Molecular and Supramolecular Photochemistry

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Fundamental Research:
The presentations/reports are **not "subject"** to the EAR – Fundamental Research as per EAR Part 734.8 (a) and (c).

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CHM 535/635
Molecular and Supramolecular Photochemistry

Absorption and Emission
Radiative Transitions

Chapters 3 & 4
Principles of Molecular Photochemistry: An Introduction
NJT, VR and JCS

2

Manifestations of Light-Matter Interactions

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

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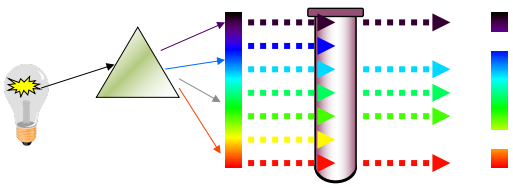
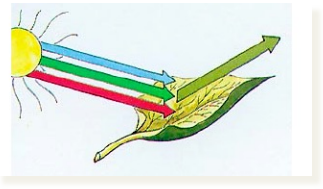
Reflection and Absorption

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.

Red light is absorbed by the chlorophylls, blue light is absorbed mostly by the carotenoids.

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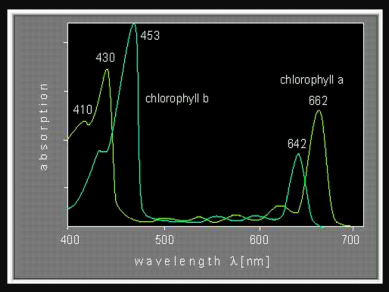
Why are most plants green?

Chlorophyll absorbs in the **red** and **blue**, and hence reflects in the **green**.



Colocasia Esculenta "Black Magic"

It would seem that leaves should be **black** in order to more efficiently absorb all of the sun's light spectrum.

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Light-Matter (Electron) Interaction

Matter → Materials → Molecules → Atoms → Nuclei & Electrons

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 and then introduced step by step.
- The molecule could be built by assuming there are no interactions between electronic, vibrational and spin motions of electrons and nuclei (Born-Oppenheimer approximation).
- Molecules remain stationary at equilibrium position.

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The Basic Laws of Photochemistry

Grotthuss-Draper law

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

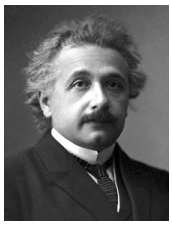
Grotthus

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

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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).

R* —— Ψ_2

$$\Delta E = E_1 - E_2 = h\nu$$

$$\nu = (E_1 - E_2)/h$$

R —— Ψ_1

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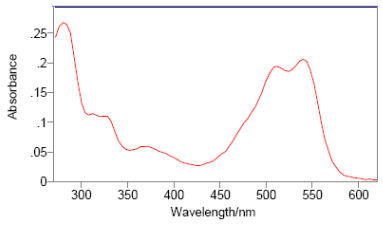
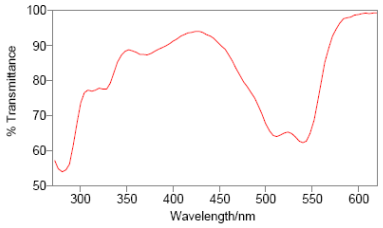
ABSORPTION & TRANSMISSION SPECTRA

•Absorption spectrum of a red textile



•Transmission spectrum of the same



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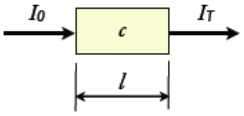
Absorption

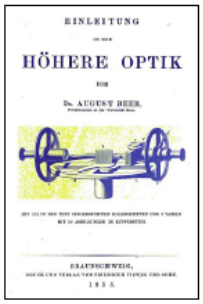
Beer-Lambert Law



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

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



August Beer
(1825-1863)

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

OD can be adjusted with concentration

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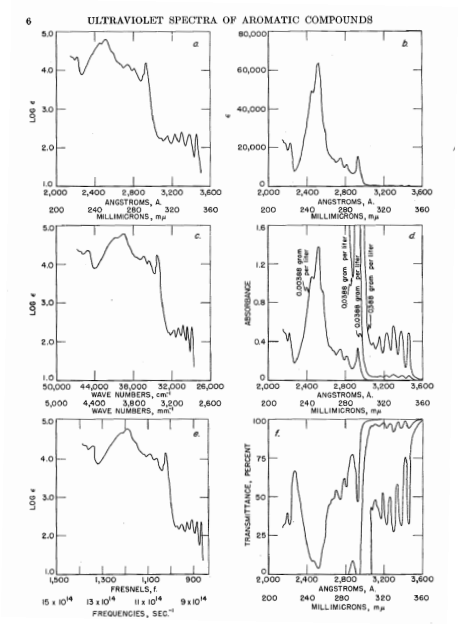
Be Watchful of the Units Used



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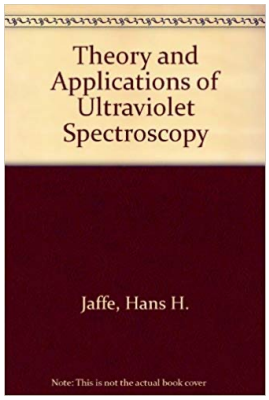
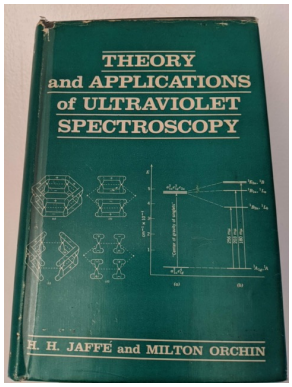
Electronic Spectra





Theory and Applications of Ultraviolet Spectroscopy, 1962
by Hans H. Jaffe and Milton Orchin

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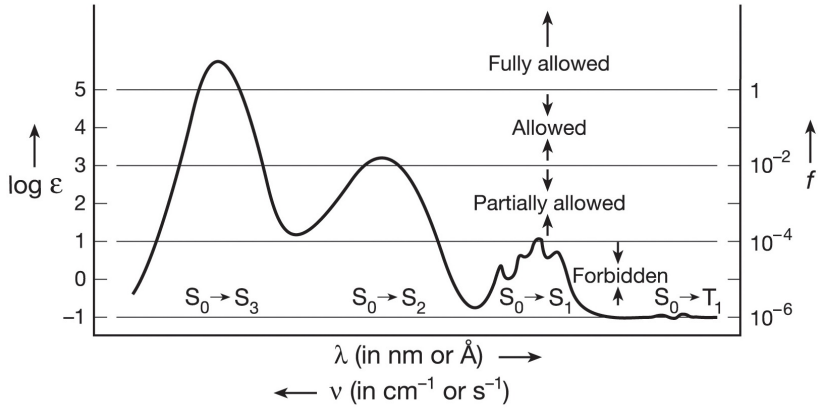
Absorption Spectra: Why the ε and *f* vary with the band?



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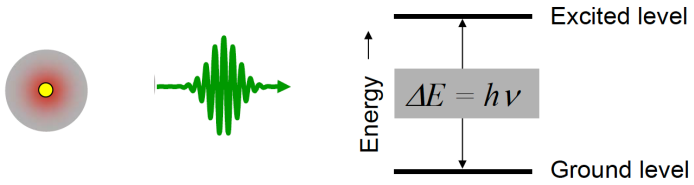
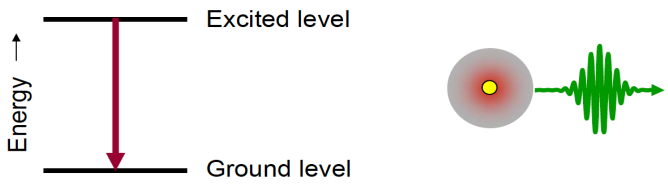
Rules for absorption and emission are the same

Absorption



Emission



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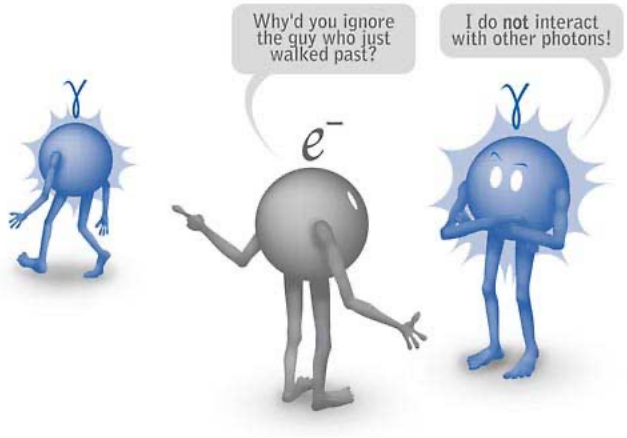
Interaction Between Photon and Electron



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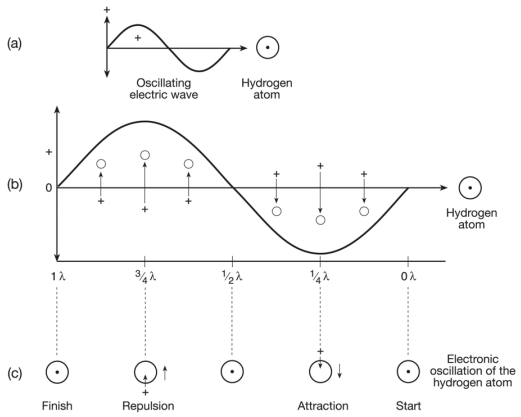
Light as an oscillating electric field



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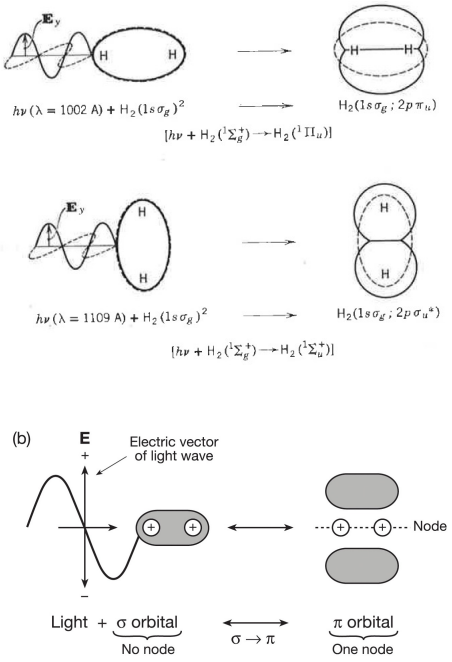

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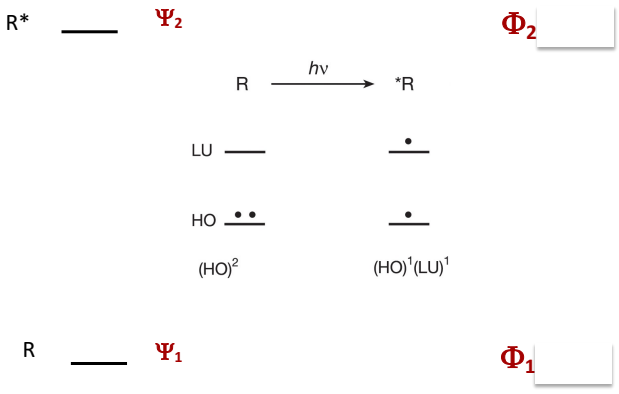
Electronic structures for various states are generated assuming the molecule is stationary and it is in its lowest energy state



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

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Oscillator Strength-Absorption

$\Psi_1 | P_{1\rightarrow 2} | \Psi_2$ **Φ. χ. *S***

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

A perfectly allowed transition has $f = 1$

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

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

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Probability of light absorption and emission
Fermi's Golden Rule

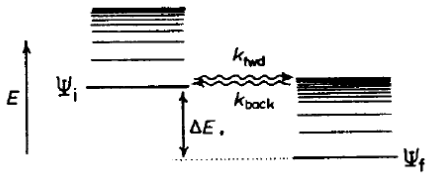
Enrico Fermi
Nobel Prize, 1938

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

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

$$\rho \, 2\pi \frac{\langle \Psi_1(R) \, | \, P_{h\nu} \, | \, \Psi_2({}^*R) \rangle^2}{\hbar}$$

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



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Fermi's Golden Rule

Bohr model couldn't predict why one spectral line is brighter than another.

