

UV and Visible spectroscopy

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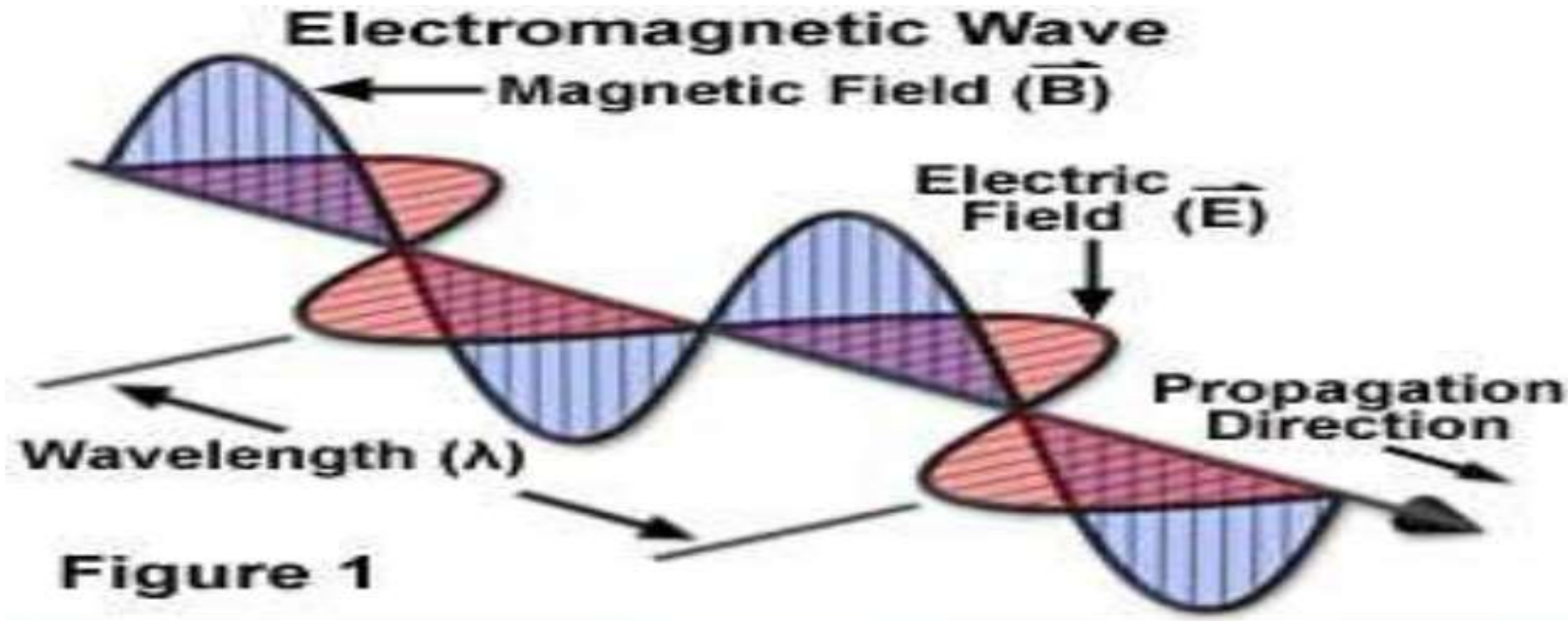


What is Spectroscopy?

Spectroscopy is the study and measurement of interaction of radiant energy and the matter

Electromagnetic Radiation

This is radiant energy and consists of mutually perpendicular Electric and Magnetic vectors which oscillates sinusoidally as wave propagates at high speed

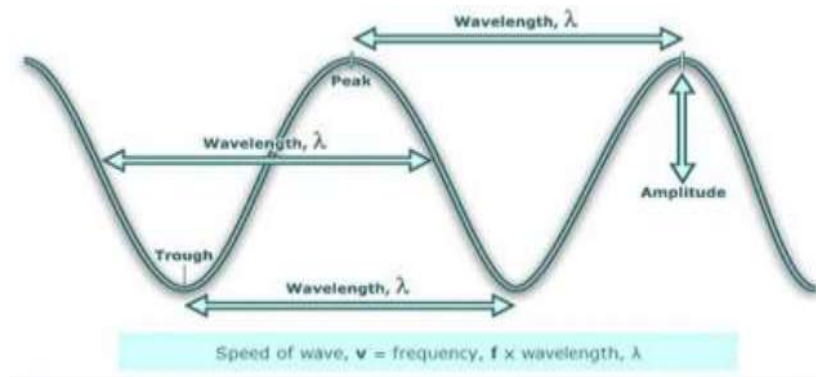


Electromagnetic Radiation:

When falls on matter there may be various phenomena depending on the nature of radiation and that of matter

- Reflection
- Emission
- Absorption
- Transmission
- Scattering

The characteristics of a wave



Wavelength (λ) : The distance between two successive crests or troughs is wavelength.

Frequency (ν) : This is the number of waves or complete cycles passing through a point per second. The unit is cycles per second or Hz

Wavenumber ($\bar{\nu}$): It is the number of cycles or wavelengths per unit distance. It is the reciprocal of wavelength.

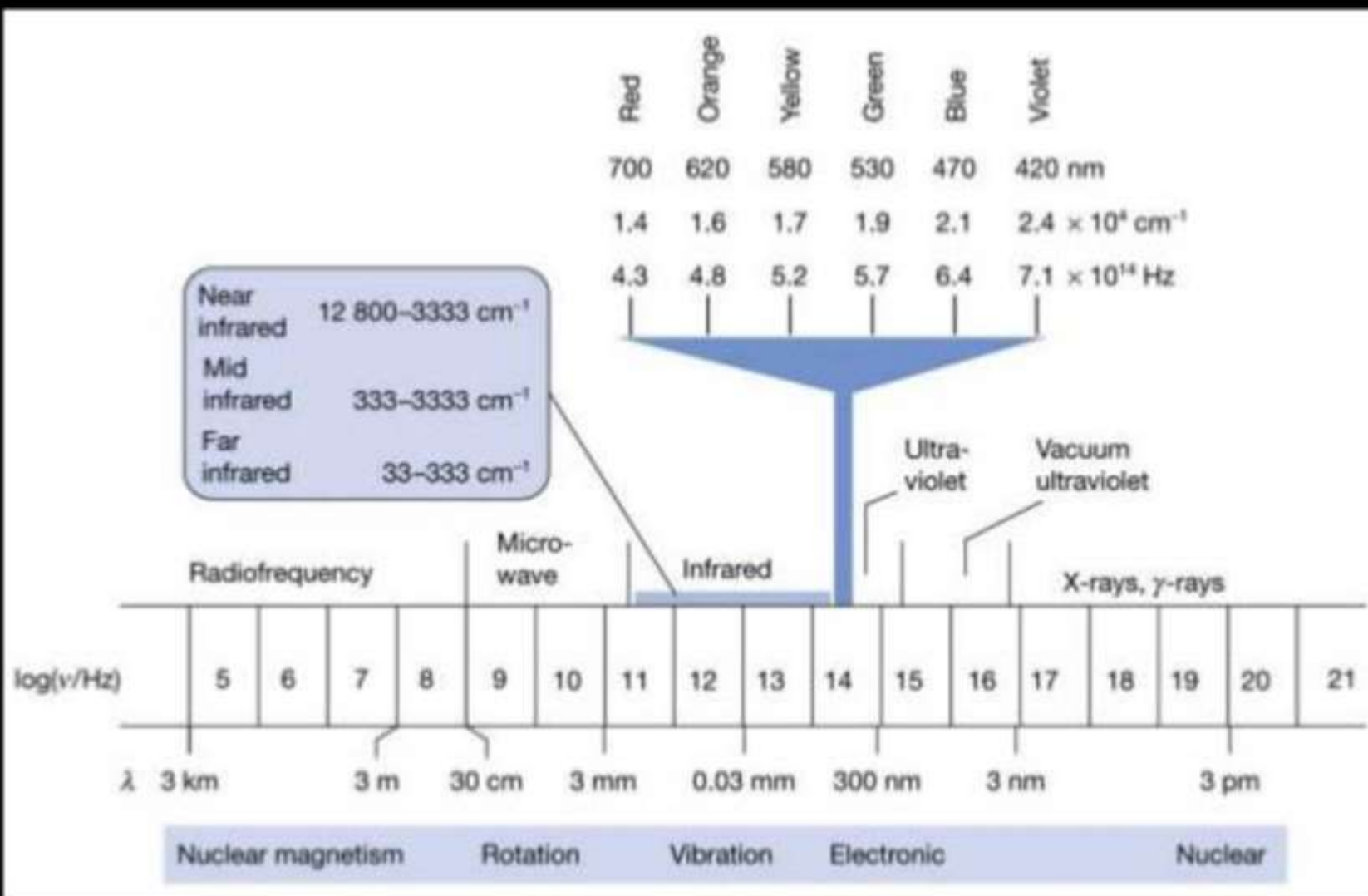
Amplitude (a) : The maximum displacement of wave from the mean position is called as amplitude.

