Molecular Absorption Spectroscopy

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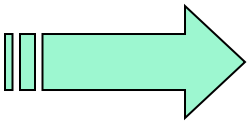
Contents

A. Introduction:
Regions of the electromagnetic spectrum

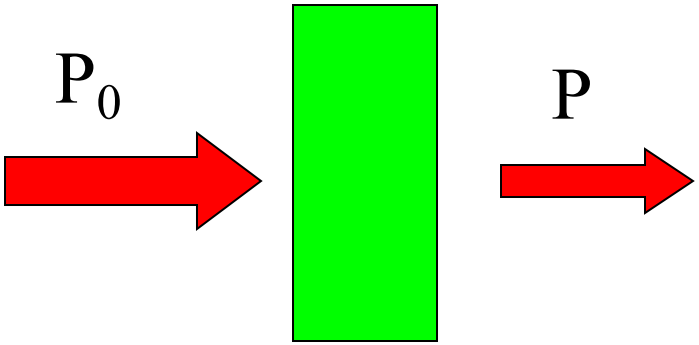
- Deep UV 10-200nm
- Near UV 200-400nm
- Visible 400-800nm

Energy ≈100Kcal



Electronic transitions

A. Introduction:
Transmittance and absorbance



Analyte solution in a transparent cell

- Transmittance : $T = P/P_0$
- Absorbance : $A = \log_{10} 1/T = \log P_0 / P$

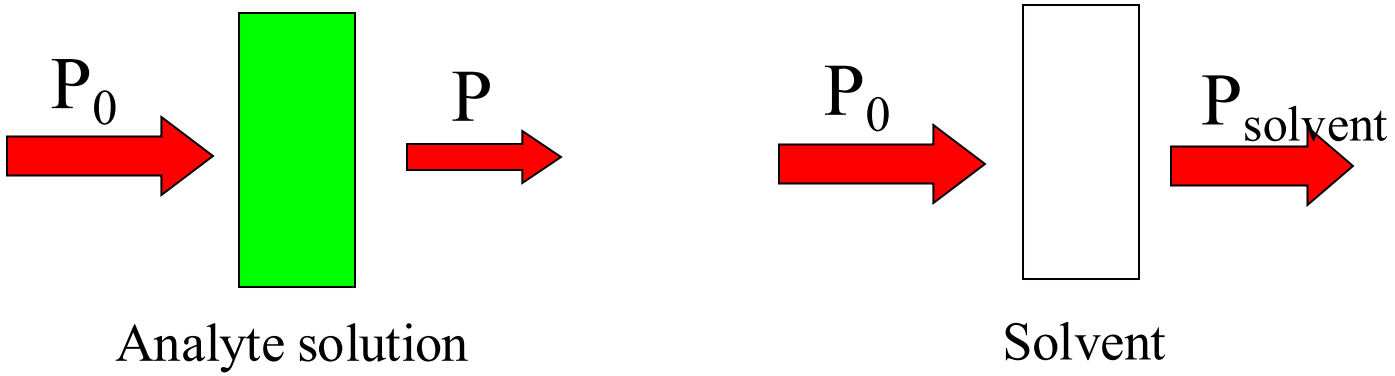
A. Introduction:
Measurement of absorbance

Beam attenuation by:

*reflection losses at solution-wall and air-wall interfaces

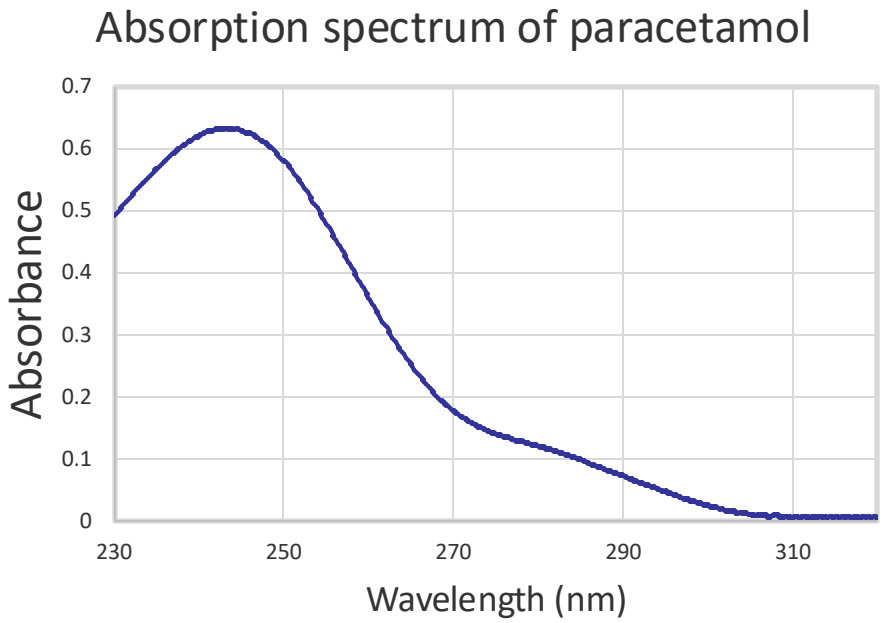
*absorption by the container walls

*scattering by larges molecules in solution



$$A = -\log T = \log P_{solvent} / P$$

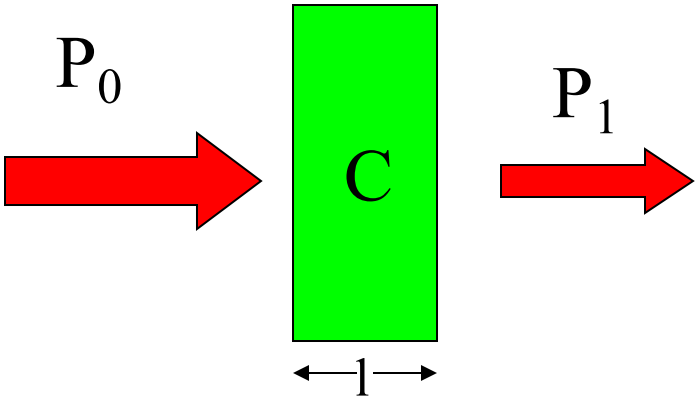
A. Introduction: Absorption spectra



*Broad bands in solution

*Gas-phase spectra and high resolution instruments to obtain narrow bands and fine structure.

