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**Spectroscopy** is the study of the interaction of electromagnetic radiation with the matter. During the interaction the energy is absorbed or emitted by the matter. It is used to study the atomic and molecular structure of the substance.

**Types of spectroscopy:**

Two types

1. **Atomic spectroscopy** deals with the interaction of the electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

2. **Molecular spectroscopy** deals with the interaction of the electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

**Difference between atomic spectroscopy and molecular spectroscopy**

<table>
<thead>
<tr>
<th>Atomic spectroscopy</th>
<th>Molecular spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. It is the study of interaction of electromagnetic radiation with atoms.</td>
<td>1. It is the study of interaction of electromagnetic radiation with molecules.</td>
</tr>
</tbody>
</table>
Absorption spectrum:

- When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule absorbs photon of energy $h\nu$ and undergoes a transition from the lower energy level to the higher energy level.
- The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy.
- The spectrum thus obtained is called the absorption spectrum.

Emission spectrum:

If the molecule comes down from the excited state to the ground state with the emission of photon of energy, $h\nu$, the spectrum is called emission spectrum.

Properties of Electromagnetic Radiation

Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. It requires no supporting media. An electromagnetic radiation is said to have a dual nature.

Wave properties of electromagnetic radiation:

- An electromagnetic radiation is an alternating electrical and associated magnetic force in space.
- Thus an electromagnetic wave has an electric component and magnetic component.
- The two components oscillate in plane perpendicular to each other.

a) Wavelength ($\lambda$)

- Wavelength ($\lambda$) is the distance between two successive maxima on an electromagnetic wave.
- It is denoted by the Greek latter lambda, $\lambda$. 

| 2. The atoms absorb radiation and gets excited from the ground state electronic energy level to higher level. | This results in transition between rotational, vibrational and electronic energy levels. |
| 3. It is also called as line spectra or emission spectra. | It is also known as band spectra or absorption spectra. |
Units are: m, cm, mm, μm, nm and Å.

A beam carrying radiation of only one discrete wavelength is said to be monochromatic and a beam having radiation of several wavelengths is said to be polychromatic or heterochromatic.

b) Frequency (v)

Frequency (v) is the number of complete wavelength units passing through a given point in unit time.

It is denoted by the Greek letter ν.

Units: cycles/second or Hertz (Hz).

c) Wave number (v)

- Wave number (v) is defined as the number of waves per centimeter in vacuum.
- This is denoted by v.
- $v = \frac{1}{\lambda}$ units: cm$^{-1}$

d) Velocity (v):

- The product of wavelength and frequency is equal to the velocity of the wave in the medium.
- Velocity $= \lambda v$
- The frequency (ν), wavelength (λ) and wave number (λ) of an electromagnetic radiation (EMR) are related by the equation $v = \frac{c}{\lambda} = c\lambda^{-1}$.

Electromagnetic spectrum:

The entire range over which electromagnetic radiation exists is known as electromagnetic spectrum.

Types of energy present in molecules:

1. Translational energy ($E_{\text{trans}}$) is concerned with the overall movement of the molecule along the three axes.

2. Rotational energy ($E_{\text{rot}}$) involves the spinning of molecules about the axes passing through their centre of gravity.
3. Vibrational energy (E_{vib}) is associated with vibrations within a molecule such as the stretching or the bending of bonds.

4. Electronic energy (E_{elec}) involves changes in the distribution of electrons by the excitation of electrons to higher levels by absorption of energy.

5. Now, if E is the energy of a molecule, it can expressed as  
\[ E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \]

**Energies Associated with Electromagnetic Radiation:**

The different regions of the electromagnetic spectrum of interest are given in the Table.

