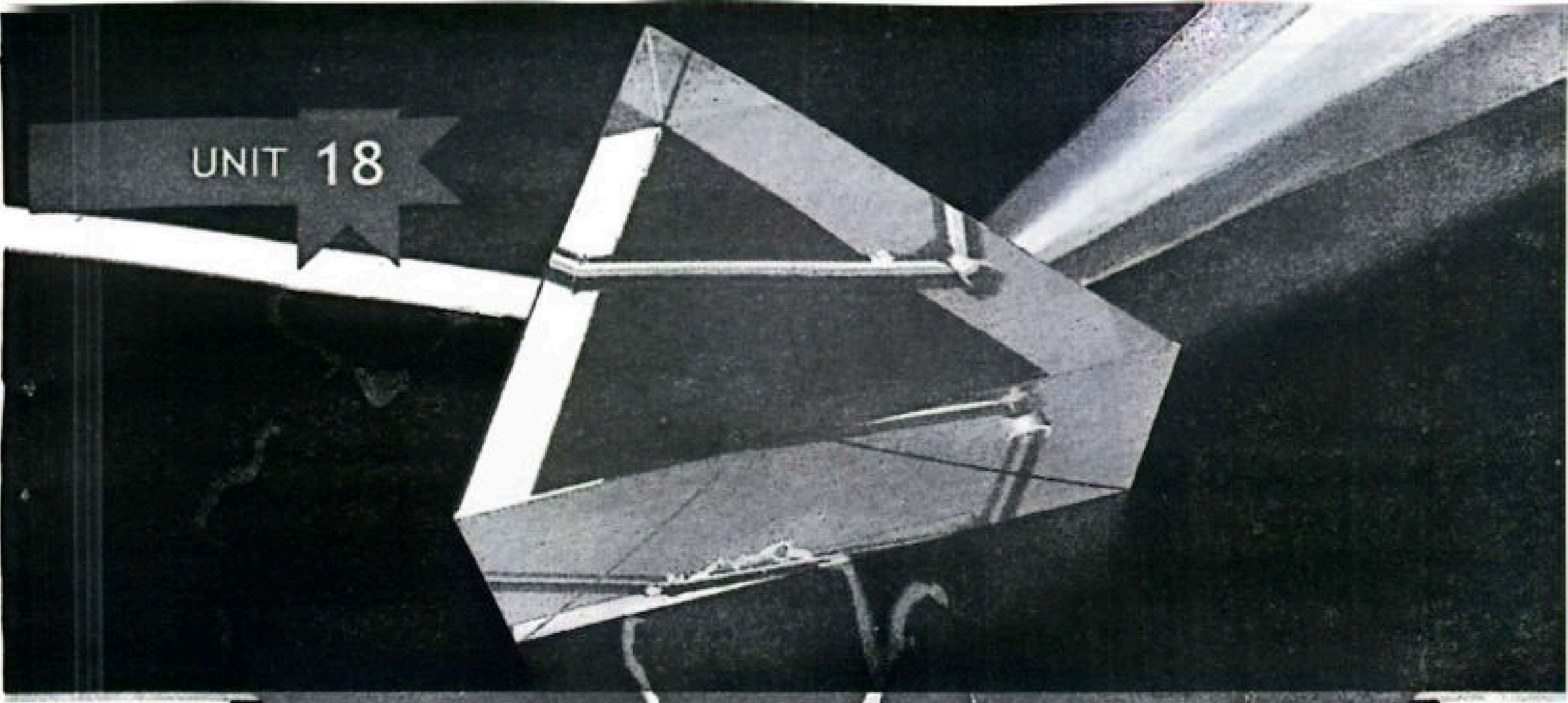
UNIT 18



SPECTROSCOPY

Student Learning Outcomes (SLOs)

- Explain that the degree of unsaturation or Index of Hydrogen Deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.
- Explore, how Mass Spectrometry (MS) proton nuclear magnetic resonance spectroscopy (1H NMR) and Infrared Spectroscopy (IR) are the techniques that can be used to help identify compounds, and to determine their structures.
- Interpret an infrared spectrum of a simple molecule to identify functional groups.
- Deduce possible structures of organic compounds using IR spectrum and molecular formula. (examples: phenol, acetone, ethanol).
- Predict weather a given molecule will absorb in the UV-Visible region.
- Predict the colour of a transition metal complex from its UV-Visible spectrum.
- Explain atomic emission and atomic absorption spectrum.
- Analyse different environments of carbon atoms present in a simple molecule using 13C-NMR spectrum.
- Using 13C-NMR to deduce possible structure of a simple molecule.
- Predict the number of peaks in 13C-NMR spectrum for a given molecule.
- Analyse different environments of protons present in a simple molecule using (proton) 1H-NMR spectrum.
- Use a (proton) 1H-NMR spectrum to deduce relative number of each type of proton present, the number of equivalent protons on the carbon atom adjacent to the one to which the given proton is attached.

- Deduce possible structures of the molecule.
- Predict the chemical shift and splitting patterns of the protons in the given molecule.
- Explain the use of Tetra methyl silane (TMS) as the standard for chemical shift measurement.
- Recognise the need for deuterated solvent e.g. $CDCl_3$ when obtaining a proton NMR spectrum.
- Describe the identification of O-H and N-H protons by proton exchange using D_2O

Spectroscopy is a technique used for structural elucidation of the molecule. It is based on the interaction of atoms or molecules with electromagnetic radiations. Spectroscopy is a very powerful technique used by the chemists of the world to determine the composition and structure of any compound. It exploits the interaction of electromagnetic radiations with matter.

Electromagnetic Spectrum

The electromagnetic spectrum is the range of all frequencies of electromagnetic radiation.

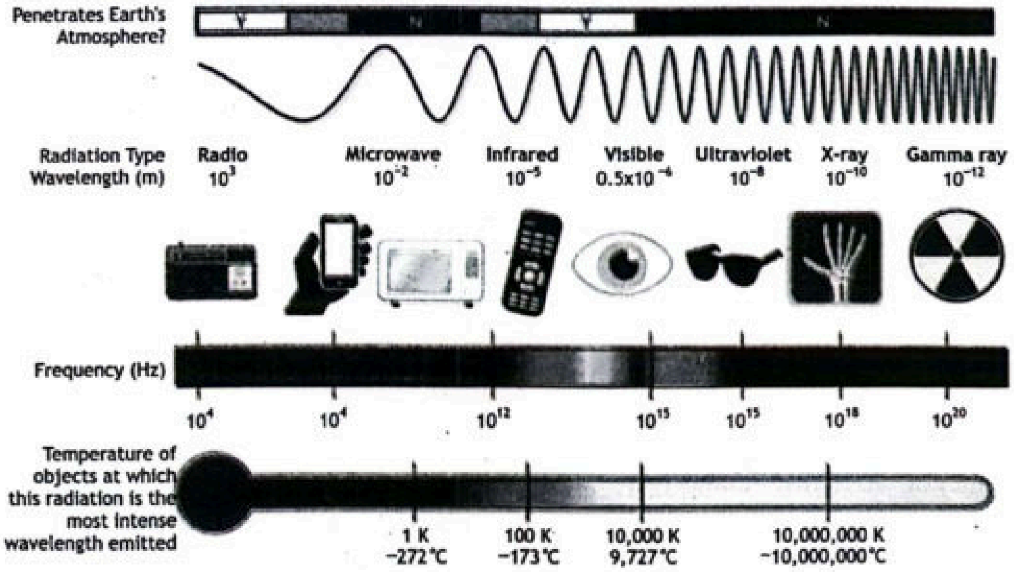


Fig 18.1: Electromagnetic Spectrum

18.1 Spectroscopic Techniques

The major spectroscopic techniques used for organic compounds are:

1. **UV-Visible** spectroscopy is used to find out the conjugation, predict the colour and concentration in compounds.
2. **IR-spectroscopy** is used for the determination of functional group in the organic compounds.
3. **NMR- spectroscopy** is used to find out the number of particular types of atoms in a molecule usually hydrogen-1and carbon-13.

