PROTON NMR

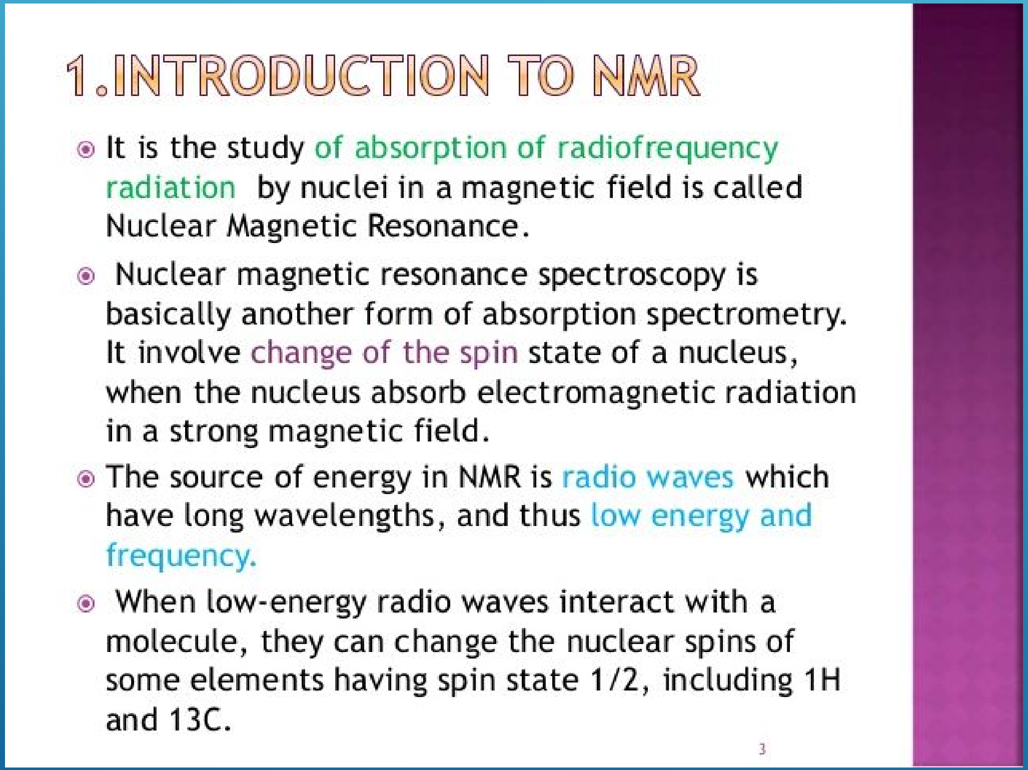
Dr. MARY JELASTIN KALA,

ASSISTANT PROFFESOR,

ST. XAVIERS AUTONOMOUS COLLEGE.

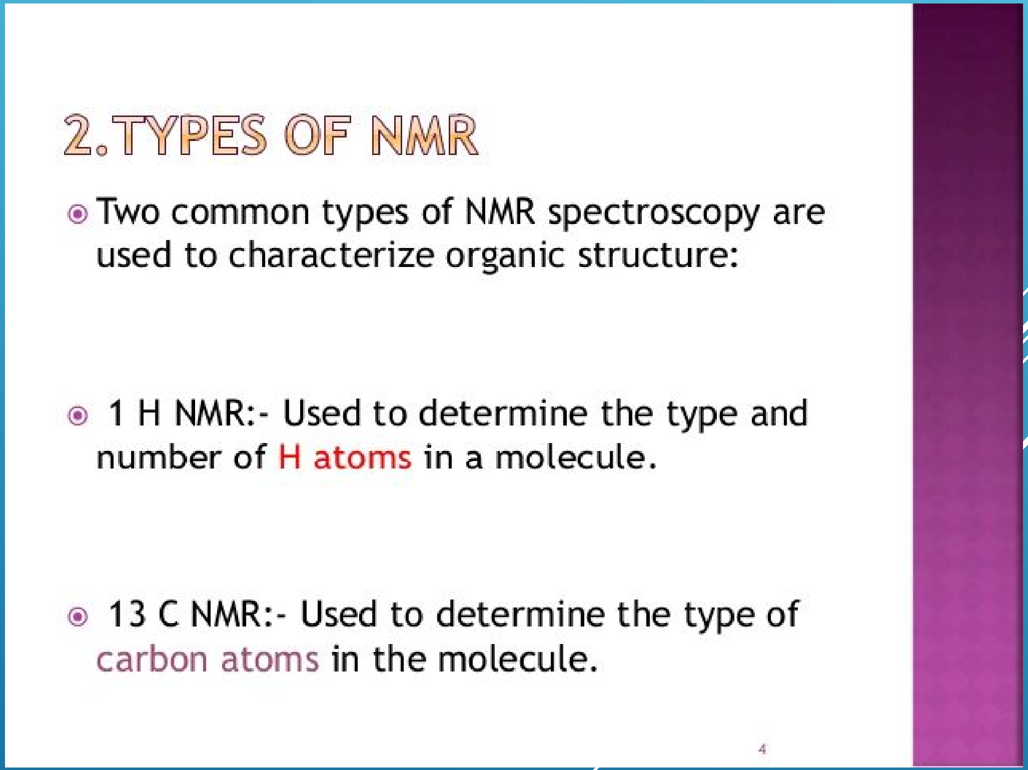
- Introduction
- Types of NMR
- Proton NMR
- Chemical Shift
- Shielding and Deshielding
- Feature of NMR

