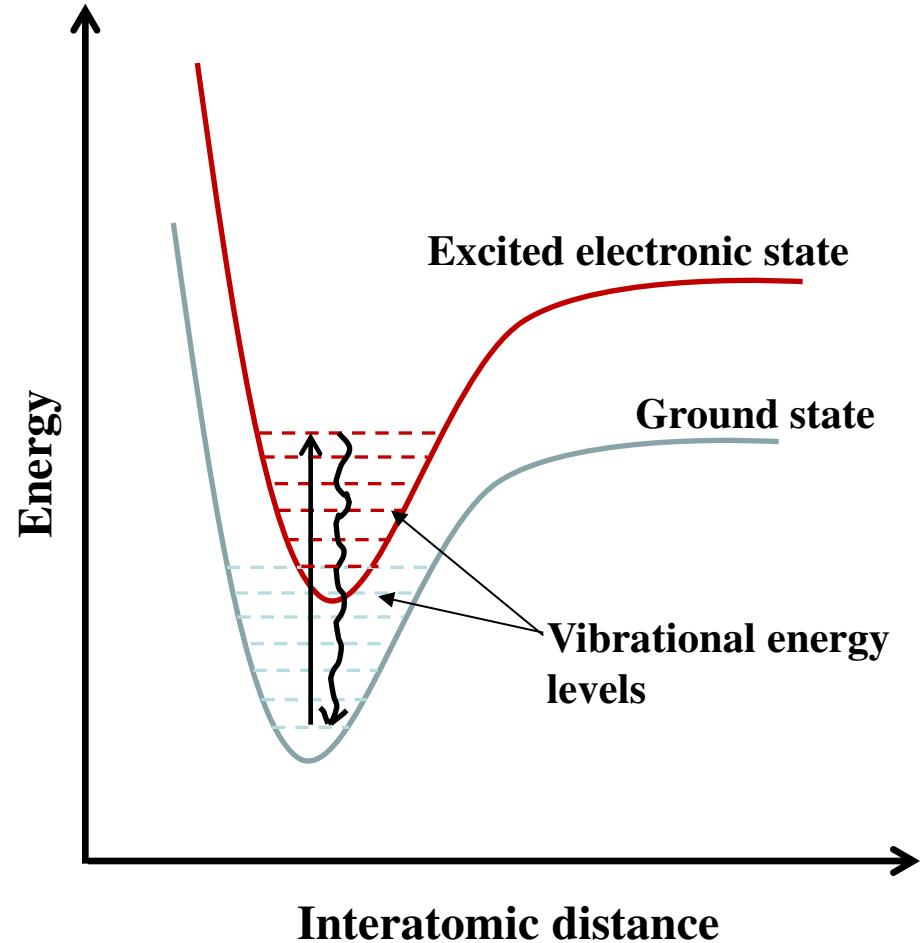


UV-Visible spectroscopy

- Absorption of light in the UV/Visible part of the spectrum (210 – 900 nm).
- The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels.
- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO).

Introduction

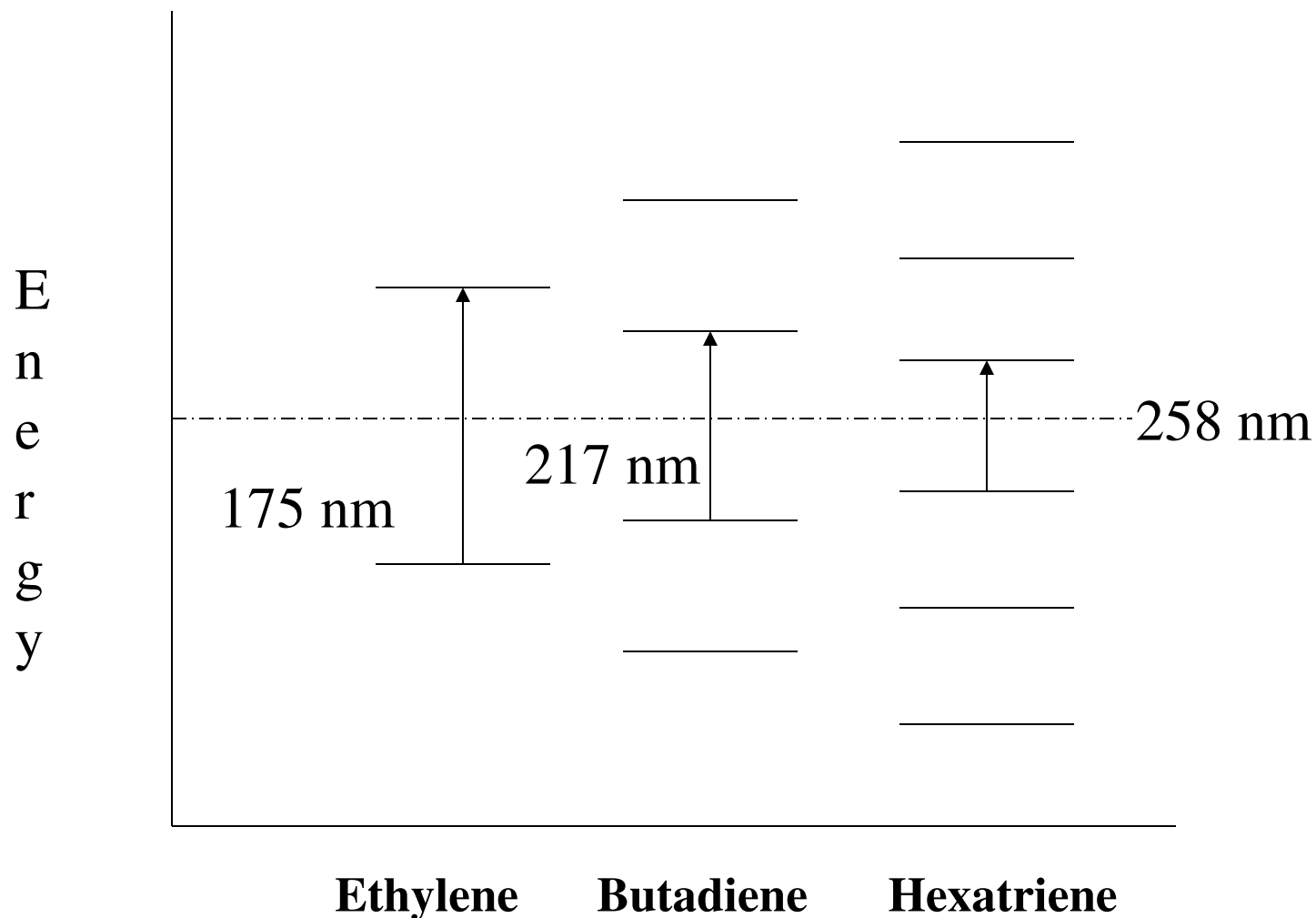
- Probes the various excited states of the system.
- Light in the UV-VIS part of the spectrum is used to promote electrons from the ground state to various excited states.
- The particular frequencies at which light is absorbed are effected by the structure and environment of the **chromophore** (light absorbing species).
- Excited electrons can return to the ground state by vibrational transitions through smaller energy increments.
- Absorbed energy appears ultimately as heat in solution.



Effect of substituents on the absorption spectra

- Bathochromic shift (red shift): a shift to lower energy or longer wavelength.
- Hypsochromic shift (blue shift): a shift to higher energy or shorter wavelength.
- Hyperchromic effect: An increase in intensity.
- Hypochromic effect: A decrease in intensity.

The effect of conjugation of alkene



Energies are quantized

$$E = \frac{1}{2}mV^2$$

$$p^2 = m^2V^2$$

$$E = \frac{p^2}{2m}$$

$$E = \frac{h^2}{2m\lambda^2}$$

$$\lambda = 2L/n$$

$$E = \frac{n^2h^2}{8mL^2}$$

A Discreet set of energy levels

There is a discreet set of energy levels for a given mass, m , and a given box length, L . As the quantum number n takes on values, 1, 2, 3, etc., the energies are

$$\frac{h^2}{8mL^2}, \frac{4h^2}{8mL^2}, \frac{9h^2}{8mL^2}, \text{ etc.}$$

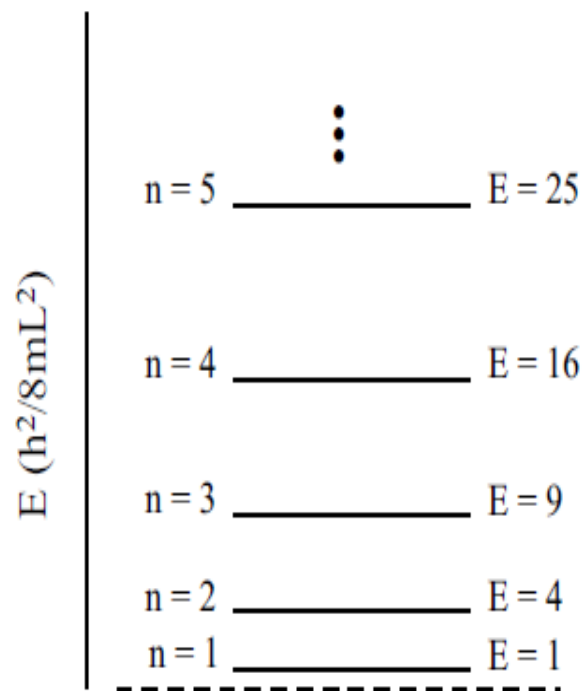


FIGURE 8.6. Particle in a box energy levels. The quantum number is n . E is the energy, which increases as the square of the quantum number. The energy is plotted in units of $h^2/8mL^2$, so that it is easy to see how the energy increases. The dashed line is zero energy. The lowest energy level does not have $E = 0$, in contrast to a classical particle in a box.