4. **Mass Spectrometry** is the technique used for finding out molecular masses, fragment mass, and relative atomic masses of isotopes of an element.
   Each molecule in a compound is very specific to absorb the electromagnetic radiations of a specific region. On absorbing specific wavelength of light each molecule undergoes a different type of change, that is observed. This gives the key to understand the structure of an organic compound.

18.2 Index of Hydrogen Deficiency or Unsaturation

The total number of rings and pi bonds can be determined by the use of index of hydrogen deficiency (IHD) or degree of unsaturation in an organic compound. It compares the molecular formula that contains all sigma bonds and the molecular formula of the given compound, in such a way that the difference of atoms which are deficient in the actual compound as compared to the fully saturated compound is obtained. A ring in the structural formula of organic compound contributes 1 in the degree of hydrogen deficiency.

Example 18.1

"Degrees of Unsaturation" (or "Index of Hydrogen Deficiency")

- In a hydrocarbon with no double bonds or rings, the number of hydrogens and carbons is related as follows:

  Number of hydrogens = (2 x number of carbons) + 2

- Each multiple bond *or* ring reduces the hydrogen count by 2, which we refer to as a "degree of unsaturation"
- The degrees of unsaturation in a molecule can be calculated from its molecular formula using the following calculation:

$$\textbf{Degrees of Unsaturation} = \frac{2C + 2 + N - H - X}{2}$$

C = #carbons

H = #hydrogens

N = #nitrogens

X = #halogens

- Note that this tells you the *sum* of [multiple bonds + rings], but does not specify exactly how many multiple bonds or rings are present.
- This simple and fast calculation is a useful first step to take when confronted with determining the structure of an unknown molecule.

Calculate the degree of unsaturation in ethene (C_2H_4)

The molecular formula of ethene is C_2H_4. To calculate the degree of unsaturation, we use the formula:

Degree of Unsaturation = (2C + 2 - H–X)/2

In this case, there are 2 carbon atoms and 4 hydrogen atoms and number of halogen atoms in the molecule. Substituting these values into the formula, we get:

Degree of Unsaturation = (2 x 2 + 2 - 4–0)/2 = 1

So the degree of unsaturation for ethene is 1.

CONCEPT ASSESSMENT EXERCISE 18.1

Calculate the degree of unsaturation in:

a. Benzene (C_6H_6) b. Ethyne(C_2H_2)

18.3 IR Spectroscopy

IR spectroscopy makes use of interaction 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 a *specific* component of the IR radiations thus it is recognised. This technique is widely used in organic and inorganic compounds. It helps in the identification of molecular structure. It has high scan speed, resolution and sensitivity which makes it a very useful tool.

18.3.1 Principle of IR spectroscopy

When an organic molecule having any functional group composed of some hetero atom is exposed to IR radiation, the electric field component of rays interacts with the dipole moment of the molecule. If the frequency of the infrared light matches the natural vibrational frequency of a bond or a collection of bonds within the molecule, absorption occurs.

The bonds start to vibrate with greater amplitude by the absorption of this energy. It leads to a change in the dipole moment of the particular bond in a molecule. More is the polarity of the bond more is the intensity of the absorption of the bond.

The frequencies of the radiations that are absorbed are the characteristic of the molecular structure and the functional groups that are present in the sample. By analysing the IR spectrum one can find out the molecular structure especially the functional groups.

The major components of infrared spectrophotometers are;

source of IR radiations, monochromator, sample chamber, detector, data collection and processing system etc.

18.3.2 Reading an IR spectrum

To interpret an infrared spectrum we have to analyse the absorption bands, in this way we can find out the functional groups present in the structure of organic compound.

Each peak in the IR spectrum corresponds to a specific bond. This provides a fingerprint of the compound.

First of all we correlate the absorption frequencies of the unknown compound with the reference for different type of bonds. We look for the major peaks and the associated functional groups by comparing it with the reference. Functional groups like C-H, C=O, O-H, N-H, are more common.

The finger print region below 1500 cm^{-1} is unique to each compound, aiding in compound identification.

18.3.3 Some common functional groups and their characteristic IR absorption ranges

Table 18.1: functional groups with wavenumber and intensity

Functional Group	Wavenumber (cm^{-1})	Intensity
	Akyl	
C–H	2853-2962	medium-strong
	Alkenyl	
=C–H	3010-3095	medium
C=C	1620-1680	variable
	Alkynyl	
≡C–H	3300	strong
C≡C	2100-2260	Variable
	Aromatic	
Ar–H	3030	variable
C=C	1400-1600	variable
	Alcohols, Phenols & Carboxylic Acids	
O–H (alcohols / phenols)	3200-3500	broad, strong
O–H (carboxylic acids)	2500-3000	broad, variable
C–H (alcohols)	1025-1060	Strong
	Aldehydes, Ketones, Esters, Carboxylic acids & Amides	
C=O (Aldehydes)	1690-1740	strong
C=O (Ketones)	1680-1750	strong
C=O (Esters	1735-1750	strong
C=O (Carboxylic acids)	1710-1780	strong
C=O (Amides	1630-1690	strong
	Amines	
N–H	3300-3500	medium

Example 18.2:

Interpret the IR spectrum of a simple molecule, ethanol (C_2H_5OH)

Problem solving strategy

- Identify significant peaks.
- Compare these peaks to known wavenumber ranges for various functional groups.
- Use this information to deduce the presence of specific functional groups in the molecule.
- This method allows you to identify and confirm the functional groups in simple molecules using their IR spectra.

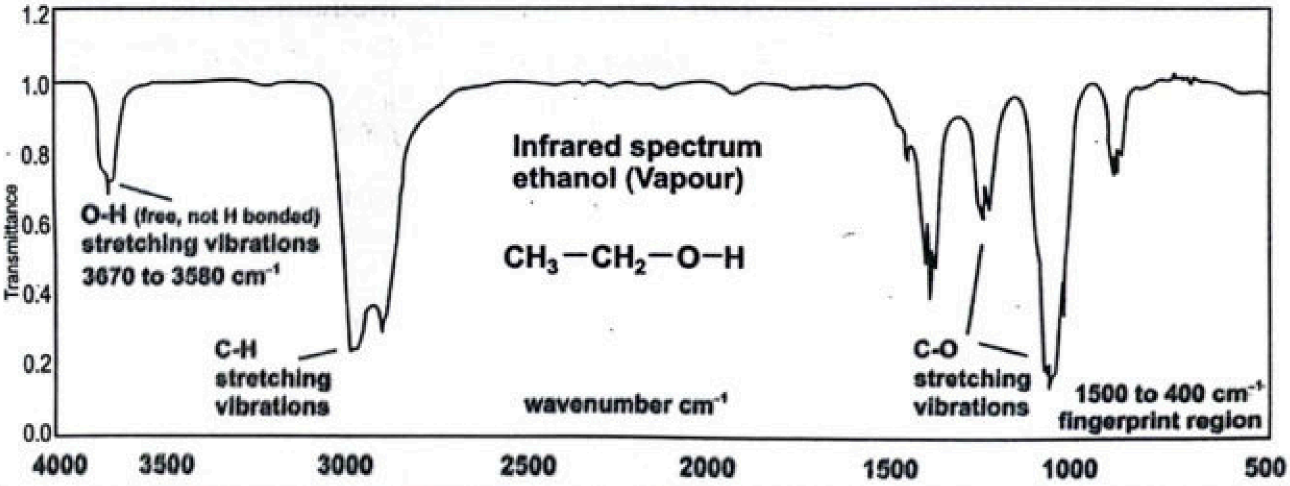


Fig 18.2: IR spectrum of ethanol

The IR spectrum of ethanol shows:

- A broad peak around 3300 cm^{-1}
- Peaks around 2850-2960 cm^{-1}
- A peak around 1050-1150 cm^{-1}

Solution

Match Peaks to Functional Groups:

- The broad peak at 3300 cm^{-1} suggests an O-H bond, confirming an alcohol functional group.
- The peaks in the 2850-2960 cm^{-1} range indicate C-H bonds, which are present in the ethyl group (C_2H_5).
- The peak around 1050-1150 cm^{-1} suggests a C-O bond, also supporting the presence of an alcohol group.