Velocity (C): It is distance travelled by wave in unit time. The velocity of radiation I vacuum is 3.0×10^8 m/s.

- Electromagnetic Spectrum :Different Regions

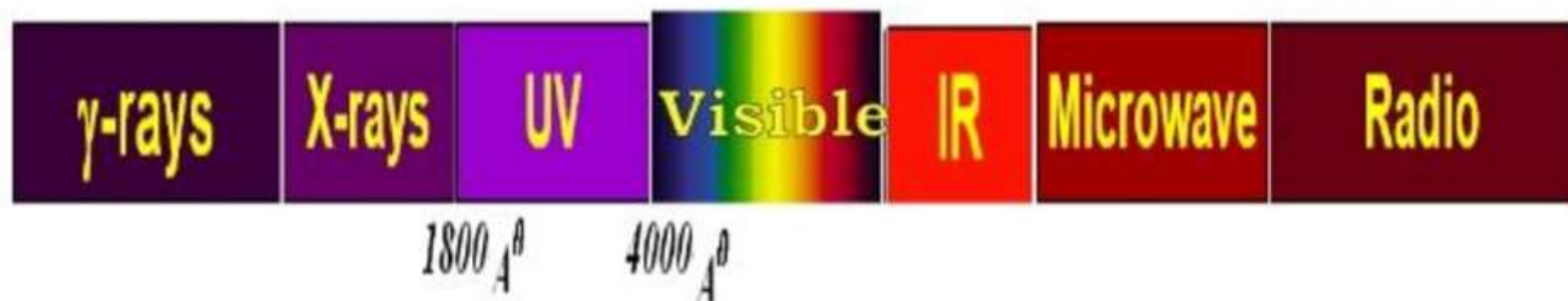
- Radio wave region
- Microwave region
- Infrared region
- Visible region
- Ultraviolet region
- X-ray region
- Gamma ray region

THE ELECTROMAGNETIC SPECTRUM



Electromagnetic Spectrum

The region beyond red is called **infra-red** while that beyond violet is called as **ultra-violet**.



Study of spectroscopy

Atomic spectroscopy:

interaction of EMR+ATOMS

Changes in energy take place at atomic level

Eg: atomic absorption spectroscopy, flame photometry

Molecular spectroscopy:

Interaction of EMR + molecules

Changes in energy take place at molecular level

Eg: UV, IR, colorimetry

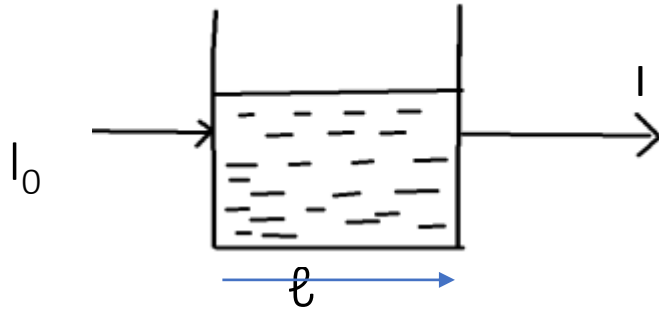
Results in transitions between vibrational, & rotational energy levels

UV AND VISIBLE RADIATIONS ARE ENERGETIC THAT THEY PRODUCE ELECTRONIC EXCITATION. HENCE, UV-VISIBLE SPECTROSCOPY IS ALSO CALLED AS ELECTRONIC SPECTROSCOPY.

UV REGION EXTENDS FROM 100-400NM. THE REGION 100-200 NM IS FAR ULTRAVIOLET REGION. FOR PRACTICAL PURPOSE, LOWER LIMIT IS 200 NM. THE SOURCE FOR UV LIGHT IS DEUTERIUM DISCHARGE LAMP.

VISIBLE REGION EXTENDS FROM 400 – 800 NM RANGE OF ELECTROMAGNETIC SPECTRUM. THE SOURCE FOR VISIBLE RADIATIONS IS TUNGSTEN FILAMENT LAMP.

Lambert's Law: When a ray of monochromatic radiation passes through an absorbing medium, its intensity decreases exponentially as the length of absorbing medium increases.



I_0 – Intensity of incident Light
 I – Intensity of transmitted light
 l – Length of absorbing medium

Mathematically,

$$I = I_0 e^{-k_1 l}$$

Beer's Law:

When a ray of monochromatic radiation passes through an absorbing medium, its intensity decreases exponentially as the concentration of absorbing medium increases.

If c is the concentration of absorbing medium,

Mathematically.

$$I = I_0 e^{-k_2 c}$$

Beer-Lambert's law:

Combining Lambert and Beer's law,

$$I = I_0 e^{-(kcl)}$$

Rearranging,

$$I / I_0 = e^{-(kcl)}$$

$$\ln I / I_0 = -kcl$$

$$2.303 \text{Log } I / I_0 = -kcl$$

$$\text{Log } I / I_0 = -kcl / 2.303$$

$$\text{Log } I_0 / I = kcl / 2.303$$

$k/2.303$ is a constant known as extinction coefficient ϵ

$$\text{Log } I_0 / I = \epsilon cl$$

$\text{Log } I_0 / I$ is known as absorbance and denoted as A

$$A = \epsilon cl$$

When concentration is expressed in mol/dm³ and path length in cm, A is called as molar absorbance and ϵ is called as molar extinction coefficient.

When $c = 1\text{M}$ and length = 1 cm,

$$A = \epsilon$$

So molar extinction coefficient is defined as molar absorbance of 1M solution of an absorbing substance in 1cm path length cuvette under given conditions of wavelength, solvent and temperature.

