30

SPECTROSCOPY-2 NMR

Student Learning Outcomes

[C-12-E-19 to C-12-E-28]

- Explain the use of tetramethylsilane, TMS, as the standard for chemical shift measurement.
- Recognize the need for deuterated solvents, e.g., $CDCl_3$, when obtaining a proton NMR spectrum.
- Analyze the different environments of protons present in a simple molecule using a ^1H (proton) NMR spectrum.
- Predict the chemical shifts and splitting patterns of the protons in a given molecule.
- Use a ^1H (proton) NMR spectrum to deduce relative numbers 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.
- Describe the identification of O-H and N-H protons by proton exchange using D_2O.
- Deduce possible structures for the molecule.
- Predict the number of peaks in a ^{13}C NMR spectrum for a given molecule.
- Analyze the different environments of carbon atoms present in a simple molecule using a ^{13}C NMR spectrum.
- Use a ^{13}C NMR spectrum to deduce possible structures of a simple molecule.

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique which is extensively used in chemistry, polymer industry, study of proteins and natural products, environment monitoring, and medical field. In chemistry, this technique is particularly used for the identification of organic compounds and determination of their structures. Proton (^1H) NMR and carbon-13 (^{13}C) NMR are two most commonly used methods in this regard.

30.1 PRINCIPLE OF PROTON (^1H) NMR

NMR spectroscopy is based on the magnetic properties (nuclear spin) of nuclei. Atoms with odd mass numbers usually show signals on NMR. The atomic nuclei of these atoms, such as hydrogen (^1H) and carbon-13 (^{13}C) behave like a tiny magnet. In the absence of a magnetic field, all the nuclei have random orientation and have the same energy. When placed in a strong magnetic field, these nuclei align themselves either with or against the field and give rise to two spin states i.e., low energy state and high energy state **(Figure 30.1)**.

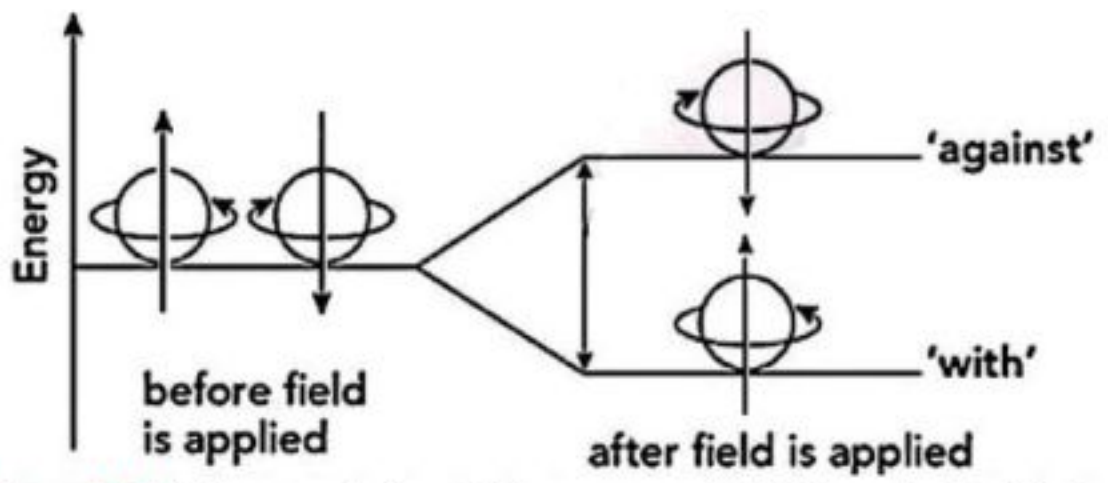


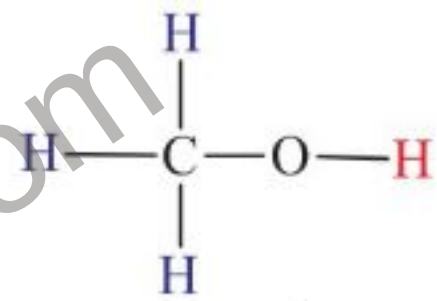
Figure 30.1 Alignment of nuclei in a magnetic field and spin flipping

Did You Know?

The atoms with even atomic and mass numbers have equal number of protons and neutrons in their nuclei. As their magnetic fields cancel out each other, there is no net magnetic field of such nuclei e.g., ^{12}C.

By irradiating with radio waves, the nuclei at low energy state can absorb energy and move to higher energy state (spin flipping). When they return to their original states, they emit energy which is detected and converted into an NMR spectrum (plural spectra). The exact energy required to flip a nucleus depends upon its position in a compound and the surrounding atoms, collectively known as the molecular environment. Thus, NMR can be used to identify different hydrogen atoms lying in different environments within one molecule. For example, in the methanol (CH_3OH) molecule, three hydrogen atoms are attached to a carbon atom and one hydrogen atom is bonded to an oxygen atom. The methyl ($-CH_3$) hydrogens and hydroxyl (O-H) hydrogen lie in different environment, so they absorb different amount of energy (different frequency of radio waves) for flipping.

Nuclei lying in different environments can be flipped by using the radio waves of same frequency, if the strength of magnetic field is varied.



methanol

30.2 SOLVENTS FOR NMR SPECTROSCOPY

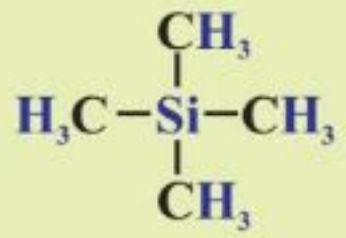
In the ^1H NMR analysis the sample to be analyzed is dissolved in excess solvent to prepare a solution. Ordinary solvents contain hydrogen atoms which produce strong signals and cause interference in the spectrum of the sample. To avoid this problem, deuterated solvents such as $CDCl_3$ (deuterated chloroform) or CD_3OD (deuterated methanol), are used. If regular $CHCl_3$ is used as a solvent, the signal from its single proton (^1H) would be intense enough to completely overlap and mask the weaker signals arising from the protons in the actual sample. In $CDCl_3$, hydrogen (H) is replaced with its isotope Deuterium (D). Deuterium requires a different frequency of radio waves for flipping, hence it neither absorbs radio frequency provided to the sample solution nor its peak appears in the ^1H NMR spectrum. This makes the solvent "silent", and only the signals of the sample are observed in the spectrum.

30.3 CHEMICAL ENVIRONMENT AND CHEMICAL SHIFT (δ)

Chemical shift is an important parameter in NMR spectroscopy and represents the position of a signal relative to a reference compound. Tetramethylsilane, $Si(CH_3)_4$ (commonly known as TMS) is used as the standard reference and its signal is assigned a value of 0.0 ppm. All other signals due to the hydrogen nuclei (protons) in the sample compounds are measured relative to this TMS zero point. The position of a peak in a ^1H NMR spectrum relative to TMS peak is called the chemical shift (δ) which is measured in parts per million (ppm) unit. Chemical shift indicates the electronic environment of a proton. Protons in different environments have different δ values, while those lying in same environment have same δ value.

