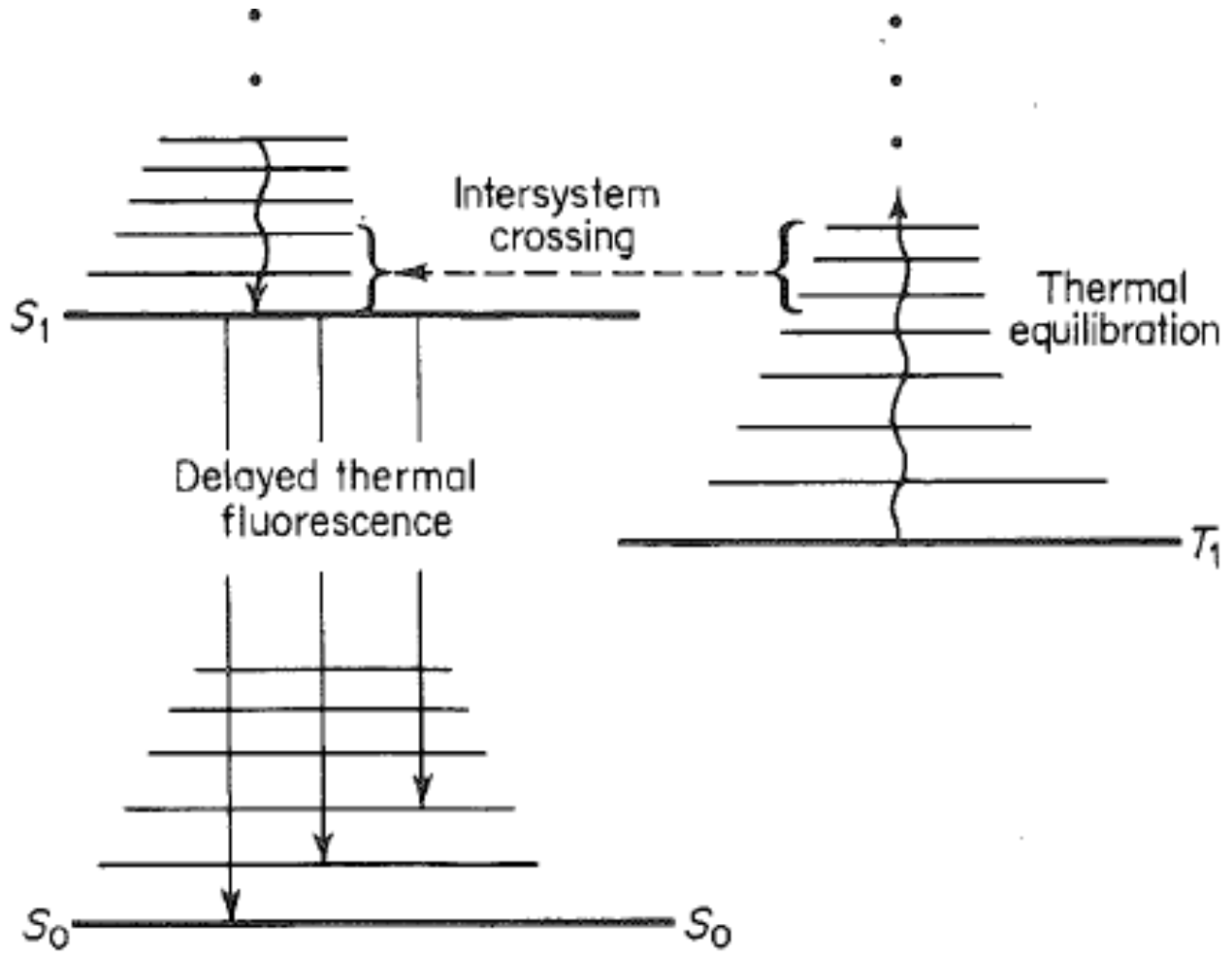
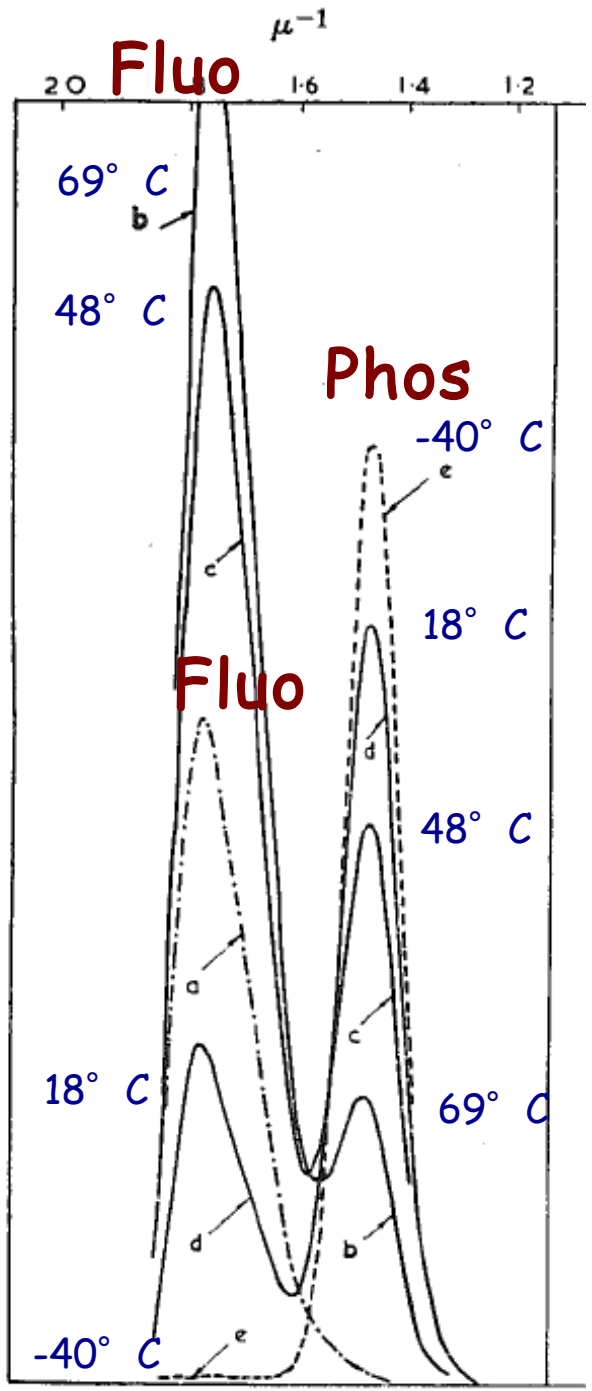
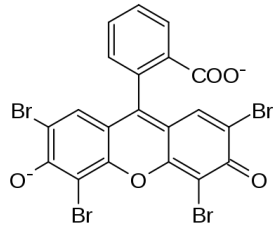


Fig. 1.11 Illustrating production of delayed thermal fluorescence (DTF).