TOPIC



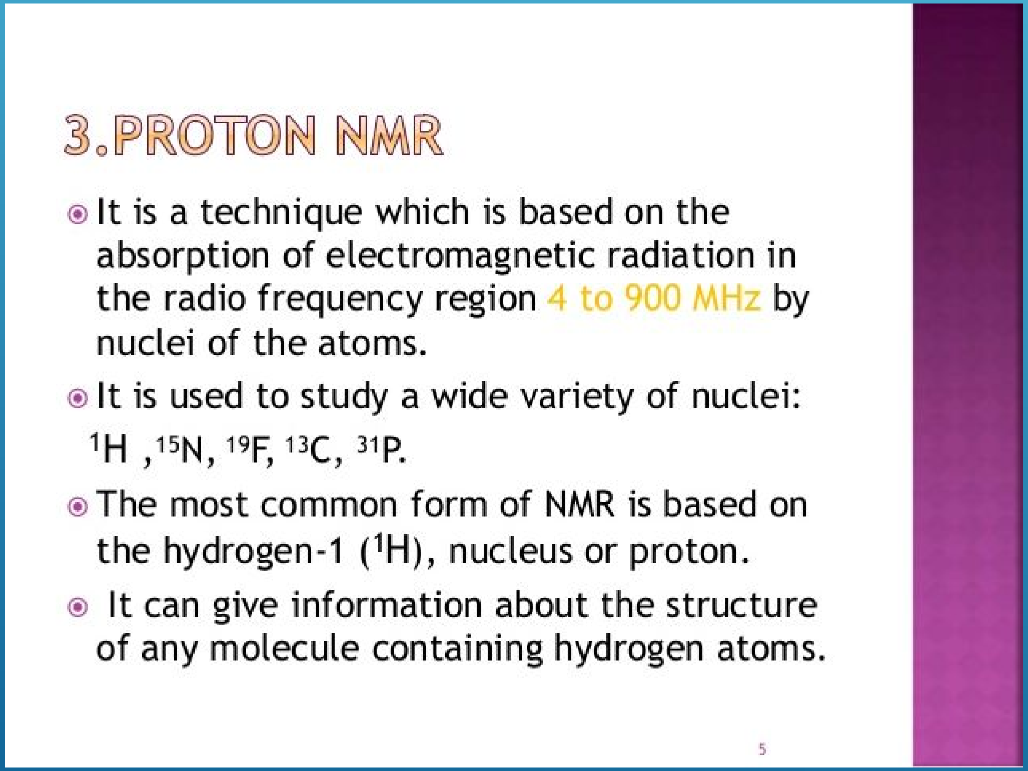
1.INTRODUCTION TO NMR

- It is the study of absorption of radiofrequency radiation by nuclei in a magnetic field is called Nuclear Magnetic Resonance.
- Nuclear magnetic resonance spectroscopy is basically another form of absorption spectrometry. It involve change of the spin state of a nucleus, when the nucleus absorb electromagnetic radiation in a strong magnetic field.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements having spin state 1/2, including 1H and 13C.



2.TYPES OF NMR

- Two common types of NMR spectroscopy are used to characterize organic structure:
- 1 H NMR:- Used to determine the type and number of H atoms in a molecule.
- 13 C NMR:- Used to determine the type of carbon atoms in the molecule.

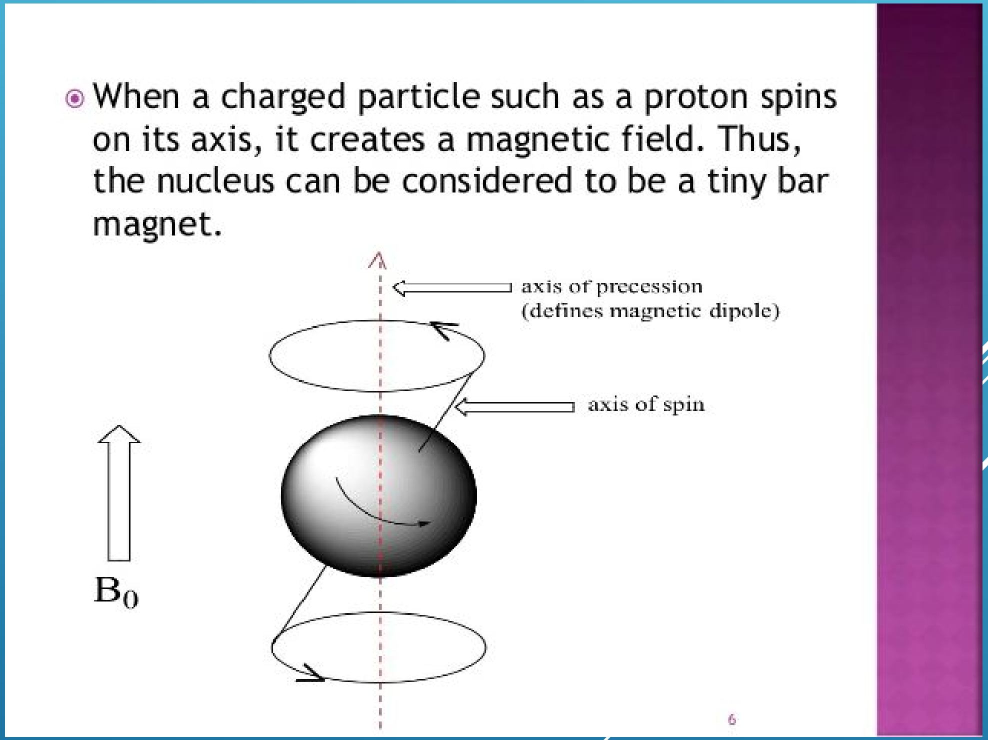


3.PROTON NMR

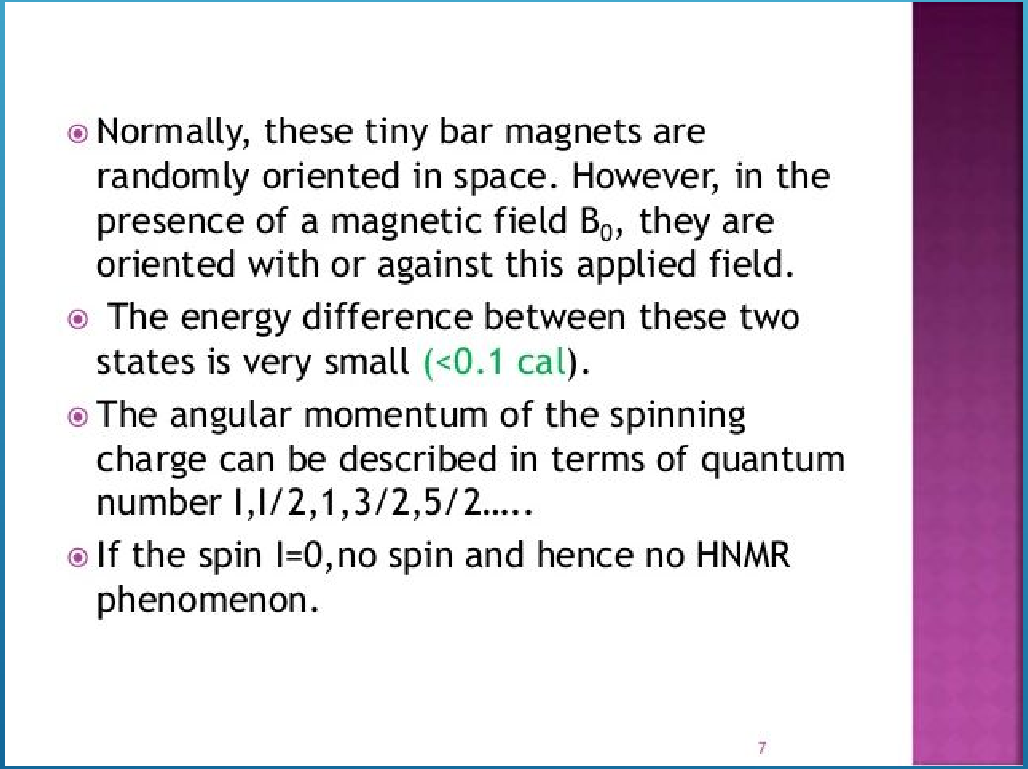
- It is a technique which is based on the absorption of electromagnetic radiation in the radio frequency region 4 to 900 MHz by nuclei of the atoms.
- It is used to study a wide variety of nuclei:

^{1}H , ^{15}N, ^{19}F, ^{13}C, ^{31}P.

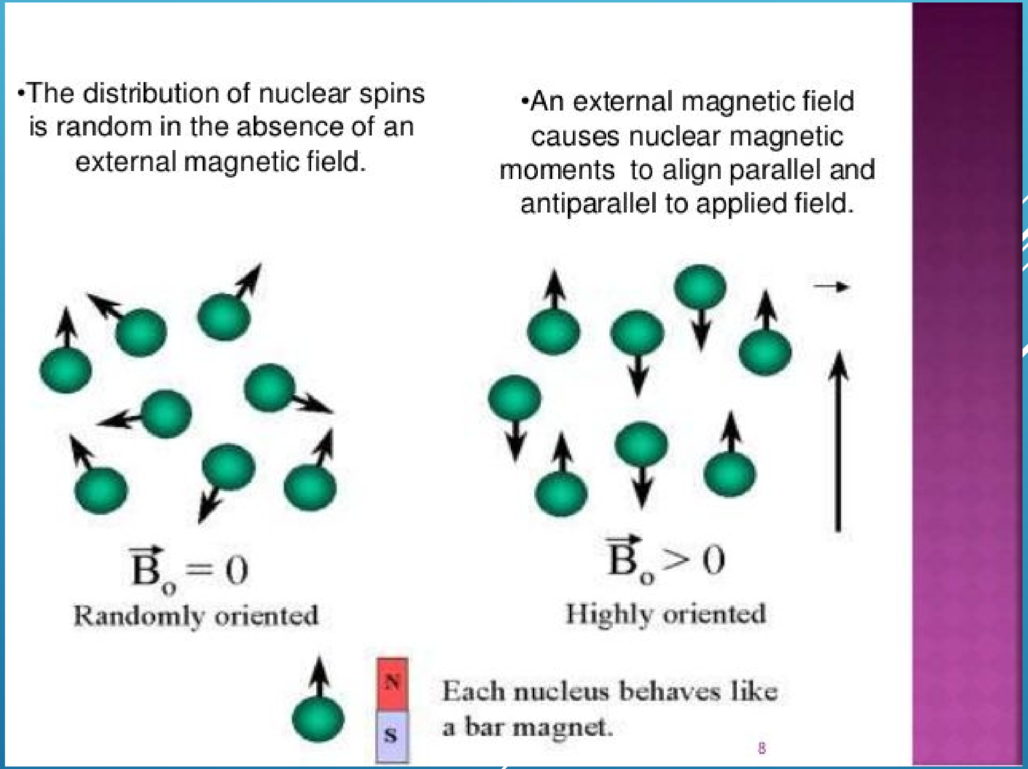
- The most common form of NMR is based on the hydrogen-1 (^{1}H), nucleus or proton.
- It can give information about the structure of any molecule containing hydrogen atoms.



- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.



- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0, they are oriented with or against this applied field.
- The energy difference between these two states is very small (<0.1 cal).
- The angular momentum of the spinning charge can be described in terms of quantum number I,I/2,1,3/2,5/2…..
- If the spin I=0,no spin and hence no HNMR phenomenon.



- The distribution of nuclear spins is random in the absence of an external magnetic field.
- An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.

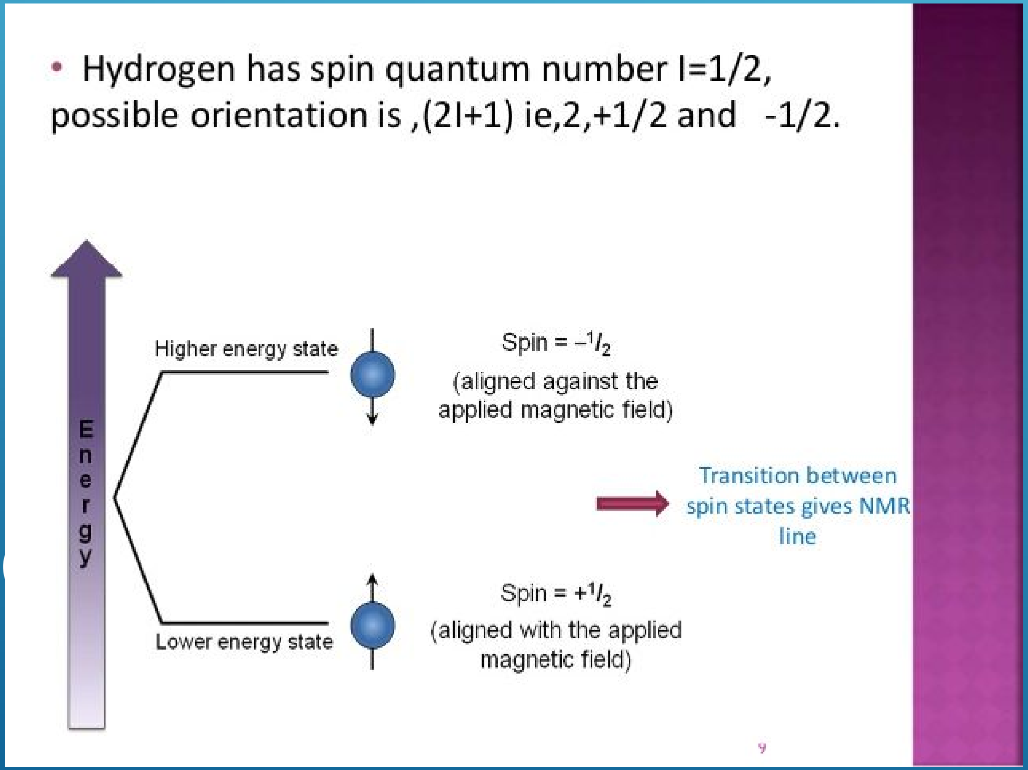
$\vec{B}_o = 0$

Randomly oriented

$\vec{B}_o > 0$

Highly oriented

Each nucleus behaves like a bar magnet.



