

Instrumentation methods and app

II electronic
etallic

- p^Hmetry - p^H meter
- conductometry - conductometer
- potentiometry - potentiometer
- UV - spectrum
- IR - spectrum
- NMR - spectrum
- chromatographic methods
- colorimetry

Spectroscopy :

* Based on spectrum

Electromagnetic radiations :-

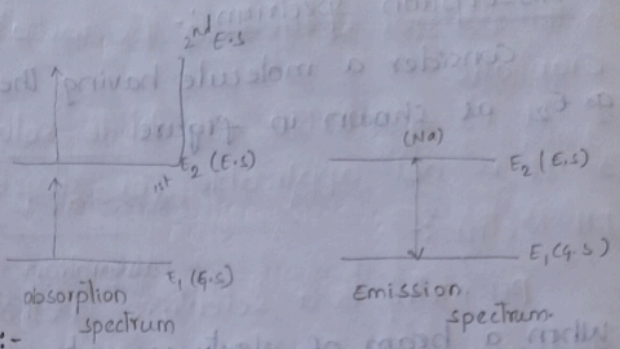
* High frequency radiations w.r.t Matter.

→ Based on atoms, molecules.

* Atomic spectroscopy

* Molecular spectroscopy

→ o.s and e.s is based on EMR



Fluorescence :- 10^{-8} sec - bulb will glow. emission is fast.

phosphoro-If time lap is their emission is slow.

Instr

Spectroscopy deals with the study of interactions of electromagnetic radiations with matter. During the interactions the energy is absorbed or emitted by the matter.

Types of spectroscopy

The study of spectroscopy can be carried out under

the following headings.

1. atomic spectroscopy It deals with the interactions of the emr with atoms. During which the atoms absorb radiations and get excited from the ground state energy level to another.

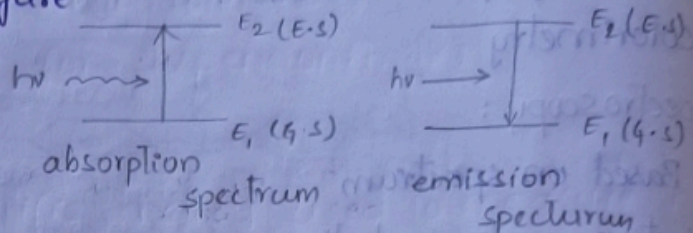
Molecular Spectroscopy :-

It deals with interactions of EMrs. with molecules. This results in the radiations between rotational, vibrational and electronic energy levels.

Spectrum :

1. Absorption Spectrum :-

Consider a molecule having the energy levels E_1 and E_2 as shown in figure



When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state. The molecule absorbs photons of energy $h\nu$ and undergoes a transition from the lower energy to higher energy level. The spectrum thus obtained is called absorption spectrum.

Emission spectrum :-

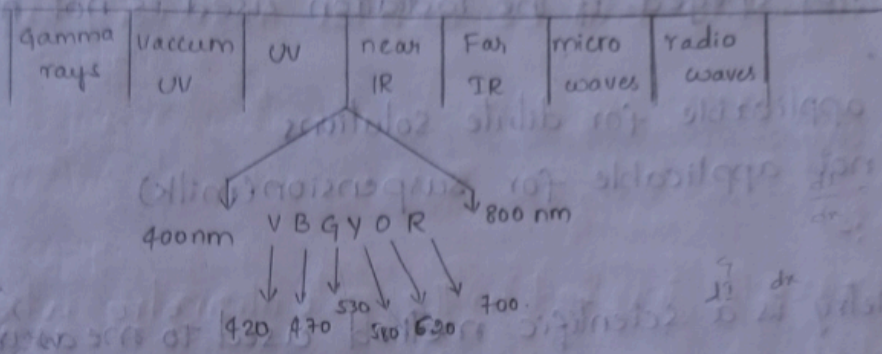
If the molecule comes down from the excited state to ground state with the emission of photons of energy $h\nu$ the spectrum thus obtained is called emission spectrum.

When the electromagnetic radiation is passed through a solution of absorbing substance the rate of matter, the following changes occur.