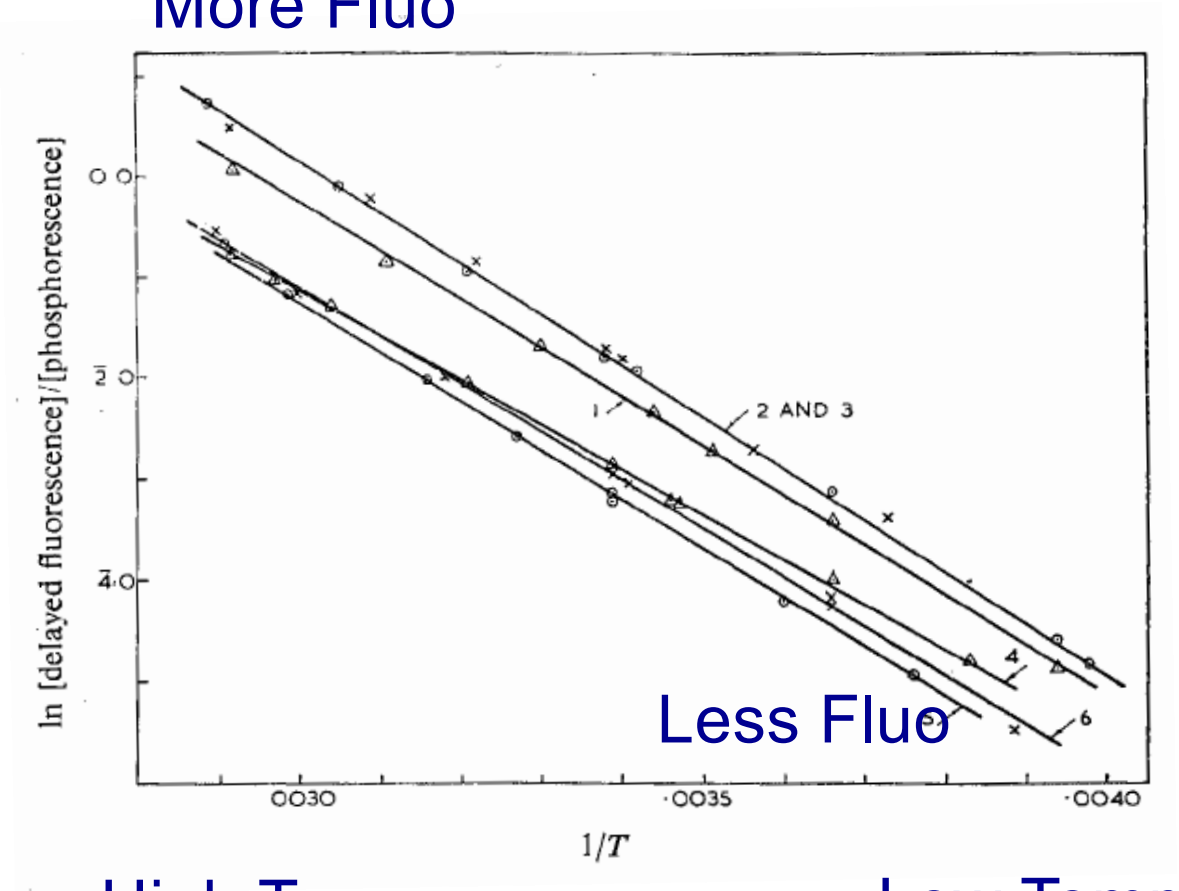
Delayed Fluorescence





Eosin Y

More Fluo



Less Fluo

High Temp

Low Temp

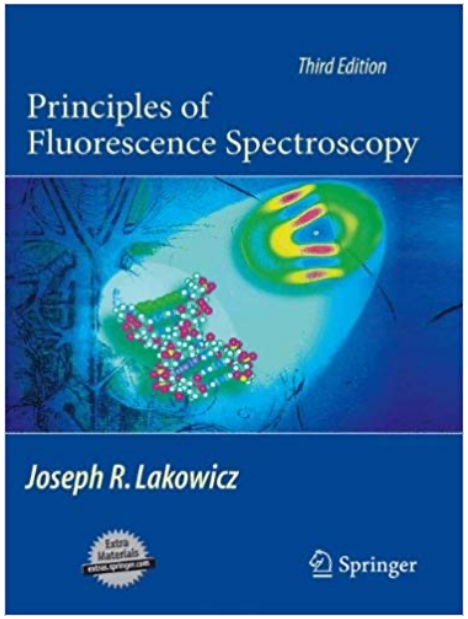
Types of emissions

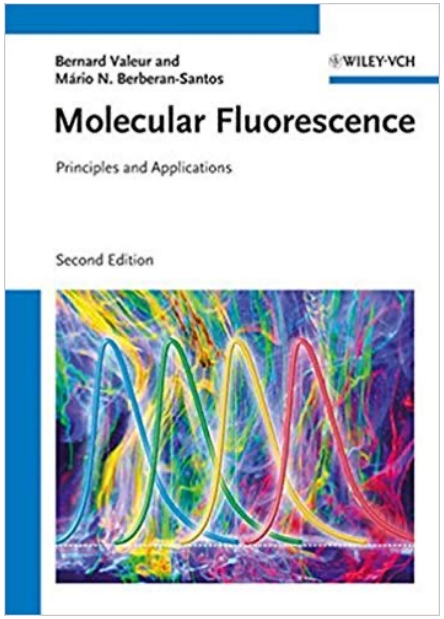
- Fluorescence
- Phosphorescence
- Emission from upper excited states
- Excimer emission
- Exciplex emission
- TICT emission
- Delayed emission

Photoluminescence of Solutions: With Applications to Photochemistry and Analytical Chemistry

