CHM 535/635

Molecular and Supramolecular Photochemistry

Absorption and Emission
Radiative Transitions

Chapters 3 & 4

Principles of Molecular Photochemistry: An Introduction

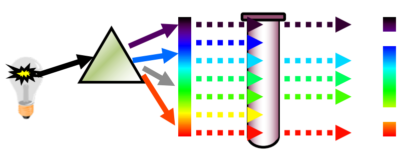
NJT, VR and JCS

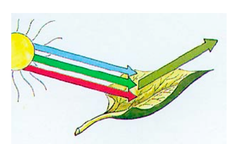
Manifestations of Light-Matter Interactions

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

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.

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.

The Basic Laws of Photochemistry

Grotthuss-Draper law

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

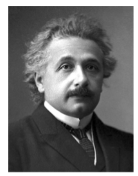
Grotthus

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

Third law of photochemistry

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

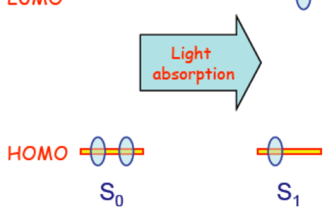
The *energy conservation rule* (Eq. 4.8): There must be an exact matching of the energy difference that corresponds to the energy required for the transition (ΔE) between orbitals and the energy of the photon (hν); that is, ΔE must exactly equal hν (Eq. 4.8).

R* —— Ψ_2

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

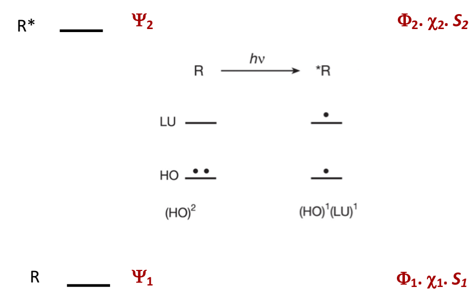
R —— Ψ_1

Light absorption and electron movement



What controls the electron movement or electronic configuration change?

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

Oscillator Strength-Absorption

$\Psi_1|P_{1\to2}|\Psi_2$ $\Phi.\ \chi.\ S$

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

A perfectly allowed transition has $f = 1$

Electronic (Φ)	{ **Orbital 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' $(\Phi.\ \chi.\ S)_1$?

Fermi's Golden Rule

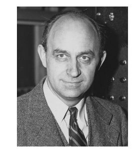
Bohr model couldn't predict why one spectral line is brighter than another.

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).

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

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

Fermi's Golden Rule



Enrico Fermi
Nobel Prize, 1938

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

Probability of light absorption and emission
Fermi's Golden Rule

$$k_{OBS} \sim P_{1\to2} \qquad \rho\, \frac{2\pi}{\hbar} [\langle\Psi_1|P_{1\to2}|\Psi_2\rangle]^2$$

k_{OBS}	allowedness of absorption or emission
ρ	density of states
$P_{1\to2}$	perturbing Hamiltonian

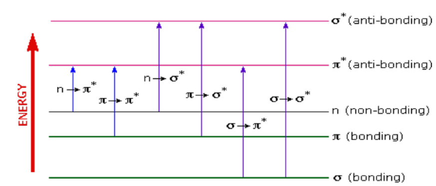
$$(R) + h\nu \rightarrow (^*R) \qquad \rho\, \frac{2\pi}{\hbar} \langle\Psi_1(R)\,|\,P_{h\nu}\,|\,\Psi_2(^*R)\rangle^2$$

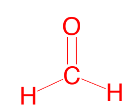
Electronic transitions: Orbital part

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

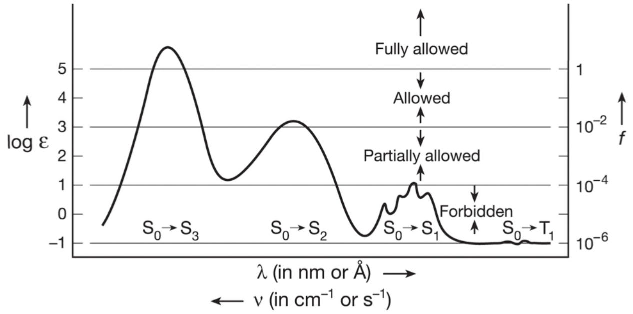
(1) *Overlap* forbiddenness, which results from poor spatial overlap of the orbitals involved in the electronic transition, example, the n,π* transition in ketones, for which the HO and LU are orthogonal to one another and the overlap integral <n│π*> is close to zero.

(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.





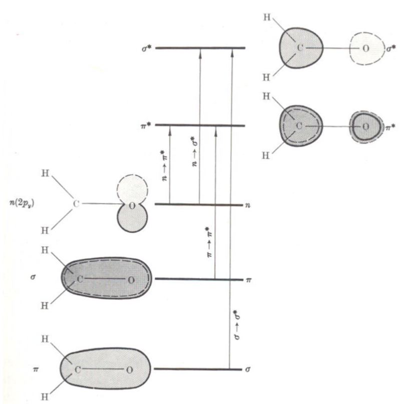
Absorption Spectra: Why the ε and *f* vary with the band?



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

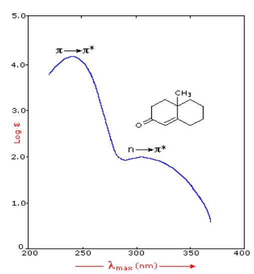
Chromophore	λ_{max}(nm)	ε_{max}	Transition type
C-C	<180	1000	σ,σ*
C=C	180	10,000	π,π*
C=C-C=C	220	20,000	π,π*
C=C-C=C-C=C	260	40,000	π,π*
C=O	280	20	n,π*
C=C-C=O	350	30	n,π*
C=C-C=O	280	10,000	π,π*
Benzene	260	200	π,π*
Pyrene	350	510	π,π*
Anthracene	380	10,000	π,π*

Electronic factor f_e

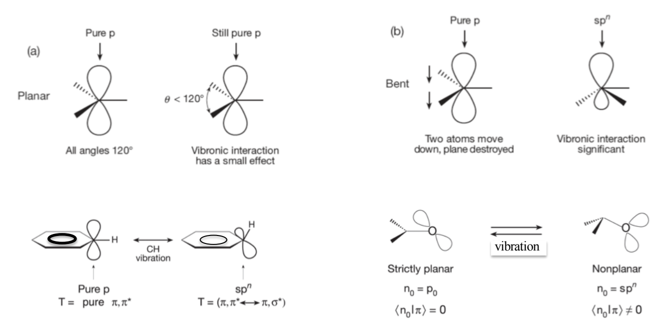


No orbital overlap n and π*

Orbital overlap π and 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*')

Terms to be familiar with

- **Allowed and forbidden electronic transitions**
- **Resonance**
- **Look alike**
- **Vibrational mixing**
- **Fermi's golden rule**
- **Density of states**

Vibronic mixing results in state mixing

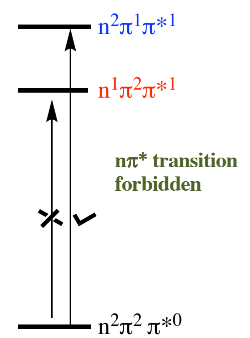
Due to vibration an n, π^* S_1 state is no longer pure but contains a finite amount of π, π^* character mixed in so the zero order wavefunction is not valid and the first order wavefunction may in fact be:

$$\underbrace{\psi(S_1)}_{\text{first order } n,\pi^*} = \underbrace{\psi(n,\pi^*)}_{\text{zero order } n,\pi^*} + \overbrace{\lambda}^{\text{Mixing coefficient}}\underbrace{\psi(\pi,\pi^*)}_{\text{zero order } \pi,\pi^*}$$