**Table: The energies of the electromagnetic spectrum**

<table>
<thead>
<tr>
<th>Region</th>
<th>Region Wavelength (nm)</th>
<th>Wavenumber ((\text{cm}^{-1}))</th>
<th>Frequency ((\text{Hz} \times 10^{-12}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-rays</td>
<td>Below 0.1</td>
<td>Above (10^6)</td>
<td>Above (3 \times 10^6)</td>
</tr>
<tr>
<td>X-rays 3</td>
<td>0.1 – 10</td>
<td>(10^9 – 10^6)</td>
<td>(3 \times 10^6 – 3 \times 10^4)</td>
</tr>
<tr>
<td>Far UV</td>
<td>10 – 200</td>
<td>(1 \times 10^9 – 5 \times 10^9)</td>
<td>(30,000 – 1,500)</td>
</tr>
<tr>
<td>UV</td>
<td>200 – 360</td>
<td>(5 \times 10^9 – 2.5 \times 10^4)</td>
<td>(1,500 – 800)</td>
</tr>
<tr>
<td>Visible</td>
<td>360 – 800</td>
<td>(2.5 \times 10^9 – 12.5 \times 10^7)</td>
<td>(800 – 400)</td>
</tr>
<tr>
<td>Near IR</td>
<td>800 – 2500</td>
<td>(12.5 \times 10^9 – 3 \times 10^7)</td>
<td>(400 – 100)</td>
</tr>
<tr>
<td>IR</td>
<td>(3 \times 10^8 – 3 \times 10^4)</td>
<td>(3300 – 300)</td>
<td>(100 – 10)</td>
</tr>
<tr>
<td>Far IR</td>
<td>(3 \times 10^4 – 3 \times 10^3)</td>
<td>(330 – 10)</td>
<td>(10 – 1)</td>
</tr>
<tr>
<td>Microwave</td>
<td>(3 \times 10^7 – 1 \times 10^9)</td>
<td>(10 – 0.01)</td>
<td>(1 – 0.0003)</td>
</tr>
<tr>
<td>Radio Frequency</td>
<td>(1 \times 10^9 – 1 \times 10^{14})</td>
<td>(1 \times 10^{-2} – 1 \times 10^{-6})</td>
<td>(3 \times 10^{-2} – 1 \times 10^{-8})</td>
</tr>
</tbody>
</table>

- **γ-ray:** the rearrangement of nuclear particles.
- **X-ray:** involve inner electrons.
- **UV-Visible:** the transfer of valence electrons from one molecular orbital to another.
- **IR:** involve vibrations of the molecule.
- **Microwave:** the rotational spectra of diatomic and polyatomic molecules.
**Radiofrequency:** the transition of nuclear spin magnetic moments in an applied magnetic field.

**ULTRA VIOLET and VISIBLE SPECTROSCOPY**

- The absorption of UV-Visible radiation by a molecule leads to transition among the electronic energy levels of the molecule and therefore it is called as **electronic spectroscopy**.
- All organic compounds absorb UV light.
- The region between 200 – 400 nm is near UV region 400 – 800 nm is visible region.
- Below 200 nm is far (or) vacuum UV region.
- Absorption bands appear rather than absorption lines because vibrational and rotational effects are superimposed on the electronic transitions, so that an envelope of transitions arises.

**TYPES OF TRANSITIONS INVOLVED IN ORGANIC MOLECULES:**

- **n→π* transition** – shown by unsaturated molecule having hetero atoms like N, O, &S.
  - It occurs at longer wavelength with low intensity.
  - **Eg. Aldehyde & ketone.**
- **σ→σ* transition** - occur in the compound in which all the electrons are involved in single bond and there are no lone pair of electrons.
- **Eg. Saturated hydrocarbons.**
- **n→σ* transition** – occur in the saturated compounds having lone pair of electrons.
- **Eg. Trimethylamine.**
- **π→π* transition** – occur in molecule having a π electron system.
  - **Eg. Ethylene.**
  - Allowed transitions are σ→σ*, n→σ* and π→π*.
- These transitions give rise to strong absorption bands but the energy involved is higher than for n→π* transition.
Forbidden transition is $n\rightarrow\pi^*$. It give rise to band with low intensity.

Order of decreasing energy for the absorption is $\sigma\rightarrow\sigma^* > n\rightarrow\pi^*>\pi\rightarrow\pi^*> n\rightarrow\pi^*$.

**Characterization of UV - Visible spectra**

1. $\lambda_{\text{max}}$:
   $\lambda_{\text{max}}$ value is the wavelength at which absorption maximum occurs.

