B. Sc. III Year (Sem-VI)

UV Spectroscopy

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Introduction of Spectroscopy

- **Introduction :**
- The study of organic compounds depends on the knowledge of their molecular structures.
- The classical methods for structure determination are very time consuming as well as they require large quantity of compound. The structure determination of organic compound require sequence of characterization as follows :
- a) Elemental analysis
- b) Find out molecular mass and molecular formula of the compound.
- c) Determination of functional groups in the compound by usual chemical tests.
- d) Melting points or boiling points.
- e) Formation of derivatives.
- During the last few decades, we have been using different spectroscopic methods for determination of structure.
- This methods are most important and useful to give accurate information about the structure in very short time.
- It is a branch of science which describes properties of molecules on the basis of electromagnetic radiation.

- **Electromagnetic radiations :**
- Emission of energy or particles is called as radiation. It consists of both properties of wave as well as particles.
- It describes as a wave occurring simultaneously in electric and magnetic field and particles in the form of photons.
- **Characteristics of EMR :** An electromagnetic wave is characterized as follows :
- **a) Wavelength (λ) :**
- It is distance between two adjacent crest or trough in a particular wave is called as wave length.
- It is denoted by λ. It is expressed in m, μm, nm.
- **b) Frequency (ϑ):**
- It is defined as number of waves passes through a point in one second.
- It is denoted by 'ϑ'. It is expressed in cycle/sec. or Hertz (Hz).
- **c) Wave number (ϑ) :**
- It is the reciprocal of wavelength or it is defined as total number of waves passes through a space of one centimeter.
- It is denoted by ϑ. It is expressed in cm^{-1}.

- **d) Energy of EMR :**
- Energy of quantum of EMR has direct relation with its frequency. Energy of a wave of a particular radiation can be calculated by applying following formula …
- $E = h \vartheta$
- Where, h = planks constant = 6.626×10^{-27} erg/sec
- ϑ = frequency
- **Electromagnetic spectrum :**
- When a beam of light passed through a prism, it splits into seven different colours. This set of colour obtained by splitting of light is called as spectrum. The electromagnetic spectrum is as follows.
- Sunlight -> Prism -> Red, Orange, Yellow, Green, Blue, Indigo, Violet.
- The electromagnetic spectrum comprises the following radiations :

S.No	Region	Wavelength
1	Cosmic rays	10^{-3} nm
2	Gamma rays	10^{-3} to 10^{-10} nm
3	X-rays	0.01 to 4 nm
4	UV rays	4 to 400 nm
5	Visible light	400 to 800 nm
6	IR rays	0.5 to 200 µ

Spectroscopy :

- Spectroscopy is a branch of science which describes properties of molecule on the basis of electromagnetic radiations. The study of spectroscopy deals with emission as well as absorption phenomenon.
- **Types of Spectroscopy :**
- There are two types of spectroscopy.
- **a) Emission spectroscopy :**
- When electromagnetic radiations passed through the substance, energy is absorbed and electron in the ground state is promoted to upper excited state. When electron from upper state jumps to lower energy, then some energy is released as radiation. This emitted radiation is analyzed by spectrophotometer. Such type of spectroscopy is called as emission spectroscopy.
- **b) Absorption spectroscopy :**
- When electromagnetic radiations passed through the substance, then radiation of certain wavelength are absorbed by the substance. The wave length which are absorbed is analyzed by spectrophotometer. Such type of spectroscopy is called as absorption spectroscopy.

Ultra Violet Spectroscopy (UV Spectroscopy)

- UV spectroscopy is used for detection of conjugation in organic compounds.
- UV spectroscopy helps to differentiate:
- conjugated and isolated dienes,
- dienes and triens,
- carbonyl compounds and α, β–unsaturated carbonyl compounds,
- cis and trans isomers.
- UV region of electromagnetic spectrum extend from 15 to 400 nm. Visible region extends from 400 to 800 nm.
- UV region is divided into following two sub regions.
- i) Far UV region   –   15 - 200 nm
- ii) Near UV region –   200 - 400 nm
- Important region of UV spectroscopy is extend from 200 to 400 nm.