B. Beer's law

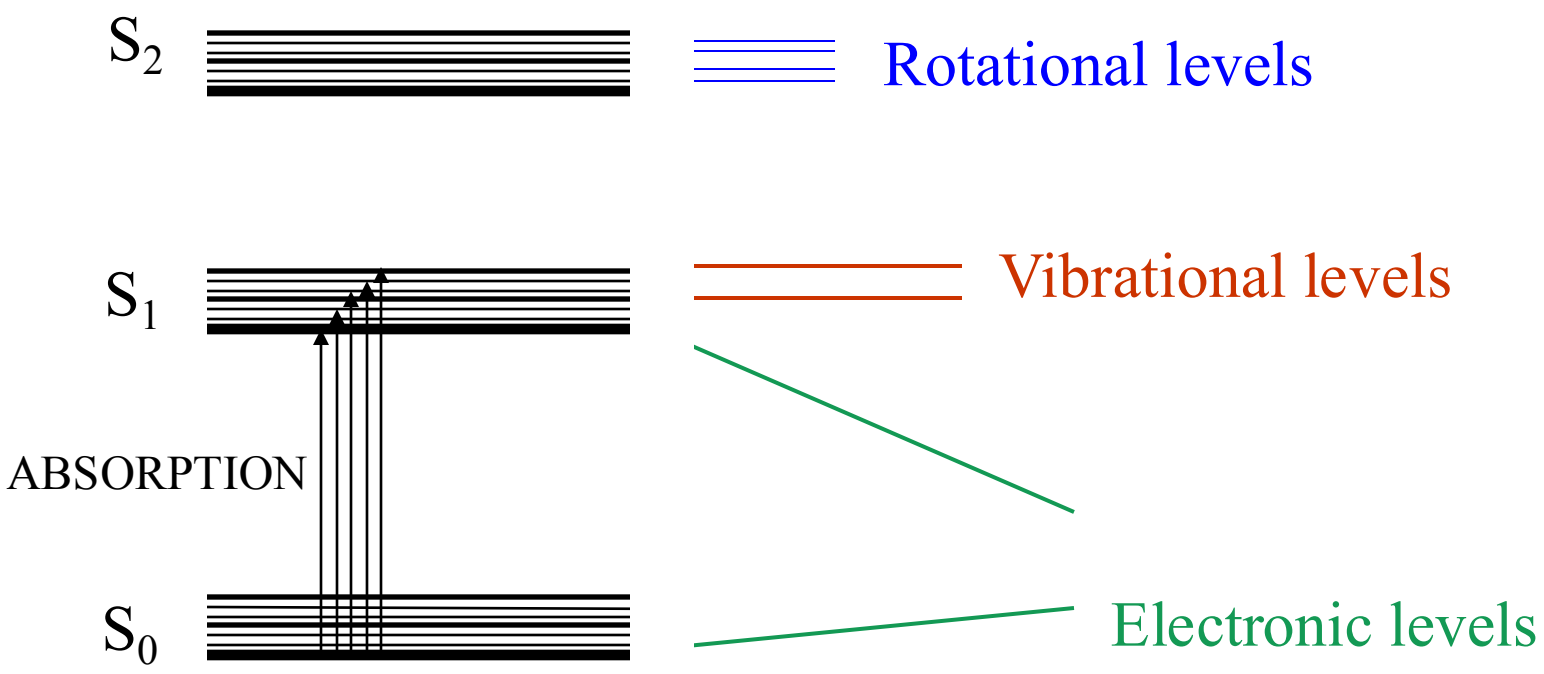


$$A = \alpha \; l \; C$$

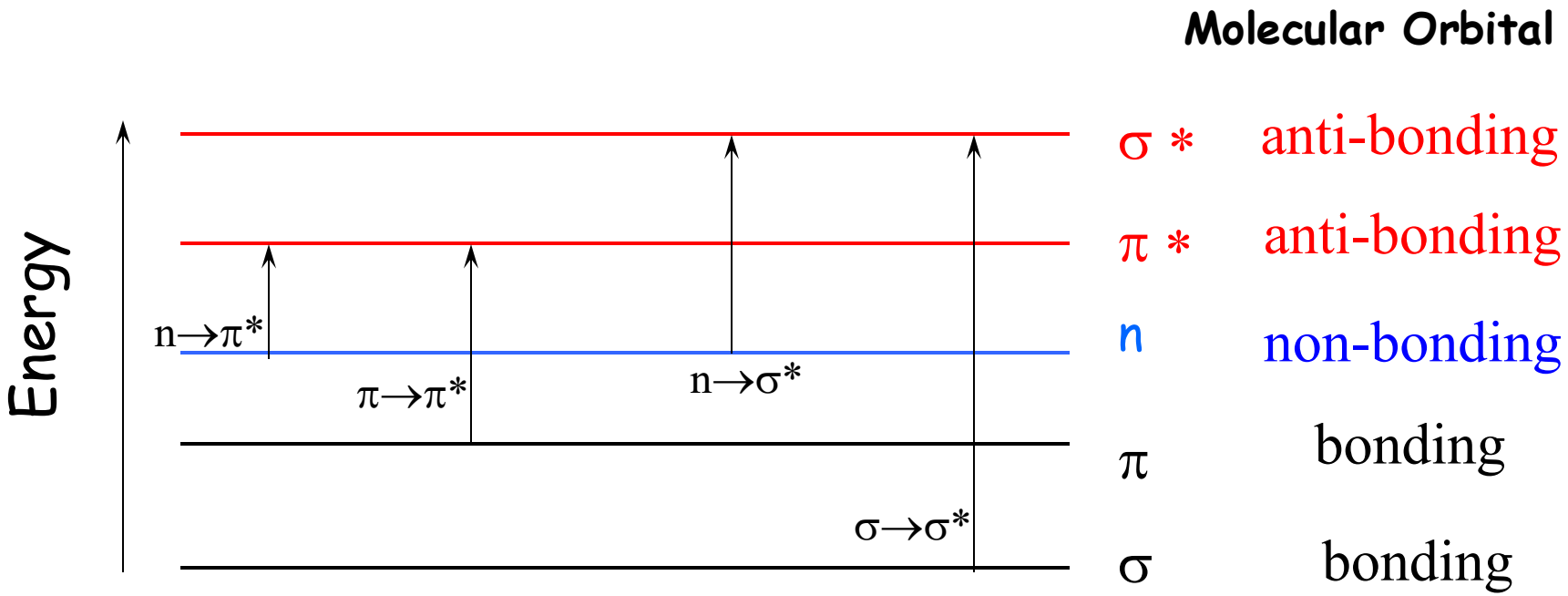
* Path lenght: l (cm)
* Concentration of absorber: C ($mol.L^{-1}$) or ($g.L^{-1}$)
* Absorptivity α (in $L.g^{-1}.cm^{-1}$): C in $g.L^{-1}$
* Molar absorptivity ε (in $L.mol^{-1}.cm^{-1}$): C in $mol.L^{-1}$

