UV- VISIBLE SPECTROSCOPY

Principle

- Ultraviolet (UV) visible – spectra arises from the transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state E_o) to higher electronic energy level (excited state E_1).
- This transition occurs due to the absorption of UV (wavelength 100- 400 nm) or visible (wavelength 400-750 nm) region of the electronic spectrum by a molecule (or) ion.

Origin of UV – visible spectroscopy

- The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons.

$$\Delta E = E_1 - E_0 = hv$$

1. Chromophores

- The presence of one or more unsaturated linkages (π-electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores .
- Examples: C=C; -CC-; -C-N; -N-N; C-O; etc.,

3. Auxochromes

- It refers to an atom or a group of atoms which does not rise to absorption band on its own, but when conjugate to chromophore will cause a red shift.
  - Examples:-OH, $-NH_2$, -Cl, -Br, -I, etc.,

Some important definitions related to change in wavelength and intensity

1.	Bathochromic shift. (red shift)	Shift to higher wave length (lower frequencies).
2.	Hypsochromic shift. (blue shift)	Shift to lower wave length (higher frequencies).
3.	Hyperchromic effect.	An increase in intensity.
4.	Hypochromic effect.	An decrease in intensity.

Illustration

In chloroethylene, CH_2 – CHCl,

C=C is a chromophore and Cl is an auxochrome.

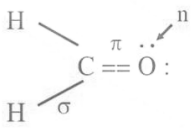
Types of electrons involved in organic molecule

- The energy absorbed by a organic molecule involves transition of valence electrons. The following three types of electrons are involved in the transition.

S. No	Electrons	Examples	Energy required to excite electrons	Present in
1.	σ -electrons	Saturated long chain hydrocarbons. (paraffins) (CH_3-CH_2-CH_2-CH_3)	Higher than UV light	Single bond
2.	π-electrons	Unsaturated hydrocarbons like trienes and aromatic compounds.	UV (or) visible light	Double bond and triple bonds. (unsaturated bond)
3.	n- electrons	Organic compounds containing N, O (or) halogens.	UV radiation	Unshared (or) non bonded electrons.

- Thus, the unsaturated hydrocarbons and compounds containing N, O, S may absorb visible (or) UV radiations.

Examples: The three types of electrons are shown in the molecule (HCHO).



Instrumentation

Components

1. Radiation source

- In visible – UV spectrometer, the most commonly used radiation sources are hydrogen or deuterium lamps.
- Requirements of a radiation source
  - (a) It must be stable and supply continuous radiation.
  - (b) It must be of sufficient intensity.

2. Monochromators

- The monochromator is used to disperse the radiation according to the wavelength.
- The essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit.
- The dispersing element may be a prism or grating (or) a filter.

3.Cells (sample cell and reference cell)

4. Detectors

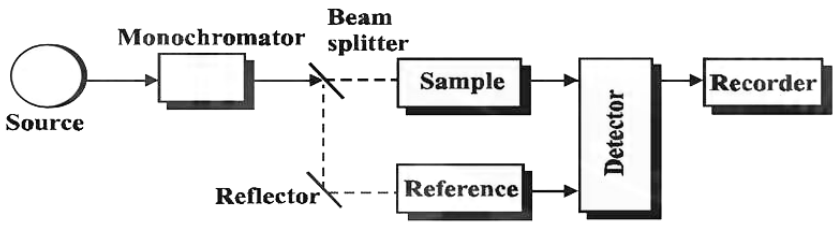
- barrier layer cell, photomultiplier tube and photocell.
- The detector converts the radiation, falling on which, into current. The current is directly proportional to the concentration of the solution.

5. Recording system

- The signal from the detectors is finally received by the recording system. The recording is done by the recording pen.

II Working of UV and visible spectrophotometer

- The radiation from the source is allowed to pass through the monochromator unit.
- The monochromator allows a narrow range of wavelength to pass through an exit slit.
- The beam of radiation coming out of the monochromator is split into two equal beams.
- One-half of the beams (the sample beam) is directed to pass through a transparent cell containing a solution of the compound to be analyzed.
- Another half (the reference beam) is directed to pass through an identical cell that contains only the solvent.
- The instrument is designed in such a way that it can compare the intensities of the two beams.
- If the compound absorbs light at a particular wavelength, then intensity of the sample beam (I) will be less than that of the reference beam (I_O).
- The instrument gives output graph, which is a plot of wavelength Vs absorbance of the light. This graph is known as an absorption spectrum.



Applications

1. Predicting relationship between different groups
2. Qualitative analysis
3. Detection of impurities
4. Quantitative analysis
5. Determination of molecular weight
6. Dissociation constants of acids and bases

7. Study of tautomeric equilibrium
8. Studying kinetics of chemical reactions
9. Determination of calcium in blood serum