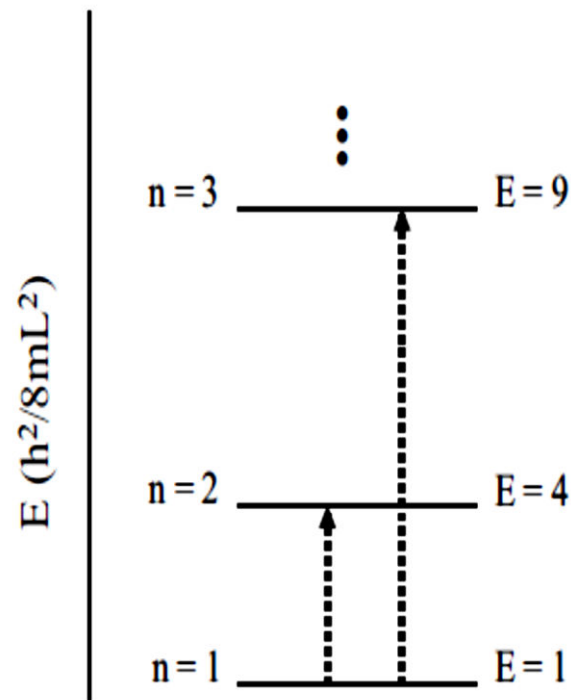


FIGURE 8.7. Particle in a box energy levels. The quantum number is n . E is the energy plotted in units of $h^2/8mL^2$. The arrows indicate absorption of photons that can take an electron from the lowest energy level, $n = 1$, to higher energy levels, $n = 2$, $n = 3$, etc. For a photon to be absorbed, its energy must match the difference in energy between two energy levels.

Why are Cherries Red and
Blueberries blue ?

The Colour of Fruit

Let's put in numbers. $h = 6.6 \times 10^{-34}$ J-s. The electron mass, $m_e = 9.1 \times 10^{-31}$ kg. For the length of the box, let's take L to be that of a medium-sized molecule, that is, $L = 0.8 \times 10^{-9}$ m (0.8 nanometers, 0.8 nm). Then,

$$\Delta E = \frac{3(6.6 \times 10^{-34})^2}{8(9.1 \times 10^{-31})(0.8 \times 10^{-9})^2} = 2.8 \times 10^{-19} \text{ J}.$$

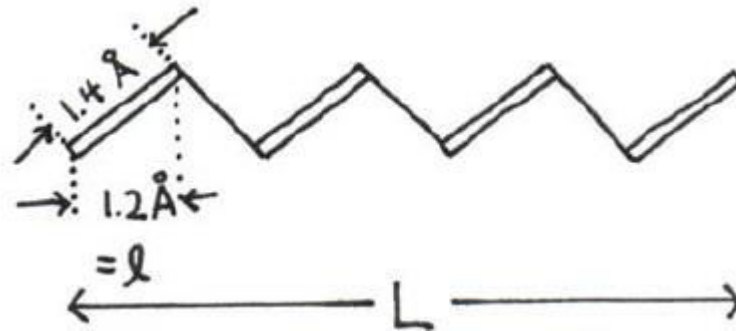
This energy corresponds to

$$\lambda = 7.06 \times 10^{-7} \text{ m} = 706 \text{ nm} \quad \Rightarrow \quad \text{Deep Red Colour}$$

If $L=0.7$ nm, $\lambda=540$ nm ~~—Green Colour~~

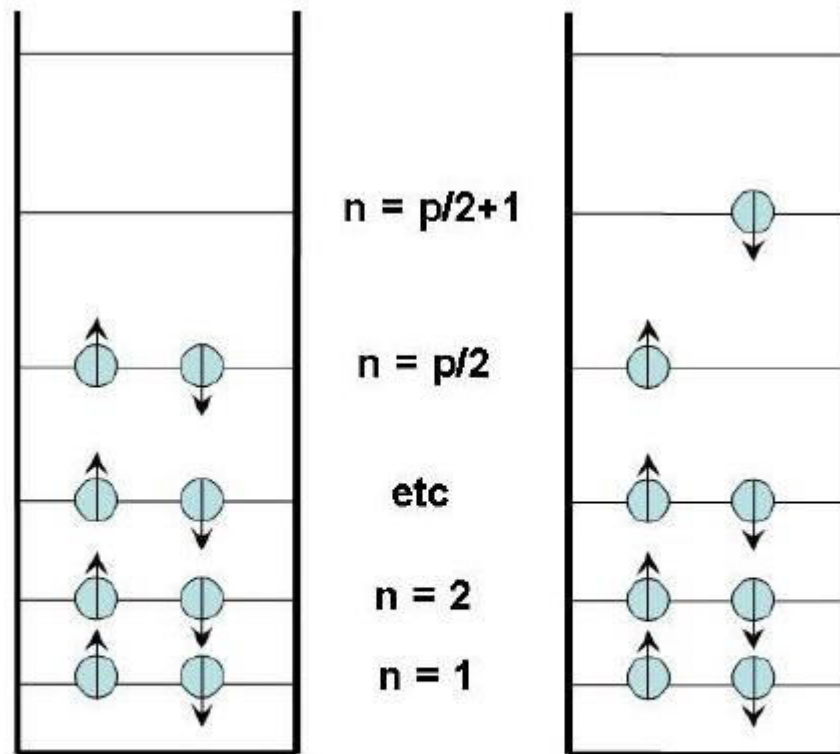
If $L=0.6$ nm, $\lambda=397$ nm ~~—Blue Colour~~

Estimating pigment length



Assumptions:

- Each atom in the path of conjugation contributes one electron to the quantum energy levels inside the box.
- By Pauli's Exclusion Principle, only two electrons can occupy the same energy state. To have the same energy, they must have opposite spins.
- A typical bond length in the path of conjugation is 1.4 \AA .



**GROUND STATE
OF THE MOLECULE**

**1ST EXCITED STATE
OF THE MOLECULE**

$$\begin{aligned}
 \Delta E_{\text{electron}} &= \frac{(j^2 - i^2)h^2}{8mL^2} \\
 &= \frac{\left[\left(\frac{p}{2} + 1 \right)^2 - \left(\frac{p}{2} \right)^2 \right] h^2}{8m((p-1)l)^2} \\
 &= \frac{(p+1)}{(p-1)^2} \frac{h^2}{8ml^2}
 \end{aligned}$$

Since $E_{\text{photon}} = \Delta E_{\text{electron}}$,

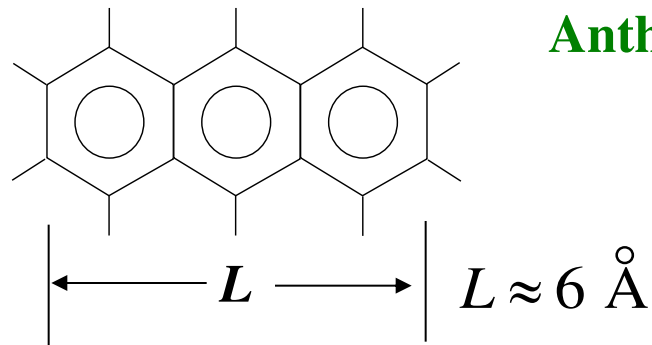
$$\frac{hc}{\lambda_{\text{photon}}} = \frac{(p+1)}{(p-1)^2} \frac{h^2}{8ml^2} .$$

Canceling an h on both sides gives us,

$$\frac{c}{\lambda_{\text{photon}}} = \frac{(p+1)}{(p-1)^2} \frac{h}{8ml^2} .$$

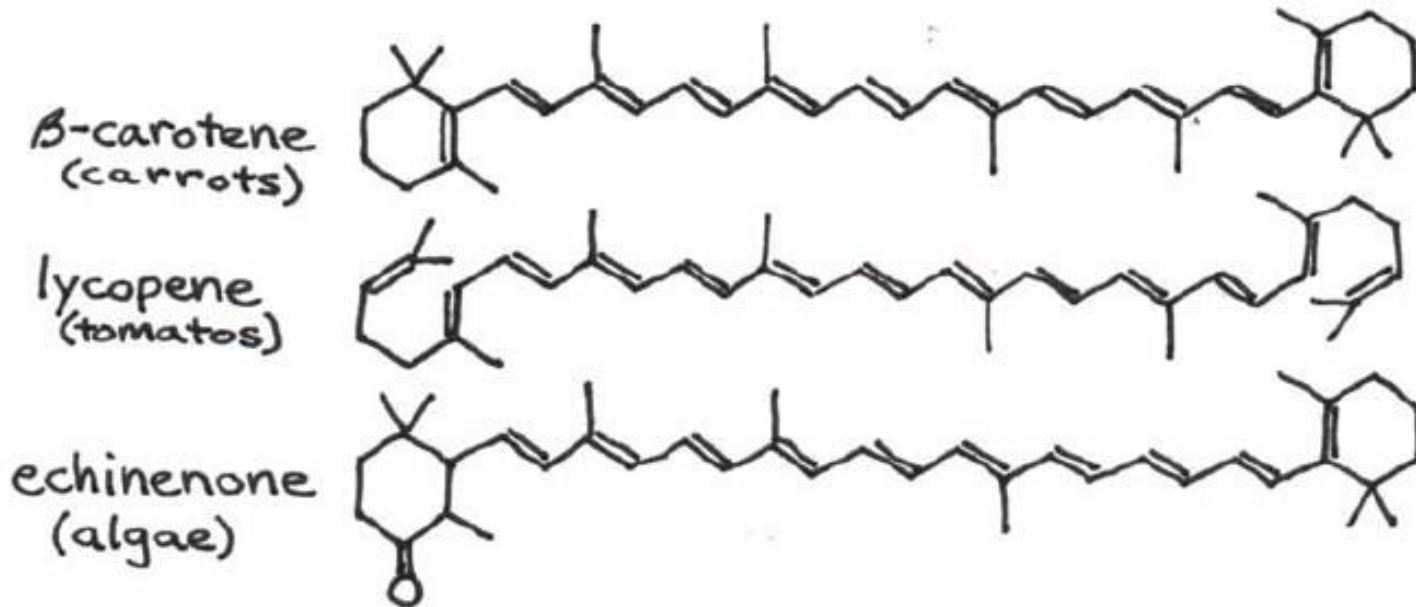
Wavelength of transition for Anthracene

Particle in a Box \longrightarrow Simple model of molecular energy levels.