C. Absorbing species
Energy states of molecules

$E_{tot} = E_{el} + E_{vib} + E_{rot}$ $E_{el} \approx 100$Kcal $E_{vib} \approx 1$kcal

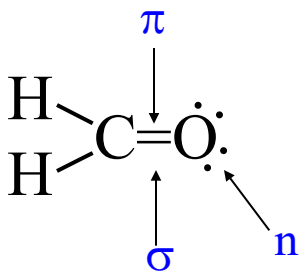


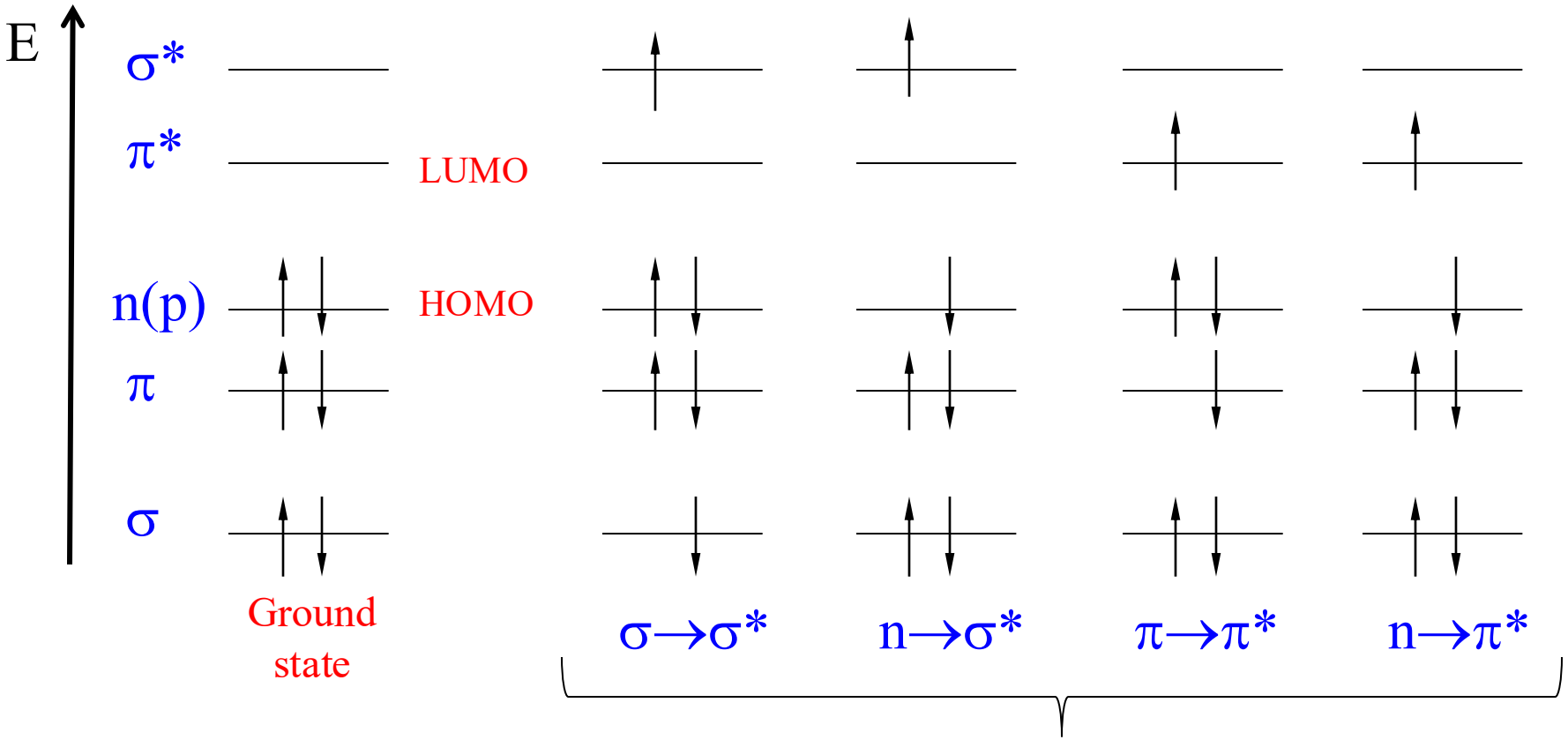
C. Absorbing species
Electronic transitions



$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$$

Example: formaldehyde





C. Absorbing species
Electronic transitions

Transitions of electrons from bonding or non bonding molecular orbitals to empty anti-bonding orbitals.

$\sigma \rightarrow \sigma^*$	ΔE high, excitation at: $\lambda < 150$nm	
$n \rightarrow \sigma^*$	ΔE lower, possible excitation between 150 and 250nm	
$\pi \rightarrow \pi^*$	ε: 1000 – 10000 $cm^{-1}L\ mol^{-1}$	ΔE low, λ between 180 and 700nm
$n \rightarrow \pi^*$	ε: 10 – 100 $cm^{-1}L\ mol^{-1}$	

C. Absorbing species: organic compounds

*All organic compounds contain single bonds and are capable of absorbing electromagnetic radiation at $\lambda<185$nm.

*A limited number of compounds contain valance electrons of low exciting energy that absorb at $\lambda>200$nm : the chromophores

Transitions $\sigma \rightarrow \sigma^*$

compounds	λ_{max}
CH_4	125
$CH_3\,CH_3$	135

Transitions n $\rightarrow \sigma^*$

compounds	λ_{max}	ε_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S$	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