Did You Know?

TMS is particularly suitable as a standard compound for NMR because all 12 of its protons have the same chemical environment and produce a single sharp peak. Moreover, the protons on TMS appear at the extreme right region of the spectrum (due to the low electronegativity of silicon) and do not overlap with most organic proton signals. TMS is chemically inert and volatile, which makes it easy to remove after use.



Tetramethylsilane (TMS)

For example, in the ^{1}H NMR spectrum of methanol **(Figure 30.2)**, the relative position of peak for methyl (-CH_3) hydrogens at 3.35 ppm compared to 0.0 ppm of TMS is the chemical shift of these protons. Similarly, O-H hydrogen of methanol has a chemical shift of 4.80 ppm.

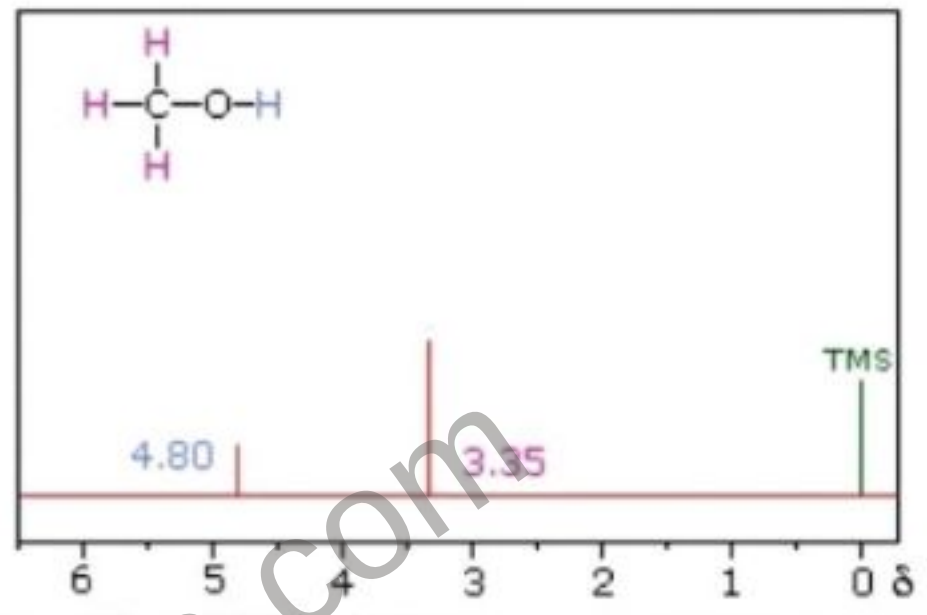
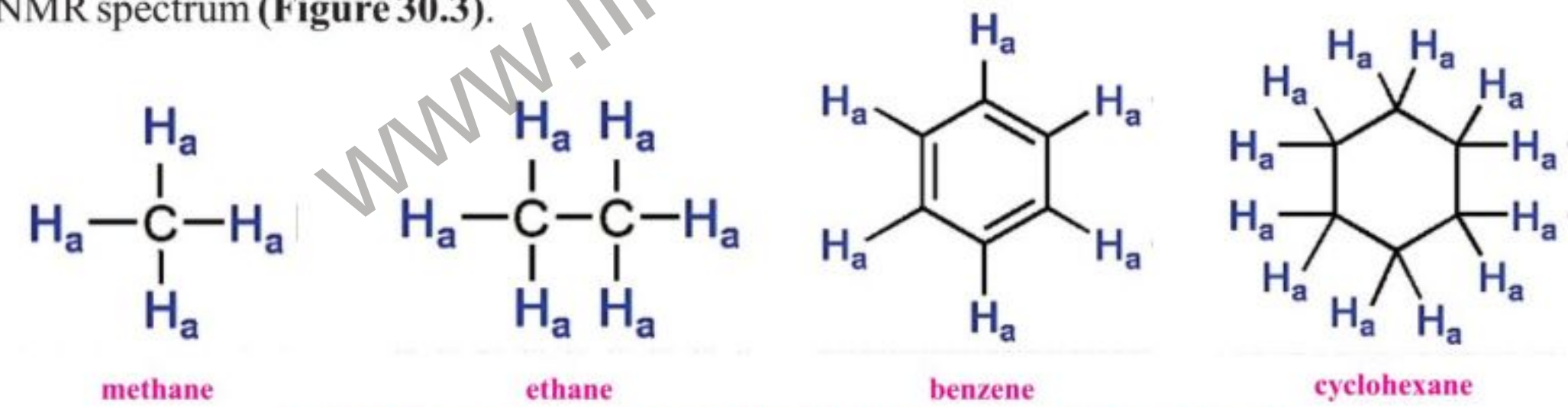


Figure 30.2 ^{1}H NMR Spectrum of Methanol

Protons (^{1}H) in a molecule are surrounded by electrons and this electron density affects the appearance of an NMR spectrum. Protons in different parts of a molecule are in different "environments" because of the atoms and bonds near them. All the protons (^{1}H) found in chemically identical environments within a molecule are chemically equivalent, and they exhibit the same chemical shift in the ^{1}H NMR spectra of that molecule. All the protons in TMS, methane, ethane, benzene and propanone (acetone) are chemically equivalent. Each of these compounds gives rise to a single absorption peak in its ^{1}H NMR spectrum **(Figure 30.3)**.



