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Class 12
Chemistry

Chapter 18
Spectroscopy
Handwritten Notes

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SPECTROSCOPY

Branch of science which deals with finding structure of molecules on basis of interaction of electromagnetic raditions with matter.

Spectroscopic Techniques

- UV-Visible: UV visible spectroscopy is used to find out the conjugation, predict the color and concentration in compounds.
- IR-spectrosopy: It is used for the determination of functional group in the organic compounds.
- NMR-spectroscopy: It is used to find out the number of particular types of atoms in a molecule usually hydrogen-1 and carbon-13.
- Mass spectroscopy: It is the technique used for finding out molecular masses, fragment mass, and relative atomic masses of isotopes of an element.

Electromagnetic radiation is form of energy known as radiation energy such as sunlight.
These radiations have properties of both wave and particle.
Electromagnetic radiations have two components ie. electric field + magnetic field.

Instrument used to measure amount of radiation absorbed by compound is called spectrometer or spectrophotometer.

IR Spectroscopy

IR spectroscopy makes use of interacation of infrared radiations with organic molecules. Its typical range of wave number is from 4000 cm^{-1} to 625 cm^{-1} and it is used to analyse the functional group present in an organic compound. Each functional group absorbs IR radiation at a specific frequency, so it can be recognized easily.

- Principle of IR Spectroscopy: When a molecule containging a polar bond or functional group is exposed to IR radiation, the electric field of the radiation interacts with the dipole movement of the bond. If the frequency of the IR radiation matches the natural vibrational frequency of the bond, abrorption takes place. As a result, the bond starts to vibrate with greater amplitude. This vibration may be in form of streetching or bending. The absorption causes a change in dipole moment of the bond. The greater the polarity of the bond, the stronger the absorption peak. Therefore, the absorbed frequencies are characteristic of the molecular structure and functional groups present in the sample.
- Main Components of IR Spectrometer: The main parts of an IR spectrometer include: source of IR radiation, monochromator, sample chamber, detector, data collection and processing system.
- Reading an IR spectrum: An IR spectrum is intrepreted by studying the absorption bands (peaks). Each peak corresponds to a specific bond vibration, so it acts like a fingerprint of the compound. Common functional groups identified include: C-H, C=O, O-H, N-H. The observed peaks are compared with reference values to determine which functional groups are present. A very important region is the fingerprint region (below 1500 cm^{-1}). This region is unique for every compound and helps in accurate identification.

UV- Visible Spectroscopy

UV-visible spectroscopy is a technique in which the absorption of ultraviolet and visible light by a compound is measured. Its typical wavelength range is 200 nm to 800 nm. It is mainly used to study electronic transitions in molecules, determine conjugation in unsaturated compounds, and find the concentration of solutions.

- Principle of UV-Visible Spectroscopy: This technique works on the excitation of electrons when a molecule absorbs UV or visible light. When light of suitable wavelength falls on the molecule, electrons absorbs energy and move from a lower energy level to a higher energy level. The common electronic transitions are; $\pi \rightarrow \pi^*$ (pi to pi star transition), $n \rightarrow \pi^*$ (n to pi star transitions), $\sigma \rightarrow \sigma^*$ (sigma to sigma star transition), $n \rightarrow \sigma^*$ (n to sigma star transition). These transitions provide information about the molecular structure and type of bonding in the compound. The absorbance is directly propotional to the concentration of

sample, which makes this technique useful for quantitative analysis.
- **Colored Compounds and Visible Region:** Colored compounds absorb light in the visible region (400–800 nm) and transmit or reflect the remaining wavelengths. The observed color is not the absorbed color, but the complementary color of the absorbed wavelength. For example, if a compound absorbs blue or voilet light, it appears yellow or yellow-green. An example is hexa-aqua titanium (III), which appears voilet because it absorbs yellow-green light.
- **Determination of Concentration:** UV-visible spectroscopy is also used to determine the concentration of an unknown solution. First, a standard curve is prepared using solutions of known concentration and their absorbance values. Then, the absorbance of the unknown solution is measured and compared with the standard curve to determine its concentration. This follows the direct relationship: $A \propto C$ (where A = absorbance and c = concentration).
- **Prediction of Absorption in UV-Visible Region:** A compound will absorb in the UV-visible region if it contains; conjugated double bonds, aromatic rings, carbonyl groups, electrons capable of $\pi \rightarrow \pi^*$ or $n-\pi^*$ transtions. The greater the conjugation the easier the absorption in this region. Example:
Benze (C_6H_6) :- conjugated π systems with alternating double bonds, $\pi \rightarrow \pi^*$, absorbs around 254 nm.
1,3-Butadiene (C_4H_6) :- conjugated system of double bonds (C=C-C=C), $\pi \rightarrow \pi^*$, absorbs around 217 nm.
Acetone (CH_3COCH_3) :- carbonyl group (C=O), $n \rightarrow \pi^*$ aborbs around 279 nm.