Limitations of Beer- Lambert's law :

- Beer-Lambert's law holds good for dilute solutions (below 0.01 M)
- The wavelength of light used should be one (monochromatic)
- The absorbing solute should not associate, dissociate
- There should not be complexation of solute particles.

Terms used in UV Visible Spectroscopy :

Chromophore:

It is a covalently unsaturated group which is responsible for absorption of UV or visible radiation and may or may not impart colour to the compound.

-N=N-, the π electrons are loosely bound. These loosely bound electrons require less energy for electronic transition and the absorption band occurs in the near UV region.

A compound which contains a chromophore is called a chromogen.

Auxochrome:

It is a saturated and unsaturated group which consists of one or more pairs of non-bonded electrons.

This group is attached to a chromophore and helps in altering the wavelength by increasing the intensity of absorption and increasing λ_{\max} .

Example of an auxochrome is -OH, -NH₂, -OR etc.

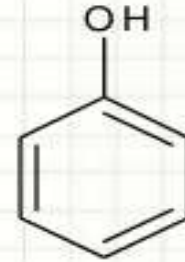
Chromophore	Example	Excitation	λ_{\max} , nm	ϵ	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C \equiv C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$	290	15	hexane
		$\pi \rightarrow \pi^*$	180	10,000	hexane
N=O	Nitromethane	$n \rightarrow \pi^*$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

Auxochrome

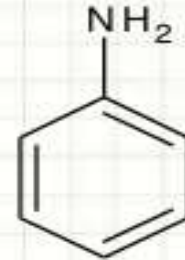
e.g. Benzene $\lambda_{\max} = 255 \text{ nm}$



Phenol $\lambda_{\max} = 270 \text{ nm}$



Aniline $\lambda_{\max} = 280 \text{ nm}$



Type of Shifts

1. Bathochromic shift (Red shift) :-

In this Types the absorption maximum shift towards longer wavelength. When two or more chromophore present in a molecule, it is responsible for bathochromic shift.

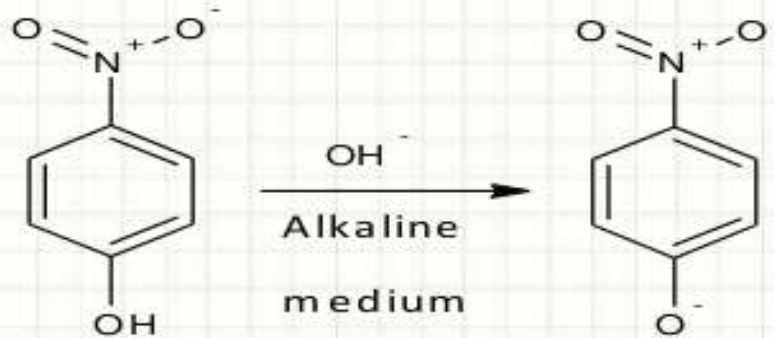
Ex. Ethene which contains unconjugated double bond shows λ_{\max} at 170 nm.

In case butadiene, it shows λ_{\max} at 210 nm.

1

• Bathochromic Shift (Red Shift)

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



p-nitrophenol

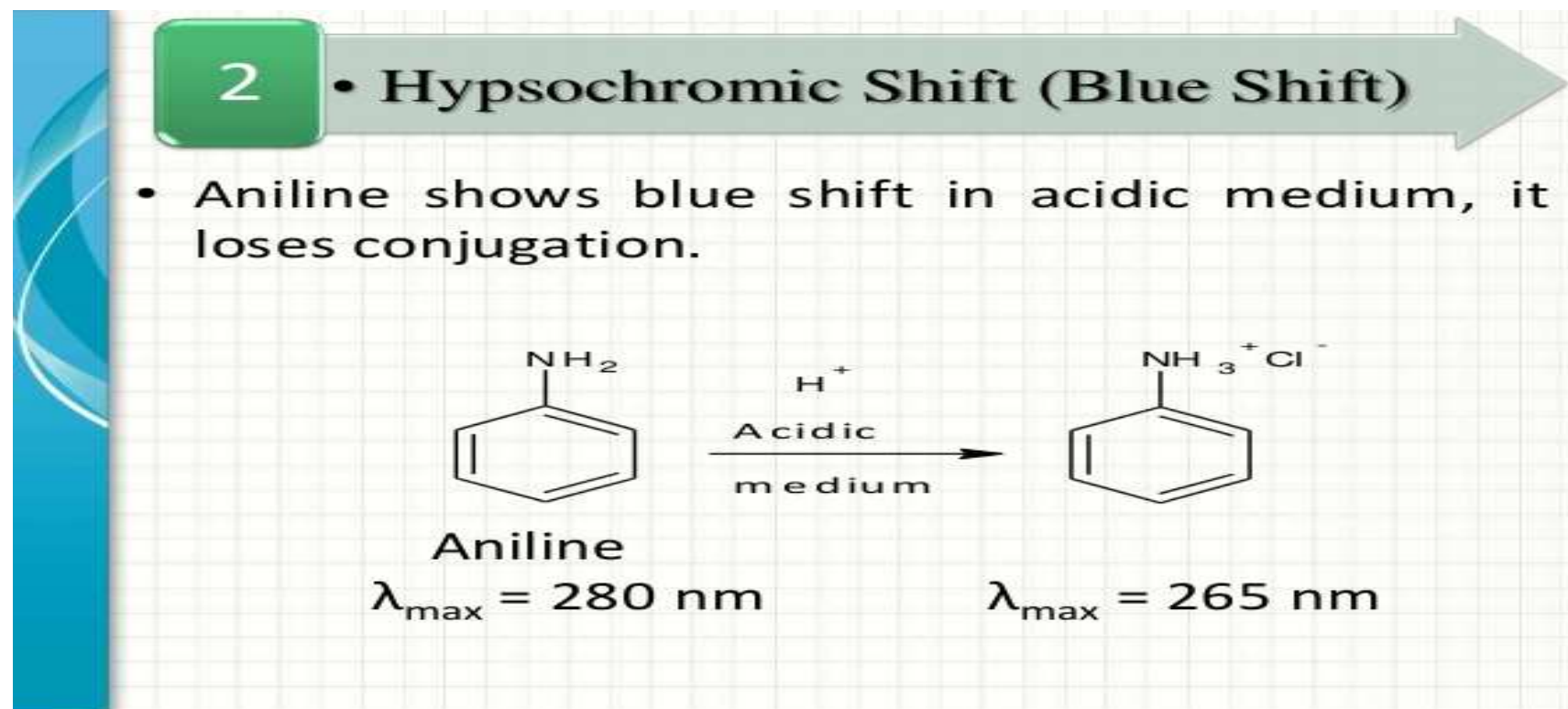
$\lambda_{\max} = 255 \text{ nm}$

$\lambda_{\max} = 265 \text{ nm}$

2. Hypsochromic shift (Blue shift) :-

In this Type the absorption maximum shift towards shorter wavelength. This shift is occur due to removal of conjugation or due to change in the polarity of the solvent.

Ex. Aniline show λ_{\max} at 280 nm because of on conjugation between lone pair of electron between nitrogen and benzene.



3. Hyperchromic shift :-

In this Type of shift increase in intensity with increase of absorption of radiation.

This is due to the introduction of Auxochrome.

Ex. Increase in intensity of the absorption of DNA due to denaturation at the λ_{\max} 260 nm.