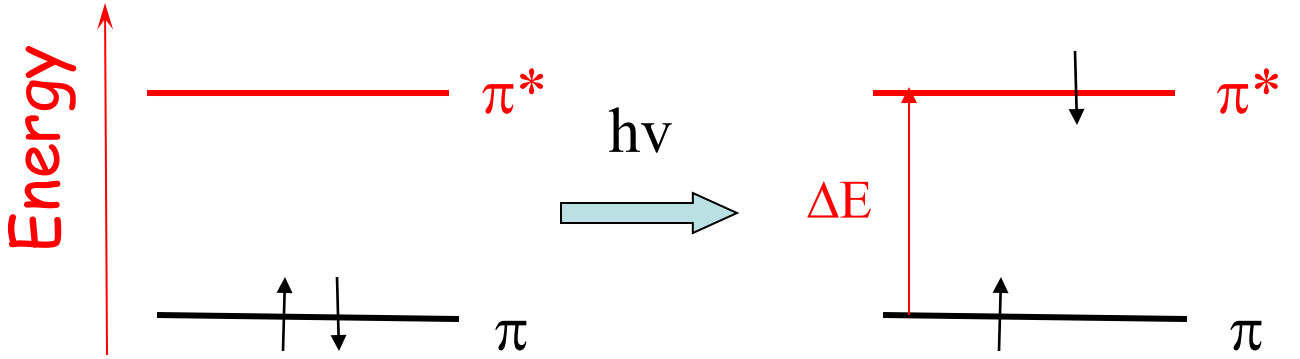
C. Absorbing species: organic compounds

Chromophores: Transitions n → π* and π → π*

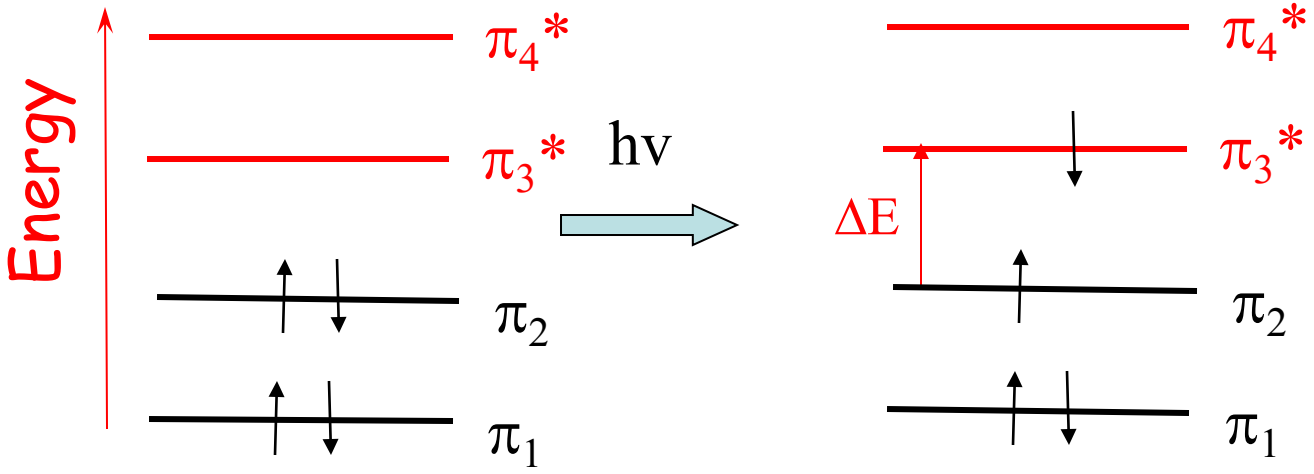
Compound	solvent	λ_{max}	ε_{max}	transition
$C_6H_{13}CH=CH_2$	heptane	177	13000	π →π*
$C_5H_{11}CH\equiv CCH_3$	heptane	178	10000	π →π*
		196	2000	
		225	160	
$CH_3(C=O)CH_3$	hexane	186	1000	n → σ*
		280	16	n →π*
$CH_3(C=O)H$	hexane	180	large	n → σ*
		293	12	n →π*
$CH_3(C=O)OH$	ethanol	204	41	n → π*
$CH_3(C=O)NH_2$	water	214	60	n → π*
$CH_3N=NCH_3$	ethanol	339	5	n → π*
CH_3NO_2	isooctane	280	22	n → π*
$C_2H_5ONO_2$	dioxane	270	12	n → π*

