INSTITUTE OF TECHNOLOGY & MANAGEMENT, GORAKHPUR
2001

Unit – 2
Spectroscopy

Spectroscopy

- ✓ Electromagnetic Radiation
- ✓ Spectrum & Types of Spectra
- ✓ Instrumentation- spectrophotometer
- ✓ Emission and Absorbance
- ✓ UV-Visible spectroscopy
- ✓ Woodwards Fieser Rule of λmax
- ✓ Rotational & Vibrational spectroscopy (IR)
- ✓ Selection Rule
- ✓ Raman Spectroscopy

Spectroscopy

Spectroscopy is the branch of science which deals with the determination of the structure of a compound through the interaction of electromagnetic radiation with the matter.

Spectroscopy are terms used to refer to the measurement of radiation intensity as a function of wavelength.

The energy of a photon is given by $\mathbf{E=h\upsilon}$

$$= hc/\lambda$$

Where,

h= Planck's constant.

speed of light **(c)** =3 x 10^{10} cm/sec.

λ **=** Wavelength of radiation

Wave number is defined as the number of wavelengths per unit distance (cm^{-1}). Wave numbers are usually measured in units of reciprocal meters
($1/m$, or m^{-1}) or
reciprocal centimeters ($1/cm$, or cm^{-1}).

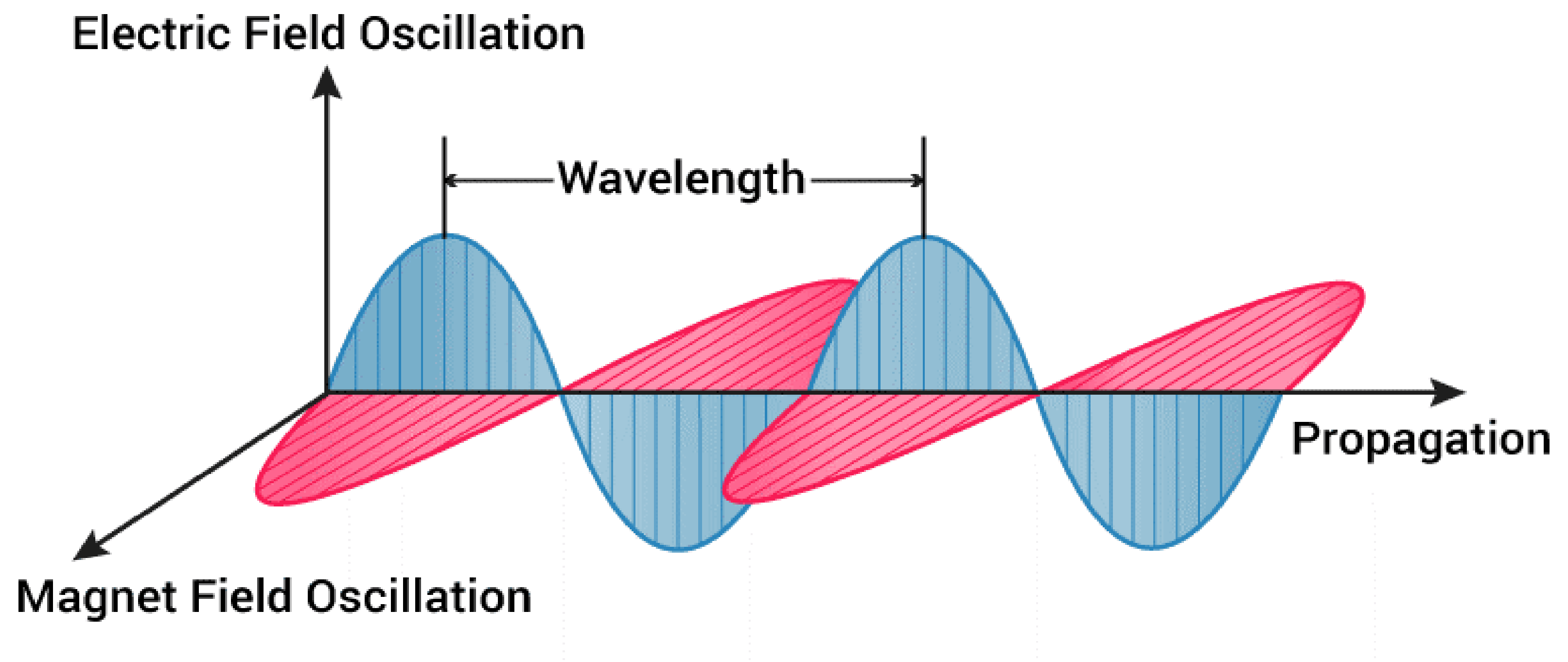
λ is the wavelength

$$\text{wavenumber}\,(\tilde{\nu}) = \frac{1}{\lambda}$$

Electromagnetic radiation

Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. Visible light is a common example of electromagnetic radiation.

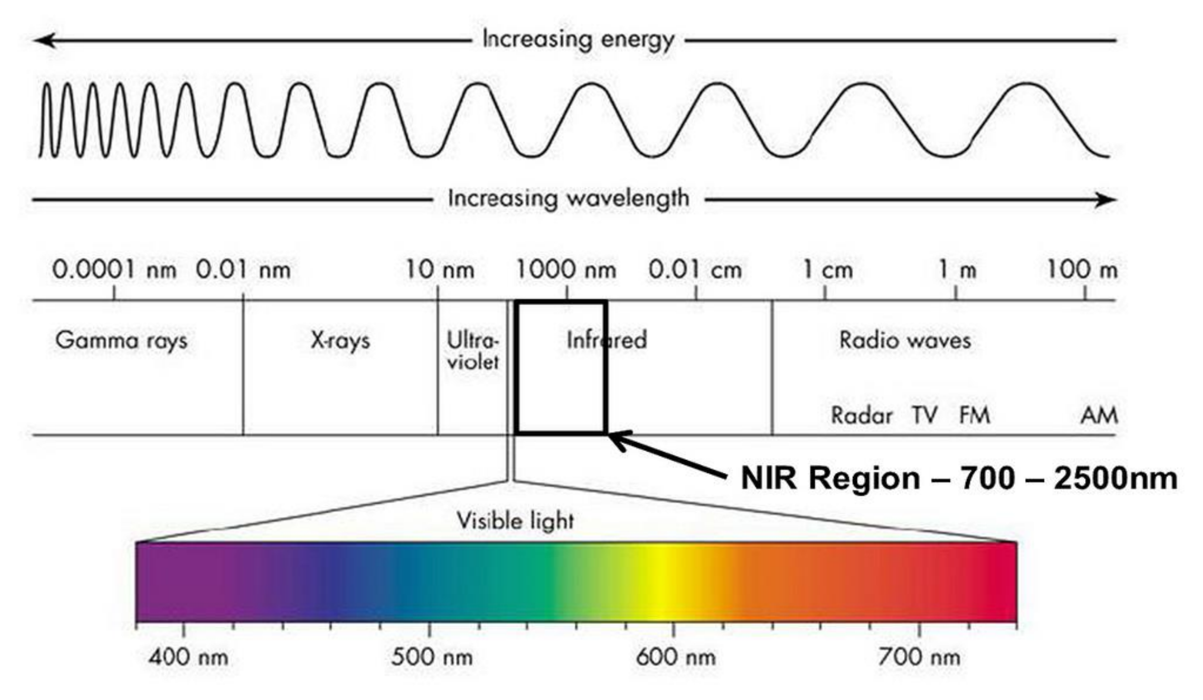
According to wave nature of radiations, the [electromagnetic waves]() consist of oscillating electric and magnetic fields mutually perpendicular to each other.