4. Hypochromic shift :-

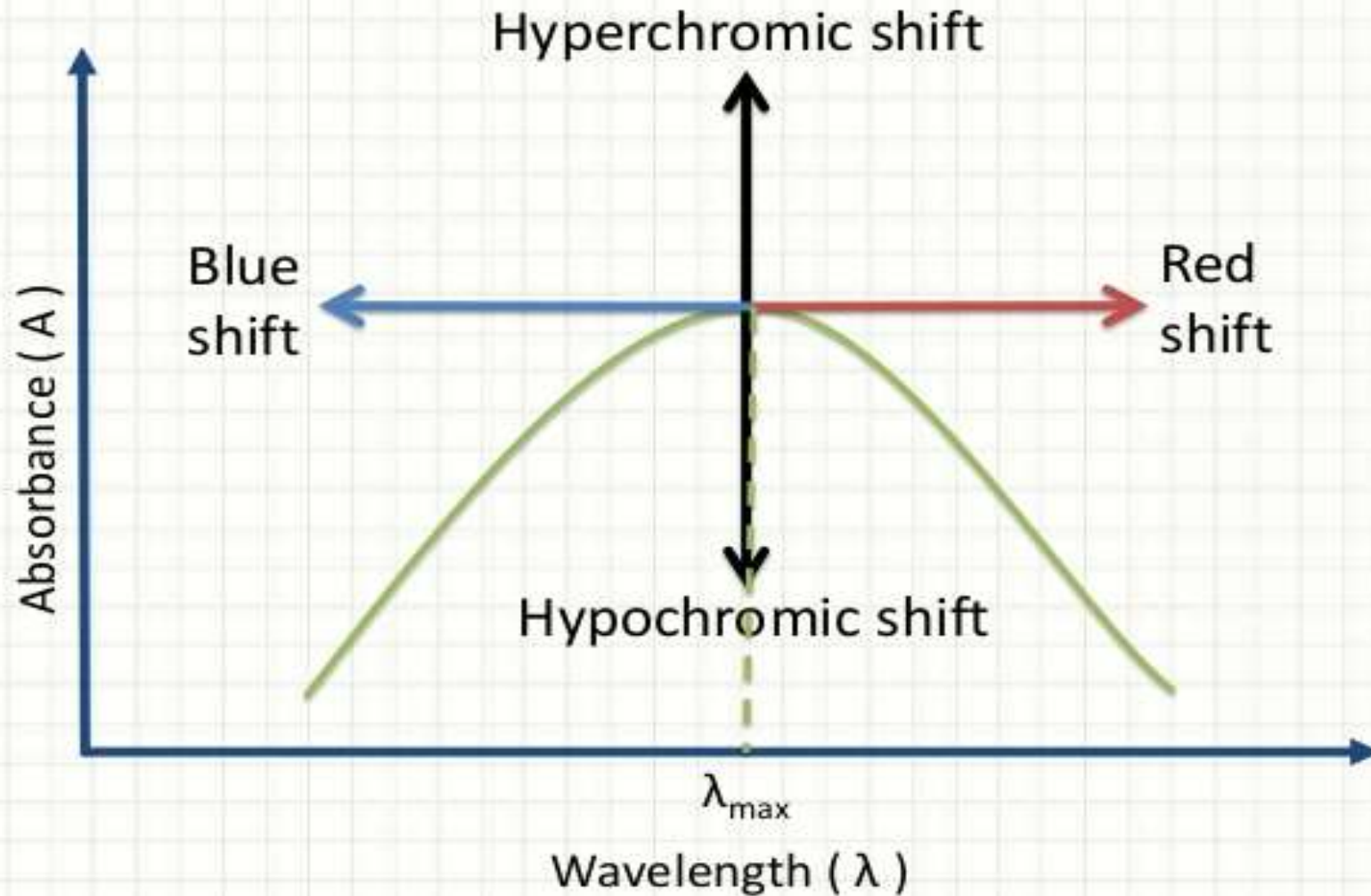
In this Type of shift decrease intensity of radiation because of decreased absorption.

It is due to presence of certain group which may cause deformation of structure of compound.

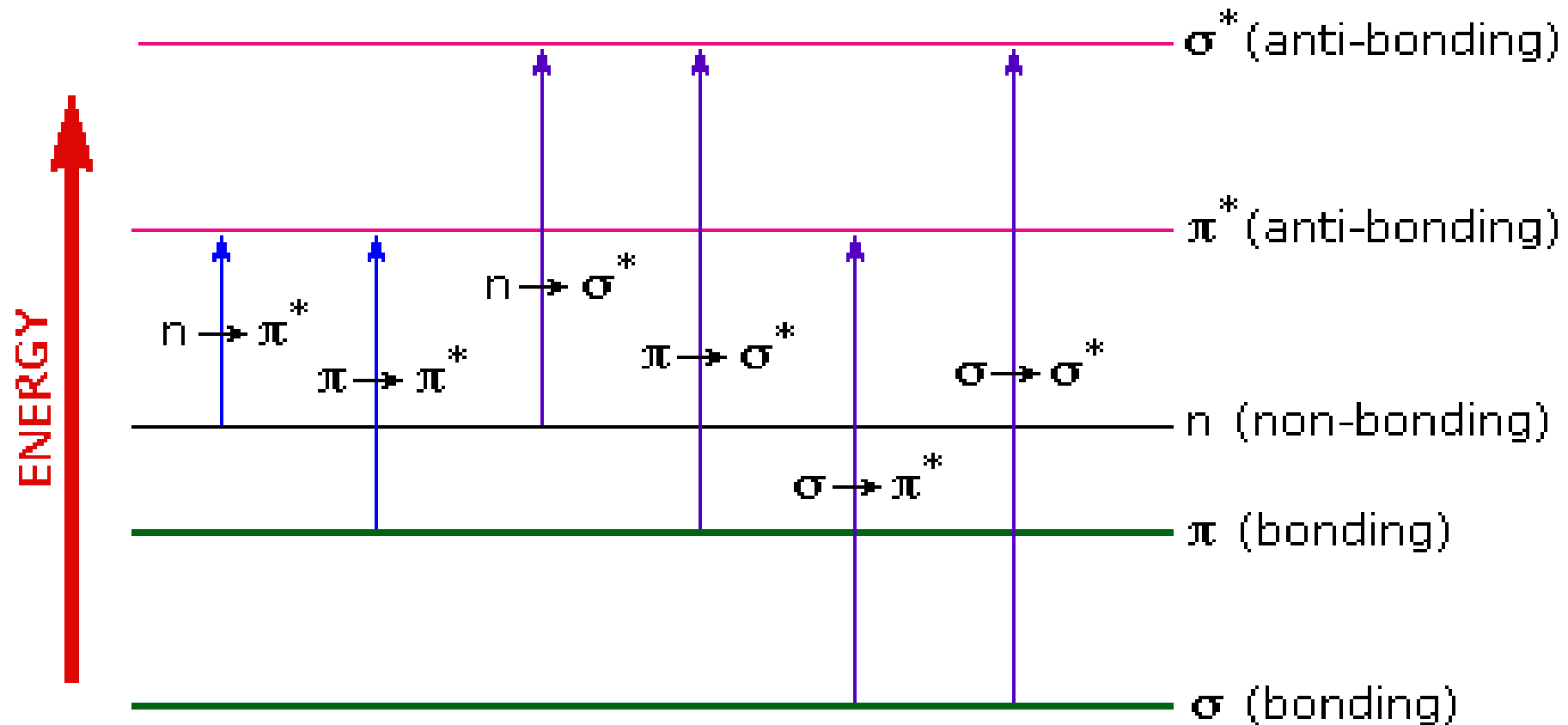
Terminology for Absorption Shifts

Nature of Shift		Descriptive Term
To Longer Wavelength	→	Bathochromic
To Shorter Wavelength	→	Hypsochromic
To Greater Absorbance	→	Hyperchromic
To Lower Absorbance	→	Hypochromic

