



Shree H.N.Shukla College of Science Rajkot

B.Sc. (Sem- 6) (CBCS)

CHEMISTRY: [602]

Unit-4 Chapter-7: NMR Spectroscopy

- NMR spectroscopy means **Nuclear Magnetic Resonance**
- **NMR** is an abbreviation for **Nuclear Magnetic Resonance**. An NMR instrument allows the molecular structure of a material to be analyzed by observing and measuring the interaction of **nuclear spins** when placed in a powerful **magnetic field**.

Learning Objective

- Know how nuclear spins are affected by a **magnetic field**, and be able to explain.
- What happens when **radiofrequency** radiation is absorbed.
- Be able to predict the number of proton and proton (**^1H**) NMR signals expected from a compound given its structure.
- Be able to predict the **splitting pattern** in the proton NMR spectrum of a compound given its structure.
- With the aid of a chart of **chemical shifts** from ^1H NMR, be able to assign peaks in an NMR spectrum to specific protons in a compound.
- Be able to interpret **integration** of NMR spectra.
- Be able to use NMR spectra to determine the **structures of compounds**, given other information such as a molecular formula.
- Be able to calculate **coupling constants(J)** from ^1H NMR spectra, and utilize the Coupling constants(J)for determining compound structure.
- Be able to determine the compound structure based on information generated from mass spectrometry, IR, NMR, and UV-Visible Spectroscopy.



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Introduction

- Spectroscopy is branch of science that deals with the **EMR** (Electro-Magnetic Resonance) interaction with **matter**.
- Nuclear Magnetic Resonance (NMR) is a nuclei (Nuclear) specific spectroscopy that has far reaching applications in various field such as physical sciences, chemistry, medical field/ industry etc.
- NMR uses a large Magnet (Magnetic) to probe the intrinsic **spin properties** of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (**radio frequency waves**) to promote transitions between nuclear energy levels (**Resonance**). Most chemists use NMR for **structure determination** of small molecules.
- In 1946, NMR was co-discovered by **Purcell, Pound and Torrey** of **Harvard University** and **Bloch, Hansen and Packard** of **Stanford University**.

Principle

- All nuclei are electrically charged and many have spin.
- Transfer of energy is possible from lower energy to higher energy levels when an external magnetic field is applied.
- The transfer of energy occurs at a wavelength that coincides with the **Radio frequency (Rf)**.
- Also, energy is emitted at the same frequency when the spin comes back to its lower level.
- Therefore, by measuring the signal which matches this transfer the processing of the NMR spectrum for the concerned nucleus is yield.

Spin and Magnetic Properties of Nuclei

- The nucleus consists of elementary particles called **neutrons** and **protons**, which contain an intrinsic property called **spin**.



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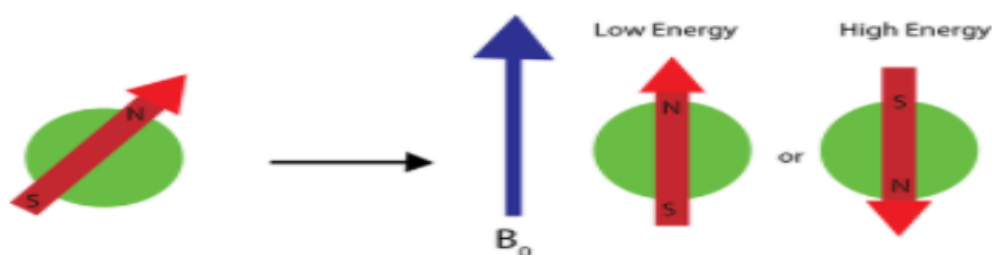
- Like electrons, the spin of a nucleus can be described using spin quantum numbers (I) and the spin in a magnetic field (m).
- Atomic nuclei with **even numbers** of protons and neutrons have zero spin ($I=0$) and all the other atoms with **odd numbers** have a non-zero spin ($I \neq 0$). Furthermore, all molecules with a non-zero spin have a **magnetic moment** (μ) given by

$$\mu = \gamma I$$

Where γ = Magnetic-gyro ratio

I = Nuclear spin

- The magnetic moment of the nucleus forces the nucleus to behave as a **tiny bar magnet**. In the absence of an external magnetic field, each magnet is randomly oriented. During the NMR experiment the sample is placed in an external magnetic field (B_0), which forces the bar magnets to align with (**low energy**) or against (**high energy**) the B_0 .
- During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy. To understand this rather abstract concept it is useful to consider the NMR experiment using the nuclear energy levels.