A transition rate depends upon the strength of the coupling between the initial and final state of a system and upon the number of ways the transition can happen (i.e., the density of the final states).

$$\lambda_{if} = \frac{2\pi}{\hbar}\left|M_{if}\right|^2 \rho_f$$

Fermi's Golden Rule

Transition probability — *Matrix element for the interaction* — *Density of final states*

Enrico Fermi
Nobel Prize, 1938

The transition probability λ applies to both absorption and emission. The general form of Fermi's golden rule apply to atomic transitions, nuclear decay, scattering ... a large variety of physical transitions such as energy and electron transfer.

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Electronic transitions: Overlap and symmetry of orbitals involved

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

(1) *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* 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.

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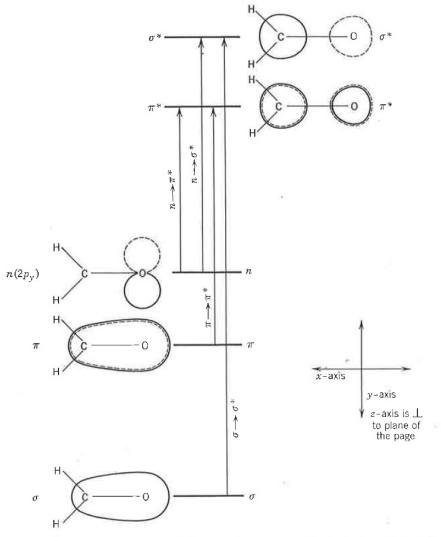
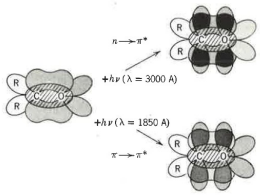
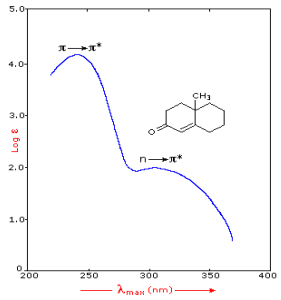
Electronic factor - Orbital overlap



No orbital overlap n and π*



Orbital overlap π and π*



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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*

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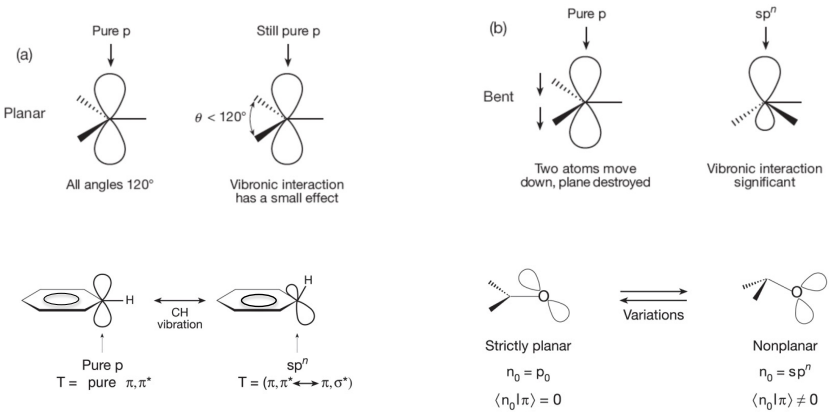
Zero Order to First Order Through Vibronic Coupling



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*')

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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:

Mixing coefficient

first order n, π* → $\psi(S_1) = \psi(n, \pi^*) + \lambda\psi(\pi, \pi^*)$

zero order n, π* zero order π, π*

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

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

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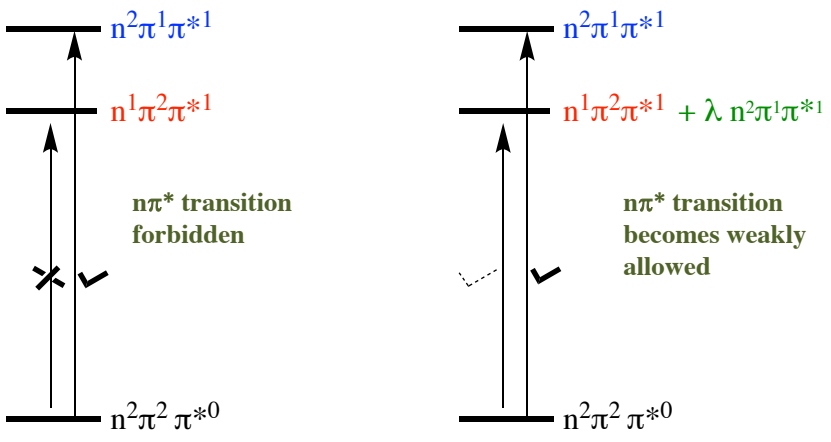
Result of vibrational – electronic mixing (vibronic coupling)



As per Bonn-Oppenheimer approximation

Vibration mixes the states, no longer pure states

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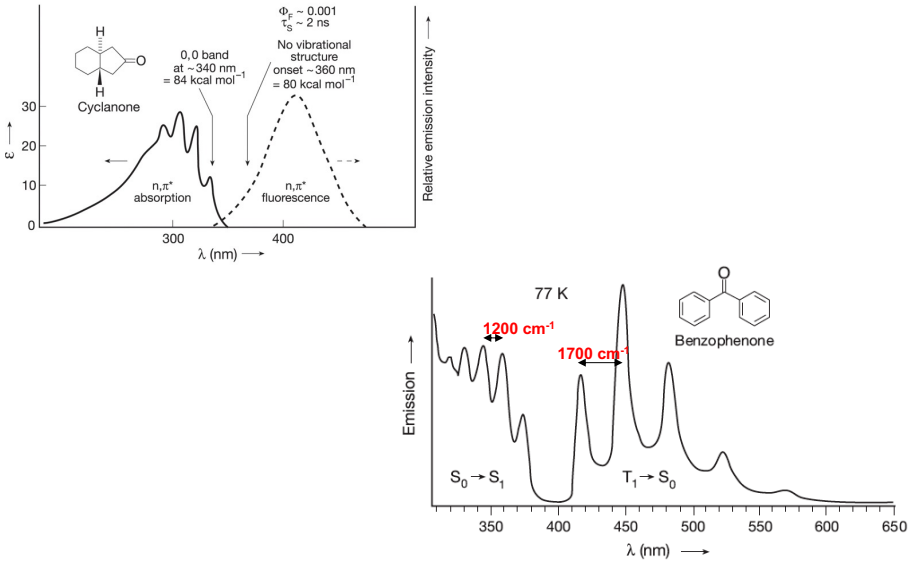
Absorption and emission spectra
Vibrational structure due to vibrational mixing



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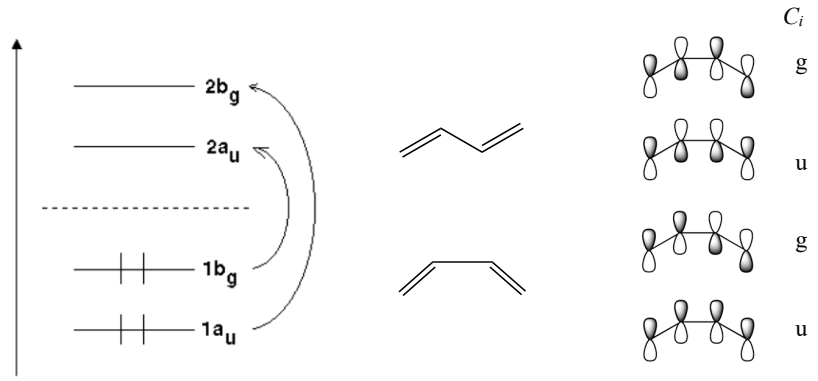
Symmetry based selection rules



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)

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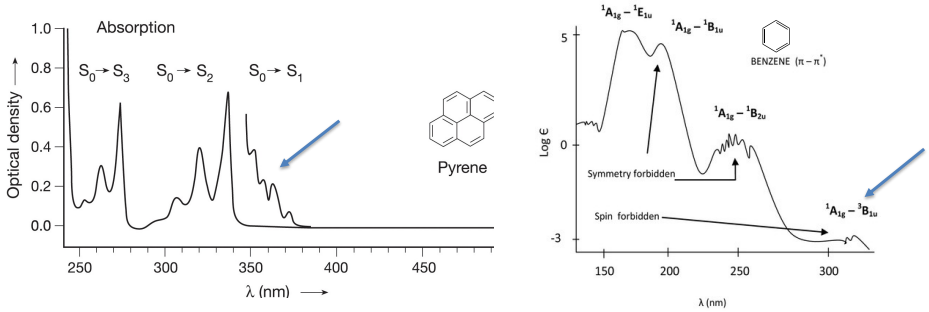
Selection Rules (Electronic part)



Orbital Symmetry (ππ*, 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.

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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

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

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

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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

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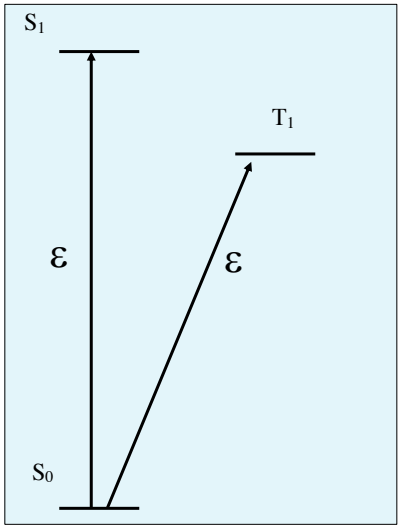
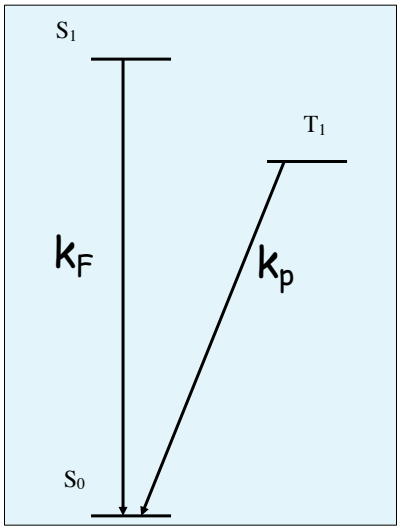
Same Rules for Excitation & De-excitation





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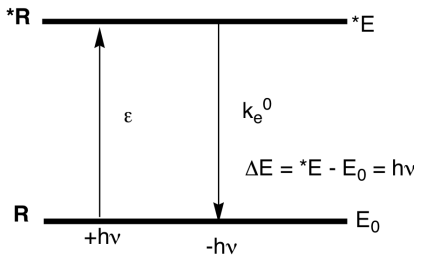