C A: Parker

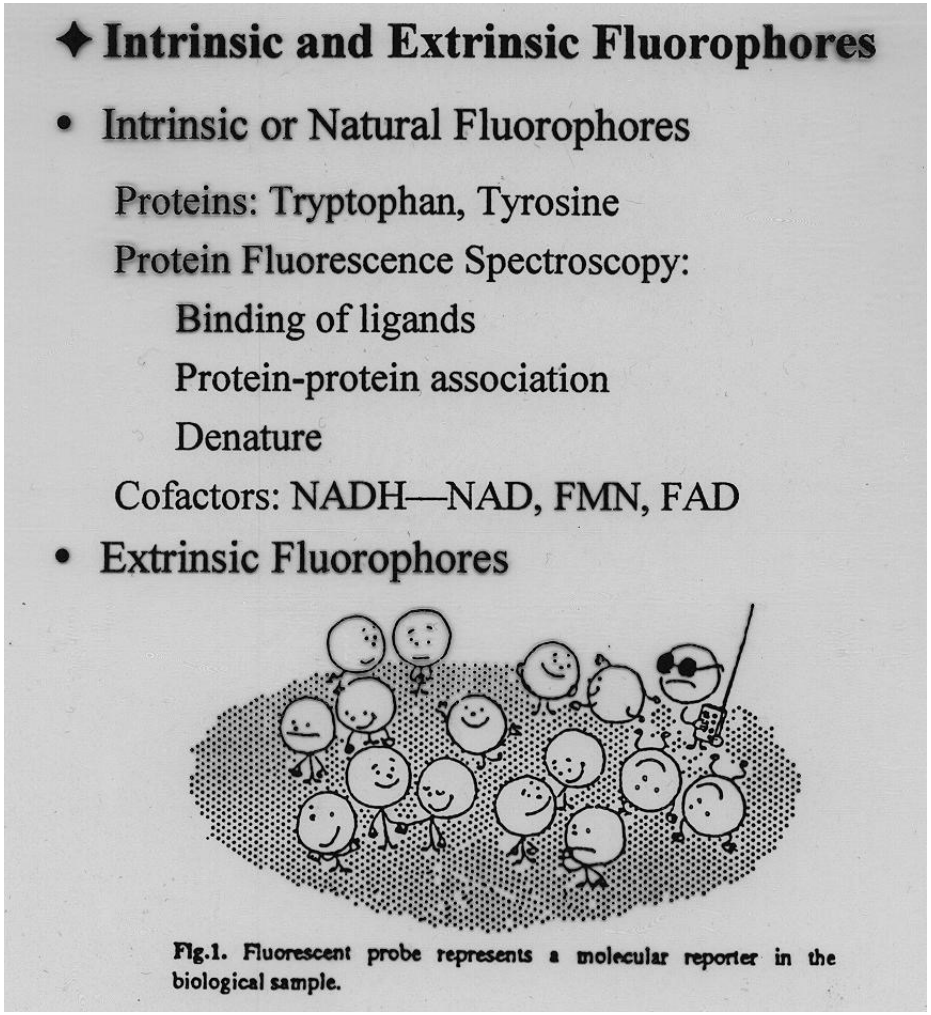
1968



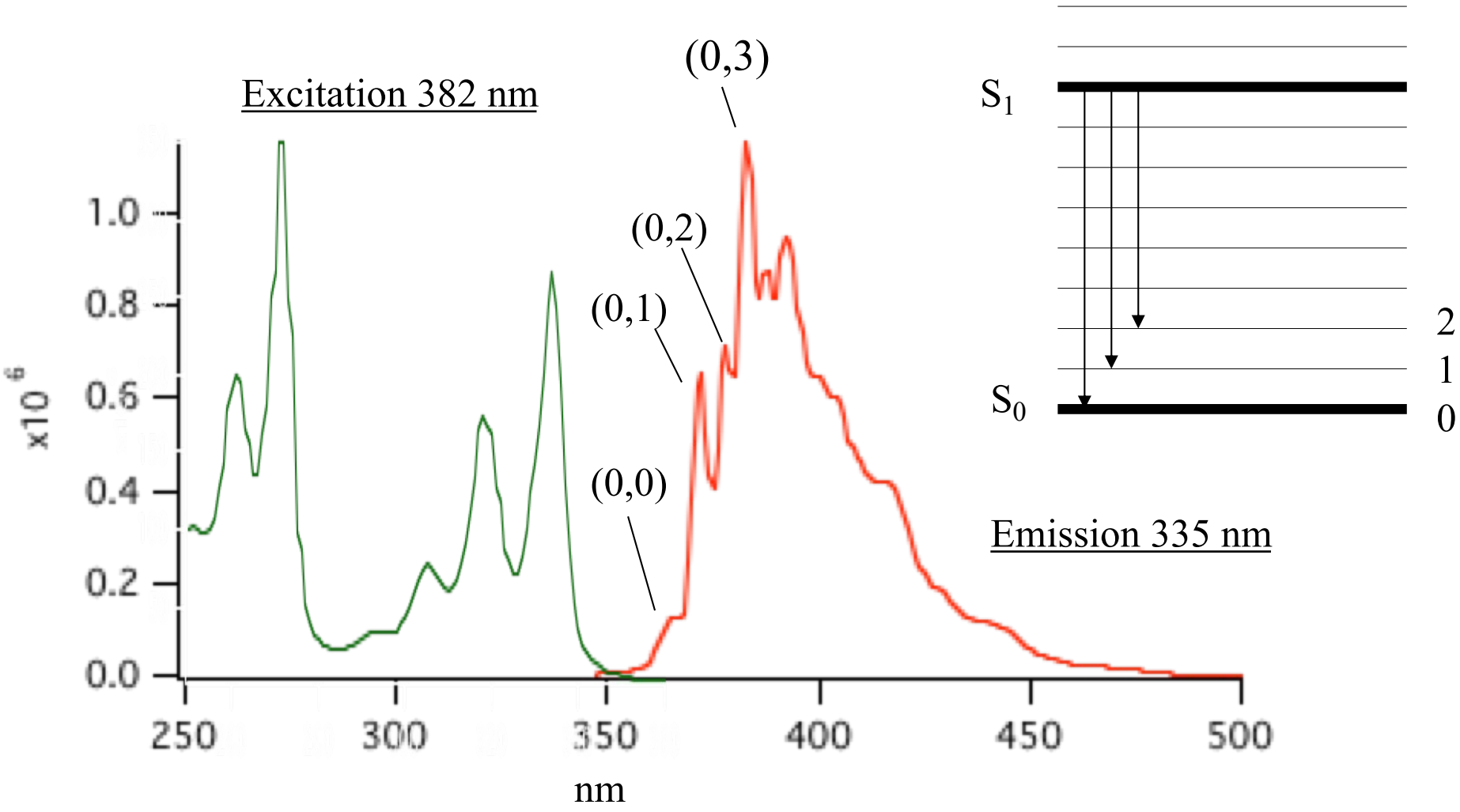


Intrinsic fluorophore and extrinsic fluorophore

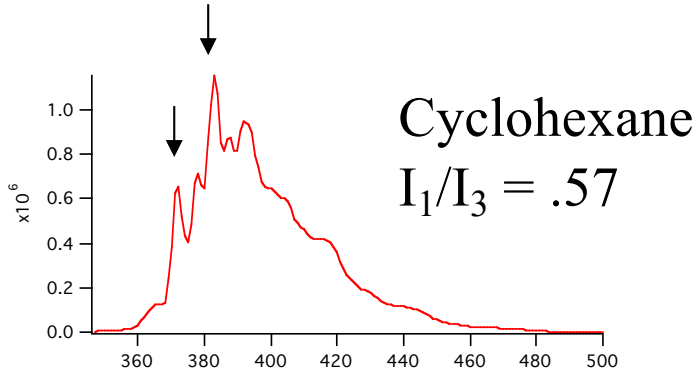
- Intrinsic fluorophores are those which occur naturally
- Extrinsic fluorophores, fluorescence probes

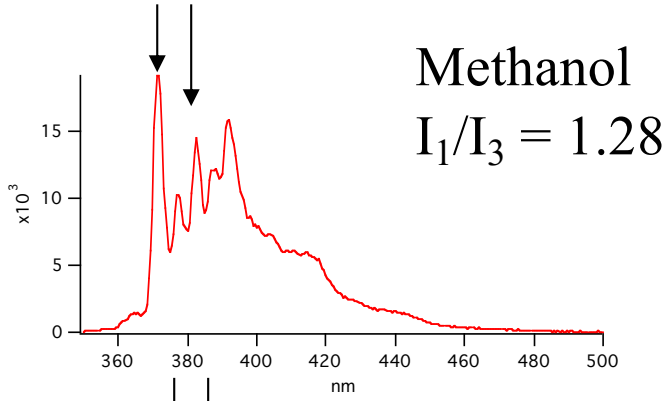


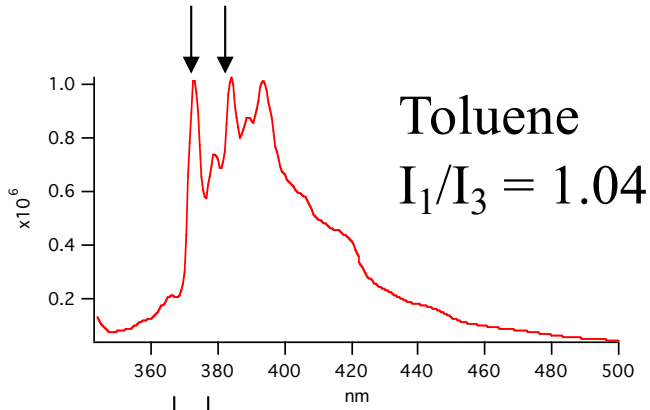
Pyrene Emission at Room Temperature Vibrational Pattern

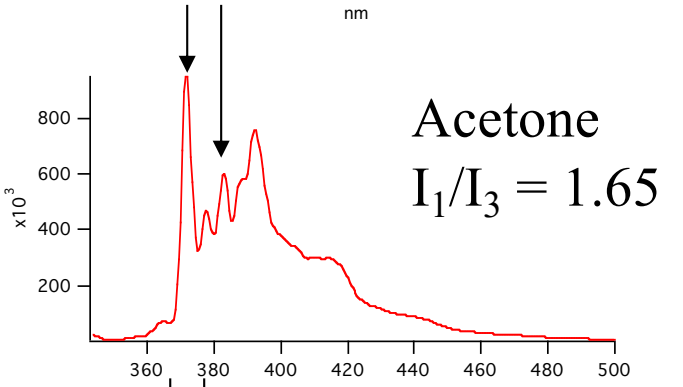


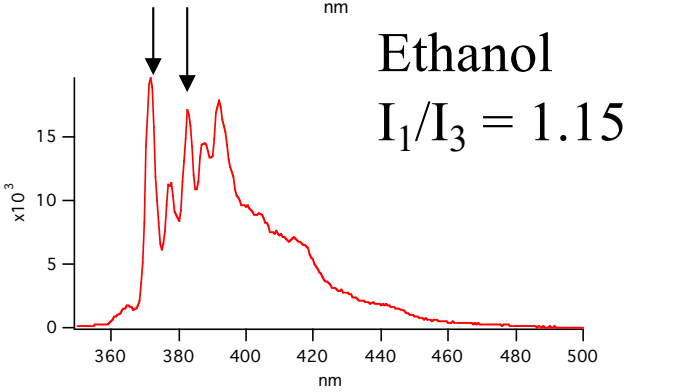
Comparison of Pyrene Emission in Different Solvents: I_1/I_3 as Polarity Probe

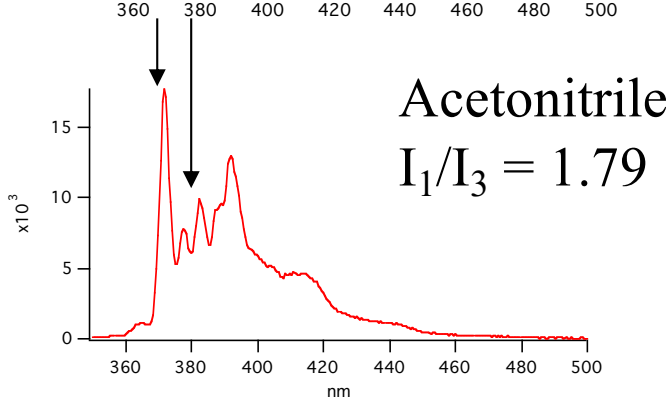










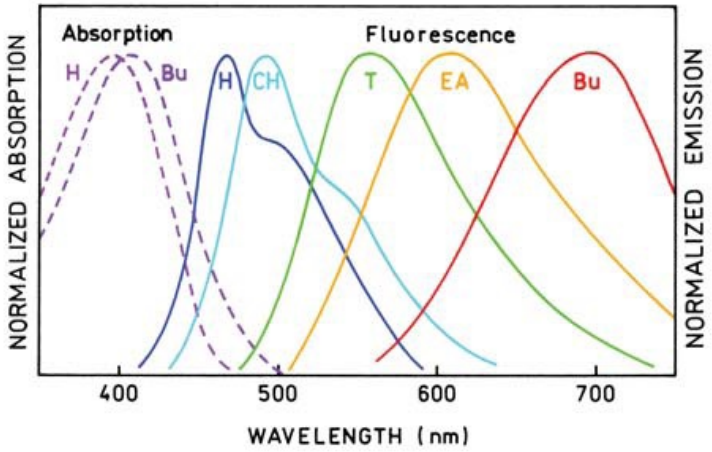


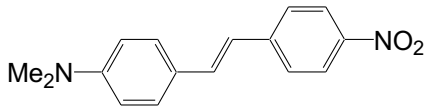
94 Solvents have been tested, showing ratios from 0.41 to 1.95. *Can. J. Chem.* 62, **1984**

Solvent Polarity Probe

Solvent Polarity: The emission wavelength generally increases with solvent polarity.

Solvent Reorganization: The energy of S_1 after solvent reorganization generally decrease with solvent polarity.