2. $\varepsilon$ value:
   The extent of absorption for a given concentration ($c$) of a compound at any given wavelength is defined by molar absorptivity (or molar absorption coefficient). Which is related to the height of the absorption band.

   These two parameters depend on the concentration and the structure of the molecules and hence are regarded as characteristic properties of a molecule.

**COLOUR and LIGHT ABSORPTION – THE CHROMOPHORE CONCEPT:**

**CHROMOPHORE** may be defined as any group which exhibits absorption of electromagnetic radiation in visible or UV region.

**Eg. Ethylenic, acetylenic, carboxylic acids, esters, etc.**

Two types of chromophores are known:

1. chromophores in which the group is having $\pi$ electrons undergo $\pi\rightarrow\pi^*$ transitions.
   **Eg. Ethylene, acetylene, etc.**

2. chromophores having both $p$ electrons and $n$ (non bonding) electrons undergo two types of transitions ie. $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$.
   **Eg. Carbonyls, nitriles, azo compounds, nitro compounds, etc.**

**AUXOCHROME:**

- Auxochrome is a group which itself does not act as a chromophore but when attached.

- to a chromophore it shifts the absorption maximum towards longer wavelength along with an increase in the intensity of absorption.
  **Eg. -OH, -NH$_2$, -OR, etc.**

- **For example**, when the auxochrome –NH$_2$ is attached to benzene ring, it absorption changes from $\lambda_{\text{max}}$ 255 nm ($\varepsilon_{\text{max}}$ 203) to $\lambda_{\text{max}}$ 280 nm ($\varepsilon_{\text{max}}$ 1430).
CHANGE IN POSITION & INTENSITY OF ABSORPTION:

1. **Bathochromic shift (or) red shift** involves the shift of absorption towards longer wavelength because of the presence of certain groups such as OH and NH₂ called **auxochromes or by change of solvent**.

2. **Hypsochromic shift (or) blue shift** involves the shift of absorption maximum towards shorter wavelength and may be caused by removal of conjugation or by change of solvent.

3. **Hyperchromic shift** involves an increase in the intensity of absorption and is usually brought out by introduction of an auxochrome.
   For example, when a methyl group is introduced in position 2 of pyridine δ_{max} increases from 2750 to 3560.

4. **Hypochromic shift** involves a decrease in intensity of absorption and is brought by groups which are able to distort the geometry of the molecule.

**PRINCIPLE:**

- Visible and UV spectra arises from the transition of valency electrons within a molecule or ion from a lower electronic energy level (E₀) to higher electronic energy level (E₁).
- This transition occurs due to the absorption of UV or visible radiation by a molecule or ion.
- The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons, E₁ - E₀ = hv.

**INSTRUMENTATION**

The various components of UV-visible spectrometer are as follows:

1. **Radiation source:**
   - The most commonly used radiation sources are hydrogen or deuterium lamps.

2. **Monochromator:**
   - It 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.

3. **Cells:**
   - The cells (containing sample and reference for analysis) must transmit the light of
the wavelength used. The most commonly used cells are made of quartz or fused silica.

4. **Detectors:**
   It converts the radiation, falling on which, into current. Commonly used detectors are Barrier layer cell, photomultiplier tube, photocell.

5. **Recorder:**
   The signal from the detector is recorded by recorder pen.

**WORKING:**

- The radiation from the source is allowed to pass through the monochromator which selects a narrow range of wavelength.
- The beam of radiation coming out of the monochromator is split into two equal beams.
- One-half of the beam is passed through the sample solution and another half is passed through the solvent (reference). The instrument compares the intensity of the two beams.
- If the compound absorbs light at a particular wavelength then the intensity of the sample beam (I) will be less than that of the reference beam (I₀).
- The instrument gives output graph which is a plot of wavelength vs absorbance. This graph is known as absorption spectrum.

**Solvent effects:**

The position and intensity of an absorption band may shift when the spectrum is recorded in different solvents. For changes to solvents of increased polarity the following pattern of shifts arise:

i) Conjugated dienes and aromatic hydrocarbons experience very little solvent shift.

ii) α,β-unsaturated carbonyl compounds show two different shifts:
   
   (a) the $\pi \rightarrow \pi^*$ band moves to longer wavelength (red shift) while
   
   (b) the $n \rightarrow \pi^*$ band moves to shorter wavelength (blue shift).