$k_e(s^{-1})$	Example	Transition type	ε_{max}	f
10^9	*p*-Terphenyl	$S_1(\pi,\pi^*) \rightarrow S_0$	3×10^4	1
10^8	Perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	4×10^4	10^{-1}
10^7	1,4-Dimethyl-benzene	$S_1(\pi,\pi^*) \rightarrow S_0$	7×10^2	10^{-2}
10^6	Pyrene	$S_1(\pi,\pi^*) \rightarrow S_0$	5×10^2	10^{-3}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

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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

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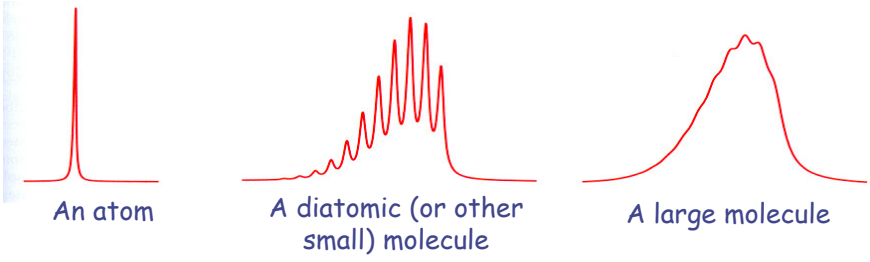
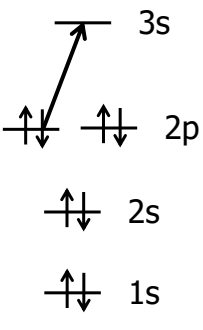
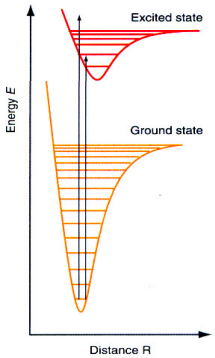
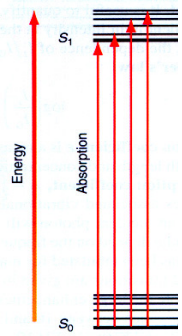
Electronic spectra of larger molecules









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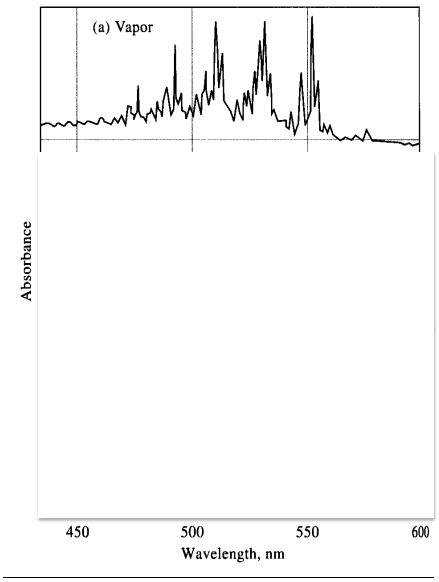
Shapes of Absorption Spectra: medium dependent



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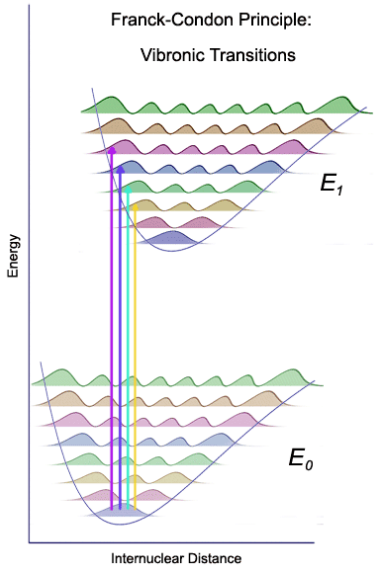
Franck-Condon principle and vertical transitions



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.

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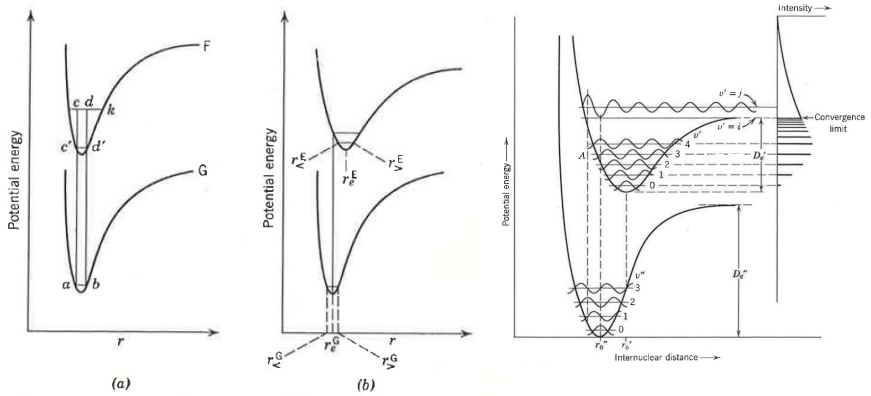

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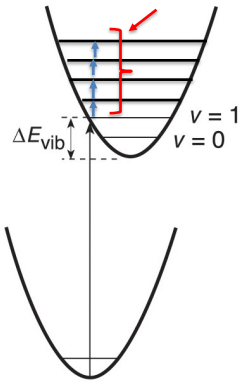
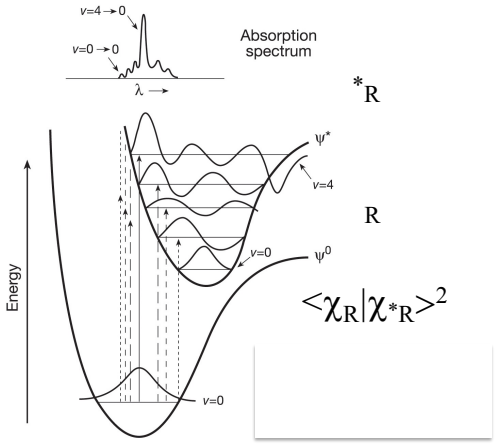
Franck-Condon principle

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

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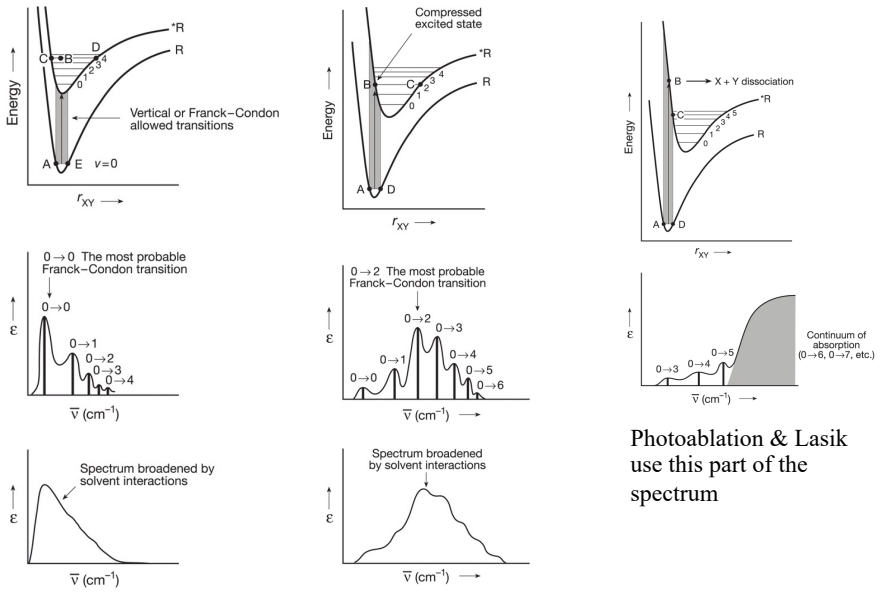
Franck-Condon Principle

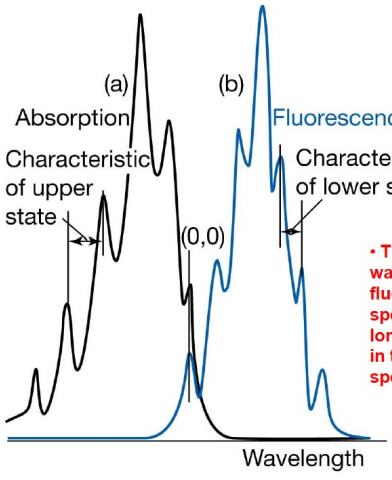


Photoablation & Lasik use this part of the spectrum

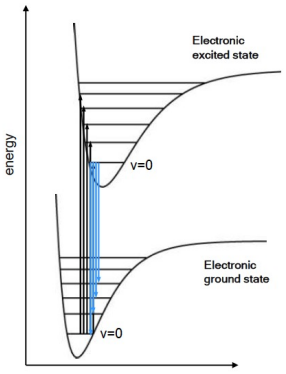
41

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.

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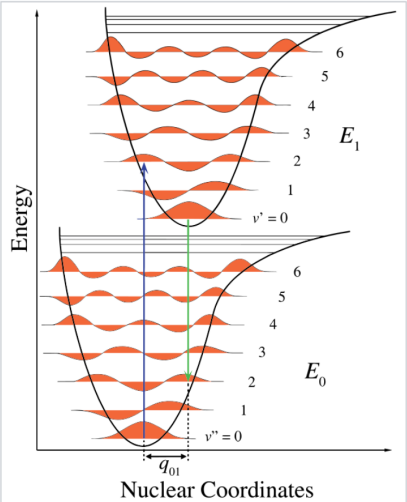
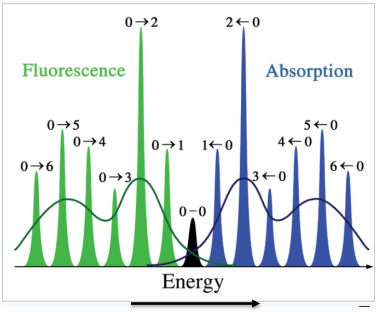
Absorption and Emission Spectra

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





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

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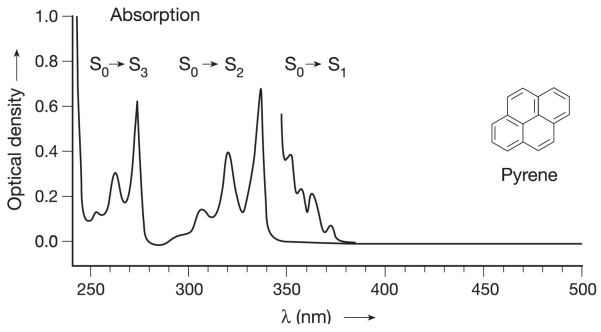
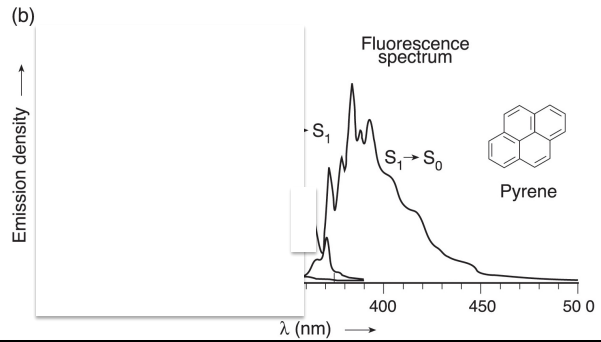
Absorption