Chromophores: Conjugation effects

C=C



C=C-C=C

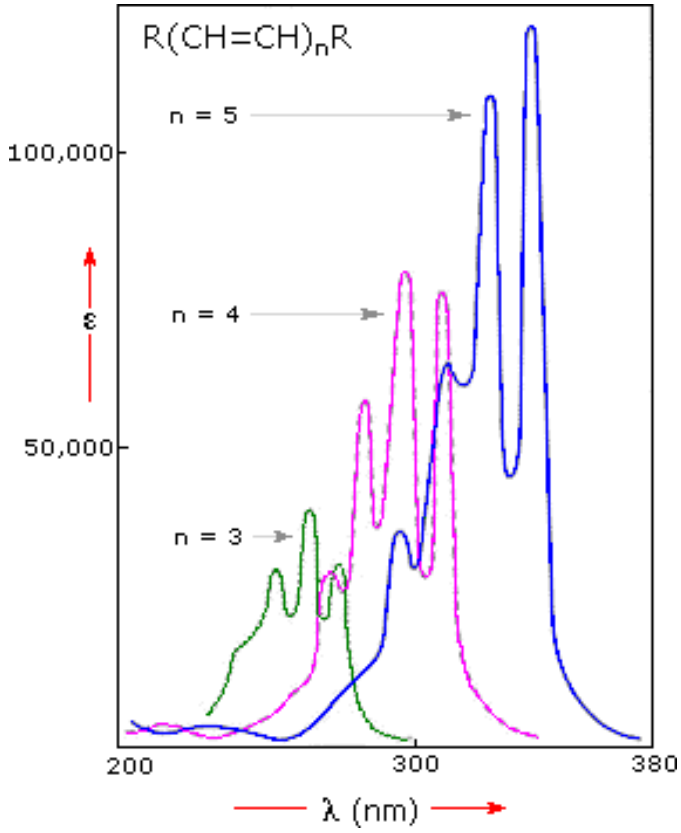


Red shift of 30-50nm

C. Absorbing species: organic compounds

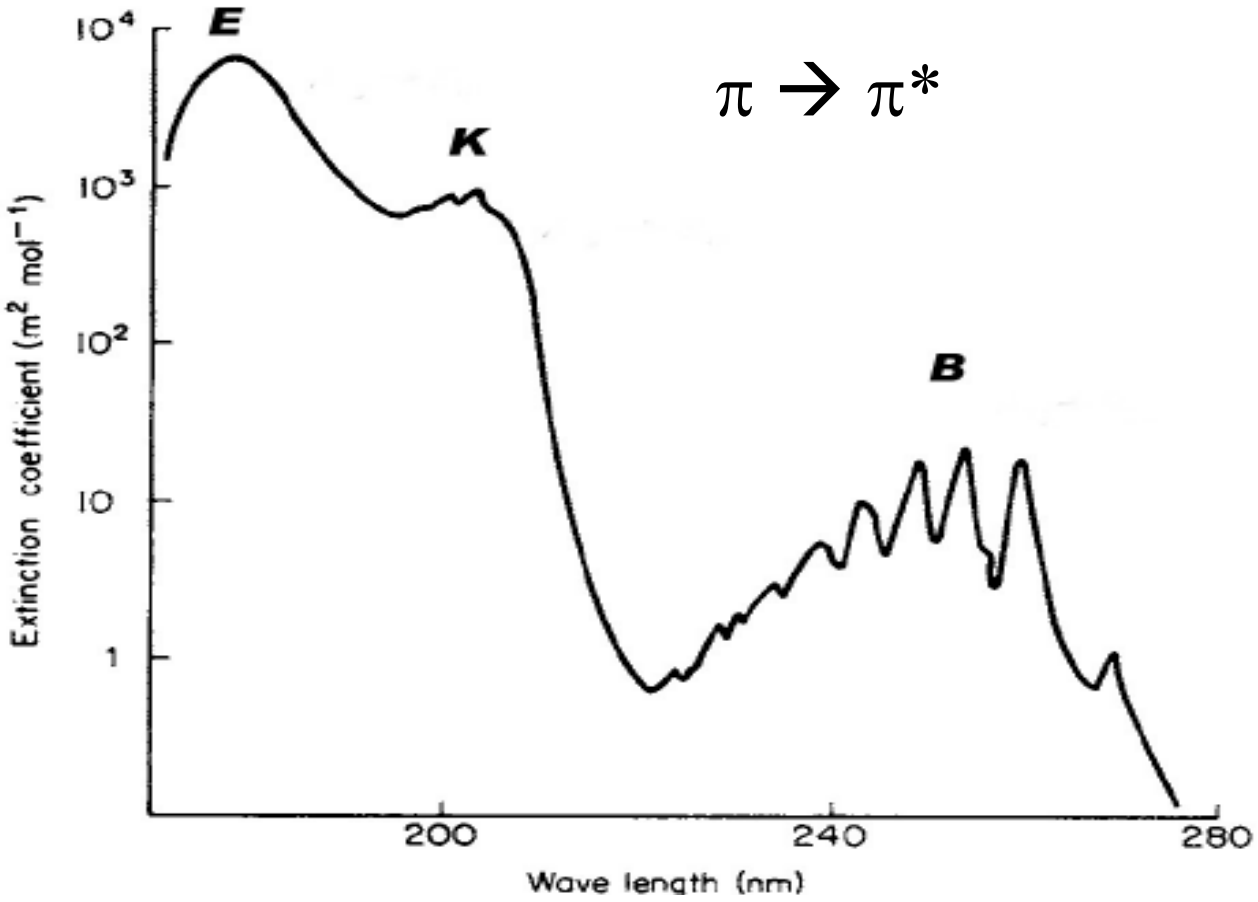
Chromophores: Conjugation effects

Compound	λ_{max}	ε_{max}
$CH_3CH_2CH_2CH=CH_2$	184	10000
$CH_2=CHCH_2CH_2CH=CH_2$	185	20000
$H_2C=CHCH=CH_2$	217	21000
$H_2C=CHCH=CHCH=CH_2$	250	
$CH_3CH_2CH_2CH_2(C=O)CH_3$	282	27
$CH_2=CHCH_2CH_2(C=O)CH_3$	278	30
$CH_2=CH(C=O)CH_3$	324	24
	219	3600



http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

BENZENE

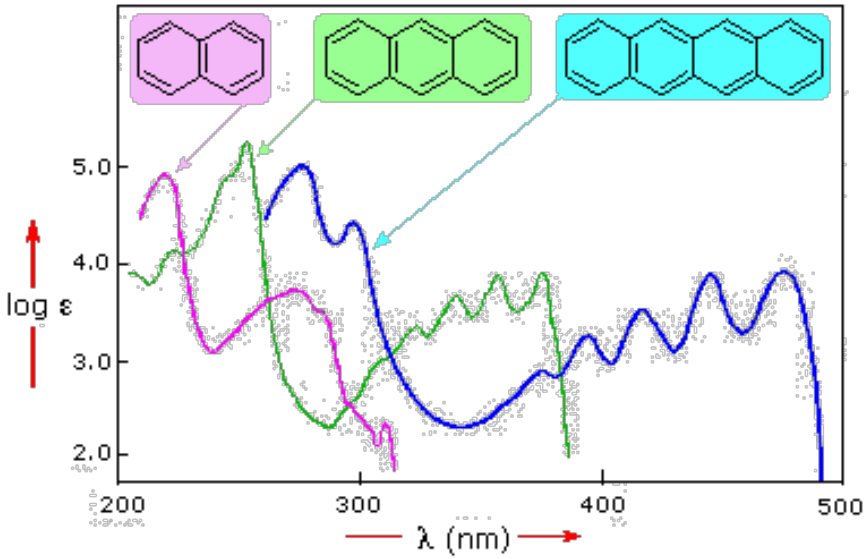


Benzene homologues:

More electronegative the substituent, more pronounced the red shift

Aromatic compounds

Transitions $\pi \rightarrow \pi^*$



http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

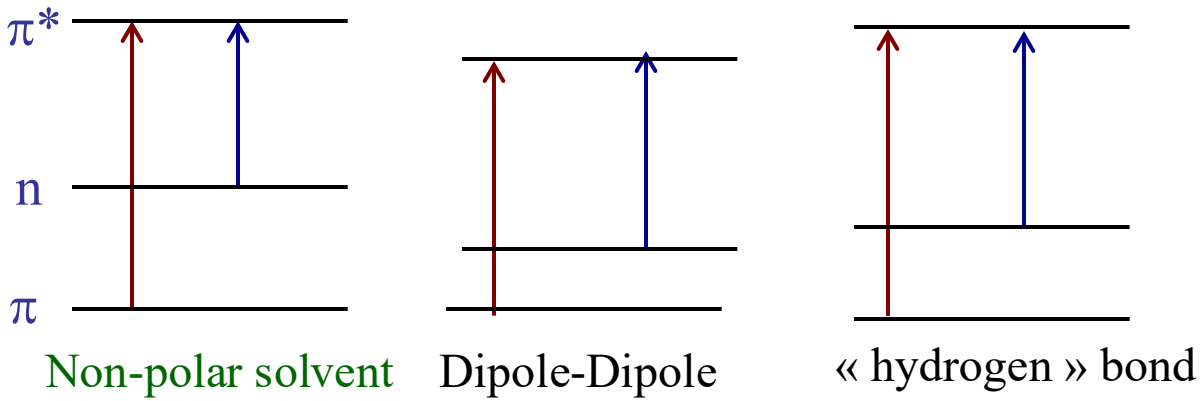
Compound		Band E_2(K)		Band B	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}
Benzene	C_6H_6	204	7900	256	200
Toluene	$C_6H_5CH_3$	207	7000	261	300
M-Xylene	$C_6H_4(CH_3)_2$			263	300
Chlorobenzene	C_6H_5Cl	210	7600	265	240
Phenol	C_6H_5OH	211	6200	270	1450
Phenolate	$C_6H_5O^-$	235	9400	287	2600
Aniline	$C_6H_5NH_2$	230	8600	280	1430
Anilinium	$C_6H_5NH_3^+$	203	7500	254	160
Naphthalene	$C_{10}H_8$	286	9300	312	289
Styrene	$C_6H_5CH=CH_2$	244	12000	282	450

Skoog/Leary, « Principles of Instrumental Analysis » 4th edition, Saunders College Publishing, 1992

C. Absorbing species
Solvent effect

Solute/solvent interactions effect energy levels

Example of ketones (C=O): **n** and π* levels are lower in polar solvents



Modification of the position, intensity and form of bands

⇨ Transition n → π* : more energy required in polar solvents (bleu shift)

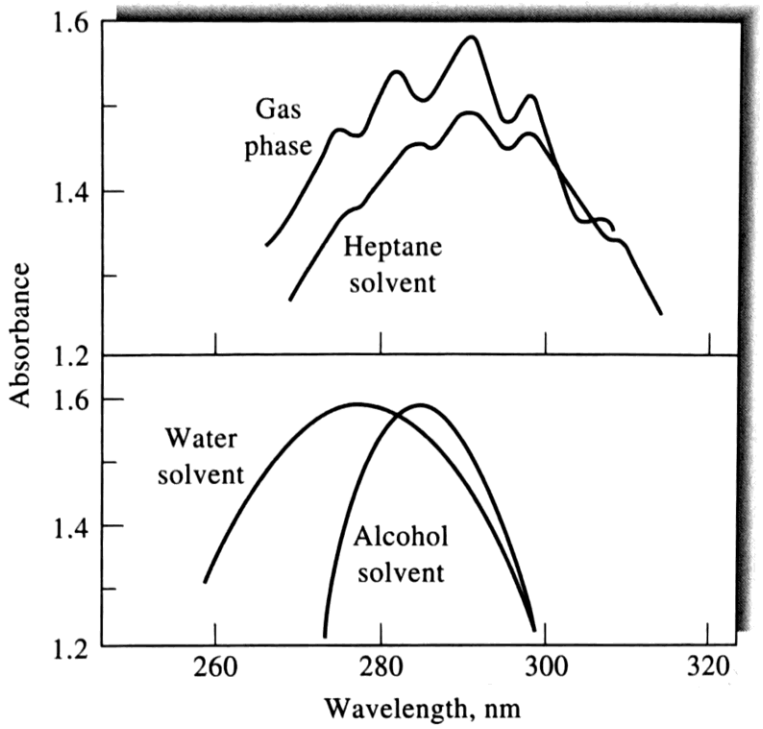
⇨ Transition π → π*: less energy required in polar solvents (red shift)

⇨ Band broadening

C. Absorbing species

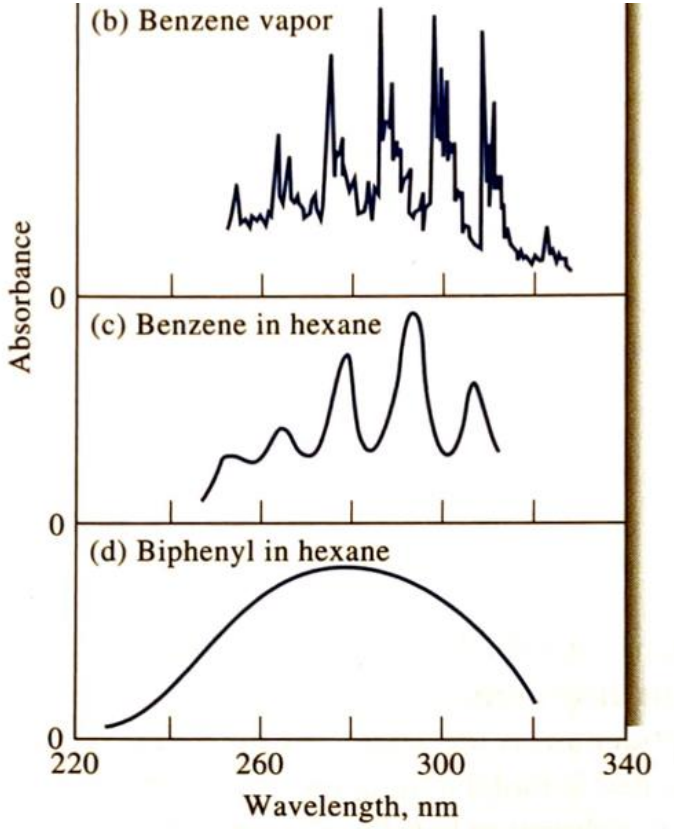
Solvent effect/Qualitative applications

Acetaldehyde



$n \rightarrow \pi^*$

Benzene derivatives



$\pi \rightarrow \pi^*$

According: D. A. Skoog, E. J. Holler, S.R. Crouch, « Principles of Instrumental Analysis », Chap. 6 & 14, 2017, Cengage Learning.