Fig : Showing Electronic Transitions

There are four types of electronic transitions in organic compounds as follows,

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a) σ-σ* transitions :

A transition in which bonding σ electrons get excited (promoted) to anti bonding σ* orbital is called as σ-σ* transitions. Sigma bonds are very strong bonds, therefore they required very high energy for this transition. These transitions occur at wavelength shorter than 165 nm.

- Ex. In methane molecule, σ-σ* transitions occur at 150 nm.

b) n-σ* transitions :

A transition in which one electron of a lone pair get excited (promoted) to antibonding σ* orbital is called as n-σ* transitions. These transition required lower energy than σ-σ* transitions. It occur at wavelength at 175 nm.

- Ex. Methyl alcohol shows n-σ* transition at 174 nm.

c) π-π* transitions (K-band) :

A transition in which bonding π electron get excited (promoted) to anti bonding π* orbital is called as π-π* transitions. These transition required lower energy than n-σ* transitions. It occur at wavelength above 200 nm.

- Ex. 1,3-butadiene shows π-π* transition at 217 nm.

d) n-π* transitions (R-band) :

A transition in which one electron of a lone pair get excited (promoted) to antibonding π* orbital is called as n-π* transition. These transition required lower energy than π-π* transitions. It occur at wavelength above 270 nm.

- Ex. Acetone shows n-π* transition at 280 nm.

Terms used in UV Spectroscopy

a) Chromophore:

- Any isolated covalently bounded group that shows a characteristic absorption in the UV or visible region, such functional group is called as chromophore.

- Ex. $CH_2=CH_2$, $CH\equiv CH$, -N=O, -COOH, $-NO_2$ etc.

  There are two types of chromophores.

- i) Chromophores which shows π-π* transition

  e.g. Ethylene and acetylene shows only π-π* transitions.

- ii) Chromophores which shows π-π* transition as well as n-π* transition

  e.g. Carbonyl and nitro shows π-π* transition as well as n-π* transitions.

b) Auxochrome :

- It is a functional group which does not absorb radiation above 200 nm but when attached to chromophore causes shift of absorption towards higher wave length.

  Common auxochromic groups are –OH, -OR, -NH$_2$, -NHR,

- Ex. Benzene shows λmax at 255 nm and aniline shows λmax at 280 nm.

c) Bathochromic Shift (Red Shift) :

- It is an effect, in which absorption maximum shifted towards longer wavelength due to the presence of an auxochrome or by change in solvent. Such effect is called as bathochromic shift or red shift.

- Ex. Benzene shows λmax at 255 nm and aniline shows λmax at 280 nm.

d) Hypsochromic Shift (Blue Shift) :

- It is an effect, in which absorption maximum shifted towards shorter wavelength due to removal of conjugation or by changing polarity of solvent. Such effect is called as hypsochromic shift or blue shift.

- Ex. Aniline shows λmax at 280 nm and acidic solution of aniline shows λmax at 254 nm.

e) Hyperchromic Shift :

- It is an effect, in which intensity of absorption maximum (ϵ_{max}) increases. Such effect is called as hyperchromic shift.

- Ex. Benzene shows ϵ_{max} at 205 and aniline shows ϵ_{max} at 1430.

e) Hypochromic Shift :

- It is an effect, in which intensity of absorption maximum (ϵ_{max}) decreases. Such effect is called as hypochromic shift.

- Ex. Biphenyl shows ϵ_{max} at 19000 and 2-methyl biphenyl shows ϵ_{max} at 10250.

Woodward-Fieser rules for calculation of λmax for conjugated dienes

S.No	System	Base Value/ Increments
1.	Open chain diene or heteroannular diene	214 nm
2.	Homoannular diene	253 nm
3.	Extended double bond in conjugation	+ 30 nm
4.	For alkyl group/ Ring residue	+ 5 nm
5.	For Exocyclic double bond	+ 5 nm

- **Examples :**
- 1) 2,4-hexadiene :

This is an example of open chain diene
Base value   214 nm
For 2-alkyl groups (2x5)   + 10 nm

                              λmax   = 224 nm

- 2) 2,4,6-octatriene :
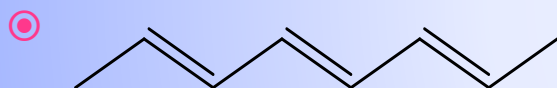
This is an example of open chain diene
               Base value   214 nm
For 2-alkyl groups (2x5)   + 10 nm
For extended double bond   + 30 nm

