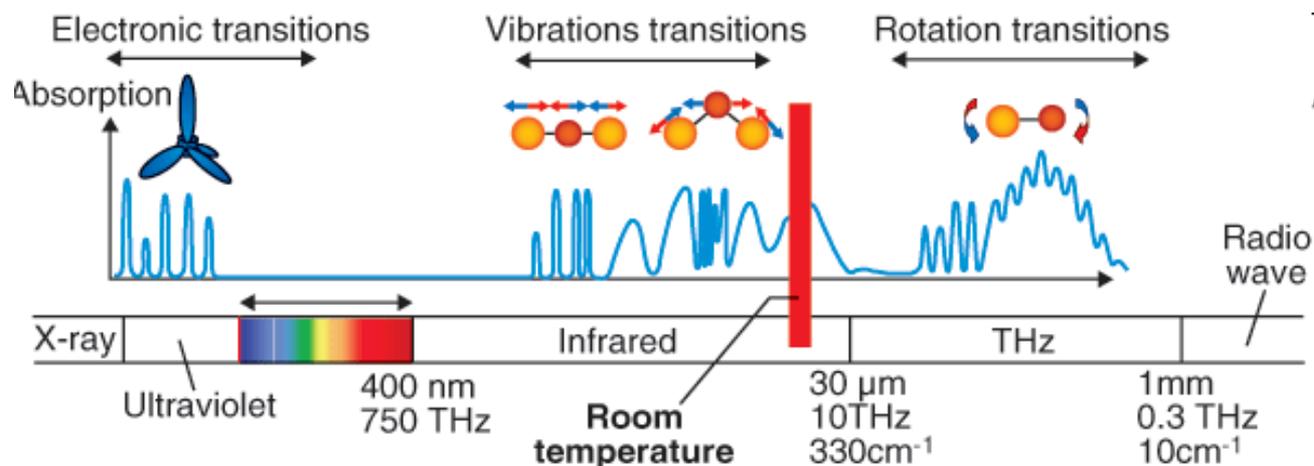


UV-VIS Absorption spectroscopy (Electronic spectroscopy)



The earliest method of molecular spectroscopy!

Quantitative analysis: concentration determination.

Qualitative analysis: identification of molecule properties
(electronic transitions of molecules ↔ UV-Vis absorption)

Quantitative Analysis

UV-Vis spectroscopy is used more for **routine analytical determinations** .

Beer-Lambert law:

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

Parameters:

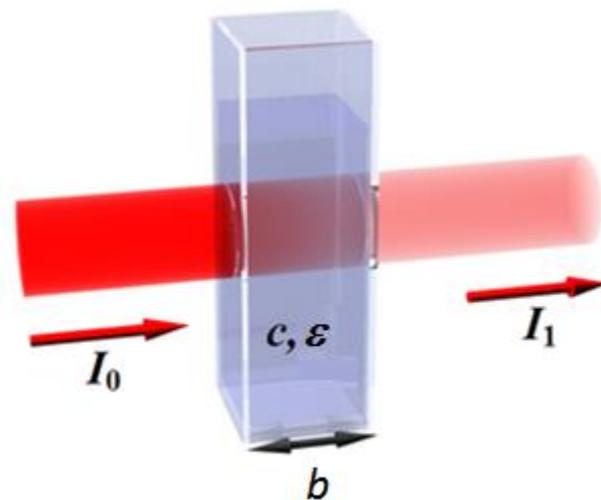
A- absorbance, ($A = \log(I_0/I_1)$)

I - light intensity

ϵ - molar absorption coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$),

b - sample pathlength (usually 1 cm),

c - concentration (mol/L).



$$I_1 = I_0 e^{-\epsilon bc}$$

$$\ln\left(\frac{I_0}{I_1}\right) = \epsilon bc$$

Conceptual Basis of Beer's Law:

- Light of a particular wavelength enters the 'sample'.
- Light *scatters* from particles in solution reducing light transmission
- Light is *absorbed* by molecules/particles and remitted at different wavelengths, reducing light transmission

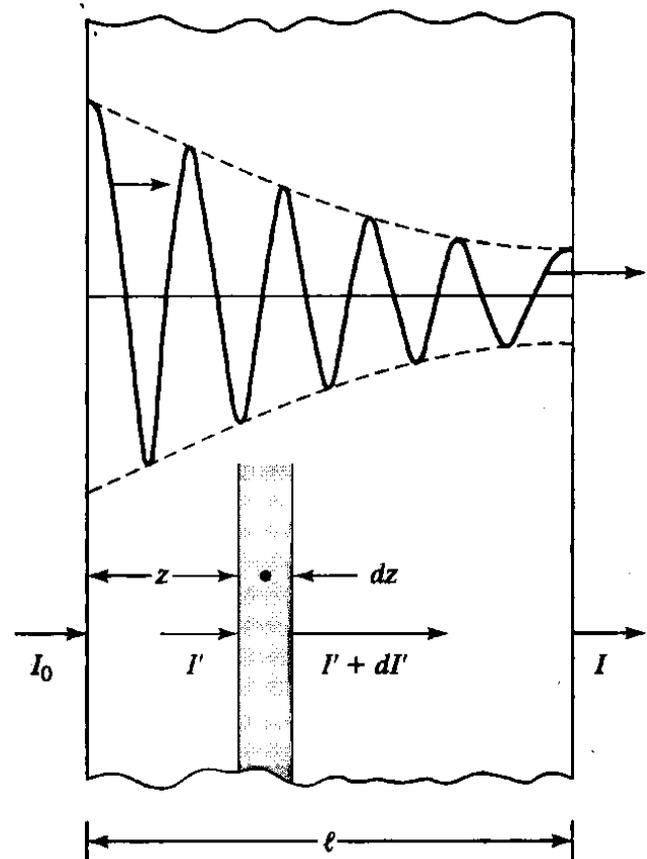
$$\frac{dI}{I} = -\epsilon c dl$$

$$\int_{I_0}^I \frac{dI}{I} = -\int_0^l \epsilon c db$$

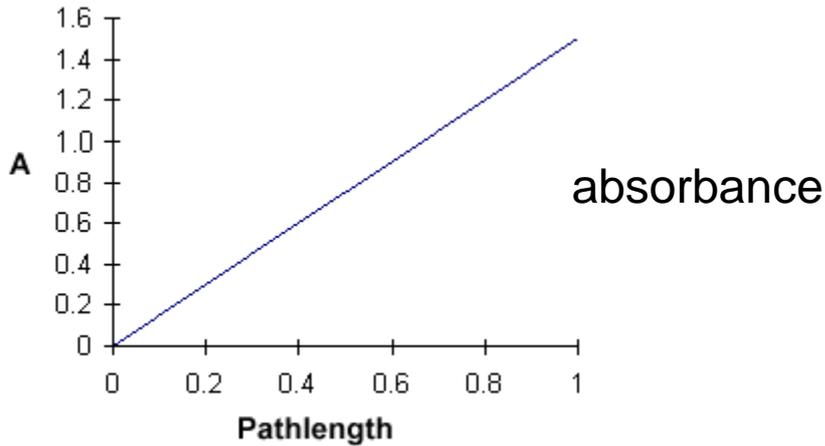
$$\ln \frac{I}{I_0} = -\epsilon cb$$

$$A = \ln \frac{I_0}{I}$$

$$A = \epsilon cb$$

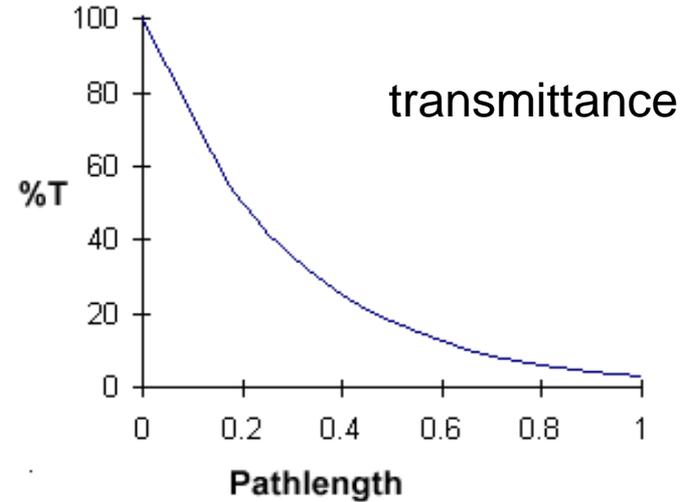


The amount of absorbed radiation may be measured in different ways:



$$A = \lg(1/T) = \epsilon \cdot b \cdot c$$

A: $[0, \infty)$

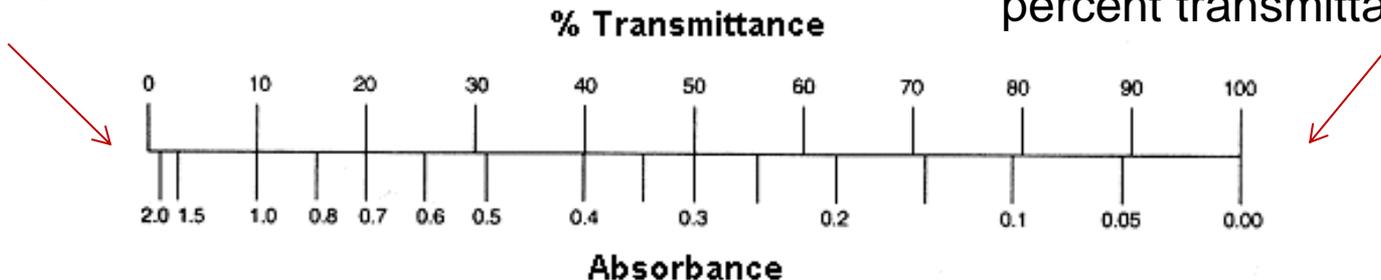


$$T = I/I_0 = 10^{-\epsilon \cdot b \cdot c}$$

%T: $[0\%, 100\%]$

If all the light is absorbed, then percent transmittance is zero, and absorption is infinite

If all the light passes through a solution *without* any absorption, then absorbance is zero, and percent transmittance is 100%.



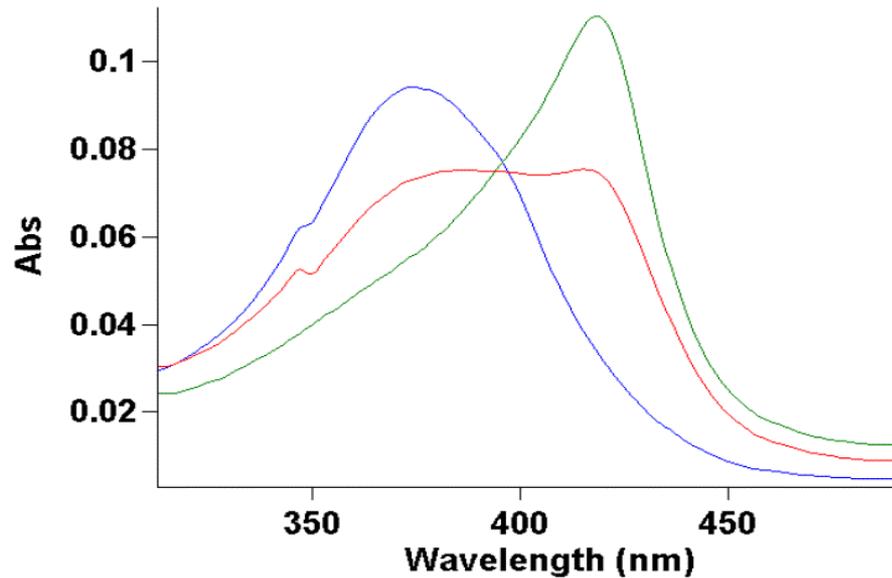
Molar absorptivity is a constant for a particular substance (at a wavelength!).

$$\epsilon = f(\text{subst}, \lambda) !!!!$$

Tab. 2.1. Examples of molar absorption coefficients, ϵ (at the wavelength corresponding to the maximum of the absorption band of lower energy). Only approximate values are given, because the value of ϵ slightly depends on the solvent

<i>Compound</i>	$\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$	<i>Compound</i>	$\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$
Benzene	≈ 200	Acridine	$\approx 12\,000$
Phenol	$\approx 2\,000$	Biphenyl	$\approx 16\,000$
Carbazole	$\approx 4\,200$	Bianthryl	$\approx 24\,000$
1-Naphthol	$\approx 5\,400$	Acridine orange	$\approx 30\,000$
Indole	$\approx 5\,500$	Perylene	$\approx 34\,000$
Fluorene	$\approx 9\,000$	Eosin Y	$\approx 90\,000$
Anthracene	$\approx 10\,000$	Rhodamine B	$\approx 105\,000$
Quinine sulfate	$\approx 10\,000$		

Absorption spectrum ($A = f(\lambda)$) represents the dependence of absorbance from wavelength

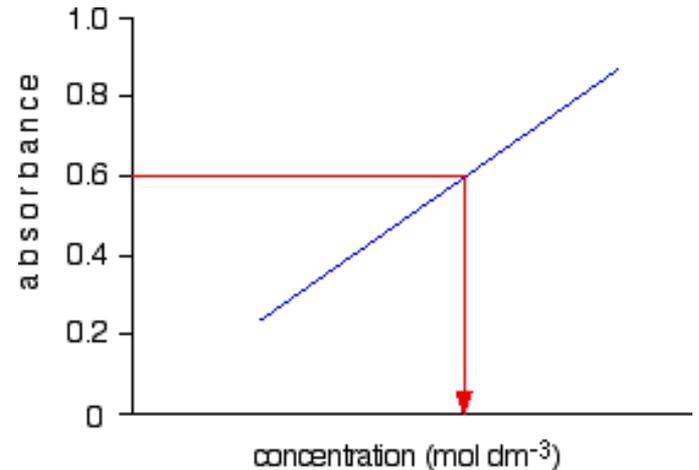


From the absorption spectrum can be determined:

- the position of the absorption maxima (λ_{max})
- the intensity of the absorption maxima (A)

For **concentration** determinations **the calibration curve** (already existing or determined in the laboratory) can be used.

According to the Beer-Lambert Law, absorbance is proportional to concentration.



To build a **calibration curve**:

- record the absorption spectra for *different knowns concentrations* of a substance
- determine the absorbance (maximum of absorption band) for each spectra
- plotted the absorbance versus concentration **$A = f(c)$** to produce a calibration 'curve'
- obtain equation of straight line ($y = mx$) from line of 'best fit'

To determine an **unknown concentration**:

- record the absorption spectra for unknown concentration of same substance use for calibration curve.
- use obtained equation to calculate the concentration.

The Beer-Lambert law is additive:

Absorbance of a mixture, at a certain wavelength, is the sum of each component absorbance at the considered wavelength: $A_{\text{tot}} = A_1 + A_2 + A_3 + \dots$

To determining the concentration of a mixture of two or more substances, UV-Vis absorption spectra of each component is needed (for a known concentration).

Usually, the number of wavelength used to determine the absorbances is equal with the number of the constituents from mixture. One option is to choose those wavelengths at which each component has the maximum of absorption.

In order to determine the concentrations of each component of the mixture (c_{Mx} , c_{Ny}) the values of molar absorptivities of the two substances M, N must be calculated (using Beer-Lambert law) from the UV-Vis absorption spectrum of each component recorded for known concentrations (c_M , c_N).

$$A_{(M+N)}^{\lambda_1} = A_{Mx}^{\lambda_1} + A_{Ny}^{\lambda_1}$$

$$A_{(M+N)}^{\lambda_2} = A_{Mx}^{\lambda_2} + A_{Ny}^{\lambda_2}$$

$$A_{(M+N)}^{\lambda_1} = \epsilon_M^{\lambda_1} b c_{Mx} + \epsilon_N^{\lambda_1} b c_{Ny}$$

$$A_{(M+N)}^{\lambda_2} = \epsilon_M^{\lambda_2} b c_{Mx} + \epsilon_N^{\lambda_2} b c_{Ny}$$

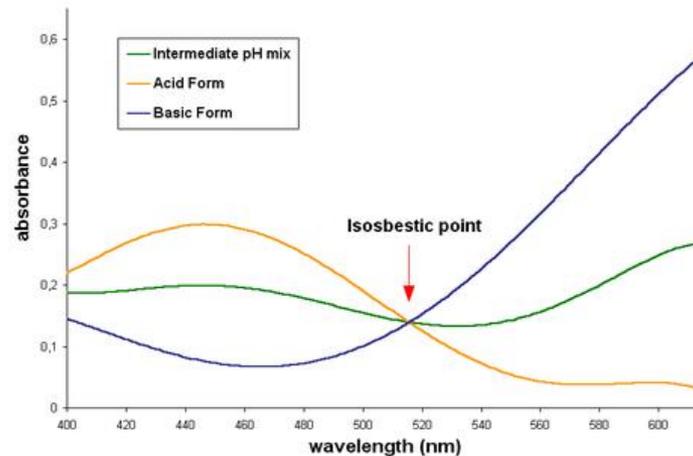
$$\epsilon_M^{\lambda} = \frac{A_M^{\lambda}}{b \cdot c_M}$$

$$\epsilon_N^{\lambda} = \frac{A_N^{\lambda}}{b \cdot c_N}$$

By solving the system, the concentrations (c_{Mx} , c_{Ny}) of the two components of the mixture can be determined.

Absorption curve is influenced by:

- **Temperature** (at higher temperatures monomers are predominant)
- **Concentration** (at higher concentrations dimers/polymers are predominant)
- **pH** (influence the balance between ionized and non-ionized forms)



Isobestic point is the intersection of all absorption curves of a solution at different pH's

Limits to Beer's Law: High Concentration and 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.