- Hydrogen has spin quantum number I=1/2, possible orientation is ,(2I+1) ie,2,+1/2 and -1/2.

Energy

Higher energy state

Spin = $-^{1}/_{2}$

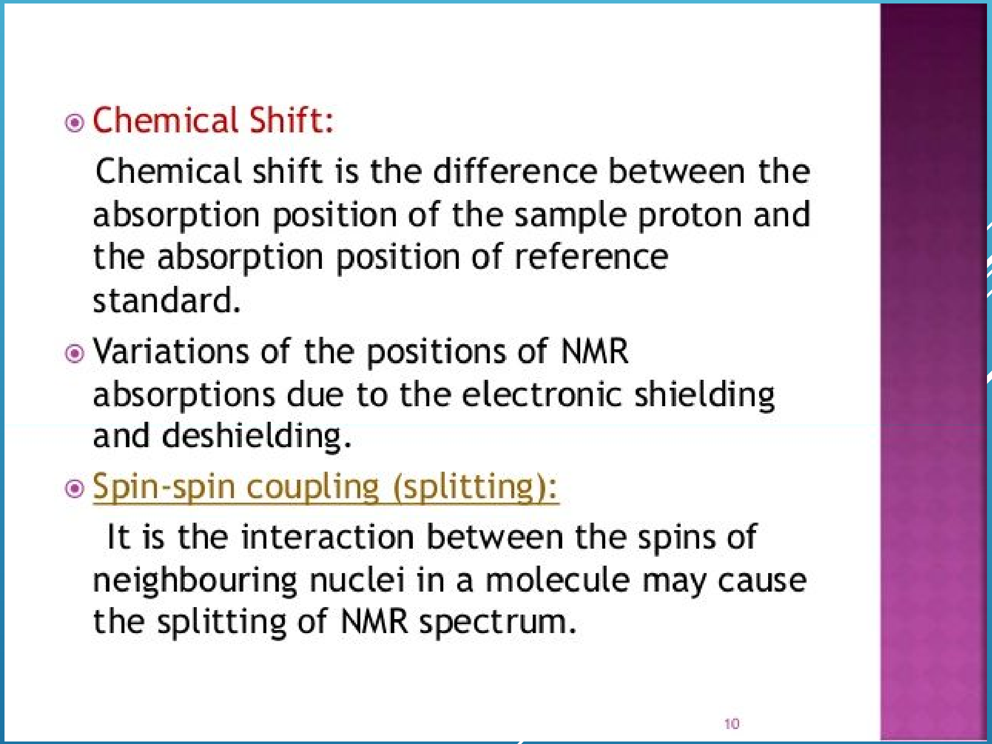
(aligned against the applied magnetic field)

Transition between spin states gives NMR line

Lower energy state

Spin = $+^{1}/_{2}$

(aligned with the applied magnetic field)

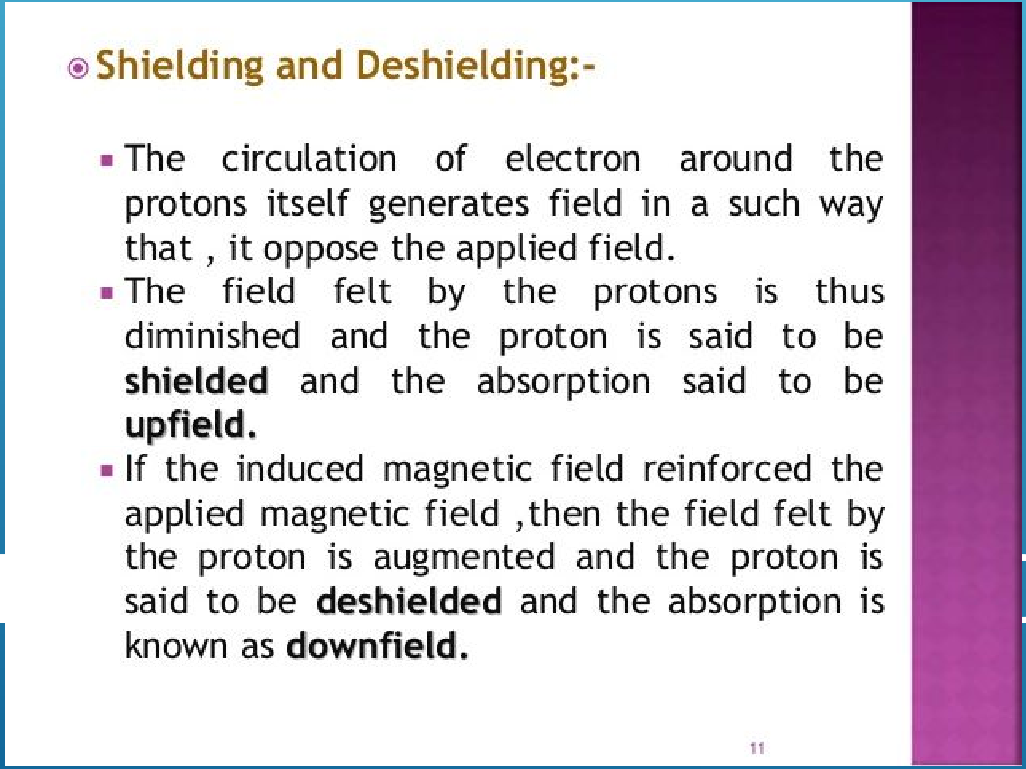


- **Chemical Shift:**

  Chemical shift is the difference between the absorption position of the sample proton and the absorption position of reference standard.
- Variations of the positions of NMR absorptions due to the electronic shielding and deshielding.
- Spin-spin coupling (splitting):