                              λmax   = 254 nm

- 3) 2,5-dimethyl-2,4,6-octatriene :
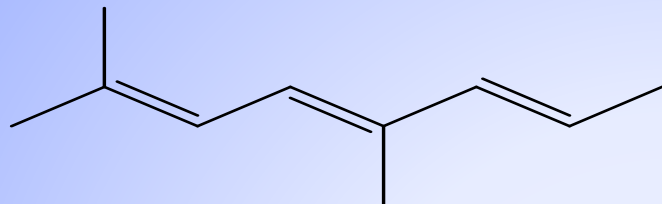
- 4) Cyclohexadiene :
-
-
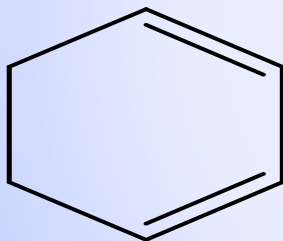
- 3) 2,5-dimethyl-2,4,6-octatriene :
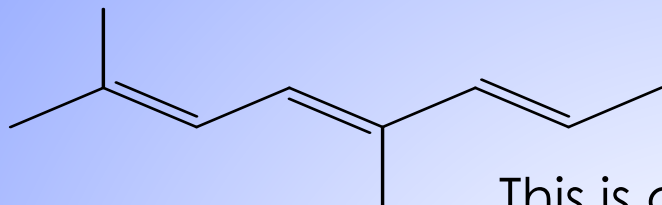
This is an example of open chain diene

Base value		214 nm
For 4-alkyl groups (4x5)	+	20 nm
For extended double bond	+	30 nm

λmax   = 264 nm

- 4) Cyclohexadiene :
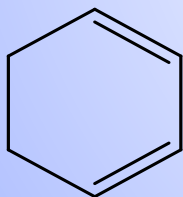
This is an example of homoannular diene

Base value		253 nm
For 2-ring residue (2x5)	+	10 nm
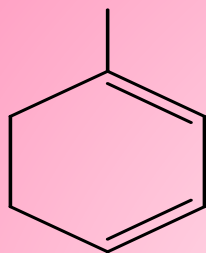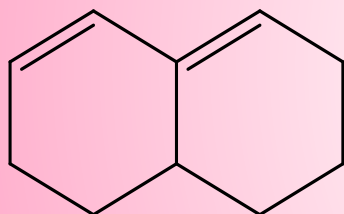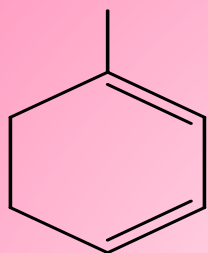
λmax   = 263 nm

5)

6)

- 5)

This is an example of homoannular diene

Base value	253 nm
For 3-ring residue (3x5)	+ 15 nm

λmax = 268 nm

- 6)

This is an example of heteroannular diene

Base value	214 nm
For 3-ring residue (3x5)	+ 15 nm
For 1-exocyclic double bond	+ 5 nm

λmax = 234 nm

- 7)
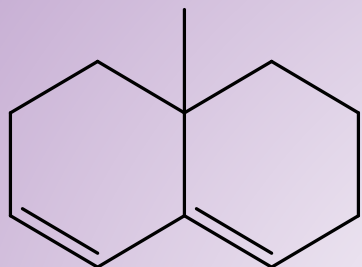
- 8)

7)
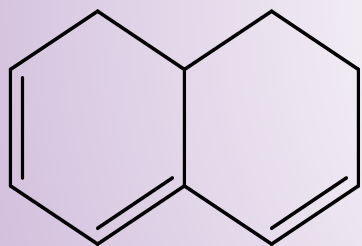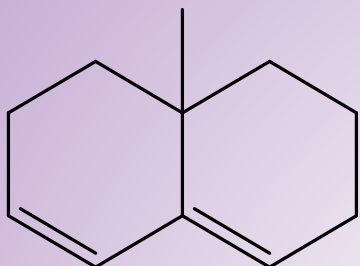
This is an example of heteroannular diene

Base value	214 nm
For 3-ring residue (3x5)	+ 15 nm
For 1-exocyclic double bond	+ 5 nm