Emission

Excitation





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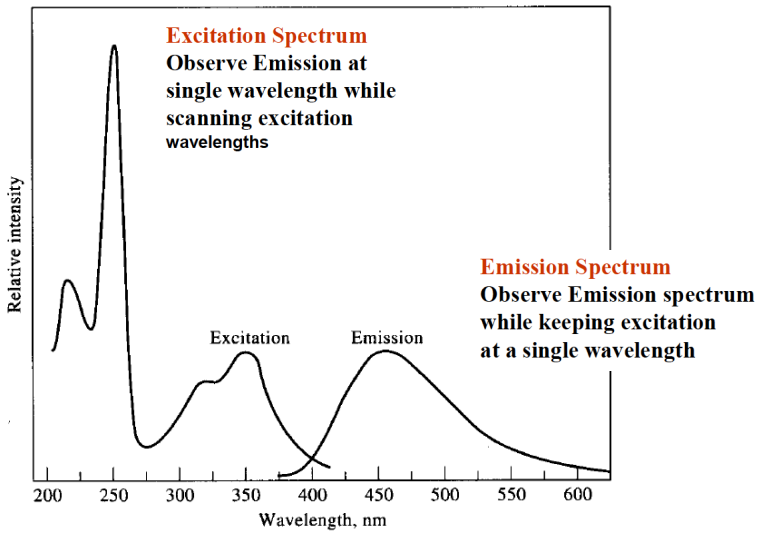
Emission and Excitation spectra



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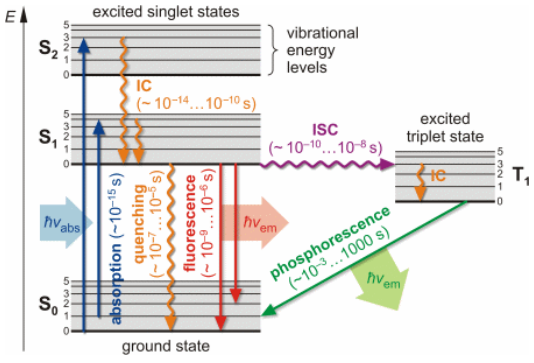
Vavilov's rule

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



S. Vavilov

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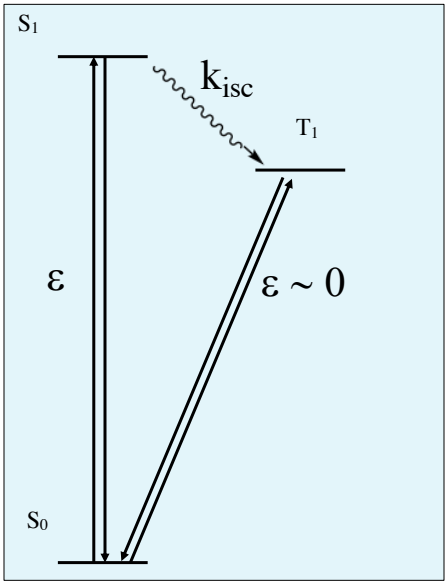
Singlet–Triplet Crossing and Phosphorescence



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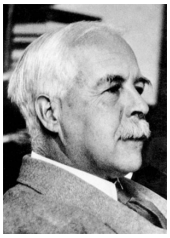
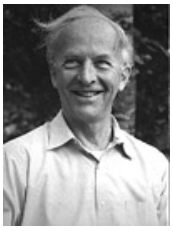
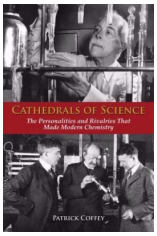
Triplet State and Phosphorescence



G. N. Lewis



Kasha



S. Vavilov

A. Terenin

Porter

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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

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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)

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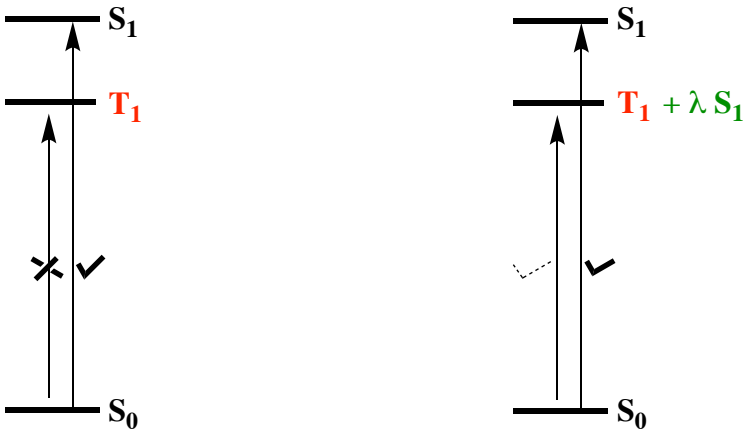
Singlet-Triplet Transitions
Role of Spin-Orbit Coupling



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

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$$\underbrace{k_{obs}}_{\text{Observed Rate Constant}} = \underbrace{k^0_{max}}_{\text{Zero-point Motion-Limited Rate Constant}} \times \underbrace{f_e \times f_v \times f_S}_{\text{"Fully Allowed Rate"}} \quad (3.7)$$

Prohibition to maximal caused by "selection rules"

Prohibition factors due to changes in electronic, nuclear, or spin configuration

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

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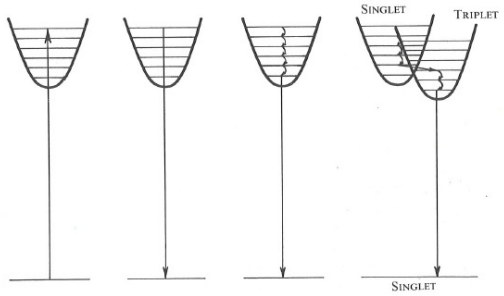
Absorption and Emission



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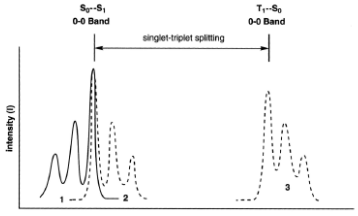
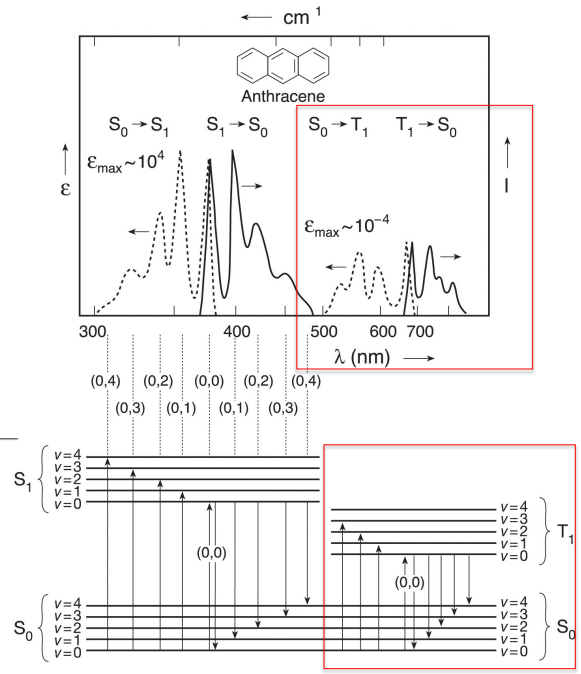
Phosphorescence





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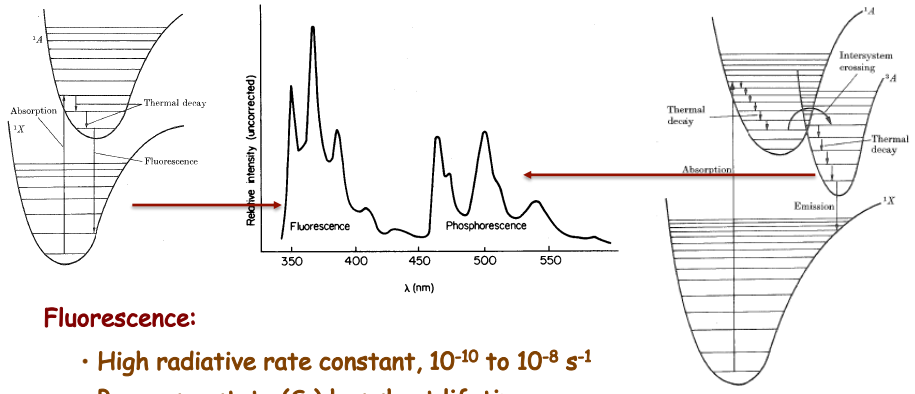

Fluorescence:

- 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

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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

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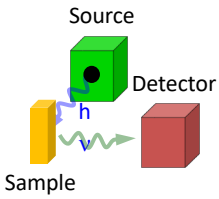
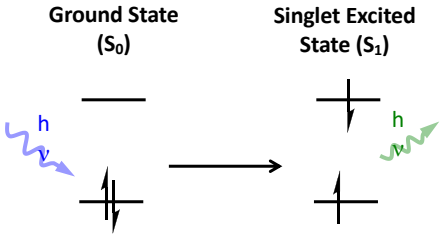
Emission Quantum Yield



Emission Quantum Yield (Φ)

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



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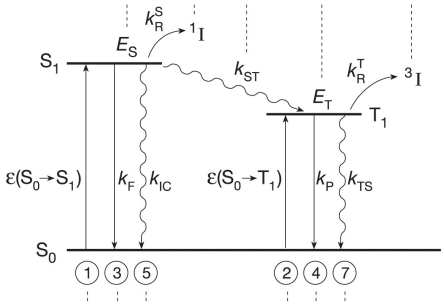
Competition with fluorescence

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

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

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

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



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

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

Lifetime

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

Radiative lifetime

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Quantum Yields of Fluorescence

$$\Phi_F = k_f(k_f + \Sigma k_i)^{-1}$$

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

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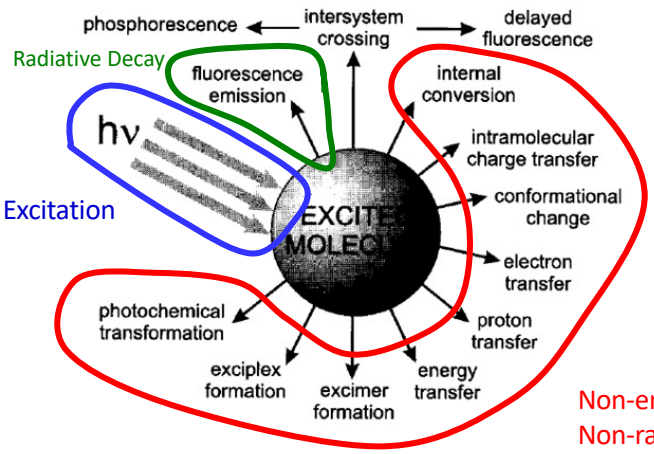
Excited State Decay



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

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Emission Quantum Yield

Table 2.4. Quantum Yield Standards

Compound	Solvent	λ_{ex} (nm)	°C	Q
Quinine sulfate	0.1 M H_2SO_4	350	22	0.577
		366	–	0.53 ± 0.023
β-Carboline[a]	1 N H_2SO_4	350	25	0.60
Fluorescein	0.1 M NaOH	496	22	0.95 ± 0.03
9,10-DPA[b]	cyclohexane	–	–	0.95
9,10-DPA	"	366	–	1.00 ± 0.05
POPOP[c]	cyclohexane	–	–	0.97
2-Aminopyridine	0.1 N H_2SO_4	285	–	0.60 ± 0.05
Tryptophan	water	280	–	0.13 ± 0.01
Tyrosine	water	275	23	0.14 ± 0.01
Phenylalanine	water	260	23	0.024
Phenol	water	275	23	0.14 ± 0.01
Rhodamine 6G	ethanol	488	–	0.94
Rhodamine 101	ethanol	450–465	25	1.0
Cresyl Violet	methanol	540–640	22	0.54

[a]β-carboline is 9H-pyrido[3,4-β]-indole.
[b]9,10-DPA, 9,10-diphenylanthracene.
[c]POPOP, 2,2'-(1,4-phenylene)bis[5-phenyloxazole].

$$\Phi = \frac{\text{\# of photons emitted}}{\text{\# of photons absorbed}} = \text{ 0 to 1}$$

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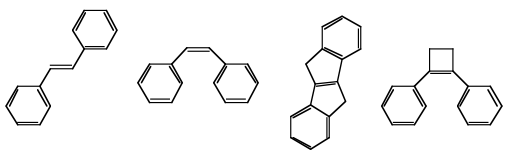
Factors Controlling Quantum Yield of Fluorescence
Rigid *vs* non-rigid molecules

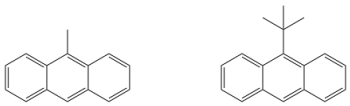
Bond rotation



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

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Ermolaev's rule

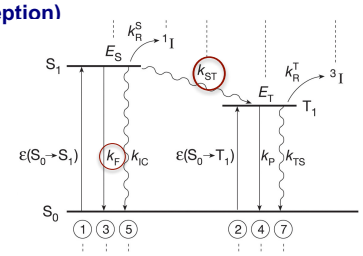
For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., internal conversion is very small with respect to the other two.