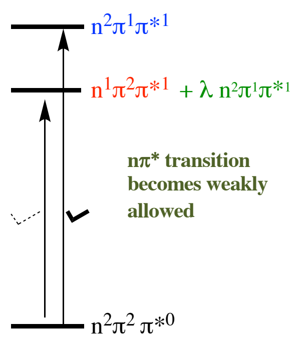
$$\lambda = \left| \frac{\langle \psi_a | H | \psi_b \rangle}{E_a - E_b} \right|$$

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

Result of vibrational – electronic mixing (vibronic coupling)

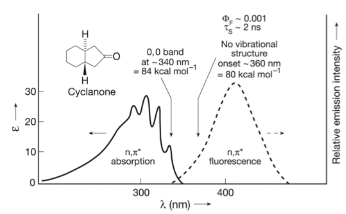


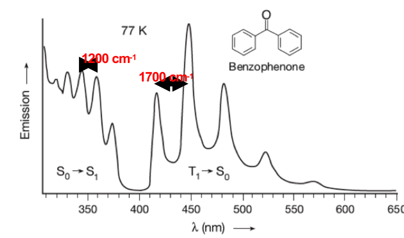
As per Bonn-Oppenheimer approximation



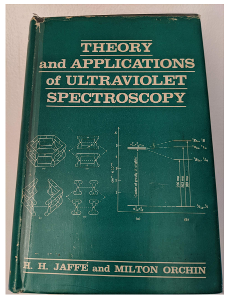
Bonn-Oppenheimer approximation relaxed
Vibrational and electronic motion coupled

Absorption and emission spectra
Vibrational structure due to vibrational mixing



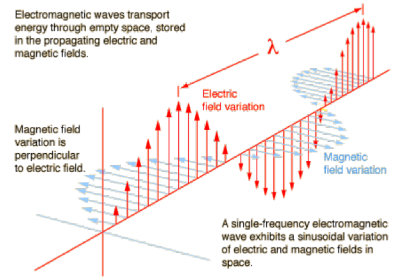


Electronic Spectra



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

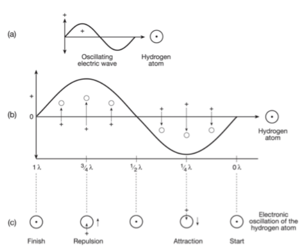
Light as EM waves

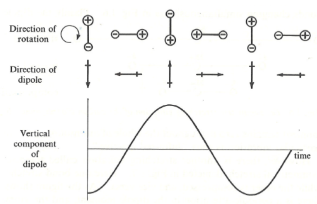


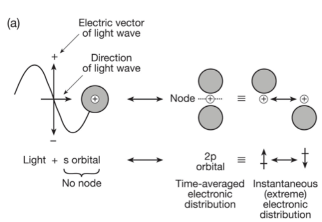
Characterized by:

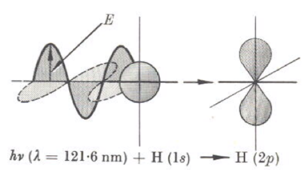
- Wavelength (λ)
- Amplitude (A)
- Frequency (ν)

$$\nu = \frac{c}{\lambda}$$

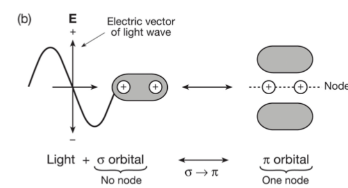


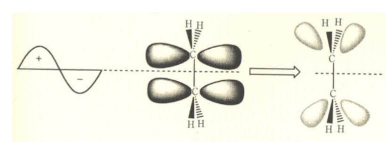




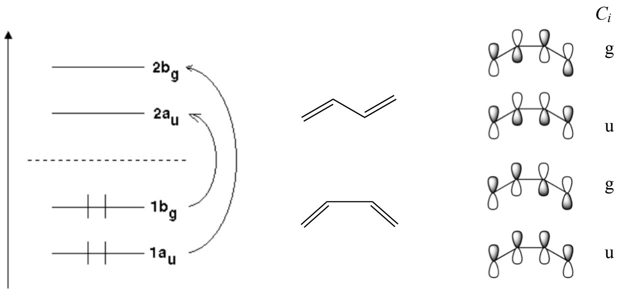


Light as an electromagnetic wave





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

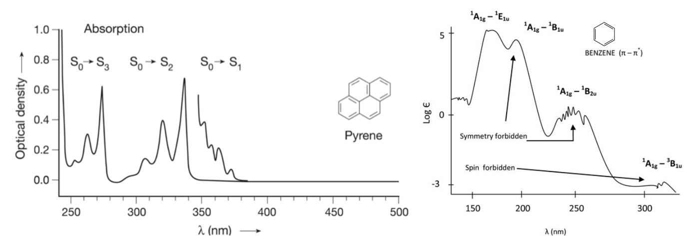
(Communicated by R. G. W. Norrish, F.R.S.—Received 14 August 1939)

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

Area under ε *vs.* wavenumber plot

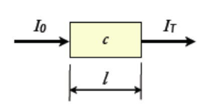
Emission follows the same rules as absorption

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

$$\mathbf{k^0_e \sim 4.3x10^{-9}\, \nu^{-2}_0 \int \varepsilon \, d\nu \sim \nu^{-2}_0 \, f}$$

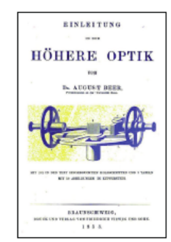
Absorption

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



August Beer (1825-1863)

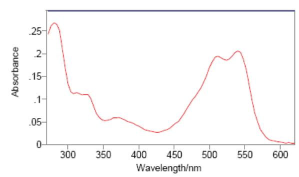
Example: $c = 10^{-3}$ M, $\varepsilon = 10^4$ mol$^{-1}\cdot$ l $\cdot$ cm^{-1}
$\Rightarrow T = 0.01,\ A = 2 \Rightarrow$ 99% of the light is absorbed within the first 2 mm of the solution

