University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

Engineering Chemistry-**II** (BS-104)
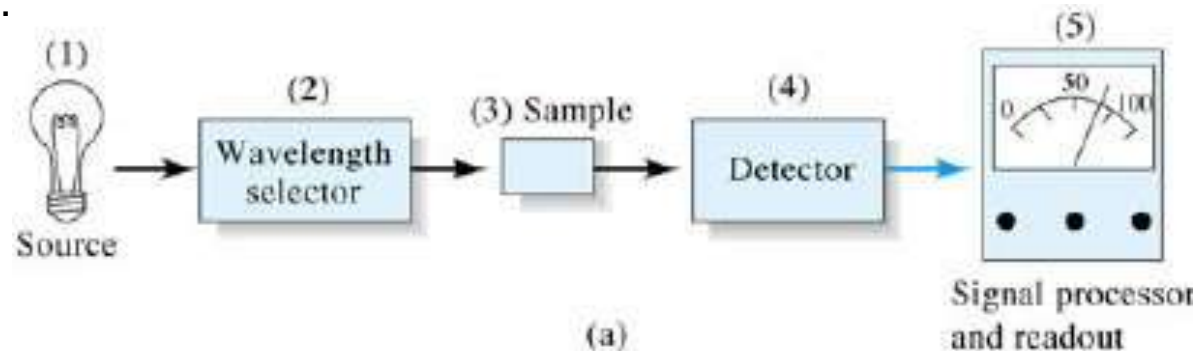
Spectroscopic Techniques-1

**Dr. Shruti Khanna Ahuja**

Assistant Professor

USAR, GGSIPU

- Study of interaction of electromagnetic radiation with matter defines the science of **spectroscopy.**

- **Spectroscopy** is that science which attempts to determine what specific energies and amounts of incident light are absorbed by specific substances, and what specific energies and amounts are later re-emitted.

- It includes different analytical techniques used for both quantitative and qualitative analyses of inorganic, organic and biological compounds.

- **Spectrometers** are optical instruments that reveal the light energies absorbed and emitted in terms of specific wavelengths or frequencies.

- **Spectra** are the records that provide us with important information pertaining to the atomic and molecular structure of the substances on which the electromagnetic energy is focused.

- These spectra provide us with "fingerprints" that are characteristic of—and therefore uniquely connected to—different elements and compounds.

A generic spectrometer

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Electromagnetic radiation** is a type of energy that is transmitted through space at enormous velocities. It is found to have dual nature - the particle nature (photons) and wave nature.

- It is a propagating wave of electrical energy with an orthogonal magnetic component oscillating with exactly the same frequency.

- Molecules absorb electromagnetic radiation in discrete packets of energy called "quanta", which are measurable by spectroscopy.

- The many different types of EM waves are categorized according to their origins and their frequency/wavelength values.
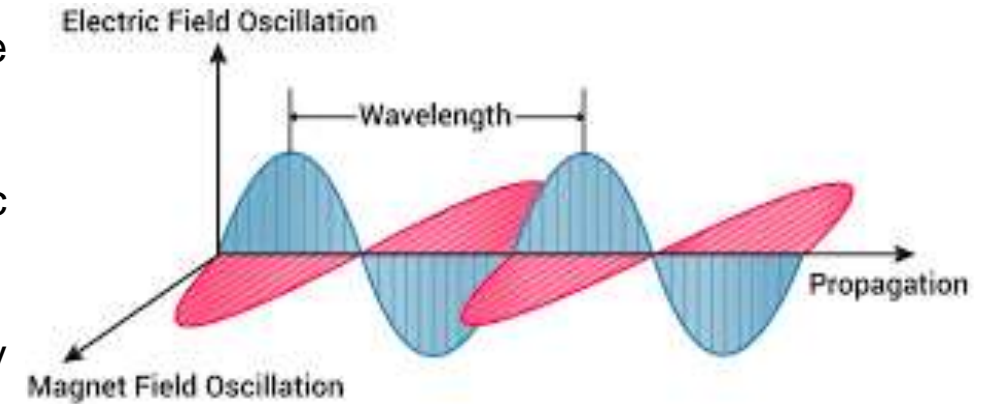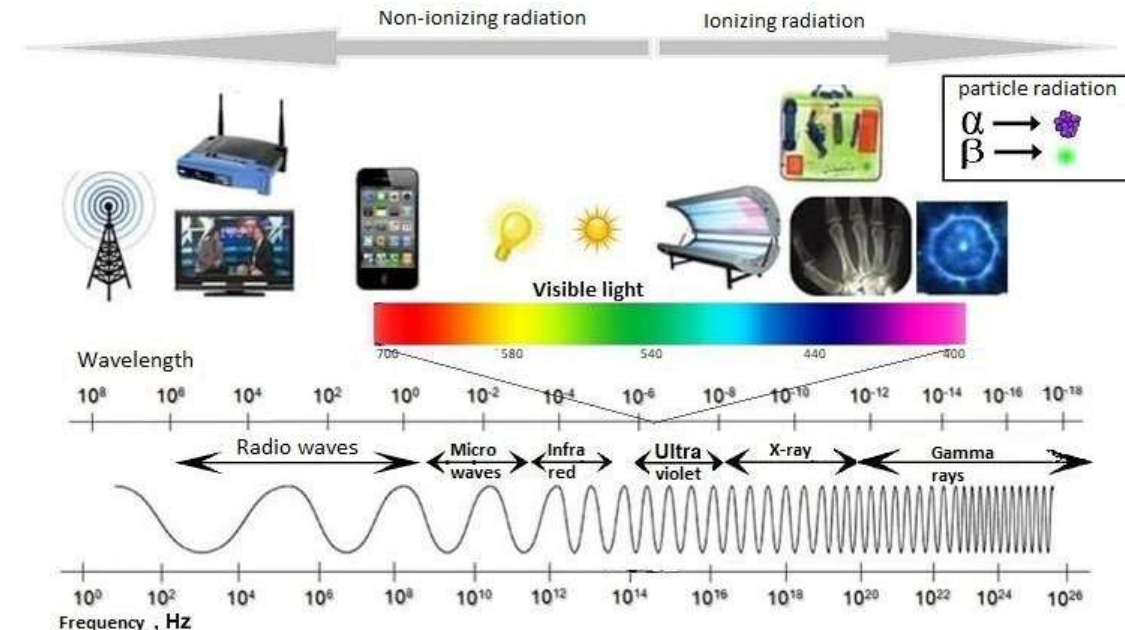

Electromagnetic radiation

$c = \lambda v$
c = speed of light = 3×10^8 m/s
λ = wavelength of radiation
v = frequency of electromagnetic radiation

Electromagnetic spectrum

$E = hv = hc/ \lambda$
E = energy of electromagnetic radiation
h = Planck's constant = 6.62×10^{-34} Js