λmax = 234 nm

8)
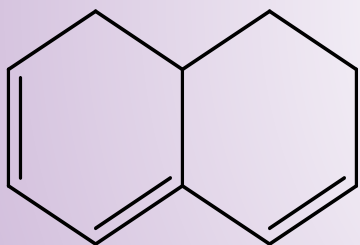
This is an example of homoannular diene

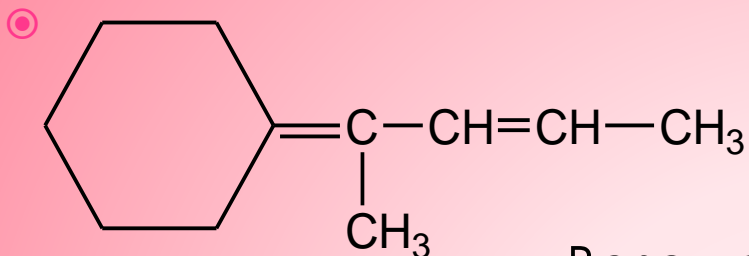|	
Base value	253 nm
For 3-ring residue (3x5)	+ 15 nm
For 1-exocyclic double bond	+ 5 nm
For 1-extended double bond in conjugation	+ 30 nm

λmax = 303 nm

- 9)

- 10)
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- 9)

$C = C - CH = CH - CH_3$

CH₃ group: CH_3
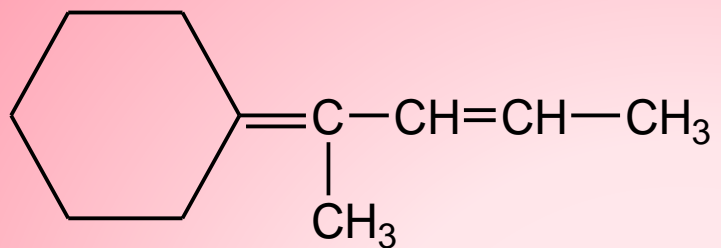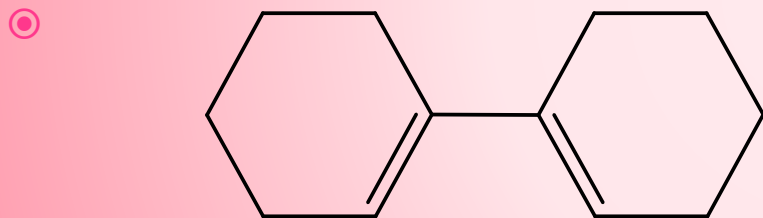
Base value	214 nm
For 2-ring residue (2x5)	+ 10 nm
For 2-alkyl group (2x5)	+ 10 nm
For 1-exocyclic double bond	+ 5 nm

λmax	= 239 nm

10)
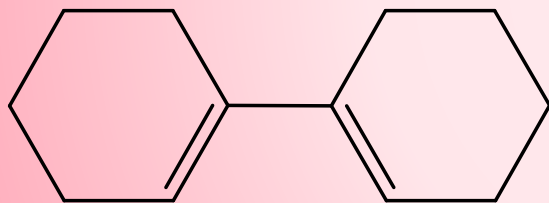
Base value	214 nm
For 4-ring residue (4x5)	+ 20 nm

λmax	= 234 nm

Woodward-Fieser rules for calculation of λmax for conjugated Enones

S.No.	System	Base Value/ Increments
1.	Open chain α,β-unsaturated ketones **or** 6-membered α,β-unsaturated cyclic ketones	215 nm
2.	Open chain α,β-unsaturated aldehyde	207 nm
3.	Open chain α,β-unsaturated esters or acids	193 nm
4.	5-membered α,β-unsaturated cyclic ketones	202 nm
5.	Ring Residue : At α-position --- At β-position --- At ϑ, δ and so on position ----------------------	+ 10 nm + 12 nm + 18 nm
6.	Extended double bond in conjugation	+ 30 nm
7.	For exocyclic double bond	+ 5 nm
8.	For homoannular diene	+ 39 nm

Examples

- **1) Prop-2-enal**
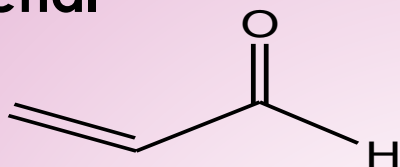
- This is an example of open chain α, β-unsaturated aldehyde