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

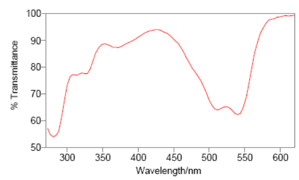
OD can be adjusted with concentration

ABSORPTION & TRANSMISSION SPECTRA

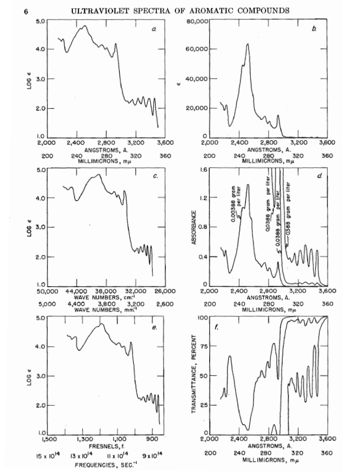
•Absorption spectrum of a red textile



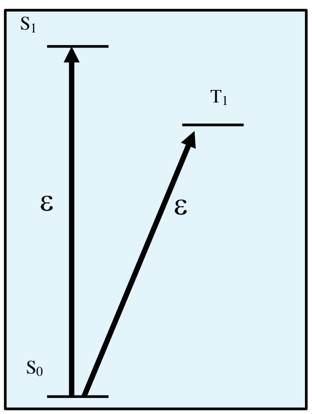
•Transmission spectrum of the same

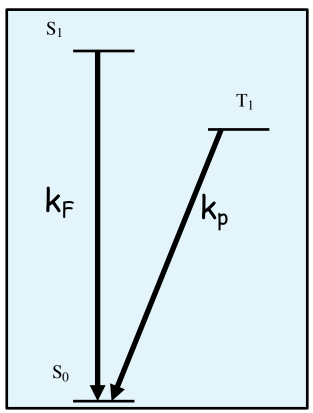


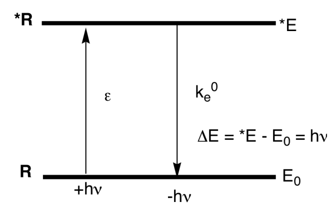
Be Watchful of the Units Used



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}

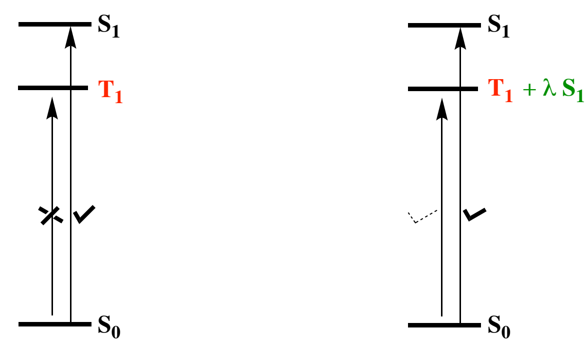
Radiative rate constant $k_e^0 = 3 \times 10^{-9} \overline{\nu}_0^2 \int \varepsilon d\overline{\nu} \cong \overline{\nu}_0^2 f$

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

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

Singlet-Triplet Transitions
Role of Spin-Orbit Coupling



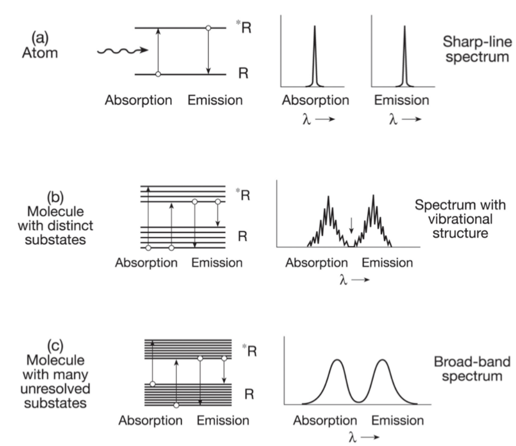
Spin-Orbit coupling mixes the states, no longer pure states

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

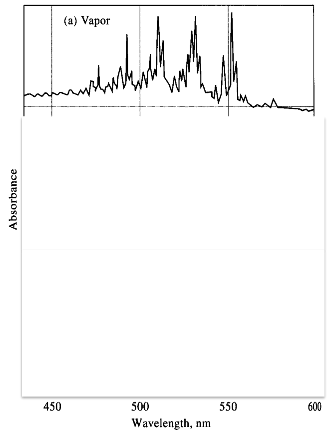
$$\underbrace{k_{obs}}_{\text{Prohibition to maximal caused by "selection rules"}} = k^0_{max} \times \underbrace{f_e \times f_v \times f_S}_{\text{Prohibition factors due to changes in electronic, nuclear, or spin configuration}} \qquad (3.7)$$

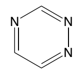
$$k_{obs} = \underbrace{\left[\frac{k^0_{max} < \psi_1|P_{vib}|\psi_2 >^2}{\Delta E_{12}^2}\right]}_{\text{Vibrational coupling}} \times \underbrace{\left[\frac{< \psi_1|P_{so}|\psi_2 >^2}{\Delta E_{12}^2}\right]}_{\text{Spin–orbital coupling}} \times \underbrace{\left[< \chi_1|\chi_2 >^2\right]}_{\text{Vibrational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

Shapes of Absorption and Emission Spectra

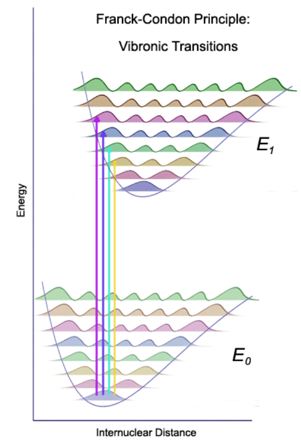


Shapes of Absorption Spectra: medium dependent





Franck-Condon principle and vertical transitions



J. Franck
1882-1964
Nobel Prize, 1925

E. Condon
1902-1974

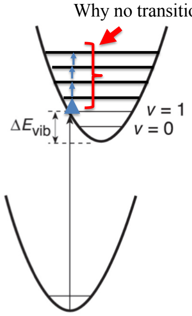
The ground state (E_0) supports a large number of vibrational energy levels. At room temperature, only the lowest vibrational level is populated, and electronic transitions originate from the v=0 vibrational level.

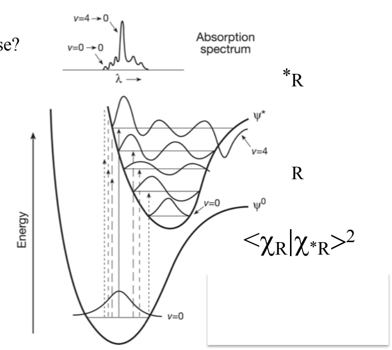
Franck-Condon principle is based on the fact that electrons move faster than nuclei that are heavier.

Franck-Condon principle

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

Why no transition to these?





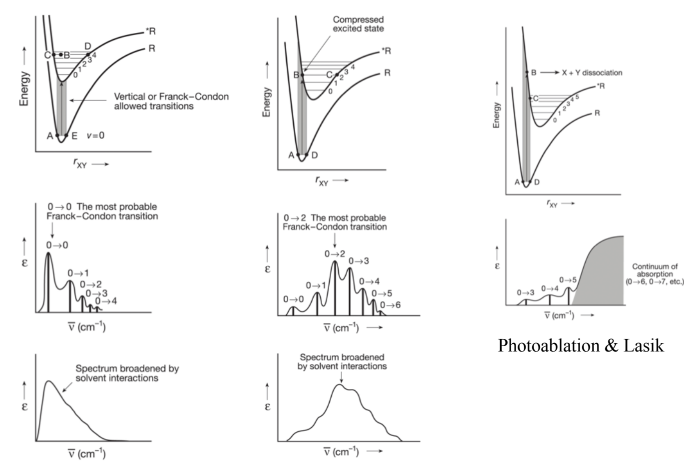
$<\chi_R|\chi_{*R}>^2$

QM harmonic oscillator

QM anharmonic oscillator

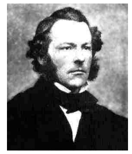
Vibrational overlap integral decides the intensity of absorption

Franck-Condon Principle

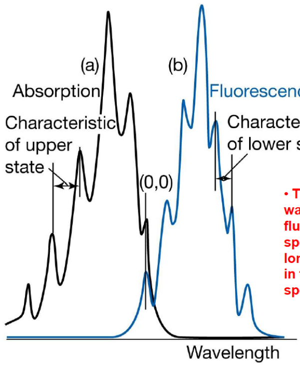


Photoablation & Lasik

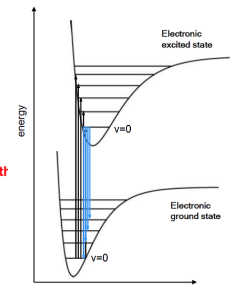
Stoke's shift: Absorption and Emission Spectra



G.G. Stokes (1819-1903)



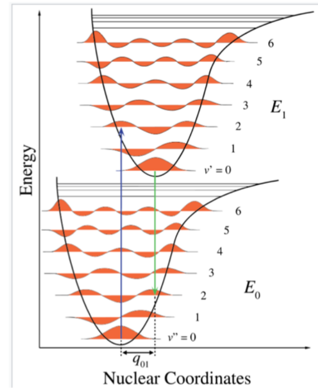
- The shortest wavelength in the fluorescence spectrum is the longest wavelength in the absorption spectrum

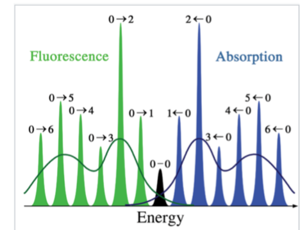


Owing to a decrease in bonding of the molecule in its excited state compared to that of the ground state, the energy difference between S_0 and S_1 is lowered prior to fluorescence emission. This is known as Stoke's shift.

