

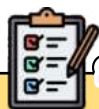
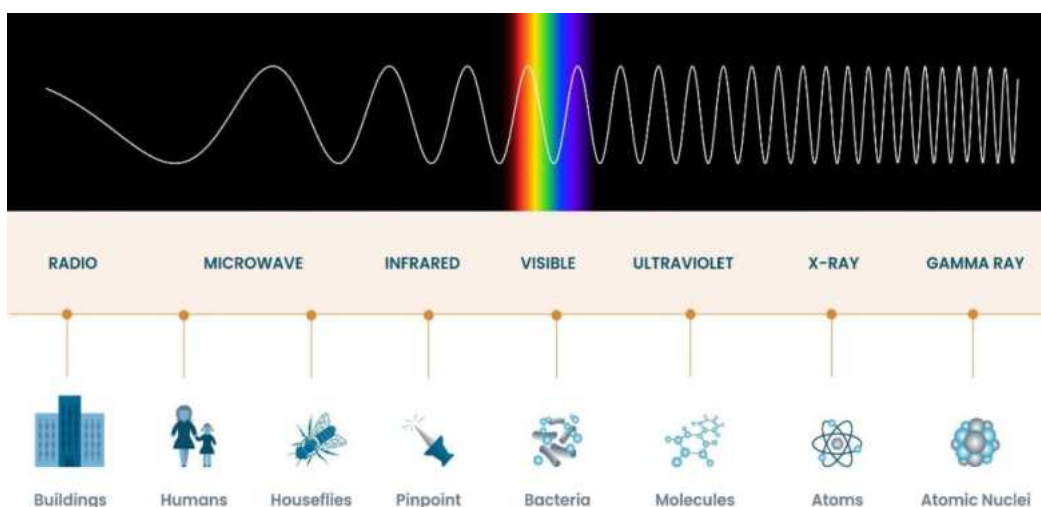


CHAPTER 13

SPECTROSCOPY



Teaching Periods	11	Assessment	02	Weightage %	09
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Students will be able to:

- ✓ Define spectroscopy and discuss its applications in different fields (Understanding)
- ✓ Enlist the regions of electromagnetic spectrum used in IR and UV/Vis spectroscopy (Applying)
- ✓ Identify Ethanol by using different techniques of Spectroscopy. (Applying)
- ✓ Explain atomic emission and atomic absorption spectrum. (Understanding)
- ✓ Describe the application of NMR, UV, IR and Mass Spectroscopy in different fields. (Understanding)



INTRODUCTION

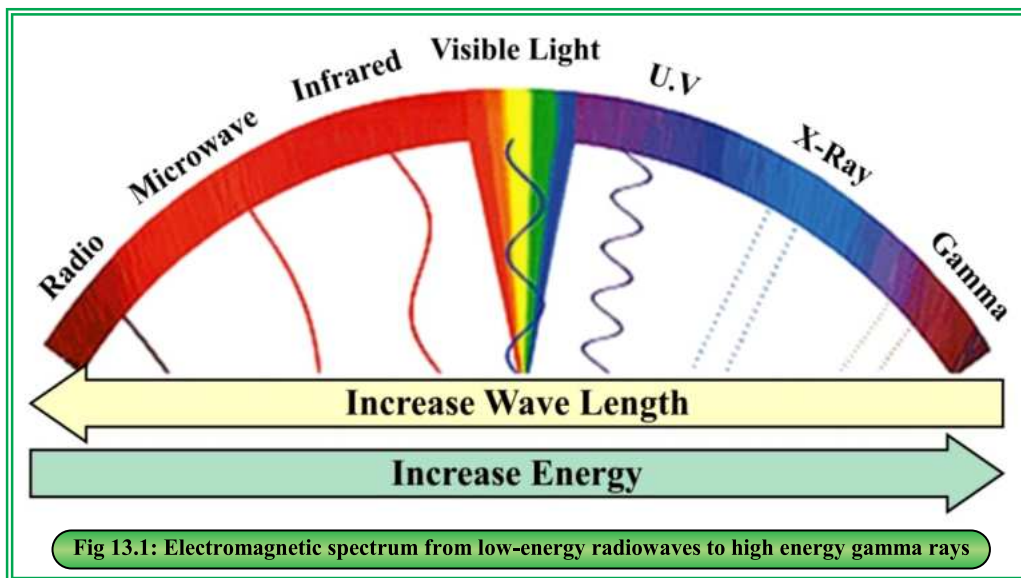
Billions of the compounds have been synthesized to date, each differing from one another based on the arrangement of atoms, bond positions and the type of functional groups present in their structures. Traditionally, the identification of compounds relied on a series of chemical tests. However, spectroscopy has now superseded the conventional methods for various reasons **“Spectroscopy is the study of interaction of electromagnetic radiation of light with matter”**. It is a powerful analytical technique for the determination of structure of molecules.