π electrons – consider “free”
in box of length L .
Ignore all coulomb interactions.

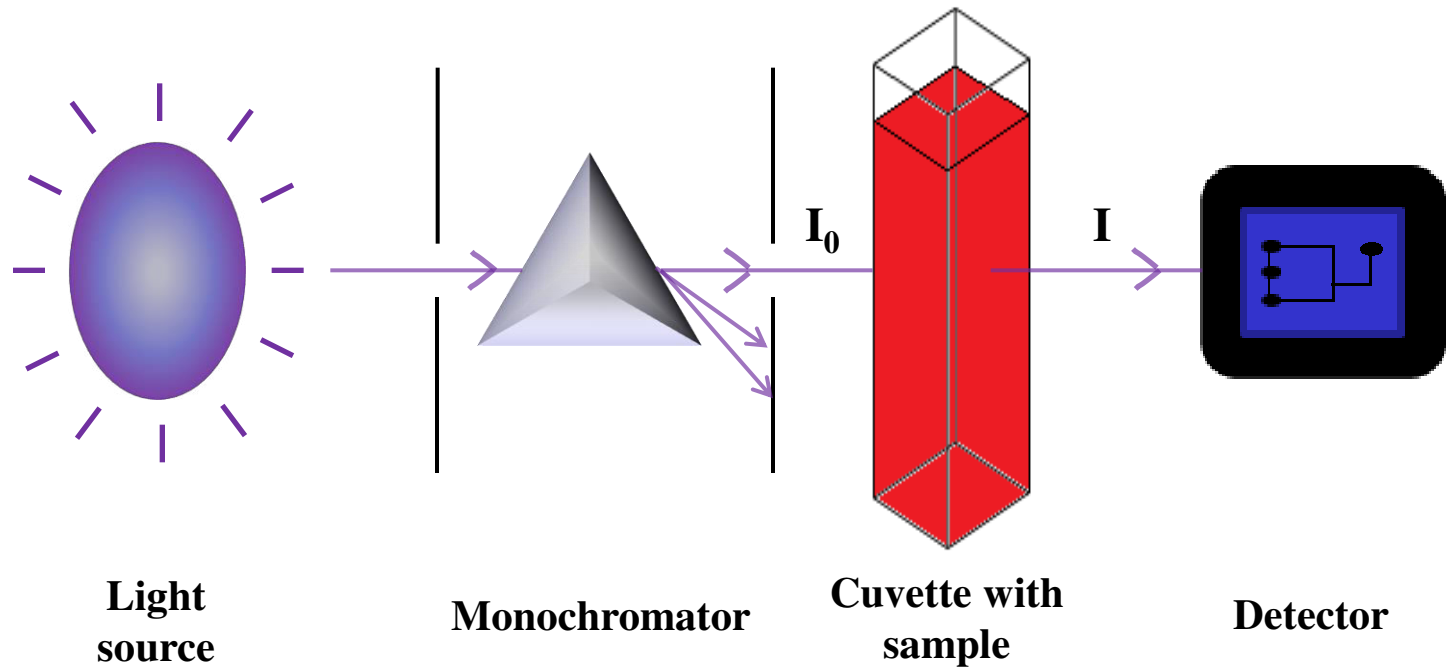
Pigments and Quantum mechanics



High degree of conjugation!!

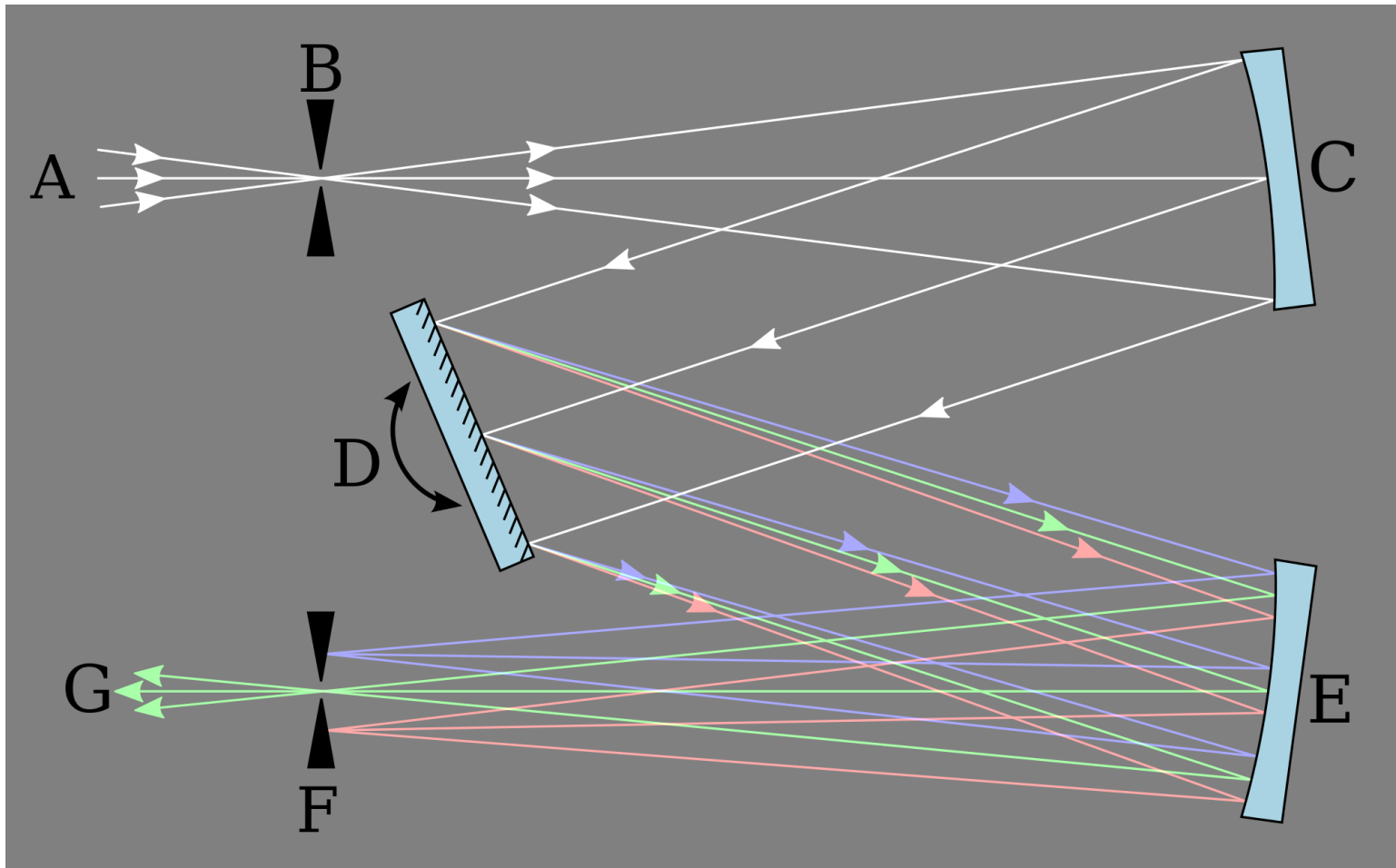
- Electrons have wave properties and they don't jump off the pigments when they reach its ends.
- These electrons resonances determine which frequencies of light and thus which colors, are absorbed & emitted from pigments

Experimental Set Up



- Various designs of spectrophotometers : Fixed and variable wavelength; Single, split and double beam
- Cuvettes: Glass or plastic – visible
Quartz – visible, UV
Acrylic – visible, UV