methane **ethane** **benzene** **cyclohexane**

All the hydrogen atoms in these molecules have same chemical environment

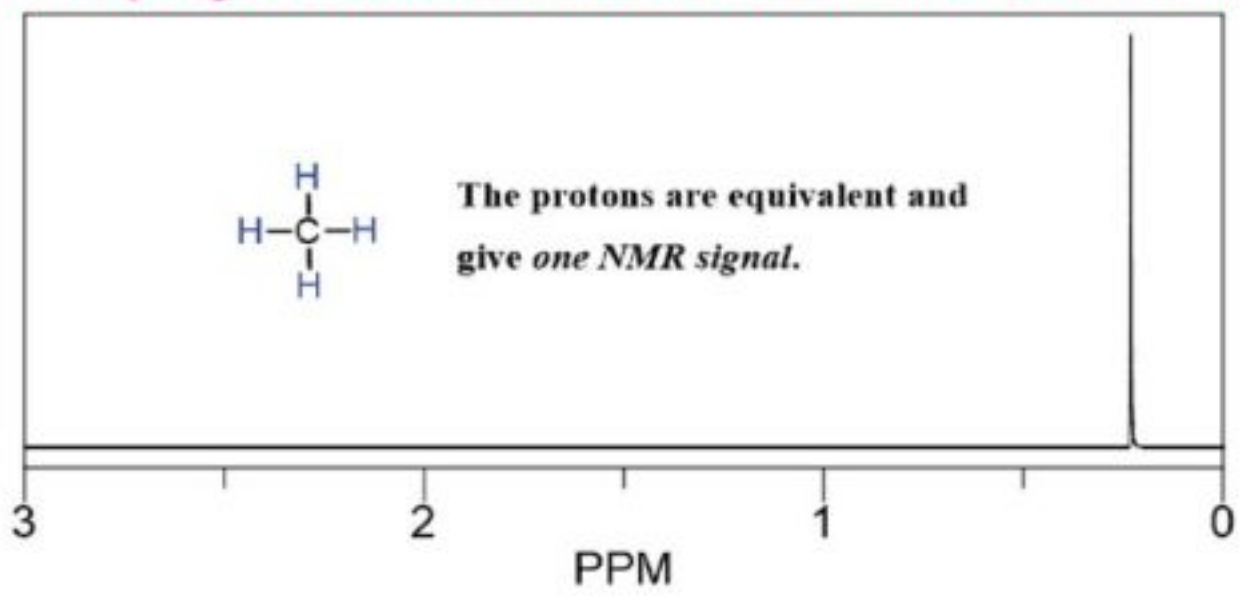
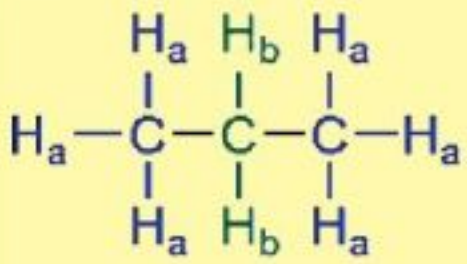
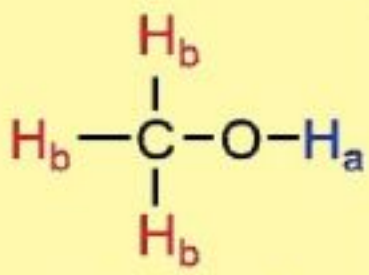


Figure 30.3 1H NMR spectrum of methane

On the other hand, a molecule which has sets of protons that are chemically different from one another, have different chemical shift and give rise to more than one peaks.

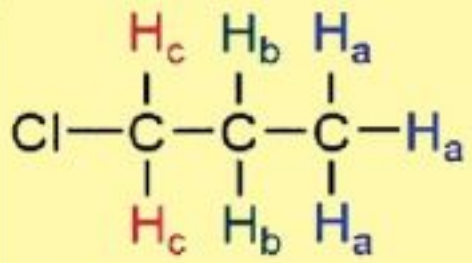


propane

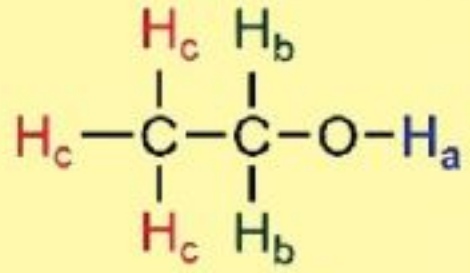


methanol

Molecules having two different chemical environments for protons



1-chloropropane



ethanol

Molecules having three different chemical environments for protons

For example, a proton on a -CH_3 group is different from the one on -CH_2- and O-H in ethanol (C_2H_5OH) molecule. Similarly, all the three protons of -CH_3 have same environment, while the two protons of -CH_2- have same environment. The chemical shift of a proton (^1H) is affected by the electron density of its surrounding chemical environment. Protons surrounded by high electron density (alkyl groups) have lower chemical shift values, whereas protons surrounded by a low electron density (near electronegative atoms like F, O, N, Cl etc.) appear at high chemical shift values. For example, methyl (-CH_3) protons in the ^1H NMR spectrum of methanol appear at 3.35 ppm due to a higher electron density around them as compared to O-H proton, which appears at 4.80 ppm due to the presence of electronegative oxygen next to it **(Figure: 30.2).**

A ^1H NMR spectrum has a chemical shift (δ) range of 0 – 12 ppm. The chemical shifts for different environments of protons have been given in **Table 30.1.** This data table is helpful in identifying and predicting the environment of protons in ^1H NMR spectrum of an unknown compound.

Table 30.1 Chemical shifts of some common types of protons

Environment of Proton	Examples	Chemical Shift Range δ (ppm)
Alkyl (alkanes)	–CH_3, –CH_2–, >CH–	0.5 – 1.5
Alkyl next to C=O (ketone/ester)	CH_3–C=O, –CH_2–C=O, >CH–C=O	2.0 – 2.6
Alkyl next to aromatic ring	CH_3–Ar, –CH_2–Ar, >CH–Ar	2.3 – 3.0
Alkyl next to electronegative atom (halogenoalkanes, alcohols)	CH_3–O, –CH_2–O, CH_3–Cl, –CH_2–Cl	3.0 – 4.5
Vinylic (alkenes)	>C=CHR	4.5 – 6.0

Aromatic (attached to aromatic ring)	Ar–H	6.5 –9.0
Aldehyde	RCHO	9.0 – 10.0
Alcohol	ROH	0.5 – 6.0
Phenol	Ar–OH	4.5 – 7.0
Carboxylic acid	RCOOH	9.0 – 13.0
Alkyl amine	R–NH–	1.0 – 5.0
Aryl amine	Ar–NH_2	3.0 – 6.0
Amide	RCONHR	5.0 – 12.0

Quick Check 30.1

a) Explain why the 12 protons in TMS produce only a single peak.
b) Identify how many chemical environments are there for protons in the following molecules. Also predict the expected chemical shift of the protons in each environment.
i) 1,1,2,2-dichloroethane ii) propane iii) propan-2-ol iv) butan-2-one
e) What proton environment does a signal at δ 7.5 ppm likely represent?

30.4 INTERPRETATION OF ^{1}H NMR SPECTRA

30.4.1 Low-Resolution ^{1}H NMR Spectra

A low-resolution ^{1}H NMR spectrum provides three main pieces of information about the structure of a compound; the number of different proton environments in the molecule, types of these environments, and the relative number of protons in each environment. While interpreting a ^{1}H NMR spectrum, three parameters are carefully analysed; total number of peaks in the spectrum, position of each peak (chemical shift δ), and the area under each peak.|The number of peaks in a ^{1}H NMR spectrum corresponds to the number of different chemical environments for protons present in the molecule. Each peak in the spectrum stands for a different chemical environment.