Spectroscopy has a wide scope of applications in various fields of science and technology and significantly favoured over conventional methods because;

- It is easier and takes very little time to analyze a sample.
- It requires a very small amount of substance which is to be analyzed.
- It provides more reliable information about chemical molecule.

Some applications of spectroscopy are given as:

- (i) Analysis of chemical compounds
- (ii) Quality control of drugs syntheses
- (iii) Analysis of water pollution
- (iv) Determination of protein structure
- (v) Analysis of forensic materials
- (vi) It helps in structure analysis





13.1 METHODS OF SPECTROSCOPY

Sunlight consists of a wide range of electromagnetic waves including radiowaves, microwaves, infrared radiations, visible radiations, ultra-violet radiations, etc. When electromagnetic radiations interact with molecule, some of the rays are absorbed by the molecules while other are transmitted. The wave length and frequency of absorbed light can provide valuable information about the structure of molecule. Various methods of spectroscopy are commonly used to analyze and characterize the compounds.



DO YOU KNOW?

After manufacturing, food, drugs and other pharmaceutical products are sent to the quality control department of the factory. In this department, various spectroscopic techniques are applied to these products to assess their purity, quality and ensure consumer safety.

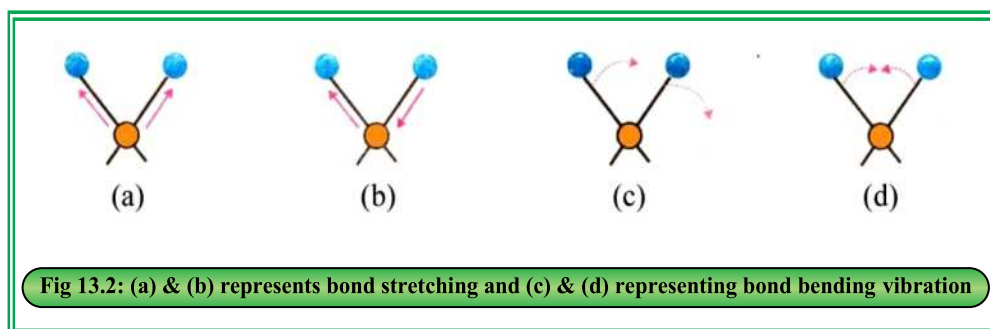
13.1.1 Infrared (IR) Spectroscopy

“Infrared spectroscopy is used to detect the type of bonds and the functional groups present in molecule”. I.R frequency is expressed in the unit of wave number (cm^{-1}). The most useful IR range lies between $4000\text{-}670\text{ cm}^{-1}$.

Table 13.1 Infrared regions

Region	Wavenumber range (cm^{-1})
Near IR	12000-4000
Middle IR	4000-200
Far IR	200-10

The atoms in a molecule already undergo vibration and rotation, in their normal routine, however when the molecule absorbs I.R radiations, it leads to increased intensity of vibrations. This vibration can be of two types namely bond stretching and bond bending. In bond stretching, the bond length increases or decreases while in bond bending the bond angle between the atoms change.

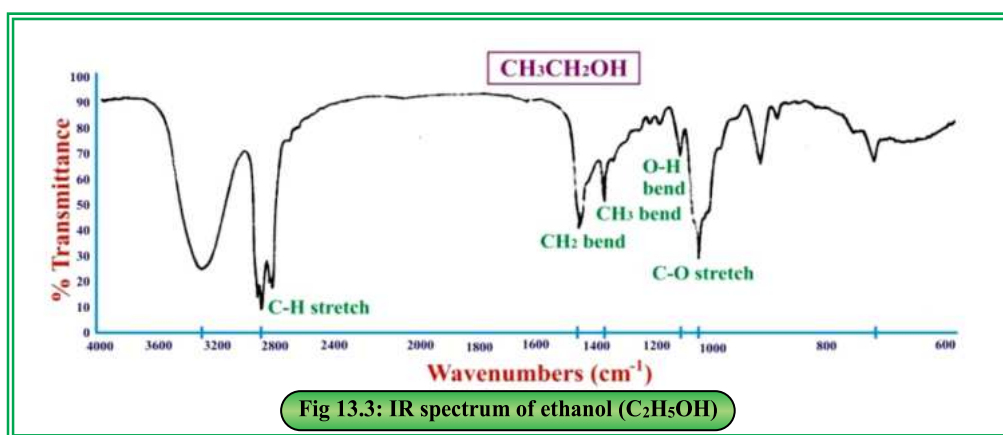


The bending and stretching of each type of bond present in the molecule occurs at a particular frequency of IR spectrum and show the signals at a particular region. There are two regions in IR spectrum;

- i. Finger print region ($1500\text{--}500\text{ cm}^{-1}$)
- ii. Functional group region ($4000\text{--}1500\text{ cm}^{-1}$)

For example if we want to identify ethanol ($\text{C}_2\text{H}_5\text{OH}$) by I.R spectroscopy. We should note the region of absorption bands, in I.R finger print and functional group regions.