Monochromator

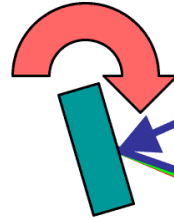


Monochromator

source

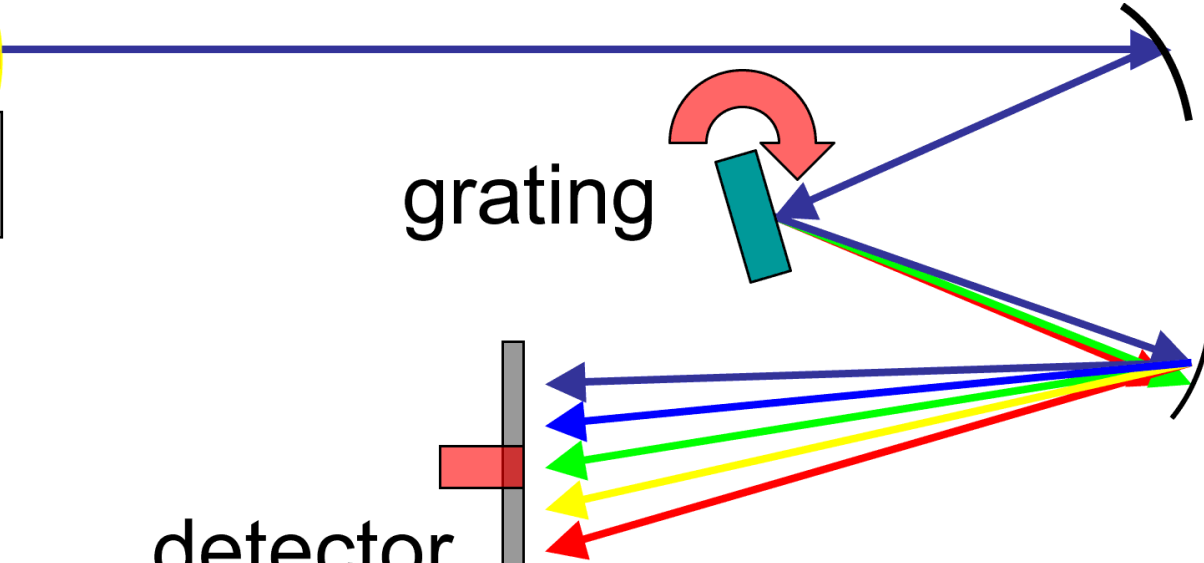
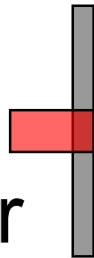


grating

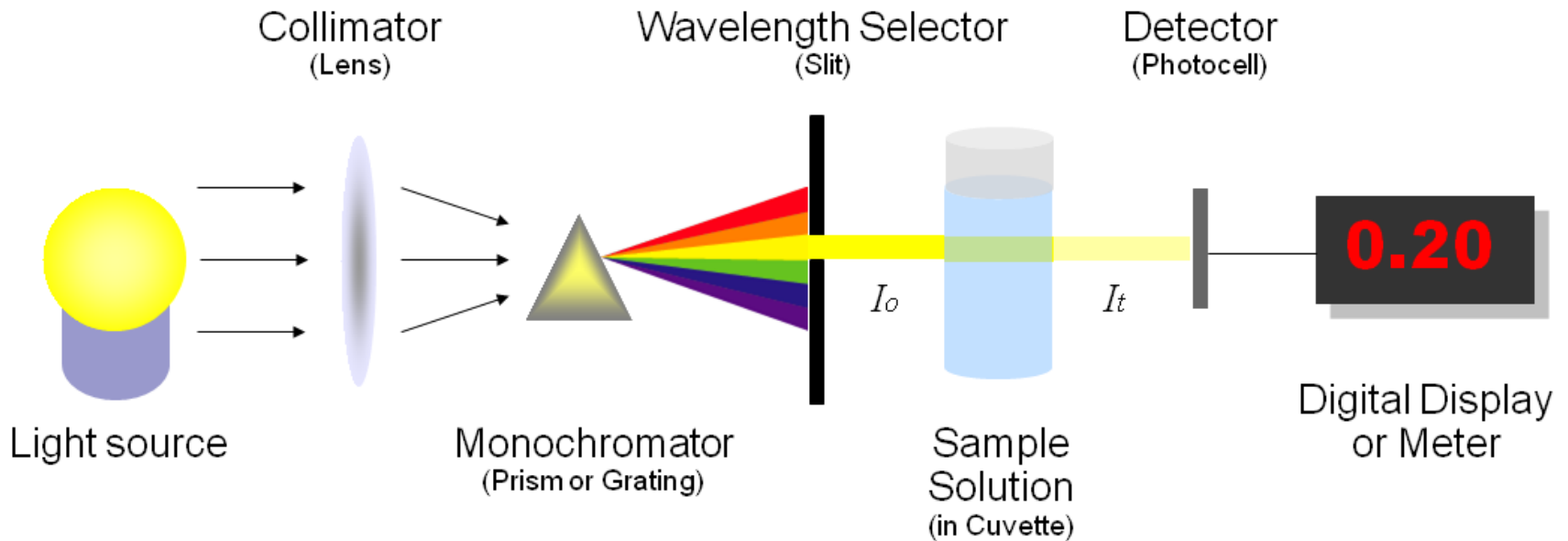


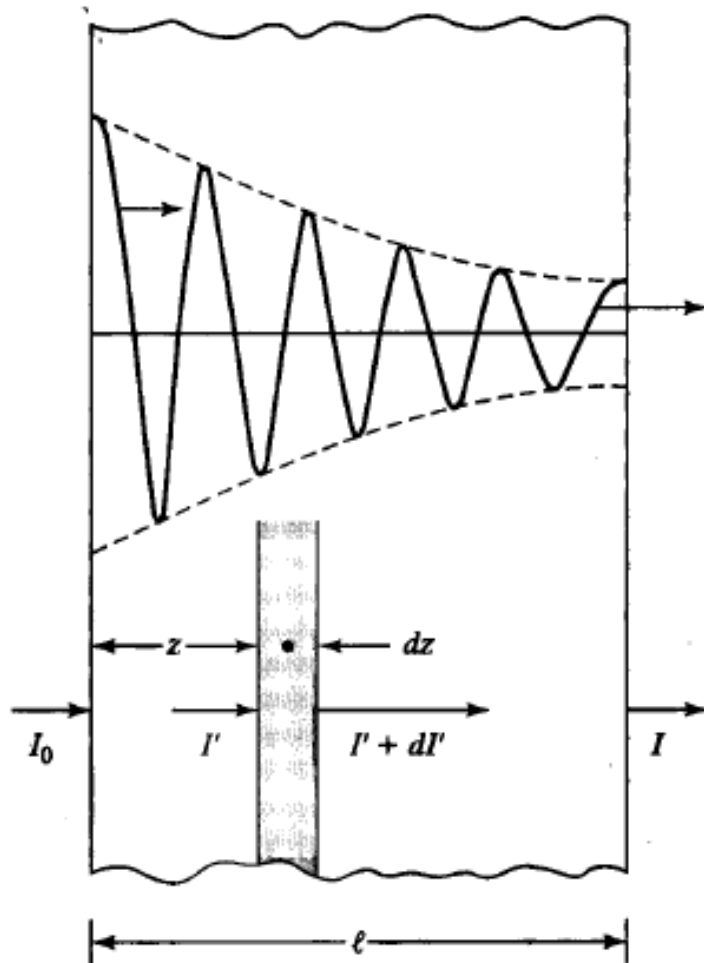
mirrors

detector



Instrumentation





$$\frac{dI}{I} = -\sigma c dl$$

$$\int_{I_0}^I \frac{dI}{I} = -\int_0^l \sigma c dl$$

$$\ln \frac{I}{I_0} = -\sigma c l$$

$$-\log \frac{I_0}{I} = -\log T = 2.303 \cdot \sigma c l$$

$$A = \epsilon l c$$

$$A = \epsilon \cdot b \cdot c$$

A - absorbance

b - length of light path through the sample

c - sample concentration

ϵ - molar absorptivity

Absorbance and the Beer – Lambert Law

The intensity of light decreases exponentially as it passes through an absorbing medium. The **absorption**, A is defined as $\log(I_0/I)$, where I_0 is the intensity of the incident light and I is the intensity of the transmitted light.

The Beer – Lambert law quantifies the process of absorption. At a given wavelength,

$$A = \epsilon cl$$

ϵ is the **Molar Extinction Co-efficient**. It is a constant for the absorbing species and defines the absorption of the species at a particular wavelength. It is determined by the number & type of chromophores present in each molecule of the absorbing species.

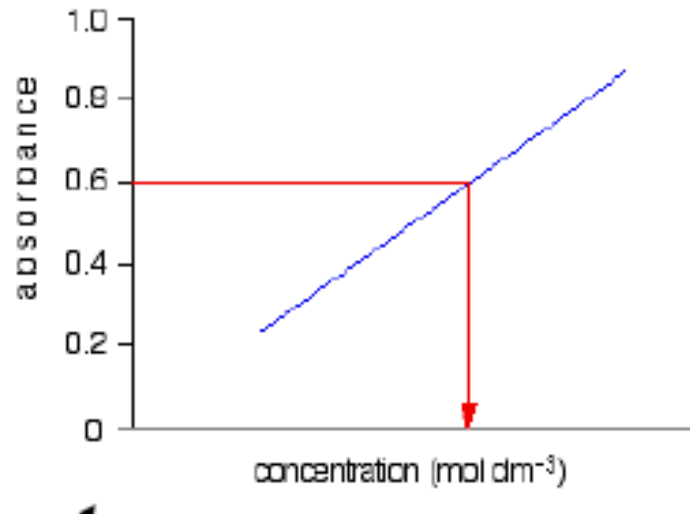
c is the **Concentration** of the sample in the cuvette.

l is the **length of the light path** through the sample.

