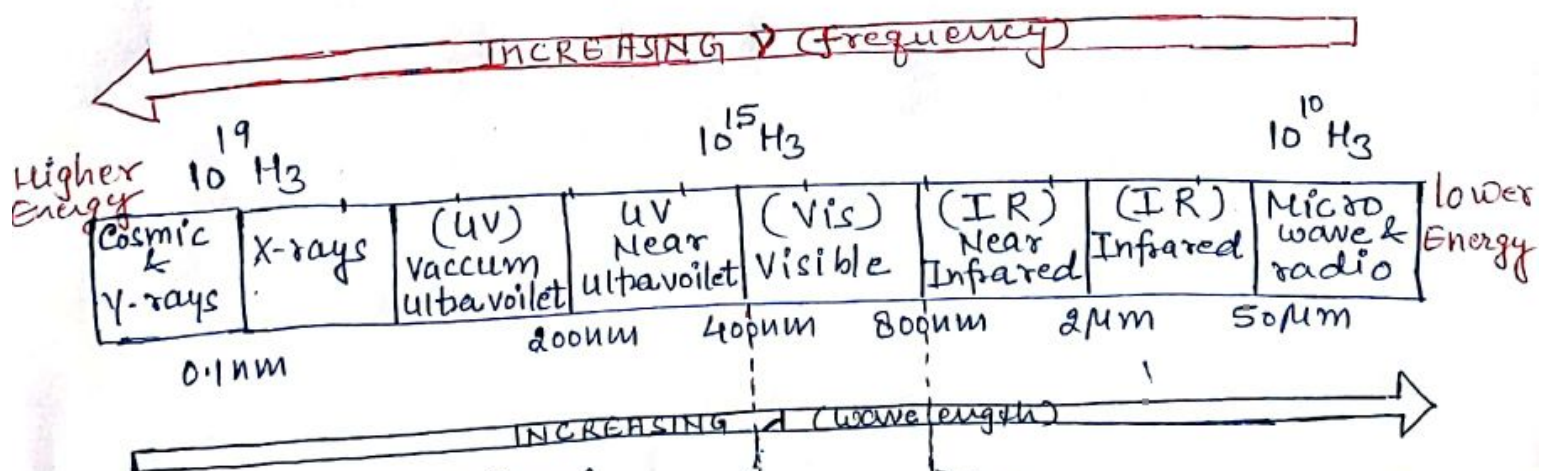


Basic Principle of Spectroscopy ⁽¹⁾

"Spectroscopy is a tool which is used to determine the structure of an unknown compound".

All organic compounds interact with electromagnetic radiation ~~that~~ i.e. they absorb energy.

Electromagnetic radiation (EM) - EM is a form of energy that is all around us and takes many forms, such as radio waves, microwaves, X-rays and gamma rays. Sunlight is also a form of EM energy, but visible light is only a small portion of the EM spectrum, which contains a broad range of electromagnetic wavelengths]



Fundamental equation of EM radiation are -

$$E = h\nu$$

E = energy of radiation

$$E = \frac{hc}{\lambda} \quad \text{or} \quad (nu) \quad \nu = \text{frequency of radiation}$$

h = Planck's Constant

V I B G Y O R

Electromagnetic spectrum

(ii)

When a molecule absorbs energy, a transformation occurs that may be either temporary or permanent.

- Lower energy [$E = h\nu$ or $\frac{hc}{\lambda}$] i.e. lower frequency or higher wavelength radiation may cause a molecular rotation or a bond vibration (Eg. in IR spectroscopy)
- ~~Low~~ Higher-energy radiation may cause the promotion of electrons to higher energy level or bond cleavage (Eg. uv. visible spectroscopy)
- When the molecule absorbs energy of a particular frequency or wavelength necessary for the transition, then transformation occurs.
- In a molecule, transformation involves molecular rotation, bond vibration or electronic transition.
- By measuring the absorption spectra of known compounds, we can correlate the wavelengths of energy absorbed with characteristic structural features.
(for Eg all proteins are absorbed in wavelength 660 nm with folin Ciocatten reagent)

(11)

This information is then used to determine the structure of unknown compounds.

Spectrophotometer -

The instrument which is used to measure the amount of electromagnetic radiation absorbed by an organic molecule is called Spectrophotometer or Spectrometer.