As the energy increases, wavelength decreases

- The field of spectroscopy is divided into two main classes:

i.   Absorption   ii. Emission

i.   Absorption spectra are produced when white light is directed onto a particular substance and certain wavelengths in the spectrum of the white light are absorbed via internal energy excitations.
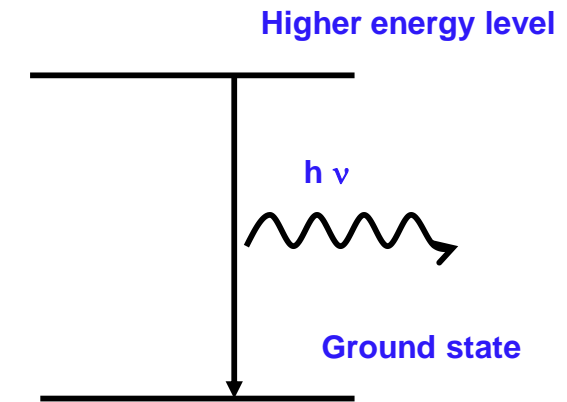
- The wavelength absorbed characterizes some specific functional group of the compound or the compound itself.

- The regions of electromagnetic radiation of greatest interest to organic chemists are 200-400 nm (UV), 400-800 nm (visible) and 800 nm-1 mm (infra-red)

- The mechanisms of absorption of energies is different in the ultra-violet, infra-red and nuclear magnetic resonance (NMR) regions, though the fundamental phenomenon is the absorption of certain amount of energy.

- Absorption in UV-vis is due to electronic transitions, in infra-red region, it is due to molecular vibrations, where as in NMR, nuclear spin transitions take place.
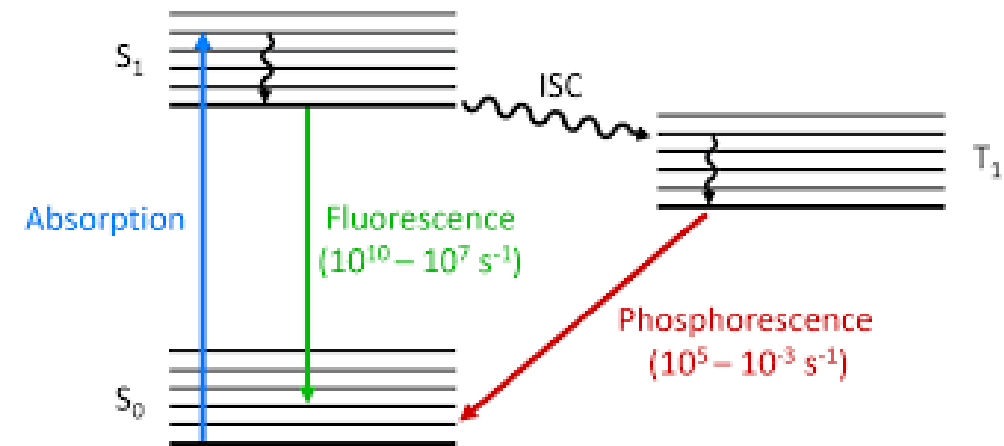
Higher energy level

$h\,\nu$

Ground state
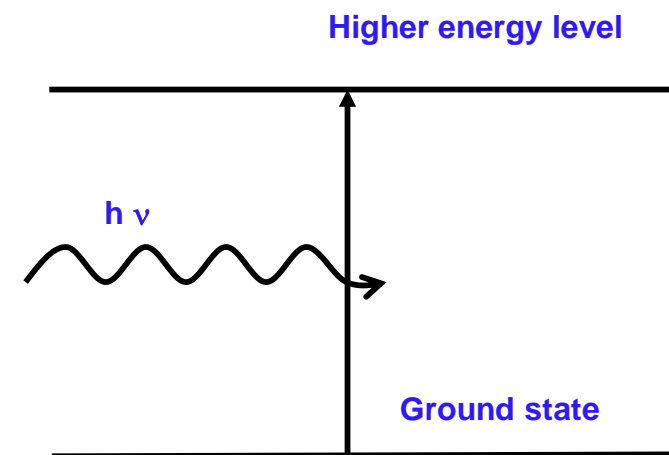
Absorption

ii. **Emission spectra** for a substance occurs when the substance receives energy from an external source, absorbs the energy to raise its electrons to higher energy metastable states (electrons having short life time here), then emits characteristic energy amounts as the excited electrons return to their previous energy levels.

Higher energy level

h ν

Ground state

Emission

- Fluorescent lights and colors obtained by heating salts of certain elements in the flame are very common examples of emission spectra

- **Fluorescence:** The electron in the excited level return to its ground state either directly or in steps with the emission of certain amount of energy. When this emission of light is instantaneous the phenomenon is known as fluorescence

- **Phosphorescence:** When the electron in the excited level return to it's ground state with the emission of light after some time lag, it is known as phosphorescence.

S_1

ISC

T_1

Absorption

Fluorescence
$(10^{10} - 10^7 \text{ s}^{-1})$

Phosphorescence
$(10^5 - 10^{-3} \text{ s}^{-1})$

S_0

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

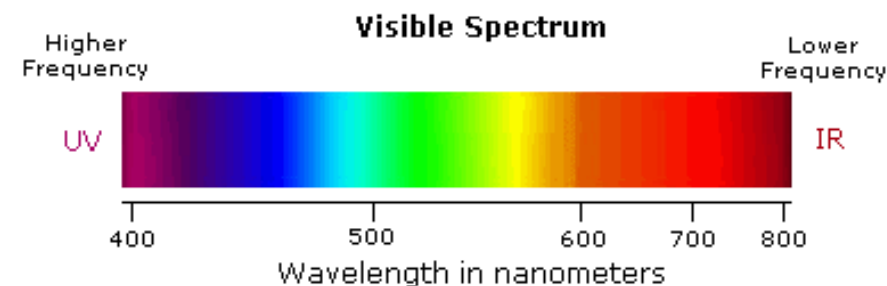**USAR**
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

1. UV-VISIBLE SPECTROSCOPY

- A region of electromagnetic radiation whose interaction with a molecule gives rise to electronic transition exists at 200-800 nm

- It requires electromagnetic radiations of higher energy

- It is primarily used to measure the multiple bonds or aromatic conjugation within the molecules.

- When monochromatic light is passed through a medium containing particles, they interact with ions and molecules and electronic transitions occur by the excitation of electrons from the ground state to the excited state.

- Molecules that absorb in UV-vis region transfer the corresponding energy from that photon to one or several of its outermost electrons.