Shifts and Effects



Types of electronic transitions



The possible electronic transitions are

1

• $\sigma \rightarrow \sigma^*$ transition

2

• $\pi \rightarrow \pi^*$ transition

3

• $n \rightarrow \sigma^*$ transition

4

• $n \rightarrow \pi^*$ transition

5

• $\sigma \rightarrow \pi^*$ transition

6

• $\pi \rightarrow \sigma^*$ transition

1

• $\sigma \rightarrow \sigma^*$ transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ^* .
- The energy required is large for this transition.
- e.g. Methane (CH_4) has C-H bond only and can undergo $\sigma \rightarrow \sigma^*$ transition and shows absorbance maxima at 125 nm.

2

• $\pi \rightarrow \pi^*$ transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π^* .
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

3

• $n \rightarrow \sigma^*$ transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.
- These transitions usually requires less energy than $\sigma \rightarrow \sigma^*$ transitions.
- The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in UV region is small (150 – 250 nm).

4

• $n \rightarrow \pi^*$ transition

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms ($C=O$, $C\equiv N$, $N=O$) undergo such transitions.
- $n \rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5

• $\sigma \rightarrow \pi^*$ transition

&

• $\pi \rightarrow \sigma^*$ transition

6

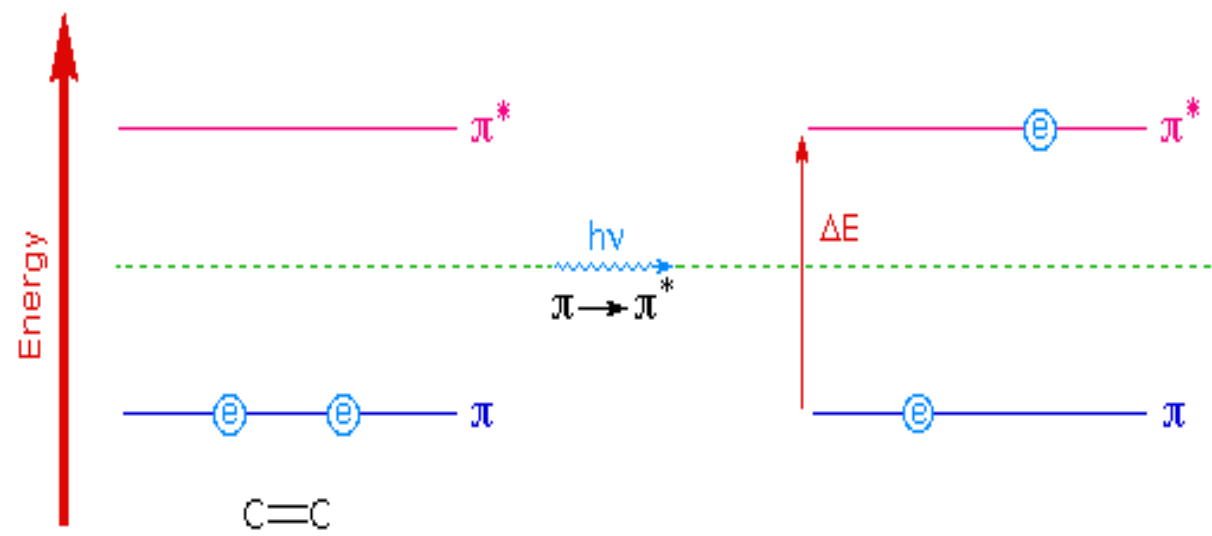
- These electronic transitions are forbidden transitions & are only theoretically possible.
- Thus, $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.
- The UV spectrum is of only a few broad of absorption.

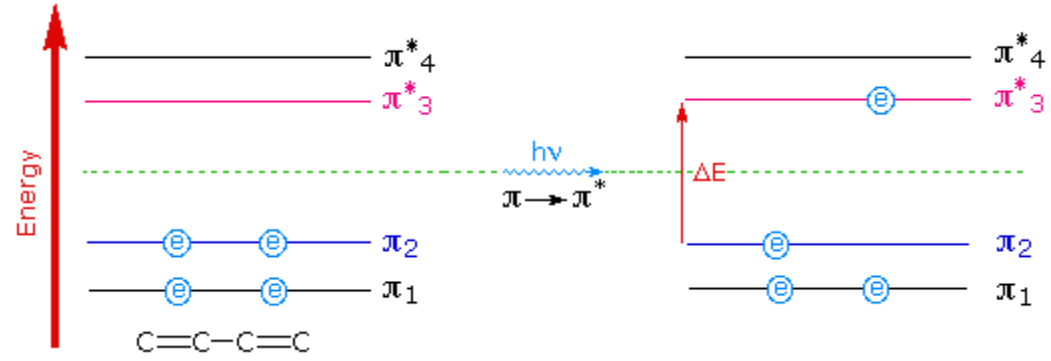
Effect of conjugation on position of UV and visible absorption band:

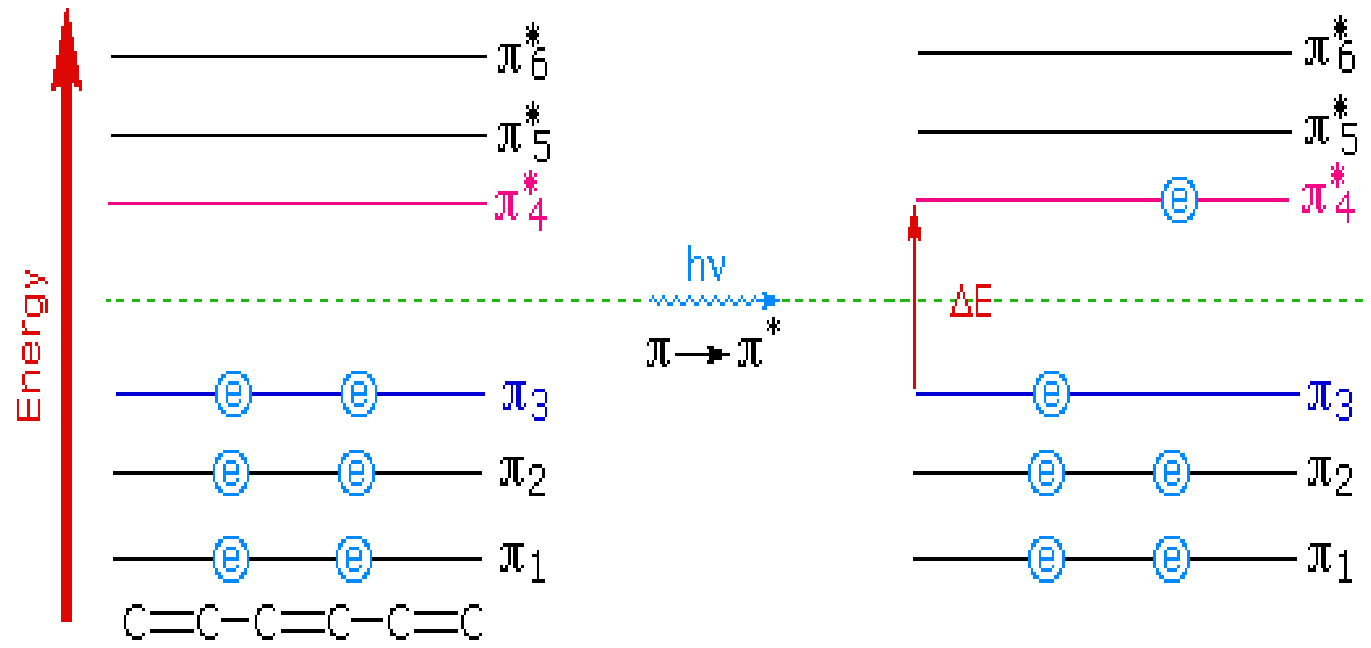
When two double bonds are conjugated, the four p-atomic orbitals combine to generate four pi-molecular orbitals out of which two are bonding and two are antibonding. In a similar manner, the three double bonds of a conjugated triene create six pi-molecular orbitals, half bonding and half antibonding.