D. Applications
Qualitative applications

Detection of chromophoric groups

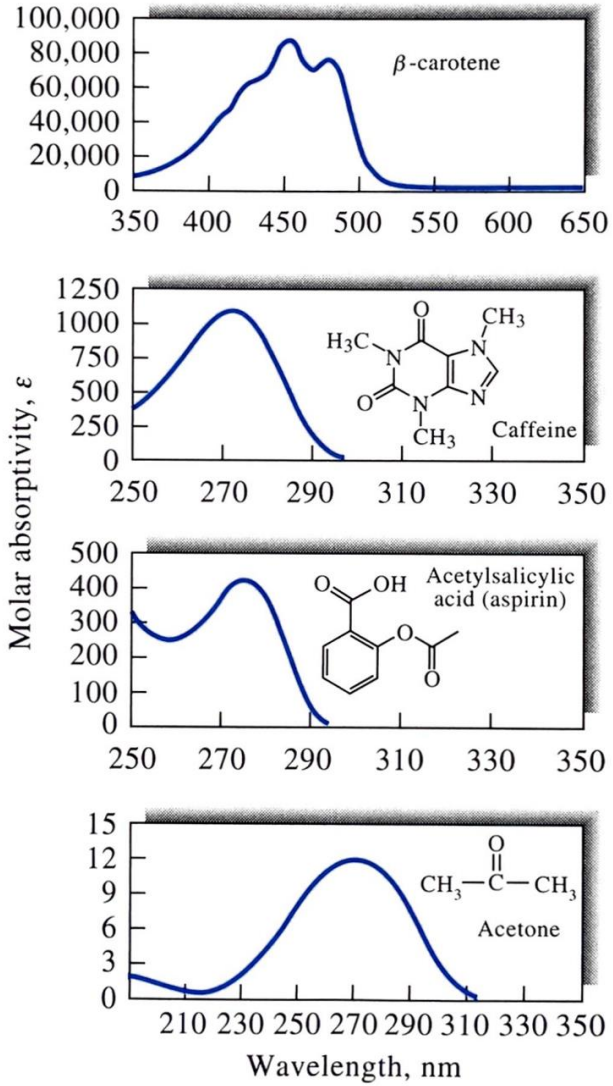
- Absorption in near UV and visible: indication of the presence of unsaturated groups or atoms as sulfur or halogens

*comparison with spectra of simple chromophores for solute identification (same solvent)

*the lack of fine structure and the dependence of the environment limits the applications

*Detection of functional groups

D. Applications
Qualitative applications



Absorption of typical organic compounds

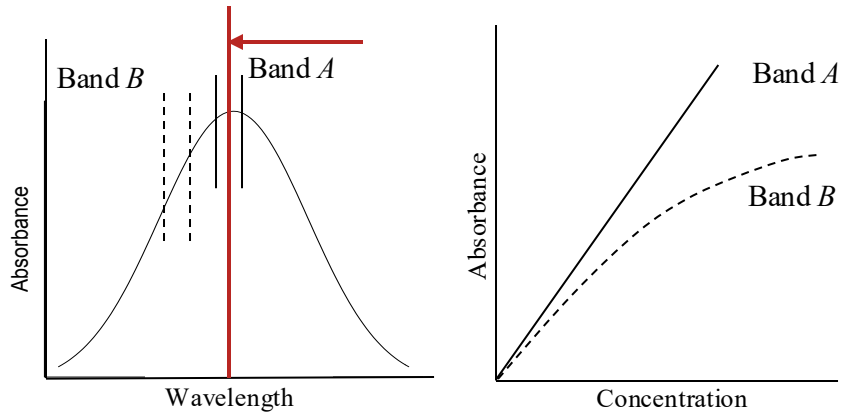
According: D. A. Skoog, E. J. Holler, S.R. Crouch, « Principles of Instrumental Analysis », Chap. 6 & 14, 2017, Cengage Learning.

D. Applications
Quantitative applications

*One of the most used techniques

-wide applicability
-typical LOD: 10^{-4}-10^{-5}M
-moderate to high selectivity
-good accuracy
-ease of data acquisition

*λ selection



➡ Highest sensitivity

➡ linearity

Fluorescence Spectroscopy

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Contents

Molecular Fluorescence

a. Introduction
b. Characteristics of fluorescence emission
c. Fluorescence and chemical structure
d. Applications

A. Introduction
Luminescence

Luminescence: emission of ultraviolet, visible or infrared light from an electronically excited species

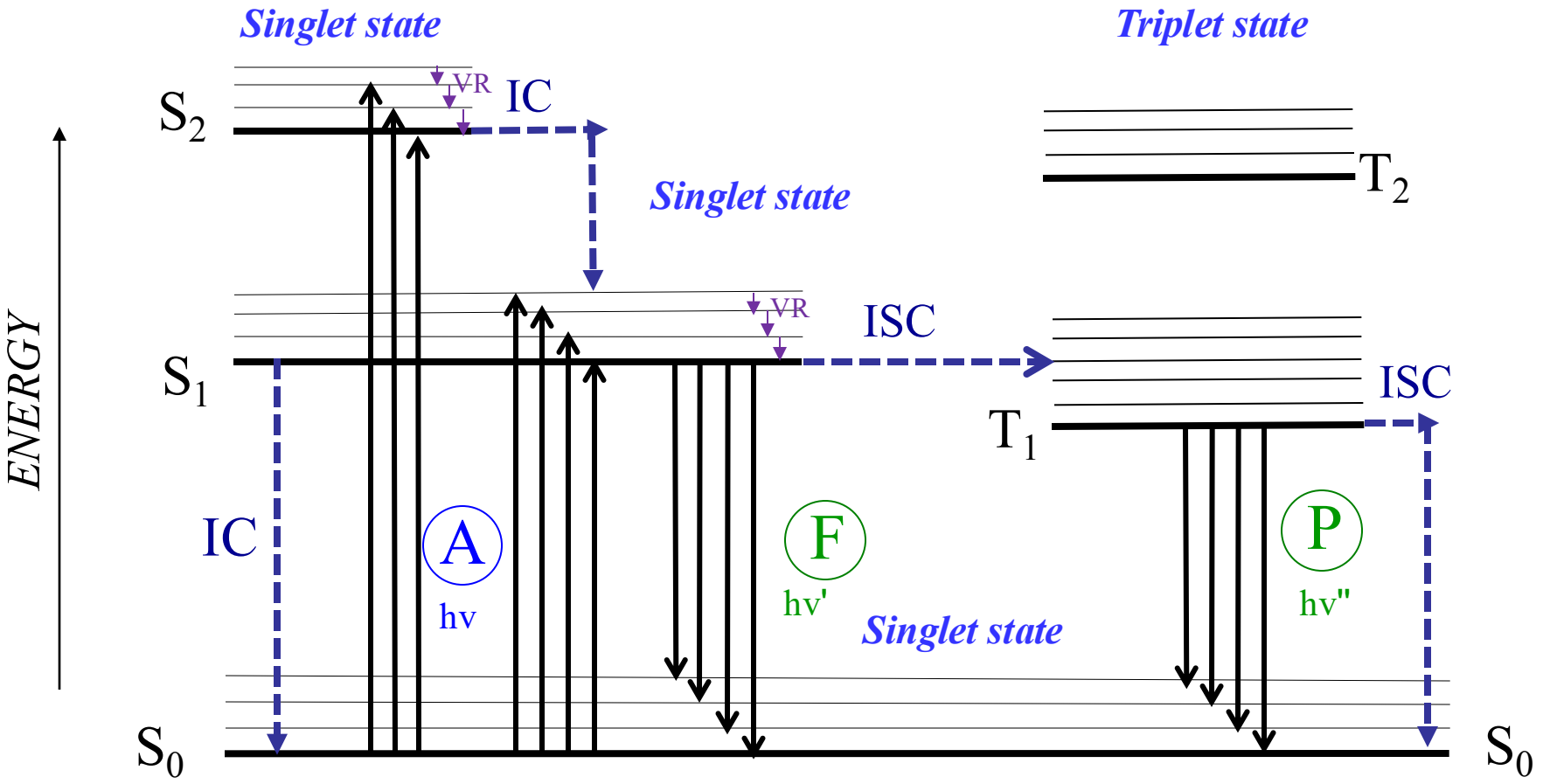
Photoluminescence: the mode of excitation is the absorption of light