Absorption and Emission Spectra

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



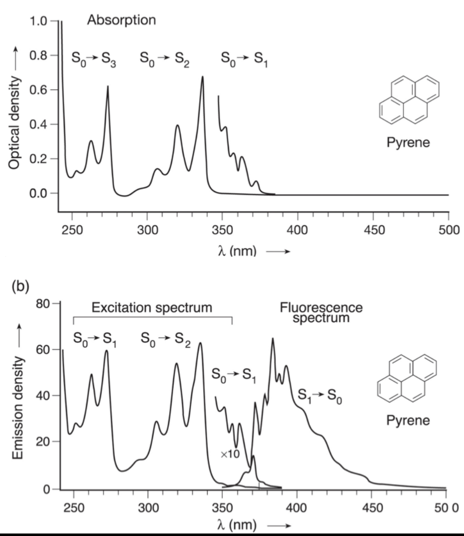


https://www.youtube.com/watch?v=ULCTTxeHI6o&t=0s

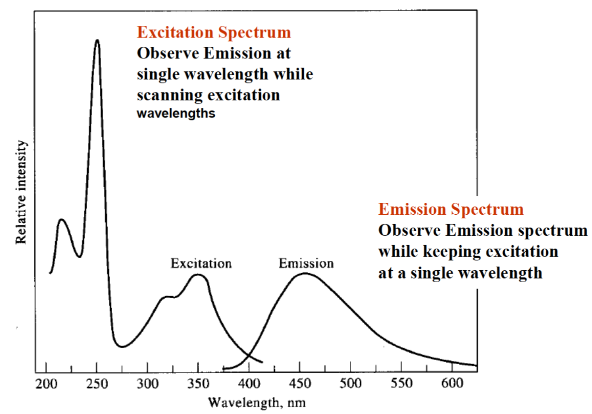
Absorption

Emission

Excitation

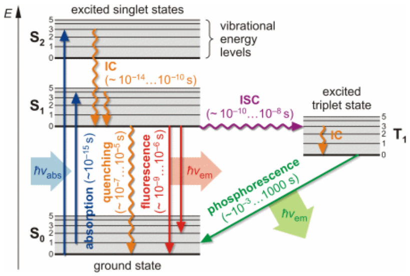


Emission and Excitation spectra



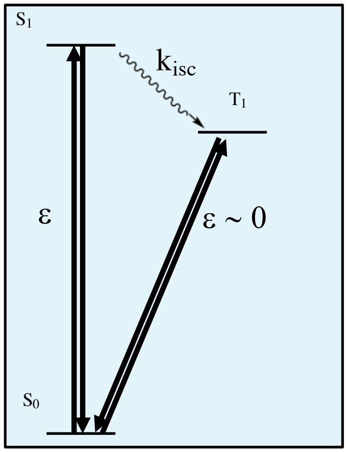
Vavilov's rule

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

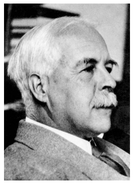


S. Vavilov

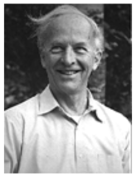
Singlet–Triplet Crossing and Phosphorescence



Triplet State and Phosphorescence

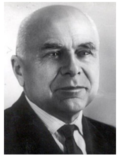


G. N. Lewis



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

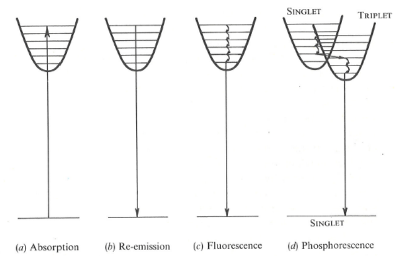
By A. Terenin and V. Ermolaev
Photochemical Laboratory, Section of Chemical Sciences, Academy of Science of U.S.S.R.
Received 21st March, 1956

Classic references on triplet state and heavy atom effect

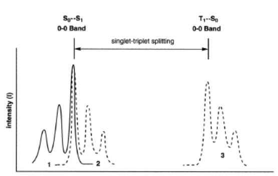
1. JACS., **63**, 3005, (1941).
2. JACS., **64**, 1916, (1942).
3. JACS., **66**, 2100, (1944).
4. JACS., **66**, 1579, (1944).
5. JACS., **67**, 994, (1945).
6. JACS., **67**, 1232, (1945).
7. Chem. Rev., **47**, 401 (1947)
8. J. Chem. Phys., **17**, 905 (1949)
9. J. Chem. Phys., **17**, 1182 (1949)
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).

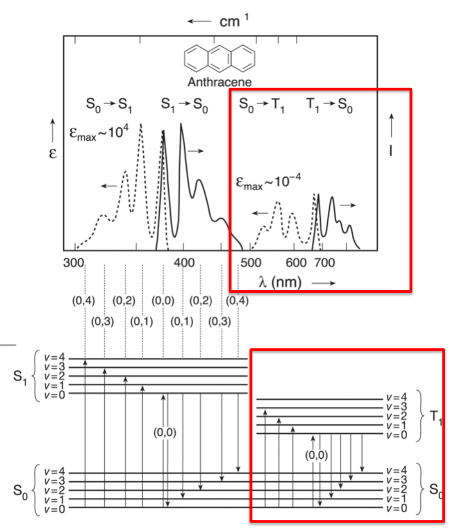
1. J. Chem. Phys., **29**, 952 (1958)
2. JACS., **82**, 5966 (1960)
3. J. Chem. Phys., **32**, 1261 (1960)
4. J. Mol. Spectroscopy, **6**, 58 (1961)
5. J. Phys. Chem., **66**, 2499 (1962)
6. J. Chem. Phys., **39**, 675 (1963)
7. J. Chem. Phys., **40**, 507 (1964)
8. Photochem. Photobiology, **3**, 269 (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)

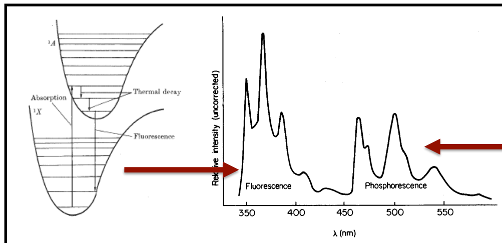
Absorption and Emission

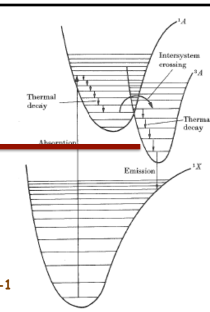


Phosphorescence









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

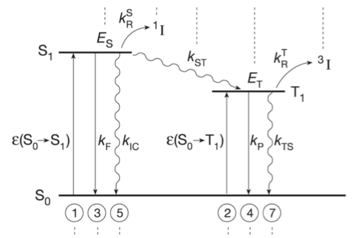
VISCOSITY OF LOW TEMPERATURE GLASSES
(Adapted from Greenspan and Fischer[208])

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

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

Quantum Yields of Fluorescence

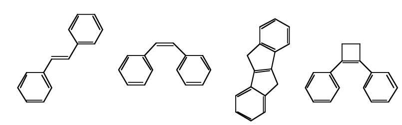
$$\Phi_F = k_f(k_f + \Sigma k_i)^{-1}$$

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

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

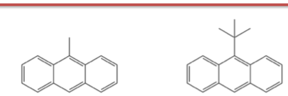
Bond rotation



25ºC	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

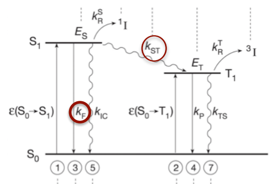
Ermolaev's rule

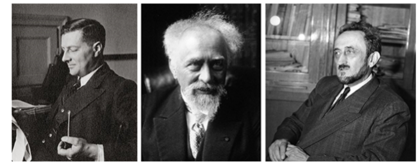
For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., internal conversion is very small with respect to the other two.