H = Hexane

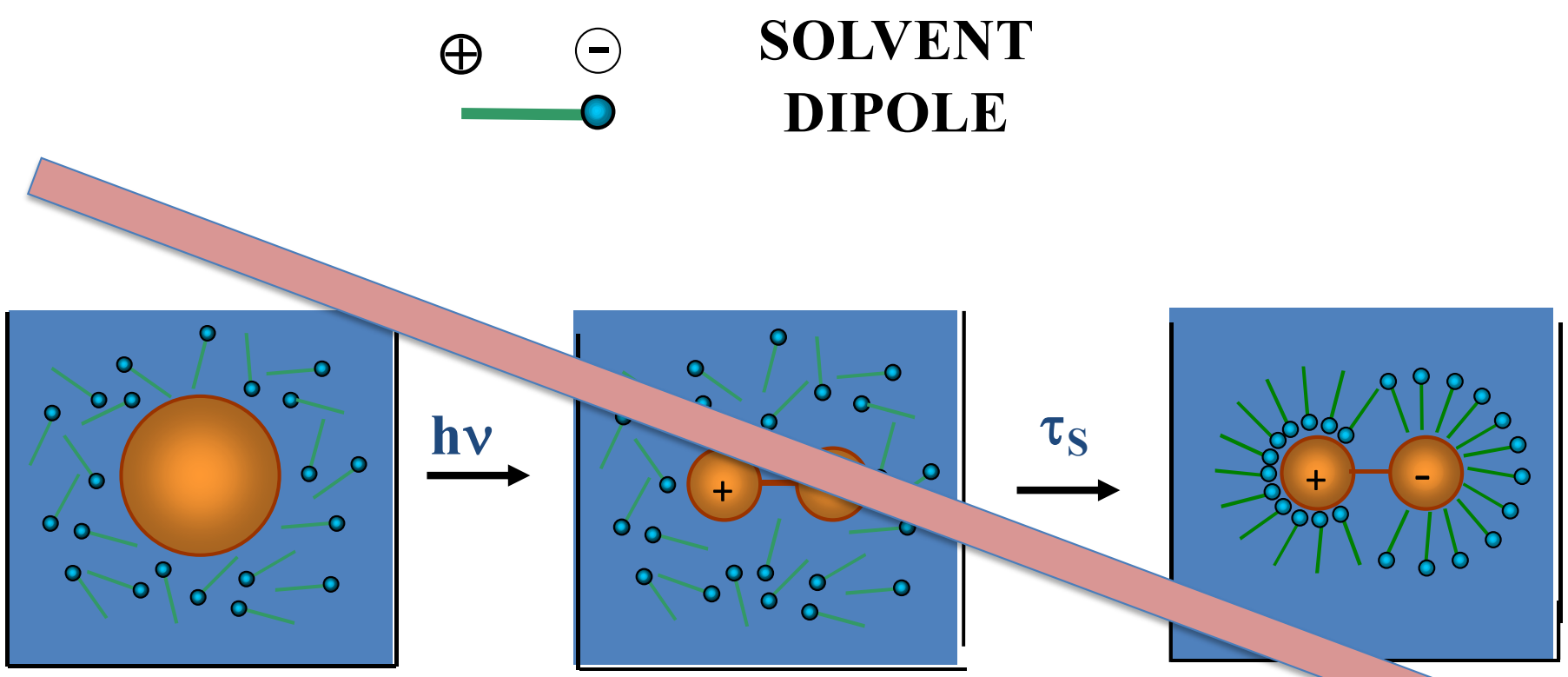
CH = Cyclohexane

T = Toluene

EA = Ethyl acetate

Bu = Butanol

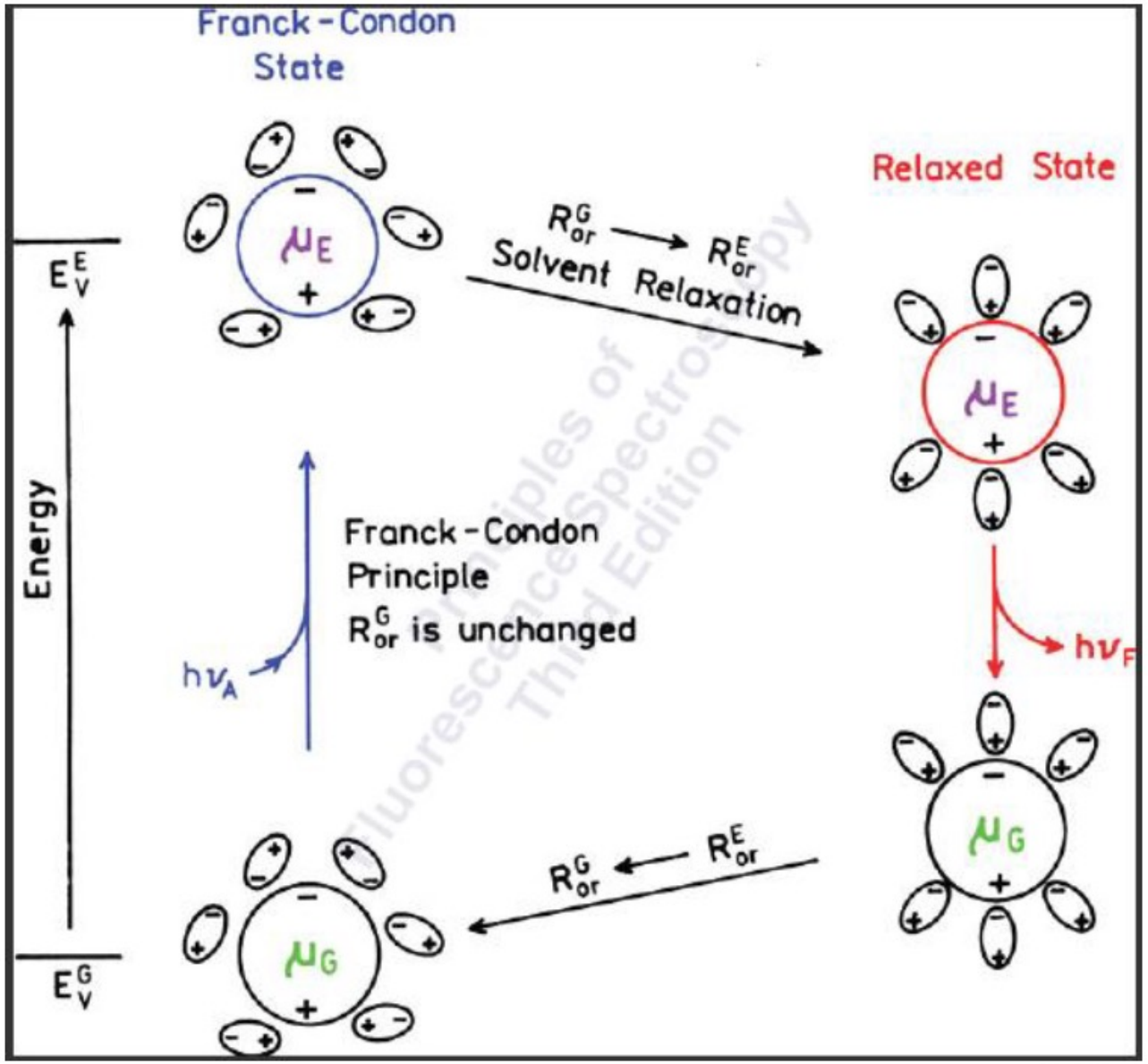
Solvation Dynamics



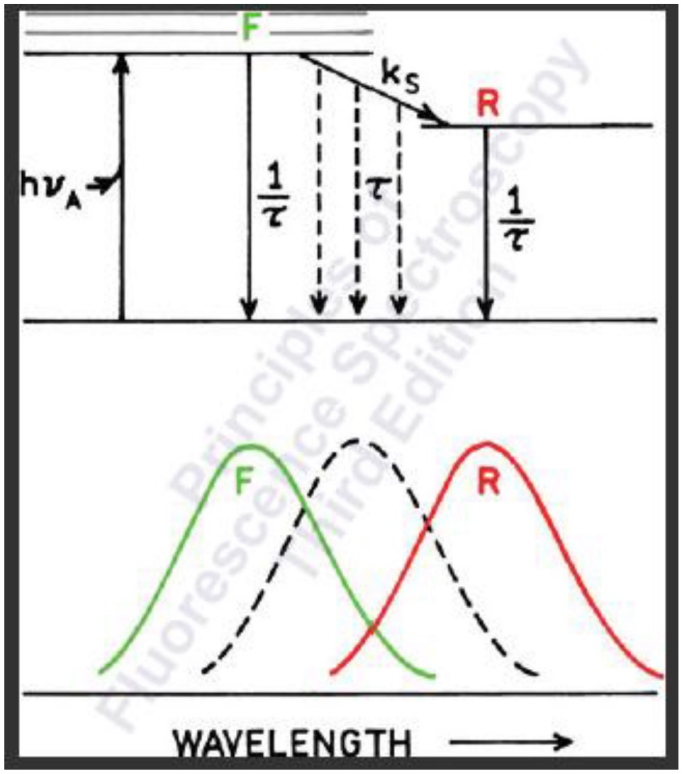
NONPOLAR SOLUTE
RANDOM SOLVENT

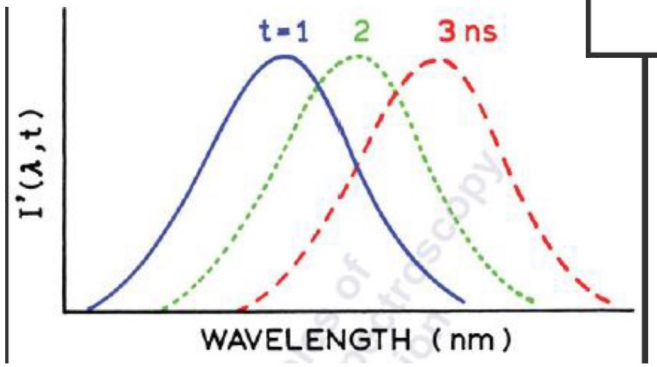
UNSOLVATED
HIGH ENERGY

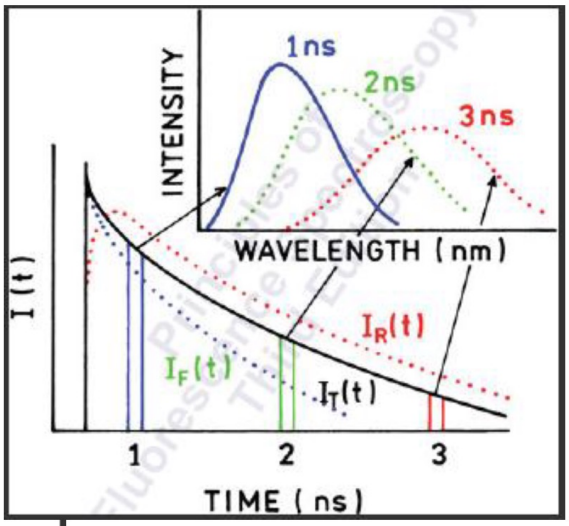
SOLVATED
LOW ENERGY

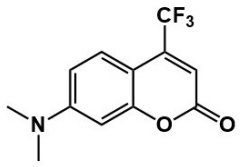

Franck - Condon
State
Relaxed State
R^G_{or} → R^E_{or}
Solvent Relaxation
μ_E
E^E_V
Energy
Franck - Condon
Principle
R^G_{or} is unchanged
$h\nu_A$
$h\nu_F$
μ_G
R^G_{or} ← R^E_{or}
E^G_V