Atomic Emission Spectroscopy

Atomic emission spectroscopy is a technique used to identify and measure elements by observing the specific wavelengths of light emitted from an excited sample. The sample is first excited using a flame, plasma, arc, or spark.
When atoms absorb energy from heat, electricity, or light, their electrons move to higher energy levels. These excited electrons are unstable and return to their ground state or lower energy level after the source of energy is removed. During this process, they release energy in the form of light (photons). The wavelength or color of the emitted light depends on the energy difference between the two levels. The emitted spectrum appears as a series of separate lines, called spectral lines, where each line represents a specific wavelength.
Each element has its own unique emission spectrum, which acts likes its fingerprint, so this technique is very useful for identifying elements in different samples.
The emitted light is then separated by a prism or diffraction grating and detected by a detector.

Atomic Absorption Spectrum

An atomic absorption spectrum is formed when free atoms in the ground state absorb specific wavelengths of light and become excited to higher energy levels. This absorption produces dark lines in the spectrum at those particular wavelengths. Both atomic emission and atomic absorption spectra are line spectra and provide the same information, as the positions of the spectral lines according to wavelength remain the same. The main difference is that in AES, bright lines appear on a dark background, while in AAS, dark lines appear on a bright background.

Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance spectroscopy (NMR), also called magnetic resonance spectroscopy (MRS), is a technique used to study the structure of molecules, especially organic compounds. It is based on the behaviour of certain atomic nuclei in an external magnetic field.
Some nuclei have a property called nuclear spin, which makes them act like tiny magnets. When these nuclei are placed is an external magnetic field, they can change their orientation by absorbing radiofrequency radiation, usually in the range of 4 to 900 MHz.
The exact frequency at which a nucleus absorbs energy depend on its chemical environment, so the NMR spectrum gives information about the functional groups present and the arrangement of nearby atoms in the molecule. Since each

compound gives a unique spectrum, NMR is one of the most important techniques for identify molecular structures.

- **Principle**: Nuclei that are NMR active normally have their spins in random orientations. When an external magnetic feild B^0 is applied, these nuclei arrange themselves into two possible spin states.
  - low-energy state → aligned with the magnetic field.
  - high-energy state → against the magnetic field.

  The difference in energy between these two states corresponds to the radiofrequency region. When the nucleus absorbs energy equal to this difference, its spin flips from low to high energy state, and this is called resonance. When the spin returns to the ground state, it realeases energy at the same frequency, producing the NMR signal or spectrum.
- **NMR Active Nuclei**: Only nuclei with non-zero nuclear spin ($I \neq 0$) can be observed by NMR. Common NMR active nuclie include; H^1, ^{13}C, ^{19}F, ^{31}P. In organic chemistry the most commonly used are ^1H NMR and ^{13}C NMR.
  Atoms having an odd number of protons or neutrons, or an odd total of both, usually have half-integar spin values such as $I = 1/2, 3/2, 5/2$. These nuclie are NMR active.

^1H NMR (Proton NMR) also called proton Magnetic Resonance Spectroscopy.
It is a type of nuclear magnetic resonance spectroscopy that studies hydrogen-1 (^1H) nuclei in a molecule. It helps in finding the structure of organic compounds by showing how hydrogen atoms are arranged in different chemical environments.

- **Use of Deutrated Solvent**: In NMR, we use deuterated solvents to avoid intereference from normal hydrogen signals. Deutriam (^2H or D) is a hydrogen isotope that is NMR inactive, so it does not disturb the spectrum.
  - Common deutrated solvents; D_2O (deuterated water), $(CD_3)_2CO$ (deutercated aceton).
  - Non-hydrogen solvents like CCl_4 and CS_2 are also used to avoid proton singles.
- **Tetramethylsilane (TMS) as Standard**: $TMS = Si(CH_3)_4$ is used as a reference standard in NMR. It gives a single sharp single. All its protons are chemically equivalent. It is highly shielded due to low electronegtivity of sillicon. Its chemical shift is defined as 0ppm.
- **Chemical Shift (δ) and Nucleus Spin Flipping**: Chemical shift is the position of a singnal in NMR, measured in ppm (parts per million). It shows how much a proton is affected by its environment.
  - In proton NMR, chemical shifts usually lie between +14 to -4 ppm.
  - The exact value depends on; magnetic field strength, electron density around the proton, chemical environment.
- **Sheilding and Deshielding**: Sheilding is when electron density around a proton is high, it reduces the effect of external magnetic field → signal appears at lower ppm.
  Deshielding is when electron density is low (near electronegative atoms like Cl, O), proton feels stronger magnetic field → signal appears at higher ppm.