1. Fluorescence : If the excited molecules re emit the radiations almost instantaneously within 10^{-8} m/s. It is called as fluorescence.
2. Phosphorescence : If the excited molecules re emit the radiation after sometime slowly is called phosphorescence.

Electromagnetic Spectrum.

The range over which electromagnetic radiations exists is known as electromagnetic spectrum. Diagrammatic representation of electromagnetic spectrum is as shown in the figure.



Beer Lambert's law:

When a beam of monochromatic radiation is passed through the solution of an absorbing substance the rate of decrease in the intensity of a radiation ' dI ' with the thickness of absorbing solution ' dx ' is proportional to the intensity of incident radiation ' I ' as well as the concentration of the solution ' c '.

It is mathematically represented as

$$-\frac{dI}{dx} = k I c$$

on integrating the equation between the limits $I = I_0$

at $x=0$ and $I=I$ at $x=x$ we get

$$\int_{I_0}^I \frac{dI}{I} = - \int_0^x k c dx \quad (1)$$

$$\ln \frac{I}{I_0} = -k c x \quad (\text{or}) \quad 2.303 \log \frac{I}{I_0} = -k c x \quad (\text{or})$$

$$\log \frac{I}{I_0} = \frac{k}{2.303} c x$$

Since $A = \log \frac{I}{I_0}$ is absorbance or optical density
 $\epsilon = \frac{k}{2.303}$ is molecular absorption coefficient.
Hence the above equation is called Beer Lambert's law.

Limitations :-

1. This is not obeyed if the radiation used is not monochromatic.
2. It is applicable for dilute solutions
3. It is not applicable for suspension (milk)

pH Metry :-

pH Metry is a scientific method used to measure the hydrogen ion concentration in water based solution indicating its acidity (or) alkalinity expressed as pH.

The pH metry usually carried out by pH meter.

Principle :-

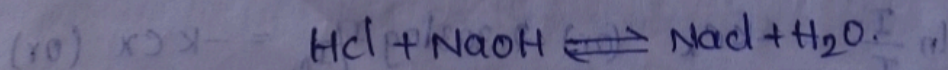
The pH meter measures the difference in electrical potential between pH electrode and a reference electrode. These electrodes are inserted into the solution to be tested.

Since the pH of the solution is related to the H^+ ions concentration by the following formula.

$$pH = -\log[H^+]$$

Measurement of pH gives the concentration of H^+ ions in the solution.

when NaOH is added slowly from the burette to the solution the fast moving H^+ ions are replaced by the slow moving Na^+ ions. As a result pH of the solution increases.



The increase in pH takes place until all the H^+ ions are completely neutralised (at the end point). After the end point

further addition of NaOH increases the pH sharply as there is an excess moving of OH^- ions.

Applications:-

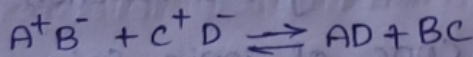
- * It is useful to monitor the pH in agriculture, water quality, environmental remediation.
- * It is useful in health care and clinical applications such as blood chemistry.
- * It is useful in the direct measurement of pH inside the living cell.

Conductometry:-

is measurement of electrolytic conductivity to monitor a progress of chemical reaction. It is applied to determine the total conductance of a solution or to analyse the end point of titrations that include ions.

principle:-

The main principle involved in this method is that the movement of ions create electrical conductivity and the movement of ions mainly depend on the concentration of ions.



Where A^+B^- is a solution of strong electrolyte. C^+D^- is a solution of reagent.

The ionic concentration of A^+ ion is determined by reacting the electrolyte solution with the reagent solution.

So, that the A^+ ions are replaced by C^+ ions. The replacement of the ions with the other ions show the conductance increase (or) decrease. This is done mainly by the replacement of H^+ ion with the other cations.

Limitations :- Applications :-

Conductometry is used in the determination

1. Ionic product of water
2. Solubility of sparingly soluble salts
3. Chemical equilibrium in ionic water
4. Water purity can be monitor in water purification system.

Potentiometry :-

Principle :-

The principle involved in the potentiometry when the pair of electrodes are placed in the sample solution it shows the potential difference by the addition of titrant or by the addition change in conc of ions.