- ☆ Fluorescence
- ☆ Phosphorescence

} Photoluminescence
-light UV, visible

B. Characteristics of fluorescence

Perrin-Jablonski diagram



A = Absorption; F = Fluorescence; P = Phosphorescence

$v > v' > v''$

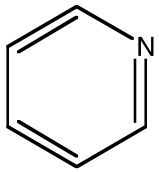
C. Fluorescence and chemical structure

*Molar coefficients 100 à 1000 times higher for transitions $\pi \rightarrow \pi^*$

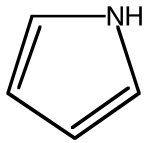
*Lifetime 10^{-7}-10^{-9}s for $\pi \rightarrow \pi^*$ but 10^{-5}-10^{-7}s for $n \rightarrow \pi^*$

*Inter-system crossing rare for π^*

Fluorophores: Aromatic compounds with $\pi \rightarrow \pi^*$ transitions of low energy

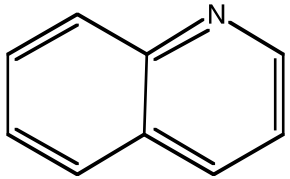


pyridine

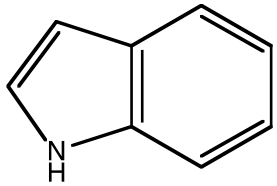


pyrrole

Non fluorescent



quinoline

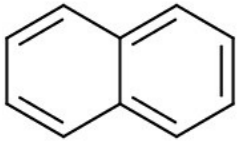


indole

Fluorescent

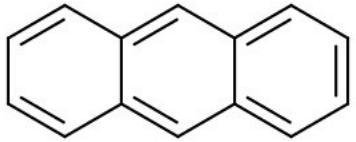
Emission: Extension of electon π conjugation

Naphtalene



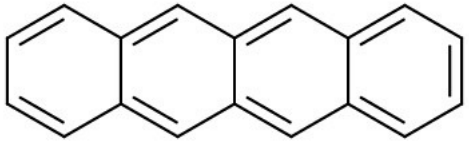
Ultra violet

Anthracene



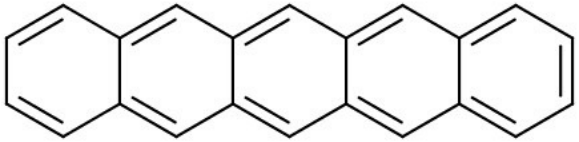
Bleu

Naphthacene



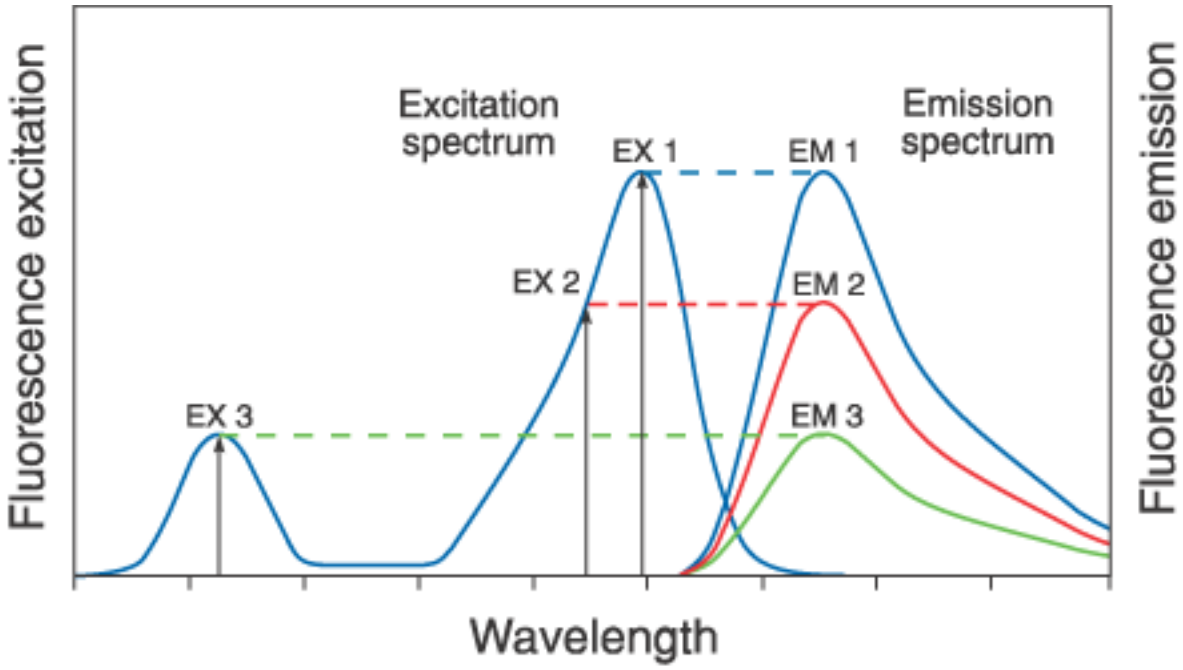
Green

Pentacene



Red

Selection of excitation and emission wavelength



D. Applications: quantitative analysis

Comparison with absorption

-lower detection limits (10 to 1000 times lower)
-increased selectivity
-limited applications

References

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