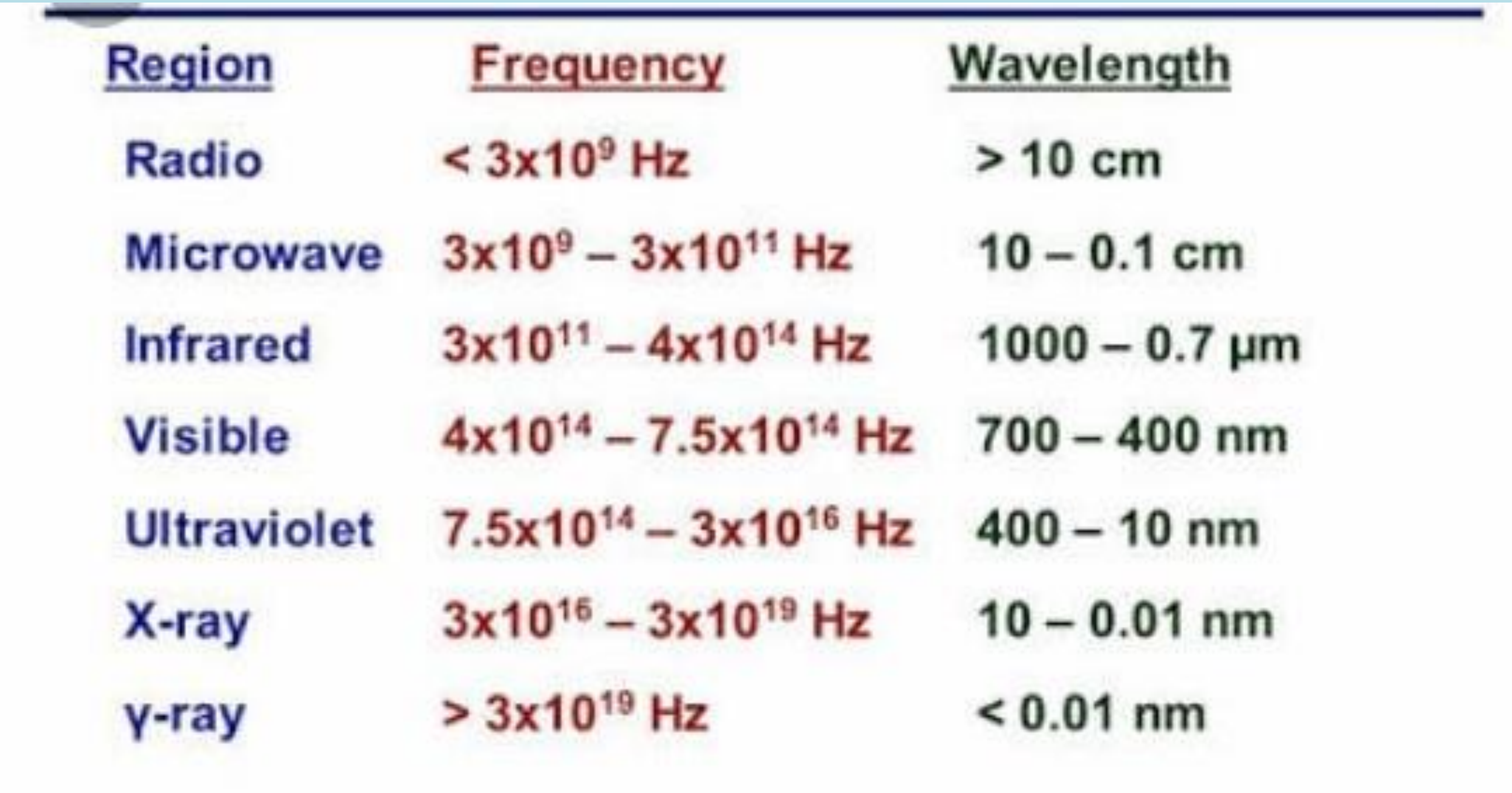


The **Electromagnetic Spectrum** is a representation of all electromagnetic waves arranged according to frequency, wavelength or wave number.

The electromagnetic spectrum includes

- Radio waves, which have longer wavelengths
- UV & X-rays, which have short wavelengths, and
- Visible light, which has wavelengths between those of radio waves and x-rays.





Region	Frequency	Wavelength
Radio	$< 3 \times 10^{9}$ Hz	> 10 cm
Microwave	$3 \times 10^{9} – 3 \times 10^{11}$ Hz	10 – 0.1 cm
Infrared	$3 \times 10^{11} – 4 \times 10^{14}$ Hz	1000 – 0.7 μm
Visible	$4 \times 10^{14} – 7.5 \times 10^{14}$ Hz	700 – 400 nm
Ultraviolet	$7.5 \times 10^{14} – 3 \times 10^{16}$ Hz	400 – 10 nm
X-ray	$3 \times 10^{16} – 3 \times 10^{19}$ Hz	10 – 0.01 nm
γ-ray	$> 3 \times 10^{19}$ Hz	< 0.01 nm

Practical Applications of Electromagnetic Waves

- The radio waves and microwaves discovered by Hertz used for wireless, television, radio and mobile communication.
- The visible light portion of the electromagnetic spectrum for visual effects of colors which can be seen by our eyes.
- The X-rays discovered by Roentgen useful in imaging of internal body structure and deformity like fracture in bones.
- The high ultraviolet radiation has energies to ionize the atoms causing chemical reactions and causes adverse effect on skin.
- The gamma rays discovered by Paul Villard are useful for ionization purposes.

