

UV-Visible spectroscopy

Introduction to UV-Visible Spectroscopy

- UV-Visible spectroscopy is an analytical technique used to study how substances absorb light in the ultraviolet (UV) and visible regions of the electromagnetic spectrum.



- **UV region:** 200–400 nm
- **Visible region:** 400–800 nm
- When light passes through a substance, some wavelengths are absorbed while others are transmitted.
- The absorbed light provides information about the structure and concentration of the substance.

Basic idea:

- Molecules contain electrons.
- When light of suitable energy strikes the molecule, electrons get excited from a lower energy level (ground state) to a higher energy level (excited state).
- The amount of light absorbed is measured and used for analysis.

Key points:

- Works mainly for compounds with π electrons or non-bonding electrons (n electrons).
- Organic compounds with double bonds, aromatic rings, or conjugation absorb UV-visible light.
- The technique is widely used for qualitative (structure) and quantitative (concentration) analysis.

Example:

- Benzene absorbs UV light due to its conjugated π -electron system.
- Colored compounds absorb in the visible region, which is why they appear colored.

Theory of UV-Visible Spectroscopy

- UV-Visible spectroscopy is based on electronic transitions in molecules.

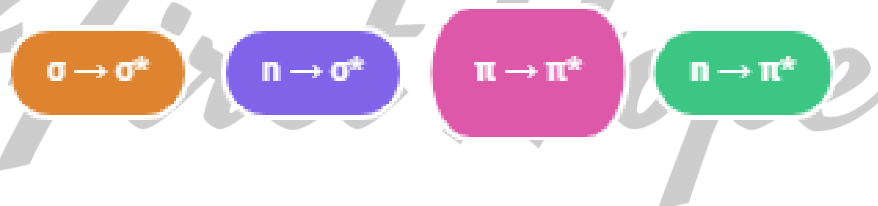
What Happens When Light Interacts with a Molecule?

- Molecules contain electrons in different energy levels
- **When UV/visible light hits the molecule:**
 - If the energy matches, electrons absorb energy
 - Electrons move from lower energy (ground state) to higher energy (excited state)

Electronic Energy Levels

- **Electrons in molecules exist in different types of orbitals:**
 - Sigma (σ) orbitals
 - Pi (π) orbitals
 - Non-bonding (n) orbitals
 - Upon absorption of UV/visible light, electrons move from lower to higher energy orbitals

Types of electronic transitions



1. $\sigma \rightarrow \sigma^*$

- Involves single bonds
- Requires high energy (deep UV region)
- Not very useful in routine analysis

2. $n \rightarrow \sigma^*$

- Involves lone pair electrons (e.g., oxygen, nitrogen)
- Occurs in UV region

3. $\pi \rightarrow \pi^*$

- Involves double bonds
- Common in organic compounds
- Strong absorption

4. $n \rightarrow \pi^*$

- Lone pair to antibonding π orbital
- Lower energy than $\pi \rightarrow \pi^*$

Important terms

- **λ_{max} (lambda max):** Wavelength at which maximum absorption occurs
- **Absorbance (A):** Amount of light absorbed
- **Transmittance (T):** Amount of light passing through
- **Bathochromic shift (red shift):** Shift to longer wavelength
- **Hypsochromic shift (blue shift):** Shift to shorter wavelength
- **Hyperchromic effect:** Increase in absorption intensity
- **Hypochromic effect:** Decrease in absorption intensity

Chromophores & Auxochromes

Chromophores

- Chromophores are the parts of a molecule that absorb UV or visible light and are responsible for the color of the compound.
 - They contain π (pi) electrons or non-bonding (n) electrons
 - These electrons get excited when they absorb light

Examples:

- C=C (double bond)
- C=O (carbonyl group)
- N=N (azo group)
- NO₂ (nitro group)

Key point:

- Chromophores determine **where (at which wavelength)** absorption occurs.

Auxochromes

- Auxochromes are groups that do not absorb strongly on their own, but when attached to a chromophore, they modify its absorption.
 - They usually contain lone pair electrons
 - They increase intensity and shift absorption

Examples:

- -OH (hydroxyl)
- -NH₂ (amino)
- -OR (alkoxy)

Effects:

- Increase absorption intensity (hyperchromic effect)
- Shift absorption to longer wavelength (bathochromic shift)

Key point:

- Auxochromes **enhance and shift the absorption** of chromophores.

Beer–Lambert Law

- The Beer–Lambert Law relates the absorbance of light to the concentration of a substance and the path length through which light passes.

Basis of the Law

The Beer–Lambert Law is a combination of two laws:

1. Lambert's Law

- Absorbance is directly proportional to the path length (b or l) of the sample

2. Beer's Law

- Absorbance is directly proportional to the concentration (c) of the solution

Mathematical Expression

$$A = \epsilon \times b \times c$$

- **Where:**

- A = Absorbance
- ϵ (epsilon) = Molar absorptivity (constant for a substance)
- b (or l) = Path length (cm)
- c = Concentration

Absorbance and Transmittance

- **Transmittance (T)**

$$T = \frac{I}{I_0}$$

- **Absorbance (A)**

$$A = \log \left(\frac{I_0}{I} \right)$$

- **Where:**

- I_0 = Incident light intensity
- I = Transmitted light intensity

Key Points

- Absorbance is directly proportional to both concentration and path length
- Widely used for quantitative analysis of solutions
- The law is valid only under ideal conditions

Deviations / Limitations of Beer–Lambert Law

1. Chemical Deviations

- Association or dissociation of molecules
- Chemical interactions affecting concentration

2. Instrumental Deviations

- Use of non-monochromatic light
- Instrumental errors

3. Concentration Effects

- At high concentrations, interactions between molecules cause deviation

Derivation of Beer–Lambert Law

Step 1: Consider a beam of monochromatic light

- **Let:**
 - I_0 = intensity of incident light
 - I = intensity after passing through solution
 - l = total path length of solution
- We divide the solution into very thin layers of thickness dx .

Step 2: Change in intensity in a thin layer

- When light passes through a very thin layer dx , a small amount of light is absorbed.
- **The decrease in intensity dI depends on:**
 - The intensity of light I
 - The thickness dx
 - The concentration c
- **So, we write:**

$$dI \propto I dx c$$

Step 3: Remove proportionality



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