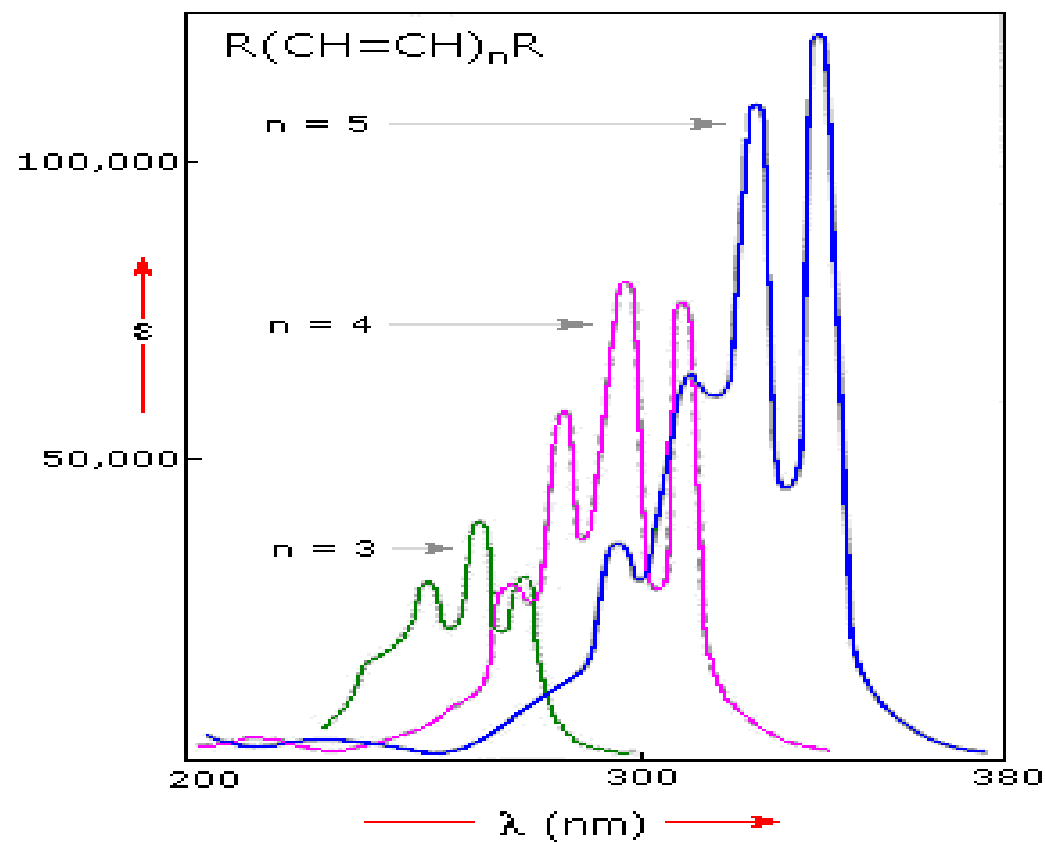
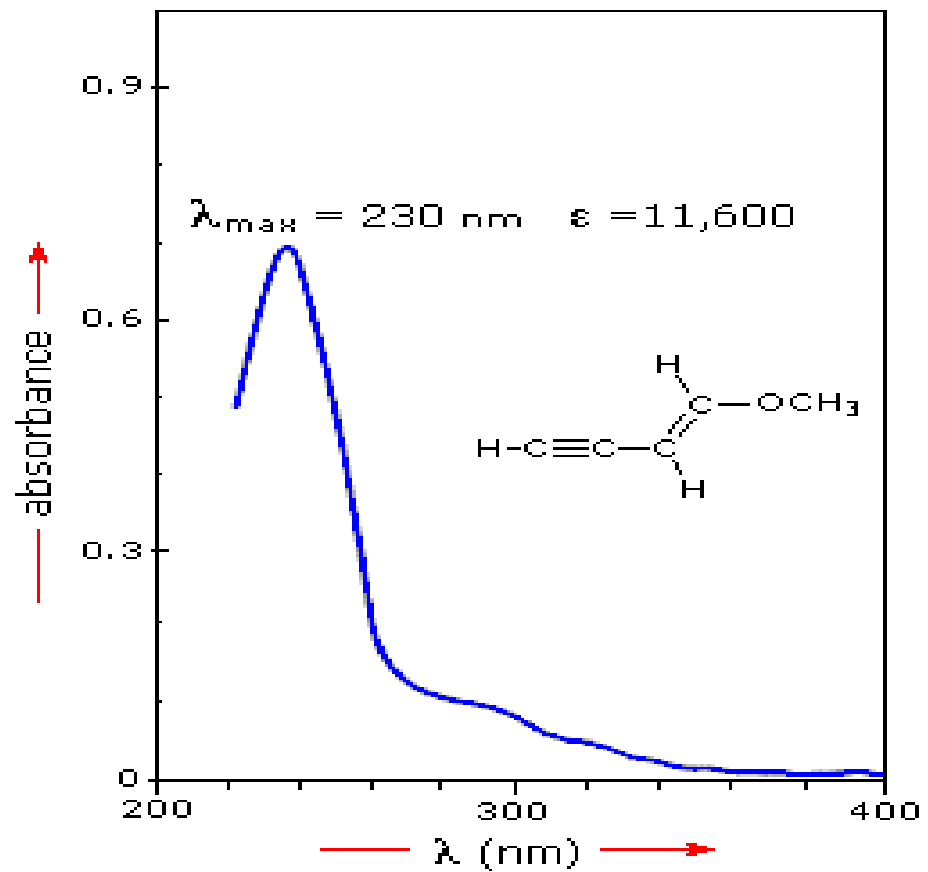
Energetically favoured electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**.