IR spectrum of acetone

This is IR spectrum of acetone (Fig 18.3) The strong absorption peak at 1700cm^{-1} to 1725cm^{-1} is the functional group C=O peak. With a small variation of wave number this peak is also visible *in the* spectrum of aldehydes, carboxylic acid and their *derivatives. At 1215*cm^{-1} to1435cm^{-1} CH_2 vibration is observed. At nearly 3000cm^{-1} C-H vibration bands are seen.

This information helps a lot in understanding the structure of the molecule.

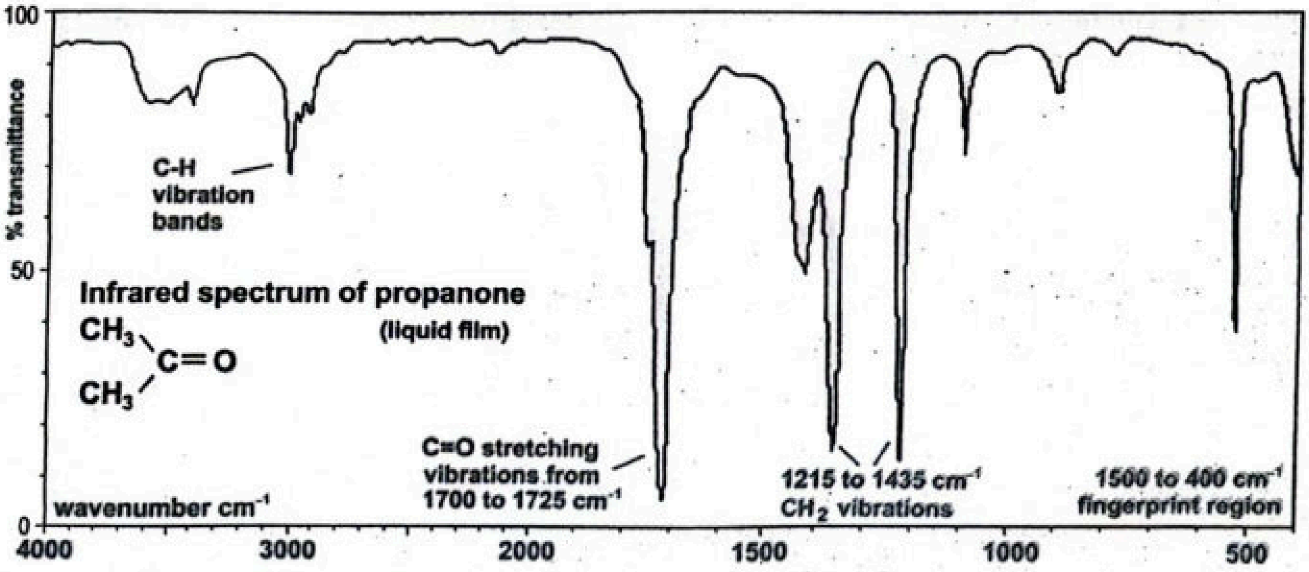


Fig 18.3: IR spectrum of acetone

IR spectrum of phenol

In the structure of phenol (Fig. 18.4) a broad and strong absorption peak represents O-H functional group attached with an aromatic ring. At around 1500 cm^{-1} conjugated double bonds absorb.

Each peak in the IR spectrum corresponds to a specific bond. This provides identification of the compound.

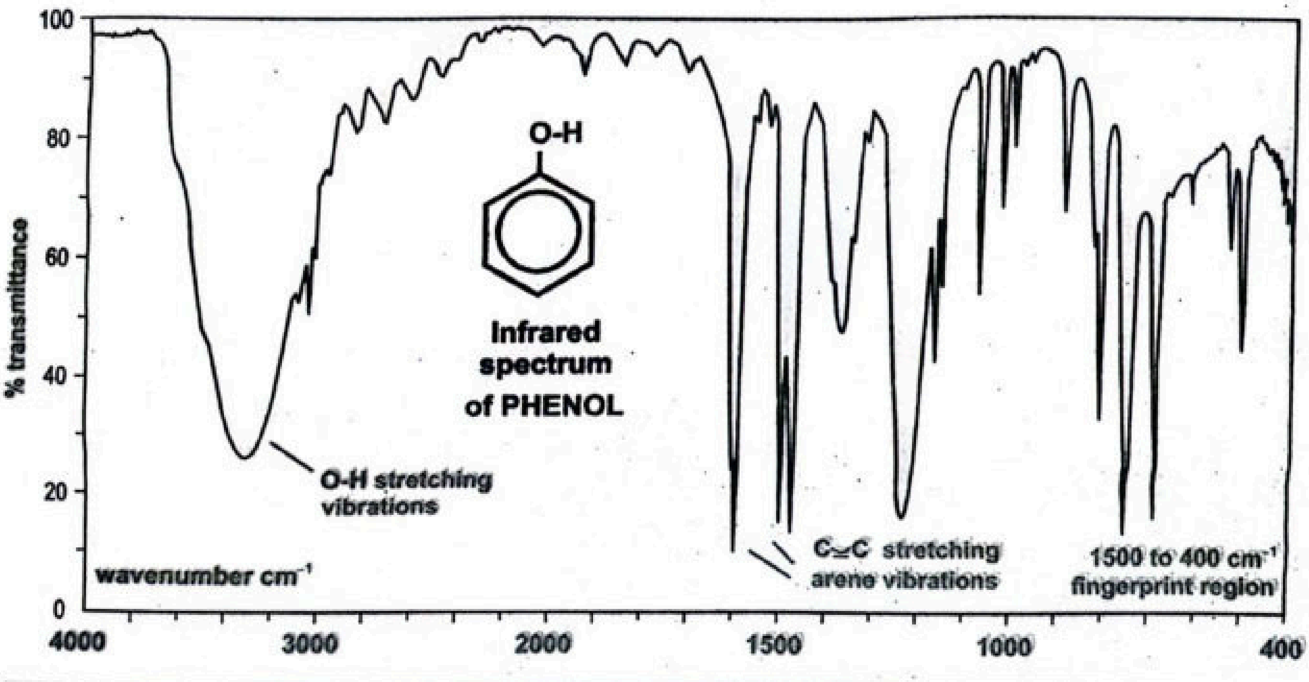


Fig 18.4: IR spectrum of phenol

18.4 UV-Visible Spectroscopy

It is the technique in which the UV and visible light absorption by any compound is measured. It's typical range of wavelength is from 200 nm-800 nm.