Base value	= 207 nm

λmax	= 207 nm

- **2) But-2-enal**
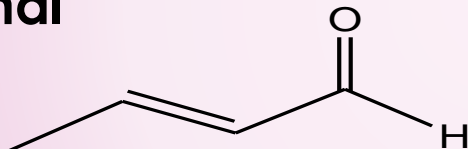
- This is an example of open chain α,β-unsaturated aldehyde

Base value	207 nm
for 1 β-alkyl group	+ 12 nm

λmax	= 219 nm

- 3) But-3-en-2-one
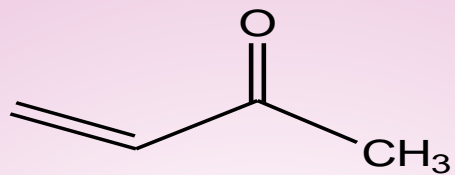
-
- 4) Cyclohex-2-enone

-
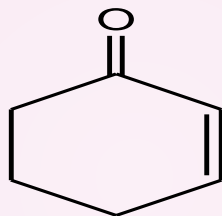
- **3) But-3-en-2-one**
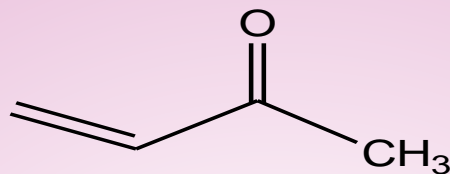
- This is an example of open chain α, β-unsaturated ketone

  Base value   = 215 nm

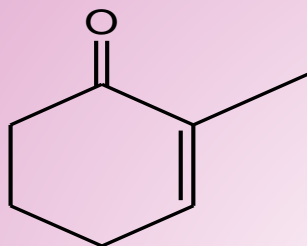
  λmax   = 215 nm

- **4) Cyclohex-2-enone**
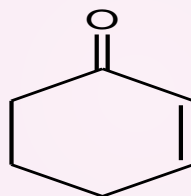
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- This is an example of open chain α,β-unsaturated 6-membered cyclic ketone
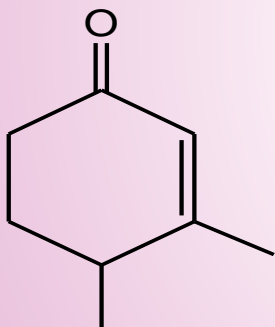
  Base value   215 nm
  for 1 β- ring residue   +   12 nm
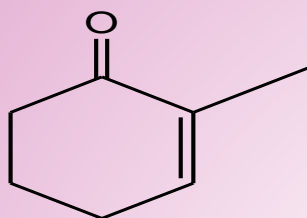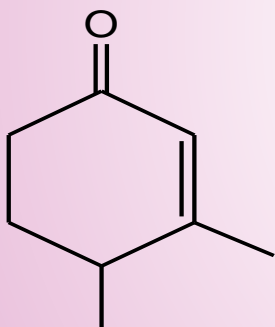

  λmax   =   227 nm

- 5)

- 6)

- 5)
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This is an example of open chain α, β-
unsaturated 6-membered cyclic ketone

Base value	215 nm
for 1 α- ring residue	+ 10 nm
for 1 β- ring residue	+ 12 nm

λmax   =   237 nm

- 6)
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This is an example of open chain α,β-
unsaturated 6-membered cyclic ketone

Base value	215 nm
for 2 β- ring residue	+ 24 nm

λmax   =   239 nm
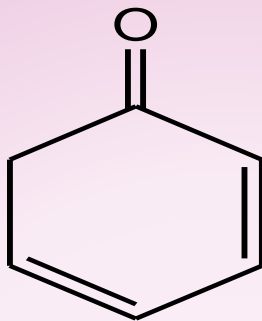
- 7)