Short Question/blanks	Answer
1. What is full form of NMR	Nuclear Magnetic Resonance
2. Which types of EMR used in NMR?	Radio wave
3. Chemist used NMR for	structure determination
4. The nuclear spin for proton _____	$I=1/2$
5. What ^{12}C nmr active _____	No



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Nuclear Energy level

→ As mentioned above, an exact quanta of energy must be used to induce the spin flip or transition. For any m , there are $2m+1$ energy levels. For a spin $1/2$ nucleus, there are only two energy levels, the low energy level occupied by the spins which aligned with B_0 and the high energy level occupied by spins aligned against B_0 . Each energy level is given by

$$E = -m\gamma\hbar B_0$$

Where E = energy of absorption

m = magnetic quantum number

γ = Magnetic-gyro ratio

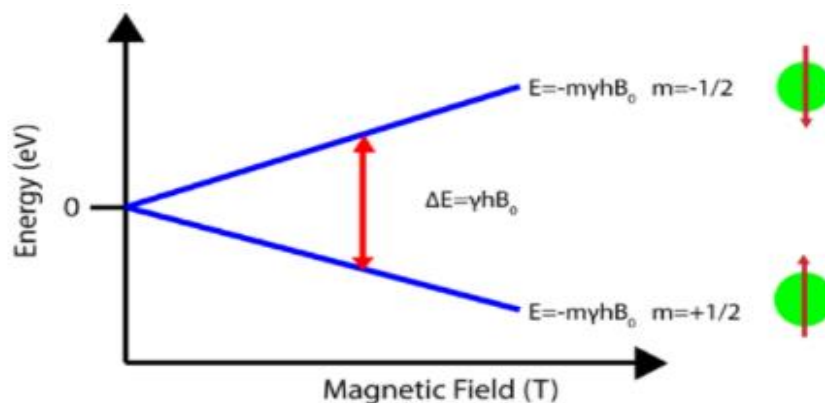
\hbar = reduced plank constant

B_0 = applied magnetic field

→ The energy difference between the energy levels is then

$$\Delta E = \gamma\hbar B_0$$

→ A schematic showing how the energy levels are arranged for a spin= $1/2$ nucleus is shown below.



→ Note how the strength of the magnetic field plays a large role in the energy level difference. In the absence of an applied field the nuclear energy levels are degenerate. The splitting of the degenerate energy level due to the presence of a magnetic field is known as **Zeeman Splitting**.

Instrumentation of NMR

→ Place the sample in a magnetic field.



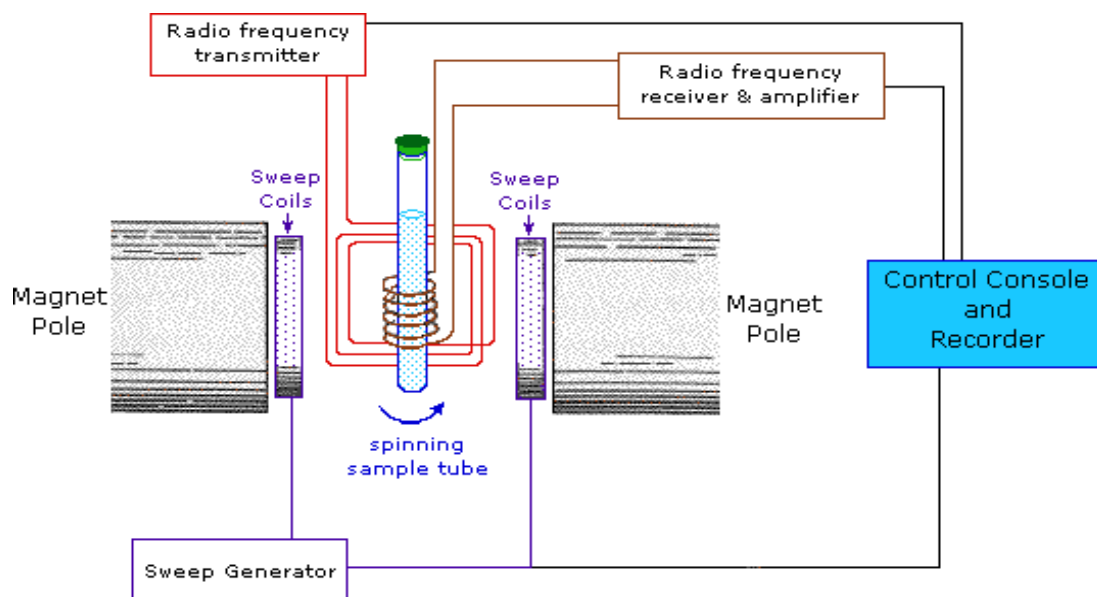
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- Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
- These NMR signals are detected with sensitive radio receivers.
- The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
- This gives details of a molecule's individual functional groups and its electronic structure.
- Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
- This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.