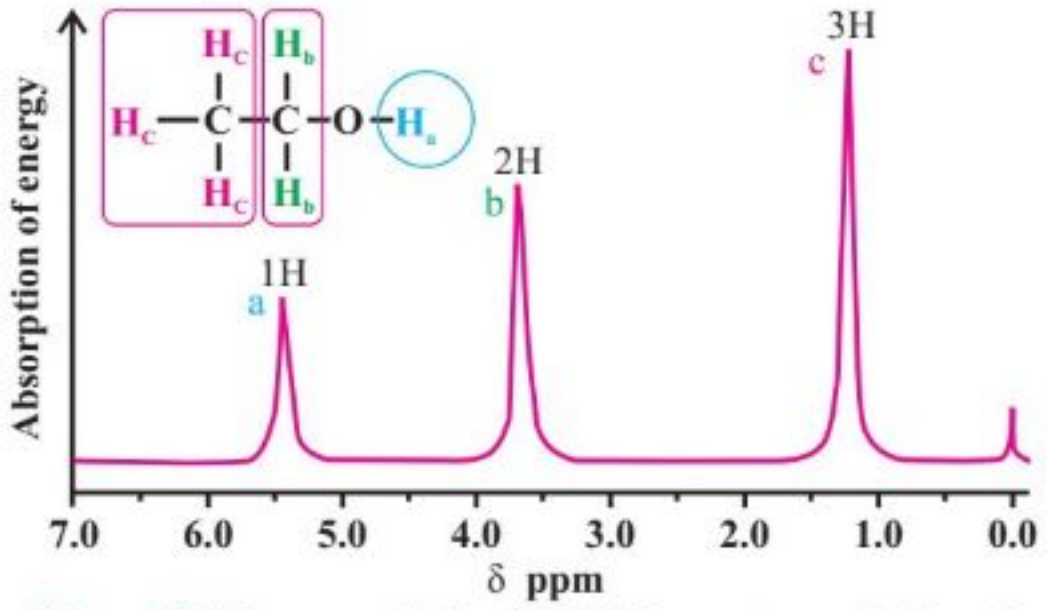


Figure 30.4 Low-resolution ^{1}H NMR spectrum of ethanol

Low-resolution ^{1}H NMR spectrum of ethanol (CH_3CH_2OH) has been illustrated in **Figure 30.4**. The spectrum has three peaks which shows that there are three different proton environments in ethanol molecule *i.e.*, the CH_3 protons, the CH_2 protons, and the OH proton.

Chemical shift of each peak corresponds to the type of chemical environment of protons giving rise to that peak. The type of proton environment can be identified by comparing the chemical shifts to standard values **(Table 30.1)**. In the spectrum of ethanol **(Figure 30.4)**, the peak at 5.4 ppm represents the presence of electrons in less electron density environment (OH). The peak having chemical shift 3.7 ppm can be identified as $–CH_2–$ next to oxygen while the signal at 1.2 ppm can be identified as methyl group ($–CH_3$ protons).

The **area under each peak** is proportional to the **number of protons** giving rise to that peak.

In the ^{1}H NMR spectrum of ethanol **(Figure 30.4),** peaks are labeled 1H, 2H and 3H to show relative peak areas in 1:2:3 ratio. This ratio matches with the number of protons in each environment (-OH has 1, $–CH_2$ has 2 and $–CH_3$ has 3 protons). Analysis of the above spectrum shows that there are three kinds of chemical environments for protons, so three signals are observed. The intensity ratio shows that they are present in the ratio of 1:2:3. **The sum of number of each type of protons gives the total number of protons present in the molecule**. Hence, there are total 6 hydrogen (1+2+3) atoms in an ethanol molecule.

Quick Check 30.2

a) What does the **number of signals** in a ^{1}H NMR spectrum represent?
b) Predict the number of peaks that will appear in the ^{1}H NMR spectra of the following molecules?
(i) 1,1,2,2-dichloroethane (ii) butane (iii) propan-2-ol (iv) pentan-3-one (v) benzene
c) Predict the number of peaks and their chemical shifts in the ^{1}H NMR spectrum of bromoethane (CH_3-CH_2-Br).
d) How many signals will be observed in the ^{1}H NMR spectrum of 2-chlorobutane. Draw its structure and identify the hydrogen atoms which will show the highest value of chemical shift.
e) What does the peak area in ^{1}H NMR represent?

30.4.2 High-Resolution ^{1}H NMR and Splitting of Peaks

The NMR signals of protons are not only affected by the nearby electrons, but also by protons on the adjacent atoms. This effect can be observed by a high-resolution NMR. When a high-resolution ^{1}H NMR spectrum of a molecule is studied, it reveals that each peak is often made up of a cluster of sub-peaks. This is due to the splitting of each signal due to the presence of protons (^{1}H) on adjacent carbon atoms. The splitting of signals into multiple peaks (e.g., doublets, triplets, quartets) indicates the number of protons (^{1}H) on the adjacent (neighbouring) carbon atom. Number of sub-peaks can be calculated by using '**n+1**' rule. A signal usually splits into n+1 sub-peaks, where n is the number of protons on adjacent carbon atoms.

Number of sub-peaks = n+1

(Where n = the number of protons on the adjacent carbon atom).

In the high-resolution ^{1}H NMR spectrum of ethanol, the -CH_3 peak is split into three sub-peaks (known as **triplet**) because the number of protons on adjacent carbon is 2 (2+1=3). Similarly, -CH_2- peak is split into four sub-peaks (known as a **quartet**) because there are 3 protons on its adjacent carbon (3+1=4). The -OH signal is not split because hydrogen is bonded to an oxygen atom instead of carbon atom **(Figure 30.5)**.