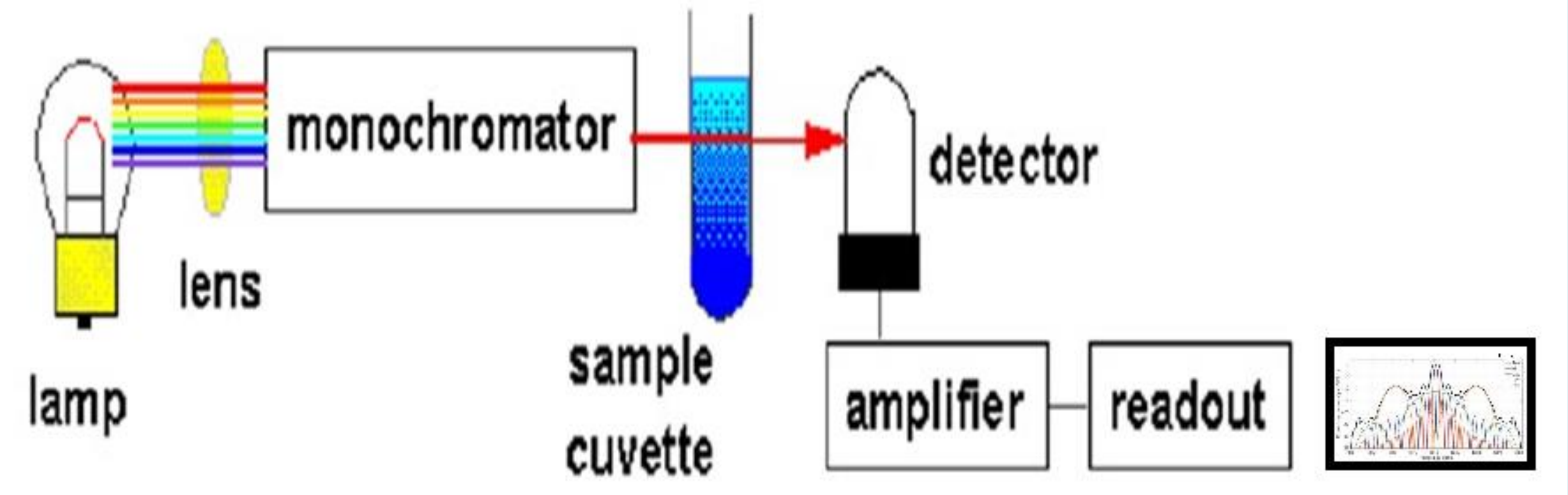
Advantages of Spectroscopic Analusis

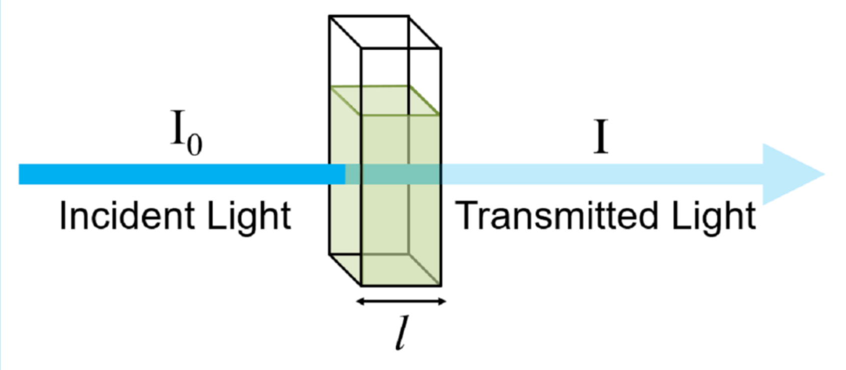
1. Fast and simple analysis
2. Little or no sample preparation is usually required.
3. Less time required.
4. Direct and non-invasive analyses are possible.
5. Non-destructive.
6. Phusical and chemical properties of sample does not alter after the analysis.
7. The substance can be used for other analysis after treatment.
8. Very less substance is required.
9. They are relatively inexpensive with respect to analysis time and reagents.
10. The results are accurate as compared to other analysis

Instrumentation

Spectrophotometer consists of following components as shown in figure.

- **Source of radiation (Lamp)**
- **Monochromator**
- **Sample or reference cell**
- **Detector**
- **Recorder**





$$\text{percent transmission (\%T)} = \frac{I}{I_o} \times 100$$

I_o = intensity of the light entering the sample

I = intensity of the light leaving the sample

Absorbance (A) and Transmittance (T)

Absorbance can be defined as the base-ten logarithm of the reciprocal of the transmittance:

$T = I/I_o$

$A = \log 1/T = –\log T = -\log I/I_o$

$A = \log 1/T$, If Transmittance is given in %

$= \log 1/T/100$

$= \log 100/T$

$= \log 100 – \log T\%$

Absorbance $A = 2 – \log T\%$

Q. Calculate absorbance if T% is 80

Solution

T% = 80 means T = 80/100

$A = \log 1/T$

$= \log 1/80/100$

$= \log 100/80$

$= \log 10 – \log 8$

$= 1 – \log 2^3$

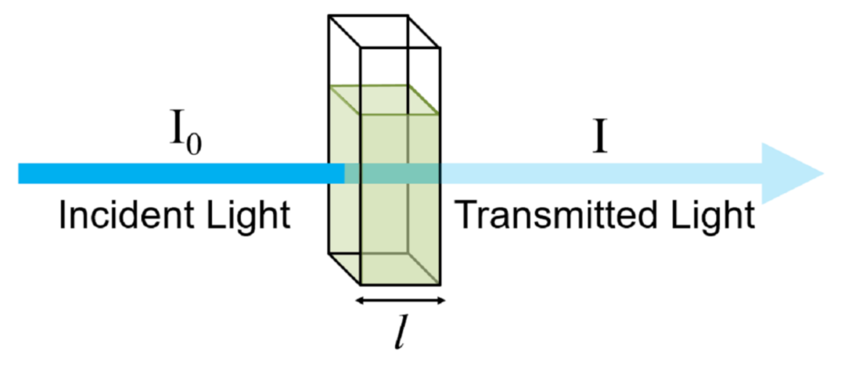
$= 1 – 3\log 2$

$= 1 – 3 \times 0.3010$

$= 1 – 0.9030$

= 0.097 Answer

Q. When UV light is passed through a solution, the radiation power is reduced to 50%. Calculate the absorbance.



Solution

Let $I_o = P_o$ and $I = P$ P=Power

$P_o = 100$ $P = 50$

$T = I/I_o$

$A = \log 1/T = -\log T = -\log I/I_o$

$= -\log P/P_o$

$= -\log 50/100$

$= -\log 1/2$

$= \log 2$

$= 0.3010$ Answer

Types of spectra

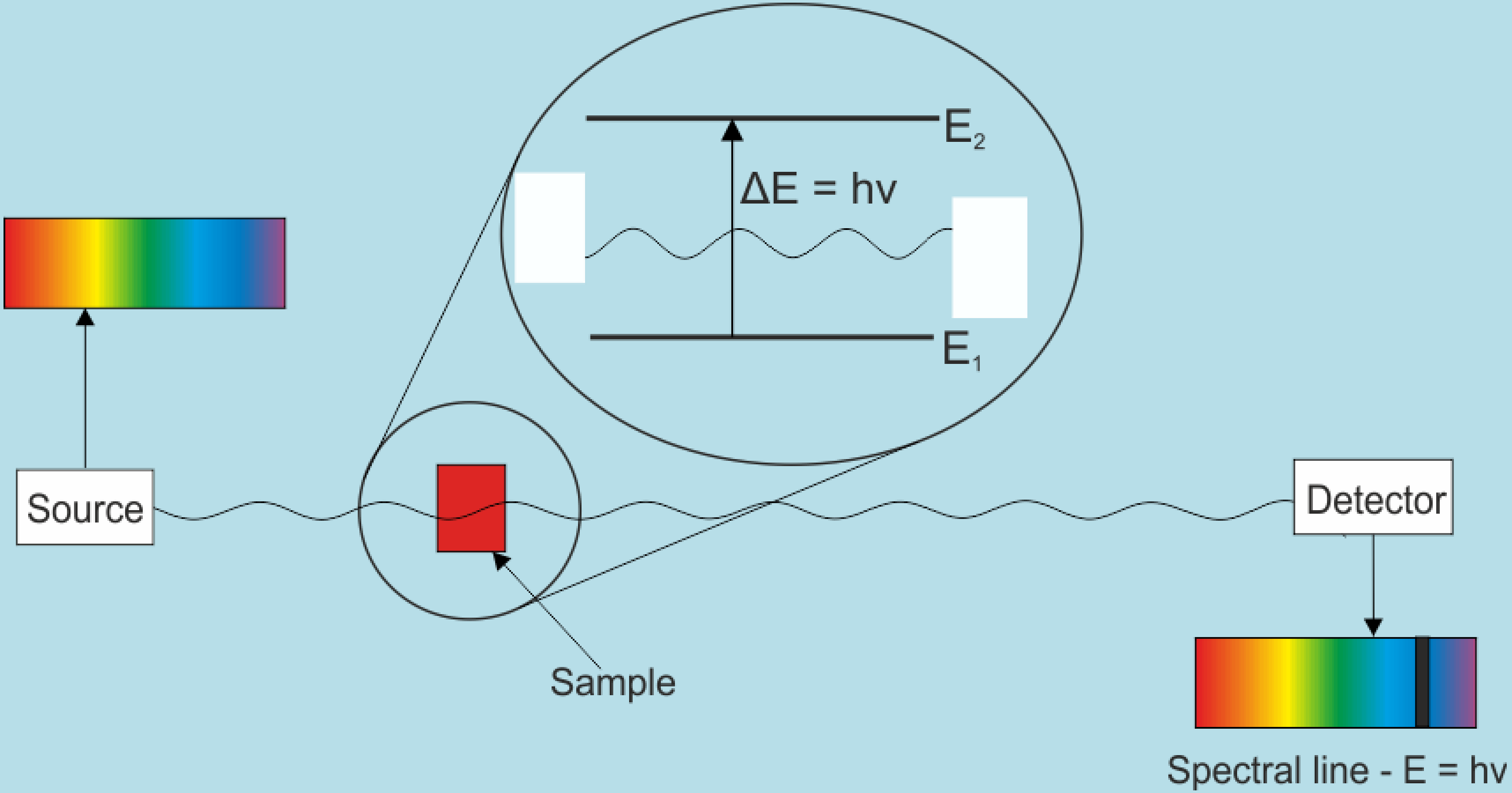
- **Absorption Spectra**
- **Emission Spectra**