The Beer-Lambert Law breaks down for solutions of higher concentration!

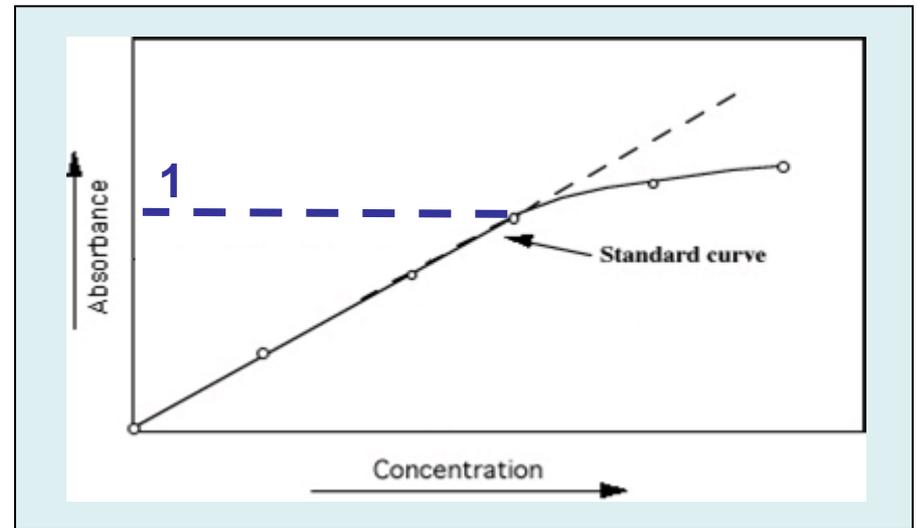
$A < 1$ for accurate results!

If $A > 1$:

- Dilute the sample
- Use a narrower cuvette

dimension of usually cuvettes:

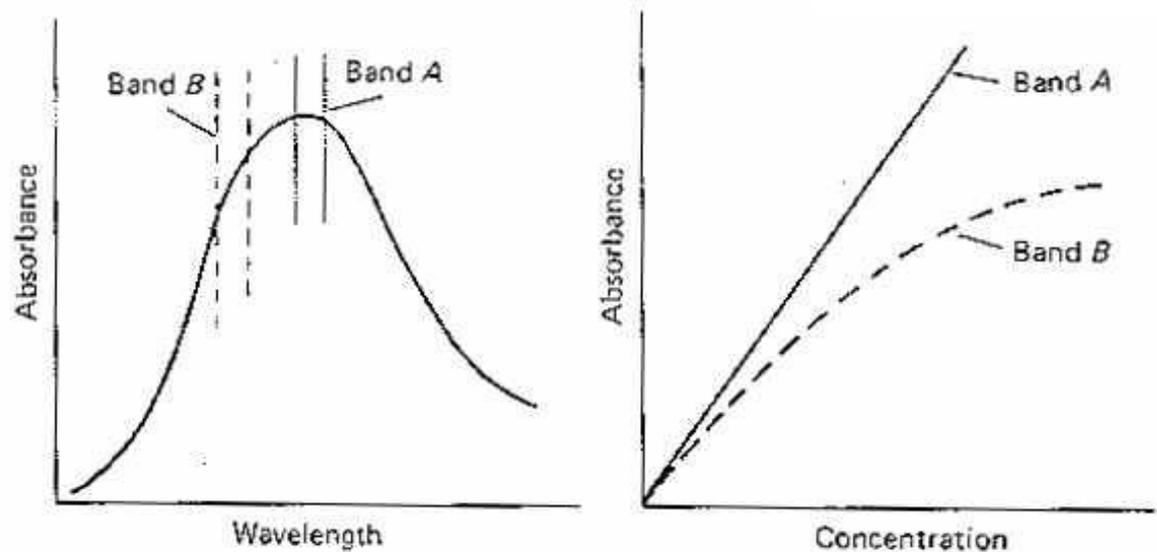
1 mm,
1 cm,
10 cm.



- chemical interactions: dissociation or reaction with the solvent

Limits to Beer's Law: Instrumental Deviations

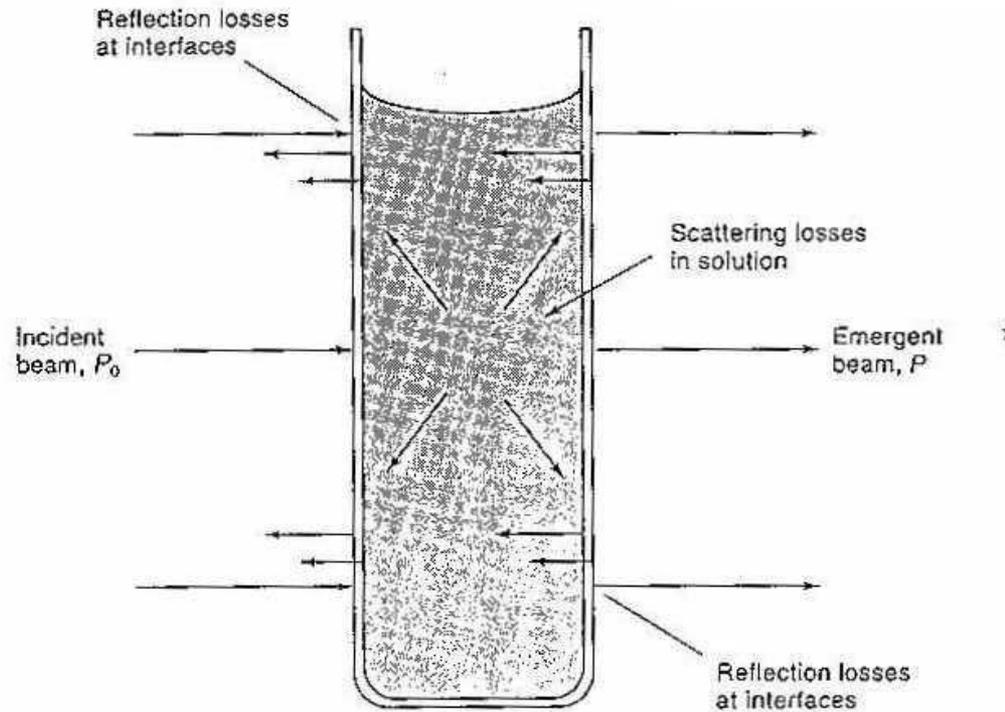
- **non-monochromatic radiation**: deviation of calibration curve from linearity



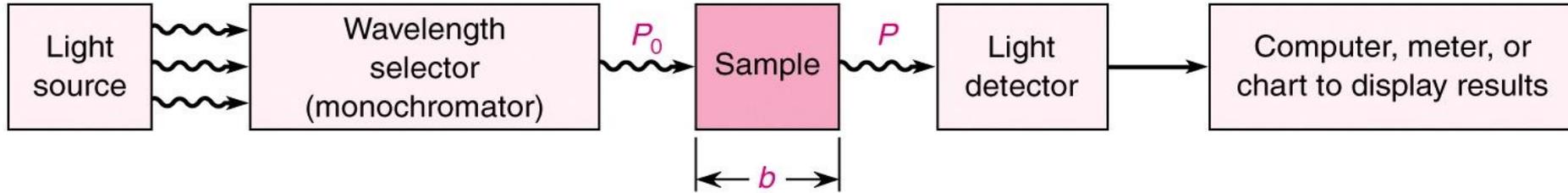
- if a significant amount of the light passed through the sample contains **wavelengths that have much lower extinction coefficients than the nominal one**, the instrument will report an incorrectly low absorbance.

Limits to Beer's Law: Experimental Deviations

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

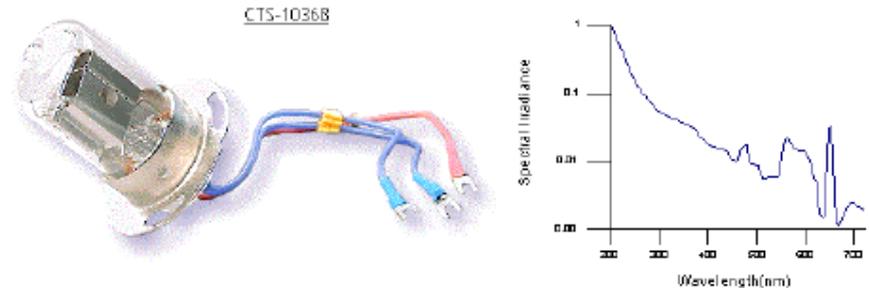


UV-VIS Absorption: *Instrumentation*



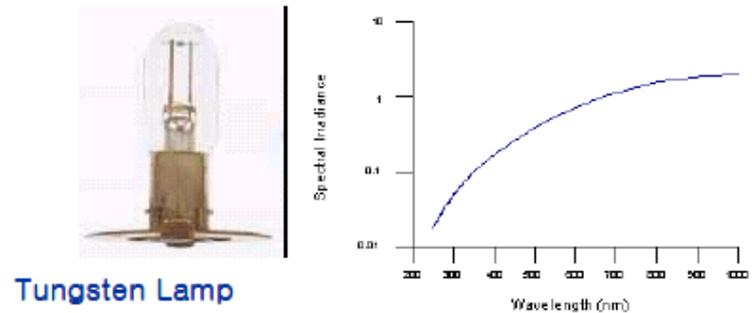
Light Source

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



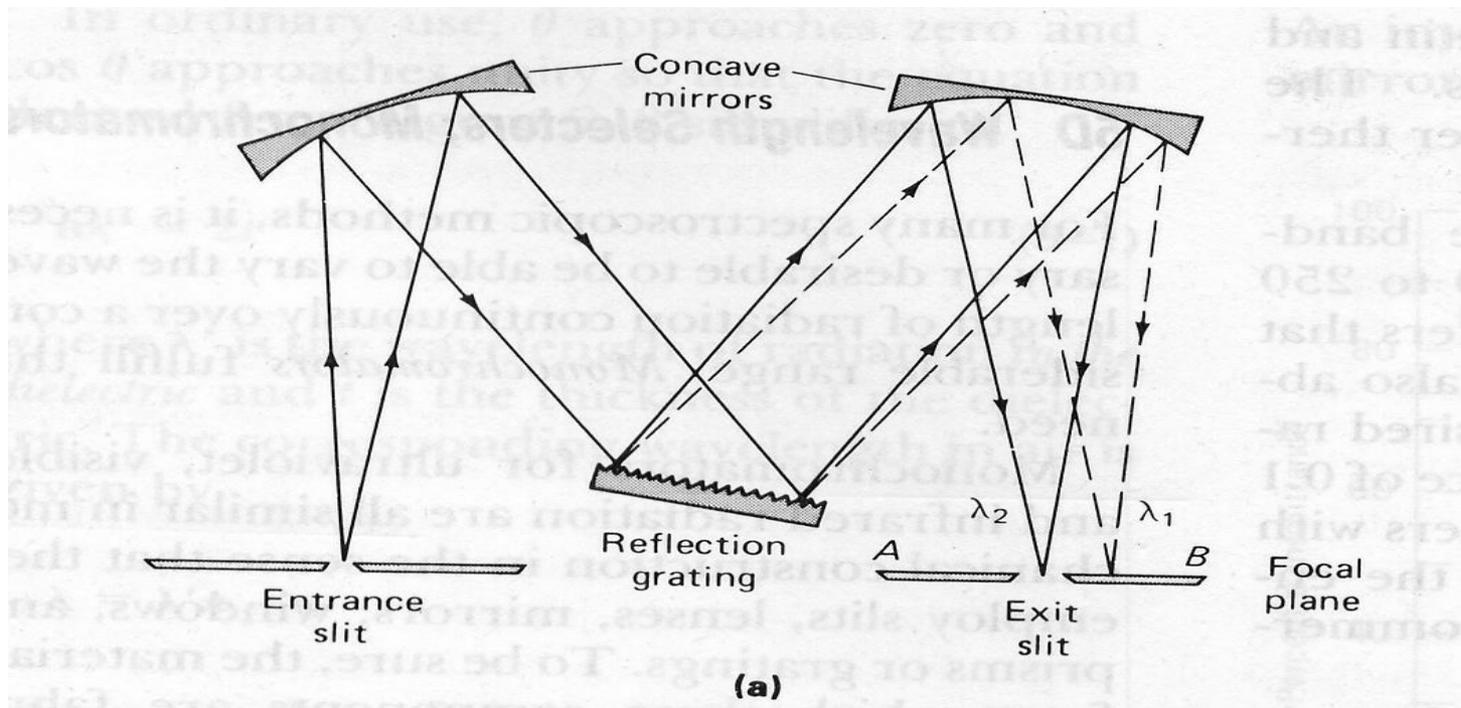
Deuterium Lamp

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



Monochromator

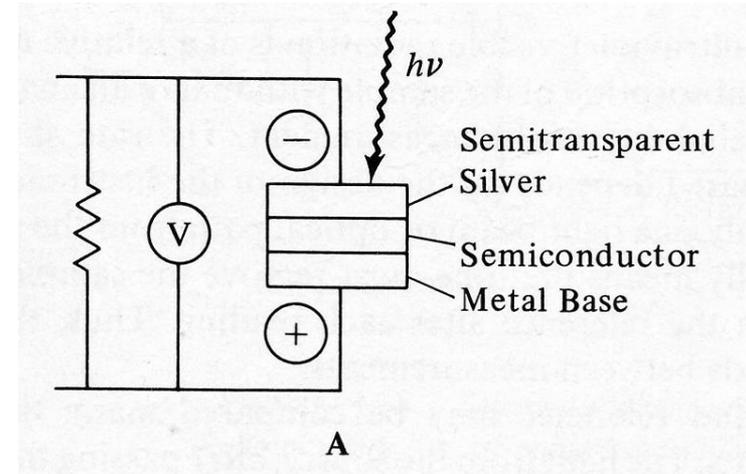
- The diffraction grating splits light into its component colours.
- The exit slit allows only light of a very narrow range of wavelengths into the rest of the spectrometer.
- By gradually rotating the diffraction grating, the light from the whole spectrum (a tiny part of the range at a time) reach into the rest of the instrument.



Detector

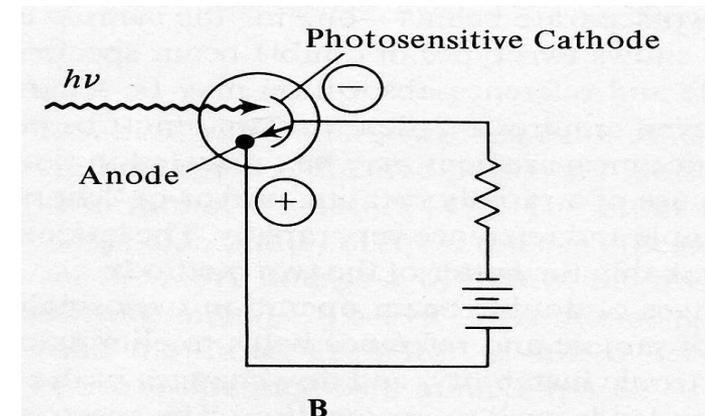
The **Photovoltaic Detector** measures the intensity of photons by means of the voltage developed across the semiconductor layer.

Electrons, ejected by photons from the semiconductor, are collected by the silver layer. **The potential** depends on the number of photons hitting the detector.



The **Phototube Detector** is a vacuum tube with a cesium-coated photocathode.

Photons of sufficiently high energy hitting the cathode can dislodge electrons, which are collected at the anode. Photon flux is measured by the **current flow** in the system.

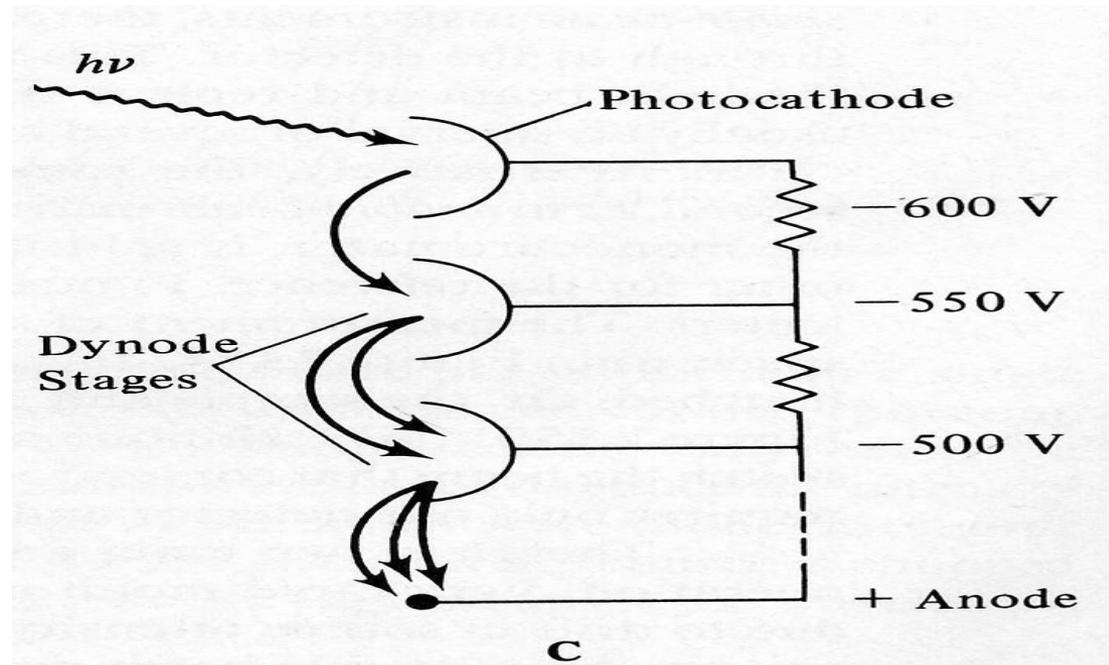


The **Photomultiplier Detector** consists of a **photoemissive cathode** coupled with a series of electron-multiplying dynode stages.