Valerii L. Ermolaev

Table 4.2 *Quantum yields for fluorescence* ($S_1 \rightarrow S_0 + h\nu$) *and intersystem crossing* ($S_1 \rightsquigarrow T_1$) *for some aromatic hydrocarbons in ethanol solution (Data from Birks, J. B. (ed.) (1975). Organic molecular photophysics, Vol. 2, Tables 2.6 and 3.4. Wiley, London)*

Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{ISC}$
Benzene	0.04	0.15	0.19
Naphthalene	0.80	0.21	1.01
Fluorene	0.32	0.68	1.00
Anthracene	0.72	0.32	1.02
Tetracene	0.66	0.16	0.82
Phenanthrene	0.85	0.13	0.98
Pyrene	0.38	0.65	1.03
Chrysene	0.85	0.17	1.03

(exception)



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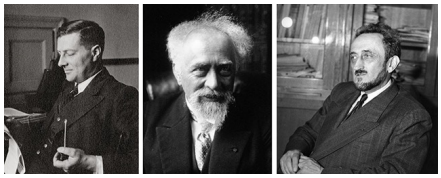
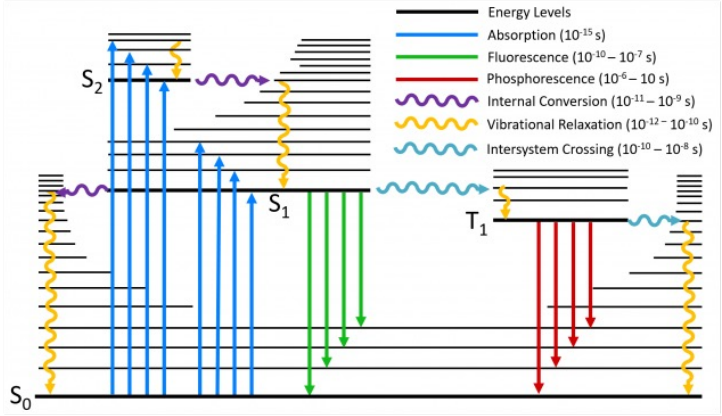
Perrin-Jablonski Diagram

A. Jablonski (1898-1980)



F. Perrin (1901-1992)

J. Perrin 1870-1942
Nobel Prize, 1926



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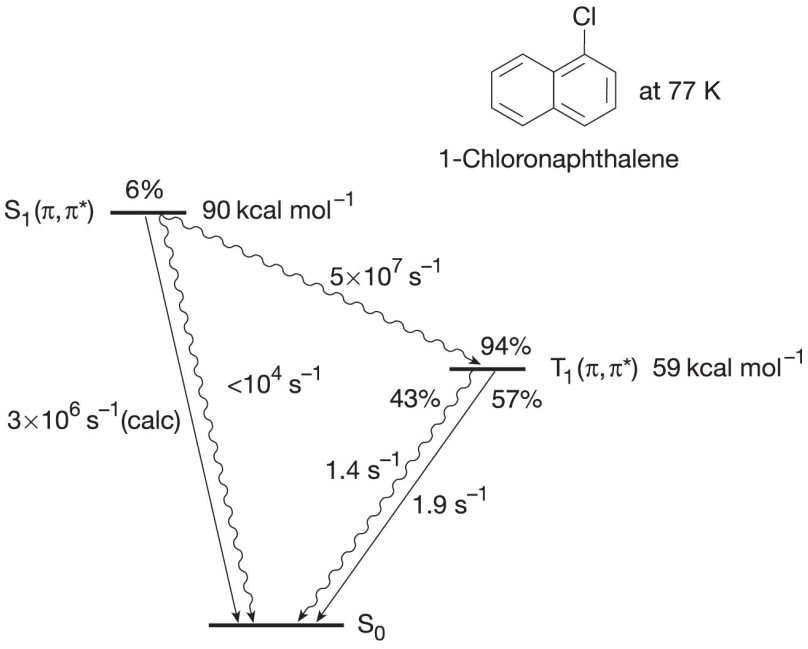

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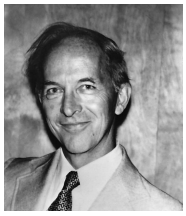
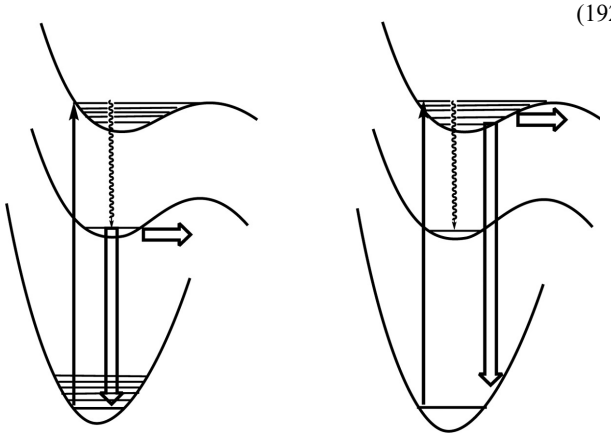
Kasha's rule

"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).



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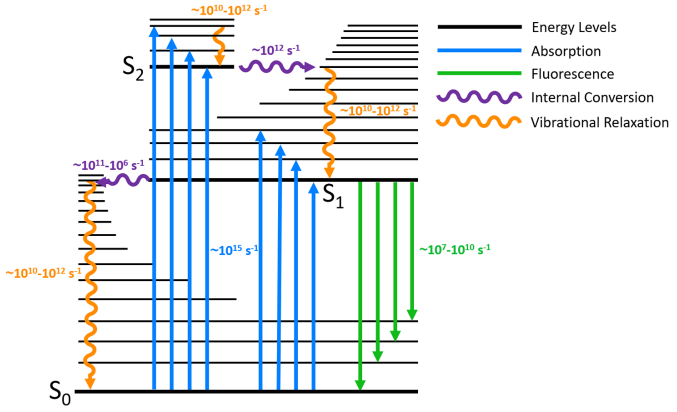
Kasha's rule

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.



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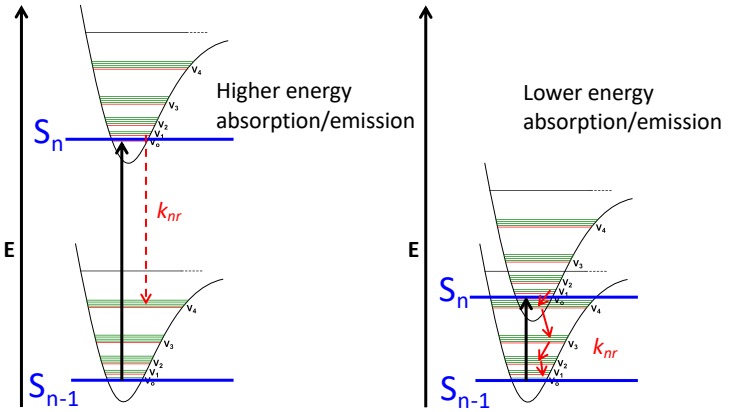
Energy Gap Law

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

Large Gap

Small Gap



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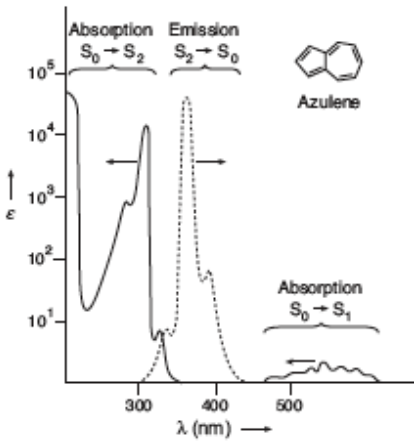
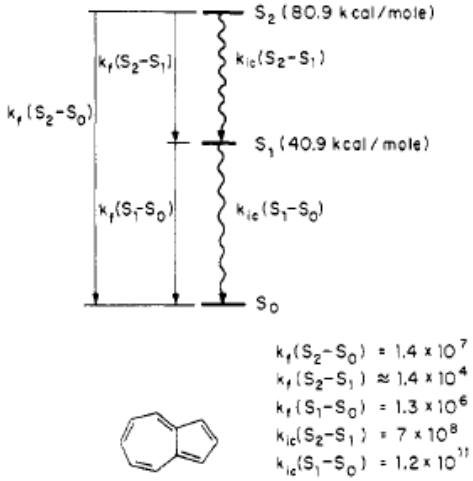
Exceptions

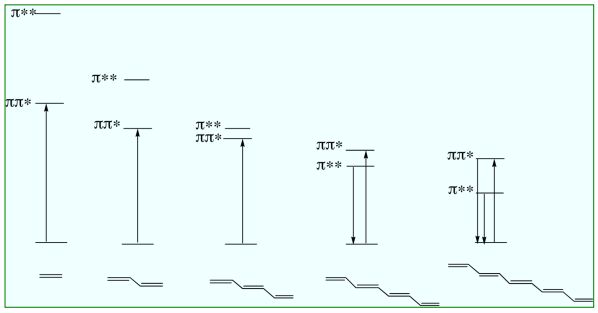


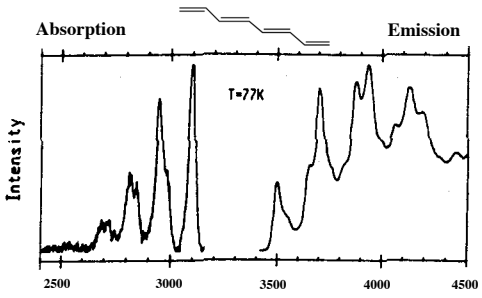


$k_f(S_2-S_0) = 1.4 \times 10^7$
$k_f(S_2-S_1) \approx 1.4 \times 10^4$
$k_f(S_1-S_0) = 1.3 \times 10^6$
$k_{ic}(S_2-S_1) = 7 \times 10^8$
$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