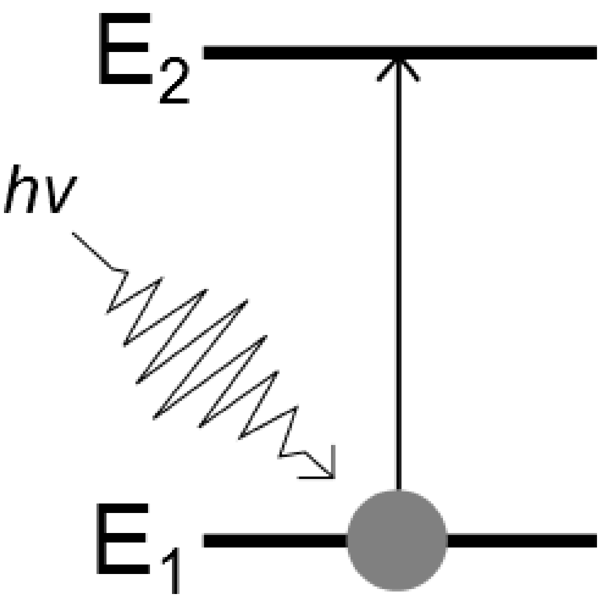
Absorption Spectra

When white light is passed through a substance and observed through a spectroscope, it is found that radiation of certain wavelengths are absorbed, the spectra obtained is called as Absorption spectra.

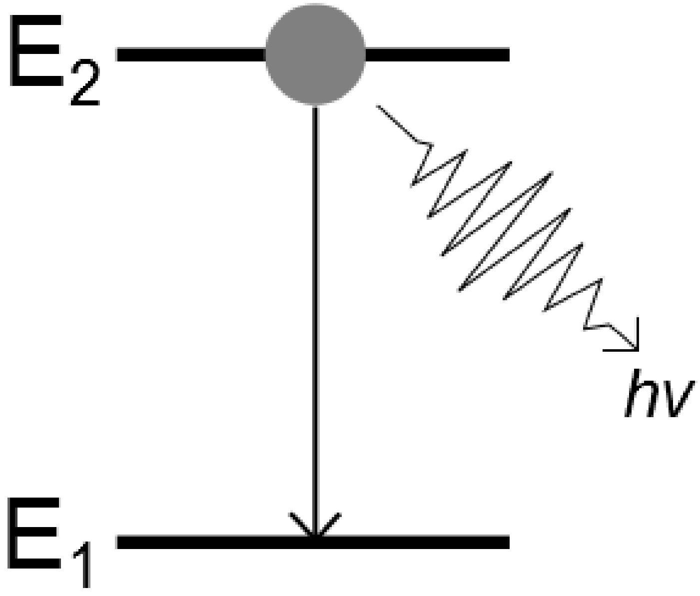
Emission Spectra

When an excited electron comes down from higher energy state to lower energy state by emitting absorbed radiation and the light emitted by the substance is passed through a prism and examined by spectroscope, the spectra obtained is called as Emission Spectra.


E_2
$\Delta E = h\nu$
E_1
Source
Sample
Detector
Spectral line - $E = h\nu$



ABSORPTION
SPECTROSCOPY



EMISSION
SPECTROSCOPY

Types of spectroscopy

1. **Rotational Spectroscopy** is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by

Microwave spectroscopy or

Far infrared spectroscopy.

2. V**ibrational Spectroscopy** or **Infrared spectroscopy (IR Spectroscopy)** is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms.

3. UV-Visible Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the ultraviolet-visible spectral region.

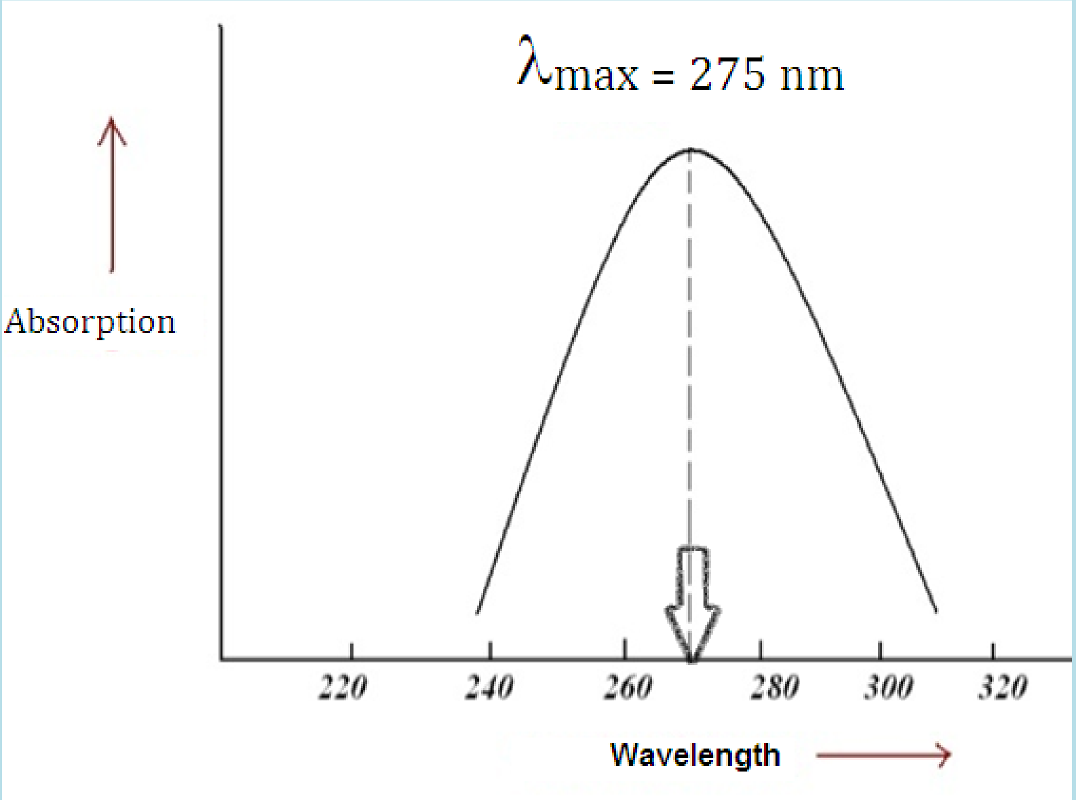
It uses light in the visible and adjacent (near-UV and near-infrared ranges.

UV/Vis spectrophotometer is used in the quantitative determination of concentrations of the absorber in the solutions of transition metal ions and highly conjugated organic compounds.

The UV region extends from 10-400 nm while the visible region extends from 400-800 nm.