The primary electrons ejected from the photo-cathode are accelerated by an electric field so as to strike a small area on the first dynode.

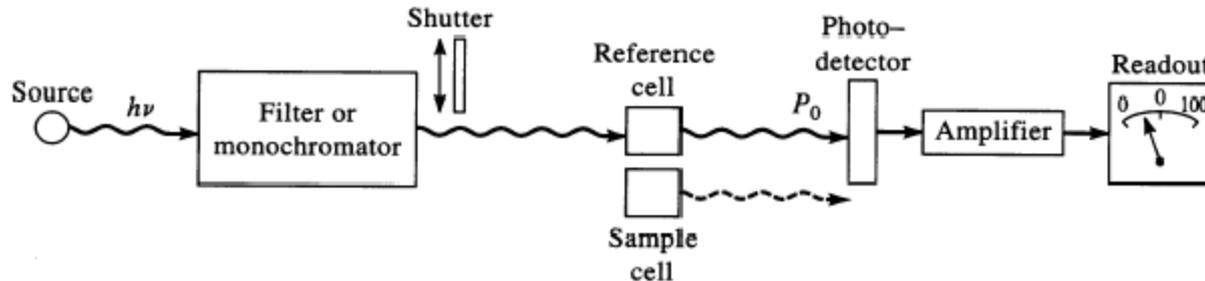
The impinging electrons strike with enough energy to eject **two to five secondary electrons**, which are accelerated to the second dynode to eject still more electrons.

A photomultiplier may have 9 to 16 stages, and overall gain of $10^6 \sim 10^9$ electrons per incident photon.

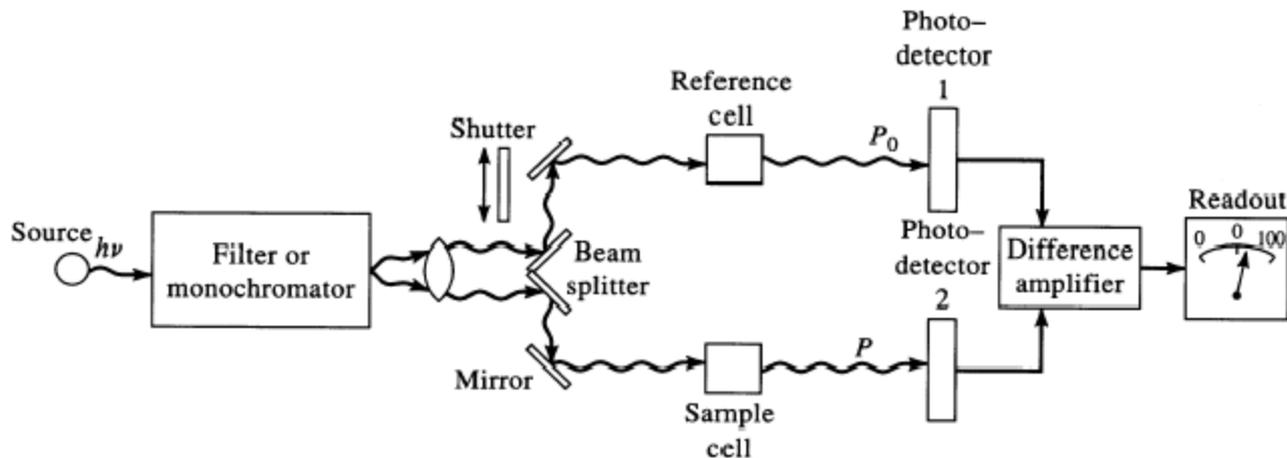


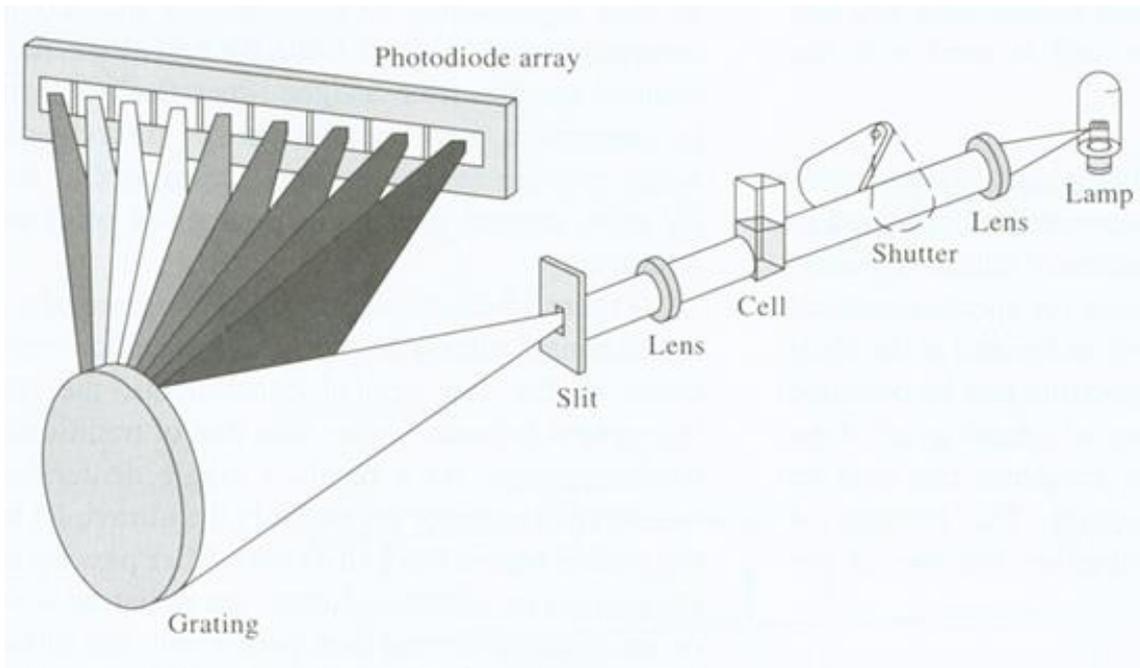
Single and Double Beam Spectrometer

- **Single-Beam:** There is only one light beam or optical path from the source through to the detector.



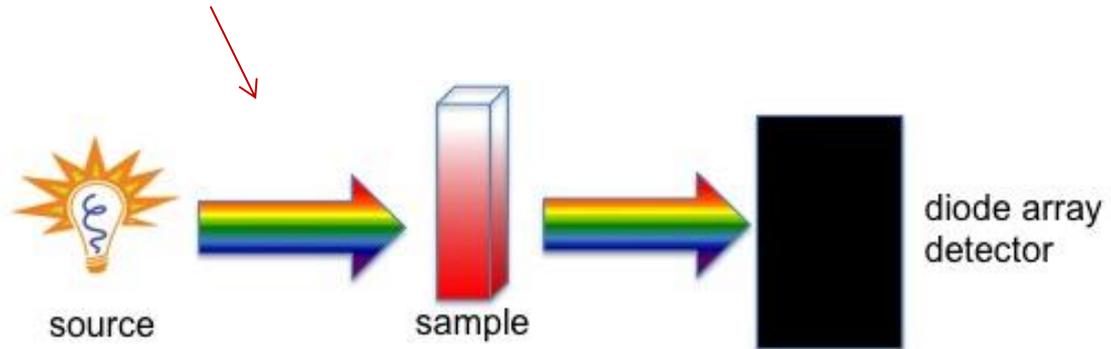
- **Double-Beam:** The light from the source, after passing through the monochromator, is split into two separate beams: one for the sample and the other for the reference.





Photodiode array (CCD) allow simultaneous detection of all wavelength.

No monochromator is needed!



Sample cell

The sample and reference cells are small rectangular containers made by:

- glass (using over Visible region)
- quartz or fused silica (Using over 190 nm)



The cells are often designed so that the light beam travels a distance of **1 cm** through the contents (1 mm for low volume).

The **sample cell** contains a solution of the substance - usually very dilute.

The solvent is chosen so that it doesn't absorb any significant amount of light in the wavelength range we are interested in (200 - 800 nm).

The **reference cell** just contains the pure solvent.

UV-Vis: Qualitative analysis

Absorption of electromagnetic radiation in the **UV-Vis** range:

- *change the distribution of electrons* in the molecule
 - *electrons are promoted* from the ground state an unoccupied orbital (excited electronic states)
- electronic transition!!!**

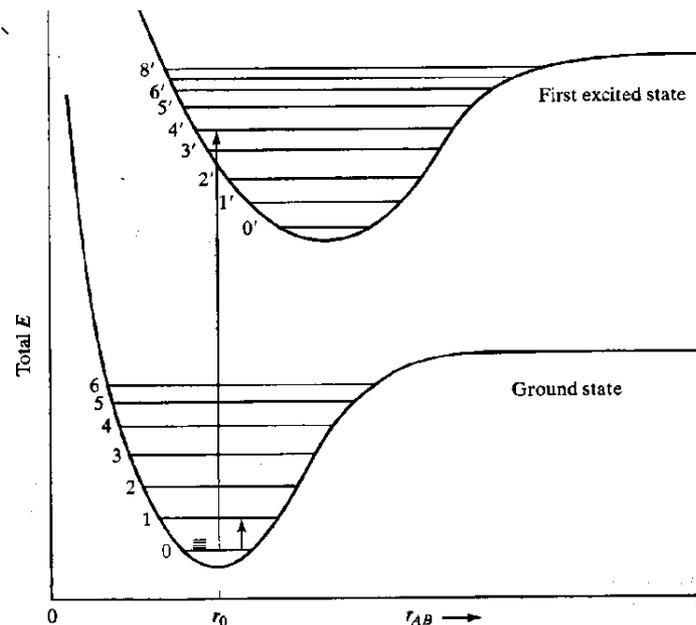
UV

$$250 \text{ nm} = 40000 \text{ cm}^{-1} = 1.2 \times 10^{15} \text{ Hz}$$

Vis

$$400 \text{ nm} = 25000 \text{ cm}^{-1} = 7.5 \times 10^{14} \text{ Hz}$$

$$750 \text{ nm} = 13333 \text{ cm}^{-1} = 4 \times 10^{14} \text{ Hz}$$



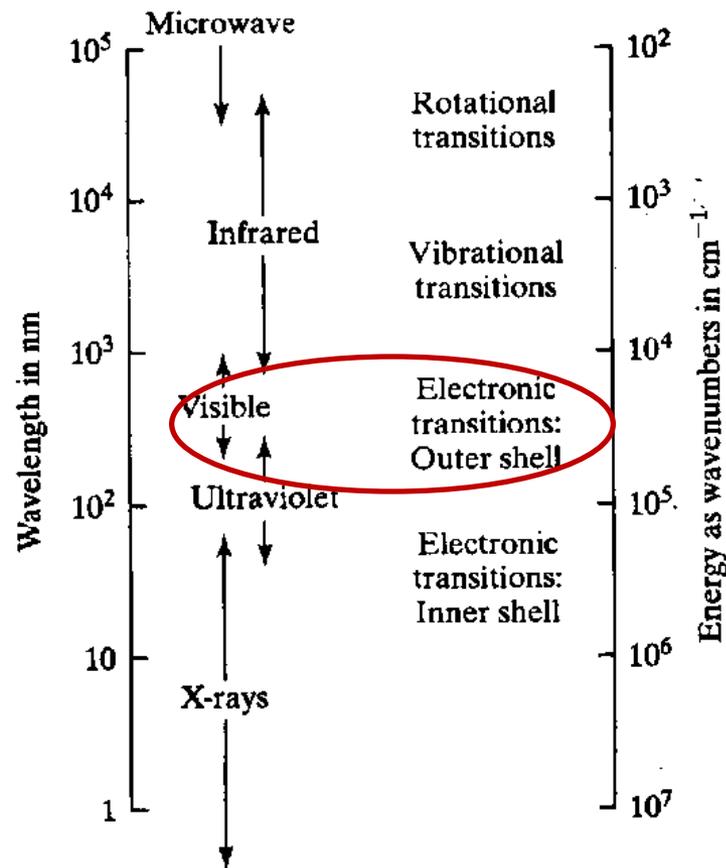
Internuclear distances and force constants corresponding to the excited electronic states differ from those corresponding to ground electronic states!

All molecules give electronic spectra!

(contrary to vibrational and rotational spectroscopies)

UV-Vis absorptions features:

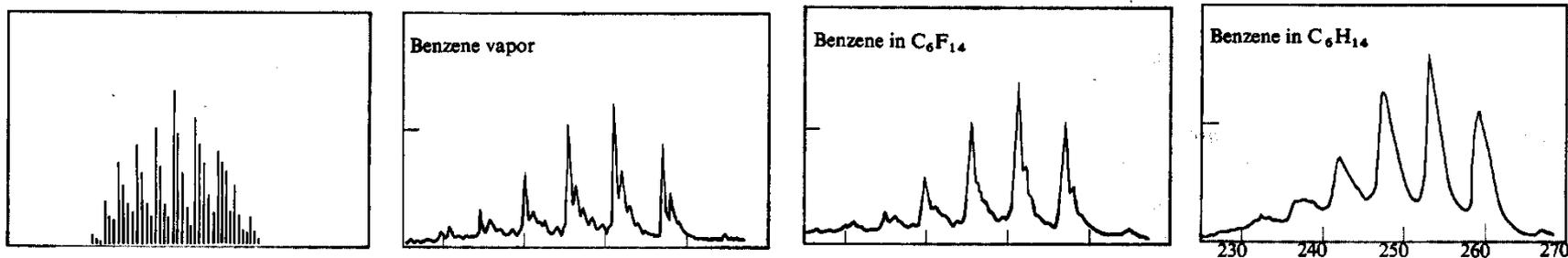
- Transitions between electronic energy levels are induced by electromagnetic radiation in the **UV-Visible** region.
- Within each electronic state are a series of vibrational and rotational levels.
- The relative **populations** of the various states are governed by **Boltzmann distributions**:
$$\frac{n_2}{n_1} = \exp\left[\frac{-(E_2 - E_1)}{kT}\right]; \quad k = 1.38 \times 10^{-23} \text{ J/K};$$
- At room temperature **nearly all molecules are in the vibrational ground state**.
(e.g., at 298 K: for $\Delta E = 10 \text{ kJ/mol} \rightarrow N_2/N_1 = 0.0176$)



- e. Electronic transitions can occur *to various vibrational-rotational states* in the *excited electronic state*.

The spectrum for a given electronic transition should consist of a **large number of closely spaced lines.**)

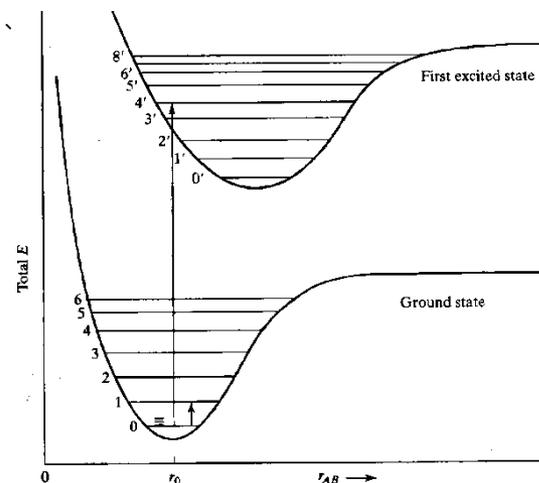
In practice, this is observed only in dilute gases or at very low temperatures.



In solution and at room temperature, the fine structure is lost due to collisions, environmental heterogeneity, Doppler shifts, etc.

- f. The electronic energy can be modeled as a harmonic oscillator near the equilibrium bond distance.

- g. *On the timescale of the electronic transition the nuclei are fixed because the electronic transitions are very fast.*



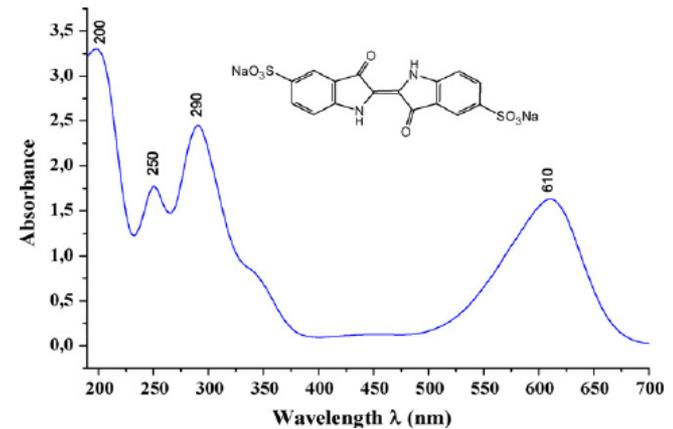
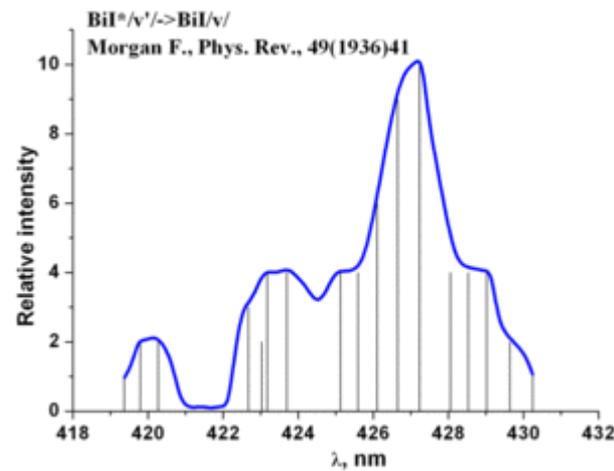
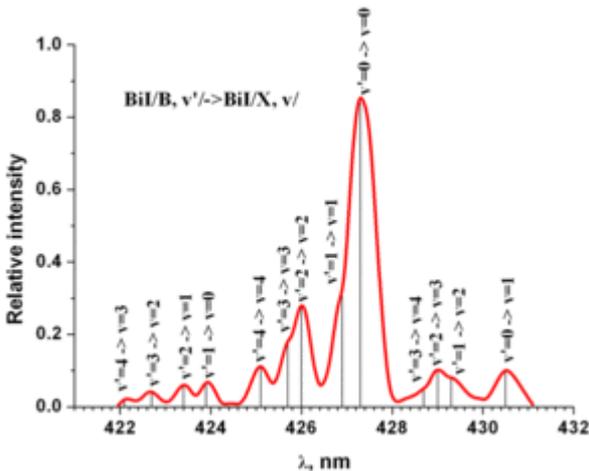
Franck-Condon Principle: electronic transitions are vertical!