- A peak around $1150\text{--}1200\text{ cm}^{-1}$ shows OH in bond bending.
- A carbon-oxygen bond stretching peak is appeared at $1050\text{--}1100\text{ cm}^{-1}$.
- A carbon-hydrogen bond bending of CH_2 and CH_3 groups are observed at $1400\text{--}1500\text{ cm}^{-1}$





Applications of IR Spectroscopy

- (i) I.R spectroscopy provides information for the presence of different functional groups in the organic molecules.
- (ii) I.R spectroscopy is also useful for identifying the impurities present in the sample to be analyzed.



DO YOU KNOW?

Chemical instruments and technology are closely inter connected.

- Chemical instruments are the tools used to analyze or measure chemical processes.
- Technology refers to the application of scientific knowledge for practical purpose.

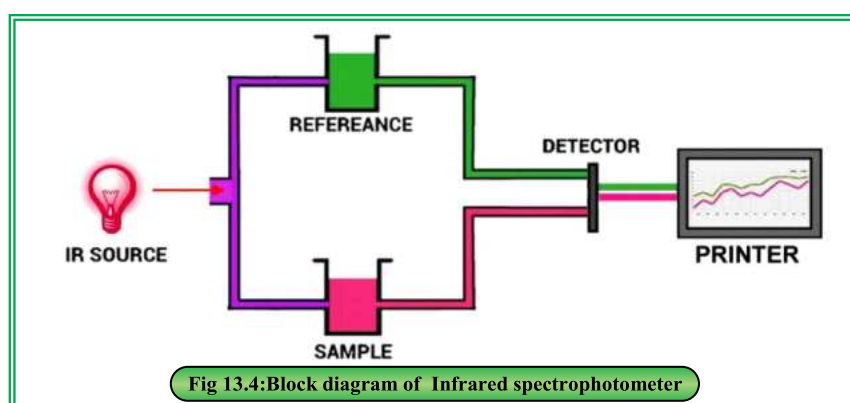


Fig 13.4: Block diagram of Infrared spectrophotometer

13.1.2 Ultra-violet/Visible (UV-Vis) Spectroscopy

“Ultra-violet-visible spectroscopy is used to determine the presence of double and triple bonds as well as conjugated system in the molecule”.

The U.V region of electromagnetic spectrum extends from 200nm to 400nm and the visible region extends from 400nm to 800nm.

When a molecule absorbs electromagnetic radiations of U.V-visible range (200nm-800nm) electronic transitions occur. Its electrons are promoted from lower

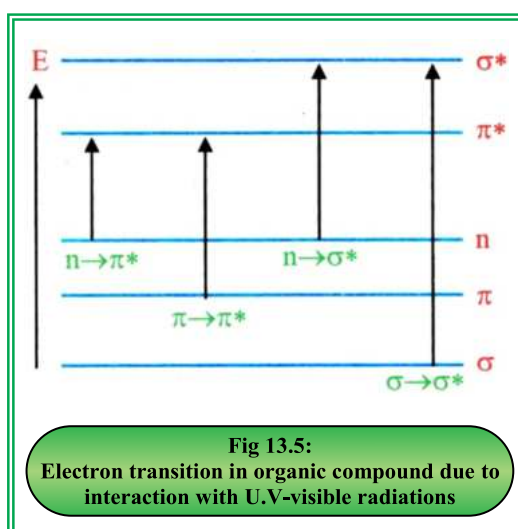


Fig 13.5:
Electron transition in organic compound due to interaction with U.V-visible radiations



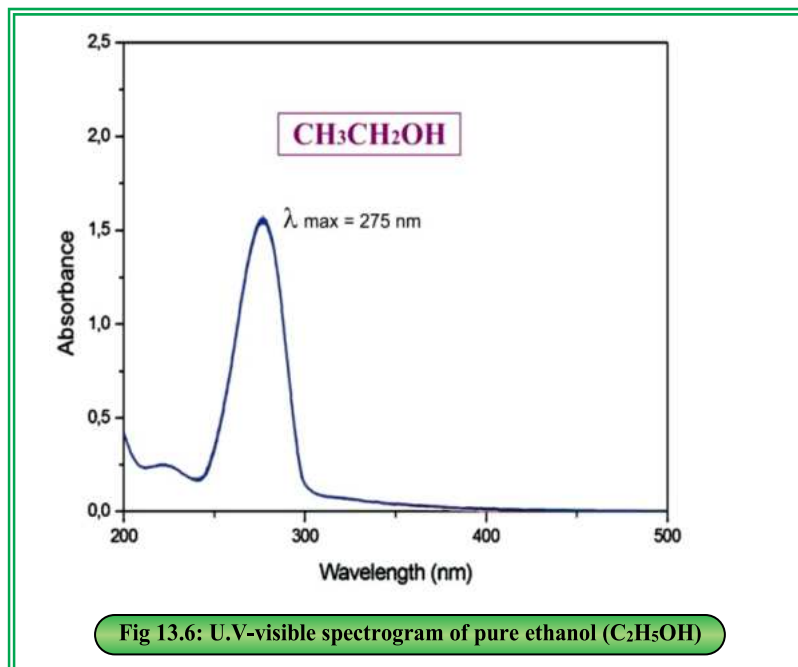
energy level to higher energy level. The transition of electrons may be of the following types.