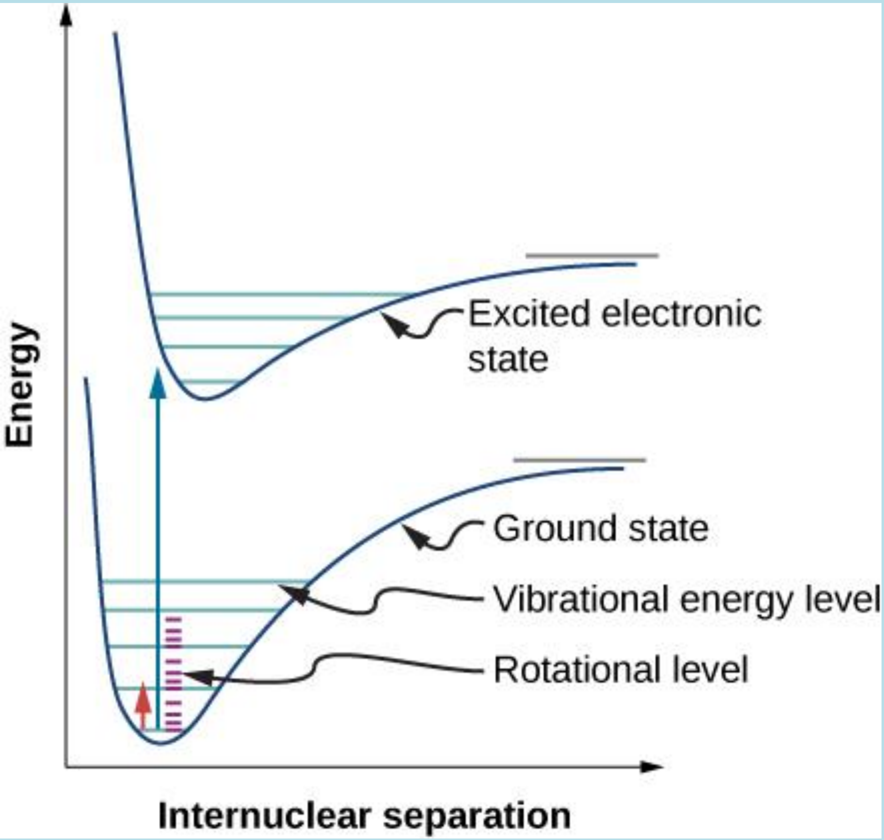
Further it is divided into two regions viz,
near UV 200-400 nm and far UV 10-200 nm.
The UV spectrum is composed of a few broad bands of spectrum.

The wavelength of maximum absorbance is referred to as λ_{max}.



Principle

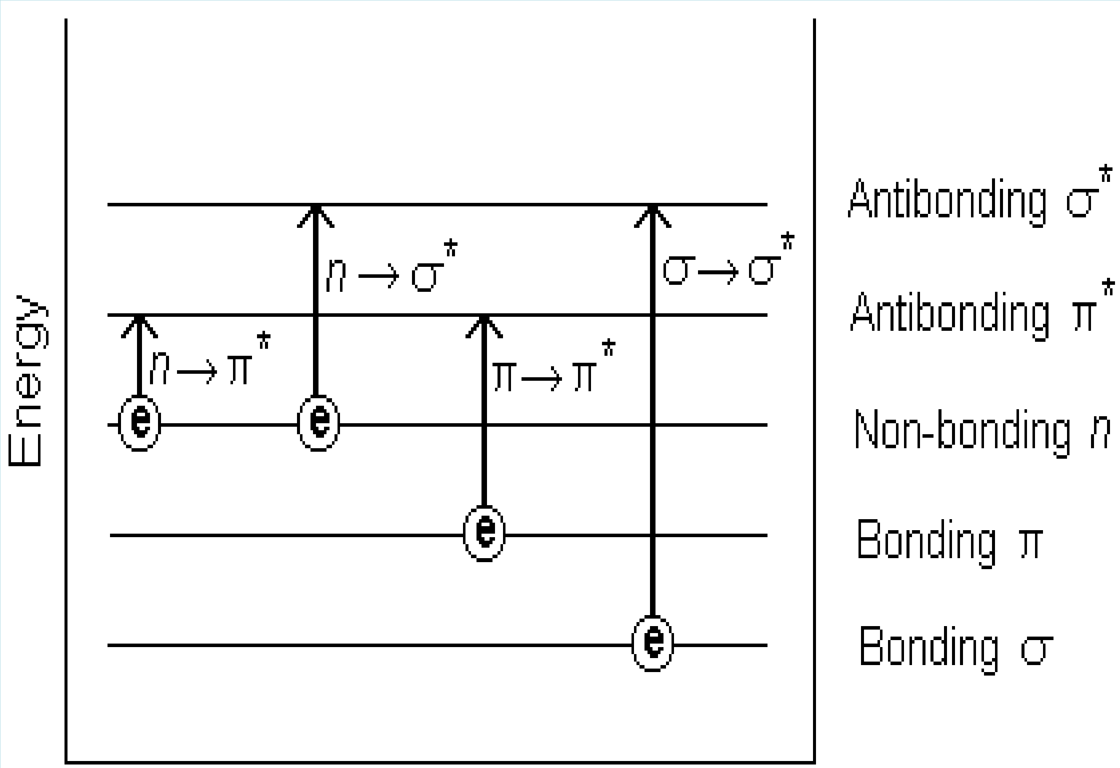
Absorption of UV-visible light brings changes in the electronic states of molecules associated with the excitation of an electron from lower to higher energy level. Each level is associated with number of vibrational sub levels and each vibrational sublevel is associated with a number of rotational sub levels.



Types of Transitions

Electronic Excitation

Electronic transition involves the excitation of electron from one orbital to another orbital of higher energy. In a molecule electron promoted may be σ-electron, a π-electron or an n-electron (nonbonding). Thus four types of transitions are possible



Low Energy n→∏* < ∏→∏* < n→σ* < σ→σ* High Energy

1. **$\sigma \rightarrow \sigma^*$ Transition:** the transition in which **σ-electron is excited to an antibonding σ* orbital**. Energy required for this transition is very high hence they occur at shorter wavelength. e.g singly bonded saturated hydrocarbon molecules- CH_4, C_2H_6

2. **$n \rightarrow \sigma^*$ Transition:** the transition in which **nonbonding-electron is excited to an antibonding σ* orbital**. e. g. compounds having nonbonding (Lone pair) electrons on oxygen, nitrogen, sulfur or halogens show this transition. NH_3, OH, SH

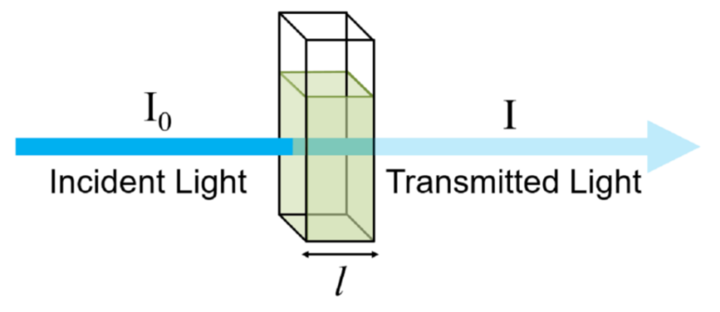
3. **$n \rightarrow \pi^*$ Transition:** the transition in which **nonbonding-electron is excited to an antibonding π* orbital.** Compounds having multiple bonds between hetero atoms containing lone pair e^- such as C=O, C=S, N=O, C≡N etc. These transition require only small amount of energy.

4. **$\pi \rightarrow \pi^*$ Transition:** the transition in which **π-electron is excited to an antibonding π* orbital.** Unsaturated hydrocarbon C=C, C≡C, $H_2C{=}CH_2$, HC≡CH

Beer-Lamberts Law

The Beer-Lambert law states that the ‘**absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length.’**

The amount of light absorbed (A) is proportional to how many molecules or the concentration (*c*) of molecules that are absorbing light, and how far the UV light must pass through this concentration or the path length *l*. These relationships are shown below.



$\mathbf{A} \propto c$

$\mathbf{A} \propto l$

$\mathbf{A} \propto c \times l$

$\mathbf{A} = \varepsilon c l$ Beer-Lambert Equation

ε is constant, The symbol **epsilon** is the molar absorptivity of the solution.

