Quadrant II – Notes

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Module Name: UV-Visible Spectroscopy Part - 1

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Introduction:

- **Spectroscopy**: Study of interaction of matter with electromagnetic radiations.
- The Electromagnetic Radiations originates in the deceleration of electrically charged particles; e-'s.
- It can be absorbed by the reverse process, contributing its energy to accelerate the particles. When the radiations are incident on the atom or molecule, a part of it is absorbed and rest is transmitted.
- The absorption can be used to determine the chemical structure of the absorbing species and the amount of radiation absorbed depends upon the concentration of absorbing substance in the solution.
- Hence spectroscopy can be regarded as an important tool for chemical analysis of molecule.
- UV, Visible and IR are widely used in Spectroscopic studies as these radiations are absorbed by various molecules.
- Radiations travel in form of Waves and a Wave is associated with **3 important wave properties** which are
- **1. Wavelength (λ)**: Length of a single wave. It is measured as the distance between 2 successive crests or 2 successive troughs of a wave.

Units: nm, **Å**, µm.

- 2. **Frequency (v)**: No. of waves which cross a given point in one second.

  {Unit – Hz} $v = \frac{c}{\lambda}$

- 3. **Wave number (ṽ)**: No. of waves in one meter distance {Unit – cm^{-1}}

  $\tilde{v} = \frac{1}{\lambda}$

Interaction of Radiation with Matter

Discussion about Interaction of Radiation with matter will be done using the concepts of Atomic Absorption and Atomic Emission.

Atomic Absorption:

- Certain region of Wavelength from the EMR is being absorbed by the molecule or atom.
- It causes excitation.
- Requires continuous supply of radiations.

Atomic Emission:

- Certain region of Wavelength from the EMR is being emitted by the molecule or atom.
- It causes relaxation.
- Does not require continuous supply of radiations.

Quantitative Calculations:

- When a beam of light passes through an absorbing medium that is a solution, a part of the light is absorbed and rest is being transmitted.

- This **amount of light** which is **absorbed depends upon the concentration of the solution** and the **length** travelled by the light through the solution.
- The quantitative relation between the amount of light absorbed, concentration of the solution and the length of the absorbing medium is governed by 2 empirical laws i.e., **Beer's Law and Lambert's law.**

Beer's Law:

- It states that "When a beam of light is allowed to pass through an absorbing medium, the **rate of decrease in intensity of light** is **directly proportional** to the **Concentration of the absorbing medium**".
- 'dI' is the small amount of light absorbed by a layer having concentration 'dc'.

I_o – Initial intensity I_t – Final or Transmitted intensity

$$2.303\ log_{10}\frac{Io}{It} = K_1.c$$ where c – Concentration.

Lambert's Law:

- It states that "When a beam of light is allowed to pass through an absorbing medium, the **rate of decrease in intensity of light** is **directly proportional** to the **Thickness of the absorbing medium**".
- If thickness 'dx' absorbs small layer of 'dI' of incident light, then the fraction dI/I is proportional to the thickness of layer dx.
- If I_o is the initial intensity, l is length of the absorbing medium and I_t is the intensity of the transmitted beam.

$$2.303\ log_{10}\frac{Io}{It} = K_2.l$$ where l – Pathlength.

Beer-Lambert's Law:

- It states that "When a beam of light is allowed to pass through an absorbing medium, the **rate of decrease in intensity of light** is **directly proportional** to the **Concentration and Thickness of the absorbing medium**".

$$\mathbf{2.303\ log_{10}\frac{Io}{It} = a.\ c.\ l}$$

a – Absorptivity of the absorbing medium, c – Concentration, l – pathlength.

$\log_{10}\frac{Io}{It} = \frac{a}{2.303}$. c. l

$\boldsymbol{log_{10}\frac{Io}{It}}$ **= A** where A – Absorbance/Optical Density

A = $\log_{10}\frac{Io}{It}$ = ε . c . l where ε – Molar absorptivity

$\boldsymbol{\frac{It}{Io}}$ **x 100 = % T** where I_t/I_o – Transmittance (T)

$$\mathbf{A = -\ Log\ T = \varepsilon\ .\ c\ .\ l}$$

Limitations of Beer-Lambert's Law:

- The linear relationship between **absorbance** and **concentration** of the solution is not observed above **10^{-2} M**. Hence **concentrated solutions do not obey Beer-Lambert's Law**.
- The law is not obeyed if reacting or absorbing species react with the solvent. **Any change in the molecular condition disobeys the law**.
- The light incident on the absorbing medium should be **monochromatic** otherwise minor deviations are observed.
- The **molar absorptivity (ε)** depends on the **refractive index** of the abs. medium which depends upon the **concentration** of absorbing medium.
- At high concentration, these changes are considerable but up to 10^{-2} M these are neglected.

- **Temperature fluctuations and entry of stray light** into the absorbing medium or system leads to deviations.

Principles of instrumentation:

1. **Sources***:* **IR** – **Globar and Nernst Glowers** are common sources.

  - The **Globar** is an electrically heated rod of **Silicon Carbide**. (1300-1700 ^{o}c)
  - **Nernst Glower** is a rod containing a mixture of **Zirconium, Yttrium and Erbium oxides** (1500-2000 ^{o}c)
  - **UV** – **Hydrogen or Deuterium Discharge lamp**.
  - **Visible light** – **Tungsten lamp** is used.

2. **Filters**: Colour filters are mainly of 2 types, **Glass/Absorption filters and Interference filters**. Filters are the simplest and least expensive component.

  - Filters of the various devices produce limited bands of radiations.
  - **Glass/Absorption filters**: It is a solid sheet of glass which is coloured by a suitable pigment. It limits the radiations by absorbing a narrow band of wavelengths. The coloured beam coming from the filter should give maximum absorbance with the sample.
  - **Interference Filters**: It contains **2 thin films of silver** separated by a film of transparent material. The material is of low refractive index.

3. **Monochromators**: It gives a monochromatic radiation i.e., radiation of one particular wavelength. It is a dispersing device which splits a beam of light into its constituent wavelengths. 2 main types – **Prisms and Diffraction Gratings.**

  - **Prisms**: When a beam of monochromatic light passes through a prism; it is bent or refracted and the amount of deviation depends upon the wavelength.

    - **Visible region – Glass prism**
    - **UV region – Quartz prism**
    - **IR region – Rock Salt**
  - **Diffraction Gratings**: It is made by cutting a large no. of perfectly parallel straight lines (grooves) into an aluminium surface; when the light is reflected at the grating surface and Dispersion takes place.

Advantages:

- It gives better dispersion than that of prism.
- Not easily attacked by moisture.
- Can be used over a longer wavelength range as compared to the prism.

4. **Cells**:

  - The **glass** cuvettes are used in the **visible** region and **quartz** cuvettes are used in the **UV** region.
  - Since both the above types of cuvettes **absorb** strongly in the **IR** region, they cannot be used for the IR absorption studies.
  - **Metal halide** cells are used for the **IR** region studies.