This technique involves the excitation of the electrons by the absorption of UV visible wavelength of light. The absorption of the light is directly proportional to the concentration of the sample having particular electrons available for excitation. UV visible spectroscopy is widely used in material sciences and biochemistry. This spectroscopy can be applied to a variety of sample types, including liquids, solids, and gases. It is used to find out the conjugation in unsaturated compounds. Usually the electronic excitations include π-π* (pi to pi star transition), n-π* (n to pi star transition), σ-σ* (sigma to sigma star transition), and n-σ* (n to sigma star transition). These transitions by the absorption of specific range of wavelength, provides the information about the molecular structure.

The coloured compounds absorb a small range of wavelength (400nm-800nm) in the visible region of electromagnetic radiations and transmit the rest of the wavelengths thus the colour appears.

The colour of the compound is not predicted by the wavelength of absorbed wavelength, but the wavelength that is reflected or transmitted.

Firstly, the wavelengths are identified that are absorbed by a coloured complex.
Secondly, we determine the energy required for the transition, the energy of the transition is related with wavelength of light absorbed. Shorter wavelength corresponds to blue and violet region while the longer wavelength region corresponds to red and orange regions.

The colour of the compound is complementary to the wavelength that are absorbed. If a complex absorbs blue or violet it will appear yellow or yellow-green etc.

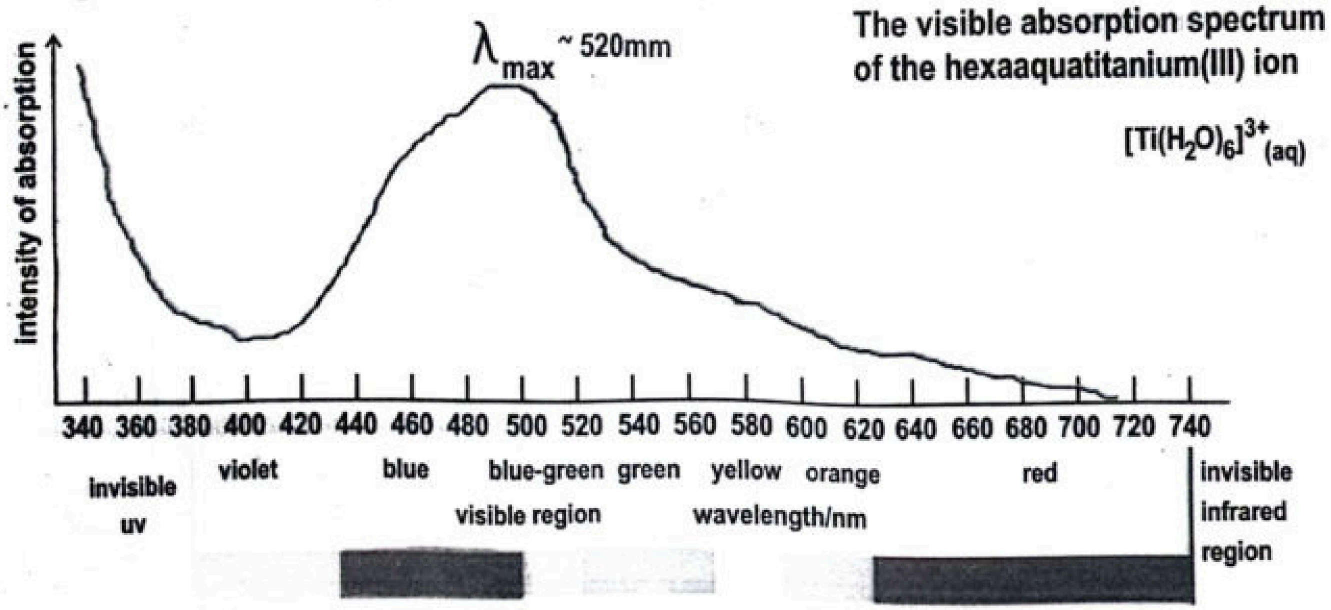


Fig 18.5: UV visible spectrum of $[Ti(H_2O)_6]^{3+}$

Table 18.2

Wavelength Absorbed (nm)	Color Observed	Color Absorbed
400-435	Yellow-Green	Violet
435-480	Yellow	Blue
480-490	Orange	Green-Blue
490-500	Red	Blue-Green
500-560	Purple	Green
560-580	Violet	Yellow-Green
580-595	Blue	Yellow
595-605	Green-Blue	Orange
605-700	Blue-Green	Red

The colour of a compound hexaaqua Titanium (III) $[Ti(H_2O)_6]^{3+}$ in figure 18.5 is violet as this compound absorbs the yellow and green colrours of visible wavelength of light, thus it appears violet. Another use of UV-Visible Spectroscopy is finding the concentration of a solution of unknown concentration quantitatively. Firstly, a standard curve is obtained by using standard solutions and analysing the intensity of absorption of particular band of wavelength. Secondly, the absorption of unknown solution is measured and compared with the standard curve.

CONCEPT ASSESSMENT EXERCISE 18.2

Q1. A compound absorbs the light with a wavelength of 500nm-560nm. What colour do you expect for this compound?

Q2. What wavelength do you suggest about the absorption of light by the components of air?

18.4.1 Predict whether a compound will absorb in the UV-visible region

To predict whether a compound will absorb in the UV-visible region, you need to understand the electronic structure of the compound, particularly the presence of certain types of electronic transitions. If a compound has conjugated double bonds, aromatic rings, or functional groups like carbonyls that enable π to π^* or n to π^* transitions, it is likely to absorb in the UV-visible region.

Example 1: Benzene (C_6H_6)

- Benzene has a conjugated π system with alternating double bonds.
- It exhibits π to π^* transitions, absorbing in the UV region around 254 nm.

Example 2: 1,3-Butadiene (C_4H_6)

- 1,3-Butadiene has a conjugated system of double bonds (C=C-C=C).
- It shows π to π^* transitions, absorbing in the UV region around 217 nm.

Example 3: Acetone (CH_3COCH_3)

- Acetone has a carbonyl group (C=O) which can undergo n to π^* transitions.
- It absorbs in the UV region around 279 nm.

18.5 Atomic Emission Spectroscopy

Atomic emission spectroscopy is a powerful technique to quantify the elements by the measurement of the specific wavelength of light emitted from a pre-excited sample. The *source of* excitation may be flame, plasma, arc or spark. Atoms of any element emit light during de-excitation after the source have been abandoned. These characteristic emitted wavelengths are used to identify the element. The emitted light is dispersed by a diffraction grating or prism then detected by a detector. It is a very useful technique used to identify the elements in different samples.

When an atom absorbs energy (e.g., from heat, electrical energy, or light), its electrons get excited to higher energy levels. These excited electrons are unstable and eventually return to their ground state or a lower energy level. During this transition, the electrons release energy in the form of photons. The wavelength (colour) of the emitted light depends on the energy difference between the two levels. The spectrum appears as a series of discrete lines, each corresponding to a specific wavelength.

Each element has a unique emission spectrum, often referred to as its "fingerprint."

These lines are known as spectral lines and represent the quantized energy levels within the atom.

18.6 Atomic Absorption Spectrum

An atomic absorption spectrum is observed when free atoms in the ground state absorb specific wavelengths of light and get excited to higher energy levels. This absorption leads to dark lines in the spectrum at those specific wavelengths.

Atomic emission and absorption spectra are always line spectra and give same information as shown in figure that placement of the spectral lines according to wavelength is same in emission and absorption spectrum of potassium. Only difference in spectrum is that in AES bright lines appear on dark background, and in AAS dark lines are visible on bright background.