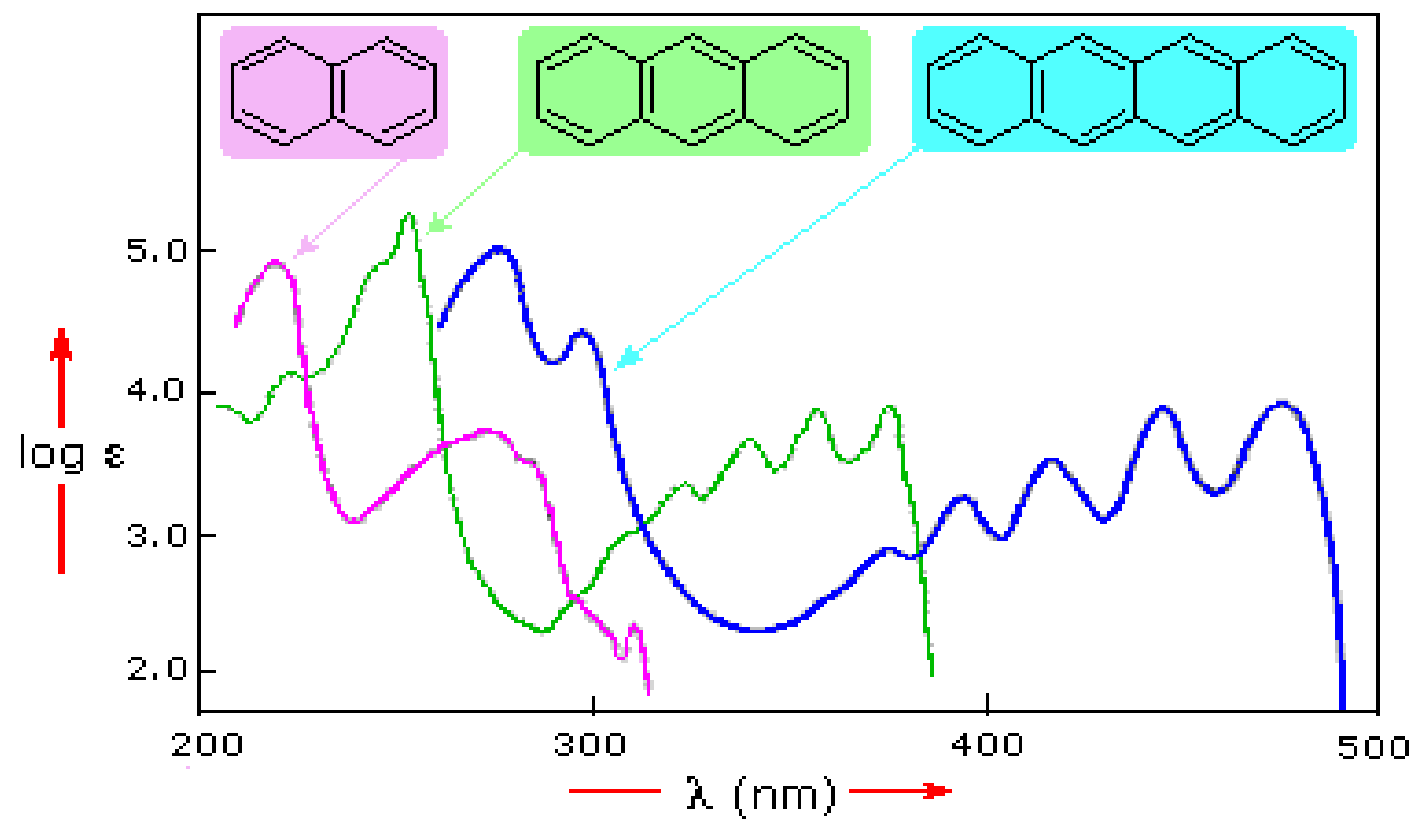
As conjugation increases, the difference between highest **occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)** goes on decreasing, making the excitation easier. That indicates conjugation causes red shift or bathochromic shift and colour of substance further deepens.



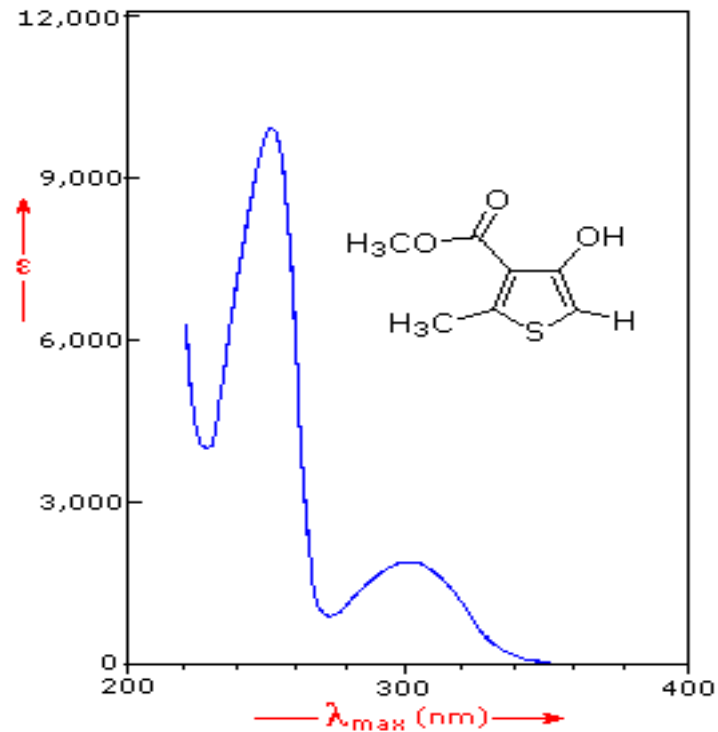
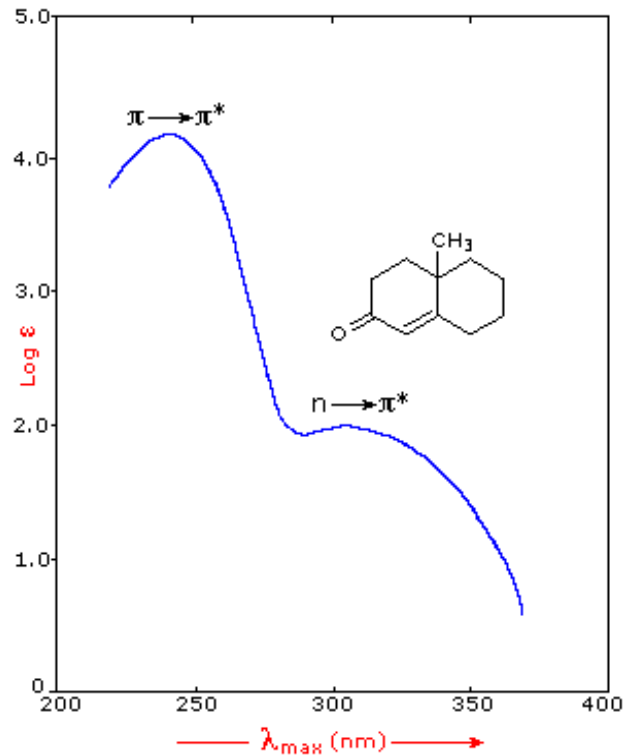