Dynamic Stokes shift

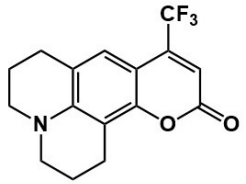




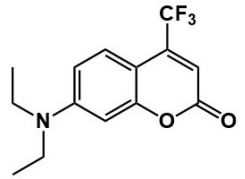




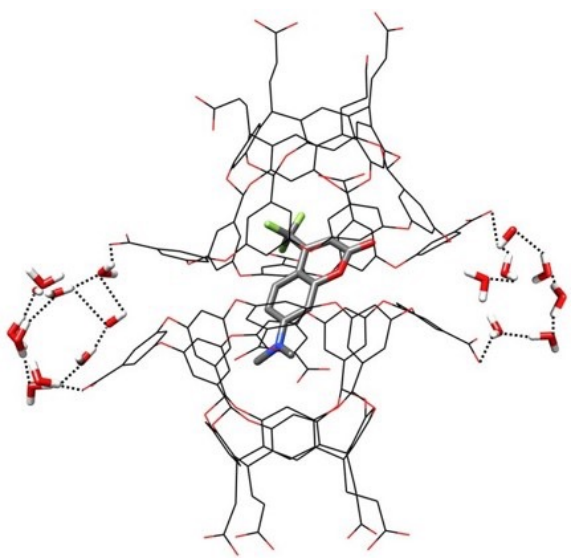
1 (C-152)

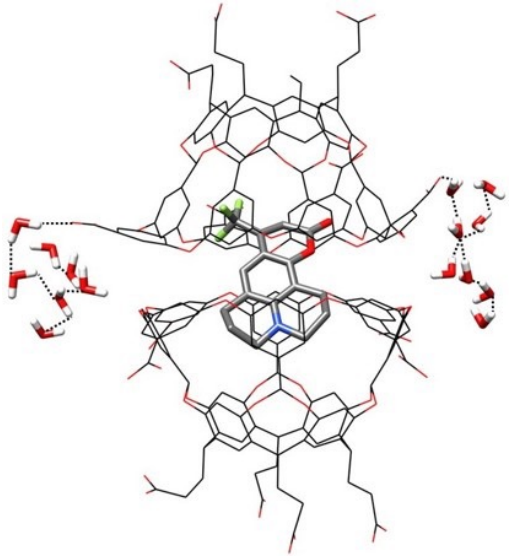


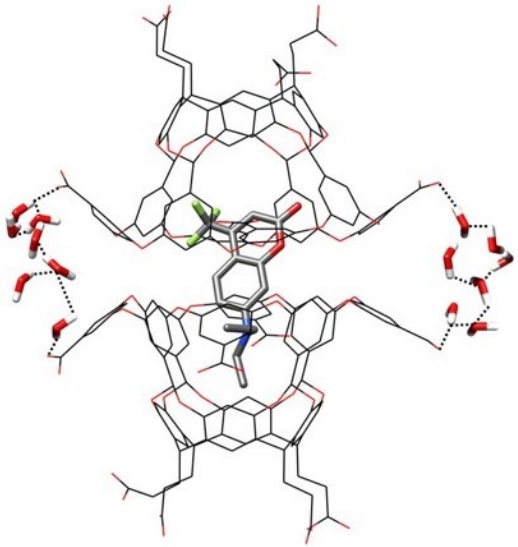
2 (C-153)

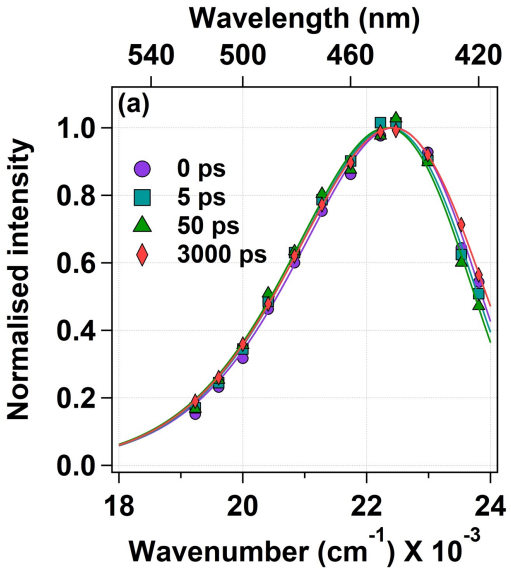


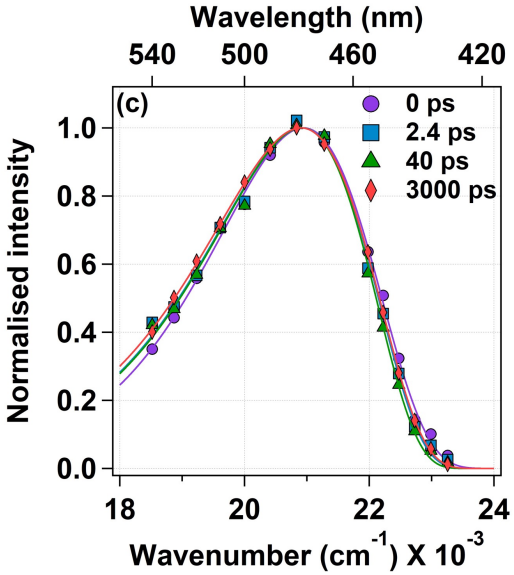
3 (C-152A)