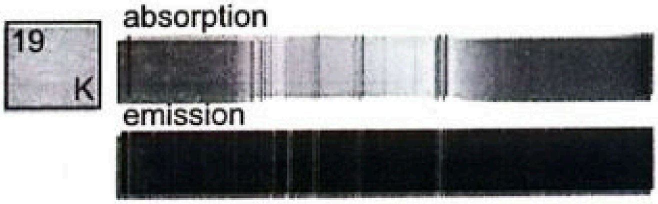


Fig 18.6: Atomic absorption and emission spectra of potassium

18.7 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique based on re-orientation of atomic nuclei with non-zero nuclear spins in an external magnetic field. This re-orientation occurs with absorption of electromagnetic radiation in the radio frequency region from roughly 4 to 900 MHz, which depends on the isotopic nature of the nucleus and increased proportionally to the strength of the external magnetic field. Notably, the resonance frequency of each NMR-active nucleus depends on its chemical environment. As a result, NMR spectra provide information about individual functional groups present in the sample, as well as about connections between nearby nuclei in the same molecule. As the NMR spectra are unique or highly characteristic to individual compounds and functional groups, NMR spectroscopy is one of the most important methods to identify molecular structures, particularly of organic compounds.

18.7.1 Principle

All those nuclei which are Nuclear magnets or NMR active have a random orientation of their spins. When an external magnetic field is applied all these nuclei acquire two spin states; one with low energy ,and aligned with applied magnetic field (B^0)and the other with high energy and against the applied magnetic field. The energy difference between these two energy states corresponds to the radio wave frequency. By absorbing the same energy to flip their spins certain equivalent nuclear magnets thus resonate. When a spin returns to its ground state, the absorbed energy is emitted at the same frequency level. The emitted radio frequency signal gives the NMR spectrum of the compound.

18.7.2 NMR active nuclei

NMR active nuclei are those possessing a property called 'spin', whereby a charged nucleus spins about an axis and generates its own magnetic dipole moment, including hydrogen (^1H), the ^{13}C isotope of carbon, the ^{19}F isotope of fluorine, and the ^{31}P isotope of phosphorus, all have magnetic moments and therefore can be observed by NMR. Organic chemists use ^1H and ^{13}C NMR.

To be NMR-active, a nucleus must have a non-zero nuclear spin quantum number ($I \neq 0$). It is this non-zero spin that enables nuclei to interact with external magnetic fields and show signals in NMR. Atoms with both an odd number of protons and an odd number of neutrons, or an odd sum of protons and neutrons, exhibit half-integer values for the nuclear spin quantum number ($I = 1/2, 3/2, 5/2$, and so on). These atoms are NMR-active.

18.8 ^1H NMR (Proton NMR)

It is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance, in order to determine the structure of its molecules.

18.8.1 Use of Deuteratedsolvent

Deuterated (deuterium = ^2H, often symbolized as D) solvents especially for use in NMR are preferred, e.g. deuterated water, D_2O, deuterated acetone, $(CD_3)_2CO$. In the non-hydrogen solvents CS_2 and CCl_4 are frequently usedin order to avoid the interference of solvent protons in the analysis.

18.8.2 Tetramethylsilane (TMS) as standard of chemical shift

TMS (Tetra methyl silane $Si(CH_3)_4$) is a tetrahedral molecule, with all protons being chemically equivalent and highly shielded by electrons due to lesser electronegativity of silicon ,giving one single signal, used to define a chemical shift (δ) = 0 ppm. Proton NMR spectra of most organic compounds are characterized by chemical shifts in the range +14 to -4 ppm and by spin-spin coupling between protons.

18.8.3 Nuclear spin flipping and chemical shift

Nuclear spin flipping is a quantum mechanical phenomenon where certain atomic nuclei absorb energy from an external source, leading to a change in their spin state.

If the nucleus is irradiated with electromagnetic radiation of the proper frequency, it can absorb energy and "flip" from the lower-energy spin state to the higher-energy state. This energy transition induces a change in the nuclear spin states.

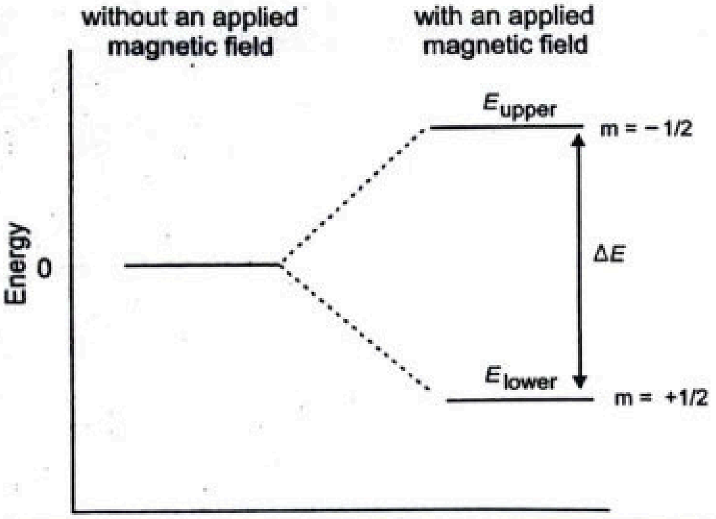


Fig 18.7: effect of external magnetic field

In nuclear magnetic resonance (NMR) spectroscopy, the chemical shift is the difference between the resonant frequency of an atomic nucleus and a standard in a magnetic field. It's expressed in parts per million (ppm) and is a key property for determining a molecule's structure.

The exact frequency required for resonance depends on the strength of the external magnetic field, the identity of the nucleus, and the electronic environment of the nucleus. The number of peaks tells you the number of different environments the hydrogen atoms are in. The ratio of the areas under the peaks tells the ratio of the numbers of hydrogen atoms in each of these environments.

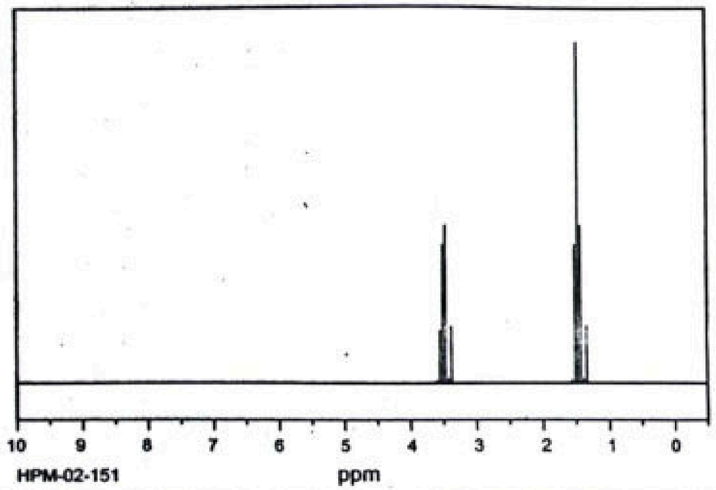


Fig 18.8: Proton NMR of Ethyl Chloride

Molecules have simple spectra. The spectrum of ethyl chloride shows a peak equivalent to three alike protons of methyl (CH_3) at 1.5 ppm and another at 3.5 ppm, corresponding to two similar protons of methylene with respect to reference peak. Two protons that absorb at 3.5 ppm are more near to highly electronegative chlorine, experience more external magnetic field due to more de-shielding as compared to the three protons absorbing at 1.5 ppm.