UV-Vis spectroscopy is related with transitions between electronic energy levels of **molecular orbitals** → electronic transitions

The frequency of absorbed light (wave number, wavelength) depends on the structure of the molecule and on its neighborhood.

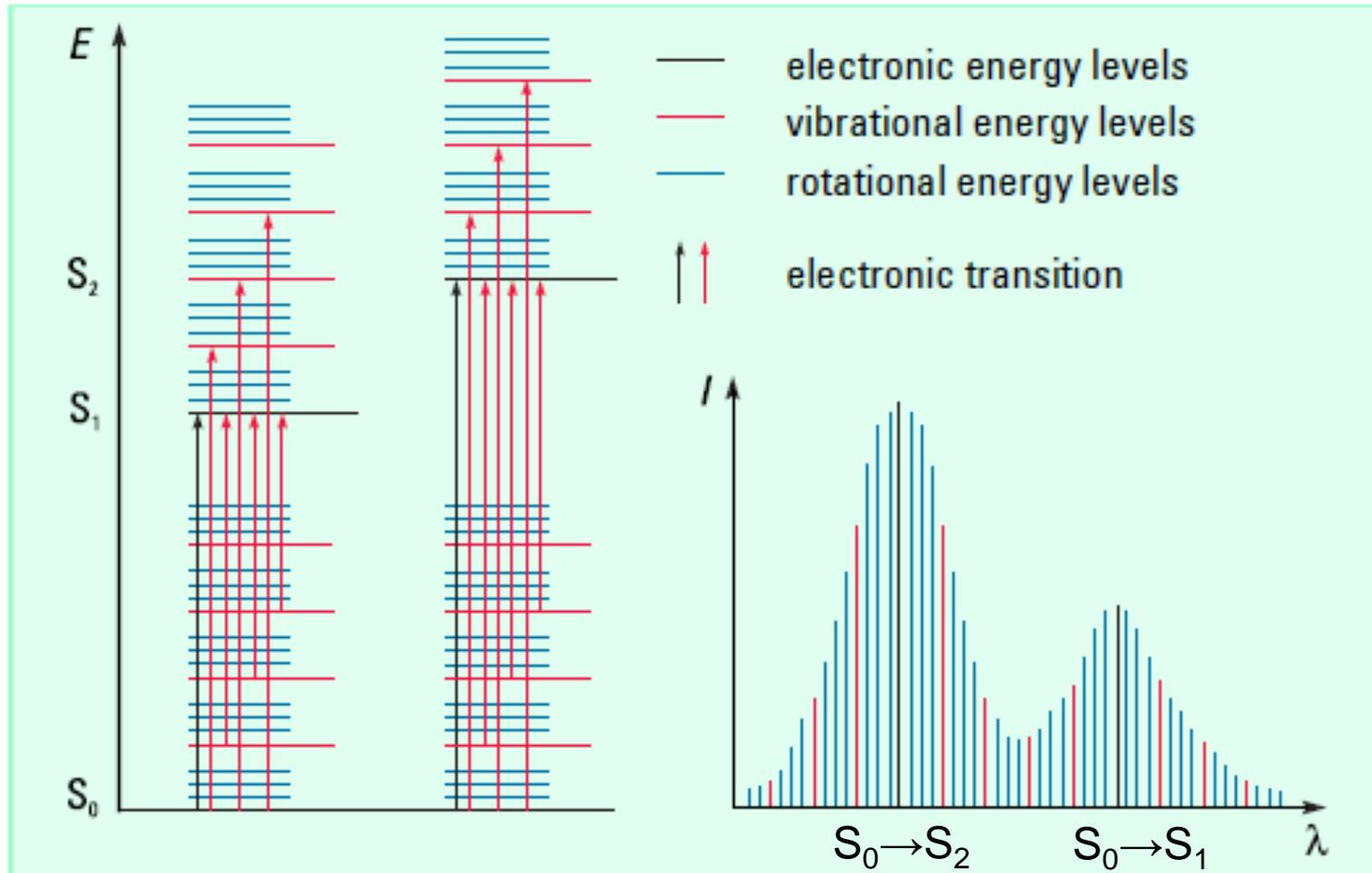
Different molecules absorb different wavelengths of radiation!

Because certain molecules absorb light in a characteristic way, this is useful to identify and quantify biological molecules.



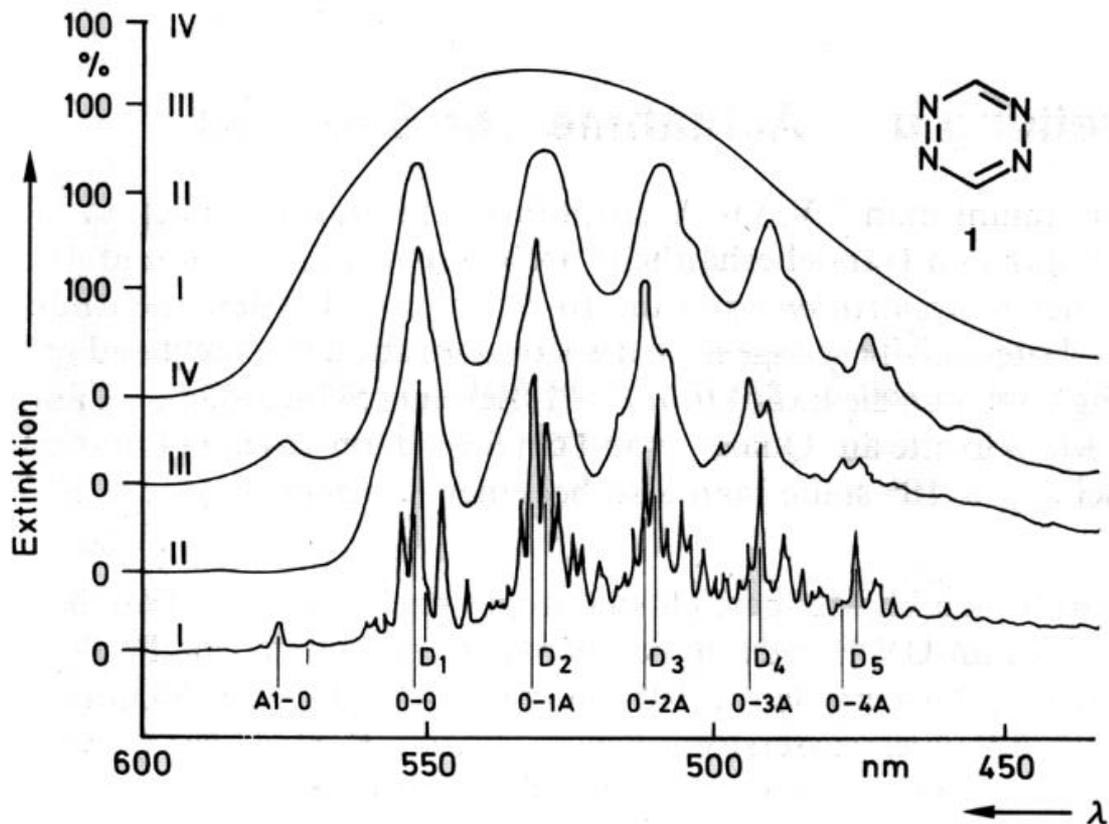
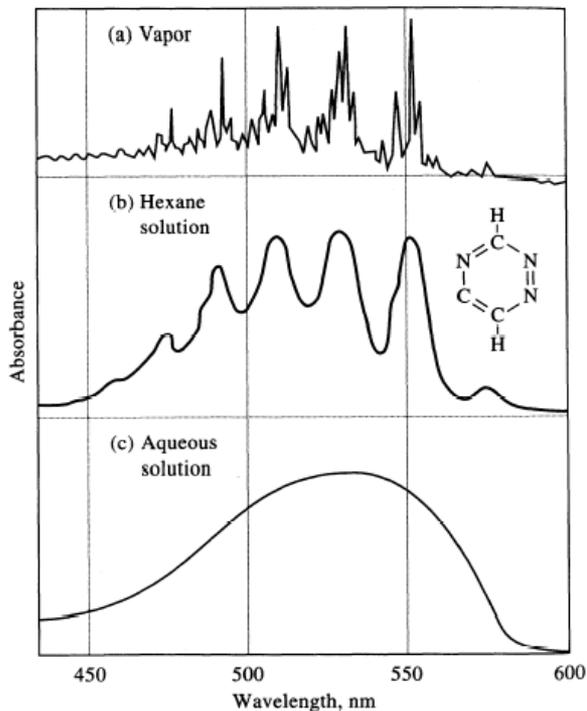
Indigo carmine: synthetic dye (blue) used in textile industry.

Vibrational changes produce a “coarse structure” on the electronic transitions
Rotational changes produce a “fine structure” on the electronic transitions.



Shape of UV-VIS Bands

The vibrational fine structure disappears for solutions but can be observed for gases.



- I Gas phase, room temperature
- II In isopentane-methylcyclohexane matrix, 77K
- III In cyclohexane, room temperature
- IV In water, room temperature

ex. 1,2,4,5-tetrazine

Electronic transition

A diatomic molecule may simultaneously undergo electronic, vibrational and rotational transitions.

The **Born-Oppenheimer approximation** (“Since the energies of the various motions are very different, motions of a diatomic molecule may be considered as independent”) allows us to express the **total molecular energy** as:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

As a result of a transition, **the change in the total energy** of a molecule is:

$$\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$$

(the approximate orders of magnitude: $\Delta E_{\text{elec}} \sim \Delta E_{\text{vib}} \cdot 10^3 \sim \Delta E_{\text{rot}} \cdot 10^6$)

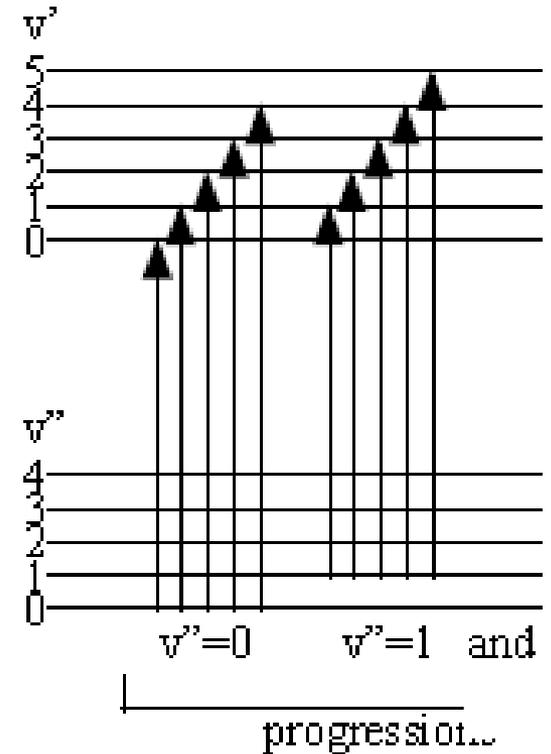
For **vibrational transitions** between different electronic levels, there is **no rule for Δv** , so that **every $v'' \rightarrow v'$ transition has some probability**, giving rise to many spectral lines.

Absorption spectra from the ground state are more likely: virtually all the molecules are in their lowest vibrational state ($v'' = 0$), so that the only transitions we observe are (0, 1), (0, 2), (0, 3) etc.

Each set of transitions in a band is called a v' **progression**, since the value of v' increases by unity for each line in the set.

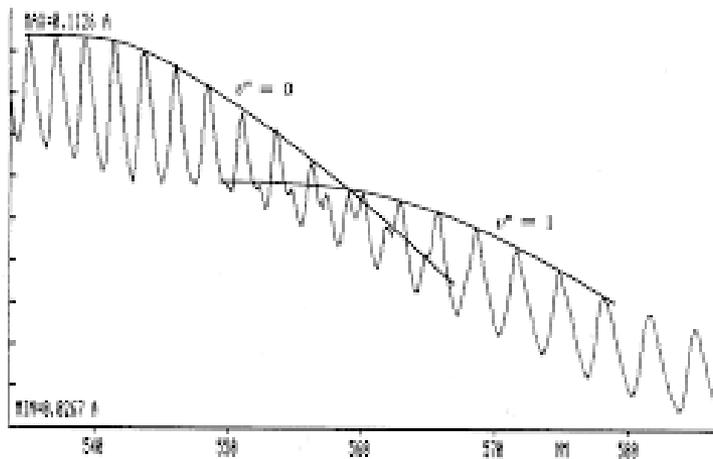
The lines in a band are closer together at high frequencies because of the **anharmonicity** of the upper state vibrations, which causes vibration energy levels to converge.

In general, the spacing of vibrational energy levels in the two electronic states is different.



v'' → vibrational quantum number of ground electronic state (initial state)

v' → vibrational quantum number of excited electronic state (final state)



Example:

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to $0 \rightarrow v'$ transitions connecting the $v'' = 0$ vibrational level of the ground electronic state to many different vibrational levels v' of the excited electronic state. Under the conditions of this experiment (i.e., low resolution), the rotational lines within each band are not resolved.

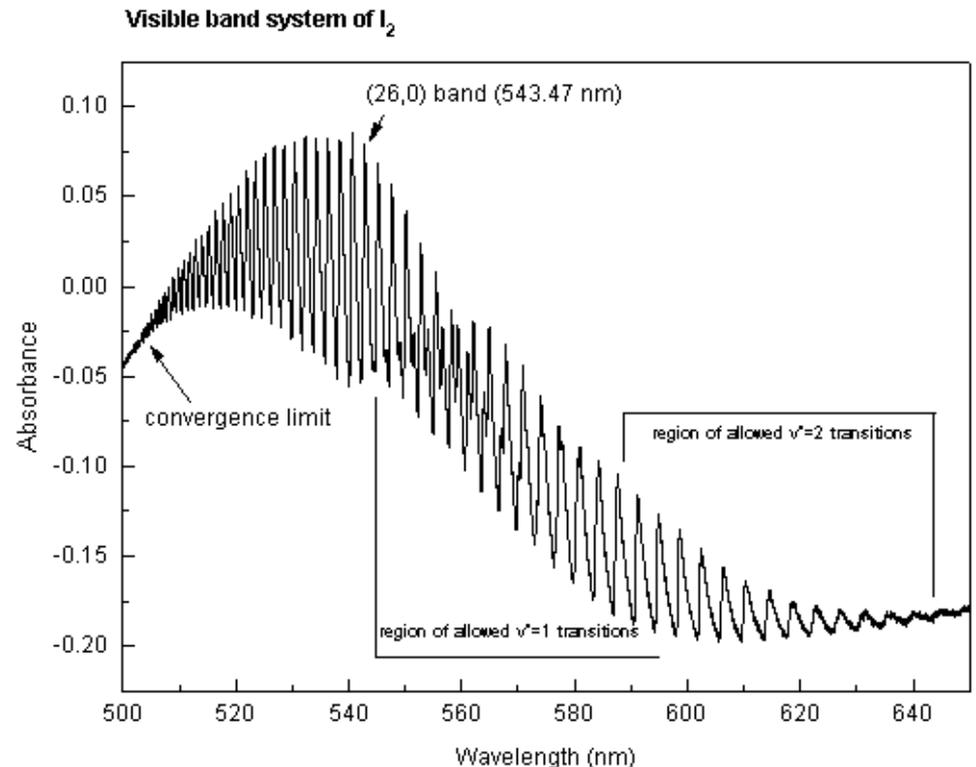
Each small peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light.

The *hot bands* arising from absorption from $v''=1$ and $v''=2$ are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero.

Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound.