Q. Calculate the molar absorptivity of a 1 x 10^{-4} M solution, which has an absorbance of 0.20, when the path length is 2.5 cm.

Solution: $A = \varepsilon\ c\ l$

$l = 2.5$ cm

$A = 0.20$

$C = 1 \times 10^{-4}$ M

$\varepsilon = ?$

So $\varepsilon = A / l\ c$

$= 0.20 / 2.5 \times 1 \times 10^{-4}$

Answer $= 800$ L/mol/cm

Q. In a spectrophotometric cell of 2.0 cm path length, the solution of a substance shows the absorbance value of 1.0. If the molar absorptivity of the compound is 2×10^4 L mol^{-1} cm^{-1} , Calculate the concentration of the substance in solution.

Solution

Path Length (L) = 2.0 cm

Molar Absorptivity (ε) = 2×10^4 L mol^{-1} cm^{-1}

Absorbance (A) = 1.0

$A = \varepsilon \times C \times L$

$1.0 = 2 \times 10^4 \times C \times 2$

$C = 1/2\times2 \times10^4$

$C = 1/4 \times10^4$

$C = 2.5 \times 10^{-5}$ mol/L

Q. A solution shows a transmittance of 20%, when taken in a cell of 2.5 cm thickness. Calculate its concentration, if the molar absorption coefficient is 12000 dm3/mol/cm.

Solution: $A = 2 - \log_{10} \%T$

$= 2 - \log_{10} 20$

$= 2 – 1.301$

$= 0.698$

$A = \varepsilon\, l\, c$

$l = 2.5$ cm

$\varepsilon = 12000$ L/mol/cm

$A = 0.698$

$c = ?$

So, $c = A / \varepsilon\, l$

$= 0.698 / 12000 \times 2.5$ Answer

$= 2.33 \text{ X } 10^{-5}$ mol / L

Q. A solution of chemical ‘X’ having its 0.14 mol L^{-1} concentration has an absorbance of 0.42. Another solution of ‘X’ under the same conditions has an absorbance of 0.36. What is the concentration of this solution of ‘X’?

$A = \varepsilon \times C \times L$

$A \propto C$

$A_1/A_2 = C_1/C_2$

$0.42/0.36 = 0.14/ C_2$

$C_2 = 0.36 \times 0.14/0.42$

$C_2 = 0.12$ mol L^{-1}

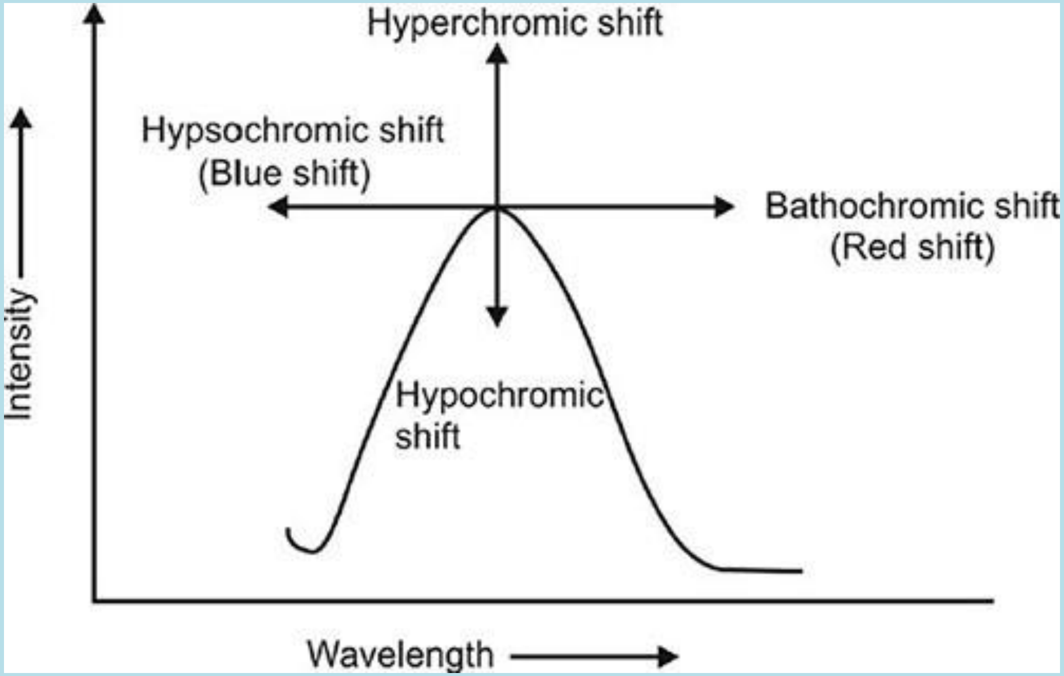
Terms used in UV-Visible spectroscopy

- **Chromophores:** the group or linkages that impart colour to the substance or the colour carrier groups are called as Chromophores. It is also defined as the substance that absorbs radiation in UV-Visible range are called as Chromophores. Presence of one or more unsaturated linkages C=C, C≡C, C=O, -C≡N etc.

- **Auxochrome:** they do not act as a chromophore means they are not responsible for colour but they are colour enhancer. In their presence the λ_{max} shifts towards Red end i.e. larger wavelength.

Examples –OR, –OH, $–NH_2$, –NHR groups etc.

- **Bathochromic Effect or Red Shift:** It is a shift of an absorption maxima towards longer wavelength due to change in medium or presence of auxochrome or addition of conjugation i.e. alternate double bonds..
- **Hypsochromic shift or Blue Shift:** **I**t is a shift towards shorter wavelength. This is caused by removal of conjugation.
- **Hyperchromic Effect: I**t is an effect leading to increased absorption intensity. Auxochromes are responsible for increased intensity.
- **Hypochromic Effect:** It is an effect leading to the decrease in absorption intensity due to distortion in geometry of molecule.



WOODWARD- FIESER RULES:

In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure.

In 1959 Louis Frederick Fieser modified these rules with more experimental data, and

the modified rule is known as

Woodward-Fieser Rules. Both are American Organic Chemist.

It is used to calculate the position and λ_{max} for a given structure

Robert Burns Woodward

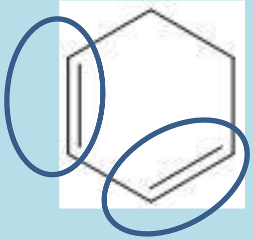
Louis Frederick Fieser

WOODWARD- FIESER RULES:

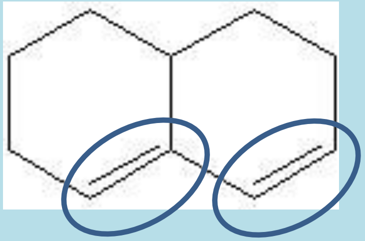
Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation (alternate single-double bonds (-C=C-C=C-C=C-)and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

CONJUGATED DIENE CORRELATIONS:

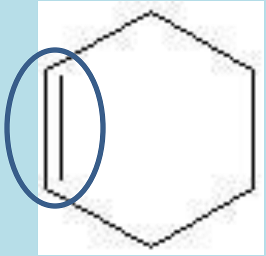
a) **Homoannular Diene:-** Cyclic diene having conjugated double bonds in same ring.



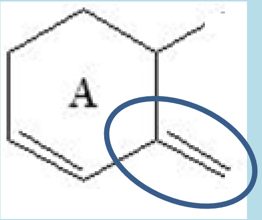
b) **Heteroannular Diene:-** Cyclic diene having conjugated double bonds in different rings.



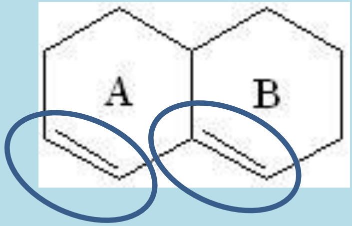
c) **Endocyclic double bond:-** Double bond present in a ring.



d) **Exocyclic double bond: -** Double bond in which one of the doubly bonded atoms is a part of a ring system.