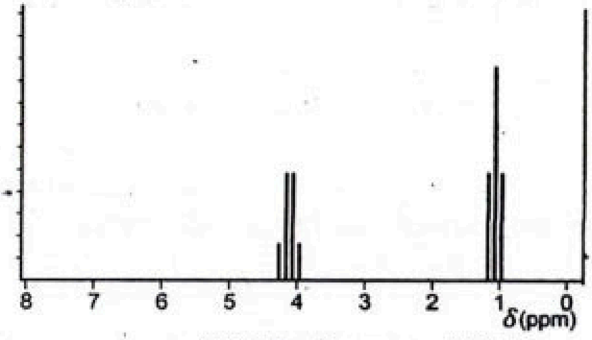
The spectrum of benzene consists of a single peak at 7.2 ppm due to the diamagnetic ring current. when the electron density is high around the nucleus, the opposing magnetic field to electrons is also bigger which in turn gives huge shielding. Deshielding is when electron density falls around the nucleus, the magnetic field opposing it reduces and then the nucleus feels more of the external magnetic field.

CONCEPT ASSESSMENT EXERCISE 18.3

Q1. How many peaks do you expect in the proton NMR of benzene?

Q2. Why the peak of two protons attached with alpha carbon of ethyl alcohol have greater chemical shift than the ethylene group of ethyl chloride?

Q3. Given is a H-NMR spectrum of an organic compound "x" with a molecular formula $C_4H_{10}O$. Deduce its structural formula by using its H-NMR spectrum.



H-NMR of compound "x"

18.8.4 Environment of a given proton (Multiplicity)

In hydrogen-1 NMR, all the hydrogen atoms attached to the same carbon have the same environment. However, hydrogen atoms on different carbons can also have the same environment, if the carbon atoms they are bonded to, exactly the same chemical groups with respect to each other.

If there are no hydrogens on the adjacent atoms, then the resonance will remain a single peak, a singlet. If there is one hydrogen on the adjacent atoms, the resonance will be split into two peaks of equal size, a doublet. If there are two equivalent protons are present on the adjacent carbon atom it will give a triplet signal, and if three protons present on adjacent C atom a quartet appears. This is governed by (N+1) rule and gives a valuable information about the neighbourhood of a given proton, shown in the figure.

Summary of Signal Splitting Patterns in ¹H NMR Spectroscopy

The pattern is that n protons split the signal into n+1 peaks, which is known as the **n+1 rule.**

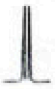
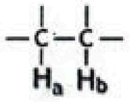
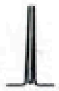
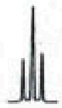
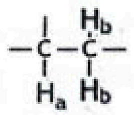
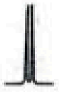
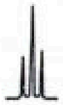
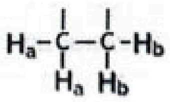
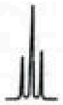
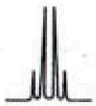
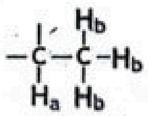
Multiplicity	N + 1	H_a	Signal	H_b	N + 1	Multiplicity
Doublet	1 + 1 = 2		 $-\overset{\vert}{\underset{H_a}{C}}-\overset{\vert}{\underset{H_b}{C}}-$		1 + 1 = 2	Doublet
Triplet	2 + 1 = 3		 $-\overset{\vert}{\underset{H_a}{C}}-\overset{H_b}{\underset{H_b}{C}}-$		1 + 1 = 2	Doublet
Triplet	2 + 1 = 3		 $H_a-\overset{\vert}{\underset{H_a}{C}}-\overset{\vert}{\underset{H_b}{C}}-H_b$		2 + 1 = 3	Triplet
Quartet	3 + 1 = 4		 $-\overset{\vert}{\underset{H_a}{C}}-\overset{H_b}{\underset{H_b}{C}}-H_b$		1 + 1 = 2	Doublet

Fig 18.9: Multiplicity of NMR peaks

This is why in the given spectrum of ethyl chloride, CH_2 peak is a quartet because of 3 neighbouring protons and the CH_3 peak is a triplet due to 2 neighbouring protons of CH_2.

18.8.5 Proton exchange by D_2O

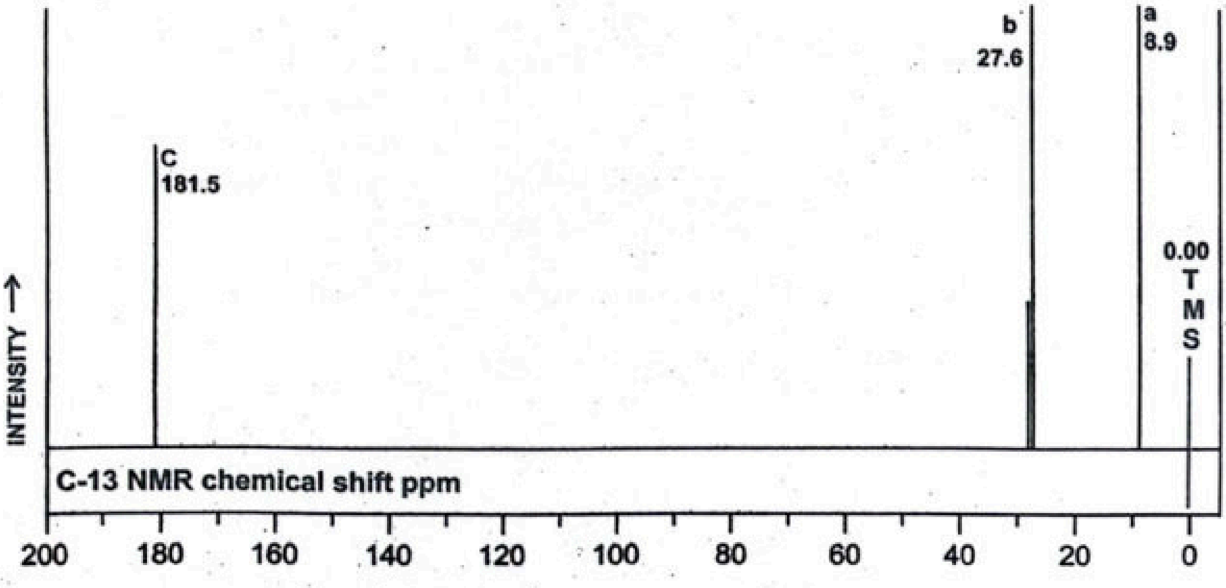
When an NMR sample that contains O-H or N-H protons is shaken with deuterium oxide (D_2O), the O-H or N-H protons exchange with the deuterium atoms in D_2O. This causes the corresponding NMR signals to disappear, which suggests the presence of an O-H or N-H proton. This is because deuterium is NMR inactive.

CONCEPT ASSESSMENT EXERCISE 18.4

Q1. How many peaks do you expect in the NMR spectrum of acetone? If it is a single peak describe the reason.

Q2. What would be the difference between the proton NMR spectrum of ethyl alcohol and ethyl chloride? Why is the chemical shift of OH proton in alcohol greater?

Q3. By using the information given in the C-13 NMR of the compound "y" answer the given questions.



C-13 NMR of the compound "y"

a. How many carbon atoms are present in compound "y"?
b. What is the chemical shift of CH_3 carbon out of these three values?
c. One C is dirty attached to two oxygen atoms, can you tell it's chemical shift?
d. Deduce the possible structure of compound "y" if its molecular mass is 74 amu.

18.9 Carbon-13 NMR

About 1% of all carbon atoms are the ^{13}C isotope; the rest (apart from tiny amounts of the radioactive C-14) is C-12. ^{13}CNMR is based on the magnetic properties of the ^{13}C nuclei. Carbon-13 nuclei are NMR active, hence a ^{13}C nucleus can behave as a small magnet. C-12 nuclei do not have this property.

It means that it can also be aligned with an external magnetic field(B^0) or opposed to it. The alignment where it is opposed to the field is less stable (at a higher energy). It is possible to make it flip from the more stable alignment to the less stable one by supplying exactly the right amount of energy. It is possible to detect this interaction between the radio waves of just the right frequency and the ^{13}C nucleus as it flips from one orientation to the other as a peak on a graph. This flipping of the ^{13}C nucleus from one magnetic alignment to the other by the radio waves is known as the resonance condition.