Q.No.	Short Question/blanks	Answers
1	How many number of energy level arise in molecule when applied field,	$2nI+1$
2	Chemist used NMR for	structure determination
3	Which cooling used in NMR?	Liquid N_2
4	Which is the base PMR spectroscopy	1H_1
5	Which is important part of instruments?	Magnet



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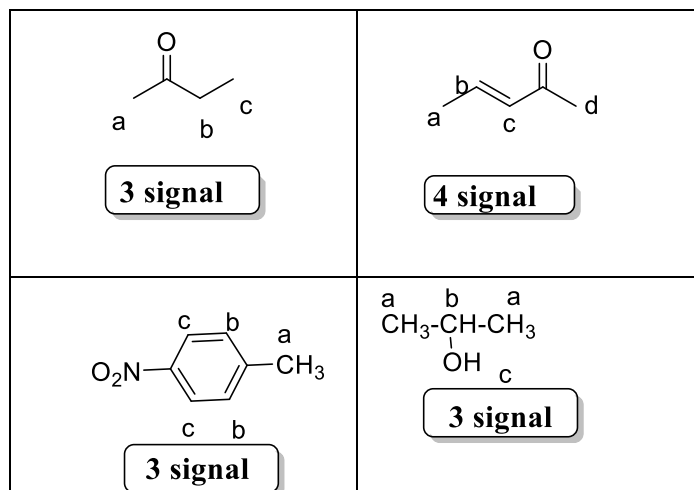
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Study of NMR spectra

1. No. of signal: It tells us about the compound containing different types of protons present and its corresponding number of signals observed in the NMR spectrum.

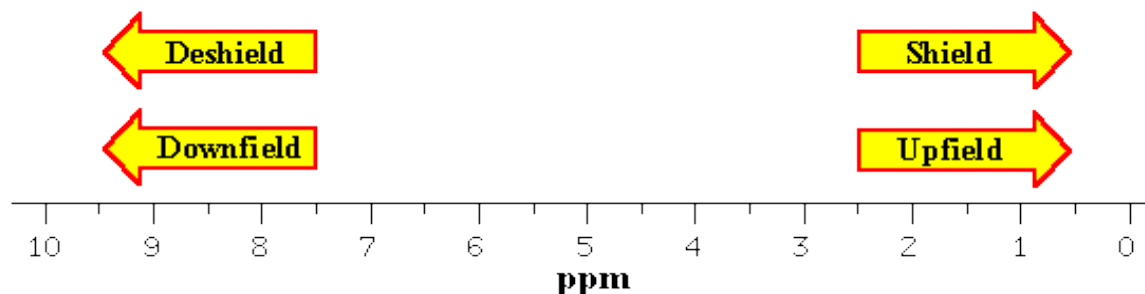


2. Position of signal: It tells us about the electronic environment surrounding the nuclei. Different types of nuclei having different positions of signal.

Chemical Shift

- The difference in the absorption position of a particular proton from the absorption position of a reference proton (TMS proton) is called the **Chemical Shift**.
- It is denoted by δ ppm or τ ppm

$$\delta = 10 - \tau$$





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Chemical shift value of different types of protons

Type of Proton	Chemical Shift (ppm)	Type of Proton	Chemical Shift (ppm)
$R-CH_3$	0.9 – 1.2	$X-CH_2R$ (X: Cl, Br, I)	3.1 – 3.8
$\begin{array}{c} R \\ \\ R-CH_2 \end{array}$	1.2 – 1.5	$R-OH$	variable, 1 – 5
$\begin{array}{c} R \\ \\ R-CH \\ \\ R \end{array}$	1.4 – 1.9	$R-NH_2$	variable, 1 – 5
$\begin{array}{c} R & & R \\ & \backslash & / \\ & C=C \\ & / & \backslash \\ R & & CHR_2 \end{array}$	1.5 – 2.5	$\begin{array}{c} R & & R \\ & \backslash & / \\ & C=C \\ & / & \backslash \\ R & & H \end{array}$	4.5 – 6.0
$\begin{array}{c} O \\ \\ R-C-CH_3 \end{array}$	2.0 – 2.6	$Ar-H$	6.0 – 8.5
$Ar-CH_3$	2.2 – 2.5	$\begin{array}{c} O \\ \\ R-C-H \end{array}$	9.5 – 10.5
$R-C\equiv C-H$	2.5 – 3.0	$\begin{array}{c} O \\ \\ R-C-OH \end{array}$	10 – 13
$(H)R-O-CH_3$	3.3 – 4.0		

Factor affecting on Chemical Shift

- Inductive effect
- Hybridization
- Size of ring
- H-bonding
- Proton attached to hetero atom(N,O,S)

TMS reference in NMR

- TMS is a **cheap** and readily available compound.
- TMS is **chemically inert**. There is no reaction between **TMS** and the **Sample**.
- TMS has a low boiling point (27 °C). It can be easily removed from the sample by **evaporation** after the spectrum is recorded.