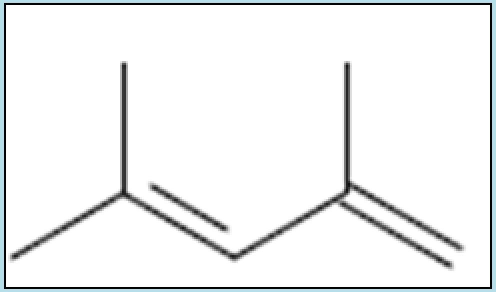
Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.



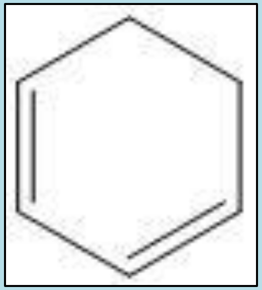
PARENT VALUES AND INCREMENTS FOR DIFFERENT SUBSTITUENTS/GROUPS:

a. Open chain conjugated diene Base Value 217 nm

b. CONJUGATED DIENE Cyclic compound :



i) Base value for homoannular diene = 253 nm (in same ring)

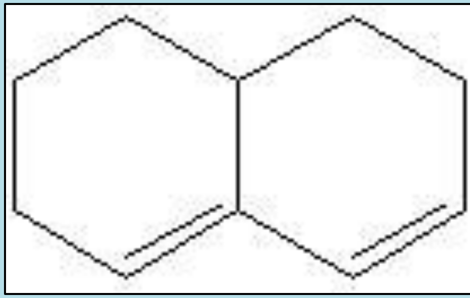


ii) Base for heteroannulardiene = 214 nm (in different rings)

iii) Alkyl substituent or Ring residue attached to the

parent diene = 5 nm

iv) Double bond extending conjugation = 30 nm

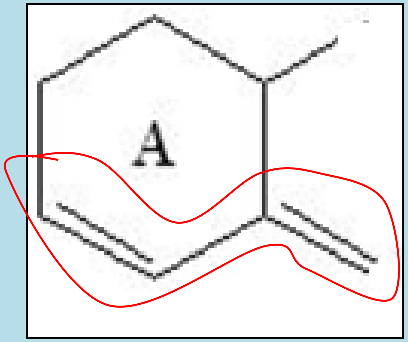


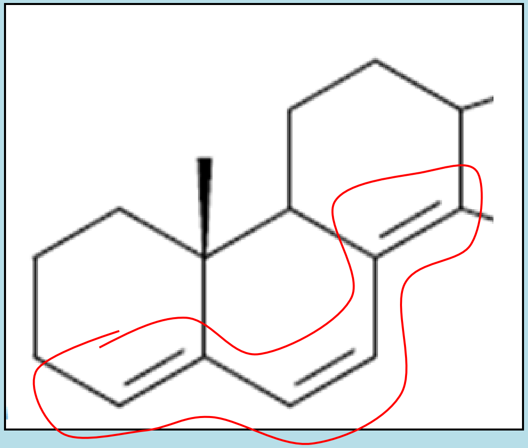
v) Exocyclic double bonds = 5 nm

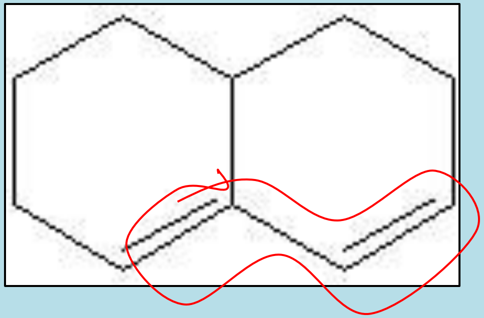
vi) Polar groups: a) -OAc = 0 nm

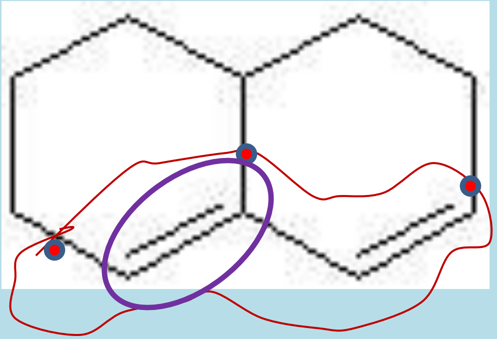
b) -OAlkyl = 6 nm

c) -Cl, -Br = 5 nm









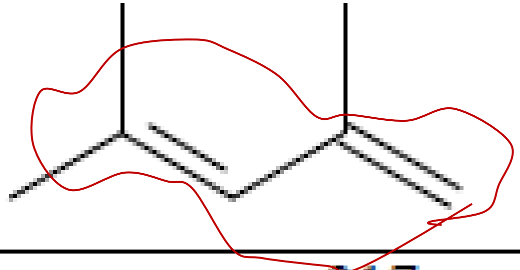
Calculate λ_{max}

Base value =		214 nm
Ring residue =	3x5 =	15 nm
Exocyclic double bond =	1x5 =	5 nm

λ_{max} = 214 + 15 + 5 = 234 nm

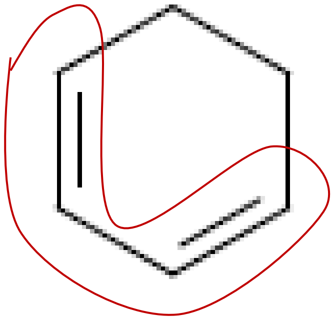
Calculation of λmax

a)



Base value:		217 nm
alkyl groups:	3x5	15 nm
calculated:		232 nm
observed:		234 nm

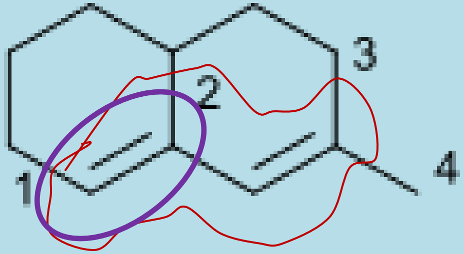
b)



Base value:		253 nm
alkyl groups:	2x5	10 nm
calculated:		263 nm
observed:		256 nm

Calculate Absorption Maxima λmax

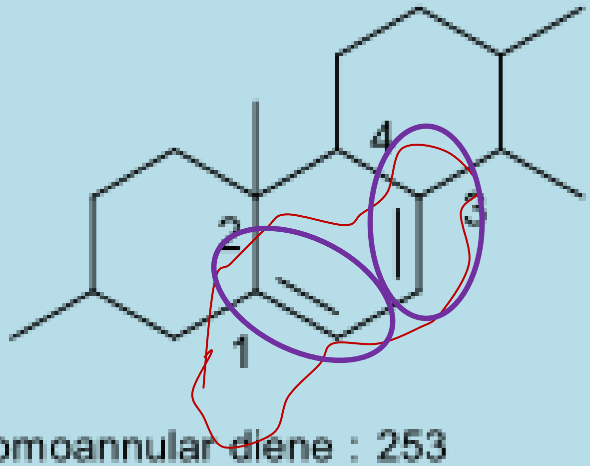
Absorption maximum : 214 + 20 + 5 = 239 nm