- This transfer of energy results in a change on the total mechanical energy associated with the molecule. The total energy will be equal to:

$$E_{tot} = E_{elec} + E_{vib} + E_{rot,}$$

where, $E_{elec} > E_{vib} > E_{rot}$

Visible Spectrum

Higher Frequency   Lower Frequency

UV   IR

400   500   600   700   800
Wavelength in nanometers

Violet: 400 - 420 nm
Indigo: 420 - 440 nm
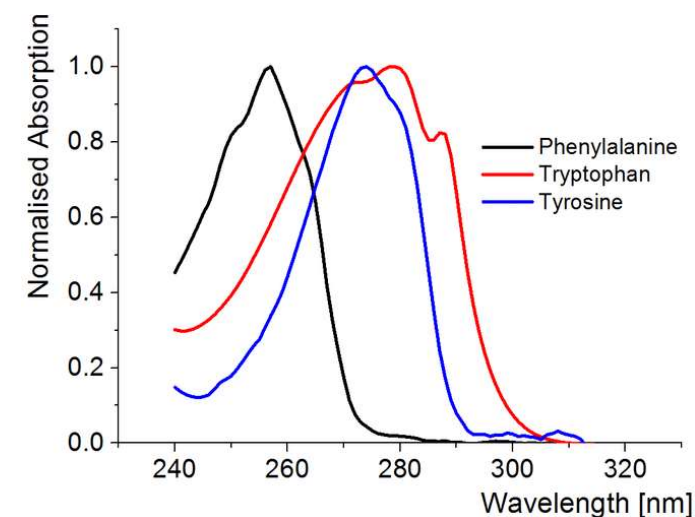**Blue:** 440 - 490 nm
Green: 490 - 570 nm
Yellow: 570 - 585 nm
Orange: 585 - 620 nm
Red: 620 - 780 nm

Phenylalanine
Tryptophan
Tyrosine

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

USAR
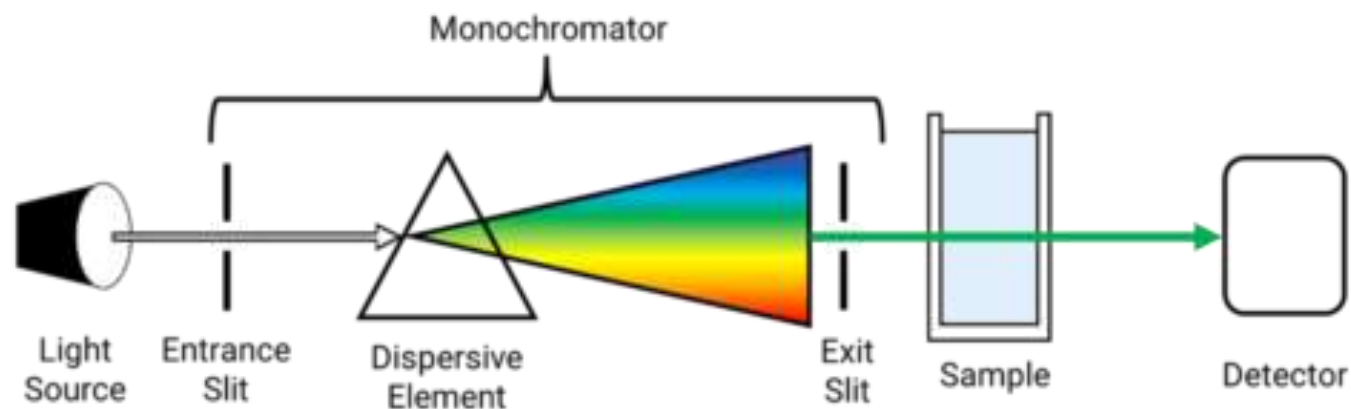UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Instrumentation:**

1. **Light Source:** Tungsten filament lamps and Hydrogen-Deuterium lamps are the most widely used and suitable light sources as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

2. **Monochromator:** Monochromators generally are composed of prisms and slits. Most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelengths to pass through the slits for recording purposes. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

3. **Sample and reference cells**: One of the two divided beams is passed through the sample solution and the second beam is passed through the reference solution. Both sample and reference solution is contained in the cells. These cells are made of either silica or quartz. **Glass can't be used for the cells as it also absorbs light in the UV region**.

4. **Detector:** Generally, two photocells serve the purpose of the detector in UV spectroscopy. One of the photocells receives the beam from the sample cell and the second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of the sample cell. This results in the generation of pulsating or alternating currents in the photocells.

5. **Amplifier:** The alternating current generated in the photocells is transferred to the amplifier. Generally, the current generated in the photocells is of very low intensity, the main purpose of the amplifier is to amplify the signals many times so we can get clear and recordable signals.

6. **Recording devices:** Most of the time amplifier is coupled to a pen recorder which is connected to the computer. The computer stores all the data generated and produces the spectrum of the desired compound.
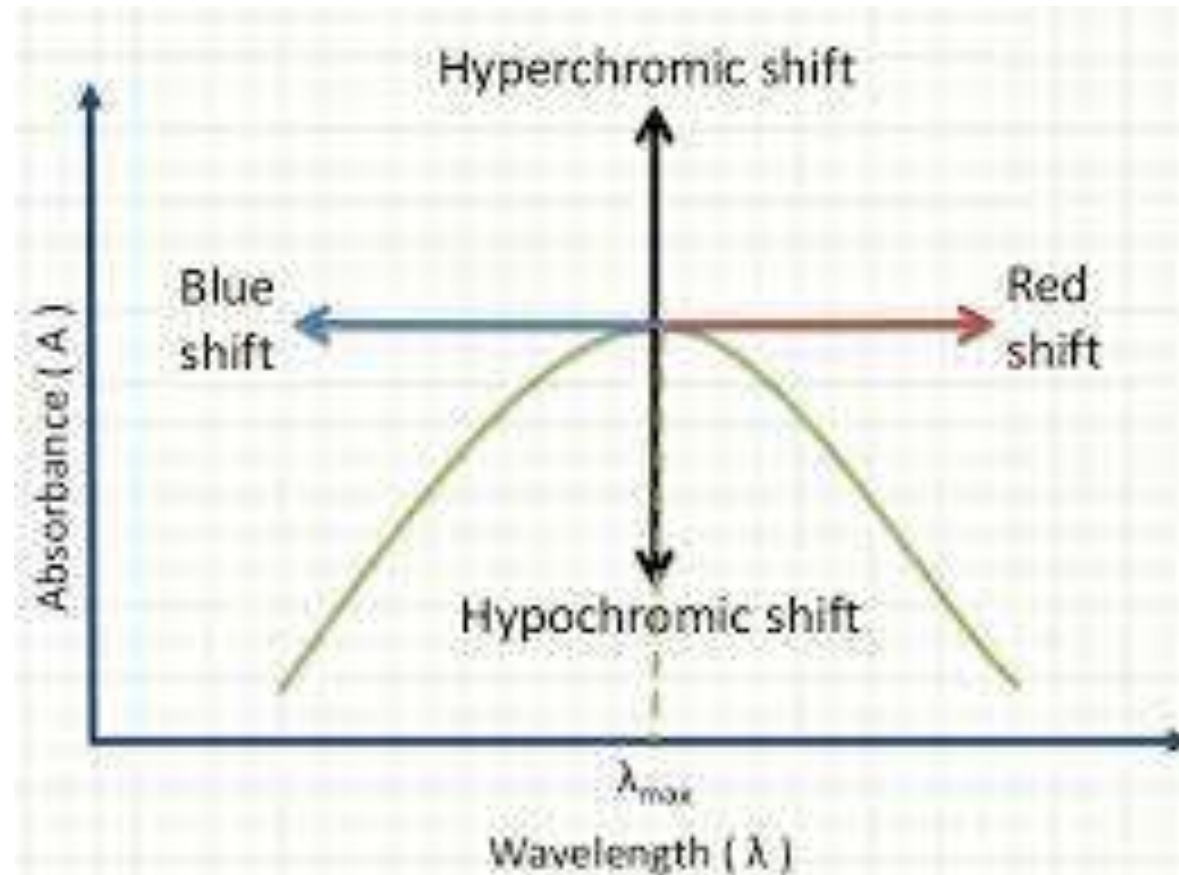