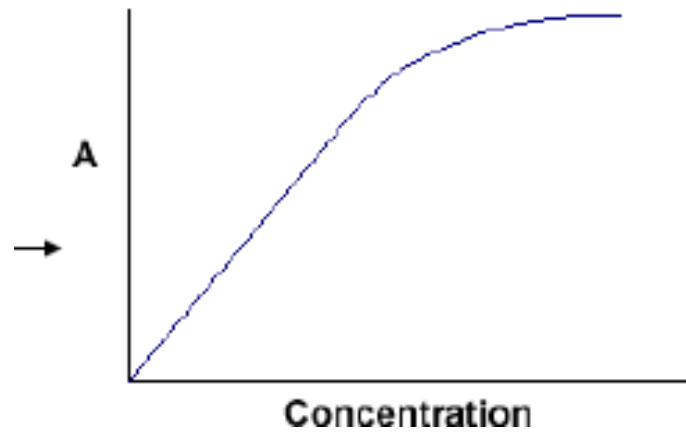
Absorbance is an additive property. The absorbance of a mixture of n species is given by,

$$A_{mixture} = \sum_{i=0}^n A_i$$

According to the Beer-Lambert Law, absorbance is proportional to concentration, and Absorbance versus concentration plot is a straight line.



Deviation from Lambert's Beer Law

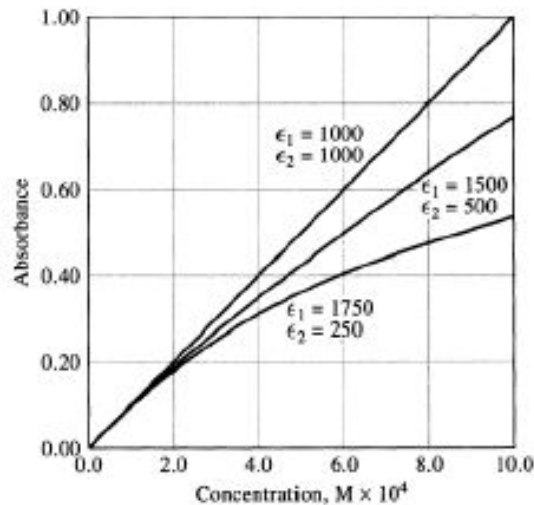
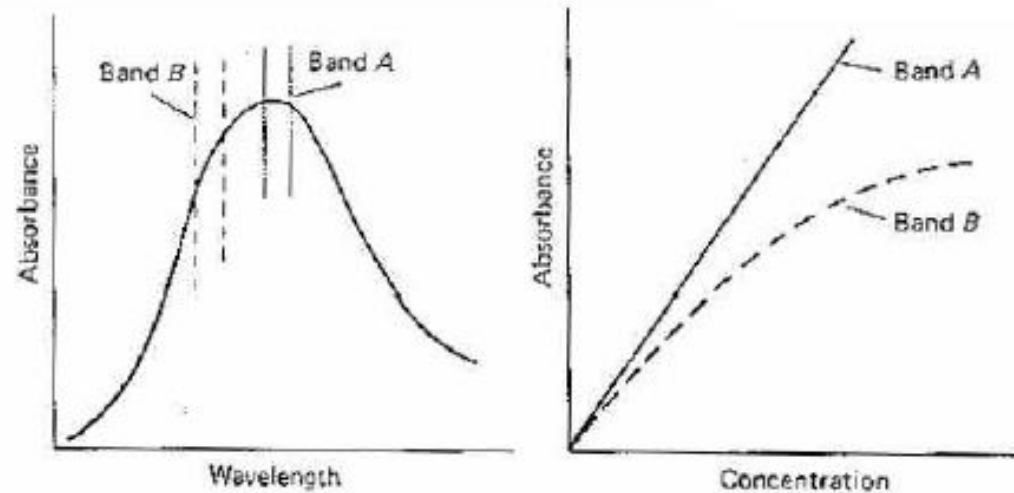


Limits to Beer's Law: Chemical Deviations

- high concentration:
 - particles too close
 - average distance between ions and molecules are diminished
 - affect the charge distribution and extent of absorption.
 - cause deviations from linear relationship.
- chemical interactions: dissociation or reaction with the solvent

Limits to Beer's Law: Instrumental Deviations

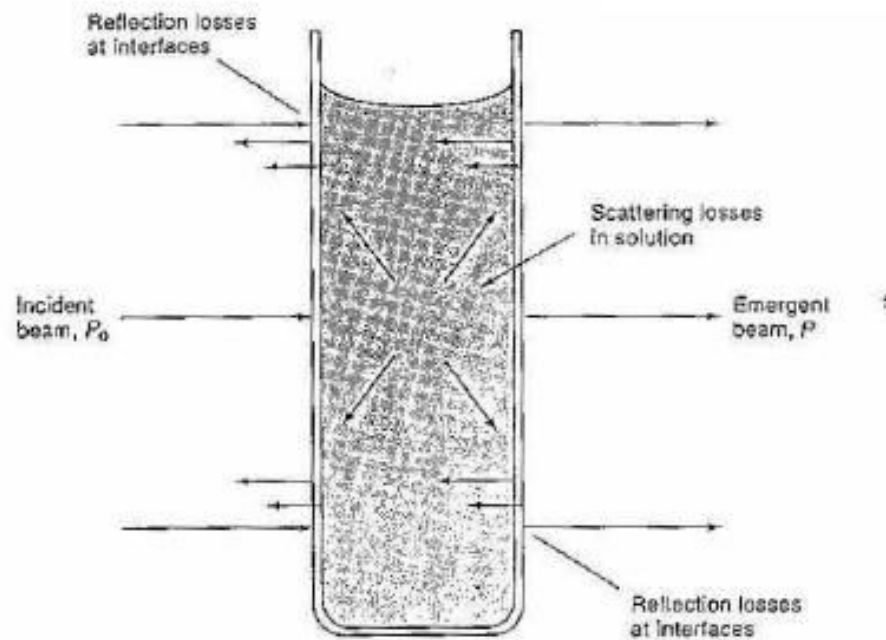
- **non-monochromatic radiation**: deviation of calibration curve from linearity



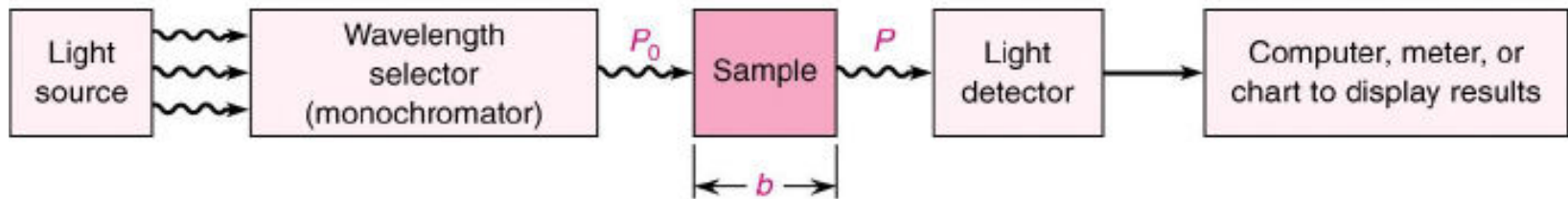
- **stray light** (policromatic light): if a significant amount of the light passed through the sample contains wavelengths that have much lower extinction coefficients than the nominal one, the instrument will report an incorrectly low absorbance.

Limits to Beer's Law: Experimental Deviations

- reflections, scattering, etc. modify the reported absorption.

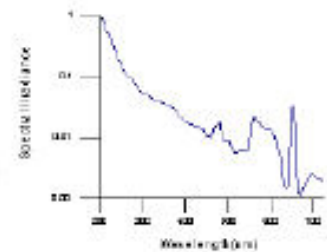


Instrumentation



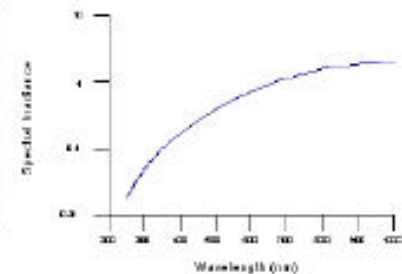
Light Source

Deuterium Lamps — a truly continuous spectrum in the **ultraviolet region** is produced by electrical excitation of deuterium at low pressure. (160nm~375nm)



Deuterium Lamps

Tungsten Filament Lamps — the most common source of **visible and near infrared radiation**.