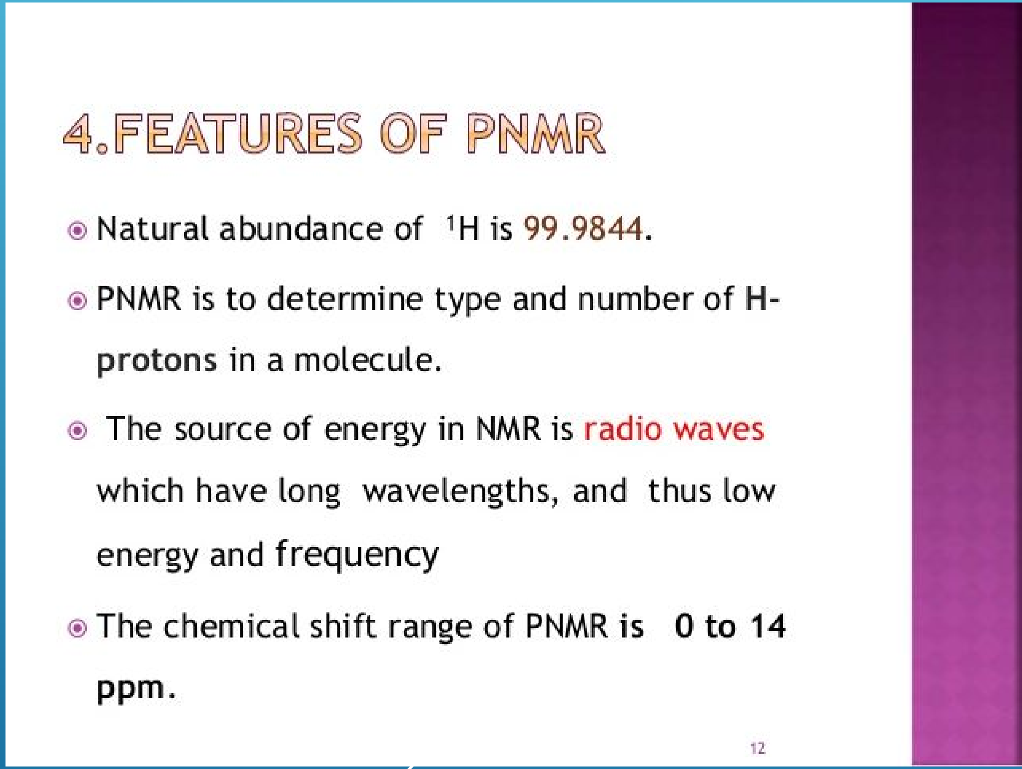
  It is the interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum.

S DLING



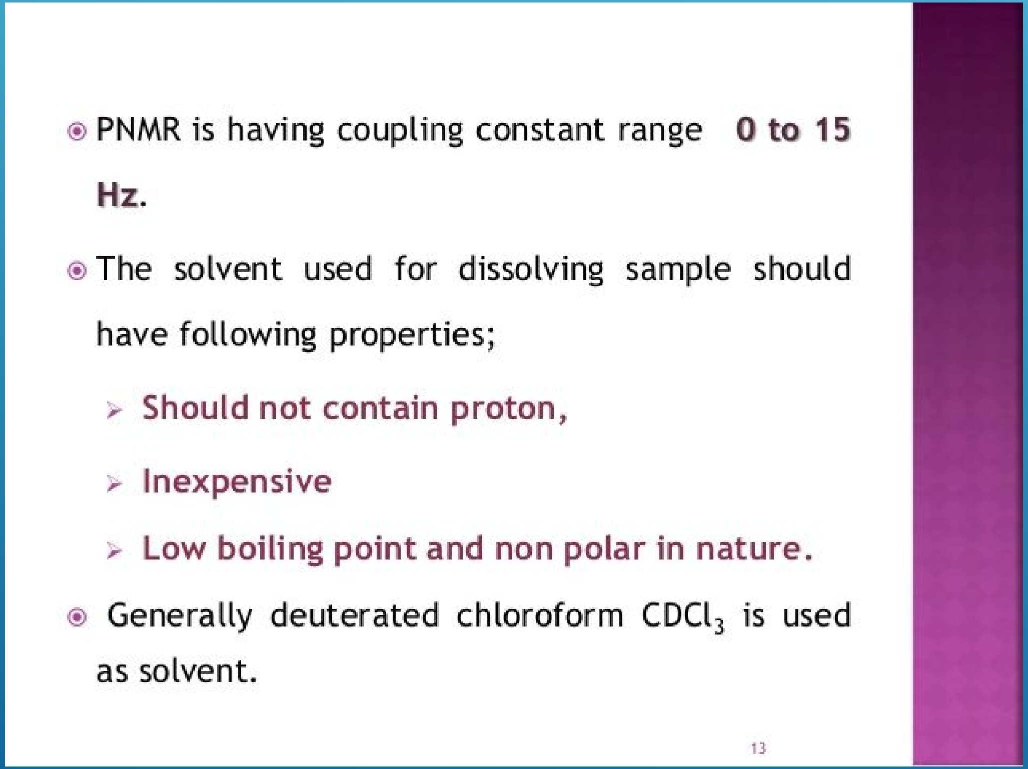
Shielding and Deshielding:-

- The circulation of electron around the protons itself generates field in a such way that , it oppose the applied field.
- The field felt by the protons is thus diminished and the proton is said to be **shielded** and the absorption said to be **upfield.**
- If the induced magnetic field reinforced the applied magnetic field ,then the field felt by the proton is augmented and the proton is said to be **deshielded** and the absorption is known as **downfield.**