Schematic Representation

UV-Vis spectrophotometer

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092
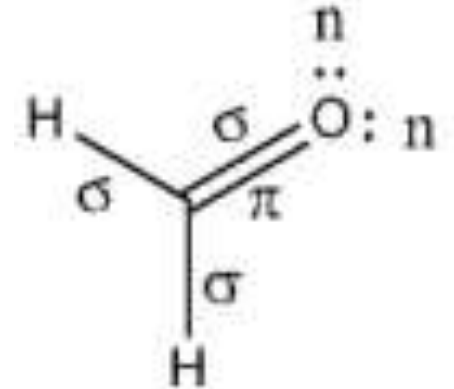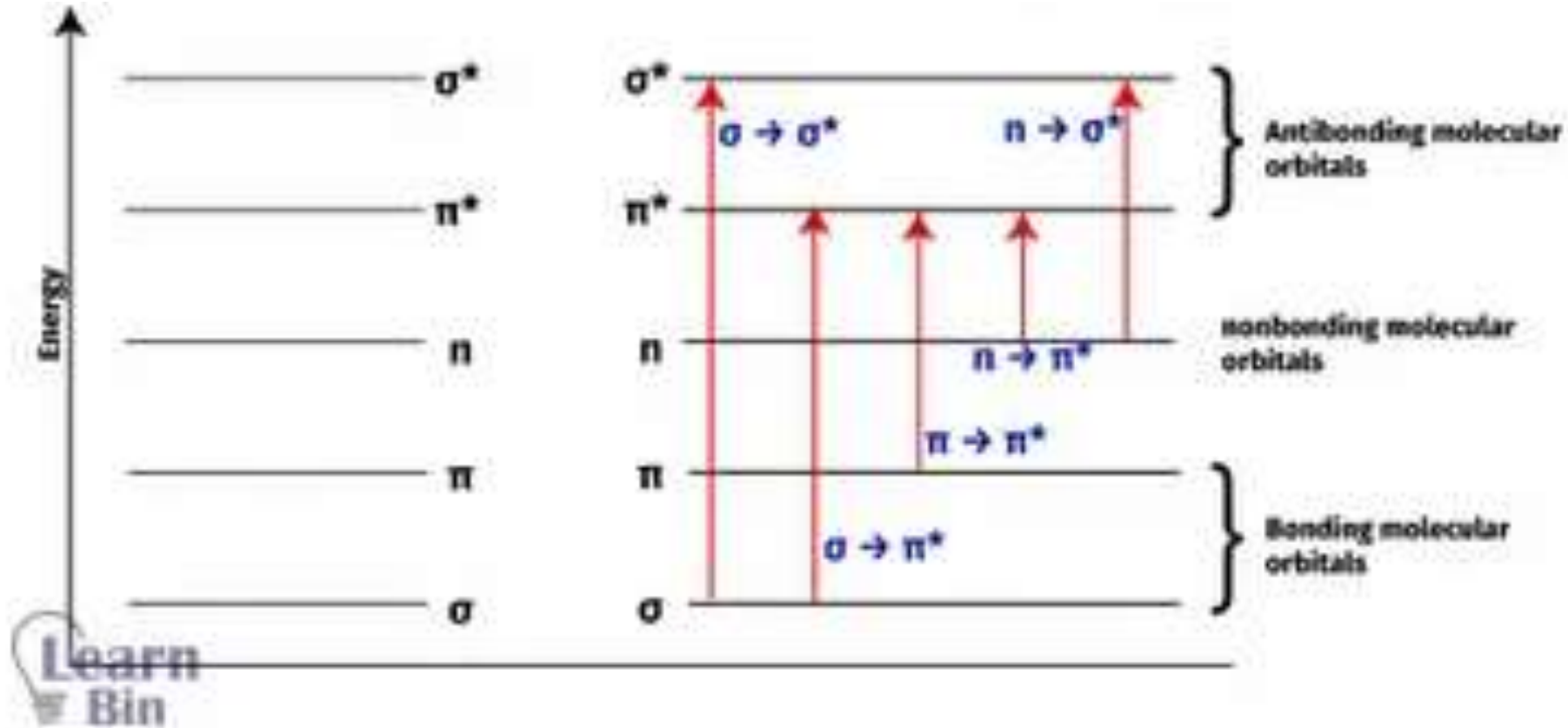
USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Chromophores:** It is a group of molecules, which is responsible for certain absorption of radiation. It is a minimum structural requirement for the absorption of radiation in the UV region, e.g. molecules having π electrons such as C=C, C=O, N=N

- **Auxochromes:** It is a saturated group containing unshared electrons which when attached to the chromophore changes both intensity as well wavelength of the absorption maxima, e.g. OH, NH2, Cl

- λ_{max} : It is a wavelength at which there is a maximum absorption. It is a physical constant and characteristic of a molecular structure and is very useful for identification of compounds. It is independent of concentration.