Tungsten Lamp

The Franck-Condon principle:

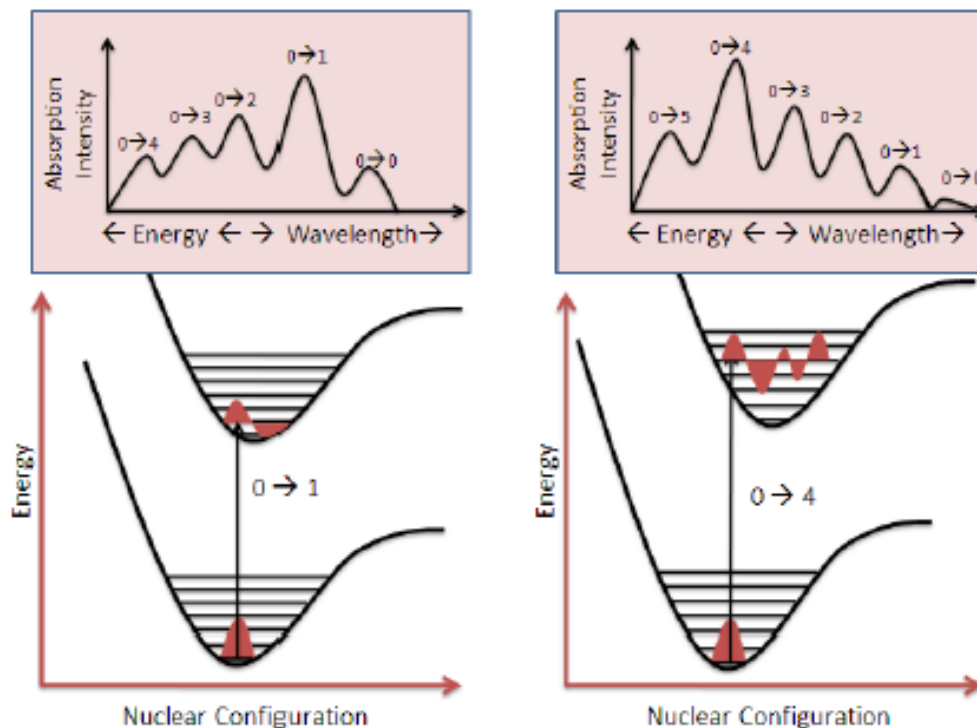
“Since electronic transitions occur **very rapidly** ($\approx 10^{-15}$ s), vibration and rotation of the molecule do not change the internuclear distance appreciably during the transition”.

The intensity of a transition is greatest for the largest of the vibrational wavefunctions.

In view of the Franck-Condon principle, electronic transitions occur “**vertically**” on a potential energy diagram.

Franck-Condon principle → explains the intensity of vibronic transitions

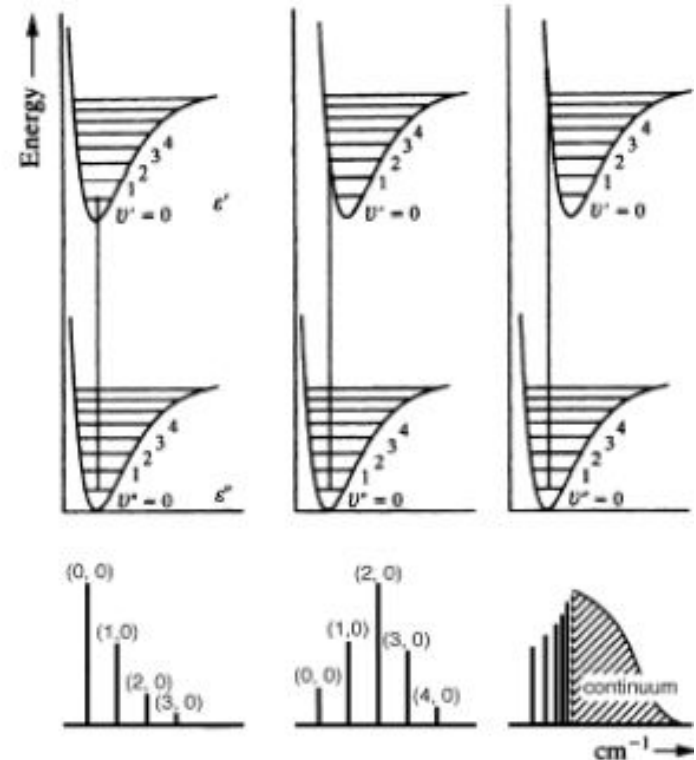
An electronic transition occur without changing the position of nuclei in the molecule.



(1) If the internuclear distances in the upper and lower states are equal ($r_e'' \approx r_e'$), the most probable transition is (0, 0) (left). However, there is a non-zero probability of (1, 0), (2, 0), (3, 0) etc. transitions. The successive lines will therefore have rapidly diminishing intensities.

(2) If the excited electronic state has a slightly larger nuclear separation than the ground state ($r_e' > r_e''$), the most probable (and thus most intense) transition is (2, 0) (center). The intensities of the neighbouring transitions are lower.

(3) When the excited electronic state has a considerably larger nuclear separation than the ground state ($r_e' \gg r_e''$) (right), the vibrational state to which the transition takes place has a high v' value. Further, transitions can occur to levels where the molecule has energy in excess of its dissociation energy.



From such states the molecule will dissociate without any vibrations and, since the fragments which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum results.

Types of electronic transitions:

- A. Transitions involving electrons π , σ and n
- B. Transitions involving charge transfer
- C. Transitions involving electrons d and f

A. Organics: Involving π , σ , n electrons

Saturated compounds

$\sigma \rightarrow \sigma^*$ (<150 nm), $n \rightarrow \sigma^*$ (<250 nm): deep UV

Double bonds/unsaturated systems

less energy to π^*

$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions: (200-700 nm)

B. Metal-ligand complexes: charge transfer transition

Electron moves between ligand and metal.

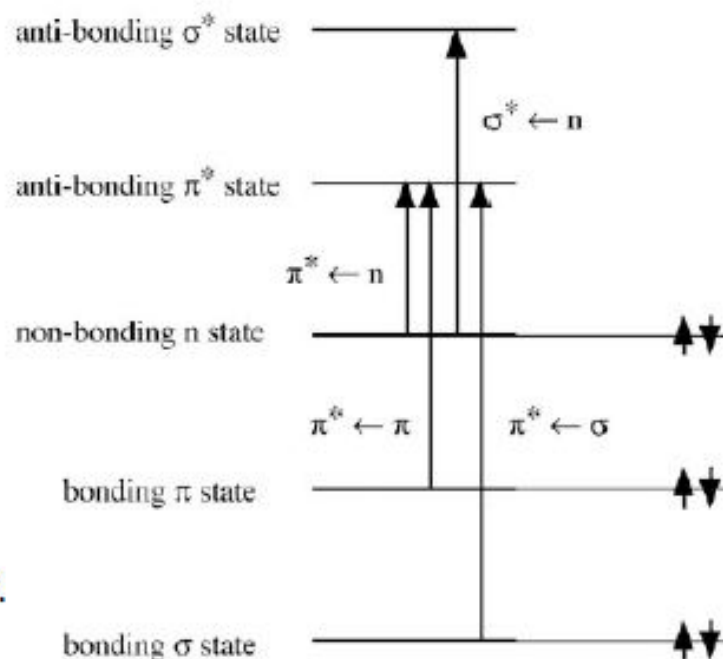
One must act as donor and other as acceptor.

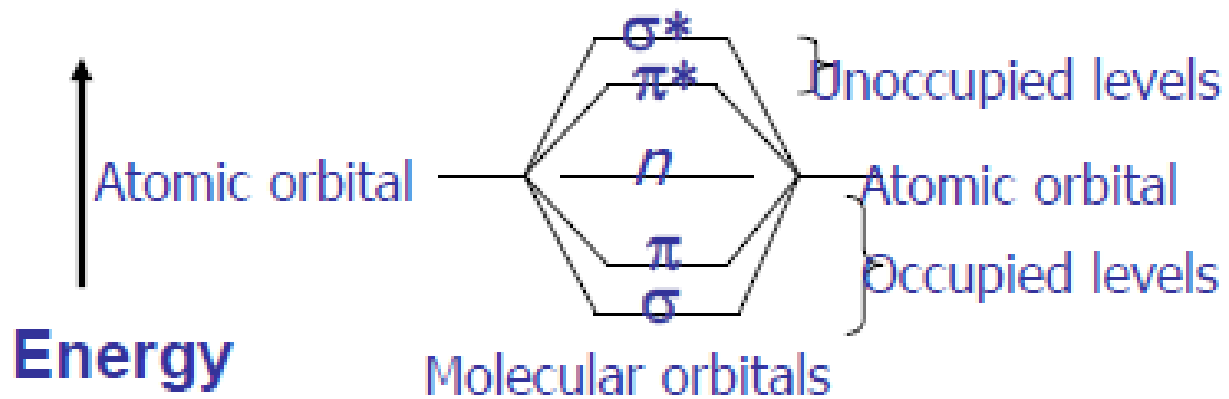
C. Inorganics: d-d transition

Additionally, transitions between d orbitals split by presence of ligand field.

Usually in visible.

The electronic structure of CH_2O



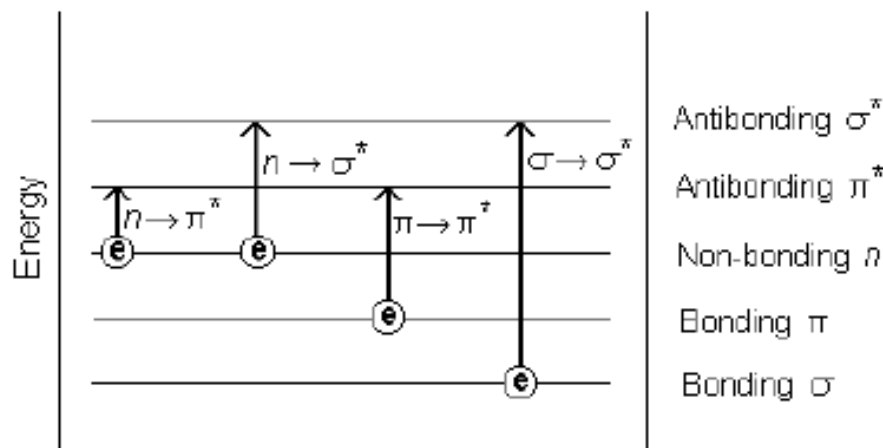


A. Transitions involving electrons π , σ and n

$\sigma \rightarrow \sigma^*$ transitions

The energy of this transitions is big. The corresponding maxima does not appear in specific UV-Vis spectra (200 - 700 nm). (UV absorption!)