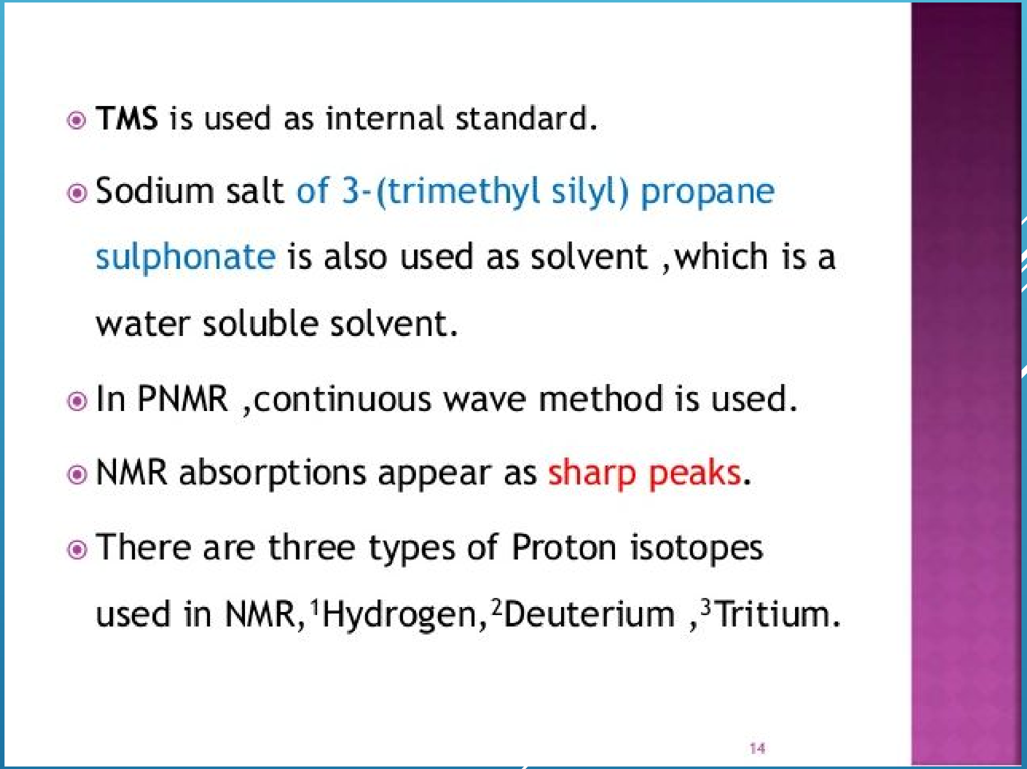


4.FEATURES OF PNMR

- Natural abundance of ^1H is 99.9844.
- PNMR is to determine type and number of H-protons in a molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency
- The chemical shift range of PNMR is **0 to 14 ppm.**



- PNMR is having coupling constant range **0 to 15 Hz**.
- The solvent used for dissolving sample should have following properties;
  - **Should not contain proton,**
  - **Inexpensive**
  - **Low boiling point and non polar in nature.**
- Generally deuterated chloroform $CDCl_3$ is used as solvent.



- **TMS** is used as internal standard.
- Sodium salt of 3-(trimethyl silyl) propane sulphonate is also used as solvent ,which is a water soluble solvent.
- In PNMR ,continuous wave method is used.
- NMR absorptions appear as sharp peaks.
- There are three types of Proton isotopes used in NMR, ^{1}Hydrogen, ^{2}Deuterium , ^{3}Tritium.

PROTON NMR

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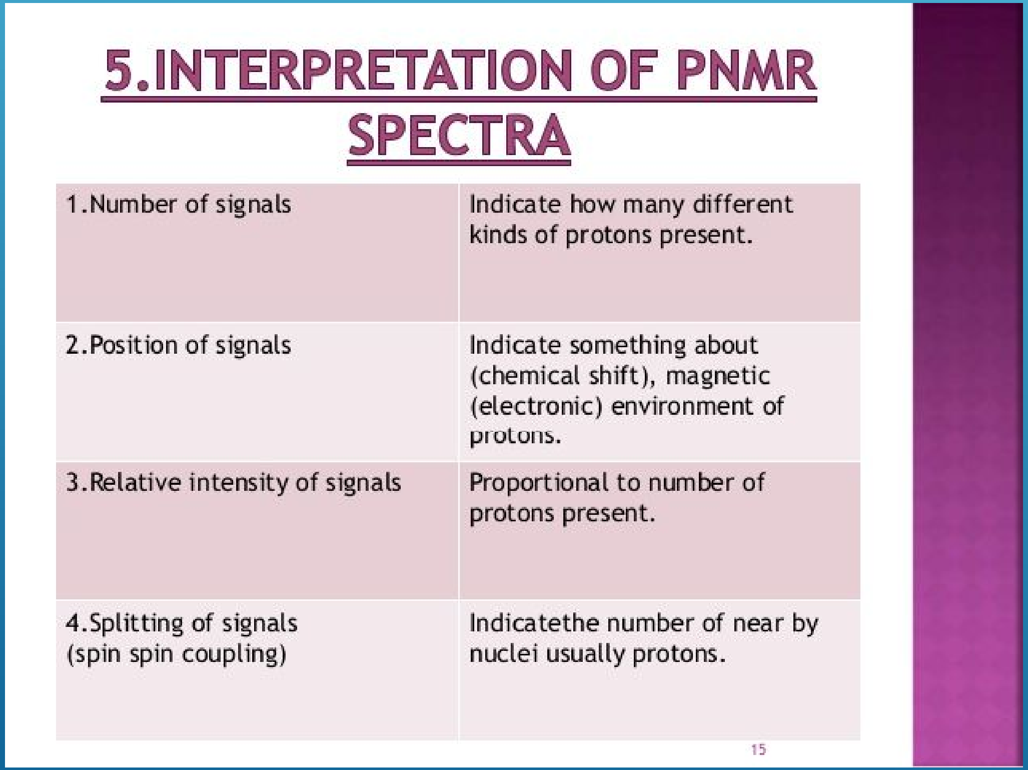
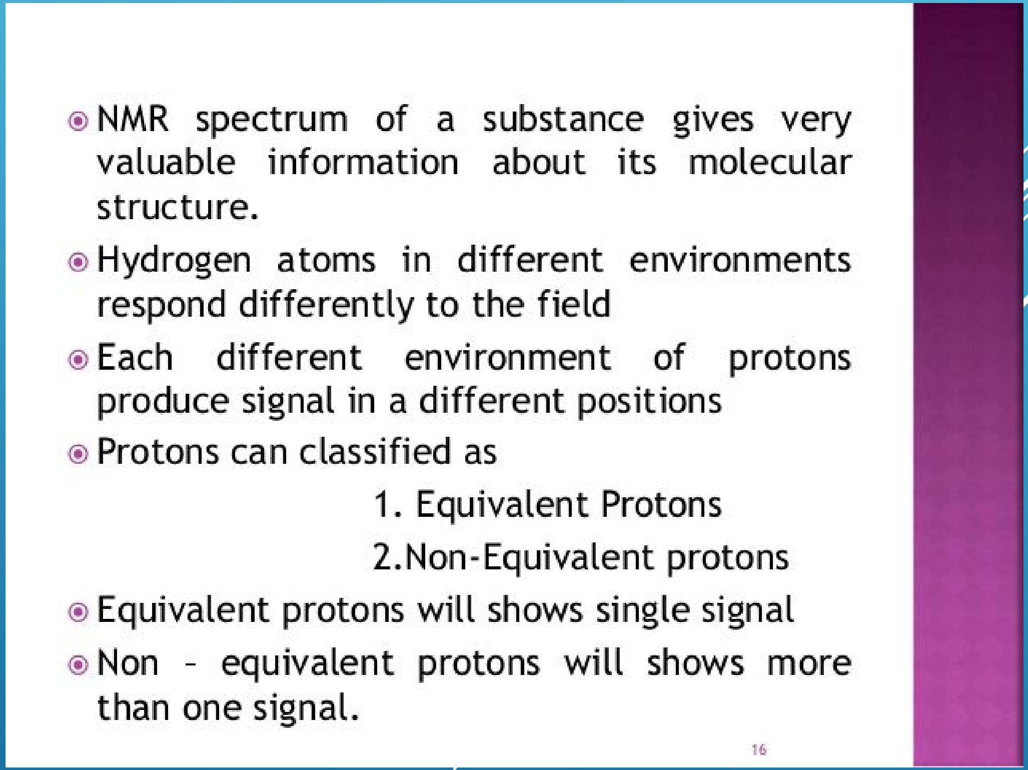
- Proton Area
- Application
- Chemical shift in PNMR