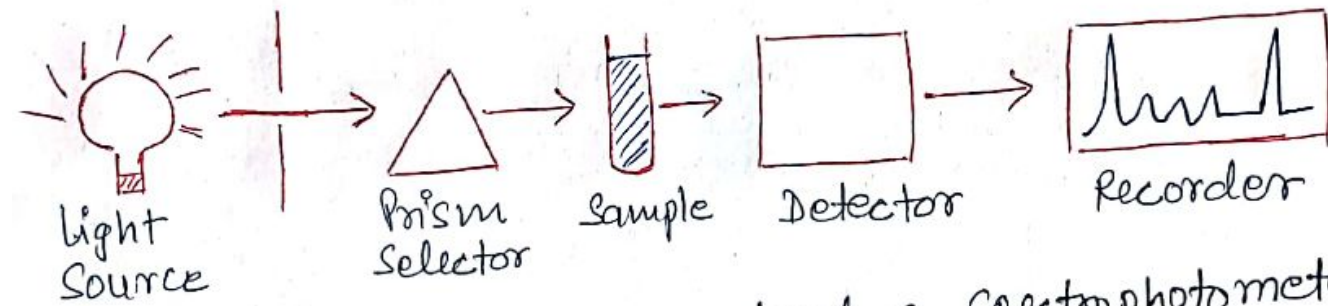


Fig- Basic Component of a Spectrophotometer

- The spectrophotometer consists of a light source of radiation, with a prism that can select the desired wavelengths, which are passed through a sample of the compound being investigated.
- The radiation of a particular frequency that is absorbed by the sample can be detected, analyzed and recorded.
- The recording is called the spectrum of the compound.

Ultra violet & visible spectroscopy.

(UV-visible spectroscopy) ①
(200 - 750 nm)

- UV-visible spectroscopy ~~involve~~ of an organic compound involves the transition of e^- from ground state to higher energy levels by absorption of radiation of a particular wavelength.
- In this process, loosely bound electrons such as non bonding electrons ($\ddot{N}-$) or electrons involved in a π -bond promotes from lower energy levels to higher energy levels.
- for absorption in this particular region of UV-~~visible~~ spectrum, the molecule must contain conjugated double bonds (like $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH}=\overset{5}{CH}-\overset{6}{CH_3}$)
2,4 Hexadiene
- If the conjugation is extensive, the molecule will absorb in the visible region.

→ The uv-visible spectrum is composed of only a few broad bands of absorption like -