Potentiometric is one in which the endpoint is detected by measuring changes in the potential of a suitable electrode during the course of reaction. No indicator is used in this titration. The electrode whose potential varies during the reaction and which depends upon the conc of ionic species is called indicator electrode. The absolute value of emf of the cell is not required. The end point of the reaction is indicated by a sharp change in the potential of the system.

Applications :-

- * In environmental chemistry for the analysis of CN^- , NH_3 , NO_3^- , F^- , in water and waste and water.
- * In agriculture for the analysis of iodine, calcium, K^+ , CN^- , Cl^- in water, in soil, in plant material, fertilizers can be analysed

* Salt contain^{ent} of meat, fish, dairy products, fruit juices are analysed

* Corrosive effects of NO_3 in canned foods.

UV Spectroscopy

UV-visible spectroscopy :-

Principle :-

UV-visible spectra arises from the transition of valence electrons within the molecule or ion from a lower electronic energy to a higher electronic energy. This transition occurs due to absorption of UV (wavelength 100-400nm) or visible wave length (400-750nm) region of electronic spectrum by a molecule or ion.

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

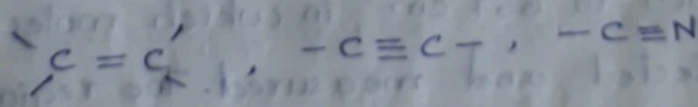
$$\Delta E = E_1 - E_0 = h\nu$$



Electronic transition depends on the electronic structure of absorbing medium. The absorption of UV visible radiation in organic molecule is mainly due to the presence of functional group.

The presence of one or more unsaturated linkages (π electrons) in a compound is responsible for the colour of the compound. This linkages are referred to as chromophores.

Examples :-



Chromophores undergo π to π^* transition in a shorter wavelength region of UV-radiation

In an atom or group of atoms which does not give rise to absorption band on its own but when conjugate to chromo

phore will cause red shift.

Example: $-\text{OH}$, $-\text{Br}$, $-\text{NH}_2$, $-\text{C}=\text{O}$, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$, $-\overset{\text{CHO}}{\text{C}}-$

Energy absorbed in the visible and UV region by a molecule causes transition of valence electrons in the mol. These transitions are $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$

Applications :-

- * UV spectroscopy is not useful in the detection of individual functional groups, but it is used in predicting the relation between the different groups.
- * It is used for the characterization and identification of aromatic compounds and conjugated olefins.
- * UV absorption spectroscopy is a best method for detecting impurities in organic compounds.
- * Kinetics of chemical reactions can be studied using UV spectroscopy.

IR spectroscopy.

IR spectra is produced by absorption of energy by a molecule in the IR region (300-1000 micrometer) and transition occurs between vibrational levels. So, IR spectroscopy is also known as vibrational spectroscopy.

IR region of the complete electromagnetic spectrum extends from 12500 to 50 cm^{-1} the most important region being 4000 to 667 cm^{-1} in which molecular vibrations can be detected and measured. The region from 4000 - 12500 cm^{-1} is called near-IR region and from 667 - 50 cm^{-1} is called far-IR region. This type of spectra is given by hetero nuclear diatomic molecules and poly atomic molecules with and without dipole moment.

In Homonuclear diatomic molecules, such as O_2 , N_2 , H_2 , Cl_2 etc are IR inactive because they have no dipole moment.

The vibrational energy of a diatomic molecule is given as

$$E_{vib} = (v + \frac{1}{2}) h\nu$$

v = vibrational quantum number (0, 1, 2, ...)

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

k = Force

μ = reduced mass.

When a molecule is in the ground state ($v=0$) then

$$E_{vib} = \frac{1}{2} h\nu$$

this is the energy of lowest vibrational level called

the zero point group (or) energy. The selection rule is

$$\Delta E = \pm 1, \Delta E_{vib} = h\nu$$

In poly atomic molecules having no dipole moment the exciting radiations can induced an oscillating dipole moment. Hence it becomes IR active.