(i) $\sigma - \sigma^*$ transition: It requires very high energy which is beyond the range of U.V-visible radiations therefore carbon-carbon single bond do not absorb U.V-visible radiations and cannot be detected.

(ii) $\pi - \pi^*$ transition: This transition occurs in the molecule that contain double or triple bonds or aromatic rings. The range of wavelength for the absorption of $\pi - \pi^*$ transition is 180-320 nm.

(iii) $n - \pi^*$ transition: This transition is associated with the molecules in which double or triple bond is connected with a hetero atom (N, O, S) for example aldehyde and ketone, etc. The range of wavelength of $n - \pi^*$ transition can vary depending upon the specific molecular system, however it is approximately 200-500nm.

(iv) $n - \sigma^*$ transition: This transition is concerned with the saturated molecule with hetero atoms like alkyl halide, alcohol etc. The range of $n - \sigma^*$ transition roughly falls around 150-300nm.





Application of U.V-visible spectroscopy

- (i) U.V spectroscopy can provide valuable information regarding the structure of a compound particularly in relation to the presence of double bond, triple bond, aromatic system and hetero atoms.
- (ii) U.V spectroscopy is extensively used for determining the concentration of unknown compounds in a solution by using Beer-Lambert's law.



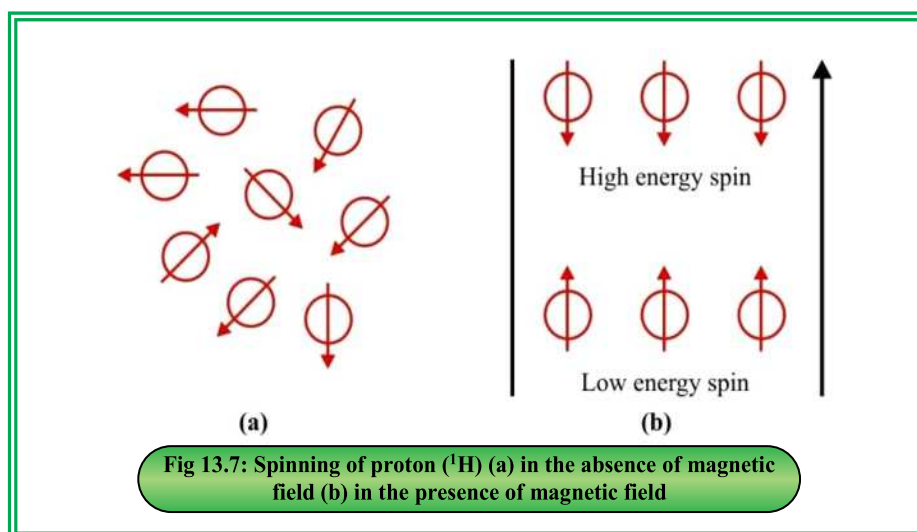
Self Assessment

What is the range of wave length typically used in U.V-visible spectroscopy?

13.1.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

The nucleus of certain elements like ^1H (proton) exhibits random spin and behave like a tiny magnet due to their charged nature. When an external magnetic field is applied, the spin of nucleus aligned in two ways.

- (i) It can align in the same direction of the applied magnetic field and it is said to be low energy spin state.
- (ii) It can be in the opposite direction of the applied magnetic field and said to be high energy spin state.





When a sample of a compound is placed in a strong magnetic field and subjected to radio frequency radiation, the nuclei with specific spin state absorb energy and flip into a high energy state, this absorption of energy is detected as signals in the NMR spectrum. The solvent used in NMR spectroscopy is usually D_2O or DMSO, since it does not interfere with NMR of the sample but with the conditions that compound is soluble in both solvents.

The graph of 1H NMR consists of following parameters.

- x-axis represents chemical shift which shows position of proton signals relative to TMS (tetramethylsilane).
- y-axis represents absorption which shows the intensity of NMR-signals.
- Peaks represent splitting pattern (singlet, doublet, triplet, quartet) due to neighboring protons.

To understand 1H NMR spectrum let us consider the example of ethanol. 1H NMR spectrum of ethanol has three types of protons.