Valerii L. Ermolaev

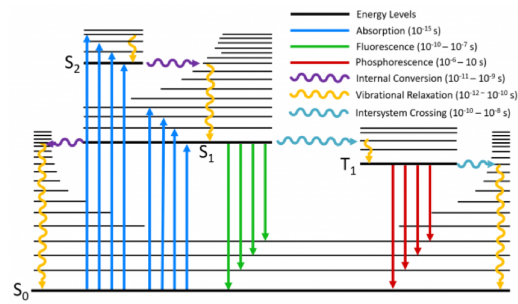
Table 4.2 *Quantum yields for fluorescence ($S_1 \rightarrow S_0 + h\nu$) and intersystem crossing ($S_1 \rightsquigarrow T_1$) for some aromatic hydrocarbons in ethanol solution (Data from Birks, J. B. (ed.) (1975).* Organic molecular photophysics, *Vol. 2, Tables 2.6 and 3.4. Wiley, London)*

Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{ISC}$	
Benzene	0.04	0.15	0.19	**(exception)**
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	

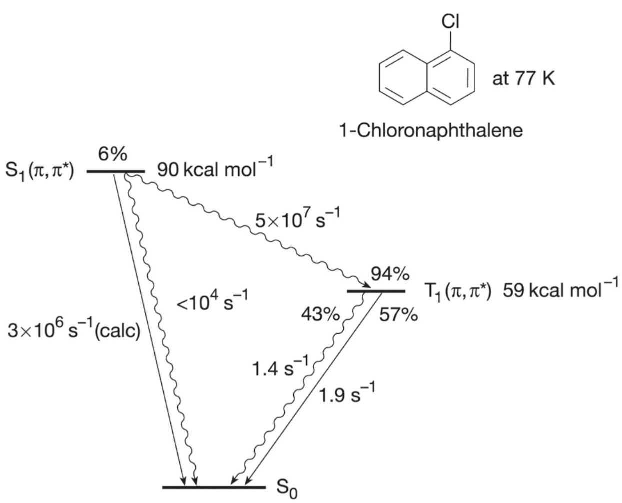




A. Jablonski (1898-1980) J. Perrin 1870-1942 Nobel Prize, 1926 F. Perrin (1901-1992)

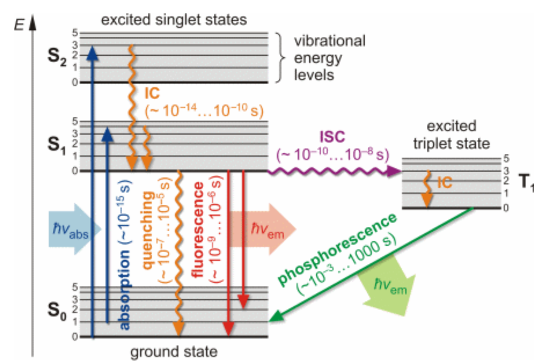


Perrin-Jablonski Diagram

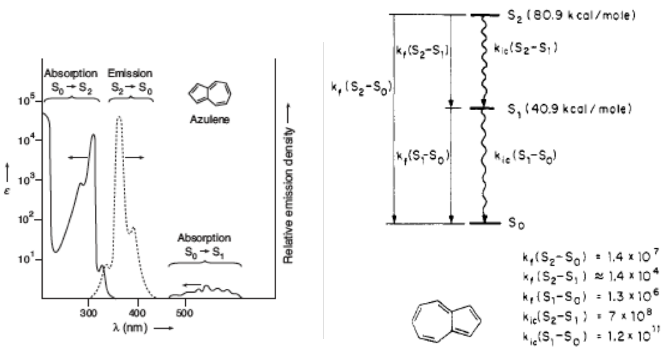


Kasha's rule

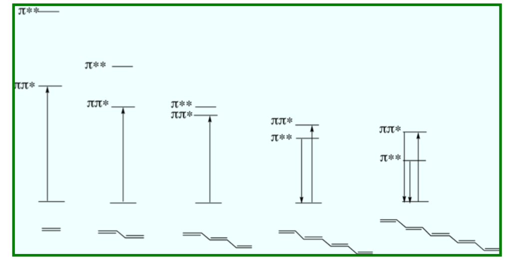
Fluorescence occurs only from S_1 to S_0; phosphorescence occurs only from T_1 to S_0; S_n and T_n emissions are extremely rare.

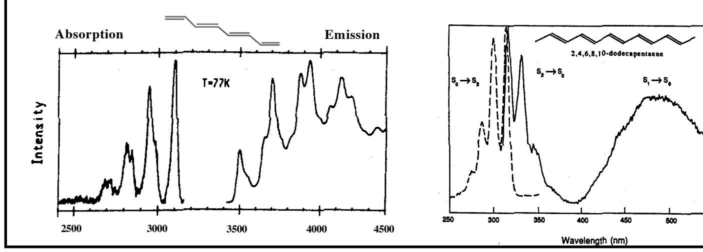


Exceptions



Ordering of excited states depends on chain length





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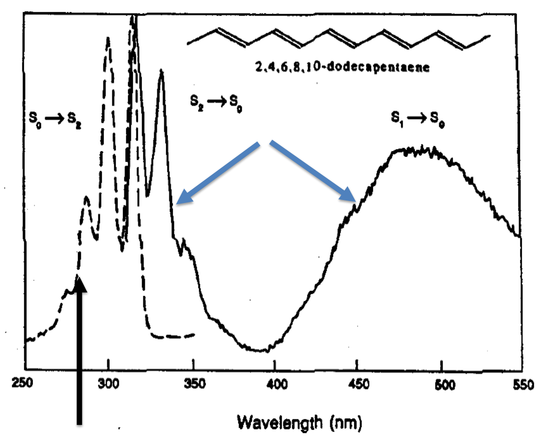
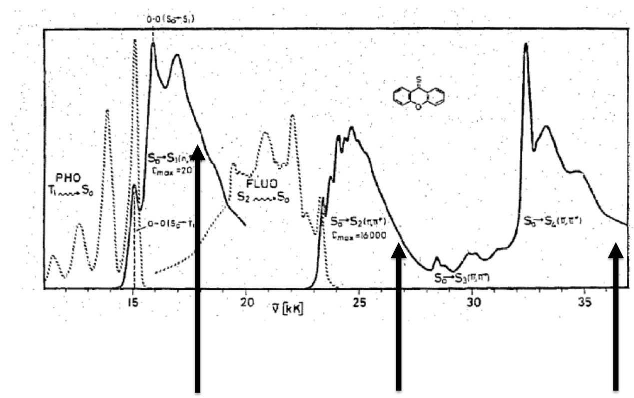