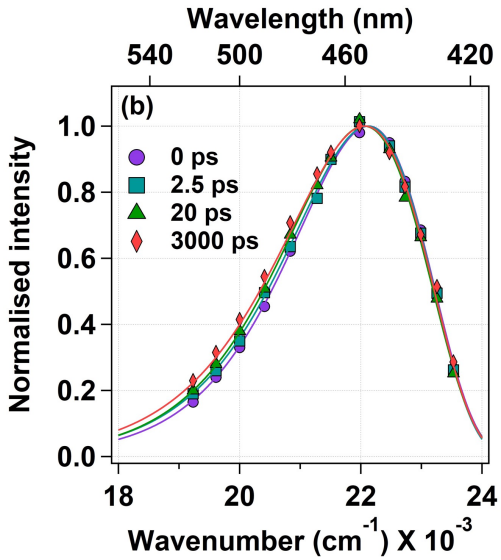


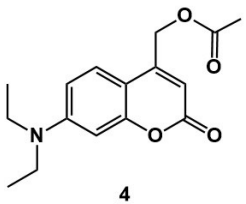




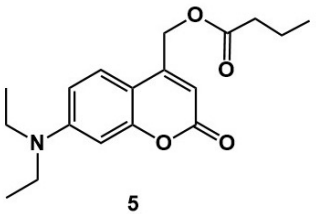




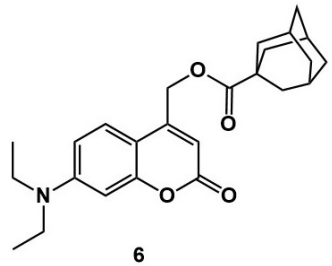



O
O
N
O
O

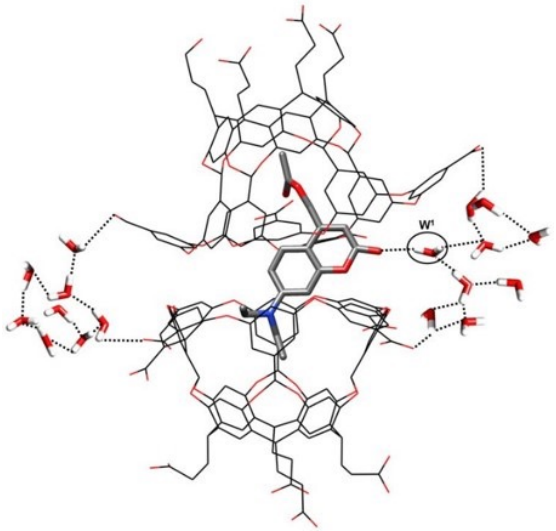
4

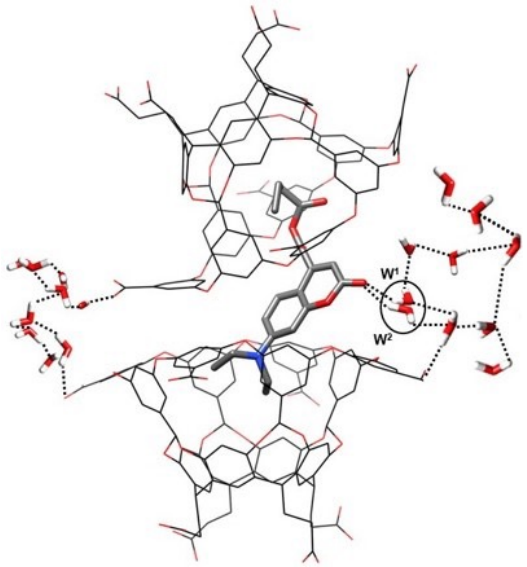

O
O
N
O
O

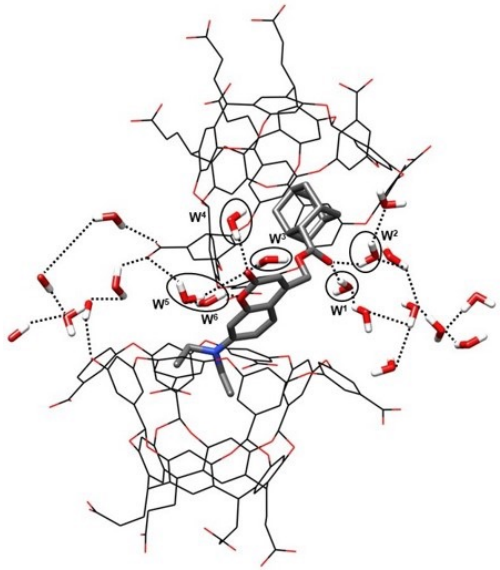
5

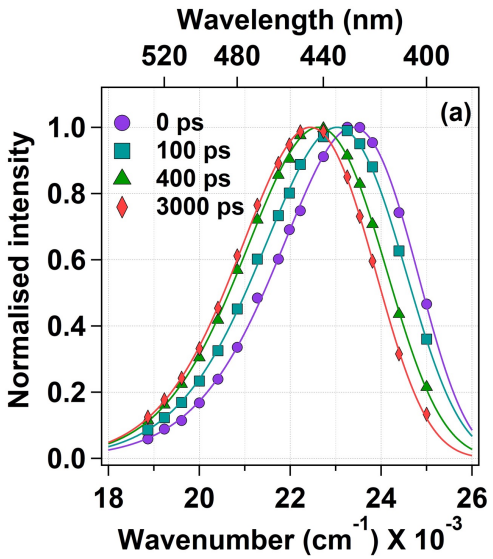

O
O
N
O
O

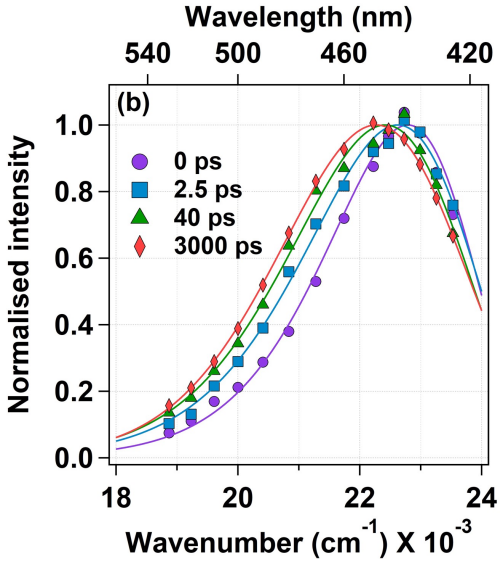
6

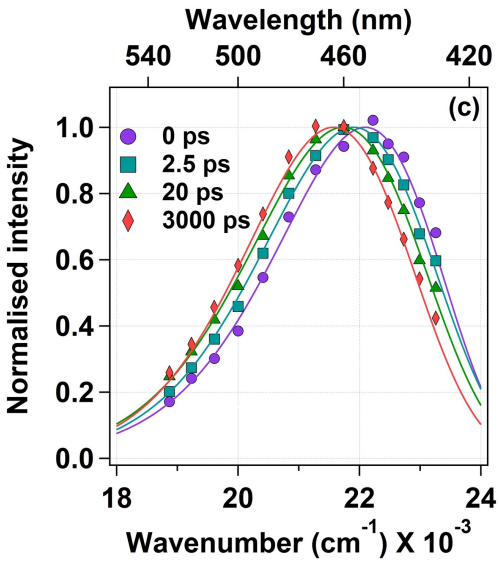

W1


W1
W2


W4
W3
W2
W5
W6
W1

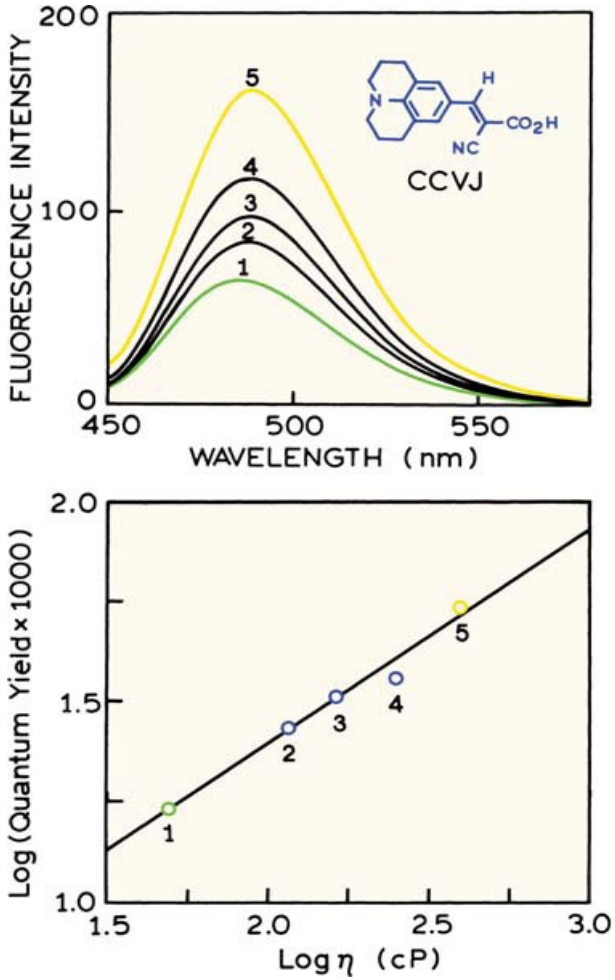

Wavelength (nm)
520
480
440
400
(a)
0 ps
100 ps
400 ps
3000 ps
Normalised intensity
1.0
0.8
0.6
0.4
0.2
0.0
18
20
22
24
26
Wavenumber (cm-1) X 10-3


Wavelength (nm)
540
500
460
420
(b)
0 ps
2.5 ps
40 ps
3000 ps
Normalised intensity
1.0
0.8
0.6
0.4
0.2
0.0
18
20
22
24
Wavenumber (cm-1) X 10-3

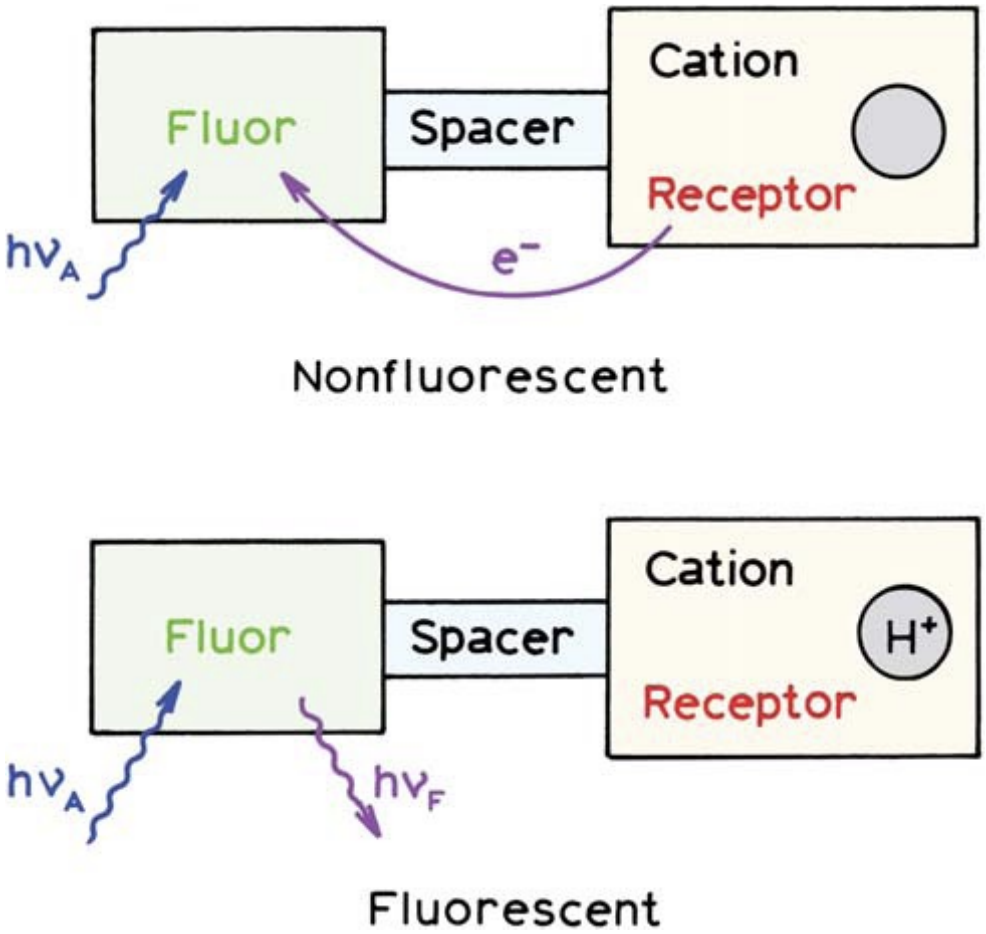

Wavelength (nm)
540
500
460
420
(c)
0 ps
2.5 ps
20 ps
3000 ps
Normalised intensity
1.0
0.8
0.6
0.4
0.2
0.0
18
20
22
24
Wavenumber (cm-1) X 10-3