69

Ordering of excited states depends on chain length

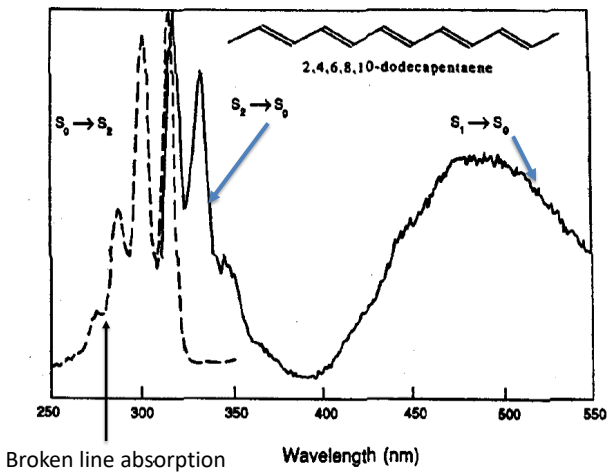




R. L. Christensen et. al., J. Phys. Chem. 1990, 94, 7429

70

Exceptions

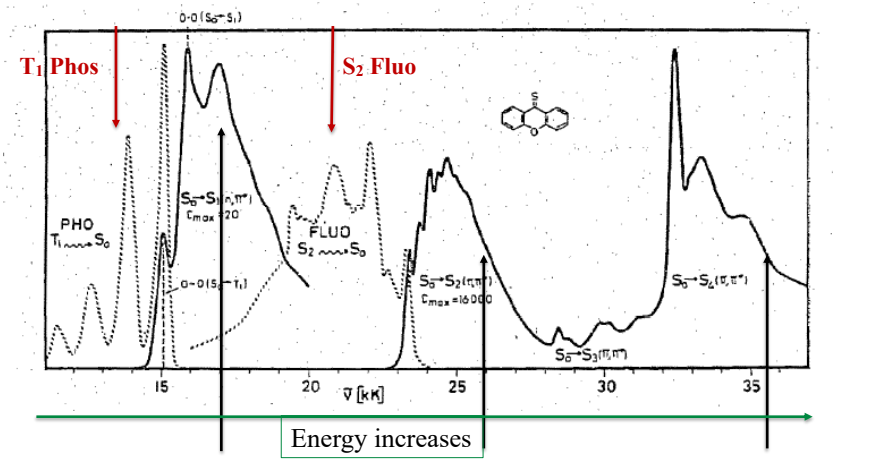


Broken line absorption

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

71

Exceptions



Energy increases

Thick line absorption Thick line absorption Thick line absorption

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

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

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Takao Itoh

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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

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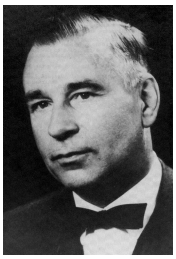
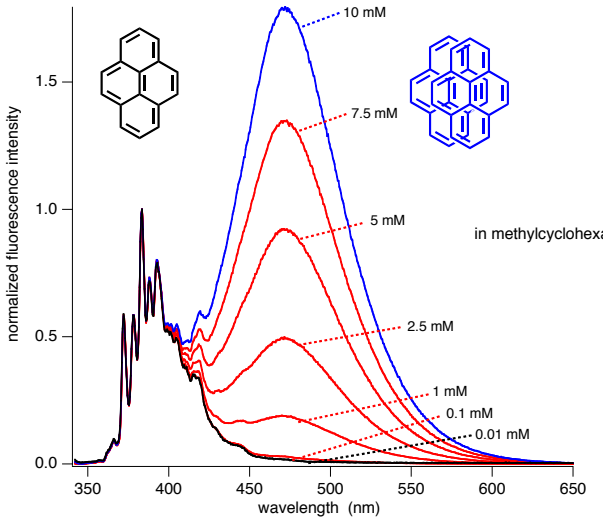
Excimers

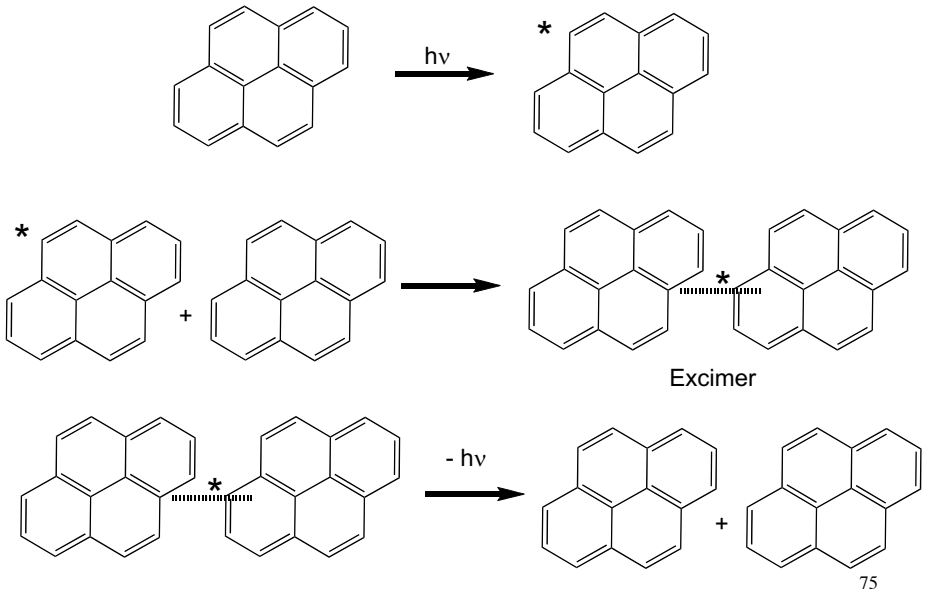


Th. Förster



74

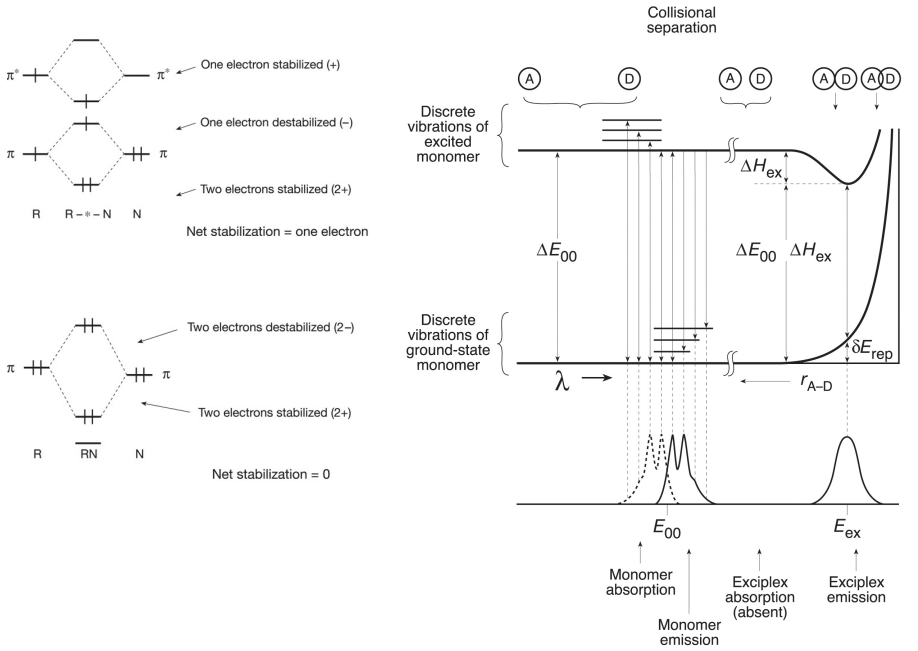
Pyrene as an exemplar of excimer formation



75

75

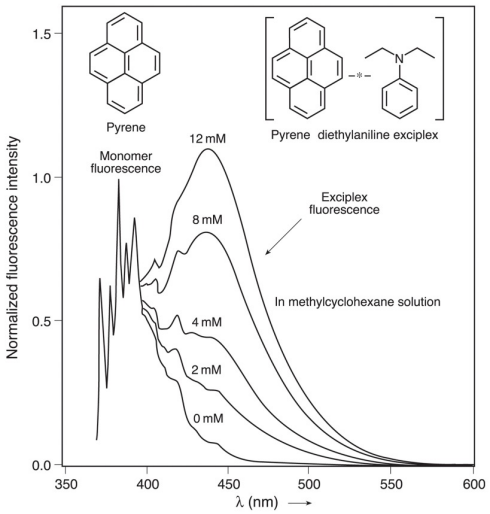
Why excited state complexes are more stable?

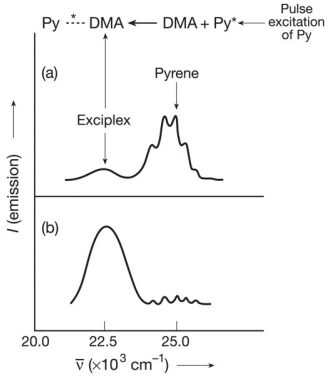


76

Excited state complexes: Exciplexes

Albert F. Weller





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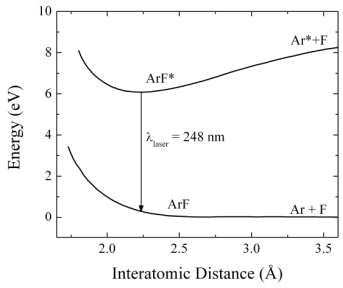
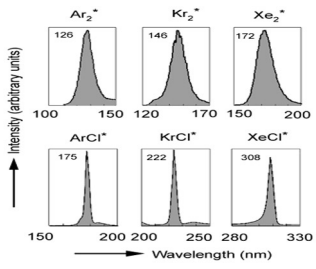
Excimer lasers