Broken line absorption

Exceptions



Thick line absorption

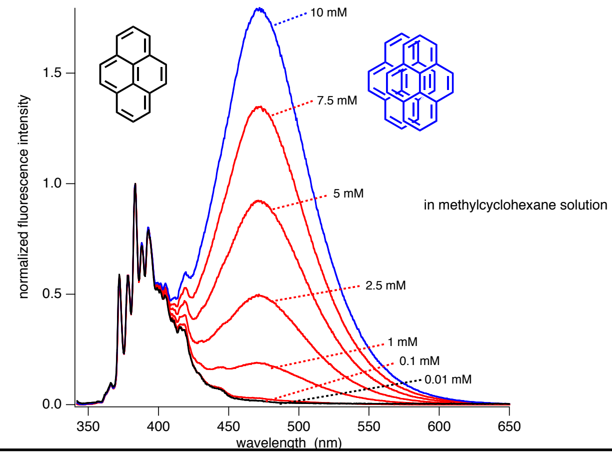
Thick line absorption

Thick line absorption

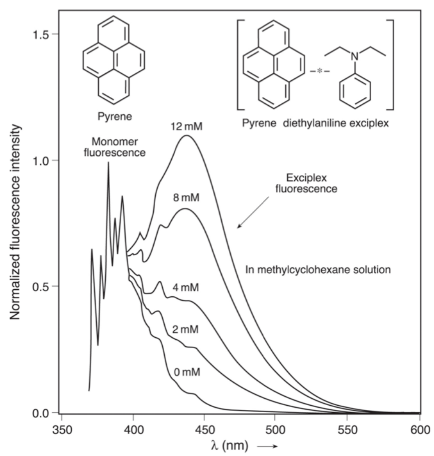
Types of emissions

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

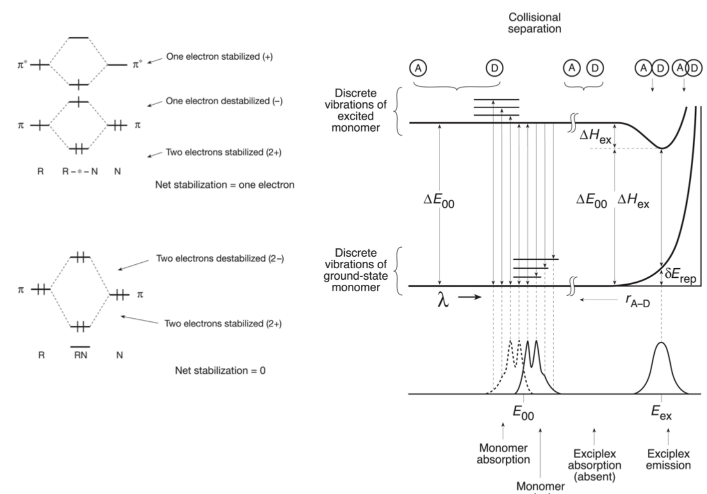
Excited state complexes: Excimers



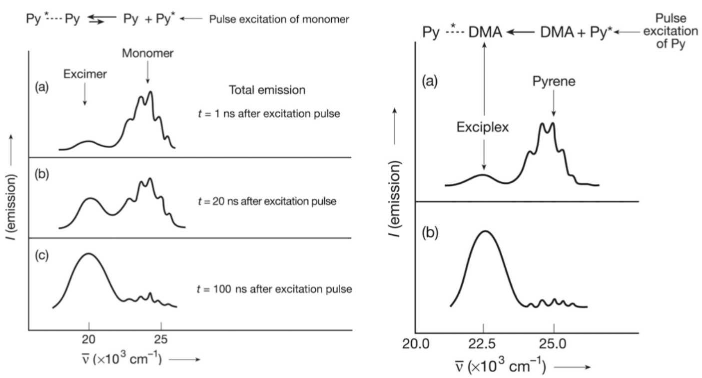
Excited state complexes: Exciplexes



Why excited state complexes are more stable?

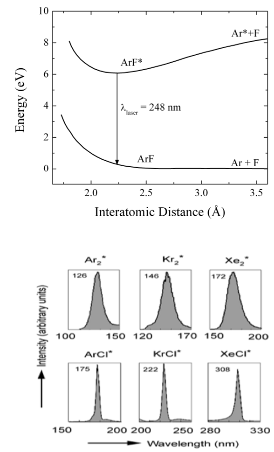


Time resolved emission spectra supports the conclusion that the excited state complexes are only stable in the excited state



Excimer lasers

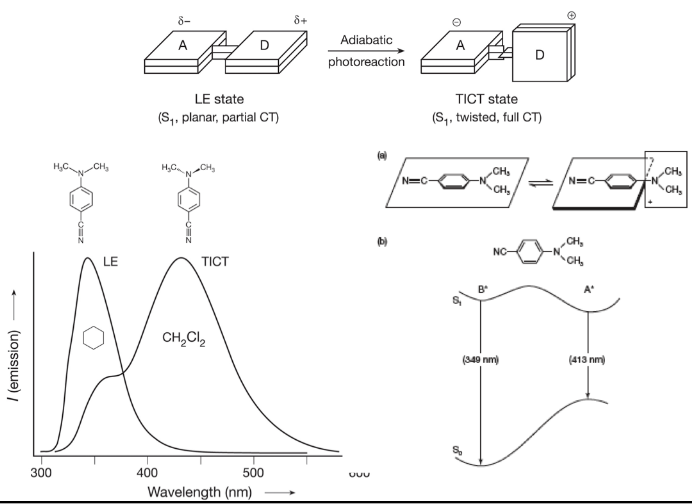
First excimer laser discovery in 1970 and further development 1970-80

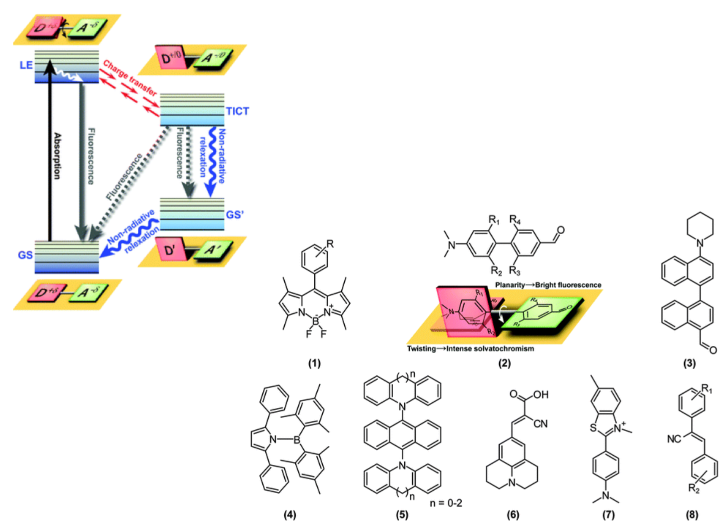


Excimer	Wavelength
F_2 (fluorine)	157 nm
ArF (argon fluoride)	193 nm
KrF (krypton fluoride)	248 nm
XeBr (xenon bromide)	282 nm
XeCl (xenon chloride)	308 nm
XeF (xenon fluoride)	351 nm

Applications: Photolithography,
Medicinal including Lasik surgery

TICT Emission





Delayed Fluorescence

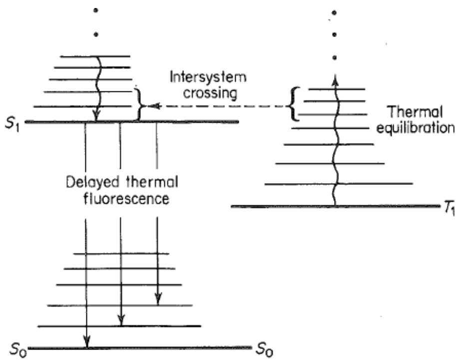
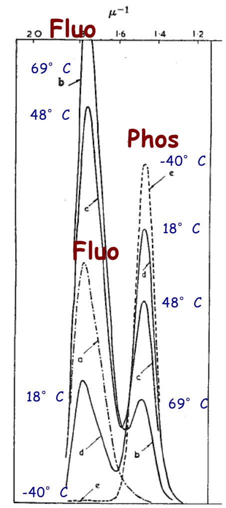
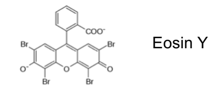
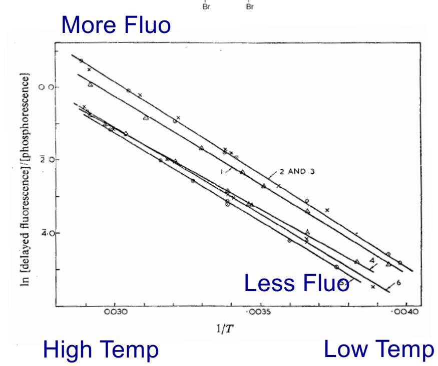


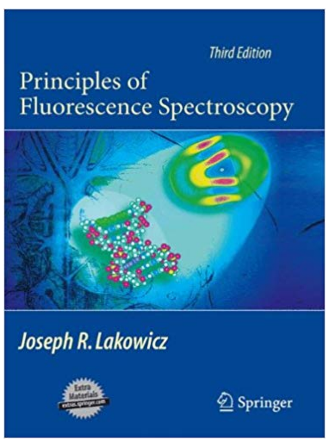
Fig. 1.11 Illustrating production of delayed thermal fluorescence (DTF).