Birge Spomer plot

The energy of a real molecule (anharmonic vibration) is:

$$E_{\text{total}} = E_{\text{elec}} + hc\left[\left(v + \frac{1}{2}\right)\bar{\nu}_e - x_e\left(v + \frac{1}{2}\right)^2\bar{\nu}_e\right]$$

The change in the total energy is: $\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}}$

$$\Delta E_{\text{total}} = E'_{\text{elec}} - E''_{\text{elec}} + hc\left[\left(v' + \frac{1}{2}\right)\bar{\nu}'_e - x'_e\left(v' + \frac{1}{2}\right)^2\bar{\nu}'_e - \left(v'' + \frac{1}{2}\right)\bar{\nu}''_e - x''_e\left(v'' + \frac{1}{2}\right)^2\bar{\nu}''_e\right]$$

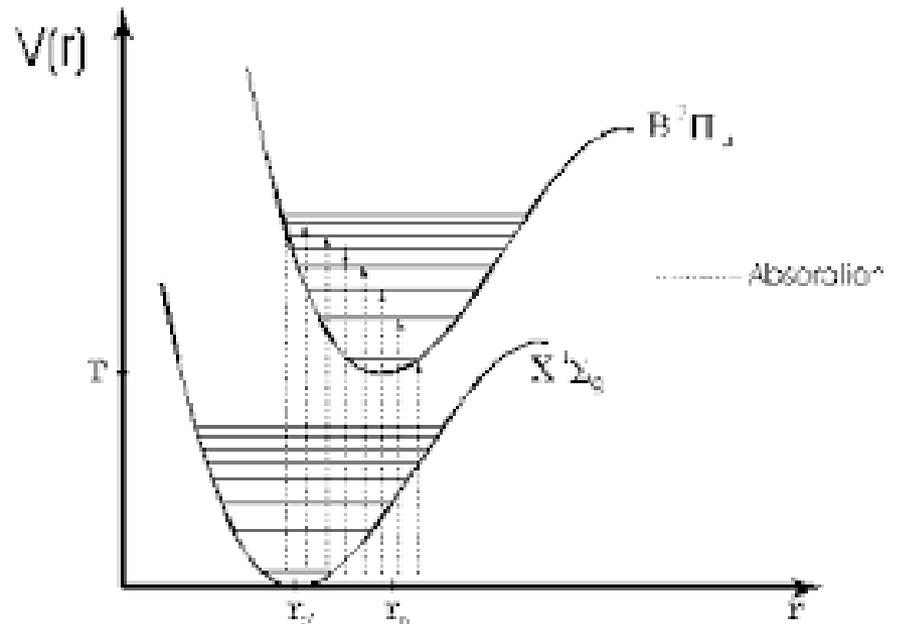
If a sufficient number (at least five) of lines can be resolved in the band, the values: x'_e , x''_e , $\bar{\nu}'_e$, $\bar{\nu}''_e$ and $(E'_{\text{elec}} - E''_{\text{elec}})$ can be calculated.

X - electronic ground state (S_0),

b - electronic excited state (S_1),

(") - lower state;

(') - higher state



For a given electronic transition: $E'_{\text{elec}} - E''_{\text{elec}} = \Delta E_{\text{elect}} = \text{constant}$.

$$\Delta E_{\text{total}} = \Delta E_{\text{elec}} + hc \left[\left(v' + \frac{1}{2} \right) \bar{\nu}'_e - x'_e \left(v' + \frac{1}{2} \right)^2 \bar{\nu}'_e - \left(v'' + \frac{1}{2} \right) \bar{\nu}''_e - x''_e \left(v'' + \frac{1}{2} \right)^2 \bar{\nu}''_e \right]$$

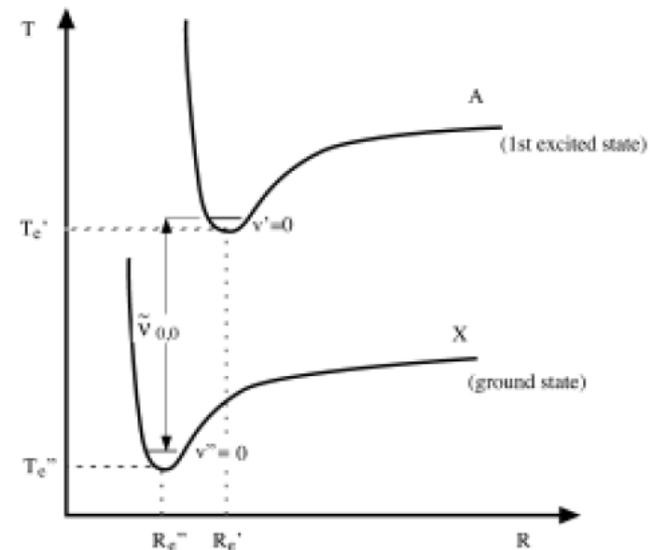
Considering only the terms $G(v') = \Delta E_{\text{total}}/hc$ from a progression (ex. $v'' = 0$)

$$G(v') = \frac{1}{hc} \Delta E_{\text{elec}} + \left[\left(v' + \frac{1}{2} \right) \bar{\nu}'_e - x'_e \left(v' + \frac{1}{2} \right)^2 \bar{\nu}'_e - \left(\frac{1}{2} \right) \bar{\nu}''_e - x''_e \left(\frac{1}{2} \right)^2 \bar{\nu}''_e \right]$$

and makes the difference between two consecutive terms, will obtain an expression which is a **first degree equation in $(v'+1/2)$** :

$$\Delta G = G(v'+1) - G(v') = \bar{\nu}'_e - 2x'_e \bar{\nu}'_e \left(v' + \frac{1}{2} \right) = f \left(v' + \frac{1}{2} \right)$$

electronic transitions



If we represent $\Delta G = f(v' + 1/2)$ will obtain the **Birge-Sponer plot**.

The slope of this line is equal to: $2x'_e \bar{\nu}'_e$

$$\Delta G = f(v' + \frac{1}{2}) = \bar{\nu}'_e - 2x'_e \bar{\nu}'_e (v' + \frac{1}{2})$$

The **y intercept** represent $\bar{\nu}'_e$ (the **vibrational frequency of harmonic oscillator**).

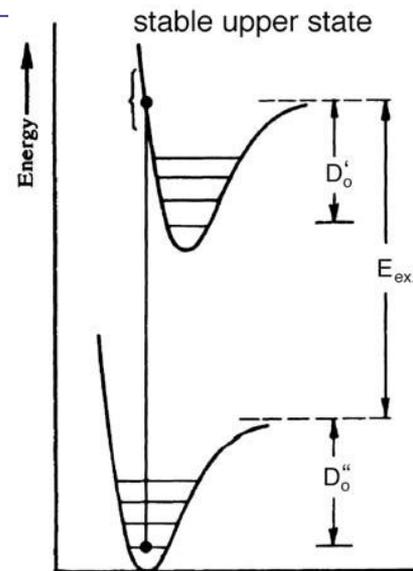
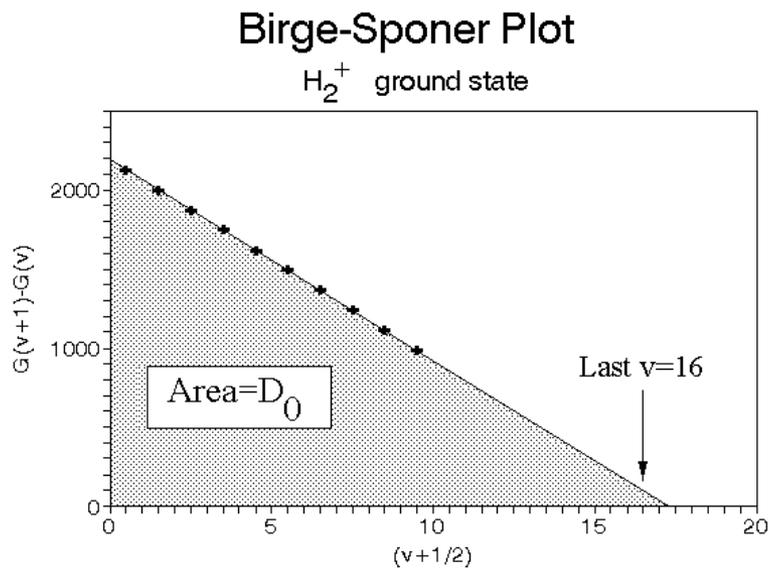
The **x intercept** represent **the number of vibrational levels** from the electronic excited state: v'_{\max}

If the terms from a series are used, the values corresponding to (") state will be obtained.

The **area below** Birge-Sponer line represent the **dissociation energy** D_0 .

D_e energy is the maximum value of $G(v)$:

$$D_e = G_{\max}(v) = \frac{\bar{\nu}'_e{}^2}{4 \cdot \bar{\nu}'_e \cdot x_e}$$



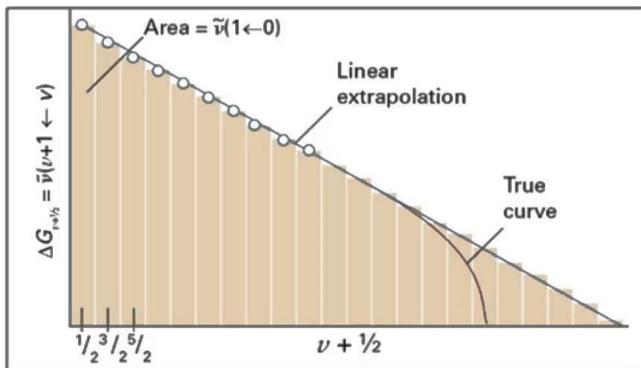


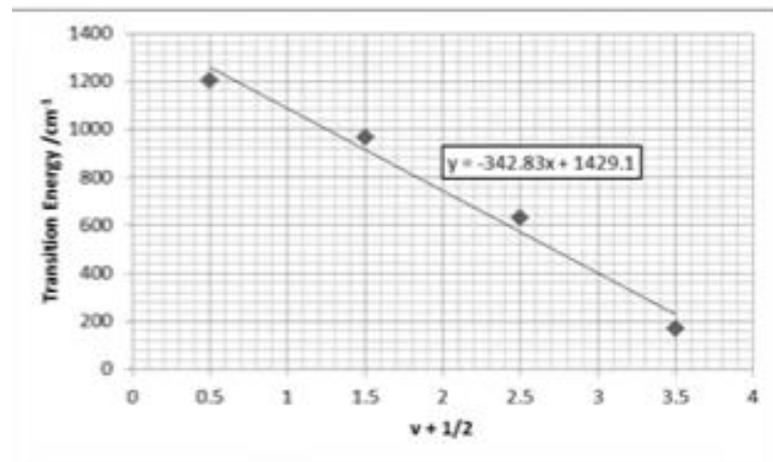
Image: Atkins, Physical Chemistry (12th Ed)

Example:

The vibrational energy levels of HgH converge rapidly and successive intervals are: (from 0→1): 1203.7, 965.6, 632.4, 172 cm⁻¹.

Estimate the dissociation energy

$$\Delta G = f\left(v'+\frac{1}{2}\right) = \bar{\nu}'_e - 2x'_e \bar{\nu}'_e \left(v'+\frac{1}{2}\right)$$



Area of triangle:

Height = y-axis intercept = 1429

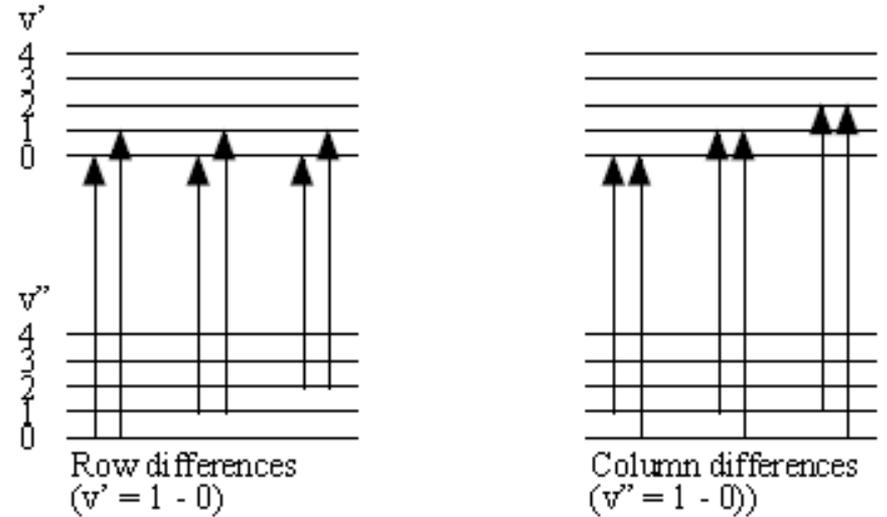
Base = x-axis intercept = 4.2

Area = Dissociation energy = 2978 cm⁻¹.
(~35.6 kJ mol⁻¹)

Vibrational band analysis: the Deslandres table

In order to draw Birge-Sponer line the Deslandres table could be used. The Deslandres table contain vibrational wavenumbers of electronic transitions and the differences between them.

The differences between rows and columns is constant, and correspond to the energy difference between a particular pair of vibrational levels in either the upper state (rows) or the lower state (columns):



	$v'' = 0$	$v'' = 1 - 0$	1	$v'' = 2 - 1$	2	$v'' = 3 - 2$	3
$v' = 0$	64748	2143	62605	2117	60488	2090	58398
$v' = 1 - 0$	1480		1480		1480		1480
1	66228	2143	64085	2117	61968	2090	59878
$v' = 2 - 1$	1440		1440		1440		1440
2	67668	2143	65525	2116	63409	2090	61319
$v' = 3 - 2$	1402		1402		1402		1402
3	69070	2143	66927	2117	64810	2090	62720

$v'' + 1/2$	λ [Å]	ν [cm ⁻¹]	$\Delta G(v''+1/2)$
0.5	5145	19436	213
1.5	5202	19222	208
2.5	5259	19015	215
3.5	5319	18800	205
4.5	5378	18594	212
5.5	5440	18382	203
6.5	5501	18179	211
7.5	5565	17968	204
8.5	5629	17764	200
9.5	5694	17564	201
10.5	5759	17363	202
11.5	5827	17161	195
12.5	5894	16967	202
13.5	5965	16765	194
14.5	6035	16571	197
15.5	6107	16374	191
16.5	6180	16182	194
17.5	6255	15988	190

Intensity of vibrational-electronic transitions (vibronic):

The vibrational lines in a progression are not of the same intensity. Intensities of the vibrational bands are determined by three factors:

- (1) The intrinsic strength of the transition
- (2) The populations of the levels involved.
- (3) The overlap of the vibrational wavefunctions (the **Franck-Condon factor**).

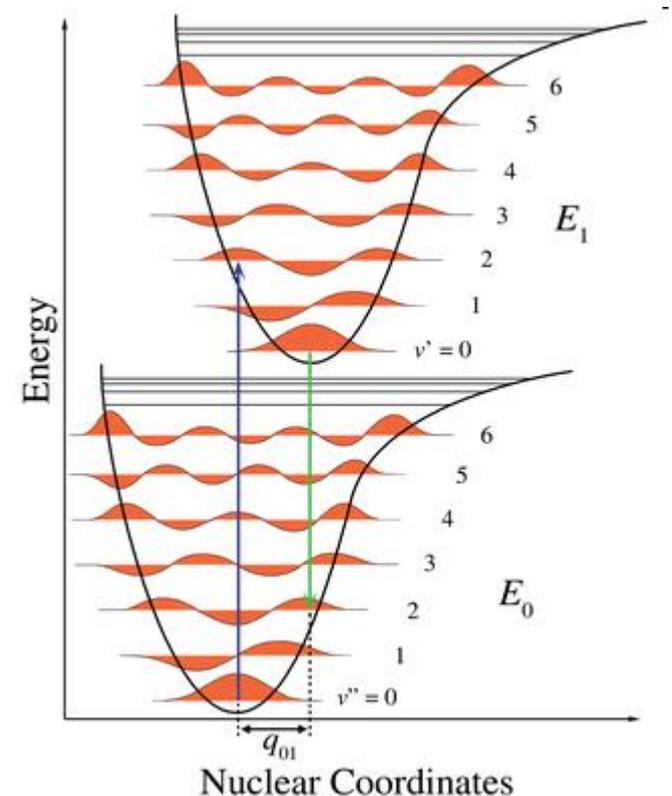
Franck-Condon Factors

- The intensity of a transition from one electronic state to another is related to the **Franck-Condon factor (FCF)**.

$$I \propto FCF = |S_{nm}|^2$$

- The quantity S_{nm} is the **overlap integral** between the ground and excited state wavefunctions.

$$S_{nm} = \int_{-\infty}^{\infty} \psi_n^{g*}(x) \psi_m^e(x) dx$$



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**”.

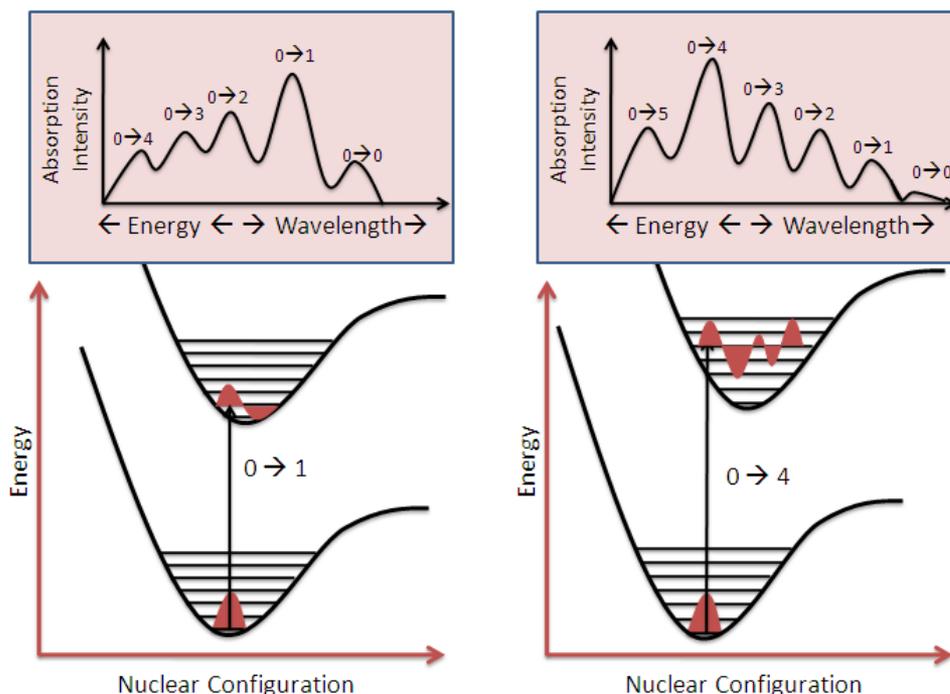
The intensity of a transition is greatest for the largest of the vibrational wavefunctions.