18.9.1 Chemical shift in ^{13}C-NMR

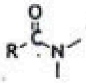
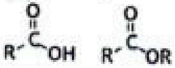
A peak at a chemical shift of 60 is said to be downfield of TMS. The further to the left a peak is, the more downfield it is. The chemical shifts for ^{13}C NMR are much bigger than for proton-NMR. In ^{13}C NMR, they range up to about 200 ppm depending on the environment of carbon.

18.9.2 Deduction of possible structure of molecule using ^{13}C-NMR

^{13}C-NMR of each different molecule is distinct. By analysing the peaks in spectrum and comparing these peaks with standard references can give the information about the types of carbon atoms present in the molecule. By a careful study of chemical shifts of all peaks in spectrum we can be able to recognise carbon atoms, or from where they belong i.e alkane, alkenes, alkynes and aromatic carbon atoms can easily be recognised based on their specific chemical shift range. The symmetrical molecules are simple and have less peaks in their NMR spectrum due to their identical positions.

Table 18.3: Chemical shift values of ^{13}C-NMR

Approximate Values of Chemical Shifts for ^{13}C NMR

$(CH_3)_4Si$	0	* I–C	-20 - 40		100 - 150		155 - 185
$R-CH_3$	8 - 30	Br–C	25 - 65		110 - 170		
$R-CH_2-R$	15 - 55	Cl–C	35 - 80				165 - 185
R_3CH	20 - 60	O–C	40 - 80	C=N	150 - 170		
R_4C	30 - 50	N–C	30 - 65	C≡N	110 - 140		190 - 220

Comparing these peak values with the appeared spectrum we can predict the structure of the molecule. Talking in general one spectroscopic technique solely does not fully work to structural elucidation. Combined information obtained from different spectroscopic techniques along with mass Spectrometry help resolve the structural formulae of organic compounds.

Let us discuss the ^{13}C-NMR spectrum of ethanol. In ethanol there are two distinct C atoms one is attached with highly electronegative O atom and the other with just three hydrogens and an alpha carbon atom. Carbon atom attached with the oxygen atom is highly de-shielded and represents a higher chemical shift and appears at 58 ppm. The second carbon atom which is methyl carbon, is slightly experiencing inductive effect thus it is better shielded. It's peak appears at 18 ppm.

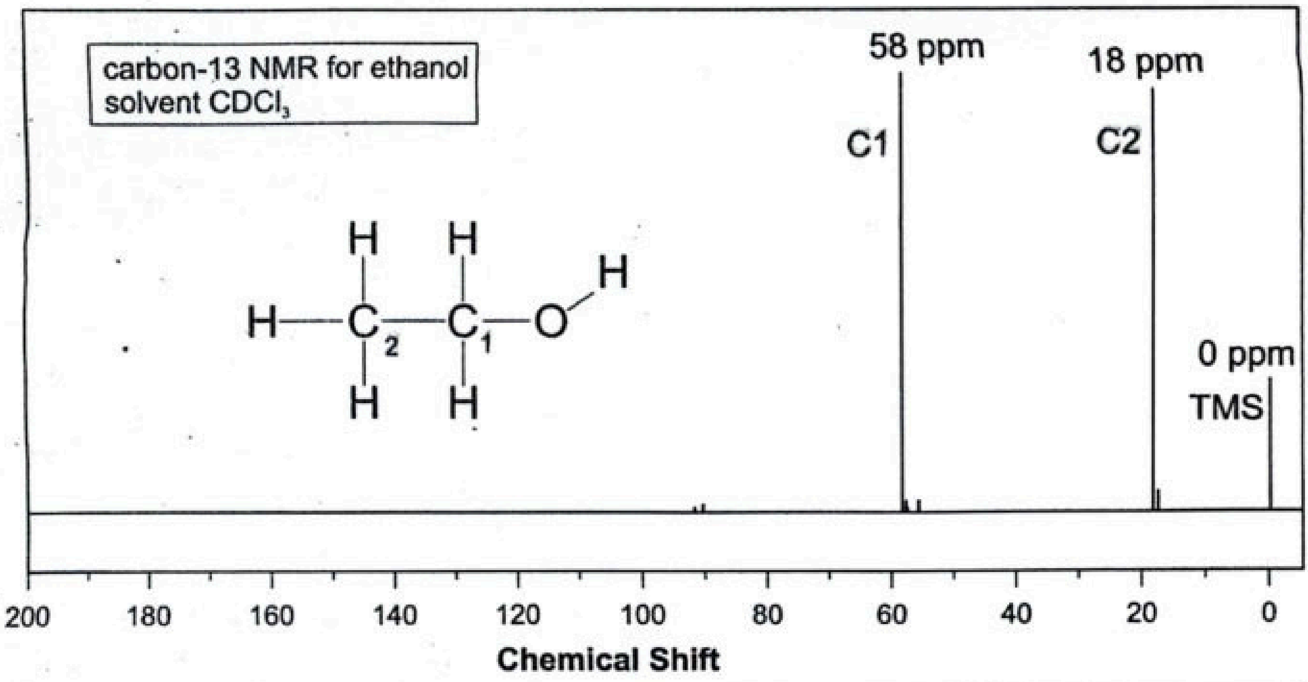


Fig 18.10: ^{13}C-NMR of ethanol

Lets take example of the acetone. In spite of having 3 carbon atoms, the spectrum is showing just two peaks. Both the methyl carbons are identical and better shielded appear at 30.8 ppm. The carbonyl carbon being more de-shielded shows it's peak at 206 ppm due to attachment with highly electronegative O atom.

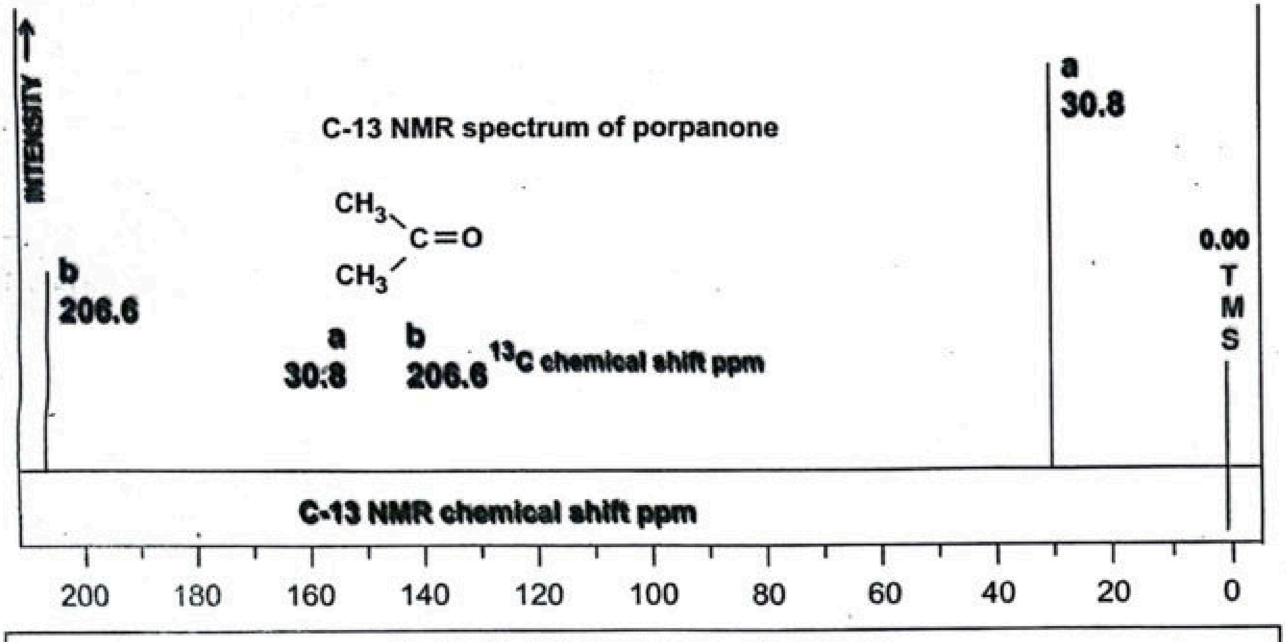


Fig 18.11: NMR spectrum of acetone

In the ^{13}C-NMR spectrum, each unique carbon environment in the molecule gives a separate peak. The number of peaks in the spectrum corresponds to the *number of chemically* different carbon atoms.