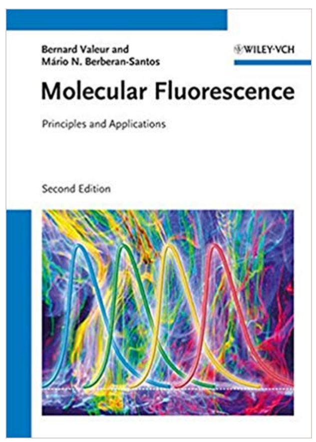
Delayed Fluorescence











Intrinsic fluorophore and extrinsic fluorophore

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

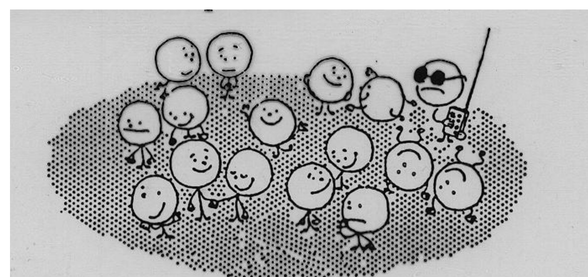
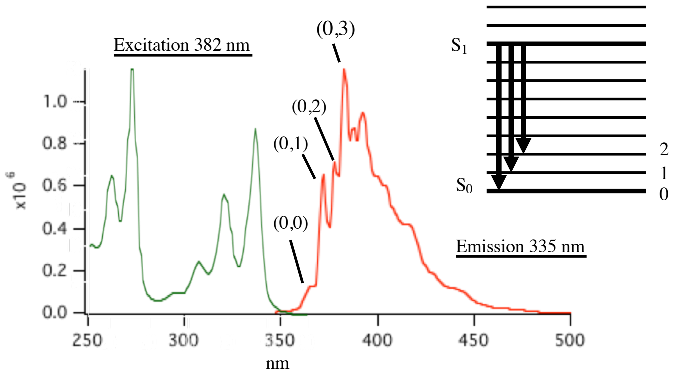
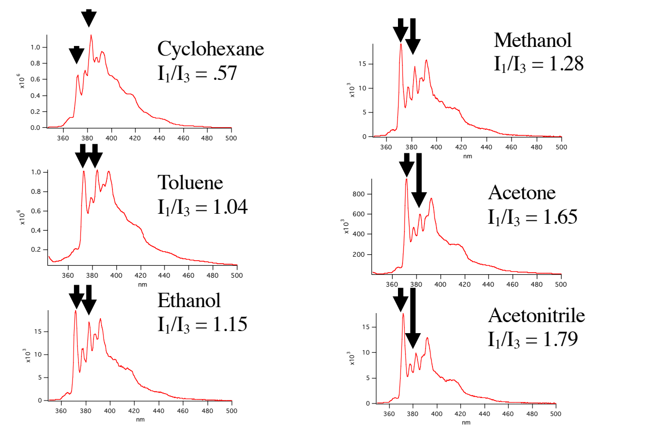


Fig.1. Fluorescent probe represents a molecular reporter in the biological sample.

Pyrene Emission at Room Temperature Vibrational Pattern



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



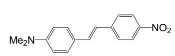
94 Solvents have been tested, showing ratios from 0.41 to 1.95. *Can. J. Chem. Vol.* 62 **1984**

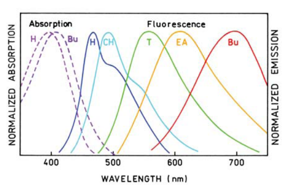
Polarity Probe

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

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

Emission Wavelength = The emission wavelength generally increases with solvent polarity





H = Hexane

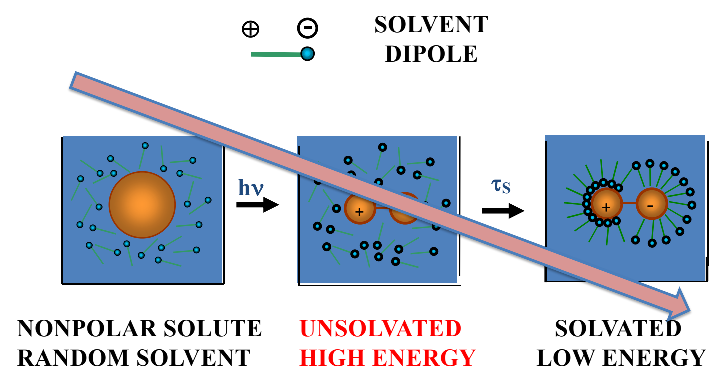
CH = Cyclohexane

T = Toluene

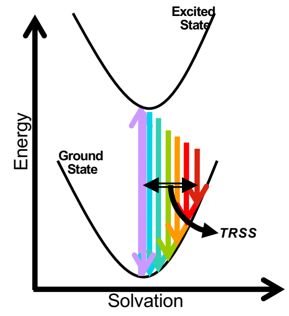
EA = Ethyl acetate

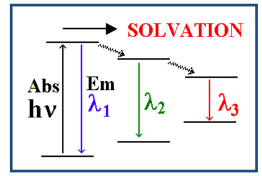
Bu = Butanol

Solvation Dynamics

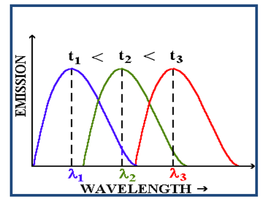


Solvation Dynamics

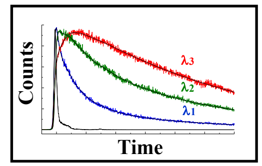




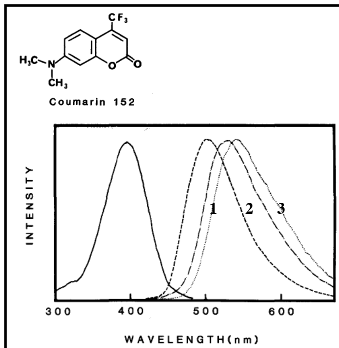
DECREASE OF ENERGY OF EXCITED DIPOLE



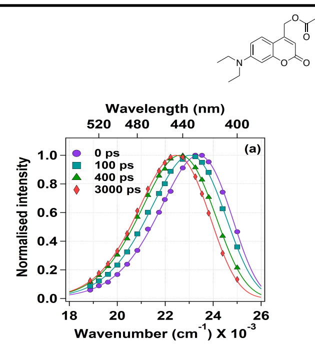
TIME DEPENDENT FLUORESCENCE STOKES SHIFT