Franck-Condon principle → explains the intensity of vibronic transitions

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

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

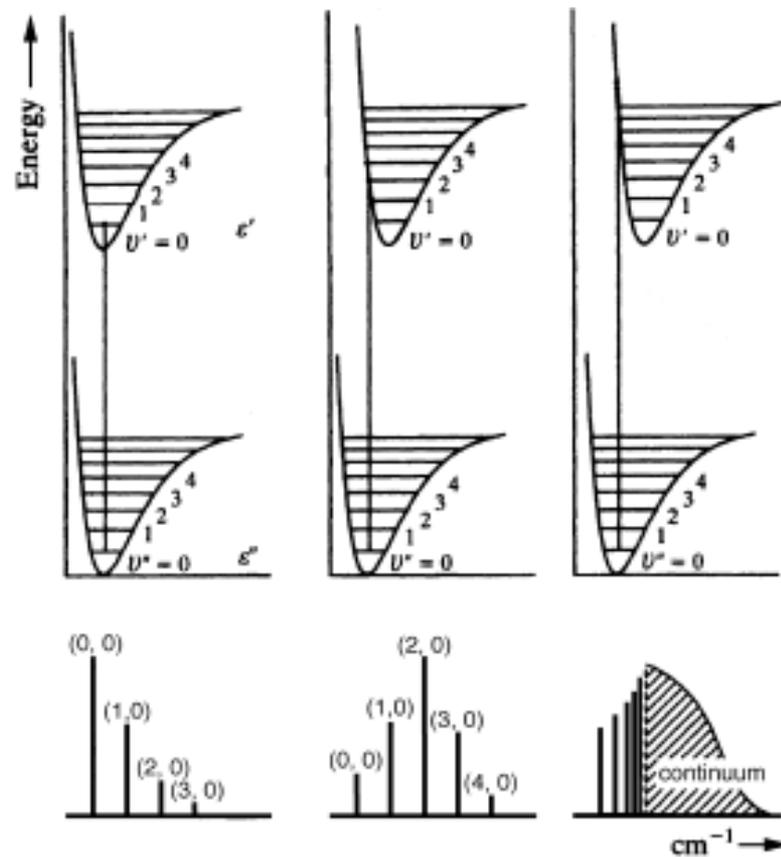
When the nucleus **realigns itself with the new electronic configuration**, the theory states that it **must undergo a vibration**.



(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.

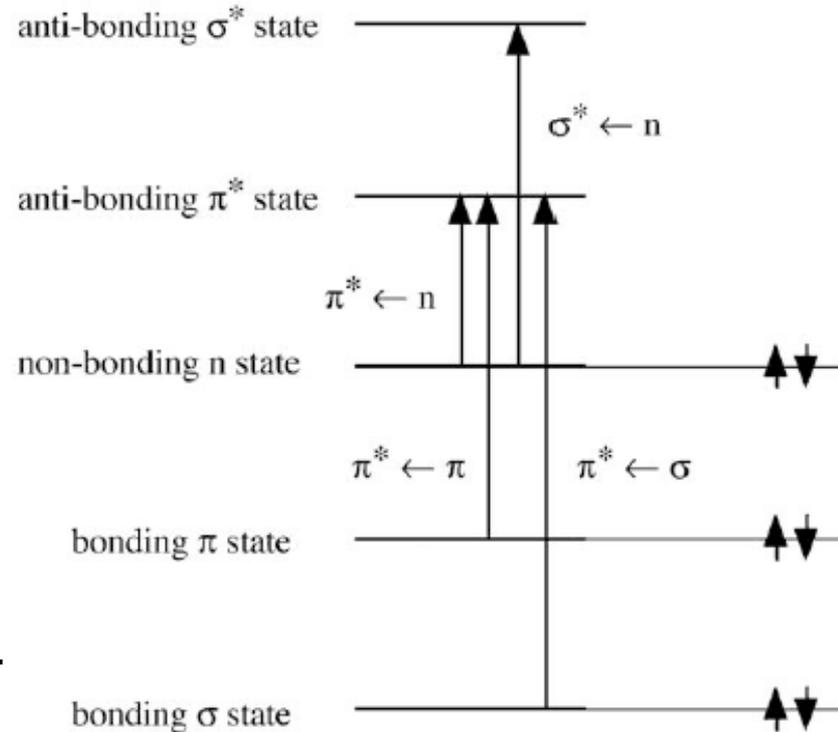
One must act as donor and other as acceptor.

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



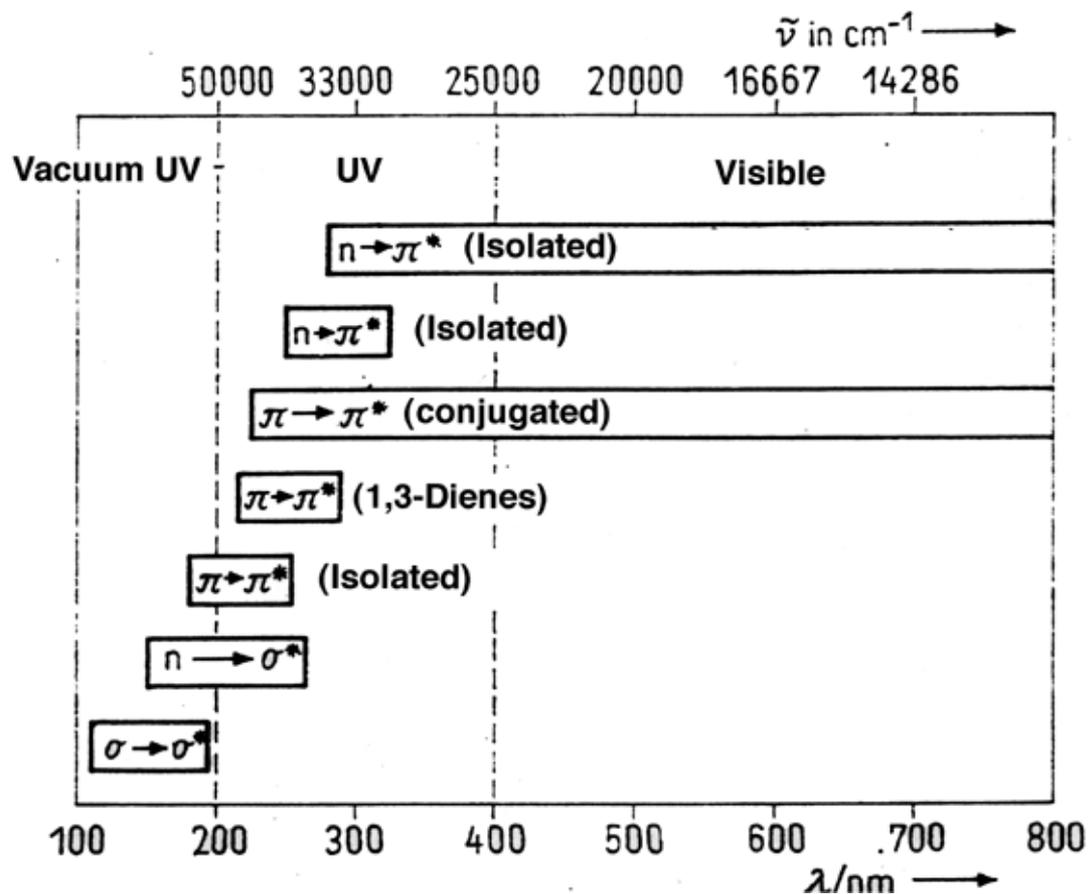
Wavelengths below 200 nm are absorbed by air therefore, can not be registered with a ordinary UV-Vis spectrometer.

"**Vacuum UV**" all parts must be maintained in a vacuum.

The vacuum UV absorption are caused by $\sigma \rightarrow \sigma^*$ transitions.

These transitions correspond to simple bonds and are common to all molecules.

$\pi \rightarrow \pi^*$ transitions depend on the conjugation, so it can reach the visible region of radiation, causing the color of substances.

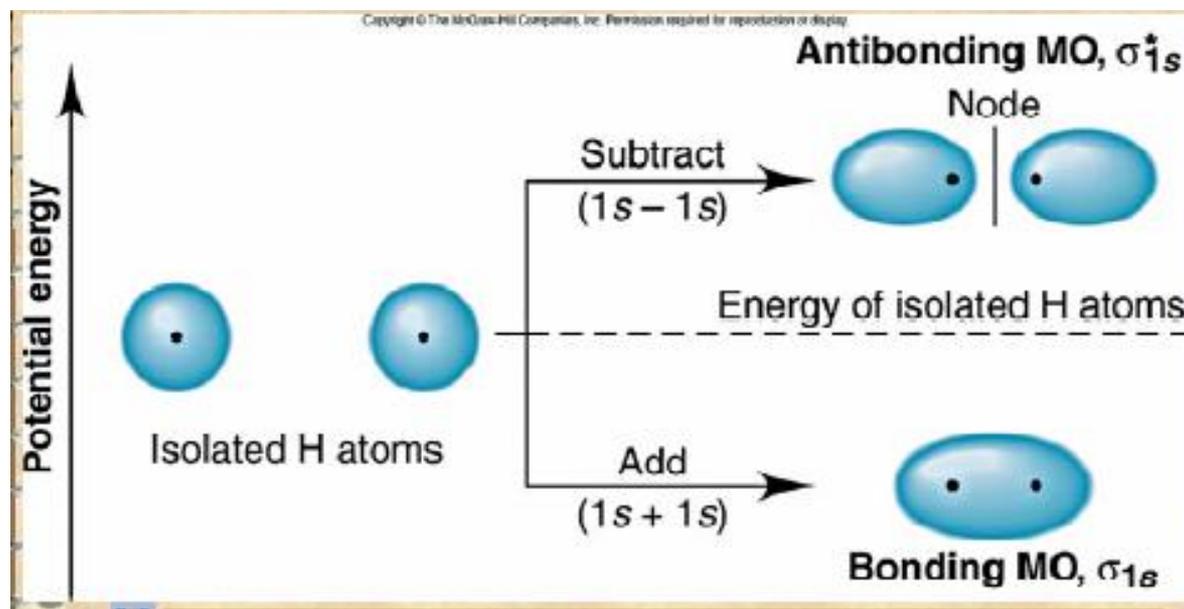
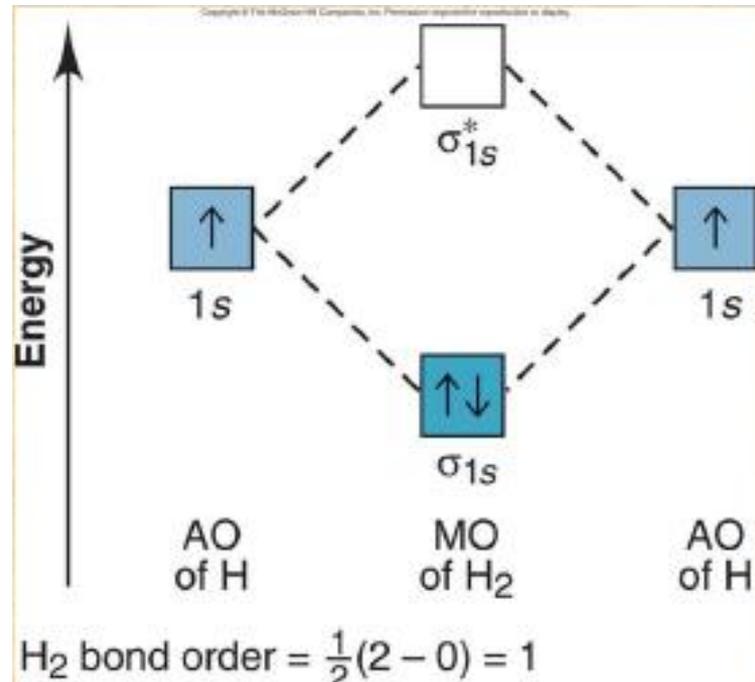


Molecular orbital theory (MO):

An *atomic orbital* is the space within which an electron belonging to the orbital spends 95% of its time.

In **molecular orbital theory orbitals embrace two or more nuclei.**

Electrons in a molecule are not tied to a particular atom, they are "scattered" throughout the entire molecule.



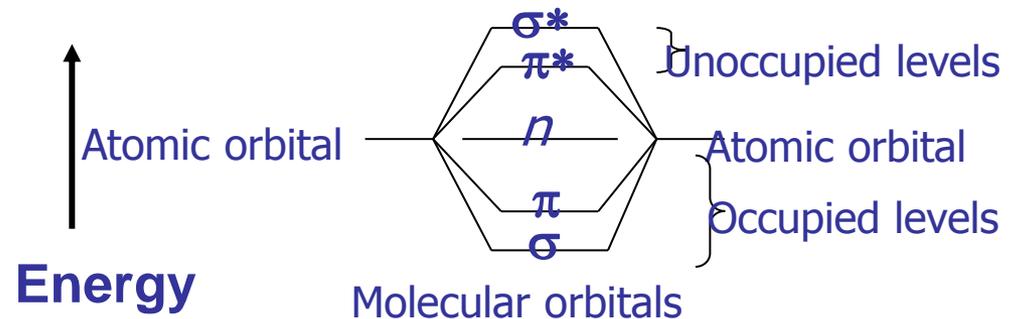
The **lowest energy transition** (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (**HOMO**) to the Lowest Unoccupied Molecular Orbital (**LUMO**)

For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every **bonding orbital** “created” from this mixing (σ , π), there is a corresponding **anti-bonding orbital** of symmetrically higher energy (σ^* , π^*)

σ -orbitals: typically are the lowest energy occupied orbitals; the corresponding **anti-bonding (σ^*)** orbital is of the highest energy

π -orbitals are of somewhat higher energy, and their complementary **anti-bonding orbital (π^*)** somewhat lower in energy than σ^* .

n -orbitals: non-bonding electrons lie at the energy of the original atomic orbital, most often this energy is higher than π or σ (since **no bond** is formed, there is no benefit in energy)



Molecular orbital wavefunction is a linear combination of atomic orbital wavefunctions.

For **bonding orbitals** the interference between the two atomic orbitals are **constructive**.
For **antibonding orbitals** the interference between the two atomic orbitals are **destructive**.

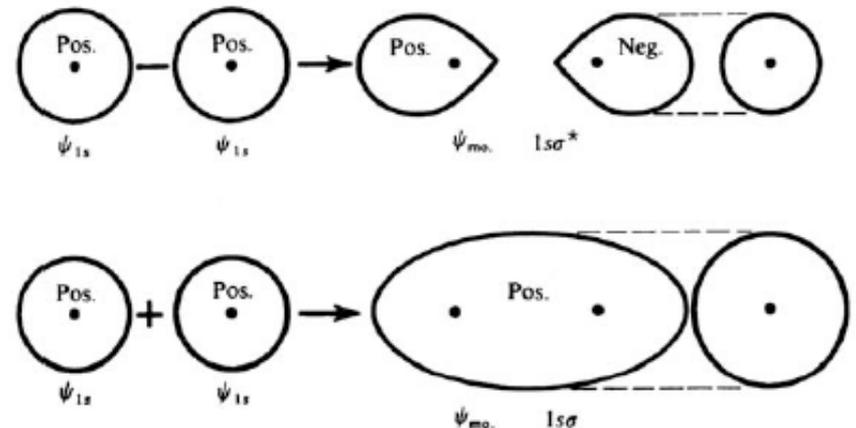
Ex: *Hydrogen molecule*:

$$\text{The sum: } \psi_{\text{H}_2}^+ = \psi_{1s} + \psi_{1s}$$

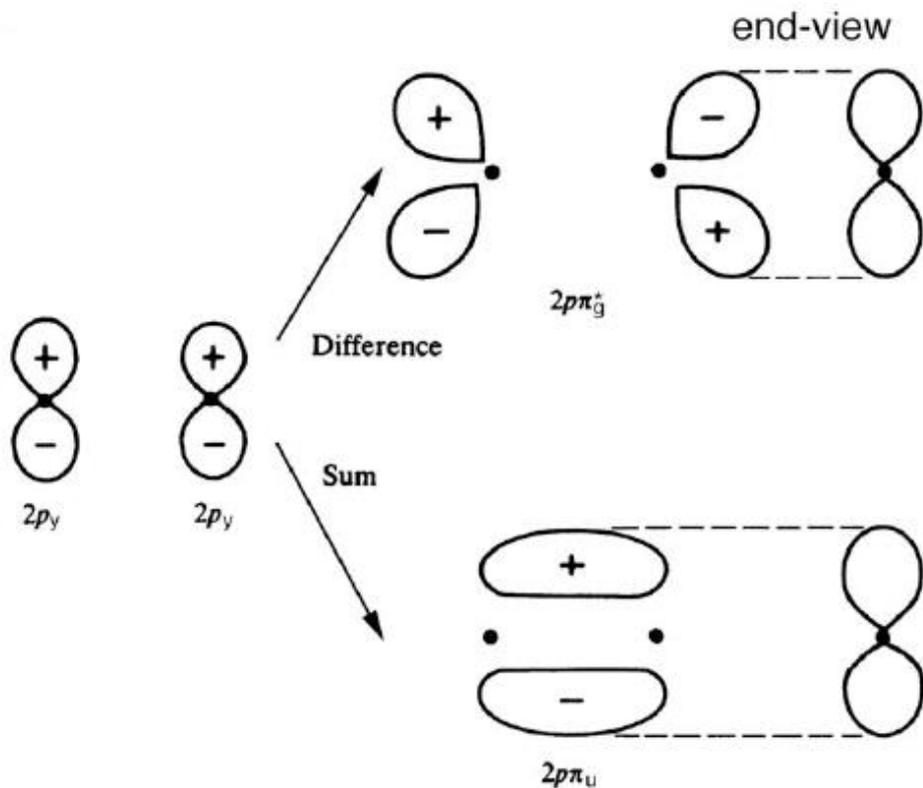
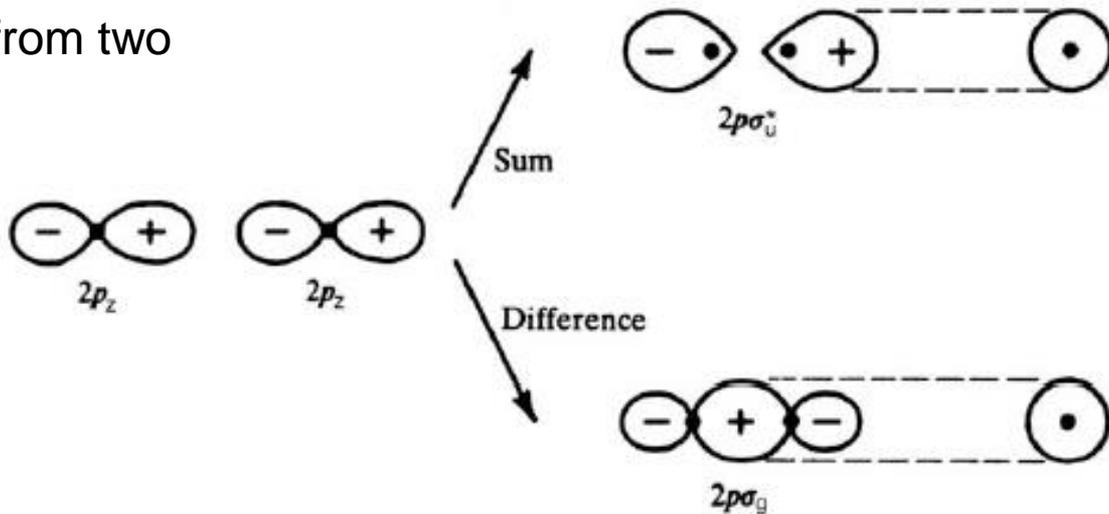
This **bonding** orbital (called $1s\sigma$, as it is produced from two s atomic orbitals) is a simple symmetrical ellipsoid. It does not change sign upon inversion about the centre of symmetry, which is marked by the subscript *g* (*gerade* = even). The orbital is thus known as $1s\sigma_g$.

$$\text{The difference: } \psi_{\text{H}_2}^- = \psi_{1s} - \psi_{1s}$$

In this **antibonding** orbital (called $1s\sigma^*$) the charge is concentrated **outside** the nuclei, which repel one another. This orbital does change sign upon inversion, which is marked by the subscript *u* (*ungerade* = odd). It is thus known as $1s\sigma_u^*$.



formation of σ_g and σ_u^* orbitals from two atomic $2p_z$ orbitals



formation of π_g and π_u^* orbitals from two atomic $2p_y$ orbitals

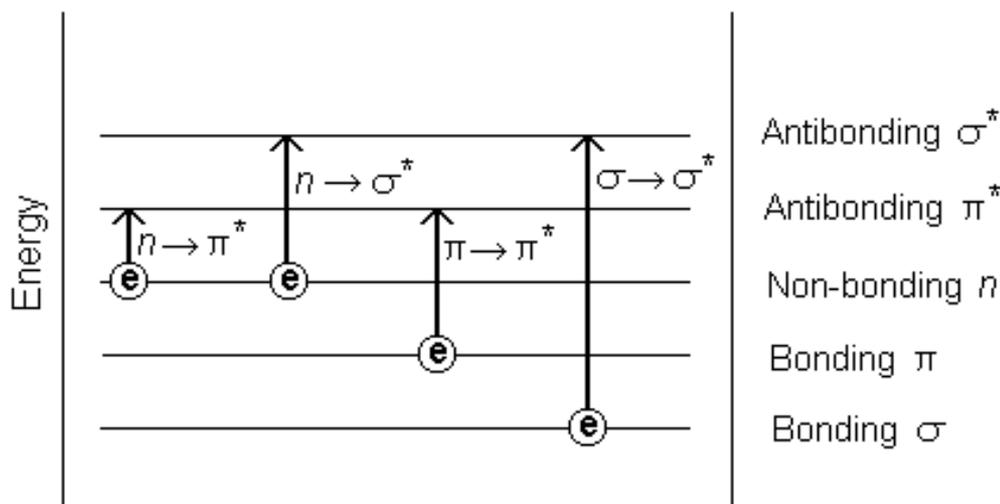
Transitions involving electrons π , σ and n

$\sigma \rightarrow \sigma^*$ 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 **decreas 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***.

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.

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

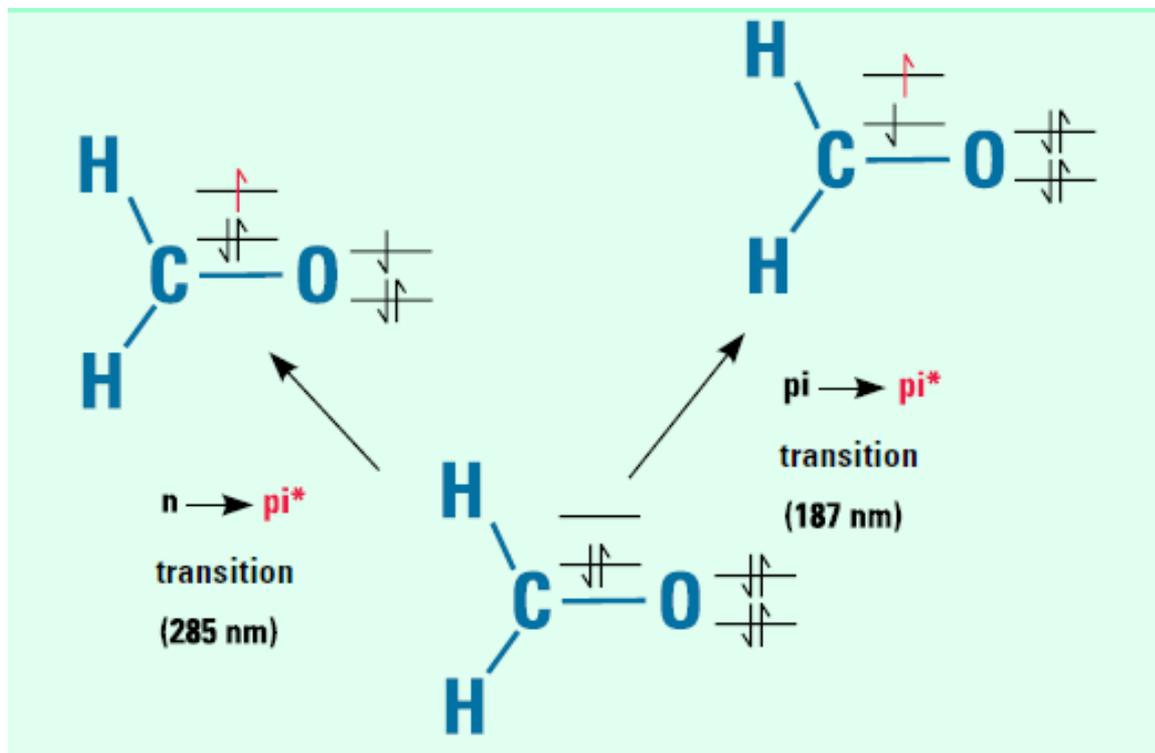
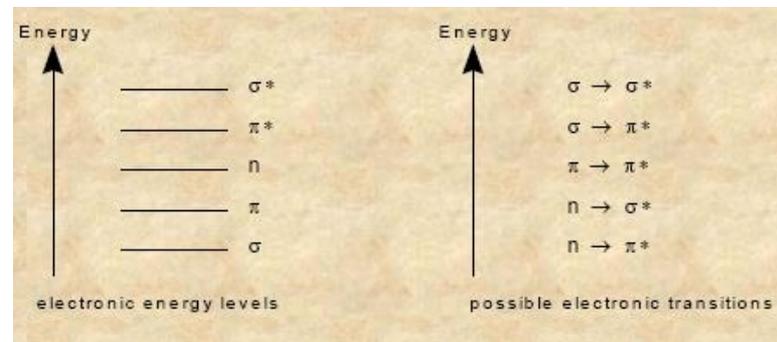
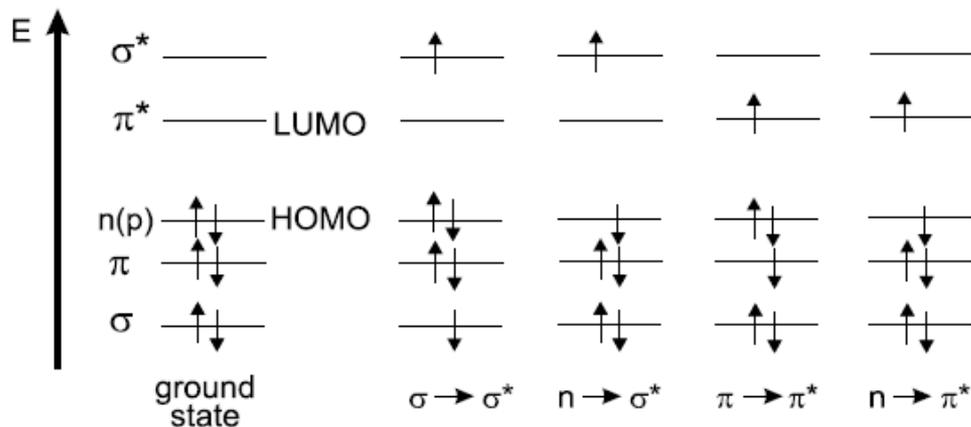
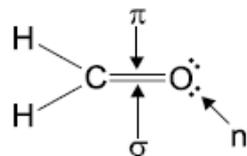


Figure 2
Electronic transitions in formaldehyde

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.



Transitions involving π and n orbitals (n = non-bonding) are important because they can be used to identify **conjugate systems**, which have strong absorption.

*The lowest energy transition is that between the **HOMO** (Highest occupied molecular orbital) and **LUMO** (Lowest unoccupied molecular orbital) orbitals.*

The absorption of electromagnetic radiation extract an electron from the HOMO and transfer it on the LUMO, creating an excited state.

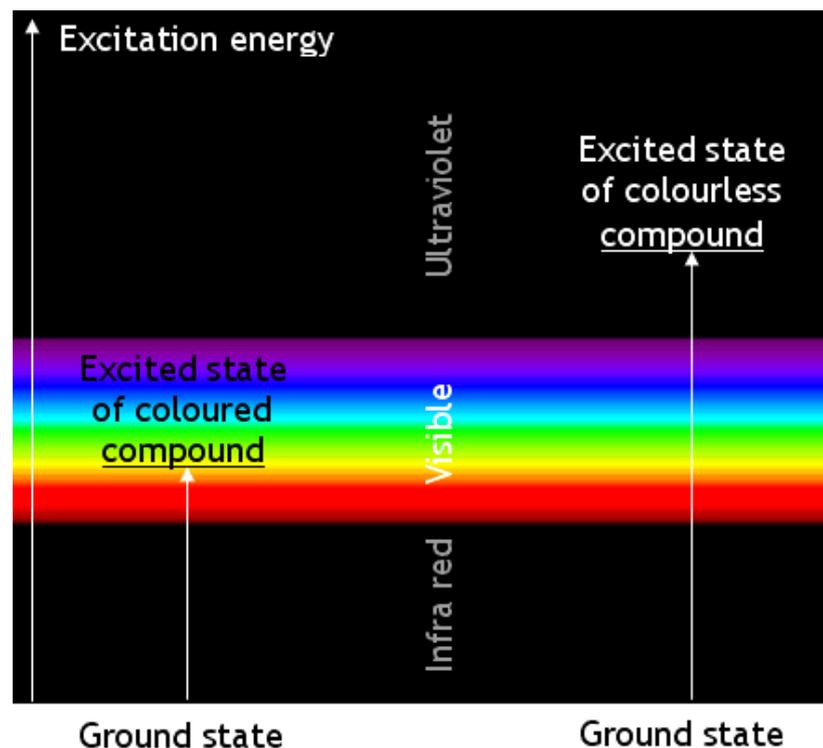
The color arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others.

Absorption spectrum consists of **absorption bands** corresponding to **structural groups** of molecules (**chromophores**)

Chromophores: atom groups acting as a light absorber!

The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum.

Visible light that hits the chromophore can be absorbed by exciting an electron from its ground state into an excited state.



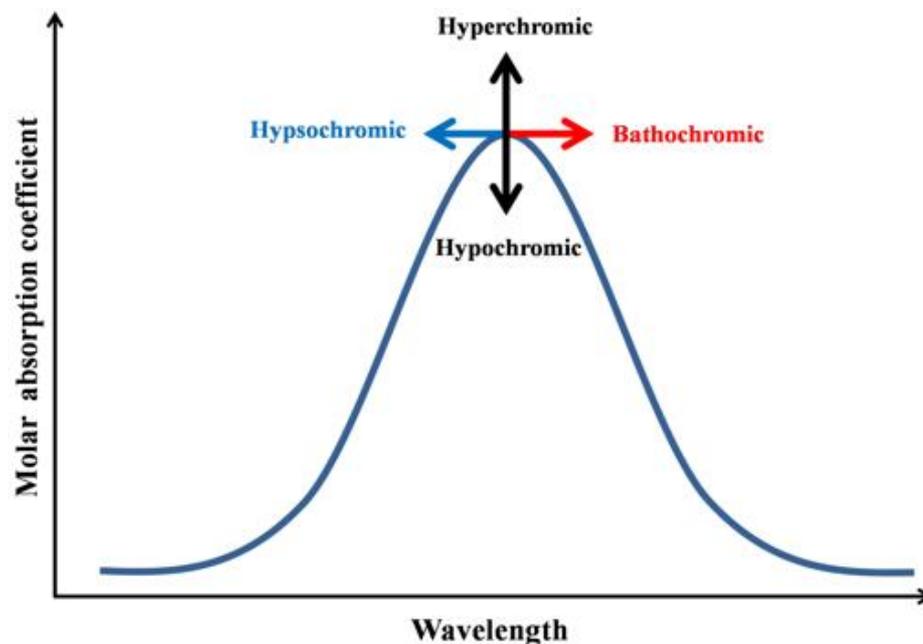
In the absorption spectrum of molecules that contain **more chromophores**, the following changes can occur due to *interaction of the chromophores*:

Hypsochromic shift ($\lambda_{\max} \downarrow$)

Bathochromic shift ($\lambda_{\max} \uparrow$)

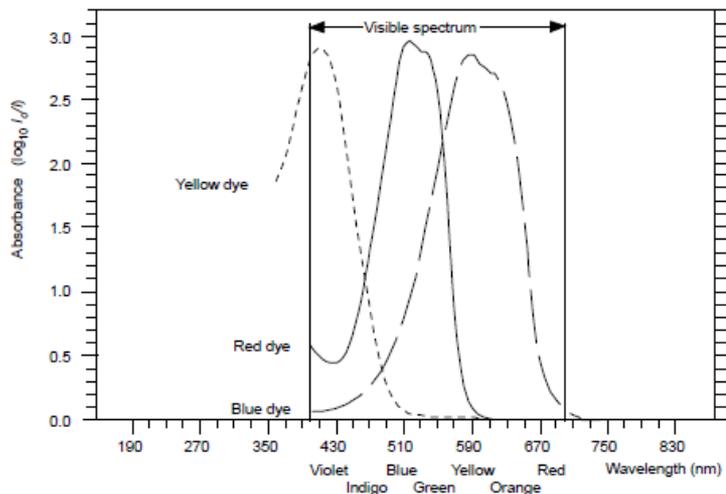
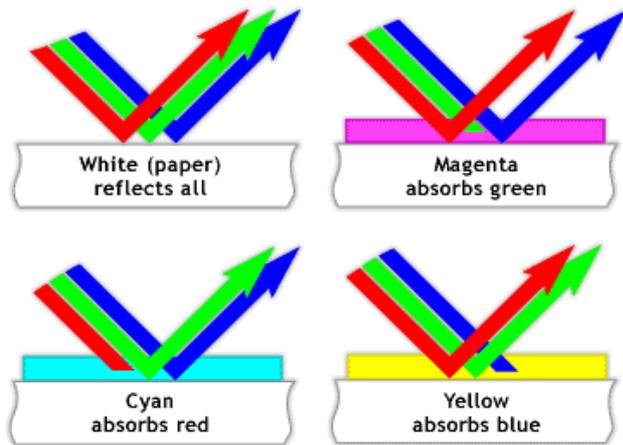
Hypochromic effect (abs. \downarrow)

Hyperchromic effect (abs. \uparrow)



The color of a substance:

- *the transmitted color* not the absorbed color
- the color that remains after subtracting from the incident light the absorbed light.