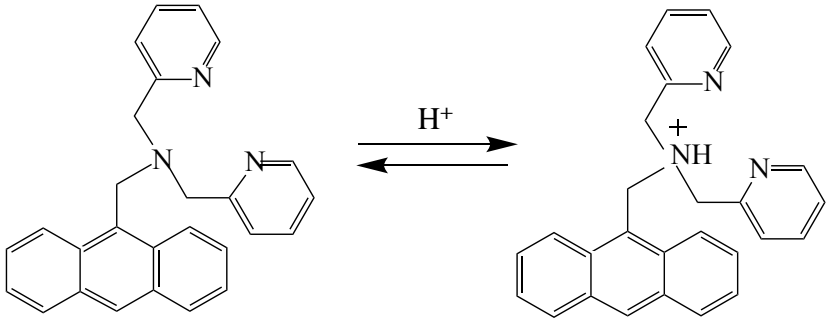
Viscosity Probes

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



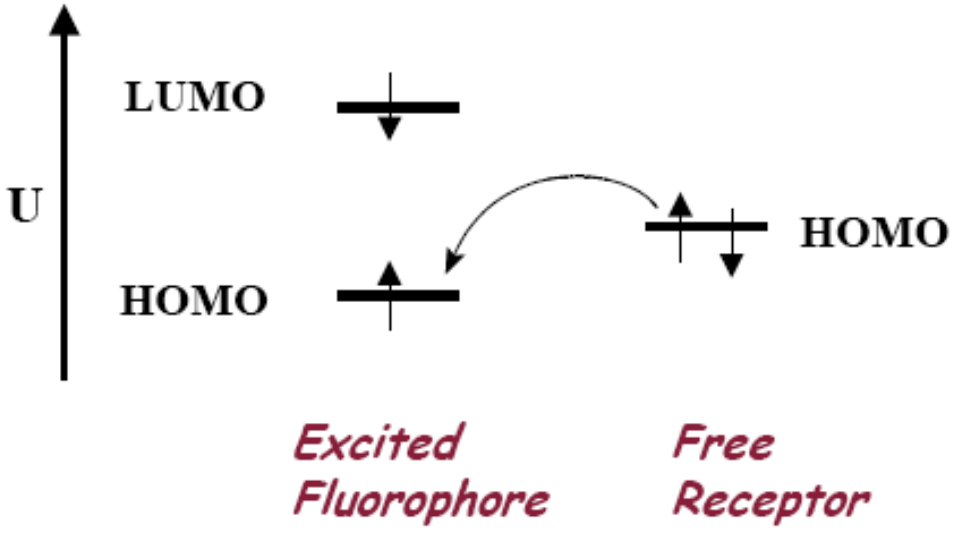
Supramolecular Sensors: Proton

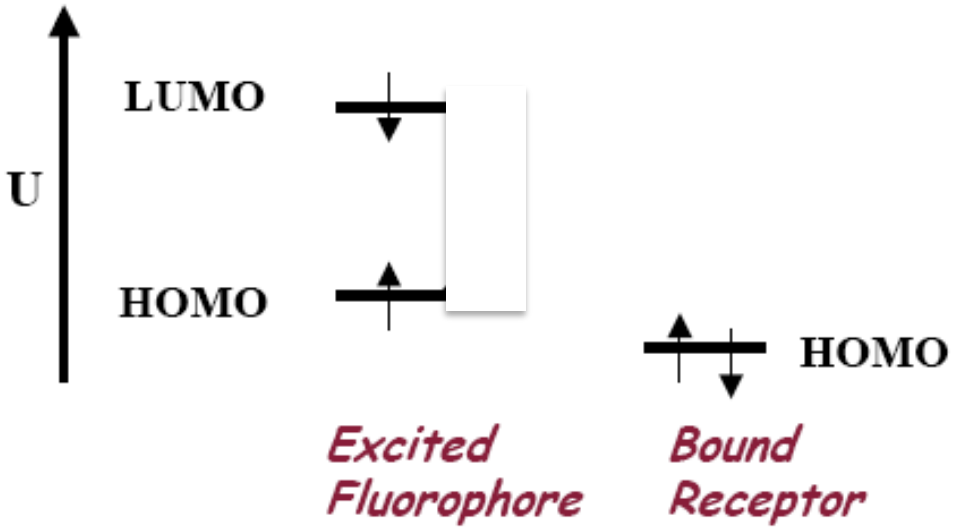


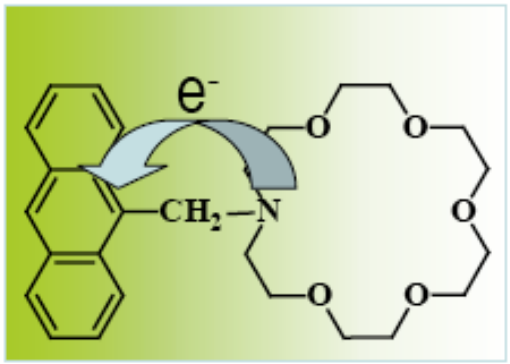


Non Fluorescent **Fluorescent**

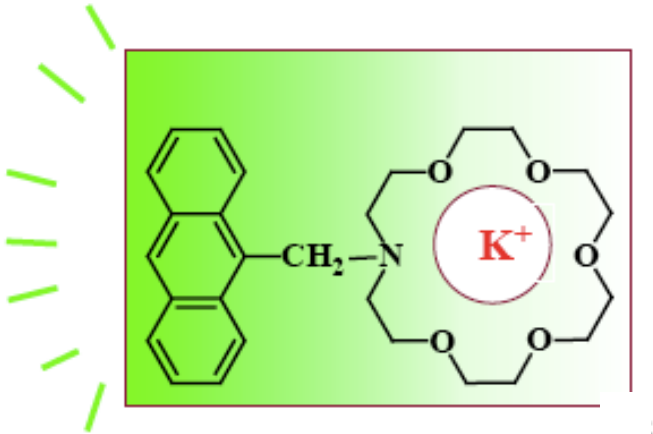
Mechanism of PET Signaling





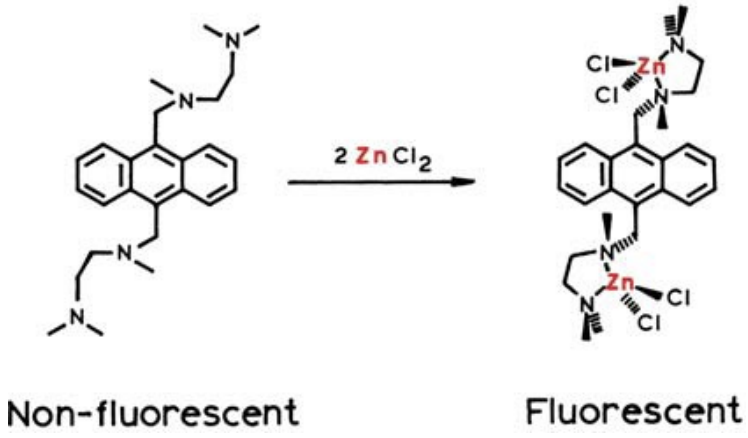


nonfluorescent

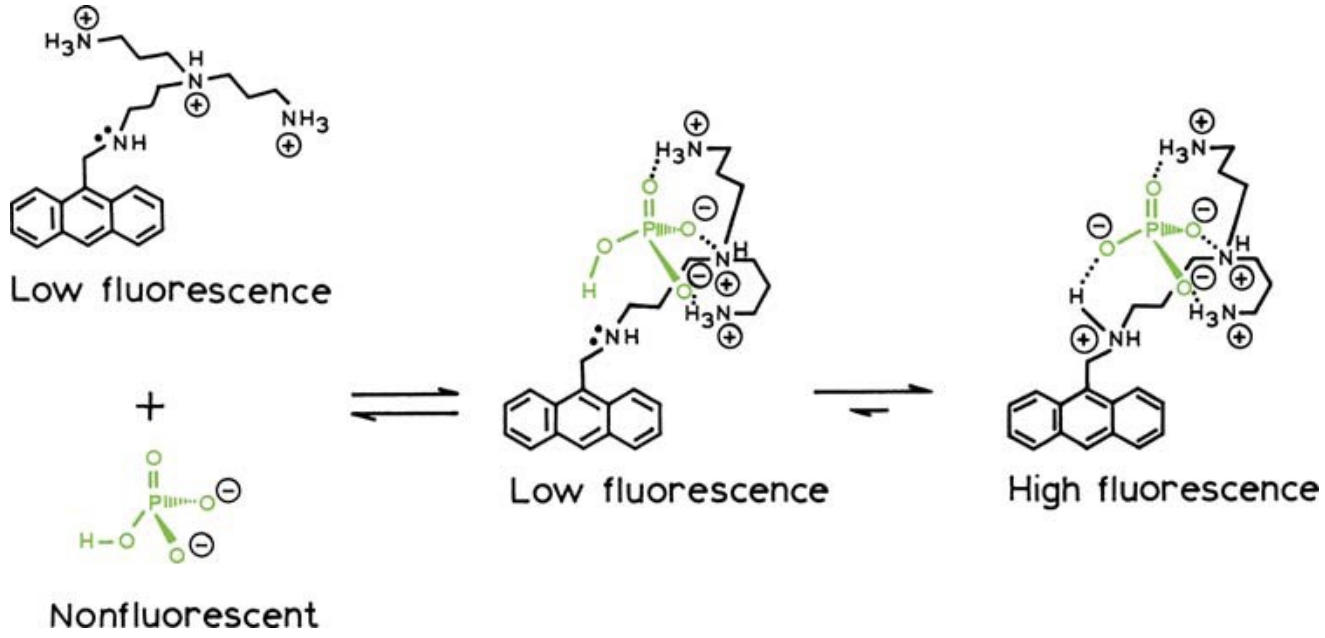


fluorescent

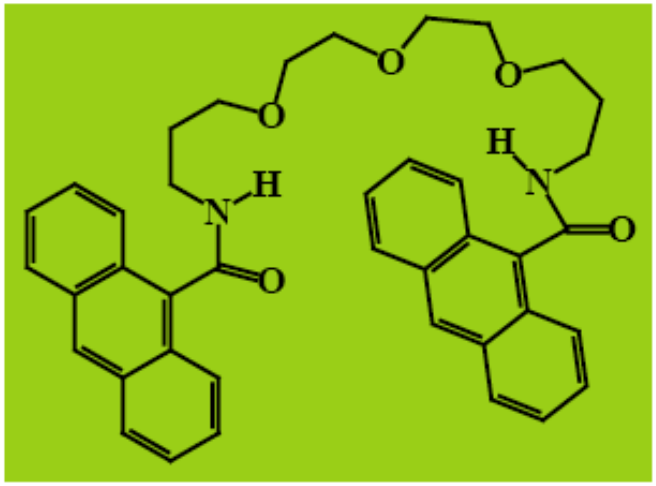
Metal ion sensing

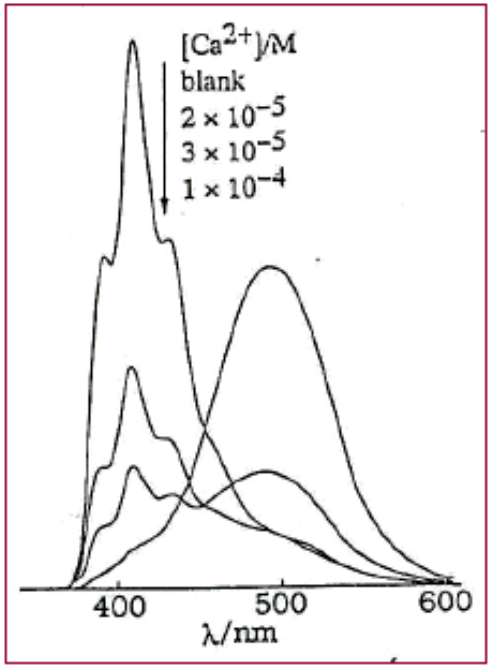


Anion sensing



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



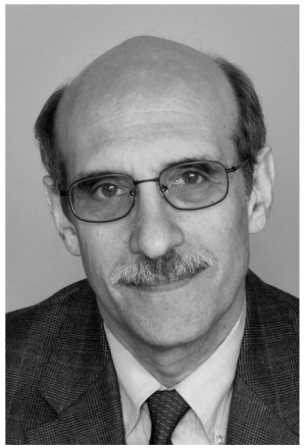


Nakamura *et al. J. Phys. Chem. B*, 2001, *105*, 2923

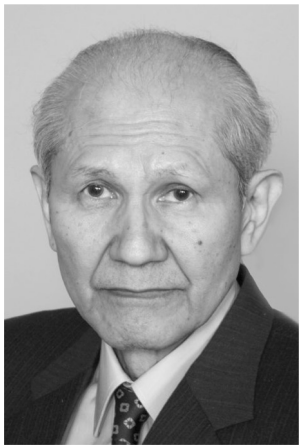
- ***A fluorescent host with anthracene moiety at each end of a linear polyether chain***