Ex: CH_4 (only C-H bond) allows only $\sigma \rightarrow \sigma^*$ transition.
The maximul of absorption is at 125 nm.



$n \rightarrow \sigma^*$ transitions

Saturated compounds containing atoms with unpaired electrons (nonbonding electrons) allows $n \rightarrow \sigma^*$ transitions. The energy necessary for those transitions is less than the energy needed for $\sigma \rightarrow \sigma^*$ transitions. Transitions may be initiated by radiation in the wavelength 150-250 nm.

The number of organic functional groups which have the maximum of absorption in UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

Most absorption bands of **organic compounds** are due to electronic transitions from fundamental levels n or π on the excited levels π^* . Absorption bands for these transitions fall in the 200 nm - 700 nm region. These transitions require the presence, in the molecule, of an *unsaturated group which has π electrons*.

$n \rightarrow \pi^*$ transitions have low molar absorptivity ($\epsilon \sim 10 - 100 \text{ L/mol}\cdot\text{cm}$).

$\pi \rightarrow \pi^*$ transitions have **high molar absorptivity** ($\epsilon \sim 1.000 - 10.000 \text{ L/mol}\cdot\text{cm}$).

The **solvent** could influence the positions of absorption bands.

With **increasing polarity** $n \rightarrow \pi^*$ transitions are shifted to lower wavelengths (**blue shift**). This shift is due to unpaired electrons (orbital energy decreases n)

With **increasing polarity** $\pi \rightarrow \pi^*$ transitions are often (not always) shifted to higher wavelengths (**red shift**). This is caused by *attractive polarization forces between the solvent and absorbent*, which determine the **decrease of ground and excited states energy**. This decrease is greater for excited state than for fundamental state, so the difference in energy between the two levels decreases, resulting in a shift of the absorption band to higher wave numbers (red shift).

This effect also influences $n \rightarrow \pi^*$ transitions but is covered by the blue shift due to *unpaired electrons*.

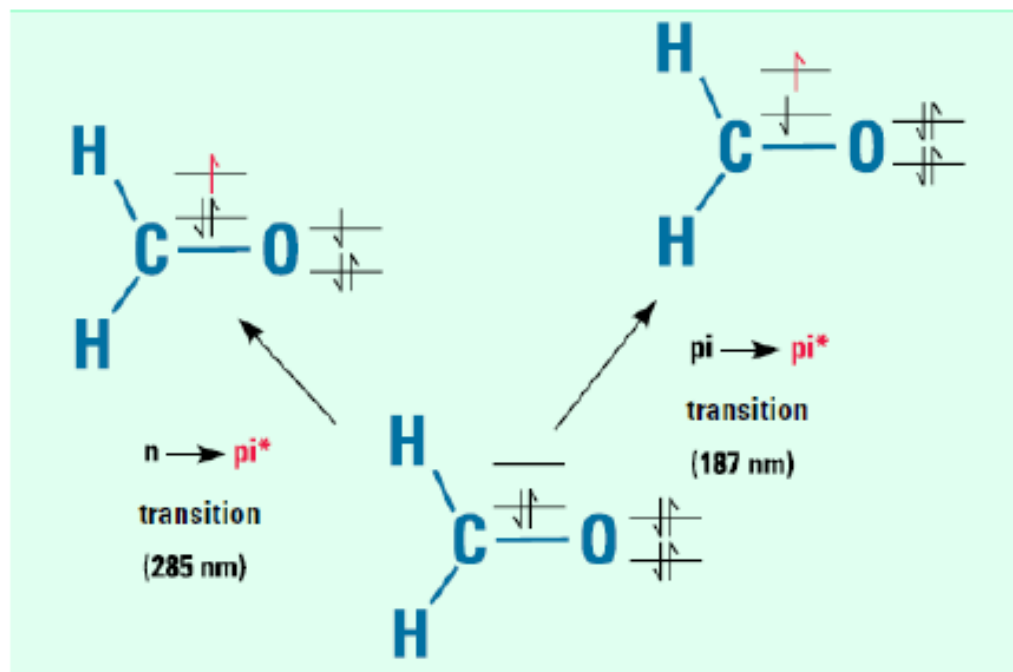


Figure 2
Electronic transitions in formaldehyde

The wavelength of light absorbed is that having the energy required to move an electron from a lower energy level to a higher energy level.

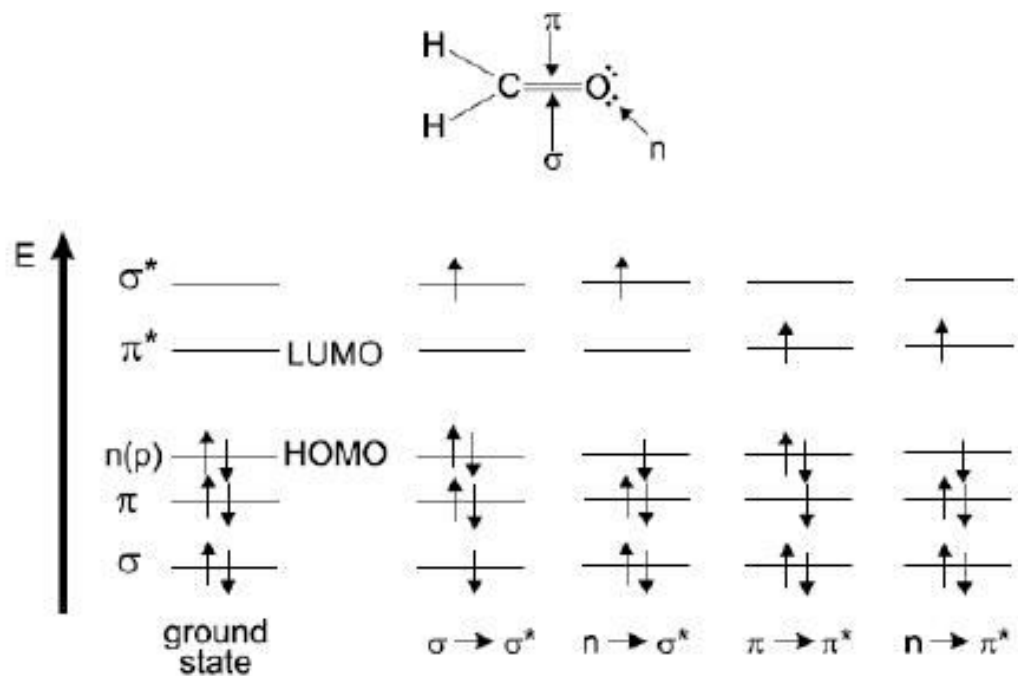
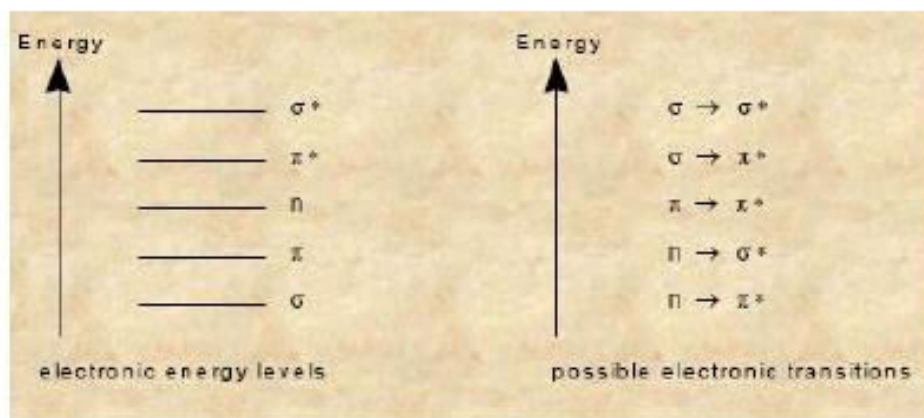
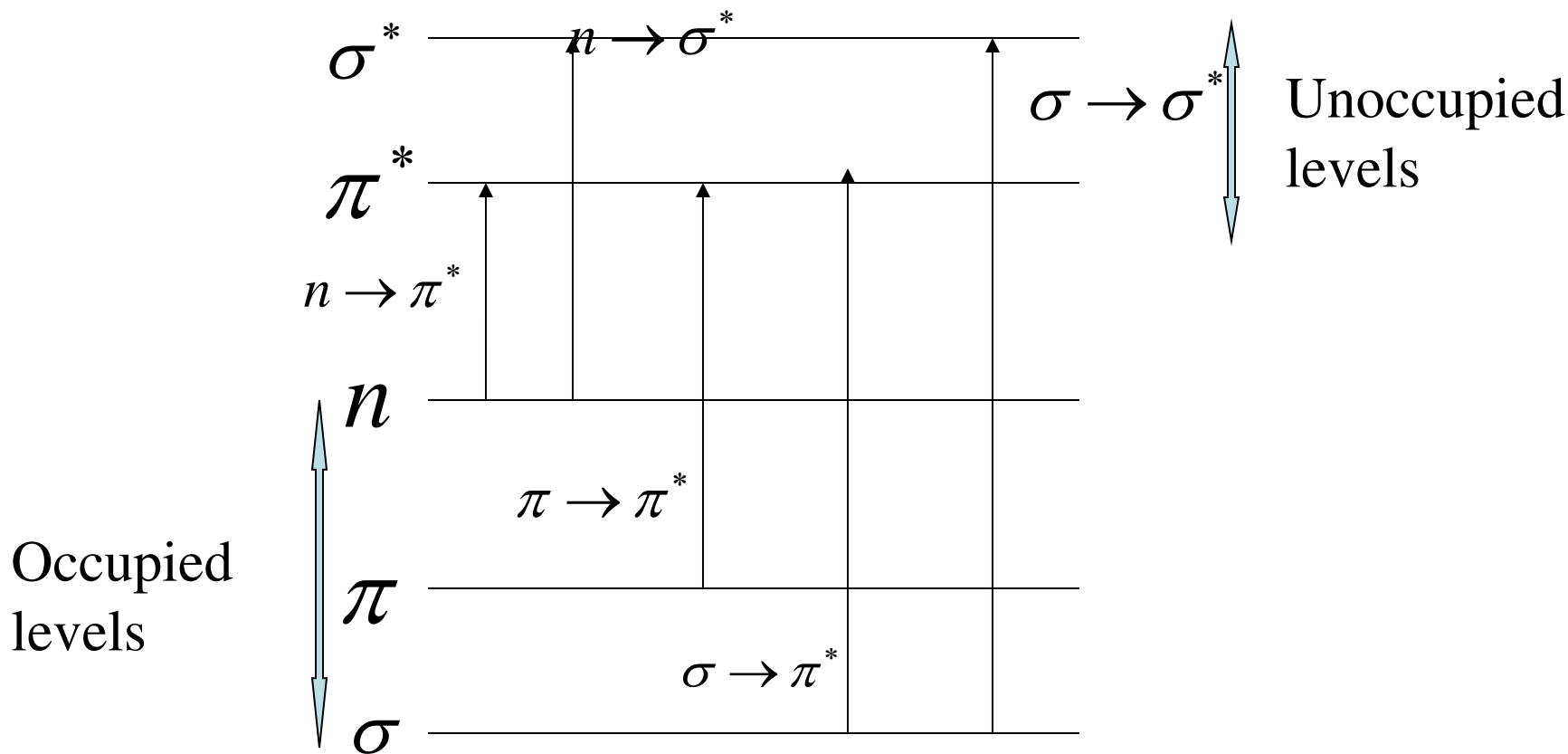