- Methyl (CH_3) protons appear as triplet at around 1.1 to 1.3 ppm.
- Methylene protons (CH_2) appear as a quartet around 3.5 to 4 ppm.
- The hydroxyl proton appears as a broad singlet around 4 to 5 ppm.



DO YOU KNOW?

Magnetic resonance imaging (MRI) is a medical imaging technique that uses strong magnetic field and radio waves to generate detailed images of the internal structure of the body.



DO YOU KNOW?

The position of signal along the x-axis of an NMR spectrum is called chemical shift. Most of the protons in compound have chemical shift values between 0-12 ppm relative to TMS. TMS is internal standard assigned 0 ppm value.

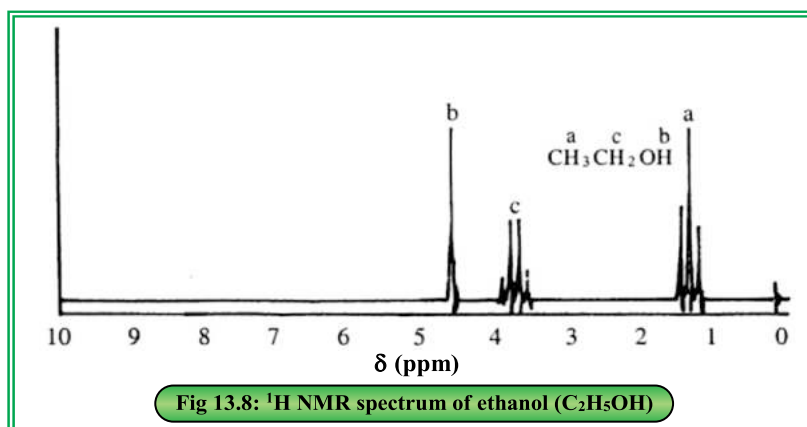


Fig 13.8: 1H NMR spectrum of ethanol (C_2H_5OH)



Applications of NMR Spectroscopy

NMR spectroscopy is a powerful analytical technique, it provides valuable information about the chemical structure of organic compounds.

Each organic compound exhibits a unique NMR spectrum acting as a “fingerprint” that allows chemists to identify them. This technique is successfully applied in drug analysis, material science, forensic analysis and many other fields.

13.1.4 Atomic Absorption and Emission Spectroscopy

Atomic absorption and emission spectroscopy are established techniques used to identify elements in various samples including metal compounds. Within an atom, electrons are distributed in different energy levels, when atom receive energy from an external source like heat or an electric discharge, electrons can be promoted to higher energy level. These excited electrons then undergo transition involving the absorption or emission of electromagnetic radiations.

Atomic absorption spectroscopy

In atomic absorption spectroscopy, the sample is exposed to a wide range of light, the atom selectively absorbs specific wavelength of light that align with the energy needed to elevate electrons to higher energy level. The absorbed wavelengths of light appear as dark lines in a unique pattern specific for that element. By examining the absorbed wavelength, a chemist can identify the presence of specific element in the given sample.

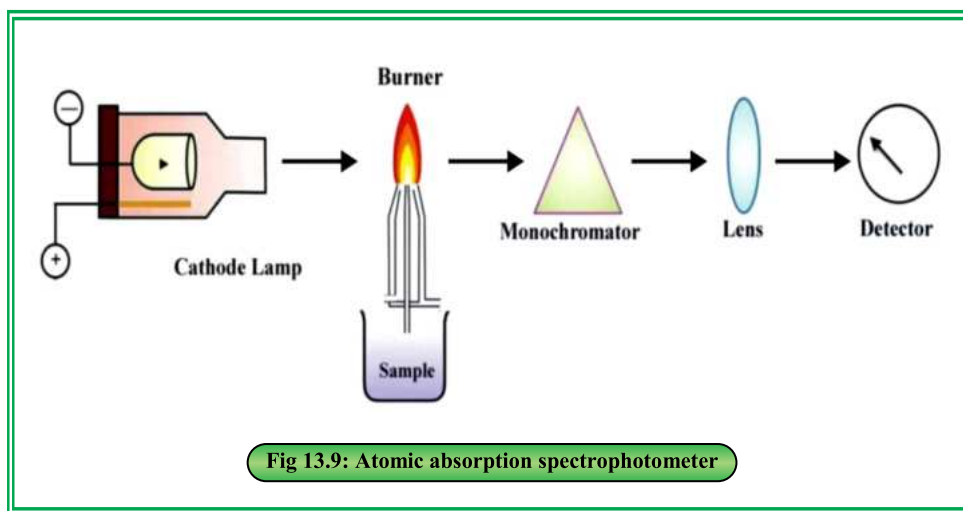


Fig 13.9: Atomic absorption spectrophotometer



Fig 13.10: Atomic absorption spectrum for Hydrogen, Helium and sodium

Atomic emission spectroscopy

In atomic emission spectroscopy the electron in an atom is first excited by providing energy from external source such as heat or electrical energy. When the excited electrons return to their ground state, they emit excess energy in the form of light of specific wavelengths.