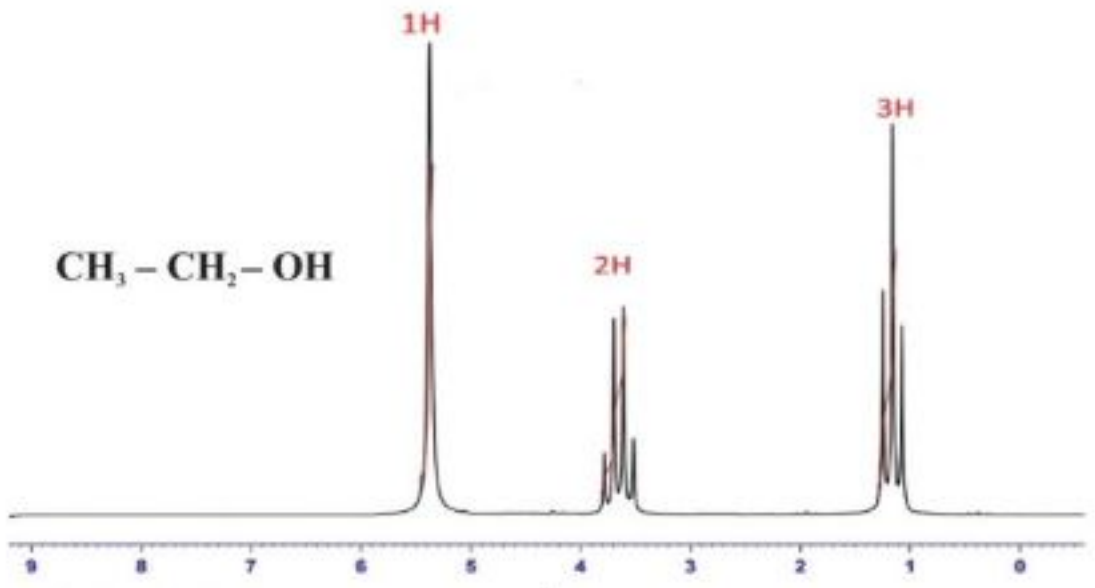


Figure 30.5 High-resolution ^{1}H NMR spectrum of ethanol

This is important to note that -OH and -NH protons usually do not show splitting, so these appear as **singlet** peak. Similarly, chemically equivalent protons do not cause splitting of their neighbouring protons. For example, the ethane (CH_3-CH_3) molecule has two methyl groups attached to each other. If one methyl group is considered, its adjacent carbon has 3 protons attached to it. However, the peak does not show splitting because all the hydrogen atoms in ethane are chemically equivalent **(Figure 30.6).**

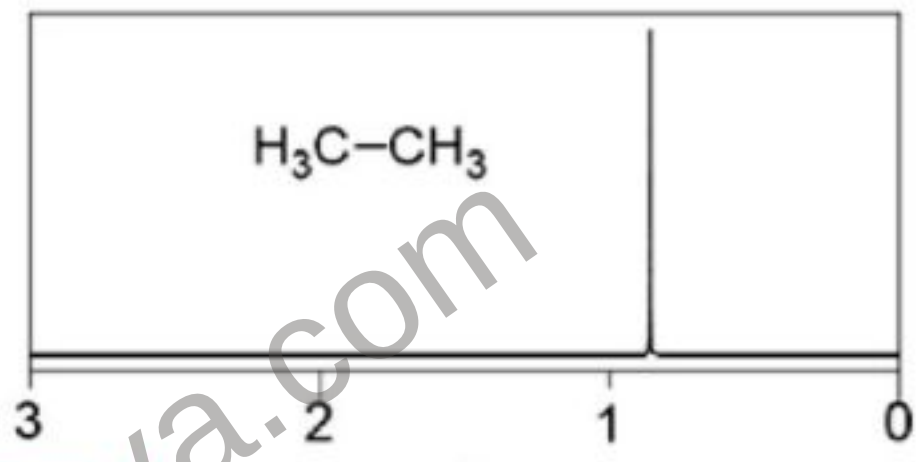


Figure 30.6 High-resolution ^{1}H NMR spectrum of ethane

The number of sub-peaks for different number of neighbouring protons and their appearance given in **Table 30.2** is useful to recognise splitting patterns in high-resolution ^{1}H NMR spectra.

Table 30.2 Common splitting patterns in high-resolution ^{1}H NMR spectra

No. of Protons on Adjacent Carbon Atom (n)	Number of Sub-Peaks (n+1)	Splitting Pattern	Abbreviation	Appearance of Split Peak
0	1	Singlet	s	
1	2	Doublet	d	

2	3	Triplet	t	
3	4	Quartet	q	

Quick Check 30.3

a) A signal in the ^{1}H NMR spectrum is a **quartet**. How many adjacent, equivalent protons ('n') are there?

b) Calculate the number of sub-peaks for each signal in the high-resolution spectra of the following compounds?

i) butan-2-ol
ii) 1-chloropropane
iii) propanone
iv) 2,2-dimethylpropane
v) methanol

30.4.3 Identification of O-H and N-H Proton in ^{1}H NMR Spectrum

The hydrogen atoms in O-H (alcohols or carboxylic acids) and N-H (amines or amides) are easily exchangeable, due to which they show a wide range of chemical shift value for their singlet peak.

$$CH_3\text{-}CH_2\text{-}O\text{-}H^a + H^b\text{-}O\text{-}H^b \rightleftharpoons CH_3\text{-}CH_2\text{-}O\text{-}H^b + H^a\text{-}O\text{-}H^b$$

Sometimes, it becomes very difficult to identify these peaks in spectra. A technique known as 'deuterium exchange' or 'D_2O shake' is used to detect whether the singlet in a ^{1}H NMR spectrum is actually due to the presence of an O-H or N-H hydrogen. In this method, the ^{1}H NMR spectrum of the compound is recorded which shows all the H atoms in the molecule including the O–H or N–H proton(s). A few drops of D_2O are then added to the NMR sample tube, the solution is shaken well and its spectrum is recorded again. The peak belonging to O–H or N–H proton disappears in the second spectrum. Comparing both spectra confirms the identity of the peak arising due to N-H or O-H.

The reason for this observation is that protons (^{1}H) attached to highly electronegative atoms like O or N are easily exchanged. When D_2O is added to the sample solution, these hydrogens are quickly exchanged with the deuterium (D) atoms.

$$R\text{–}O\text{–}H + D_2O \rightleftharpoons R\text{–}O\text{–}D + HOD$$

As deuterium atom requires different energy for spin flipping as compared to ^{1}H, it does not show a peak in the ^{1}H NMR spectrum making it '*invisible*'.

Quick Check 30.4

a) Why do **O-H or N-H peaks** disappear after a D_2O shake?

b) State the expected **peak area** and **splitting patterns** for $(–CH_2CH_2NH_2)$.

30.5 PREDICTION OF ^{1}H NMR SPECTRUM FOR A GIVEN MOLECULE

After understanding the concepts of chemical environment, chemical shift and splitting of peaks, one can predict the ^{1}H NMR spectrum of a given molecule by analyzing its structure. This can be done in the following steps:

Step I: Identify different proton environments in the molecule.

Number of different environments = Number of peaks expected in spectrum

Step II: Estimate the chemical shift (δ) for each set of protons having same chemical environment by using known ranges from the data table **(Table 30.1)**. If the data table is not available, check the nearest bonds and atoms. The protons near electronegative elements have higher chemical shift (δ), while those with alkyl groups generally have lower chemical shift.

Step III: Predict the splitting pattern of each peak by applying the 'n+1' rule.

Step IV: Assign integration ratios according to the number of hydrogen atoms in each environment.

Example 30.1:

Predict the ^{1}H NMR spectrum of chloroethane (CH_3-CH_2-Cl).

Solution:

No. of peaks

Two different chemical environments are present in the molecule.

No. of peaks in the ^{1}H NMR spectrum of chloroethane = 2

Chemical shift

The -CH_2- is attached to an electronegative element, it will show a higher value of chemical shift (3.0 – 4.5 ppm). The methyl protons will show lower value of chemical shift (0.5 – 1.5 ppm).