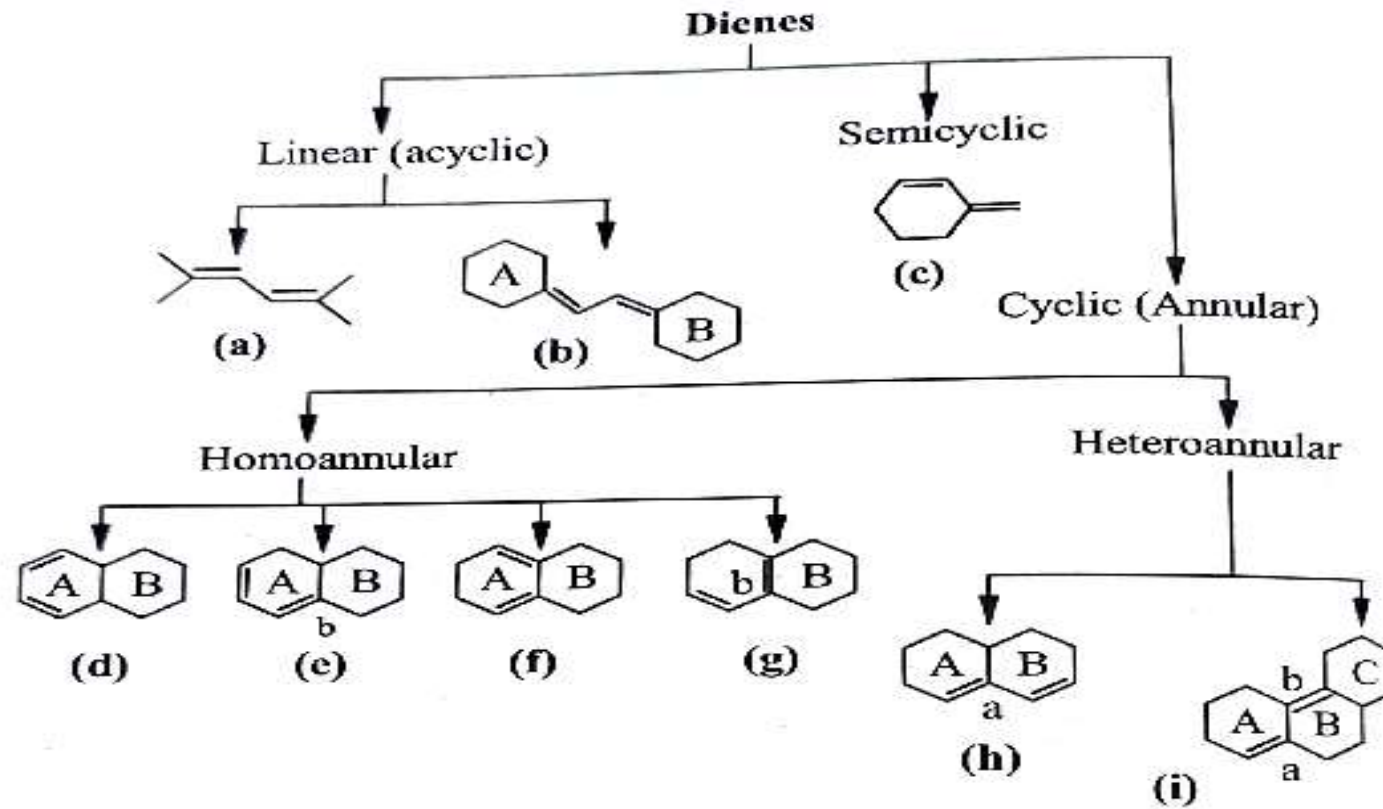




Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the advantage of a logarithmic display of molar absorptivity. The $\pi \rightarrow \pi^*$ absorption located at 242 nm is very strong, with an $\epsilon = 18,000$. The weak $n \rightarrow \pi^*$ absorption near 300 nm has an $\epsilon = 100$.




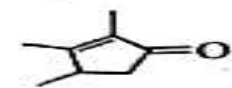
Types of Diene



Woodward - Fiesers' rules for calculating λ_{\max} of conjugated dienes

Parent diene	Base value
Acyclic diene	214 nm
Heteroannular diene	214 nm
Homoannular diene	253 nm
<i>Nature of substituent</i>	Add Increment
– R alkyl (including ring residues)	5
– OR alkoxy	6
– Cl, – Br	5
– O, COR acyloxy	0
Double bond extending conjugation	30
One double bond exocyclic to one ring	5
If exocyclic to two rings simultaneously	10

Woodward - Fiesers' rules for calculating λ_{\max} of enones

Parent skeleton	Base value
$\begin{array}{c} \beta \quad \alpha \\ \quad \\ -C=C-C=O \\ \text{(acyclic)} \end{array}$	215 nm
 (hexacyclic ring)	215 nm
 (5 membered ring)	202 nm
$\begin{array}{c} \quad \quad \quad H \\ \quad \quad \quad \\ -C=C-C=O \\ \text{(aldehydes)} \end{array}$	207 nm
$\begin{array}{c} \quad \quad \quad @ \\ \quad \quad \quad \\ -C=C-C=O \\ \text{(acids @ = OH; esters @ = OR)} \end{array}$	197 nm
extended conjugation	add, 30 nm
homodiene component	add, 39 nm
If one double bond is exocyclic to one ring	5 nm
If exocyclic to two rings simultaneously	10 nm
$\begin{array}{c} \delta \quad \gamma \quad \beta \quad \alpha \\ \quad \quad \quad \\ -C-C-C-C-C-O \end{array}$	Increments for each group at ... position
	α β γ δ and above
- R alkyl (including part of carbocyclic ring)	10 12 18 18 18
- OR alkoxy	35 30 17 31 --
- OH hydroxy	35 30 -- 50 --
- SR thioether	-- 80 -- -- --
- Cl chloro	15 12 -- -- --

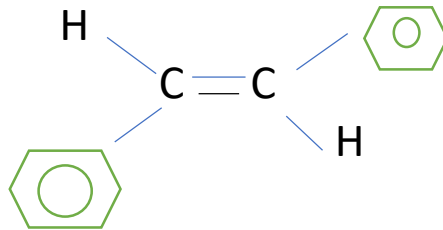
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Application of UV visible spectroscopy:

- 1. Extent of conjugation: Higher the λ_{\max} value longer the conjugation and vice versa

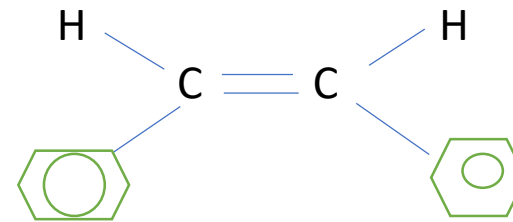
So distinction between conjugated and non conjugated diene can be done.

- 2. Detection of chromophore: A strong absorption ($\epsilon = 10000 - 20000$) is characteristic of $\pi \rightarrow \pi^*$ transition. A weak absorption ($\epsilon = 10 - 100$) suggest $n \rightarrow \pi^*$ transition.
- 3. Detection of geometrical isomers : Compared to cis isomer the trans isomer shows absorption at higher lambda max value with larger extinction coefficient.



$$\lambda_{\max} = 272\text{nm}$$

$$\epsilon_{\max} = 15900$$



$$\lambda_{\max} = 268\text{nm}$$

$$\epsilon_{\max} = 10700$$

4. Structure of organic compound: The presence or absence of chromophore can be identified by use of UV visible spectroscopy. Saturation, unsaturation can be identified , but it is not possible to detect complete structure.

5. Quantitative Analysis: This determination is based on Beer-Lambert's law.

$$A = \epsilon cl$$

6. Qualitative analysis : Characterization of aromatic compounds and aromatic olefins is done by comparing absorption spectrum with spectra of known compounds.

7. Presence of impurities: A comparison of spectra of sample with standard material at specific wavelength is done. Presence of additional peaks in the spectra hints presence of impurity.

THANK YOU