> **Nucleus Spin flipping:**
> When a nucleus absorbs energy from radio waves in a magnetic field, its spin changes from a lower to higher energy state. This absorption gives the NMR signal.

- **Number of Peaks and Information**:
  - Number of peaks = number of different proton environments.
  - Area under peaks = ratio of hydrogen atoms in each environment.
- **Example Spectra**:
  - Ethyl chloride (CH_3-CH_2Cl): CH_3 gives a triplet (~1.5 ppm) due to 2 neighbouring H atoms. CH_2 gives a quartet (~3.5 ppm) due to 3 neighbouring H atoms. CH_2 is more deshielded because of chlorine.
  - Benzene: Shows a single peak at 7.2 ppm due to ring current effect.
- **Multiplicity (Splitting of Signals)**: spilliting depends on neighbouring hydrogen atoms and follows the n+1 rule.
  - No neighbouring H → singlet.
  - 1 neighbouring H → doublet.
  - 2 neighbouring H → triplet.
  - 3 neighbouring H → quatert

- **Proton Exchange with D_2O:** If a compound has –OH or –NH groups, shaking it with D_2O causes exchange of H with D.
  - The NMR signal dissappears
  - Confirms presence of OH or NH protons
  - Because deutrium is NMR inactive.

Carbon-13 NMR

Only about 1% of carbon atoms are ^{13}C isotopes, while most are ^{12}C. ^{13}C is NMR active, which means its nucleus behaves like a small magnet and can be studied in NMR spectroscopy, while ^{12}C is NMR inactive.
When placed in an external magnetic field (B_0), the ^{13}C nucleus can align with or against the field. The opposed alignment is higher in energy and less stable. When the nucleus absorbs the correct amount of radiofrequency energy, it flips to the higher energy state. This is called the resonance condition, and it appears as a peak in the spectrum.

- **Chemical Shift in ^{13}C NMR:** Chemical shift in ^{13}C NMR is measured in ppm and compared with TMS (0 ppm).
  - Peaks to the left side are called downfield.
  - ^{13}C chemical shifts usually range from 0 to 200 ppm.
  - The exact value depends on the carbon's environment.

  Carbons attached to electronegtive atoms or double bonds appear at higher ppm values because they are deshielded.
- **Using ^{13}C NMR to Find Structure:** Each chemically different carbon atom gives one separate peak. So:
  - Number of peaks = Number of unique carbon environments.
  - Symmetrical carbons give one common peak.
  - Different neighboring atoms or bonds give different peaks.

  This helps identify whether the carbon belongs to an alkane, alkene, alkyne, aromatic ring, or carbonyl group.
- **How to Predict Number of Peaks:** To predict peaks, look for symmetry, identify different carbon environments, equivalent carbons give one peak.

> ^{13}C NMR alone may not fully determine structure. It is usually used with ^{1}H NMR and mass spectrometery.

- **Examples:** <u>Ethanol (C_2H_5OH)</u>:-

  Structure: CH_3CH_2OH

  Ethanol has 2 different carbon atoms, so it gives 2 peaks.
  - CH_3 carbon (methyl group): 1 peak (10-20 ppm)
  - CH_2 carbon (methylene group): 1 peak (50-60 ppm).

  The carbon attached to oxygen is more deshielded, so it appears at higher ppm.

  <u>Acetone (C_3H_6O)</u>:-

  Structure: $(CH_3)_2CO$

  Although acetone has 3 carbon atoms, it shows only 2 peaks because both CH_3 carbons are equivalent.
  - CH_3 carbons (methyl group): 1 peak (20-30 ppm)
  - Carbonyl carbon (C=O): 1 peak (190-210 ppm)

  <u>Butane (C_4H_{10})</u>:-

  Structure: $CH_3CH_2CH_2CH_3$

  Butane gives 2 peaks because of symmetry
  - Terminal CH_3 carbons: 1 peak (10-20 ppm)
  - Middle CH_2 carbons: 1 peak (20-40 ppm)

  <u>Benzene (C_6H_6)</u>:-

  Structure: C_6H_6

  All six carbons in benzene are equivalent because of symmetry. Only 1 peak.
  - Aromatic carbons: 1 peak (120-140 ppm).