Splitting of Peaks

No. of sub-peaks for -CH_3 = 2 + 1 = 3 (The carbon adjacent to -CH_3 has 2 protons)

-CH_3 signal will split into a **triplet**.

No. of sub-peaks for -CH_2- = 3 +1 = 4 (The carbon adjacent to -CH_2- has 3 protons)

-CH_2- signal will split into a **quartet**.

Relative peak area

The ratio of peak area for -CH_3 and -CH_2- will be 3:2.

Quick Check 30.5

For the compound $(CH_3)_2CHOH$, predict the following:

a) The number of peaks
b) The type of proton and chemical shift
c) The relative peak areas
d) The splitting pattern

30.6 DETERMINATION OF THE POSSIBLE STRUCTURE OF A MOLECULE FROM ^{1}H NMR

The structure of an unknown compound can also be deduced by analyzing its ^{1}H NMR spectrum. It can be done by putting together the following key pieces of information like a puzzle. To determine the structure:

1. Count the number of peaks in the spectrum.

   No. of peaks = No of protons

2. Use the chemical shift of each peak to identify functional groups (use data table).
3. Use peak area to find the actual number of hydrogen atoms for each peak (this gives the no. of hydrogen atoms present in each environment)
4. Analyze the splitting pattern and calculate the number of adjacent protons

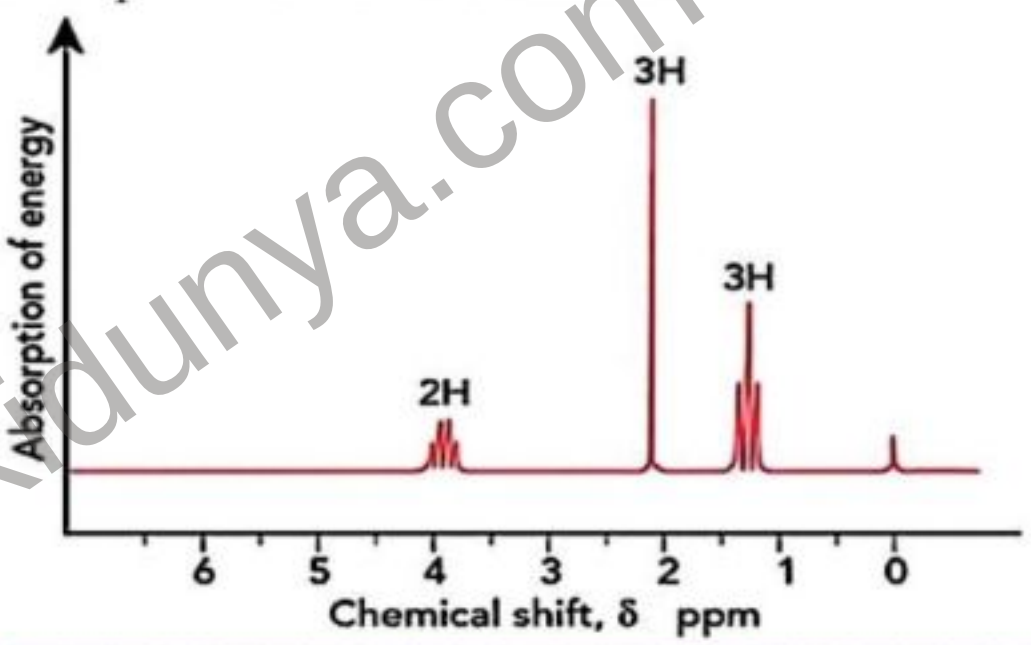
   No. of sub-peaks = n +1

   n = No. of sub-peaks – 1

5. Combine this information to assemble the complete molecular structure.

Example 30.2

The ^{1}H NMR spectrum of an ester is given below. Deduce the structure of the ester.



Solution:

The solution is given in the table below.

No.	Peak Chemical Shift (ppm)	No. of Equivalent protons	Responsible Group	Splitting	No. of Neighbouring Protons
1	1.3	3H	$-CH_3$ next to $-CH_2$	Triplet	3-1 = 2H (CH_3-CH_2-)
2	2.2	3H	$-CH_3$ next to C=O	Singlet	1-1 = 0 (CH_3-C=O)
3	3.9	2H	CH_2- next to an electronegative O atom	doublet	2-1 = 1 (CH_3-CH_2-O) Combining information from 1 and 3
Overall Structure	$H_3C-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$				

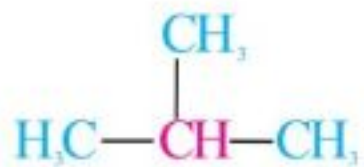
30.7 ^{13}C NMR SPECTROSCOPY

The nucleus of ^{12}C does not have magnetic properties because of even number of protons and neutrons (even mass number), and is, therefore, NMR inactive. However, the ^{13}C nucleus possesses magnetic spin due to its odd number of neutrons. On the basis of the magnetic properties of carbon-13 isotope, ^{13}C NMR spectra can be recorded for carbon compounds. Like ^{1}H NMR, chemical shift (δ in ppm) in ^{13}CNMR is compared to the reference molecule TMS (δ = 0.0 ppm). However, the ^{13}C NMR has a range of chemical shift from 0 – 220 ppm. The deuterated chlorofom ($CDCl_3$) is usually used as a solvent which produces a small signal near 80 ppm.

30.7.1 Chemical Environment of Carbon

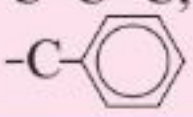
A carbon atom's environment is determined by the types of atoms directly attached to it. Carbon atoms that are in the same environment are chemically equivalent, and show the same chemical shift. For example, both carbon atoms in ethane have the same environment. Carbon atoms in different environments are chemically non-equivalent and they will appear at different positions (chemical shifts) in ^{13}C NMR spectra. For example, all three methyl carbon atoms in 2-methylpropane have the same environment, while the tertiary carbon has different environment than these three carbon atoms.

The type of environment can be predicted by looking at atoms or bonds around carbon atoms. The chemical shifts of different carbon environments are given in **Table 30.3.**



2-methylpropane

Table 30.3 Chemical shifts of different carbon environments

Hybridization of carbon atom	Environment of carbon atom	Examples	Chemical Shift Range δ (ppm)
sp^3	Alkyl	CH_3, $-CH_2-$, >CH–, >C<	0 – 50
sp^3	Carbon atom next to alkene or aryl ring	–C–C=C, 	25 – 50
sp^3	Carbon atom next to carbonyl or carboxyl	–C–COR, –C–COOR	30 – 65
sp^3	Carbon atom next to halogen	C–X	30 – 60
sp^3	Carbon atom next to oxygen	C–O	50 – 70

sp^2	Alkene or aryl carbon	>C=C<, 	110 – 160
sp^2	Carboxyl carbon	R–COOH, –COOR	160 – 185
sp^2	Carbonyl carbon	R–CHO, R–CO–R	190 – 220
sp	Nitrile	R–C≡N	100 – 125

30.7.2 Predicting ^{13}C NMR Spectra

The ^{13}C NMR spectrum is simpler than ^{1}H NMR in which each peak (or signal) corresponds to a single, different environment or type of carbon atom. Chemical shift of each peak tells about its environment.