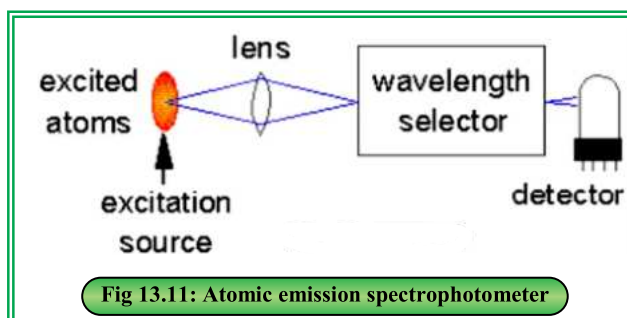


Fig 13.11: Atomic emission spectrophotometer

This emitted light commonly found U.V visible or rarely in IR range. This emitted light appears as a series of bright lines against a dark background. Since each element has its distinct set of bright lines, chemist can identify the element based on this information.



Fig 13.12: Atomic emission spectrum for Hydrogen, Helium and sodium

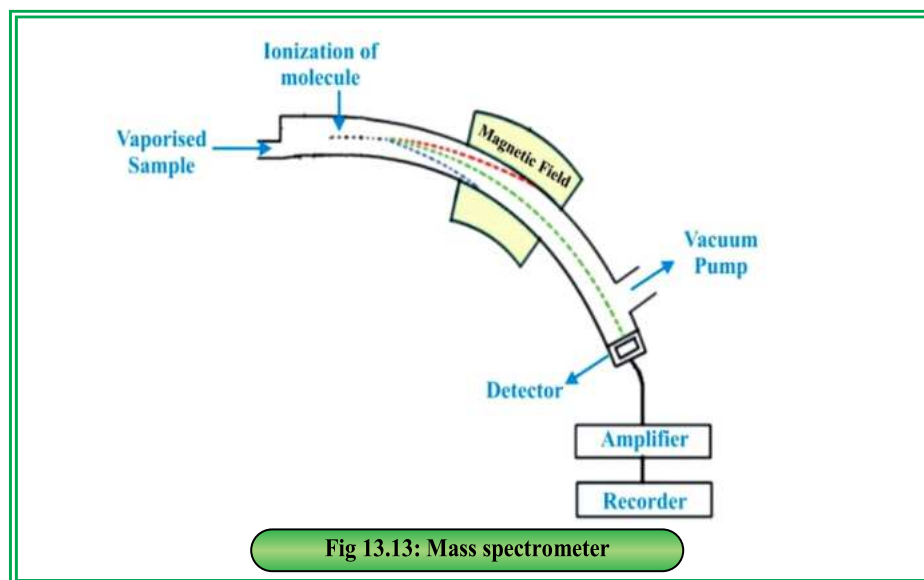


Self-Assessment

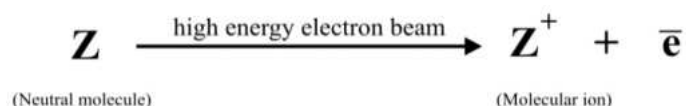
What is the principle behind atomic emission spectroscopy?

13.1.5 Mass Spectrometry

“Mass spectrometry is technique used to determine the mass to charge ratio (m/z) of ions in a sample”. It provides information about the mass of different fragments of the molecule and play an important role in the structure elucidation of molecule.

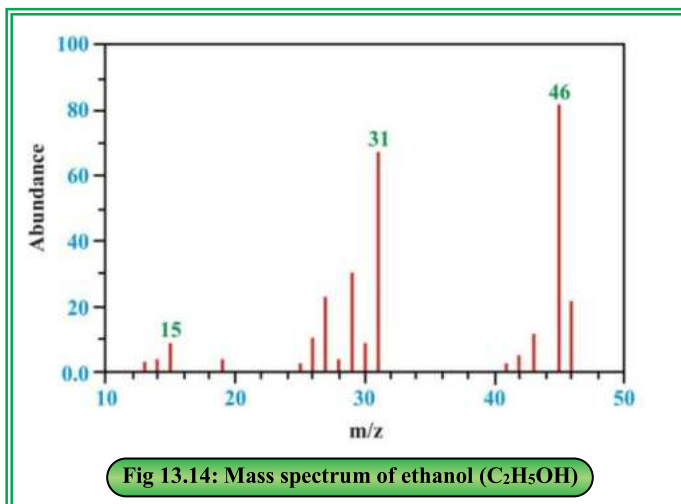


In mass spectrometry, the vapours of compounds are bombarded with beam of high energy electrons from electron gun that makes the neutral molecule loose an electron and change into molecular ion. These molecular ions further break into smaller possible fragments of specific charge to mass ratio (m/z).