- This is an example of open chain α,β-unsaturated 6-membered cyclic ketone

-
        Base value   215 nm
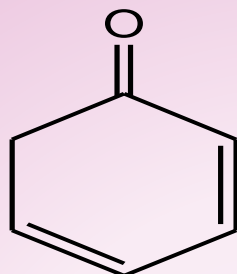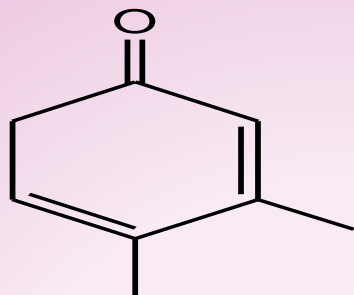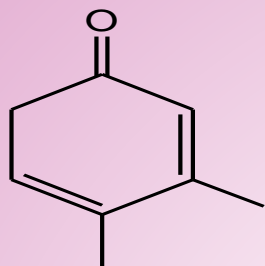   for 1 δ- ring residue   + 18 nm
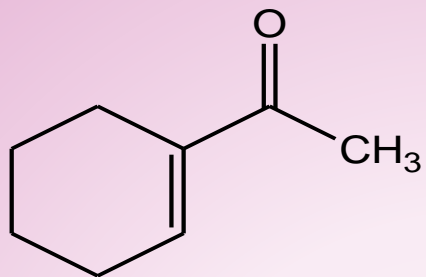   for 1 extended double bond

         in conjugation   + 30 nm
        for homoannular dienes   + 39 nm

        λmax   =   302 nm

- 8)

- 8)

- This is an example of open chain a,β-unsaturated 6-membered cyclic ketone

Base value	215 nm
for 1 β- ring residue	+ 12 nm
for 1 ϑ- ring residue	+ 18 nm
for 1 δ- ring residue	+ 18 nm
for 1 extended double bond in conjugation	+ 30 nm
for homoannular diene	+ 39 nm

λmax   =   332 nm

- 9)

9)

Base value   215 nm
for 1 α- ring residue   +   10 nm
for 1 β- ring residue   +   12 nm

λmax   =   237 nm

10)
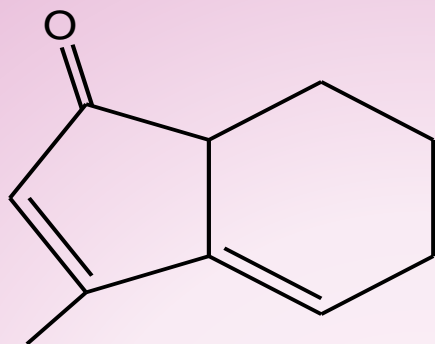
10)
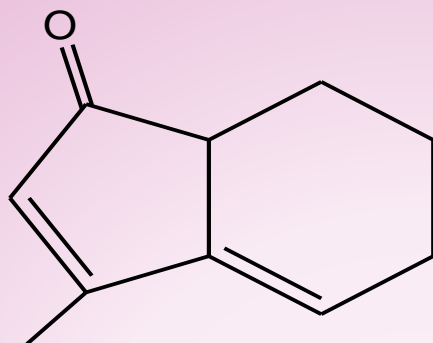
Base value   202 nm
for 1 β- ring residue   +   12 nm
for 1 ϑ- ring residue   +   18 nm
for 1 δ- ring residue   +   18 nm
for 1 extended double

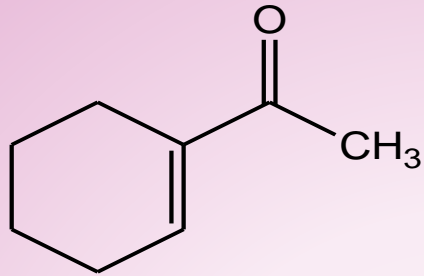bond in conjugation   +   30 nm
for 1 exocyclic double bond   +   5 nm

λmax   =   285 nm

- **Lambert's – Beer's Law :**

- **i) Lambert's Law :**
- When a beam of monochromatic light passes through homogeneous absorbing medium, the intensity of the incident light decreases as the thickness of the absorbing medium increases.
- Mathematically it is expressed as,
- $\text{Log} \dfrac{Io}{I} = a \times b$

  Where, Io = intensity of incident light
- I = Intensity of light after passing through absorbing medium
- a = absorption coefficient
- b = path length
- **ii) Beer's Law :**
- When a beam of monochromatic light passes through homogeneous absorbing medium, the intensity of the incident light decreases as the thickness as well as concentration of the absorbing medium increases.
- Mathematically it is expressed as,
- $\text{Log} \dfrac{Io}{I} = a \times b \times c$

  Where, Io = intensity of incident light
- I = Intensity of light after passing through absorbing medium
- a = absorption coefficient
- b = path length
- c = concentration

Thank You ……