TOPIC



5.INTERPRETATION OF PNMR SPECTRA

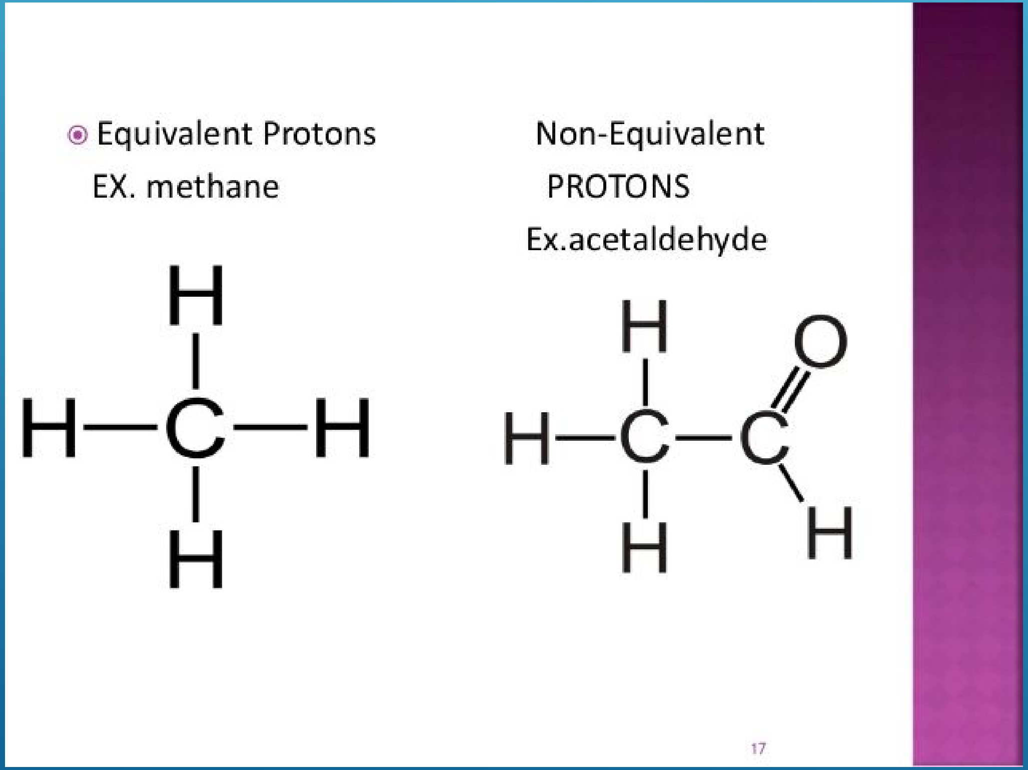
1.Number of signals	Indicate how many different kinds of protons present.
2.Position of signals	Indicate something about (chemical shift), magnetic (electronic) environment of protons.
3.Relative intensity of signals	Proportional to number of protons present.
4.Splitting of signals (spin spin coupling)	Indicatethe number of near by nuclei usually protons.



- NMR spectrum of a substance gives very valuable information about its molecular structure.
- Hydrogen atoms in different environments respond differently to the field
- Each different environment of protons produce signal in a different positions
- Protons can classified as

  1. Equivalent Protons

  2.Non-Equivalent protons
- Equivalent protons will shows single signal
- Non – equivalent protons will shows more than one signal.