These molecular ions then pass through magnetic field where they follow a curved path. A highly sensitive detector is attached in mass spectrometer which detects the molecular mass of ions and record on paper as specific lines.



Self-Assessment

What is mass spectrum? What is the role of detector in mass spectrometer?

Applications of mass spectroscopy

- (i) It is used to determine the molecular mass of unknown compounds on the basis of mass to charge ratio.
- (ii) It is used for the identification and purification of drugs and other pharmaceutical products.



SOCIETY, TECHNOLOGY AND SCIENCE

Use of MS in forensic test

Mass spectrometry provides precise and reliable data for the identification, analysis and interpretation of evidence found at crime scenes such as hairs, blood, illegal drugs, harmful substances, explosive residues, DNA analysis etc. Use of MS help forensic scientists to determine the nature of substance involved in crime and assisting forensic investigators in solving crimes and presenting scientific evidence in court.



SUMMARY

- Spectroscopy is the study of interaction of electromagnetic radiation of light with matter.
- Sunlight consists of a wide range of electromagnetic waves including radio waves, microwaves, infrared radiations, visible radiations, ultra-violet radiations etc.
- Infrared spectroscopy is used to detect the type of bonds and functional groups present in the molecule.
- Ultra violet-visible spectroscopy is used to determine the presence of double and triple bonds as well as conjugated system in the molecule.
- The U.V region of electromagnetic spectrum extends from 200 nm o 400 nm and the visible region extends from 400 nm to 800 nm.
- ^1H NMR spectroscopy is carried out when the sample of compound is placed in a strong magnetic field and subjected to radio frequency waves.
- In atomic absorption spectroscopy absorbed wavelength of light appears as dark lines with bright background.
- In atomic emission spectroscopy absorbed wavelength of light appears as bright lines with dark background.
- Mass spectroscopy is technique used to determine the mass to charge ratio (m/z) of ions in a sample.



EXERCISE

Multiple Choice Questions

- (i) The energy of IR radiations is:
(a) Higher than radio waves (b) Higher than U.V waves
(c) Lower than micro waves (d) Higher than x-rays
- (ii) The fingerprint region of an IR spectrum typically found in the range of:
(a) $1500\text{--}4000\text{cm}^{-1}$ (b) $2000\text{--}4000\text{cm}^{-1}$
(c) $1500\text{--}500\text{cm}^{-1}$ (d) $4000\text{--}8000\text{cm}^{-1}$
- (iii) Which unit of measurement is used for the wave number of IR spectrum:
(a) Nanometer (nm) (b) Angstrom (\AA)
(c) Centimeter $^{-1}$ (cm^{-1}) (d) Hertz (Hz)
- (iv) Electronic excitation occurs in electromagnetic spectrum if the molecule absorbs:
(a) I.R radiations (b) U.V-visible radiations
(c) Radio waves (d) Micro waves
- (v) In NMR spectroscopy, the hydroxyl proton of $\text{C}_2\text{H}_5\text{OH}$ appears as a broad singlet around:
(a) 1 – 2 ppm (b) 2 – 3 ppm
(c) 4 – 5 ppm (d) 6 – 7 ppm
- (vi) Atomic absorption spectrum is represented by:
(a) Dark lines against bright background
(b) Bright lines against dark background
(c) Bright lines against bright background
(d) Dark lines against dark background
- (vii) Infrared spectroscopy is a technique use to determine _____ in the given organic molecule:
(a) Double and triple bonds (b) Mass to charge ratio
(c) Functional group (d) Conjugated system



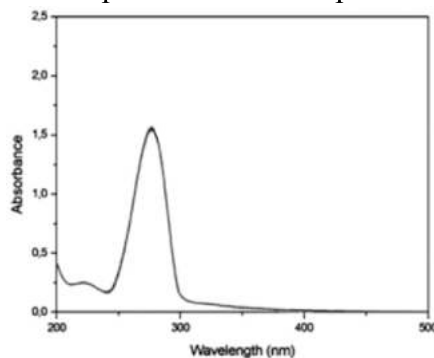
- (viii) Highest U.V-visible absorption energy require for the transition of:
- | | |
|----------------------------|----------------------|
| (a) σ to σ^* | (b) π to π^* |
| (c) n to σ^* | (d) n to π^* |
- (ix) NMR spectroscopy is carried out if radiations interact with molecules in high magnetic field:
- | | |
|----------------------|-------------------|
| (a) U.V-visible rays | (b) Radio rays |
| (c) X-rays | (d) Infrared rays |
- (x) In which of the following spectroscopy technique D_2O can be used as solvent:
- | | |
|------------------------------------|----------------------|
| (a) Mass spectroscopy | (b) NMR spectroscopy |
| (c) Atomic absorption spectroscopy | (d) I.R spectroscopy |

Short Questions

- What types of nuclei are detected in proton NMR spectroscopy?
- Name the components which represents x-axis and y-axis of a proton NMR spectrum.
- Differentiate between atomic absorption and emission spectroscopy.
- What is the purpose of U.V-visible spectroscopy? What is its applications in chemistry and biology?