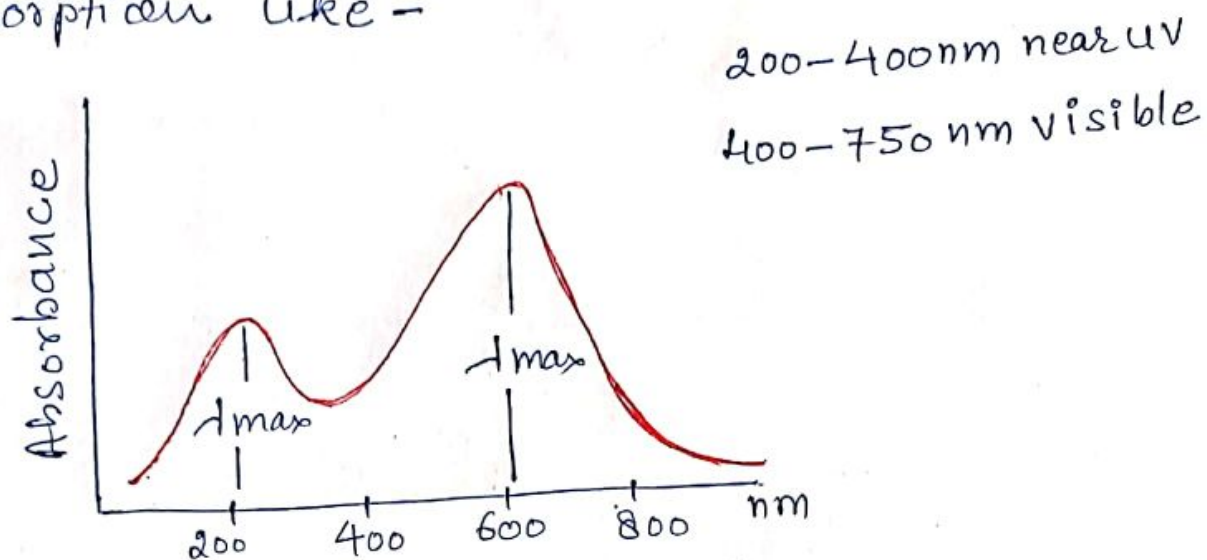


Fig- A Sample of uv-vis spectrum

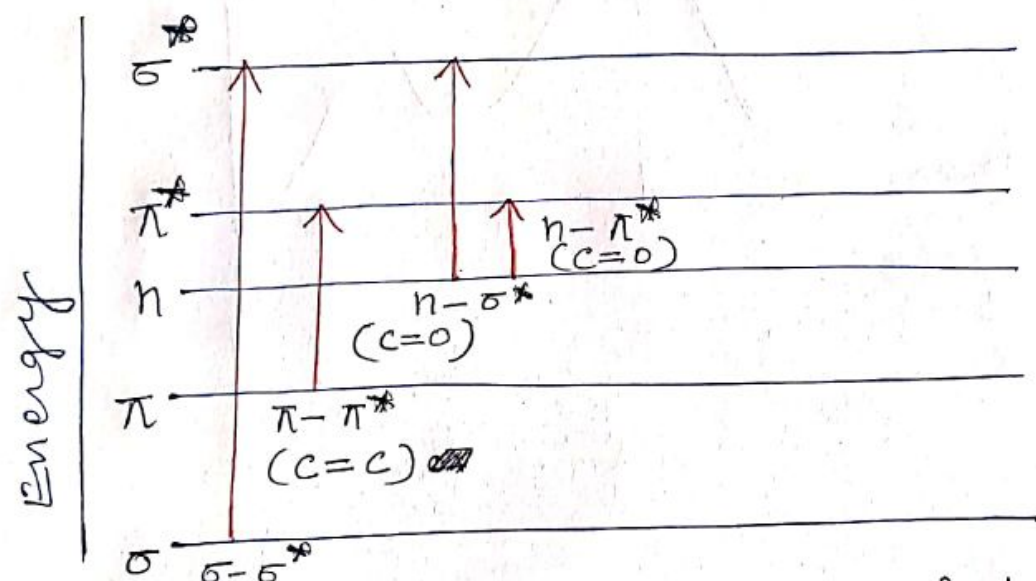
→ The wavelength of maximum absorbance is referred to as λ_{max} .

If an organic compound does not absorb uv-vis radiation, it means that the compound does not contain conjugated double bonds.

If an organic compound absorbs uv-vis radiation, it means that the compound contains a carbonyl group ($>C=O:$) or conjugated double bonds ($-C=C-C=C-$). For example, conjugated dienes, carbonyl compounds and aromatic

Compounds all absorb in the UV-Vis (3) region.

The relation between energy ($E = \frac{hc}{\lambda}$) and various types of electronic transitions in organic molecules are as follows-



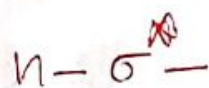
(C-C) fig- Types of electronic transition

The relative energy required for the various transitions obey the order-

$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

$\sigma - \sigma^*$ - In alkane the only transition available is the promotion of an e^- from low lying σ orbital to high energy σ^* antibonding orbital.

$\pi - \pi^*$ - In alkene, several transitions are available, but the lowest energy transition ($\pi - \pi^*$) is the most important one.



In ketones, the most important ^④ transition is $\pi - \pi^*$.

Applications of uv- visible spectroscopy

① uv- visible spectroscopy is very useful to measure the number of conjugated double bonds and aromatic conjugation between various molecules -

Eg -

molecule	λ_{max} (wavelength)	ϵ_{max} (Absorption)
① $CH_2=CH_2$ Ethylene	170	21,000
② $H_2C=C(CH_3)-C(CH_3)=CH_2$ 2,3 dimethyl 1,3 buta- diene	226	21,400
③ $H_2C=CH-CH=CH-CH=CH_2$ 1,3,5 Hexatriene	254	21,400

② It is very useful to distinguish between cis and trans isomers.
cis isomer absorbs at shorter wavelength.

③ saturated carbonyl compounds ($>C=O$)^⑤
gives two transitions i.e.

$\pi - \pi^*$ at $\lambda_{max} \cdot \epsilon_{max}$
170nm 10,000

$n - \pi^*$ at 290nm $\epsilon \sim 20$

④ Impurities can be detected on
the basis of UV spectroscopy.