- **Bathochromic shift:** It is the shifting of the absorption peak to the higher wavelength due to the effect of a substituent group or solvent. It is also known as **red shift**. E.g., λ_{max} of ascorbic acid is 243 nm, while that in alkali medium is 299 nm

- **Hypsochromic shift:** It is the shifting of the absorption peak to the lower wavelength. It is also known as **blue shift**. E.g., λ_{max} of phenol in basic media is 297 nm, while that in acidic media is 277 nm

- **Hyperchroism:** Increase in absorption intensity due to substituent, solvent, pH or some other factors

- **Hypochroism:** Decrease in absorption intensity due to substituent, solvent, pH or some other factors

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

Shifts in absorption position and intensity

- **Electronic energy levels and transitions:**
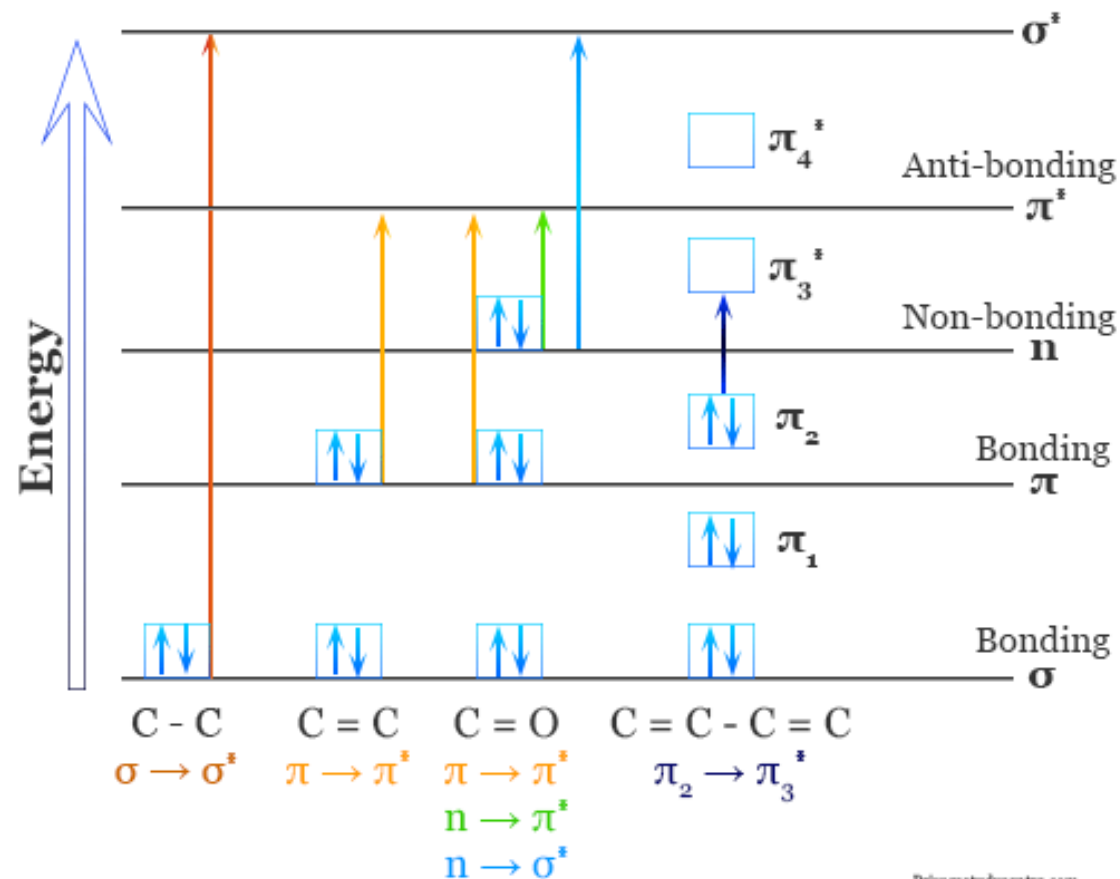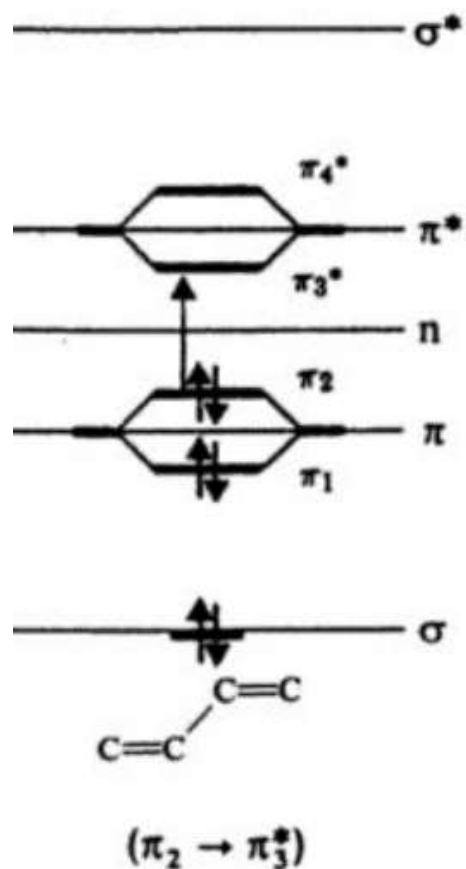
- **Types of electronic transitions:**

i. **σ–σ* transition:** An electron is excited from bonding σ orbital to higher energy anti-bonding σ* orbital. Sigma bonds, in general, are very strong and therefore the energy required for this transition is large and the band appear at short wavelengths <150 nm. It is observed with saturated compounds such as alkanes e.g. λ_{max} for methane is 122 nm. This regions is usually less informative.

ii. **n–σ* transition:** This transition involves saturated compounds with one heteroatom having unshared pair of electrons (n electrons) e.g. saturated alkyl halides, alcohols, ethers, aldehydes, ketones and amines etc. These transitions require comparatively lesser energy than σ–σ* transitions. In saturated alkyl halides the energy required for this transition decreases with increase in size of the halogen atom (less electronegativity => loosely bound outermost electron => less energy) e.g. λ_{max} for methyl chloride of 173 nm and that of methyl iodide is 258 nm. This transition is sensitive to H-bonding with the solvent molecules as in alcohols, amines thereby shifting the absorption peaks to shorter wavelength.

iii. **π–π* transition:** It occurs in the compounds with unsaturated centers such as simple alkene, aromatics, carbonyl compounds. This transition is lesser in energy than n–σ* transition. Unconjugated alkenes generally absorb in 170-205 nm.

iv. **n–π* transition:** An electron form non-bonding orbital of a heteroatom is promoted to anti-bonding π* orbital. It requires least energy out of all transitions and the absorption band appear at higher wavelengths.

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

v.   Conjugated systems: In conjugated dienes, the π orbitals of the separate alkene groups combine to give new orbitals, i.e., the new bonding orbitals designated as π_1 and π_2 and two anti-bonding orbitals, π_3^* and π_4^*. The relative energy of $\pi_2 \rightarrow \pi_3^*$ of a conjugated diene is of very low energy than $\pi \rightarrow \pi^*$ transition in an unconjugated alkene. e.g. λ_{max} for ethene is 171 nm while the peak is shifted bathochromically in butadiene with λ_{max} at 217 nm.