Applications :-

- * Widely used to detect functional groups in a chemical substance.
- * A potential tool to discriminate between a set of geometrical isomers.
- * In Biology IR spectroscopy is commonly employed to quantitate secondary structure or to determined changes in this structure.

finger print region :-

The vibrational spectral region at $1400 - 700 \text{ cm}^{-1}$ gives very rich and intense absorption band. This region is termed as fingerprint region. The region $400 - 1430 \text{ cm}^{-1}$ is known

as group frequency region.

uses:-

* finger print region can be used to detect the presence of functional groups and also to identify and characterize the molecules just as a ^{finger} print can be used to recognise a person.

Proton - NMR [^1H - NMR] spectroscopy:-

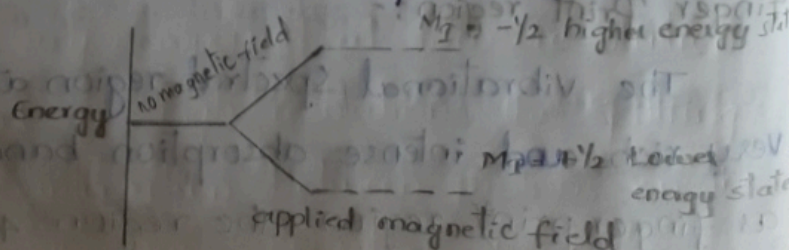
NMR - nuclear magnetic resonance.

NMR is a powerful tool in investigating the nuclear structure of atoms and molecules. In NMR spectra radio frequency waves induced transition between magnetic energy levels of the nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in magnetic field. In hydrogen nucleus (proton) spins about its own axis due to its +ve charge. The spinning proton generates magnetic momentum and hence behaves like a small magnet. But in the absence of external magnetic field the energy levels are equal. If the proton is placed in the strong magnetic field the two energy levels separate.

⇒ if m_I is equal to $+1/2$ will be parallel to the direction of magnetic field. Hence lower energy level.

→ if m_I is equal to $-1/2$ will be antiparallel to the direction of magnetic field. Hence higher energy level.

The energies of 2 states are represented in the following figure.

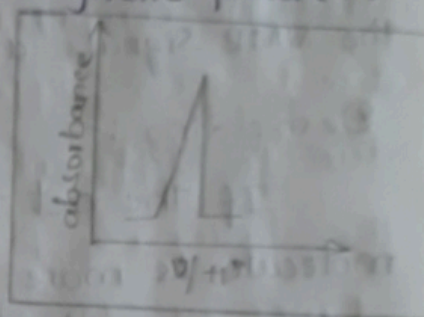


The transition from lower energy state to higher energy state can be obtained by the difference in energy between the two states, ΔE and vice versa in case of upper energy state to that with lower energy state.

The frequency absorbed or emitted by a nucleus moving from one energy level to another energy level is directly proportional to the applied magnetic field and gives the NMR spectra. Thus NMR spectra is plotted between absorption signal and the strength of magnetic field (H°).

Chemical shift

Chemical shift is the difference between the resonance frequency of observed proton and tetra methyl silane (TMS).



TMS is a common reference compound in NMR spectra.

The separation in the position of the signal of different protons from that of the standard is called chemical shift.

It is due to the screening effect of electrons. The position of NMR signals gives an idea about the kinds of protons.

Ex: aliphatic, ~~exo~~ aromatic, primary and secondary.

Different kinds of protons gives different peaks in NMR.

The difference is represented by chemical shift.

$$\text{chemical shift } (\delta) = \frac{\nu(\text{reference}) - \nu(\text{sample})}{\nu(\text{reference})} \times 10^6 \text{ ppm}$$

(or)

$$\delta = \frac{\nu(\text{sample}) - \nu(\text{reference})}{\nu(\text{reference})}$$

The normal reference compound used in the hydrogen molecule in organic compound is tetra methyl silane (TM_4).
Shielding and Deshielding :- (or) causes of chemical shift.

Shielding :-

If the net magnetic field of the nucleus in a molecule is less than the applied magnetic field, the nucleus is said to be shielded. High electron density around the nucleus shields the nucleus from the external magnetic field. Thus the NMR signals are upfield (low δ value).