**Effect of Conjugation and Auxochrome:**

- The conjugation of double bonds has a bathochromic shift (shift of an absorption band to a region of longer wavelength).

- Benzene, with its six p electrons shows appreciable absorption in the near ultraviolet.
The introduction of conjugated unsaturated side chain causes a shift to longer wavelengths (Bathochromic shift), e.g. Stillbene C₆H₅CH=CHC₆H₅.

The conjugation is destroyed by an introduction of a –CH₂ group in the unsaturated chain and causes a shift of the absorption band to shorter wavelengths (-CH₂ group causes a hypsochromic shift), e.g. C₆H₅(CH=CH)₂C₆H₅ is greenish yellow, but C₆H₅CH₂(CH=CH)₂C₆H₅ is colourless.

The -N=N- group also behaves similar to –CH=CH- group.

For example, CH₃N=NCH₃ has an absorption band at 3450 Å, but C₆H₅N=NC₆H₅ absorbs strongly at 4450 Å. If one or two–CH₂ groups are introduced, as in C₆H₅CH₂N=NCH₃C₆H₅ the absorption band appears at short wavelength region.

In the case of dyes, the intense colour is due to the presence of chromophore and auxochrome. Consider phenol in alkaline solution. The C₆H₅O⁻ ion is colourless. The introduction of –NO₂ group in the para position, produces a yellow colour p-NO₂C₆H₄O⁻ ion (-NO₂ group acts as auxochrome).

The auxochromic groups are of two types:

(i) Basic or positive groups, such as –OH, -OR, -NR₂, -NHPh, -NH₂, etc. These are effective in acid solutions.
(ii) Acidic or negative groups, such as –NO₂, -NO₃, -CO₂-, -CN, etc. These are effective in alkaline solutions.

Substitution in the ortho and para positions gives the greatest intensification of colour, but meta substitution has little or no influence.

APPLICATIONS:

1. Detection of impurities:
   a. The band due to impurities is very intense.

2. In quantitative analysis to determine the concentration of compound in solution by using Beer-Lambert’s law A = εcl

3. Determination of dissociation energy of a molecule with great accuracy.

4. In identification of cis or trans isomers of a compound.

5. It can be used to study the kinetics of reaction.

6. Determination of structure of organic compounds.

7. It can be used to determine the percentages of various keto and enol form present in a tautomeric equilibrium.
8. Molecular weights of compounds can be measured.

INFRARED SPECTROSCOPY (IR SPECTRA)

IR spectroscopy provides useful information about the structure of molecule quickly over the other methods. When infrared light is passed through a sample of an organic compound, some of the frequencies are absorbed while other frequencies are transmitted through the sample.

If we plot the percent absorbance or transmittance against frequency, the result is an infrared spectrum.

**Principle:**

Infrared spectra is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels. So, IR spectroscopy is also known as vibrational spectroscopy.

**Range of infrared radiation:**

\[ \text{IR} = 650 - 4000 \text{cm}^{-1}; \quad \text{Far IR} = \text{lower than} \ 650 \text{cm}^{-1}; \quad \text{Near IR} = \text{higher than} \ 4000 \text{cm}^{-1}. \]

**MOLECULAR VIBRATIONS:**

At ordinary temperature, organic molecules are in a vibration state, each bond having its characteristic stretching and bending frequency and being capable of absorbing light of that frequency.

The stretching energy of a bond is greater than the bending energy and stretching absorption of a bond appear at higher frequencies in the ir spectrum than the bending absorption of the same bond.

**MODES OF VIBRATIONS:**

For a non-linear molecule with \( n \) atoms, the number of vibrational modes is \((3n-6)\); eg. \( \text{CH}_4 \) possesses 9.

For a linear molecules, the number of vibrational modes is \((3n-5)\); eg. \( \text{CO}_2 \) possesses 4 modes of vibrations.