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
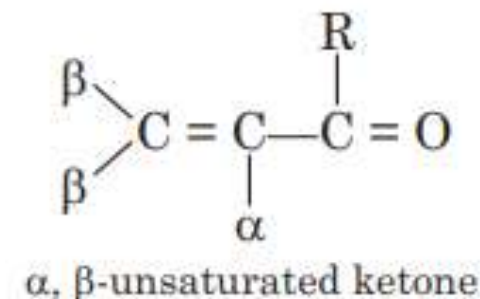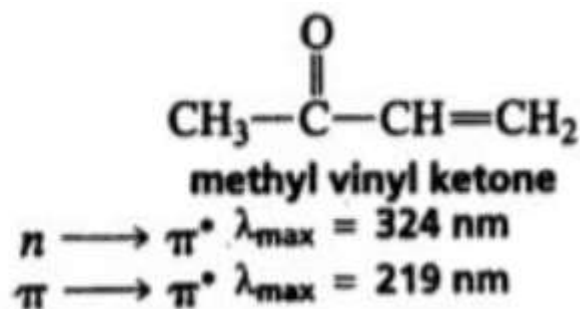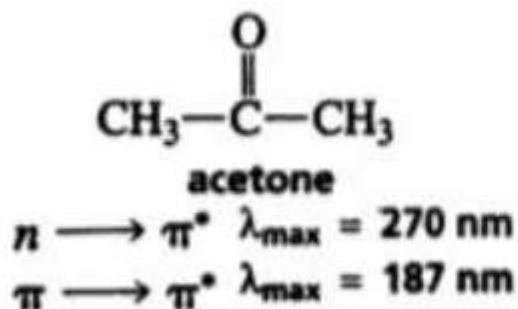Delhi – 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Types of absorption bands:** They occur due to electronic transition of a molecule.

i. **R-bands:** These are observed in compounds containing **double bonds with heteroatoms** such as carbonyls (C=O), nitro (-NO_2) etc. An electron from non-bonding orbital is promoted to anti-bonding π^* i.e. they undergo n–π^* transition. This transition require minimum energy of out of all transitions and shows absorption band at longer wavelength around 300 nm e.g. in acetone absorption band appear at 279 nm. Saturated aldehyde show both type of transitions: lower energy n–π^* and higher energy π–π^* thereby exhibiting absorption peaks at 290 and 180 nm, respectively. The ε_{max} value is less than 100.

ii. **K-bands:** These arise from π–π^* transitions in **π–π conjugated systems** like alkenes, alkynes, carbonyls, nitriles and aromatic compounds. The show ε_{max} greater than 10,000. e.g. 1,3,5-hexatriene exhibits λ_{max} at 258 nm

iii. **B-bands:** These are due to **aromatic and hetero-aromatic systems**. The λ_{max} values are between 230-270 nm and ε_{max} less than 2000. These bands are called benzenoid bands. In the presence of K-bands the position of the B-band is shifted to larger wavelengths. The UV spectrum of benzaldehdye contains K, R and B bands.

iv. **E-bands:** These are also known as **ethylenic bands** and are characteristic of the aromatic systems as are the B-bands. They are classified as E_1 and E_2 bands wherein E_1 bands appear at smaller wavelengths and are usually more intense, while E_2 bands for the same compound appear at longer wavelengths e.g. in naphthalene E_1 band is at 221 nm and E_2 band at 286 nm. The ε_{max} values of these bands vary from 2000- 14000. The presence of auxochromic group shifts an E-band to a higher wavelength.

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Woodward-Fieser's rules for calculation of λmax values in conjugated systems:**

1) **For α, β-unsaturated aldehydes and ketones:** Compounds in which C=O is conjugated with a C=C (enones) exhibit absorption band at longer wavelengths due to low energy n–π* (R-band) and π–π* transitions (K-band). e.g.

CH₃–C(=O)–CH₃
acetone
$n \longrightarrow \pi^*$ λ_{max} = 270 nm
$\pi \longrightarrow \pi^*$ λ_{max} = 187 nm

CH₃–C(=O)–CH=CH₂
methyl vinyl ketone
$n \longrightarrow \pi^*$ λ_{max} = 324 nm
$\pi \longrightarrow \pi^*$ λ_{max} = 219 nm

α, β-unsaturated ketone
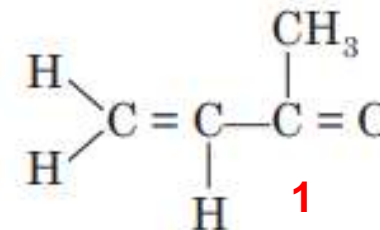
- **Rules:**

i.   The base value of the chromophore (C=C and C=O) in an acyclic and a 6-membered ring system is assigned as 215 nm

ii.   For each α-substituent (methyl) 10 nm is added to the base value

iii. For each β-substituent (methyl) 12 nm is added to the base value

iv.   For each ring system (5 or 6 membered) to which the C=C is exocyclic (double bond outside ring), 5 nm is added to the base value

v.   If the C=C and the C=O are in 5-membered ring i.e. cyclopentenone, the base value is 202 nm

➤ When cross conjugation i.e. α, β –unsaturation on both sides, λmax is calculated by considering most highly substituted conjugated system.

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

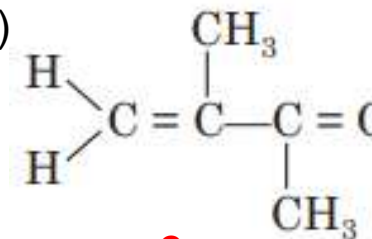USAR
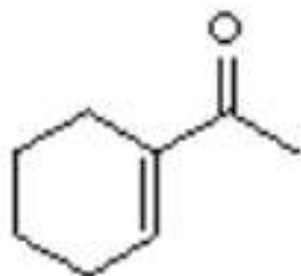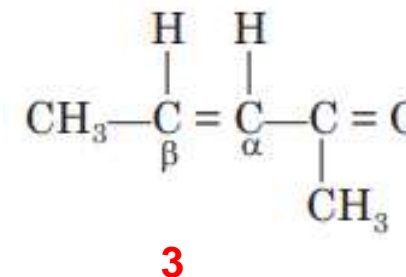UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Examples:**

1. Methyl vinyl ketone: No α and β substituents present, Cal λ_{max}: 215 nm (Obs. : 213 nm)

2. 2-Methyl-1-butene 3-one: one methyl at α-position, Cal. λ_{max}: 225 nm (Obs. : 220 nm)

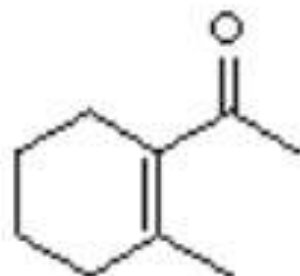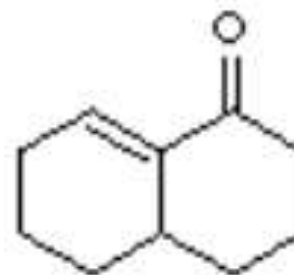3. 3-pentene-2-one: one methyl at β-position, Cal. λ_{max}: 227 nm (Obs. : 224 nm)