The number of peaks = The number of different carbon environments

^{13}C NMR spectrum of ethane shows only one peak as both the carbon atoms have the same environment. In propane **$CH_3-CH_2-CH_3$**, there are two types of carbon environments, the two terminal -CH_3 carbons have the same environment while the middle -CH_2- carbon has a different environment. The ^{13}C NMR spectrum of propane shows two peaks, one for the methyl carbon atoms while the other for -CH_2- carbon atom. Similarly, two peaks are observed in the ^{13}C spectrum of ethanol (CH_3–CH_2–OH), due to the presence of two types of environments in this molecule **(Figure 30.7).**

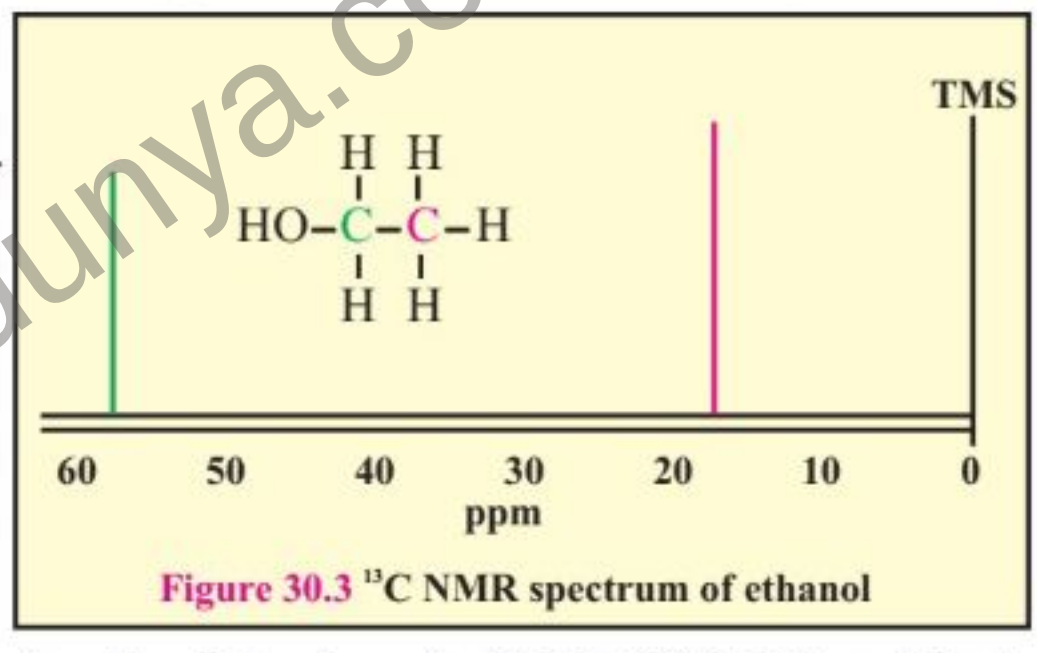


Figure 30.3 ^{13}C NMR spectrum of ethanol

Analyzing the ^{13}C NMR spectrum of ethanol by using the data given in **Table 30.3**, it is evident that the peak at 18 ppm is for -CH_3 carbon, while the peak near 57 ppm is due to -CH_2- carbon atom.

There are two key differences between ^{1}H NMR and ^{13}C NMR spectra. The relative peak area in ^{13}C NMR is usually not proportional to the number of carbon atoms unlike ^{1}H NMR in which peak area shows the number of protons. Secondly, the peaks do not show splitting, hence these appear as vertical lines. Due to this, ^{13}C NMR technique is less sensitive than ^{1}H NMR.

Quick Check 30.6

a) How many signals do you expect to observe in the ^{13}C NMR spectrum of **butane**? Justify your answer.
b) Predict the ^{13}C NMR spectrum of butan-2-ol.
c) Predict the chemical shift of carbon atoms in propanoic acid.

30.7.3 Determination of Structure of a Molecule

The ^{13}C NMR a spectrum can be used to figure out a molecule's structure. The steps during the analysis of a spectrum are:

1. Count the Peaks

The number of peaks in the spectrum tells the number of different types (environments) of carbon atoms in the molecule. If a molecule has 5 carbon atoms but only 3 peaks, it means there are 2 pairs of carbons, which are identical (chemically equivalent).

2. Look at the Position of Peak (Chemical Shift δ)

The position (ppm value) of each peak tells whether the carbon atom is present in an alkane, alkene, alkyne, aromatic or carbonyl compound. The assignment of the chemical shift value can be made according to the data provided in **Table 30.3.**

3. Work out the spectrum for possible structures

Use the information from the peak count and positions to draw possible structures that fit the molecular formula of the compound.

If the formula of a compound is $C_4H_{10}O$ and its ^{13}C NMR spectrum shows 3 peaks **(Figure 30.8)**. It means that 3 different carbon environments are present in the molecule. The three possible molecules for this formula are butan-1-ol, butan-2-ol and 2-methoxypropane. The structure of the unknown compound cannot be butan-1-ol or butan-2-ol (which are expected to show 4 peaks). It must be a structure with 3 chemical environments; 2-methoxypropane which has 3 peaks.