heteroannular diene : 214

alkyl substitutents 4 x 5 = 20

exocyclic double bond : 5

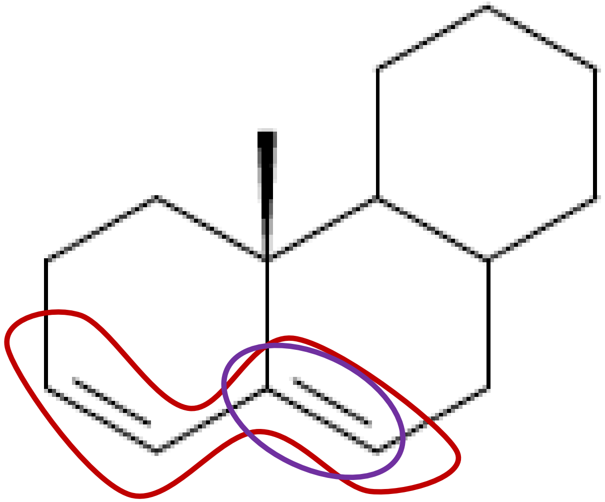


homoannular diene : 253

alkyl substituents : 4 x 5

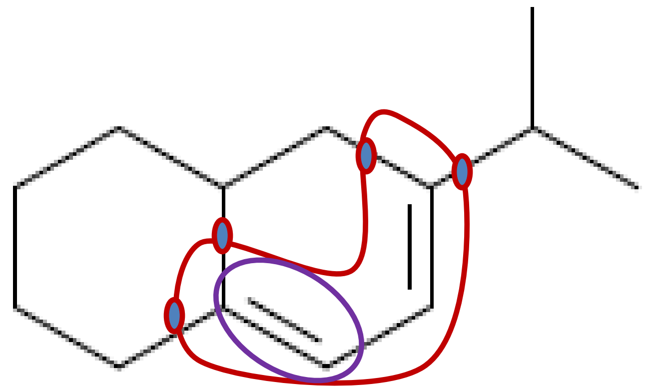
exocyclic double bond : 2 x 5

Absorption maximum : 253 + 20 + 10 = 283 nm c)



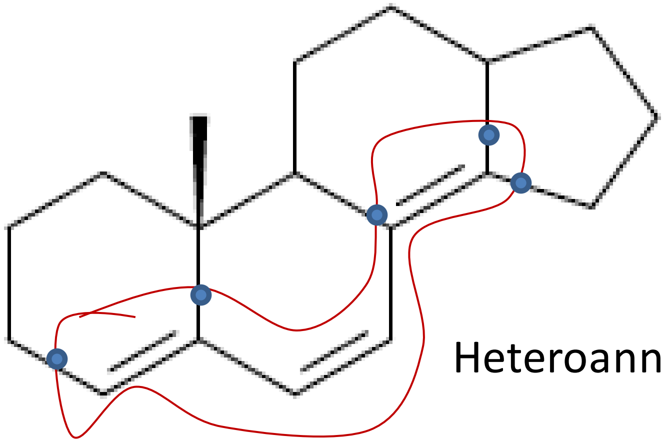
Base value:		214 nm
alkyl groups:	3x5	15 nm
Exocyclic double bond:		5 nm
calculated:		234 nm
observed:		235 nm

Answer



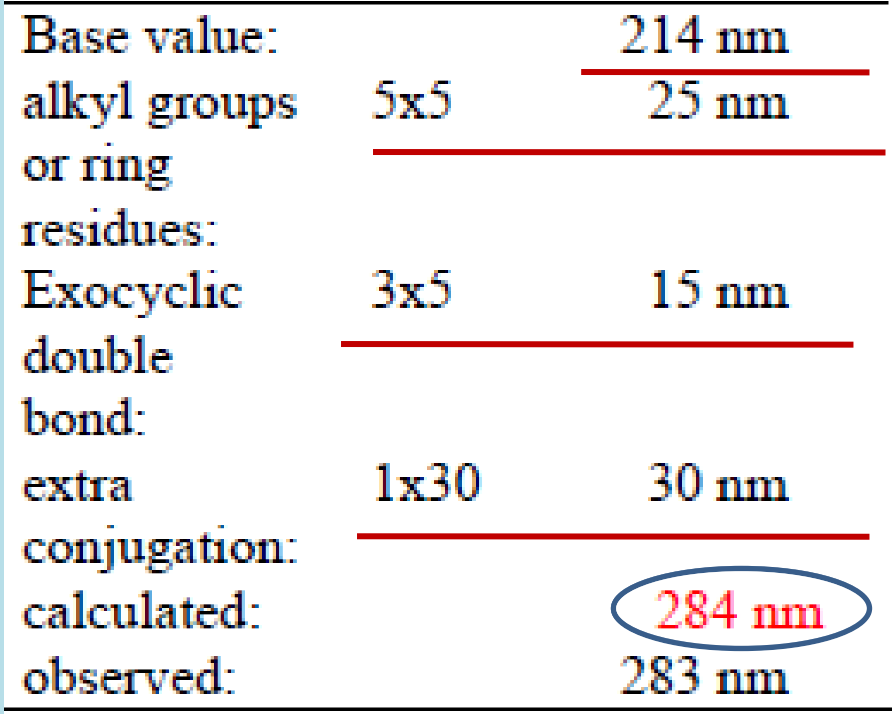
d)

Base value:		253 nm	
alkyl groups or ring residues:	4x5	20 nm	
Exocyclic double bond:		5 nm	
calculated:		278 nm	**Answer**
observed:		275 nm	

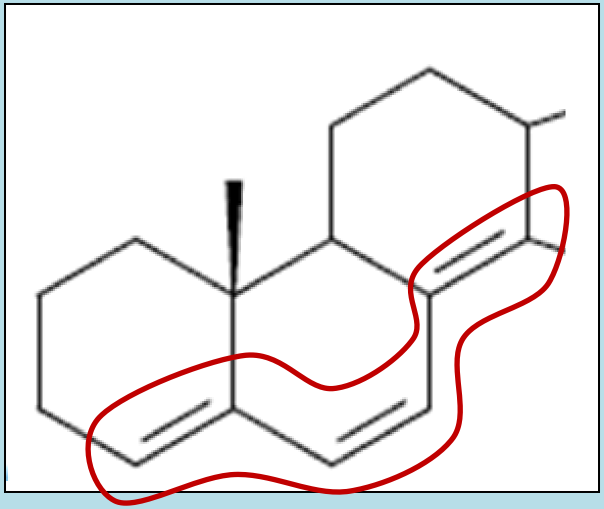


Heteroannular

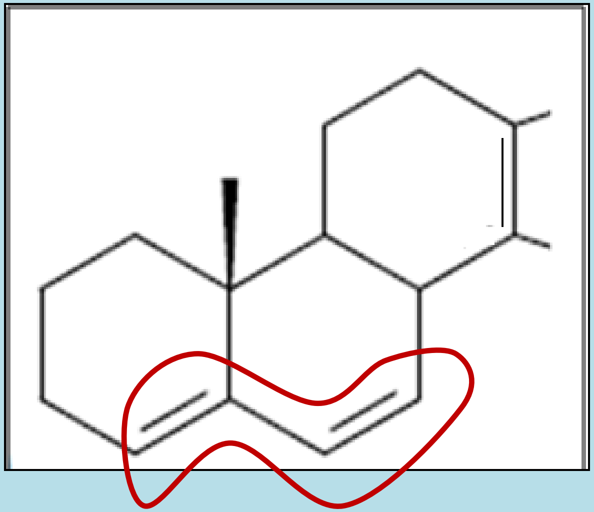
e)



Base value:		214 nm
alkyl groups or ring residues:	5x5	25 nm
Exocyclic double bond:	3x5	15 nm
extra conjugation:	1x30	30 nm
calculated:		284 nm
observed:		283 nm



Structure -1



Structure-2

Q. Two isomers of a compound have different λmax. The α isomer has lower λmax and β isomer shows higher λmax.

Which one of the above structures is α isomer and which is β isomer ?

Answer. Due to extended conjugation in structure-1, λmax is higher (β isomer) and in structure-2, λmax will be lower (α isomer)

Thank You

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