1

2

3

233 (13,000)
calc: 237

4

245 (6,500)
calc: 249

5

245 (5,500)
calc: 242

6

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
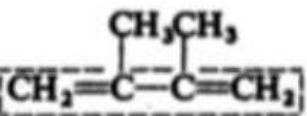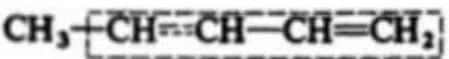Delhi - 110092
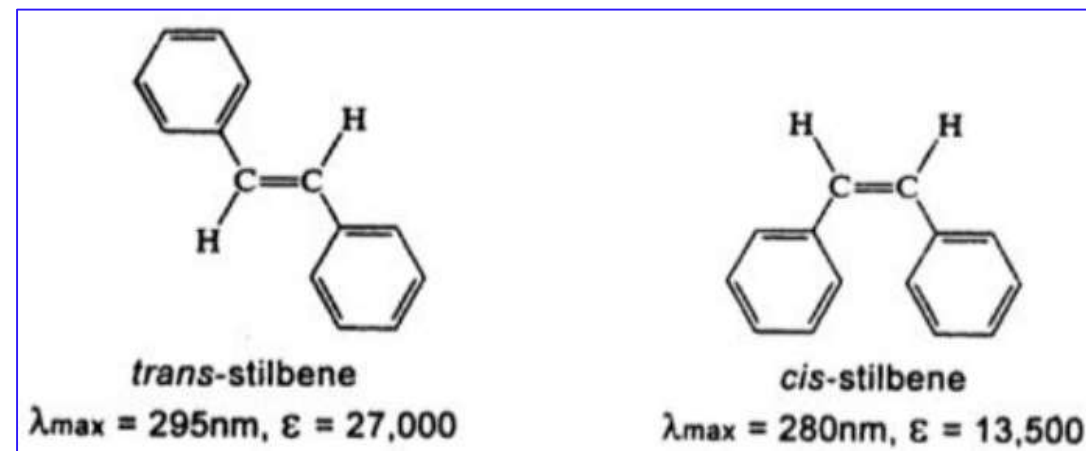
USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

2) Conjugated dienes (acyclic): Conjugation shifts the absorption band to higher wavelength.

e.g. λ_{max} for ethene, 1,3-butadiene and 1,3,5-hexatriene is 171, 217 and 258 nm, respectively

• **Rules:**

i. The base value for acyclic conjugated dienes and cyclic conjugated dienes containing a non-fused 6-membered ring system is 217 nm

ii. For each acyclic alkyl substituent 5 nm is added to the base value

iii. If C=C is exocyclic (double bond outside ring), 5 nm is added to the base value

iv. Trans-isomer absorbs at a longer wavelength due to steric effects. For effective overlap of π-orbitals and low π–π* transition energy, the molecule should be coplanar. Cis-isomer adopts a non-planar conformation due to steric effects

2,3-Dimethyl-1,3-butadiene

λ_{max}^{calc}
217   (base value,1,3-butadiene)
+ 5 x 2 [two alkyl substituents]
227 nm

λ_{max}^{obs} = 226 nm

1,3-Pentadiene

λ_{max}^{calc}
217 (base value,1,3-butadiene)
+ 5 (1 alkyl substituent).
222 nm

λ_{max}^{obs} = 223 nm

trans-stilbene
λ_{max} = 295nm, ε = 27,000

cis-stilbene
λ_{max} = 280nm, ε = 13,500

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

3) Conjugated dienes (cyclic):

- **Rules:**

i.   The base value for heteroannular conjugated dienes (tansoid) is 214 nm

ii. The base value for homoannular conjugated dienes (cisoid) is 253 nm

iii. For each acyclic alkyl substituent 5 nm is added to the base value

iv. If C=C is exocyclic (double bond outside ring), 5 nm is added to the base value

Homoannular diene is bathochromically shifted by 39nm compared to heteroannular diene.

Homoannular diene
(cisoid or s-cis)
Less intense,
ε = 5,000-15,000
λmax = 273nm

Heteroannular diene
(transoid or s-trans)
More intense,
ε = 12,000-28,000
λmax = 234nm

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Examples:**

One alkyl substituent (C-substituent) on the parent chromophore *i.e.*, the diene.

λ_{max}^{calc}

214 (base value)
+ 5 (one alkyl substituent).
219nm

Myrcene

$\lambda_{max}^{obs} = 224$ nm

An exocyclic double bond adds another 5 nm to the calculated λmax.

OR

+5
+5
+5

β–Phellandrene

λ_{max}^{calc}

214   (base value)
+ 5   (1 exocyclic double bond).
+ 5 x 2 (2 carbon substituents)
229 nm

$\lambda_{max}^{obs} = 232$ nm

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Examples:**

α-Terpinene

λ_{max}^{calc}
253 (base value) homoannular diene
+ 5 × 4 (4 alkyl substituents)
273 nm

λ_{max}^{obs} = 265 nm

α-Phellandrene

λ_{max}^{calc}
253 (base value) homoannular diene
+ 5 × 3 (3 alkyl substituents)
268 nm

λ_{max}^{obs} = 263 nm

(I)
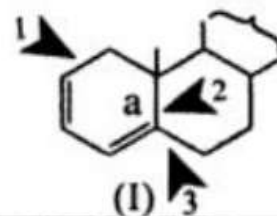
λ_{max}^{calc}
253 (base value) homoannular diene
+15 (3 ring residues,1,2,3, i.e., alkyl substituents).
+ 5 (1 exocyclic double bond, a)
273 nm

λ_{max}^{obs} = 275 nm

(III)
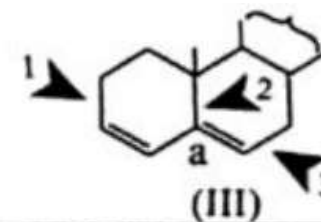
λ_{max}^{calc}
214 (base value) heteroannular diene
+15 (3 ring residues,1,2,3, i.e., alkyl substituents).
+ 5 (1 exocyclic double bond, a)
234 nm

λ_{max}^{obs} = 235 nm
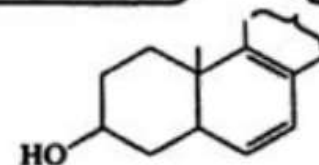
(II)
No exocyclic double bond
(the diene has four alkyl substituents.
λ_{max}^{calc} = 273 nm ; λ_{max}^{obs} = 275 nm;

- **Applications of UV-Vis spectroscopy in analytical chemistry:**

- **Qualitative analysis:**

  ➢ Detection of functional groups

  ➢ Extent of conjugation

  ➢ Identification of unknown compound

  ➢ Detection of impurities

- **Quantitative analysis:** Determination of unknown concentration of a given sample using Beer-Lambert's Law

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Beer-Lambert's Law:**

➤ When the monochromatic radiation passes through a sample containing an absorbing species, the radiant power of a beam is progressively decreased as more energy is absorbed by the particles of that species. The decrease in power is expressed by