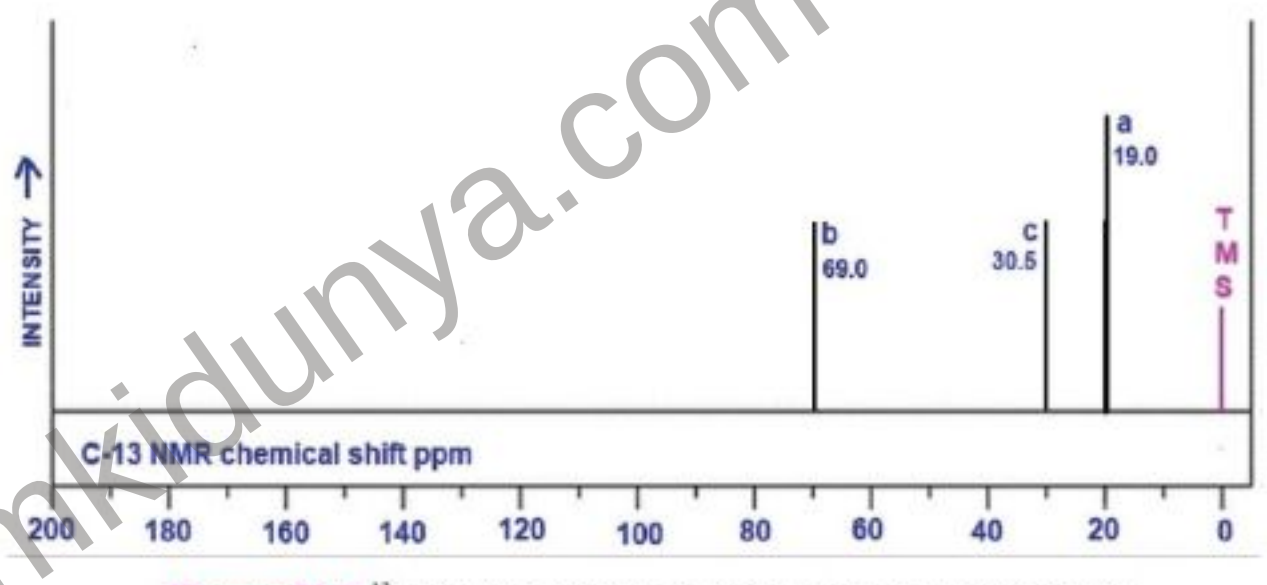


Figure 30.8 ^{13}C **NMR spectrum of an unknown molecule**

Quick Check 30.7

Draw the structures of butan-1-ol and butan-2-ol.

i) Using the spectrum given in **Figure 30.8,** explain why this spectrum does not match with the structures of these two molecules.

ii) Which peaks (mention chemical shift) would you expect in the spectra of butan-1-ol and butan-2-ol?

Exercise

Q1. MULTIPLE CHOICE QUESTIONS

I. NMR relies on the magnetic properties of nuclei known as:

a) Chemical shift
b) Nuclear density
c) Nuclear spin
d) Signal intensity

II. Chemical shift (δ) in the ^1H NMR spectroscopy is measured relative to TMS and is expressed in:

a) Tesla (T)
b) Hertz (Hz)
c) Parts per million (ppm)
d) Degrees Celsius (°C)

III. Deuterated solvents ($CDCl_3$) are used in ^1H NMR to:

a) Increase magnet strength
b) Split the signals
c) Provide a reference signal
d) Avoid solvent signal interference

IV. The primary purpose of measuring the peak area in ^1H NMR is to find the:

a) Chemical shift
b) Number of neighboring protons
c) Total carbon atoms
d) Relative number of protons

V. Splitting is typically not observed for O-H or N-H protons because of:

a) NMR-inactivity
b) Longer bond
c) Deuterated solvent
d) Rapid chemical exchange

VI. In the n+1 splitting rule, 'n' represents the number of protons on:

a) the entire molecule
b) the carbon being analyzed
c) adjacent carbon atoms
d) the signal's total area

VII. The chemical shift (δ) of a ^{13}C peak identifies the:

a) Number of adjacent carbons
b) Functional group environment (C=C, C=O, etc.)
c) Molecule's symmetry
d) Number of protons

VIII. The number of peaks in a ^{13}C NMR spectrum equals the number of:

a) Total carbon atoms
b) Chemically non-equivalent carbons
c) Adjacent hydrogen atoms
d) ^{12}C atoms

IX. How many ^{13}C peaks does propane ($CH_3CH_2CH_3$) show?

a) 1
b) 2
c) 3
d) 4

X. What is the splitting pattern for a proton with 2 neighbouring protons (n=2)?

a) Singlet
b) Doublet
c) Triplet
d) Quartet

Q2. SHORT-ANSWER QUESTIONS

a) State two reasons why TMS is a standard for ^1H NMR.

b) Why does deuterium (D) not appear in a ^1H NMR spectrum?

c) A compound ($C_4H_{10}O$) has a ^1H NMR peak area ratio of 1:3:6. How many protons does each signal represent?

d) What is the purpose of the D_2O shake test in ^1H NMR?

e) List the key features used to interpret a ^1H NMR spectrum.

f) What does the number of peaks in a ^{13}C NMR spectrum represent?

Q3. CONSTRUCTED RESPONSE QUESTIONS

a) A $-CH_2-$ group is lying between a $-CH_3$ and a $-CH<$ group. What is the splitting pattern for the $-CH_2-$ signal? Show your calculation.

b) Predict the ^1H NMR spectrum of 1-butanoic acid.

c) An organic compound has a molecular formula C_2H_5Cl. The ^1H NMR of the compound is given below. Deduce the structure of the compound by using its spectrum. Explain your working in detail.

d) An organic compound has a formula C_4H_8O. In laboratory, the compound gives 2,4-DNPH and iodoform tests positive but Fehling's test shows a negative result. The ^1H NMR of the compound is shown below. Deduce the structure of the compound and justify your answer.

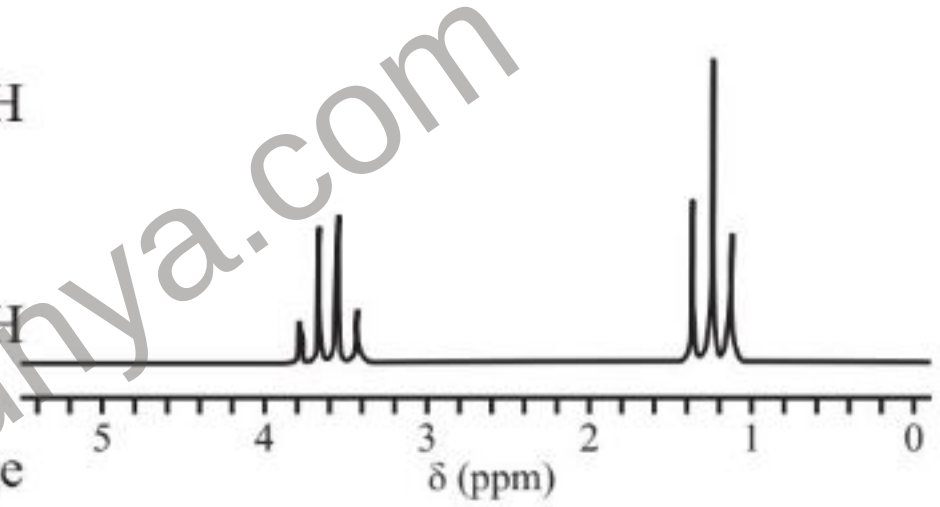
DESCRIPTIVE QUESTIONS

Q4. A chemist suspects a sample contains an O-H group.

a) Describe the "D_2O shake" procedure.

b) What is the expected observation in the ^1H spectrum after the shake?

c) Write the equilibrium equation for the exchange and explain why it causes this observation.



Q.5 Predict the number of ^{13}C NMR peaks for the following two isomers:

a) Pentane

b) 2,2-dimethylpropane

Justify each answer by identifying the sets of equivalent carbons.