**Stretching vibrations** – the bond length increases or decreases.

**Bending vibrations** – a change in bond angle. The bending vibration is also called as deformation vibration.

Only those molecules which exhibit change in dipole moment during a vibration can exhibit ir spectra. The vibrational frequency of a bond is expected to increase when the bond strength increases.
INSTRUMENTATION:

1. Radiation source:

   The main sources are

   a) Nichrome wire and
   b) Nernst glowers.

   When they are heated nelectrically at 1000 to 1800°C, they glow and produce IR radiation.

2. Monochromator:

   It selects the desired frequencies from the radiation source and reject the radiations of other frequencies. There are two types of monochromators:

   i) prism monochromator and  ii) grating monochromator.

3. Sample cells and sampling of substances: The material containing the sample must be transparent to IR radiation.

4. For, solid sample – KBr pellet technique is used.

5. Liquid sample – NaCl cell (or) Nujol is used (solvent can also be used).

6. Detectors: IR detectors convert thermal energy into electrical energy. Commonly used detectors are

   i) Photo conductivity cell;  ii) Thermocouple;  iii) Pyroelectric detectors.

7. Recorder: It records the signal coming out from the detector.

WORKING OF IR SPECTROPHOTOMETER:

The radiation emitted by the source is split into two identical beams having equal intensity.

1. One of the beams passes through the sample and the other through the reference.

2. The sample beam comes out from the sample cell is with less intensity compared to the reference beam.

3. When the two beams recombine, they produce an oscillating signal which is measured by the detector and the signal is recorded by the recorder.

FACTORS INFLUENCING VIBRATIONAL FREQUENCIES:

...
Many factors influence the frequency of a molecular vibration. Some of them are discussed below:

1. **Primary mass effects:**

   The C=O stretching frequency in the ketone RCOCH₃ is lower than in RCOCl. The change in frequency is due to the difference in mass between CH₃ and Cl.

2. **Vibrational Coupling:**

   - It takes place between two bonds vibrating with similar frequency provided the bonds are close in the molecule.
   - The coupling vibrations may both be fundamentals (AX₂) or a fundamental vibration may couple with the overtone of some other vibration.
   - The latter coupling is called Fermi resonance.

3. **Hydrogen bonding:**

   - Hydrogen bonding, especially in O-H and N-H compounds, gives rise to a number of effects in IR spectra.
   - The hydrogen bond can be regarded as a resonance hybrid of I and II so that hydrogen bonding involves a lengthening of the original O-H bond.
   - This bond is consequently weakened (ie. its force constant is reduced), so the stretching frequency is lowered.
   - For example, alcohols – at low concentrations a sharp band appears at 3650 cm⁻¹ which is O-H str. in free alcohol molecules; the frequency of hydrogen bonded alcohol molecules is 3500 cm⁻¹ (broad).

4. **Electronic effects:**

   Conjugation lowers the frequency of C=O stretching and C=C stretching. For example, acetone – 1720 cm⁻¹ whereas for methyl vinyl ketone & acetophenone. 1700 cm⁻¹.

5. **Bond angles:**

   In ketones, the highest C=O frequencies arise in the strained cyclobutanones. The C-CO-C bond angle is reduced below the normal 120° leading to increased s character of the C=O bond. The C=O bond is shortened and therefore strengthened and so the frequency increases. If the bond angle is pushed outwards above 120°, the opposite effect appears.

**APPLICATIONS OF IR SPECTROSCOPY:**
1. In the identity of the compounds and complexes.

2. To ascertain hydrogen bonding in a molecule (as the dilution is increased, the absorption band, due to intermolecular hydrogen bonding diminishes while that due to intramolecular hydrogen bonding remains unchanged).

3. In detecting impurities in a sample.

4. It provides valuable information of molecular symmetry, dipole moments, bond lengths, etc.

5. Distinguishing positional isomers of a compound.

6. It is useful for identifying isomers. Eg. cis-alkenes 970 cm\(^{-1}\); trans-alkenes 730 – 650 cm\(^{-1}\).

7. It may also be used for quantitative analysis of a mixture of compounds, in pollution detection, in milk analysis, etc.
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