Fig. 21. Energy levels of molecular orbitals in formaldehyde (HOMO: Highest Occupied Molecular Orbitals; LUMO: Lowest Unoccupied Molecular Orbitals) and possible electronic transitions.



Electronic levels and transitions



$\sigma \rightarrow \sigma^*$	Alkanes
$\sigma \rightarrow \pi^*$	Carbonyl compounds
$\pi \rightarrow \pi^*$	Alkenes, carbonyl compn, alkyne etc.
$n \rightarrow \sigma^*$	Oxygen, nitrogen, sulfur and halogen compounds
$n \rightarrow \pi^*$	Carbonyl compounds

Typical absorptions of simple chromophores

Class	transition	Wavelength max (nm)
R-OH	$n \rightarrow \sigma^*$	180
R-O-R	$n \rightarrow \sigma^*$	180
R-NH ₂	$n \rightarrow \sigma^*$	190
R-SH	$n \rightarrow \sigma^*$	210
R ₂ C=CR ₂	$\pi \rightarrow \pi^*$	175
R-C \equiv C-R	$\pi \rightarrow \pi^*$	170

Typical absorptions of simple chromophores

Class	transition	Wavelength max (nm)
R-CHO	$\pi \rightarrow \pi^*$	190
	$n \rightarrow \pi^*$	290
R ₂ CO	$\pi \rightarrow \pi^*$	180
	$n \rightarrow \pi^*$	280
RCOOH	$n \rightarrow \pi^*$	205
R-COOR'	$n \rightarrow \pi^*$	205

B. Charge-transfer transitions

These electronic transitions usually appear in light absorption of **inorganic molecules**.

For a molecule to allow a charge-transfer transition must have a component (atom, group) able to **donate an electron** and another component must be able to **accept an electron**.

The absorption of radiation involves an **electron transfer** from an orbital of a donor to an orbital associated with an acceptor.

Charge-transfer transitions have high molar absorptivity ($\epsilon > 10.000 \text{ l/mol}\cdot\text{cm}$).

Charge transfer transitions are common in **metal-ligand complexes**.

→ **Typical metal-ligand transition**: an electron **from** an orbital of the **metal** is transferred to a π^* orbital of the **ligand**.

→ If the metal has an empty d orbital, it is possible a transfer from ligand to metal.

C. d-d transitions

d-d transitions correspond to the transition of an electron from a metal d orbital to another metal d orbital.

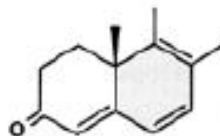
Problem: → d orbitals have the symmetry g (even)
→ d-d transition is forbidden "symmetry forbidden".

Vibronic coupling: some vibration can remove the center of symmetry of the molecule.
d-d transitions are "weakly allowed".

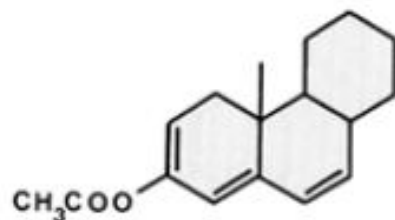
The intensity of d-d transitions is very low, because d-d transitions are forbidden.

Molar absorptivity is under 100 L/mol·cm.

type of transition	Molar absorptivity ϵ (L/mol·cm)
π - π^*	thousands
σ - σ^*	hundred - thousands
d-d	10-100
charge transfer	>10.000



	nm
base value	215
2 additional conjugated double bonds	60
exocyclic double bond	5
homoannular diene system	39
C-substituent in β	12
3 additional C-substituents	54
solvent correction	0
	<hr/>
estimated:	385 nm (ethanol)
determined:	388 nm (ethanol)



	nm
base value (homoannular)	253
additional conjugated double bond	30
exocyclic double bond	5
3 C-substituents	15
	<hr/>
estimated:	303 nm
determined:	306 nm

Selection rules:

1. Spin rule: Changes in spin multiplicity are forbidden

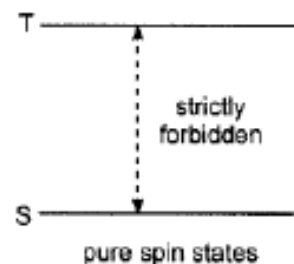
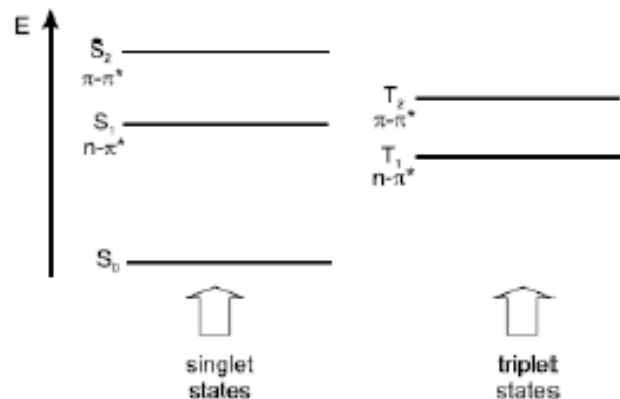
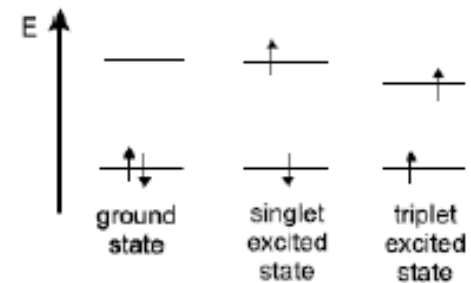
Therefore, transitions between states with different multiplicity are forbidden

allowed transitions: singlet \rightarrow singlet or triplet \rightarrow triplet

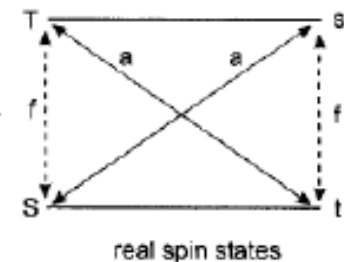
forbidden transitions: singlet \rightarrow triplet or triplet \rightarrow singlet

Always there is a weak interaction between different wave functions due to the **multiplicity spin-orbit coupling**. Therefore the wave function corresponding to the singlet state containing a small fraction of the triplet wave function and vice versa.

This leads to the occurrence of singlet-triplet transitions (intersystem crossing) with very low absorption coefficient, but still noticeable.



spin-orbit coupling



f : forbidden
a : allowed

2. Laporte rule: In an electronic transition there must be a change in the parity (symmetry)

Therefore, a transition may be forbidden for symmetry reasons.

Electric dipole transition can occur only between states of opposite parity.

allowed transitions: $g \rightarrow u$ or $u \rightarrow g$

forbidden transitions: $g \rightarrow g$ or $u \rightarrow u$

g (*gerade* = even), u (*ungerade* = odd)

A symmetry forbidden transition may be observed due to **vibronic coupling** (result in a far from perfect symmetry).

Molar absorptivity is **very small** and the corresponding absorption bands have well-defined vibronic bands

Example: $n \rightarrow \pi^*$ transitions of most solvents that can not form hydrogen bonds. ($\epsilon \sim 100\text{--}1000$ L/mol·cm)