Deshielding :-

If the net magnetic field of the nucleus in a molecule is more than the applied magnetic field and the nucleus is said to be deshielded. Low electron density around the nucleus deshields the nucleus from the external magnetic field. Thus the NMR signals are downfield (higher δ value).

The following are important factors that influence chemical shift.

* Electron density

* Electronegativity of neighbouring group

* Magnetic anisotropy

* Hydrogen bonding

Spin-spin coupling (or) Spin-spin splitting

In NMR spectrum if any compound at low resolution gives broad signals but at high resolutions the splitting of NMR signal due to the interaction between protons on the adjacent atoms gives spin-spin interactions. Hence

referred to a spin-spin coupling or spin-spin splitting.

The following are the conditions for spin-spin splitting

- * chemically equivalent protons will not cause spin-spin coupling
- * non equivalent protons will have coupling.
- * protons present in an adjacent carbon atoms will couple
- * (n+1) selection rule: The multiplicity of the signal can be calculated by using (n+1) rule. If 'n' no. of protons are present in a near by nucleus. The peak will split into n+1 lines.

Ex: 1 If no hydrogen is present in neighbouring group then
 $n+1 = 0+1 = 1$ (gives single peak)

Ex: 2 If one hydrogen is present in the neighbouring group then
 $n+1 = 1+1 = 2$ (gives double peak)

Ex: 3 If two hydrogen are present in the adjacent group then
 $n+1 = 2+1 = 3$ (gives Three peaks).

Applications :-

- * NMR spectroscopy is used to determine the molar ratio of the components in a mixture.
- * It is used to study the hydrogen bonding in metal chelates and organic compounds.
- * It is used in the determination of total concentration of a given magnetic nucleus in a sample.
- * It is useful to study ketoenol
- * Gas chromatography:-

Principle: Gas chromatography is used to analyse a mixture of volatile organic compounds. The basic principle involved

involved in GC is the differential distribution of various components between mobile phase and stationary phase. The mobile phase generally used as nitrogen gas and the stationary phase used as a solid or liquid.

In gas chromatography small amount of sample mixture is vapourised in the mobile carrier gas and passed at a constant flow through a column containing the stationary point maintaining temperature. The components of sample mixture gets separated due to their differential migration through the column due to differential in their boiling point, solubilities in the stationary phase.

Types of gas chromatography:

Based on the nature of stationary phase gas chromatography classified in two types.

1. Gas solid chromatography (GSC)
2. Gas liquid chromatography (GLC)

Gas solid chromatography: If column is packed with a solid stationary phase like silica, alumina is known as gas solid chromatography.

Adsorption occurs between gas and solid.

Gas liquid chromatography:-

If column is packed on or with non volatile liquid held as a thin layer over the solid. is known as gas liquid chromatography, partitioning occurs between gas and liquid.

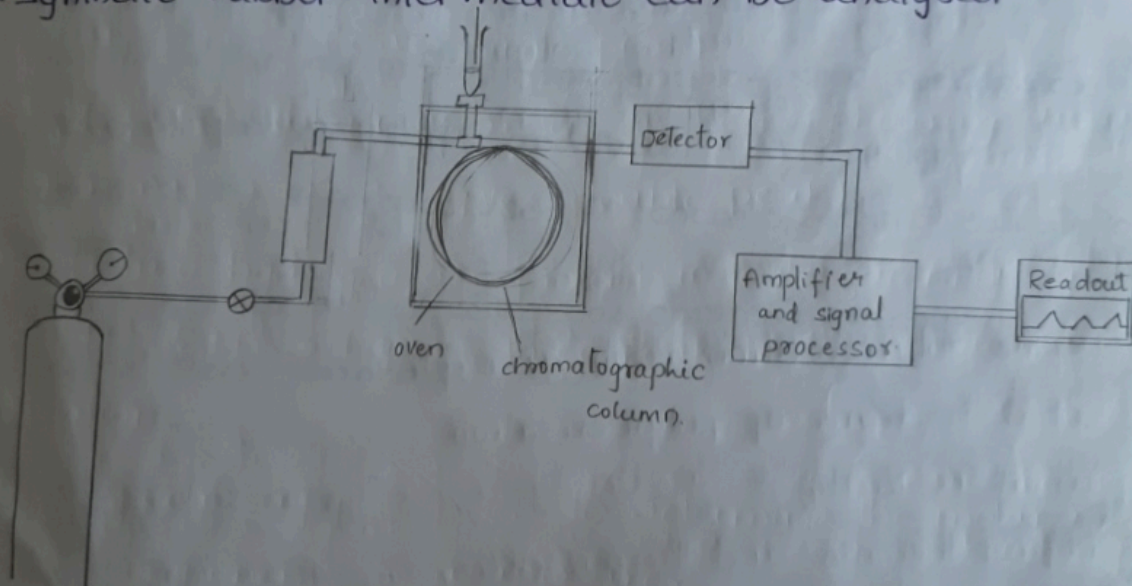
factors affecting Gas chromatography:

The separation efficiency depends on

- * nature of stationary phase
- * temperature of the column
- * length of the column
- * flow rate of carrier gas

Applications:-

- * Ethyl alcohol content can be determined by using the Gas chromatography.
- * separation of compounds having close boiling points can be done easily by Gas chromatography
- * Refinery gases can be carried out easily by G.C
- * Synthetic rubber intermediate can be analysed.



HPLC - High performance liquid chromatography

Principle:-

HPLC is an advanced method of column chromatography. The particle size of the adsorbent improves the resolution. The solvent is passed through the column under high pressure using pressure pumps. In general the adsorbent with small particle size (3 μ m, 5 μ m, 10 μ m) with a narrow size distribution will greatly improve the resolution. High pressure in the column can be created by using pump.

For example if the illustration is done with a mixture of gaseous methane and ammonia is taken along with the water as a mixture, ammonia being soluble in water will go into water phase whereas methane being insoluble will remain in gas phase. Such a separation of methane and ammonia is a one-stage partition between gas and liquid phase. This partition procedure is a tedious process.

However partitioning can be achieved automatically by using chromatographic columns in which stationary phase is in contact with the mobile phase.

Instrumentation

Applications :-

1. Clinically diagnosis of diseases and disorders can be analysed by HPLC. In food industry for quality control check HPLC method is used. For the separation of similar molecules in ^{Pharma} pharmaceutical labs for analysis.

Short :-

- 1) what are electromagnetic radiation give there rangers?
- 2) Give the principle of uv visible spectra.
- 3) what is finger print region?
- 4) Explain about shielding and deshielding effect?
- 5) write a short note on spin-spin coupling or spin-spin splitting.
- 6) Give the principle of vibration spectroscopy.
- 7) what are stretching and bending vibrations.
- 8) Give the applications of NMR spectroscopy.
- 9) Expand NMR, - IR, UV, GC, HPLC
- 10) Give the applications of GC and HPLC?
- 11) what is the absorption frequency of NMR spectroscopy?
- 12) Define chemical shift and how is it denoted?
- 13) what is the reference used in chemical shift calculation in NMR
- 14) Label the factor effecting gas chromatography.
- 15) Define Beer-Lamberts law?

Polymers - Essay.

1. Define polymer. Explain different types of polymerisation with example.
 2. Write a short of basic concepts of polymers.
 3. In detail explain the mechanism
 - a) cationic, anionic, σ -free radical, chelation (or) catalytic
 4. Define elastomers. Give the synthesis and properties and application of a) Teflon b) nylons (c) Bakelite
 - 5) Define elastomers. Give the preparation, properties and applications of Buna-S, Buna-N, polyurethane.
 - 6) what are conducting polymers. Give the mechanism of p-doping conducting polymer.
 - 7) Explain the mechanism of n-doping with poly-acetylene as example.
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- 1) Define polymerisation with an example.
 - 2) what is degree of polymerisation.
 - 3) what is tacticity.
 - 4) Define thermo and thermosetting
 - 5) Difference b/w thermo and thermosetting
 - 6) what are elastomers.
 - 7) what is the monomeric unit of rubber given the name of the molecule.
 - 8) Define vulcanization.
 - 9) write a brief note compounding of rubber.
 - 10) Define conducting polymers.
 - 11) Define condensation polymerisation with an example.