First excimer laser discovery in 1970 and further development 1970-80

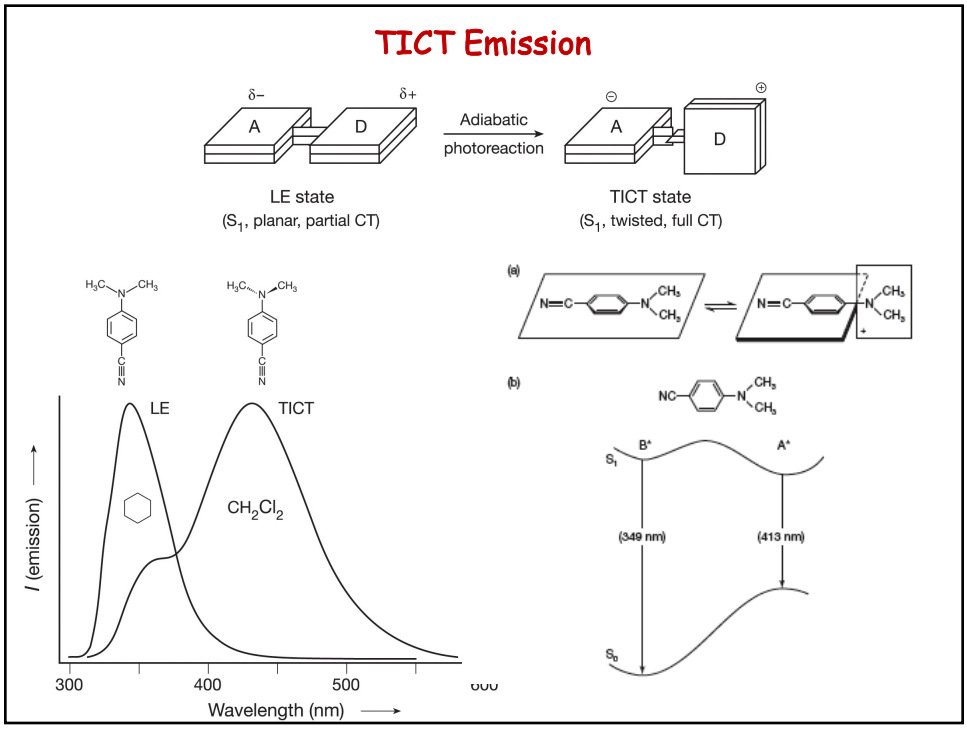




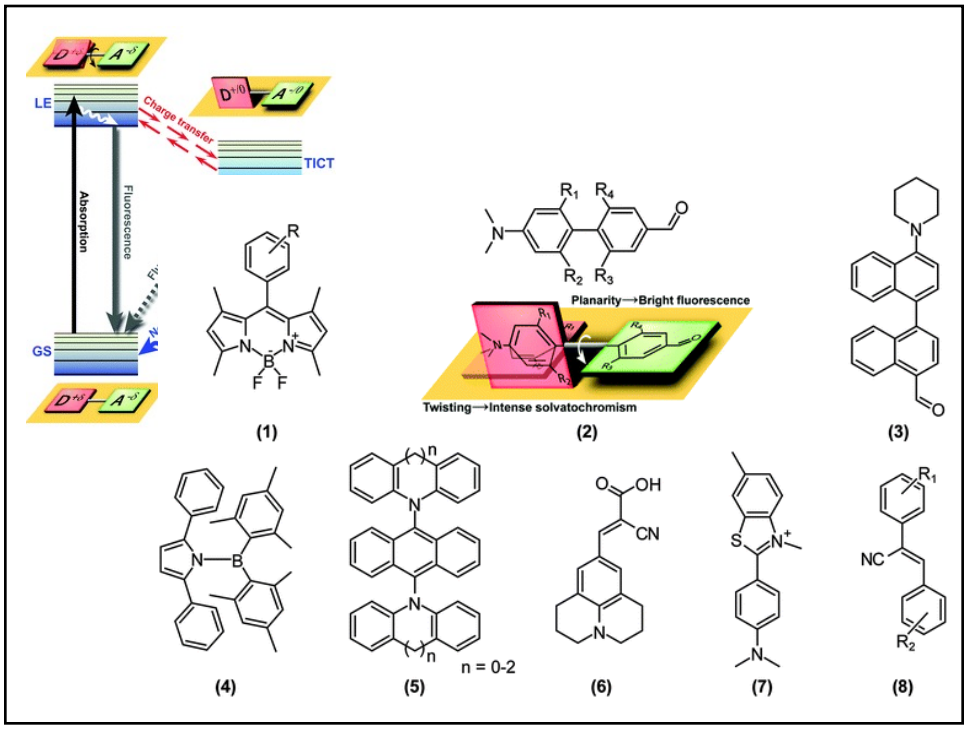
Excimer	Wavelength
F_2 (fluorine)	157 nm
ArF (argon fluoride)	193 nm
KrF (krypton fluoride)	248 nm
XeBr (xenon bromide)	282 nm
XeCl (xenon chloride)	308 nm
XeF (xenon fluoride)	351 nm

Applications: Photolithography, Medicinal including Lasik surgery

78


TICT Emission
δ−
δ+
A
D
Adiabatic
photoreaction
LE state
(S1, planar, partial CT)
TICT state
(S1, twisted, full CT)
LE
TICT
CH2Cl2
I (emission)
300
400
500
Wavelength (nm)
(a)
(b)
B*
A*
S1
S0
(349 nm)
(413 nm)

79


LE
TICT
Charge transfer
Absorption
Fluorescence
GS
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
n = 0-2
Planarity→Bright fluorescence
Twisting→Intense solvatochromism

80

Delayed Fluorescence

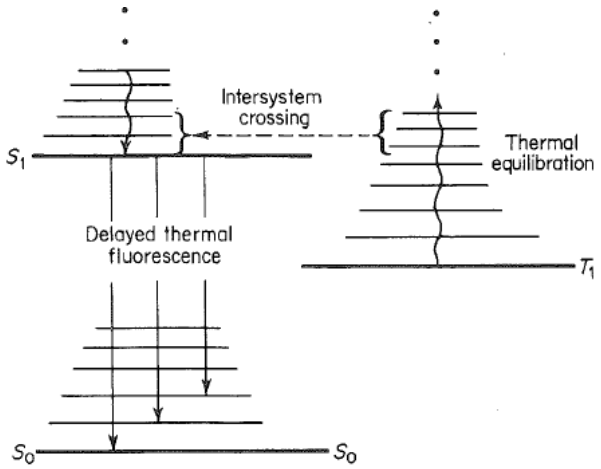
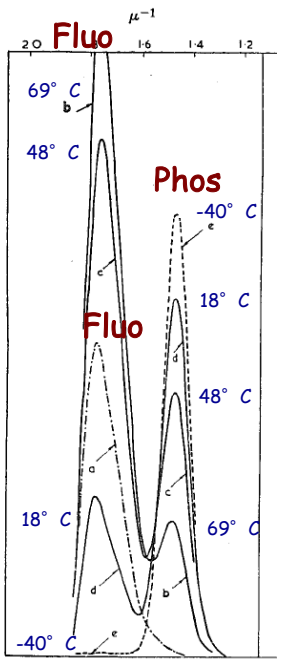
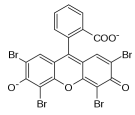


Fig. 1.11 Illustrating production of delayed thermal fluorescence (DTF).

81

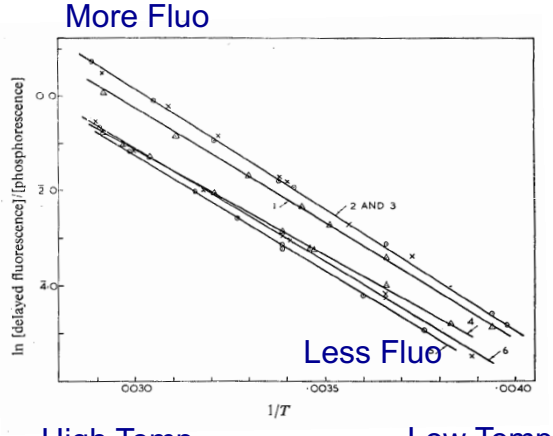
Delayed Fluorescence





Eosin Y

More Fluo



Less Fluo

High Temp

Low Temp

82

Types of emissions

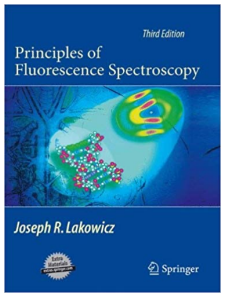
- Fluorescence
- Phosphorescence
- Emission from upper excited states
- Excimer emission
- Exciplex emission
- TICT emission
- Delayed emission

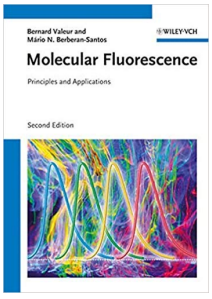
83

Photoluminescence of Solutions: With Applications to Photochemistry and Analytical Chemistry

C A: Parker

1968

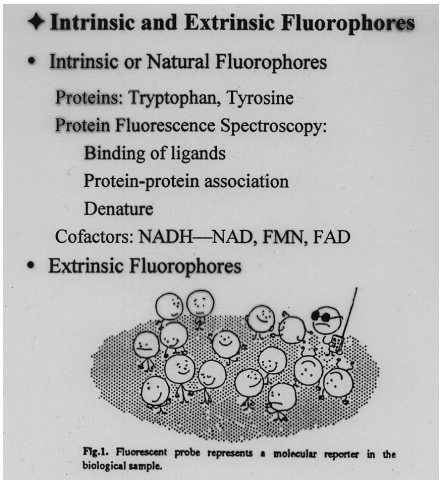




84

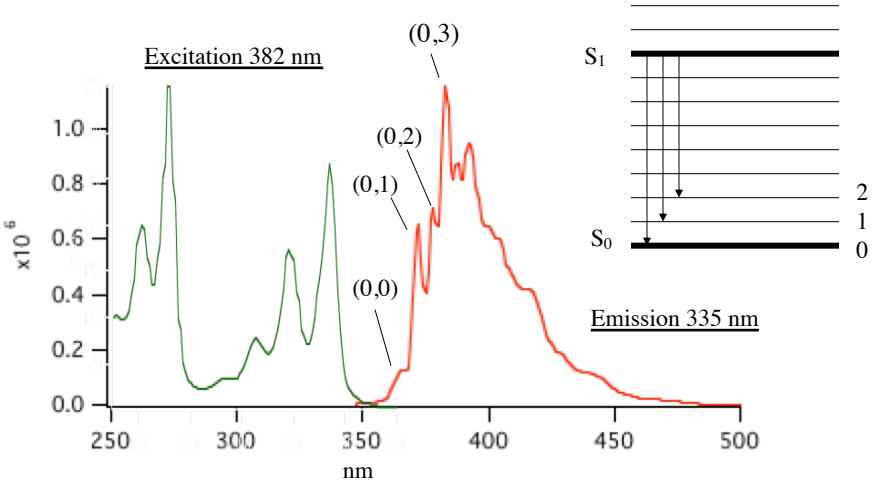
Intrinsic fluorophore and extrinsic fluorophore

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



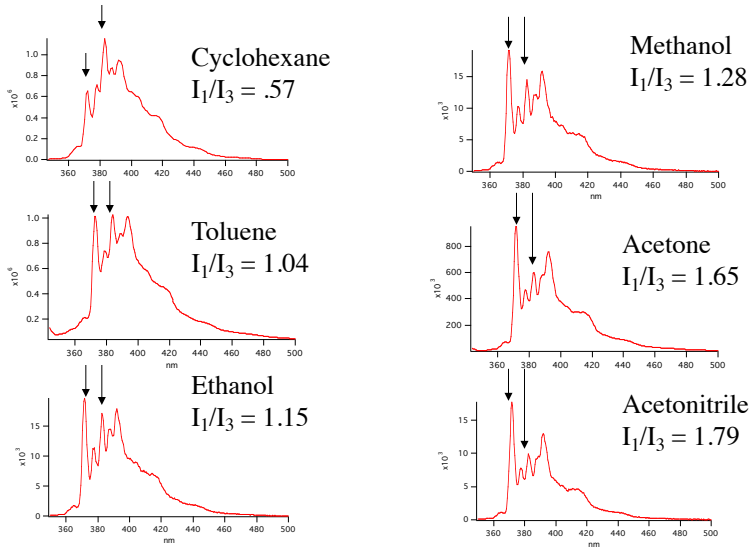
85

Pyrene Emission at Room Temperature Vibrational Pattern



86

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



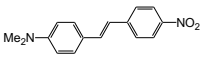
94 Solvents have been tested, showing ratios from 0.41 to 1.95. *Can. J. Chem.* 62, **1984**