Descriptive Questions

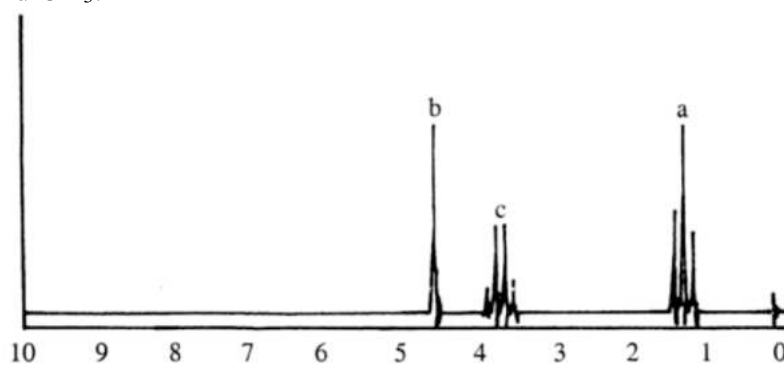
- What information about the structure of a molecule we can get from mass spectroscopy? Give the applications of mass spectroscopy.
- What is proton NMR spectroscopy? How does it work? Give its applications.
- Explain λ_{\max} with the help of U.V-visible spectrum of ethanol (C_2H_5OH).



Spectrum of ethanol



4. Explain the graph of proton NMR of ethanol ($\text{C}_2\text{H}_5\text{OH}$) proton peaks of OH, CH_2 and CH_3 .





APPENDIX - 1

Some IR Absorptions for Common Functional Groups

Bond	Type of Compound	Frequency (cm ⁻¹)
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	alkanes	2800-3000
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	alkenes, aromatics	3000-3100
$\equiv\text{C}-\text{H}$	alkynes	3300
$-\text{O}-\text{H}$	alcohols, phenols	3600-3650 (free)
$-\text{O}-\text{H}$	carboxylic acids	3600-3650 (H-bonded) (broad) 2500-3300
$\begin{array}{c} \\ -\text{N}-\text{H} \end{array}$	amines	3300-3500 (doublet for NH ₂)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	aldehydes	2720 and 2820
$\begin{array}{c} \quad \\ -\text{C}=\text{C}- \\ \quad \end{array}$	alkenes	1600-1680
$\begin{array}{c} \quad \\ -\text{C}=\text{C}- \end{array}$	aromatics	1500-1600
$-\text{C}\equiv\text{C}-\text{H}$	alkynes	2100-2270
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	aldehydes, ketones, carboxylic acids	1680-1740
$-\text{C}\equiv\text{N}$	nitriles	2220-2260



APPENDIX - 2

MCQS ANSWER KEYS

Chap #	MCQs No.									
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
1	a	c	d	a	c	c	b	a	b	a
2	c	c	b	b	c	d	d	a	c	d
3	d	d	d	a	c	c	b	d	a	c
4	a	c	c	b	b	d	d	c	c	d
5	b	d	b	b	a	b	b	d	d	b
6	b	a	c	c	b	c	a	a	d	a
7	b	c	c	b	d	c	d	c	b	c
8	b	b	b	c	a	a	c	a	a	c
9	d	d	c	c	b	c	b	c	b	a
10	c	c	b	a	a	d	a	b	b	c
11	a	a	b	b	c	b	c	b	b	d
12	d	c	d	b	c	d	b	a	b	c
13	a	c	a	b	c	a	c	a	b	b



APPENDIX - 3

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

Name	Melting Point °C	Boiling Point °C
Methane	-182	-162
Ethane	-183	-88
Ethene	-169	-104
Ethyne	-82	-84
Cyclopropane	-128	-33
Cyclohexane	6.5	81
Benzene	5.5	80
Phenol	43	182
Toluene	-95	110
Benzoic acid	122	249
Chlorobenzene	-45	132
Nitrobenzene	5.7	210
Methanol	-98	64
Ethanol	-115	78
Dimethyl ether	-141	-25
Diethyl ether	-116	34
Methyl amine	-93	-6.3
Ethyl amine	-81	17
Formic acid	8.4	101
Acetic acid	16.6	118
Acetyl chloride	-112	51
Acetic anhydride	-73	140
Methyl formate	-100	32
Ethyl acetate	-84	77
Formaldehyde	-92	-21
Acetaldehyde	-121	21
Acetone	-95	56



APPENDIX - 4

REFERENCE BOOKS

1. Organic Chemistry by Francis A. Carey (third edition).
2. Organic Chemistry by Robert T. Morrison and Robert N Boyed (sixth edition).
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