- ***Upon addition of Ca^{2+} fluorescence spectrum changes from monomer emission to excimer emission***

Chalfie, Shimomura and Tsien

The Nobel Prize in Chemistry 2008 was awarded for the discovery and development of the



Martin Chalfie
Columbia University



Osamu Shimomura
Marine Biological Laboratory
and Boston University Medical School

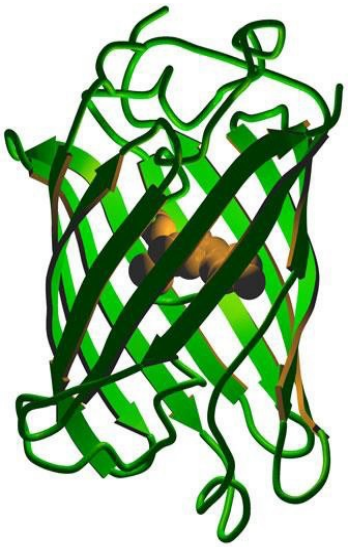
Roger Y. Tsien
University of California,
San Diego

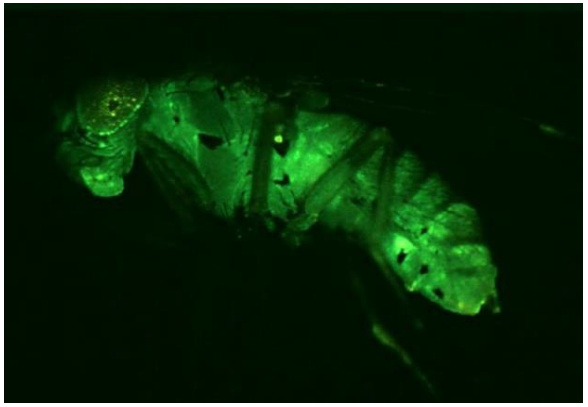
The Nobel Prize in Chemistry 2008
www.nobelprize.org

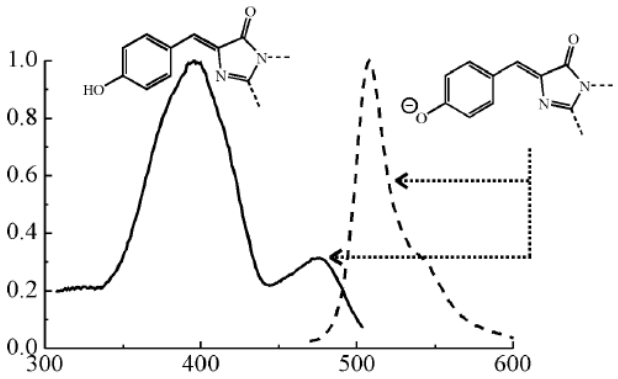
Fluorescent Protiens

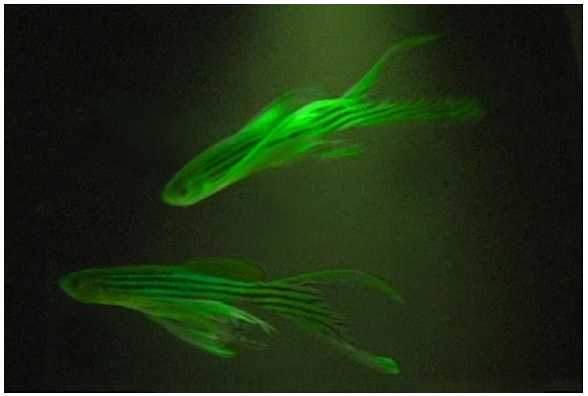
- Green fluorescent proteins can be expressed in living organisms

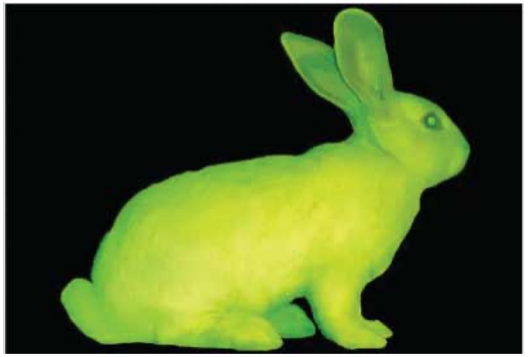
GFP











Rabbit expressing GFP

Modifications of Green Fluorescent Protein

Mutants = Mutations in the amino acid sequence can be exploited to regulate the absorption and emission properties of the chromophore