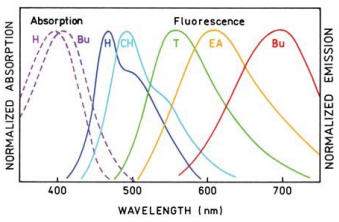
87

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

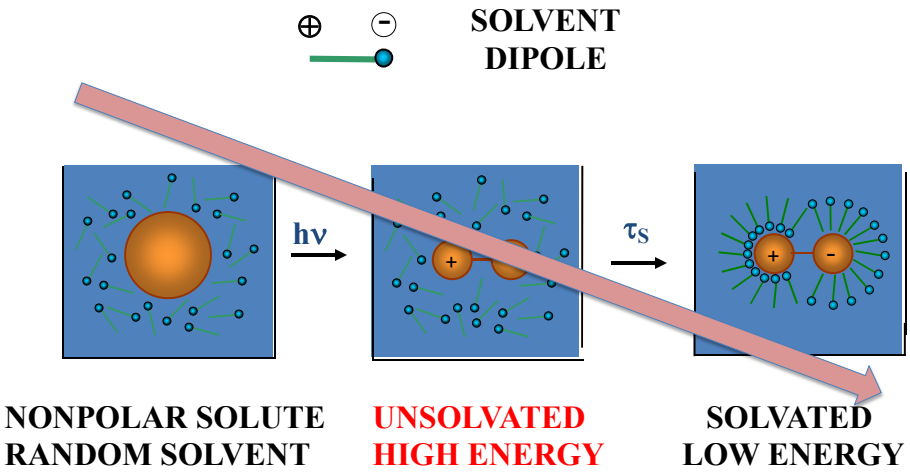
T = Toluene

EA = Ethyl acetate

Bu = Butanol

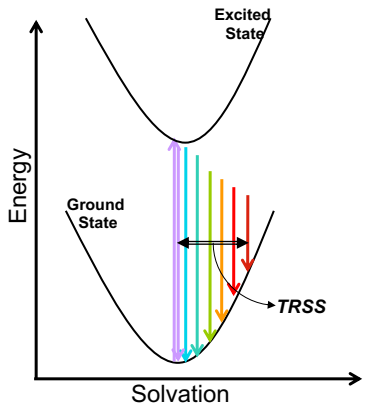
88

Solvation Dynamics

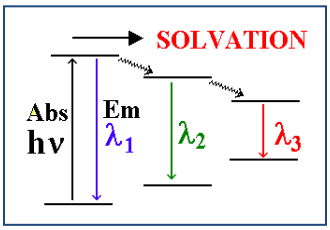


89

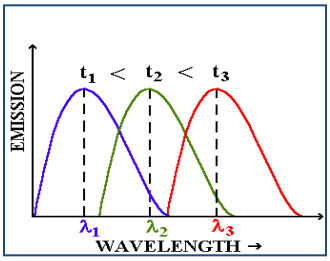
Solvation Dynamics



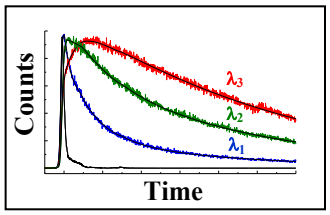
90



DECREASE OF ENERGY OF EXCITED DIPOLE

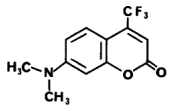


TIME DEPENDENT FLUORESCENCE STOKES SHIFT

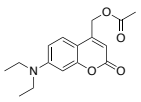


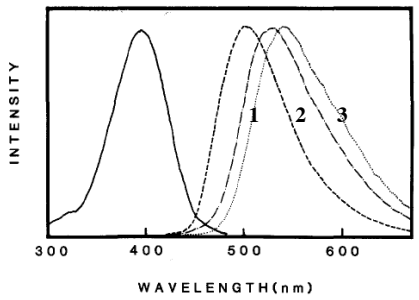
EM. WAVELENGTH DEPENDENT FL. DECAYS

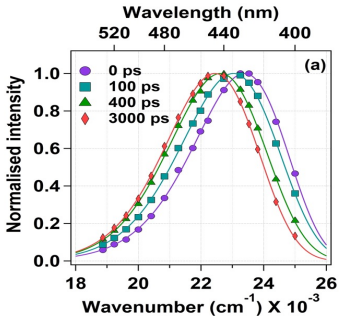
91



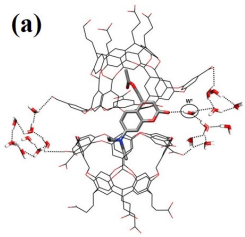
Coumarin 152







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



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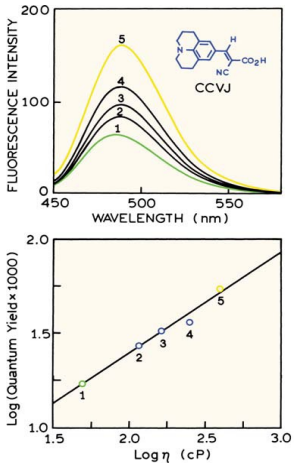
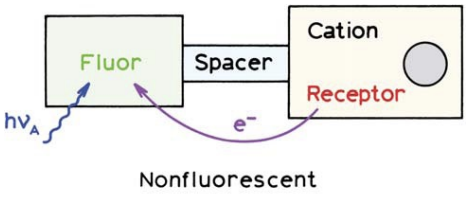
Viscosity Probes

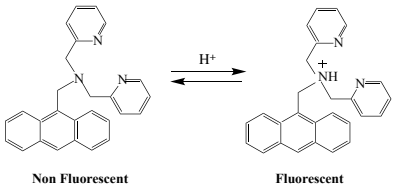
Viscosity Probes = An increase in the viscosity of the medium surrounding a fluorophore can restrict conformational freedom and alter the quantum yield



93

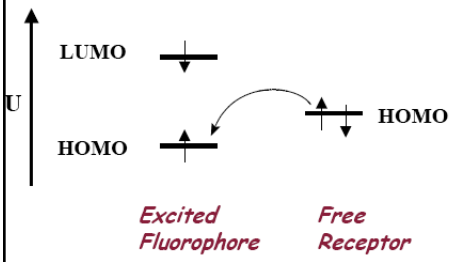
Supramolecular Sensors: Proton





94

Mechanism of PET Signaling



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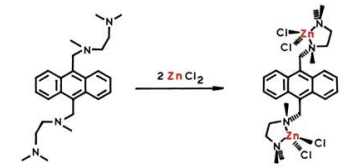
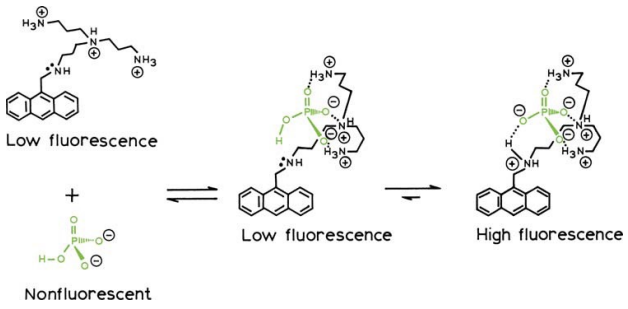
Metal ion sensing

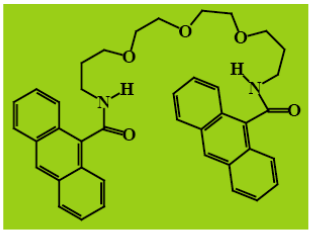


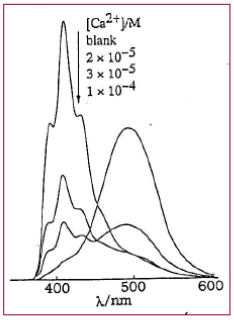
Anion sensing



96

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





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

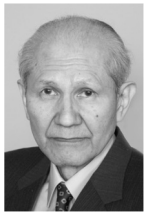
- *A fluorescent host with anthracene moiety at each end of a linear polyether chain*
- *Upon addition of Ca^{2+} fluorescence spectrum changes from monomer emission to excimer emission*

97

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

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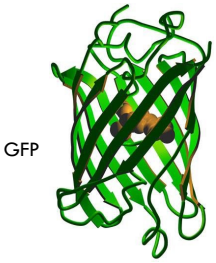
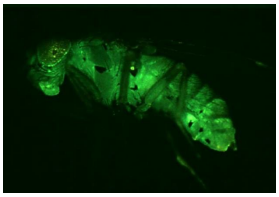
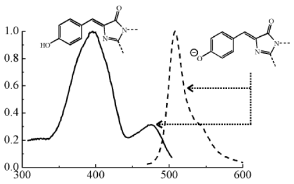
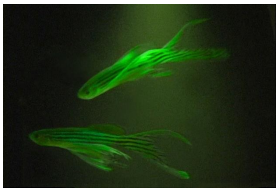
Fluorescent Protiens

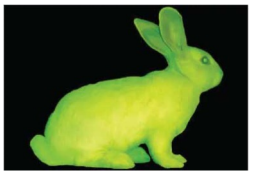
- Green fluorescent proteins can be expressed in living organisms











Rabbit expressing GFP

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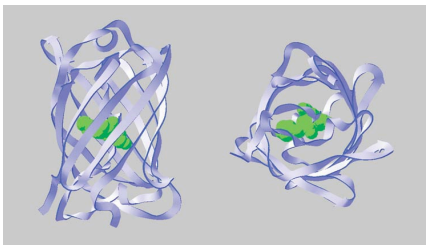
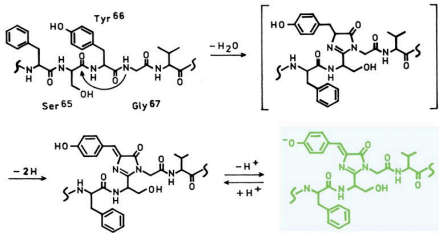
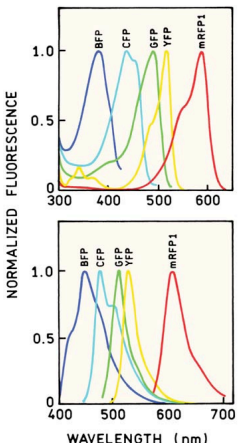
Modifications of Green Fluorescent Protein

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







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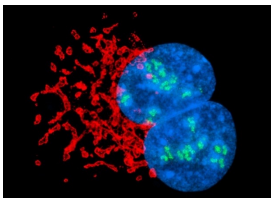
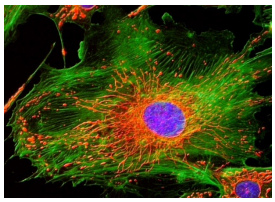
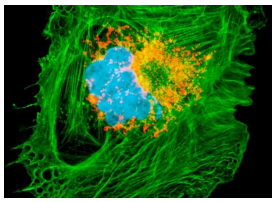
Watching Cells in Multicolor



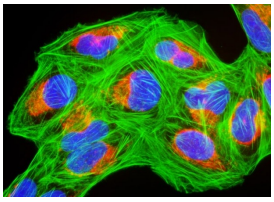
African Green Monkey Kidney Fibroblast Cells



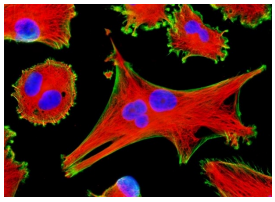
Bovine Pulmonary Artery Endothelial Cells



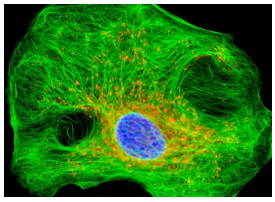
Chinese Hamster Ovary Cells



Human Bone Osteosarcoma Cells



Human Brain Glioma Cells



Human Lung Carcinoma Cells

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