      1) Lambert's law

      2) Beer's law (or) Beer - Lambert's law

➤ $I_{absorbed} = I_0 - I_t$

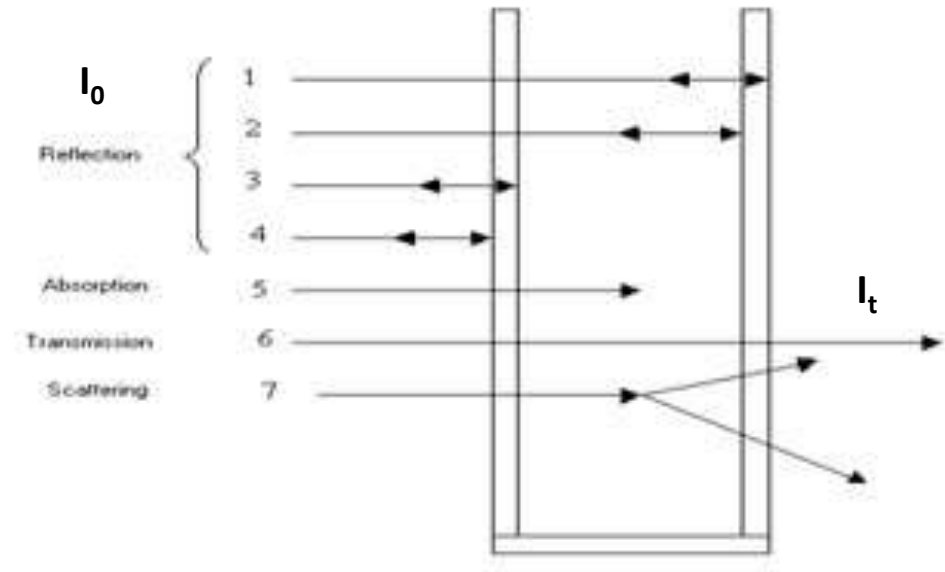   where, I_0 = intensity of incident light

          I_t = intensity of transmitted light

      The transmittance (T) is given by :

      $T = I_t / I_0$

      and $\%T = 100 \, I_t / I_0$

➤ Transmittance is defined as the amount of light that "successfully" passes through the substance and comes out from the other side

Reduction of the intensity of light by reflection, absorption, scattering

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Lambert's Law:**

➢ It states that "when a beam of monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease of intensity of the radiation 'dI' with thickness or path length of absorbing medium '*dl*' is proportional to the intensity of the incident radiation 'I' ".

$$-dI/dl = kI \qquad \text{.......... (1)}$$

On integrating the equation (1), between the limits $I = I_0$ at $l = 0$ and $I = I$ at $l = l$, we get

$$\int_0^I \frac{dI}{I} = -\int_0^l k\, dl \qquad \text{......... (2)}$$

where, k = absorption coefficient

i.e., $\boxed{\ln \frac{I}{I_0} = -k\, l}$ or, $\log \dfrac{I_0}{I_t} = \dfrac{k_1\, l}{2.303}$ ....(3) This is called Lambert's law

where $\log I_0 / I_t$ is called **Absorbance or optical density**

➢ Absorbance is reciprocal of transmittance

$$A = \log_{10} \frac{I_0}{I_t} = \log_{10} \left(\frac{1}{T} \right) = -\log_{10} T = 2 - \log(\% \, T).$$

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi – 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Beer's Law:**

  It states that "when the monochromatic radiation passes through a sample containing an absorbing species, the decrease in the radiant power of a beam is directly proportional to the concentration (C) of the sample".

  $$\log \frac{I_0}{I_t} = \frac{k_1 C}{2.303} \qquad \ldots\ldots\ldots\ldots(4) \qquad \text{This is called Beer's law}$$

- **Beer- Lambert's Law:** When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation 'dI' with thickness or path length of the absorbing solution 'dl' is proportional to the intensity of the incident radiation 'I' as well as the concentration of the solution 'C'.

  On combining equations (3) and (4)

  $$A = \log \frac{I_0}{I_t} = \frac{k\, C\, l}{2.303}$$

  or, $\boxed{A = \varepsilon\, C\, l}$ ....(5)   This is called Beer-Lambert's law

  where $\varepsilon = k/ 2.303$ is known as molar absorptivity coefficient

➢ The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in mol L^{-1} and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L mol^{-1} cm^{-1}

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Applications of Beer- Lambert's Law:** It can be used to determine the unknown concentration of a solution.

➢ A standard solution of known concentration C_s is first taken and it's absorbance A_s is measured. Then according to Beer-Lambert's law:

$$\frac{A_s}{C_s} = \varepsilon \ x \qquad\qquad \text{.........(1)}$$

Let C_u be the unknown concentration of the solution which is to be determined. The absorbance A_u of the given solution is measured.

$$\frac{A_u}{C_u} = \varepsilon \ x \qquad\qquad \text{..........(2)}$$

From equation (1) and (2), we get

$$\frac{A_s}{C_s} = \frac{A_u}{C_u}$$

$$=> \quad C_u = \frac{A_u}{A_s} \times C_s \qquad\qquad \text{...........(3)}$$

We already know the concentration of standard solution C_s and the absorbance A_u and A_s were experimentally measured and hence the unknown concentration Cu can be calculated from the equation (3).

- **Limitations of Beer- Lambert's Law:**

- This law can be used only for

  i.   dilute solution.

  ii. monochromatic radiation.

  iii. the system maintained at constant temperature.

- **Specific Absorbance:** When absorbance is measured for 1% (w/v) solution in a 1 cm cell, then the equation takes the form:

$$A = A^{1\%}_{1cm} \cdot C \cdot l$$

where, $A^{1\%}_{1cm}$ is known as specific absorbance

- **Colorimetric analysis:** It is also based on Beer-Lambert's law. Here, the visible light is used to analyze colored samples

University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092

USAR
UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

- **Solved Examples:**

Question 1: The solution of concentration of 2.5×10^{-4} M has the percentage transmittance of 25% in a 1 cm cell.

Determine   i) the absorbance (A) and ii) the molar absorption coefficient (ε).

Solution : Given : % T = 25% (or) 0.25, C = 2.5×10^{-4} M ; l = 1 cm

i)   Absorbance :   A = – log T = – log 0.25   = 0.6021

ii) The molar absorption coefficient, ε = A / C l

$$= 0.6021 / 2.5 \times 10{-4}$$

$$= 2408$$

Question 2: A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution given that ε= 6000 dm^3 mol^{-1} cm^{-1}.

Solution : Given : % T = 40% (or) 0.40, ε= 6000 dm^3 mol^{-1} cm^{-1}; l = 2 cm

i)   Absorbance :   A = – log T = – log 0.40   = 0.3980

ii) The molar absorption coefficient, C = A / ε l

$$= 0.3980 / 6000 \times 2$$

$$= 3.316 \times 10^{-5} \text{ mol } dm^{-3}$$