18.9.3 Steps to Predict the Number of Peaks

- Look for symmetry in a molecule. Symmetrical carbons are equivalent and give one peak.
- Identify each unique carbon medium. Carbons in different chemical environments (different neighbouring atoms or bonds) produce distinct peaks.

Example 1: Ethanol (C_2H_5OH)

Structure: CH_3CH_2OH

Spectrum Analysis:

- CH_3 (methyl group): The carbon in the methyl group is bonded to three hydrogens and one carbon.
- CH_2 (methylene group): The carbon in the methylene group is bonded to two hydrogens, one carbon, and one oxygen.
- OH (hydroxyl group): Although the oxygen doesn't appear directly in the 13C-NMR spectrum, the carbon bonded to it will have a distinctive chemical shift due to the electronegativity of oxygen.

Number of Unique Carbons: 2

- Methyl carbon: One peak
- Methylene carbon: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbon: Appears around 10-20 ppm
2. Methylene carbon: Appears around 50-60 ppm

Example 2: Acetone (C_3H_6O)

Structure: $(CH_3)_2CO$

Spectrum Analysis:

- CH_3 (methyl groups): Both methyl groups are equivalent and bonded to the same carbonyl carbon.
- CO (carbonyl group): The carbonyl carbon is in a distinct environment due to its double bond with oxygen.

Number of Unique Carbons: 2

- Methyl carbons: One peak
- Carbonyl carbon: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbons: Appear around 20-30 ppm
2. Carbonyl carbon: Appears around 190-210 ppm

Example 3: Butane (C_4H_{10})

Structure: $CH_3CH_2CH_2CH_3$

Spectrum Analysis:

- CH_3 (methyl groups): The two terminal methyl groups are equivalent.
- CH_2 (methylene groups): The two methylene groups are equivalent.

Number of Unique Carbons: 2

- Methyl carbons: One peak
- Methylene carbons: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbons: Appear around 10-20 ppm
2. Methylene carbons: Appear around 20-40 ppm

Example 4: Benzene (C_6H_6)

Structure: C_6H_6

Spectrum Analysis:

- Aromatic Carbons: All six carbons in the benzene ring are equivalent due to the symmetry of the molecule.

Number of Unique Carbons: 1

- Aromatic carbons: One peak

Expected Peaks: 1 peak

Spectrum:

- Aromatic carbons: Appear around 120-140 ppm

CONCEPT ASSESSMENT EXERCISE 18.5

Q1. How many types of C atoms are present in ethoxy ethane (diethyl ether)? Draw an approximate ^{13}C-NMR spectrum of this molecule taking help from the given table of chemical shifts.

Q2. Why are the chemical shifts in ^{13}C-NMR spectrum much greater as compared to the ^{1}H-NMR?

KEY POINTS

- Spectroscopy is a technique used for structural elucidation of the molecule. It is based on the interaction of atoms or molecules with electromagnetic radiaction.
- Mass Spectrometry is the technique used for finding out molecular masses, fragment mass, and relative atomic masses of isotopes of an element.
- The total number of rings and pi-bonds can be determined by the use of index of hydrogen deficiency (IHD) or degree of unsaturation in an organic compound.
- IR spectroscopy makes use of interaction of infrared radiations with organic molecule. It is used to analyse the functional group present in an organic compound.
- In UV-Visible spectroscopy the UV and visible light absorption by any compound is measured. It's typical range of wavelength is from 200 nm to 800 nm. It is used to find unsaturation and conjugation in an organic compound.

- The coloured compounds absorb small part in visible (400 nm-800 nm) region of electromagnetic radiations and transmit the rest of the wavelengths, thus the colour appears.
- Atomic emission spectroscopy is a powerful technique to quantify the elements by the measurement of the specific wavelength of light.
- NMR active nuclei are those possessing a property called 'spin', whereby a charged nucleus spins about an axis and generates its own magnetic dipole moment.
- TMS (Tetramethylsilane $Si(CH_3)_4$) is a tetrahedral molecule, with all protons being chemically equivalent and highly shielded by electrons. It works as a reference whose chemical shift is zero.
- When an NMR sample that contains O-H or N-H protons is shaken with deuterium oxide (D_2O), the O-H or N-H protons exchange with the deuterium atoms in D_2O, this is called deuterium exchange.

Reference

1. Organic spectroscopy and chromatography by M Younas, 2011
2. Introduction to Spectroscopy Donald L Pavia, 2008

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Select the correct choice from the given options.
Spectroscopy is a technique in which matter interacts with:

a) Light b) Sulphuric acid c) Magnetic field d) Plasma

ii. Which technique is used to detect conjugation in an unsaturated hydrocarbon.

a) NMR b) UV-Visible spectroscopy
b) Mass Spectrometry d) IR spectroscopy

iii. Coloured compounds absorb in the wavelength between:

a) 1nm to 200 nm b) 200 to 400 nm c) 400 to 600 nm d) 400 to 800 nm

iv. IR Spectroscopy is used to detect:

a) Functional group b) Conjugation c) Type of hydrogens d) Number of rings

v. Which radiations are used in NMR spectroscopy?

a) UV b) Visible c) X-rays d) Radio waves

vi. Which bond shows greater chemical shift in 1H NMR?

a) O-H b) N-H c) C-H d) SI-H

2. Short Answer Questions

i. Write basic principle of IR spectroscopy.
ii. How can you identify functional group of an organic compound by using IR spectroscopy?
iii. With the help of UV- Visible spectrum of an unseen compound, how can you predict it's colour?
iv. Draw a rough UV-Visible spectrum of a compound which is yellow in colour.
v. Explain principles of AES and AAS.
vi. How is atomic absorption spectroscopy different from atomic emission spectroscopy?
vii. What are NMR active nuclei? How can you tell about a nucleus, whether it is NMR active or not?
viii. What is the effect of external magnetic field on the spinning nuclei?
ix. Explain chemical shift.
x. Why do the peaks in NMR spectrum split into doublet, triplets or quartets etc?
xi. What is deuterium exchange method and what is it's use?
xii. Why does acetone give a single peak in proton-NMR and two peaks in ^{13}C-NMR? Explain with reason.
xiii. What is TMS? Tell its significance?
xiv. Why deuterated solvents are used in proton NMR spectroscopy?

3. Long Answer Questions

i. Write the details of IR spectroscopy including its principle, spectrum and uses.
ii. Explain the uses of UV-visible spectroscopy.
iii. Nuclear magnetic resonance is a powerful tool for the elucidation of structures of organic compounds. Defend the statement.
iv. How is PMR different from CMR?

PROJECT

Draw approximate proton NMR spectrum and ^{13}C-NMR spectrum of 3-pentanone.