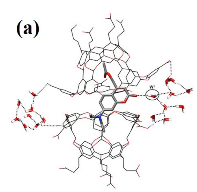


EM. WAVELENGTH DEPENDENT FL. DECAYS



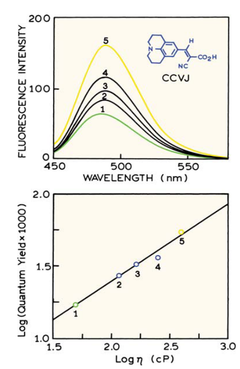
1: ethyl acetate; 2: propylene carbonate
3: methanol



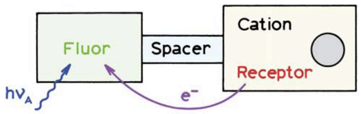


Viscosity Probes

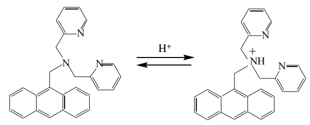
Viscosity Probes = An increase in the viscosity of the medium surrounding a fluorophore can restrict conformational freedom and alter the quantum yield



Supramolecular Sensors: Proton



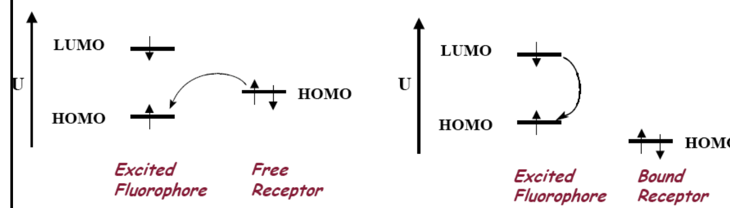
Nonfluorescent



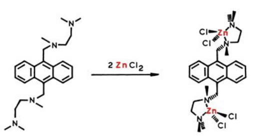
Non Fluorescent

Fluorescent

Mechanism of PET Signaling



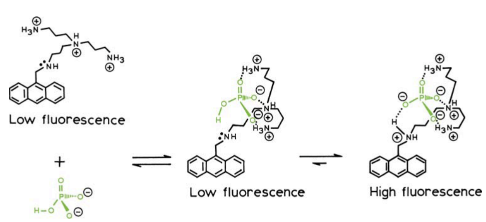
Metal ion sensing



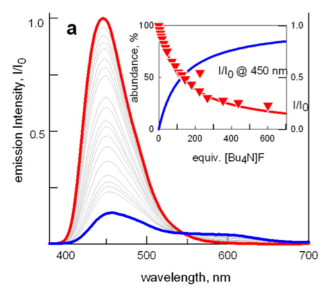
Non-fluorescent

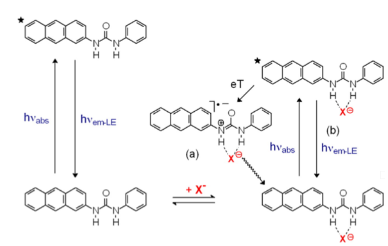
Fluorescent

Anion sensing

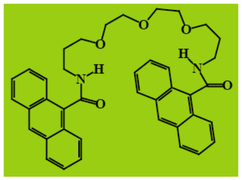


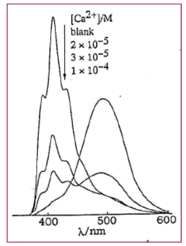
Fluoride ion sensing





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



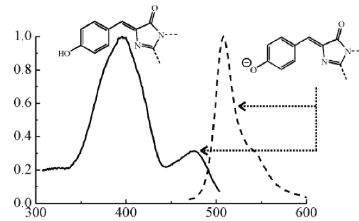


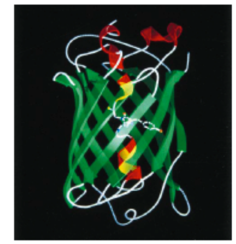
Nakamura *et al. J. Phys. Chem. B*, 2001, *105*, 2923

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

The Nobel Prize in Chemistry 2008

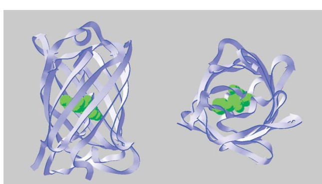
Green Fluorescent Protein (GFP) = GFP incorporates a fluorescent chromophore within the barrel of a b-sheet and can be expressed genetically in cells

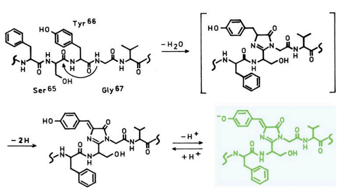


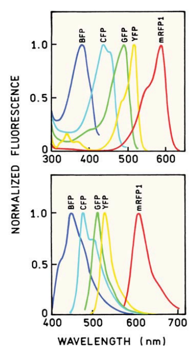


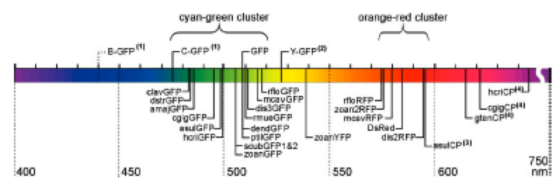
Modifications of Green Fluorescent Protein

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

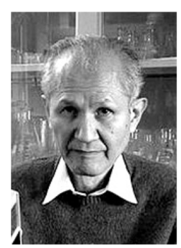


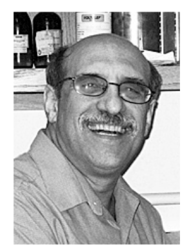






The Nobel Prize in Chemistry 2008


Osamu Shimomura


Martin Chalfie


Roger Y. Tsien

Molecular and Supramolecular Photochemistry - Class Quiz 1
V. Ramamurthy

1. Photon is
   1. Wave
   2. Particle
   3. Both

2. Triplet is
   1. Two electrons with the same spin
   2. Two electrons with different spin
   3. Two electrons with no spin
   4. One electron with α or β spin

3. Which moves faster?
   1. Nucleus
   2. Electron
   3. Both at the same speed

4. Which one has the most energy
   1. IR
   2. UV
   3. Microwave

5. Energy of the triplet state
   1. is higher than singlet
   2. is lower than singlet
   3. same energy as singlet

6. The concept that photon energy is quantized came from
   1. Max Planck
   2. Albert Einestein
   3. Linus Pauling

7. Which one has most singlet-triplet gap
   1. $n\pi^*$ state
   2. $\pi\pi^*$ state
   3. Ground state

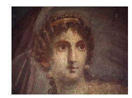
8. Which one has shorter lifetime?
   1. Excited singlet (S_1)
   2. Excited triplet (T_1)
   3. Both have the same lifetime

8. How is jaundice currently cured?
   1. Exposing the patient to infrared radiation
   2. Irradiating the patient to X-ray radiation
   3. Irradiating the patient with UV-Visible light

9. Photodynamic therapy involves
   1. Singlet oxygen as the reactant
   2. Cis-trans isomerization
   3. A sensitizer that absorbs where the blood also absorbs

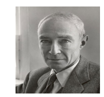
10. Photolithography is a technique used in
    1. Printing newspapers
    2. Dyeing T-shirts
    3. Synthesis of Rose-oxides

11. The main person responsible for the current understanding of light is



Lucretius

De Broglie



Oppenheimer

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12. Chemistry of vision involves
    1. Cycloaddition reaction
    2. Cis-trans isomerization
    3. Reaction with oxygen

13. Photosynthesis is a process
    1. by which camels get energy to survive in a desert
    2. by which we gain energy to walk
    3. by which plants generate energy for survival

14. Survival of the human civilization with enormous energy needs depends on
    1. Emulating photosynthesis to make use of sunlight to generate energy
    2. Making cheaper cars
    3. Using coal instead of gasoline (petrol) to drive cars

15. Absorption and emission of molecules
    1. Are generally separated by more than 20 kcal/mol
    2. Absorption appears at longer wavelength than the emission
    3. In most molecules absorption and emission overlap at 0-0 band

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