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- The **12 protons of TMS** produce a sharp signal. Even at lower TMS concentrations, the reference signal can be easily recognized.

Shielding and de-shielding effect

- Higher electron density around hydrogen atoms creates **greater opposition** to the applied magnetic field (H_0). As a result, the H atom experiences a lower magnetic field than applied field and can resonate at a **lower frequency**. The peak on the NMR spectrum for this H atom would shift **upfield**(or lower δ ppm) . These H atoms are referred to as being **shielded**. It is known as **shielding effect**.
- If the H atom is surrounded by elements that reduce the electron cloud, then, it would experience a **higher magnetic field** and would resonate at a **higher radio frequency**. This phenomenon is called **de-shielding**.

Q.No.	Short Question/blanks	Answers
1	What is symbol of chemical shift ?	δ ppm
2	n-propane No.of nmr signal	2 signal
3	What is TMS?	Internal reference standard in nmr
4	What is Shielding?	The Nucleus feels weaker magnetic field.
5	Deshielded proton present in_____	downfield region

3. Intensity of signal: The intensity of the signal is proportional to the number of hydrogens that make the signal.

- The integrated intensity of a signal in a ^1H NMR spectrum gives a ratio for the number of hydrogens that give rise to the signal, thereby helping calculate the **total number of hydrogens** present in a sample.
- Now that we've seen how the signal intensity is directly proportionate to the number of hydrogens that give rise to that signal, it makes sense to conclude that the more hydrogens of one kind there are in a molecule (equivalent hydrogens, so in the same chemical environment), the more intense the corresponding NMR signal



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4. Splitting of signal: The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, **non-equivalent** NMR-active nuclei.

→ In NMR spectrum splitting of signal by **N+1 rule**. Splitting of signal and its multiplicity given below table.

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	$1+1 = 2$				$1+1 = 2$	Doublet
Triplet	$2+1 = 3$				$1+1 = 2$	Doublet
Triplet	$2+1 = 3$				$2+1 = 3$	Triplet
Quartet	$3+1 = 4$				$1+1 = 2$	Doublet

Coupling constant (J)

→ The space between multi-plate signal is a constant and is called as the **Coupling constant (J)**.

→ It is denoted by **J** and its expressed in **Hz** or **cps(cycle per second)**.

→ It is independent of **applied magnetic field & operating radio frequency**.

→ **Different types of coupling constant described below.**



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1. Geminal Coupling: Proton attached to same atom but its different chemical environment is. It is also called **Geminal coupling**.

→ 2J coupling, means **two intervening bond** between interaction nuclei. It is also called 2J coupling.

→ This coupling ranges from **-20 to 40 Hz**.

2. Vicinal Coupling: **Non-equivalent** proton on adjacent atom couple with each other. It is also called **Vicinal Coupling**.

→ Vicinal coupling occurs though **three bonds (3J)**

→ The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules.

→ In addition, vicinal coupling constant ranges from **8 to 10 Hz**

3. Long range coupling: Coupling occur between beyond more than **three bond (>3)** is called Long range coupling.

→ It is observed in **unsaturated** aromatic compounds only with higher resolution spectrophotometers.

Q.No.	Short Quesition/blanks	Answers
1.	NMR signal splitted by _____	N+1 rule
2.	What is unit of coupling constant(j) ?	Hz
3.	The magnitudes of geminal coupling____	8-10 Hz
4.	Splitting of signal by _____	Neighboring non-equivalent nuclei.
5.	Coupling constant of vicina proton depend on_____	Dihedral angle



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Learning Outcome

- Knows the basic principles and terms related to NMR spectroscopy.
- Understands the physical principles underlying the NMR phenomenon and realizes the possibilities of NMR spectroscopy in analyzing the structures of molecules.
- Is aware of the principles on NMR sample preparation.
- Knows chemical shifts and its related to shielding and deshielding effects.
- Known NMR instrumentation and its component.
- Familiarizes her/himself with measuring NMR spectra.