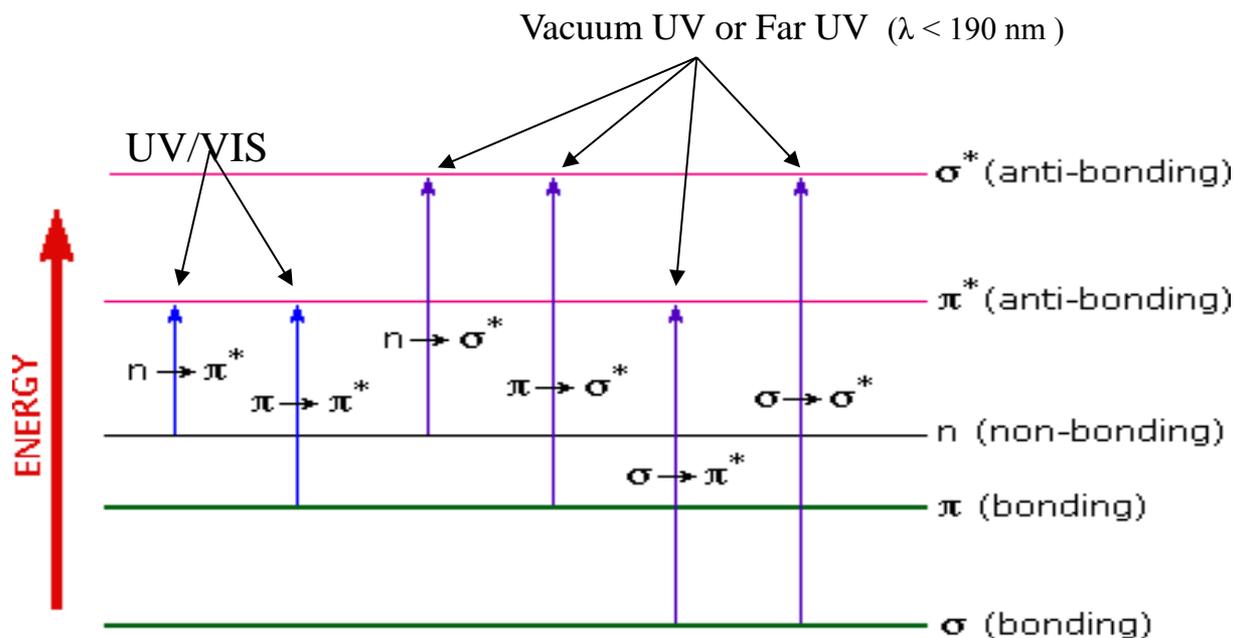


Absorbed Light		Observed (transmitted) color
Wavelength nm	Corresponding color	
400	violet	yellow-green
425	indigo blue	yellow
450	blue	orange
490	blue-green	red
510	green	purple
530	yellow-green	violet
550	yellow	indigo blue
590	orange	blue
640	red	blue-green
730	purple	green

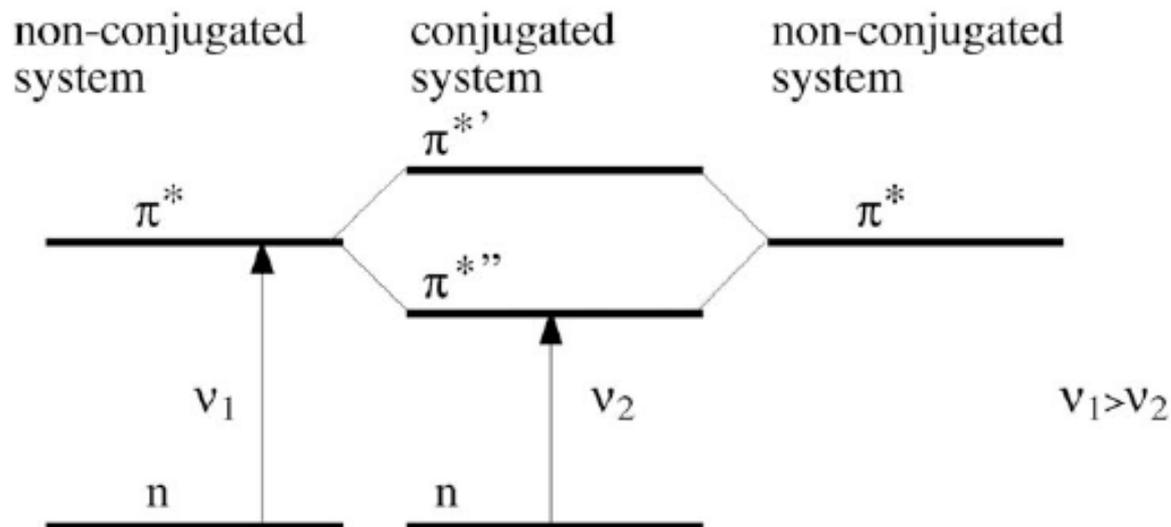
The color we see in ink, dyes, flowers, etc. is due to conjugation of organic molecules!

If the system is conjugated, the gap between HOMO and LUMO became lower, so the frequency of radiation absorbed is smaller (the wavelength of radiation absorbed is greater).

Conjugated molecules are those in which there is an alternation of single and double bonds along a chain of carbon atoms.



When two isolated double bonds are brought into conjugation, both levels are shifted to give bonding and anti-bonding orbitals.



The effect of conjugation is that the LUMO π^* orbital is shifted downwards, and the $n \rightarrow \pi^*$ absorption shifts to lower energy (longer wavelengths).

Repeated conjugation increases this effect.

Absorption by a C=C double bond excites a π electron into an antibonding π^* orbital. The chromophore activity is due to an $\pi \rightarrow \pi^*$ transition, corresponding to absorption at 180 nm.

When the double bond is part of a conjugated chain, the energies of the molecular orbitals lie closer together, and the $\pi \rightarrow \pi^*$ transition moves to longer wavelengths (lower energy). It may even lie in the visible region if the conjugated system is long enough.

An important *example* is the *photochemical mechanism of vision*.

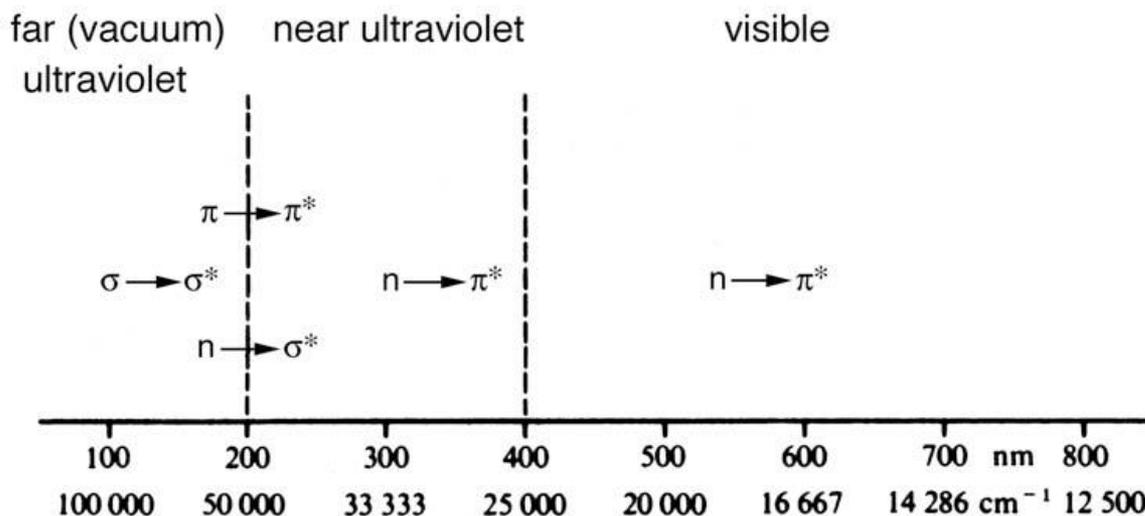
The retina of the eye contains “*visual purple*”, a combination of a protein with 11-*cis*-retinal, which acts as a *chromophore* and is a receptor of photons entering the eye.

11-*cis*-retinal itself absorbs at 380 nm, but in combination with the protein the *absorption maximum* shifts to ca. 500 nm and tails into the blue.

The **conjugated double bonds** are responsible for the ability of the molecule to absorb over the entire visible region. They play another important role: in its electronically excited state the conjugated chain can isomerize by twisting about an excited C=C bond, forming 11-*trans*-retinal.

The primary step in vision is photon absorption followed by isomerization, which triggers a nerve impulse to the brain.

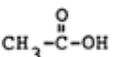
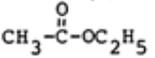
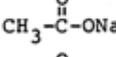
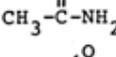
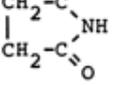
regions of the electronic spectrum

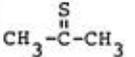


Chromophores have well know absorption maxima:

Chromophore	Example	Excitation	λ_{\max} , nm	ϵ	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C \equiv C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

$\text{—C}\equiv\text{C—}$	175-215 nm
$\begin{array}{l} \text{R} \\ \text{R} \end{array} \text{C=O}$	270 nm
$\begin{array}{l} \text{R} \\ \text{H} \end{array} \text{C=O}$	290 nm
—OH	186 nm
—N=N—	345 nm
	200, 268 nm

Chromophore	Compound	Transition	λ_{\max} [nm]	ϵ_{\max}	Solvent
C-C	CH ₃ -CH ₃	$\sigma \rightarrow \sigma^*$	135	strong	gas
C-H	CH ₄	$\sigma \rightarrow \sigma^*$	122	strong	gas
C-O	CH ₃ OH	$n \rightarrow \sigma^*$	177	200	hexane
	CH ₃ -O-CH ₃	$n \rightarrow \sigma^*$	184	2500	gas
C-N	(C ₂ H ₅) ₂ NH	$n \rightarrow \sigma^*$	193	2500	hexane
	(CH ₃) ₃ N	$n \rightarrow \sigma^*$	199	4000	hexane
C-S	CH ₃ -SH	$n \rightarrow \sigma^*$	195	1800	gas
		$n \rightarrow \sigma^*$	235	180	gas
	C ₂ H ₅ -S-C ₂ H ₅	$n \rightarrow \sigma^*$	194	4500	gas
		$n \rightarrow \sigma^*$	225	1800	gas
S-S	C ₂ H ₅ -S-S-C ₂ H ₅	$n \rightarrow \sigma^*$	194	5500	hexane
		$n \rightarrow \sigma^*$	250	380	
C-Cl	CH ₃ Cl	$n \rightarrow \sigma^*$	173	200	hexane
C-Br	n-C ₃ H ₇ Br	$n \rightarrow \sigma^*$	208	300	hexane
C-I	CH ₃ I	$n \rightarrow \sigma^*$	259	400	hexane
C=C	CH ₂ =CH ₂	$\pi \rightarrow \pi^*$	162.5	15000	heptane
	(CH ₃) ₂ C=C(CH ₃) ₂	$\pi \rightarrow \pi^*$	196.5	11500	heptane
C=O	(CH ₃) ₂ -C=O	$n \rightarrow \sigma^*$	166	16000	gas
		$\pi \rightarrow \pi^*$	189	900	hexane
		$n \rightarrow \pi^*$	279	15	hexane
		$n \rightarrow \pi^*$	200	50	gas
		$n \rightarrow \pi^*$	210	50	gas
		$n \rightarrow \pi^*$	210	150	water
		$n \rightarrow \pi^*$	220	63	water
			191	15200	aceto-nitrile
C=N	H ₂ N-C(=NH)-NH ₂ ·HCl		265	15	water
	(CH ₃) ₂ C=NOH		193	2000	ethanol
	(CH ₃) ₂ -C=NONa		265	200	ethanol
N=N	CH ₃ -N=N-CH ₃		340	16	ethanol

N=N	CH ₃ -N=N-CH ₃	340	16	ethanol
N=O	(CH ₃) ₃ C-NO	300	100	ether
		665	20	
	(CH ₃) ₃ C-NO ₂	276	27	ethanol
	n-C ₄ H ₉ -O-NO	218	1050	
		313-384	20-40	ethanol
	C ₂ H ₅ -O-NO ₂	260	15	ethanol
C=S		460	weak	
		495	weak	ethanol
C≡C	HC≡CH	173	6000	gas
	n-C ₅ H ₁₁ -C≡C-CH ₃	177.5	10000	hexane
		196	2000	
		222.5	160	
C≡N	CH ₃ -C≡N	<190		
X=C=Y	CH ₂ =C=CH ₂	170	4000	
		227	630	
	(C ₂ H ₅) ₂ C=C=O	227	360	
		375	20	
	C ₂ H ₅ -N=C=N-C ₂ H ₅	230	4000	
		270	25	
	C ₂ H ₅ -N=C=S	250	1200	hexane

The color of conjugated systems

The conjugation of double or triple bonds lead to increased absorptivity and determine the shift of λ_{\max} to higher wavelengths (bathochromic shift):

	λ_{\max} . (nm)	ϵ
—C=C—	170	16 000
—C=C—C=C—	220	21 000
—C=C—C=C—C=C—	260	35 000

The word "**conjugation**" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when π systems are "linked together".

An "**isolated**" π system exists only between a single pair of adjacent atoms (e.g. **C=C**)

An "**extended**" π system exists over a longer series of atoms (e.g. **C=C-C=C** or **C=C-C=O** etc.).

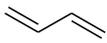
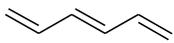
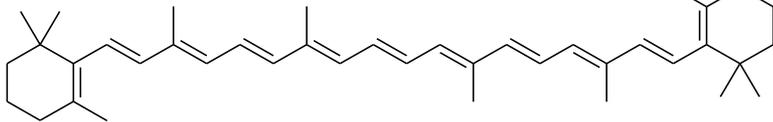
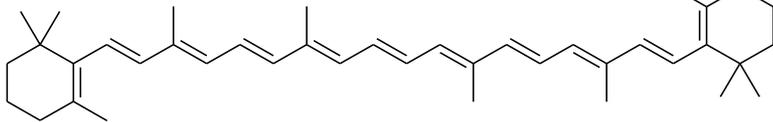
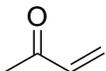
An extended π system results in an extension of the chemical reactivity.

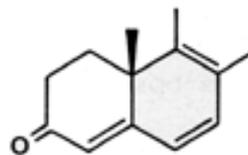
A conjugated system requires that there is a continuous array of " π " orbitals that can align to produce a bonding overlap along the whole system.

If a position in the chain does not provide a " π " orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point.

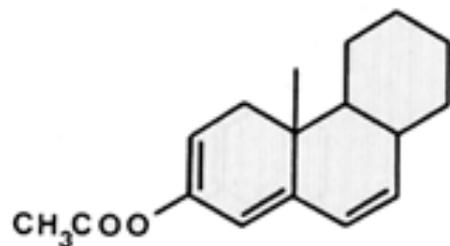
The result of conjugation is that there are extra π bonding interactions between the adjacent π systems that results in an overall stabilisation of the system.

Conjugation = most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

	λ_{\max} (nm)	ϵ
$\text{H}_2\text{C}=\text{CH}_2$ 	175	15,000
	217	21,000
	258	35,000
 β-carotene	465	125,000
	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 189	12 900
	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 213	27 7,100



	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

UV-Vis Selection rules:

1. Spin rule: Changes in spin multiplicity are forbidden

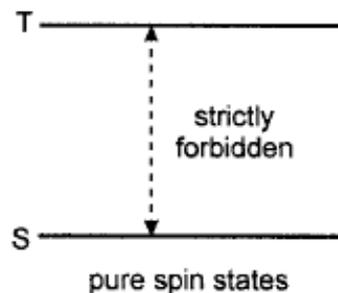
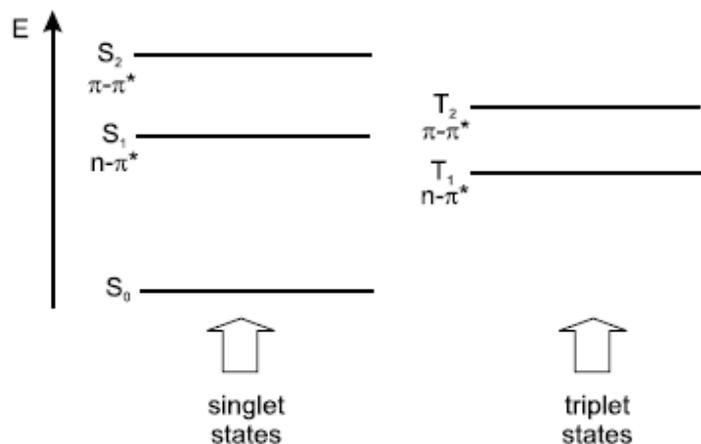
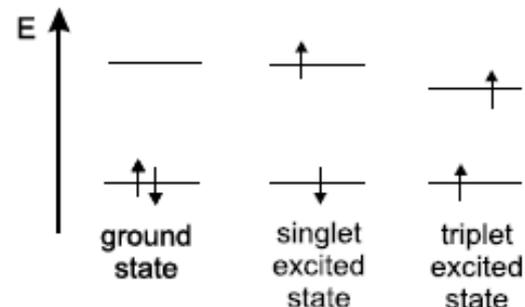
Therefore, transitions between states with different multiplicity are forbidden

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

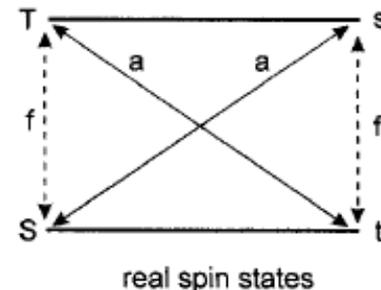
forbidden transitions: singlet \rightarrow triplet or triplet \rightarrow singlet

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)