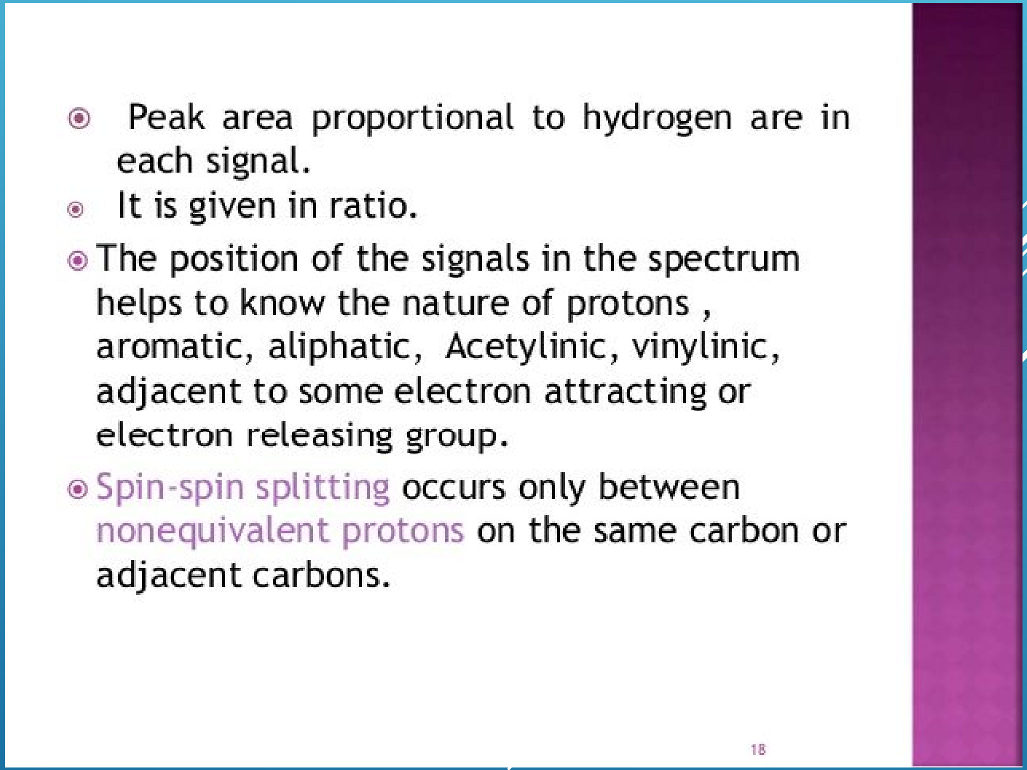
- Equivalent Protons

  EX. methane

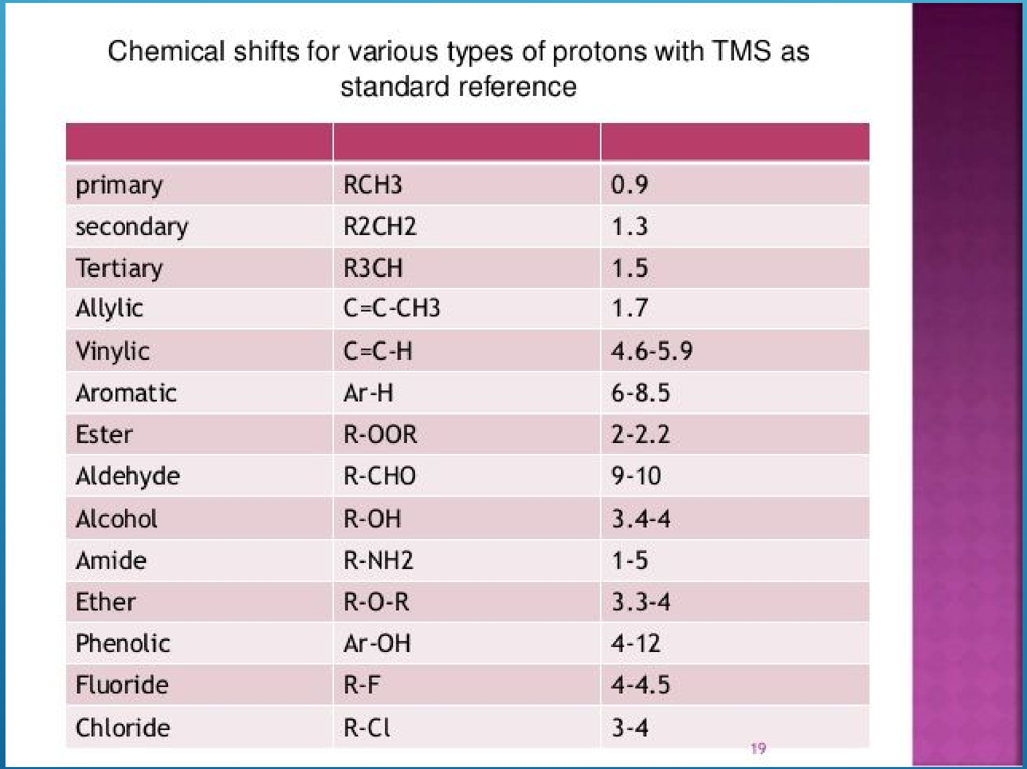
Non-Equivalent

PROTONS

Ex.acetaldehyde

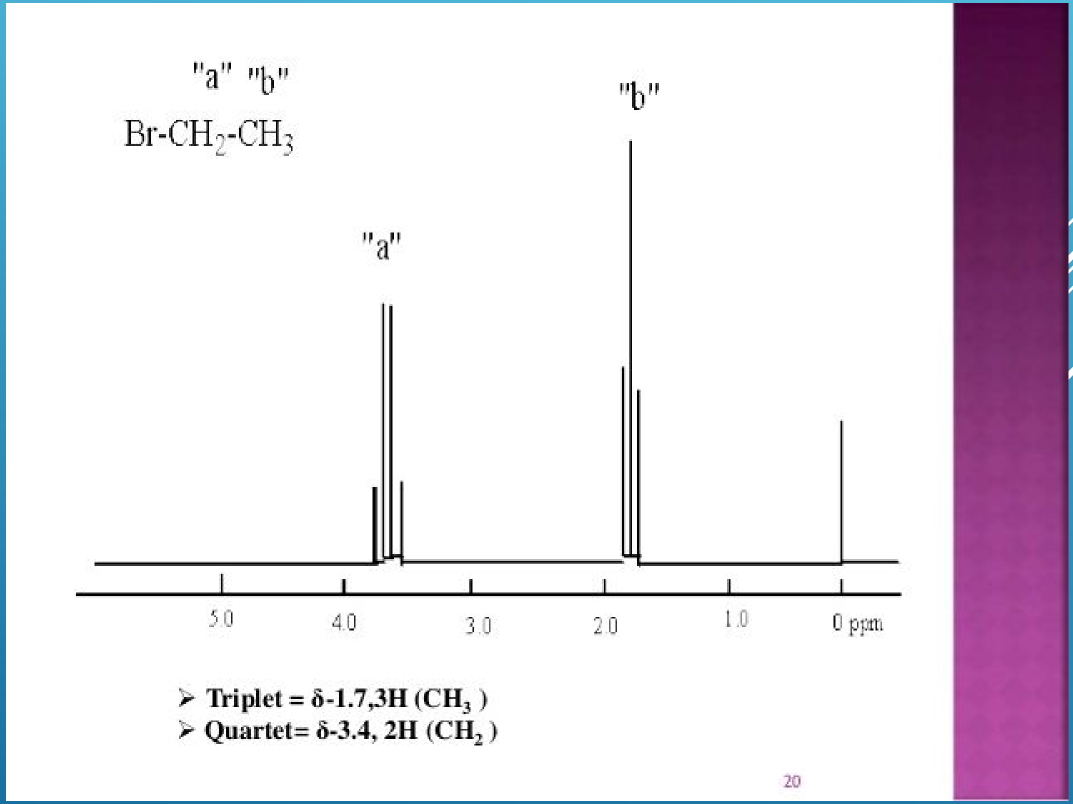


- Peak area proportional to hydrogen are in each signal.
- It is given in ratio.
- The position of the signals in the spectrum helps to know the nature of protons , aromatic, aliphatic, Acetylinic, vinylinic, adjacent to some electron attracting or electron releasing group.
- Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.

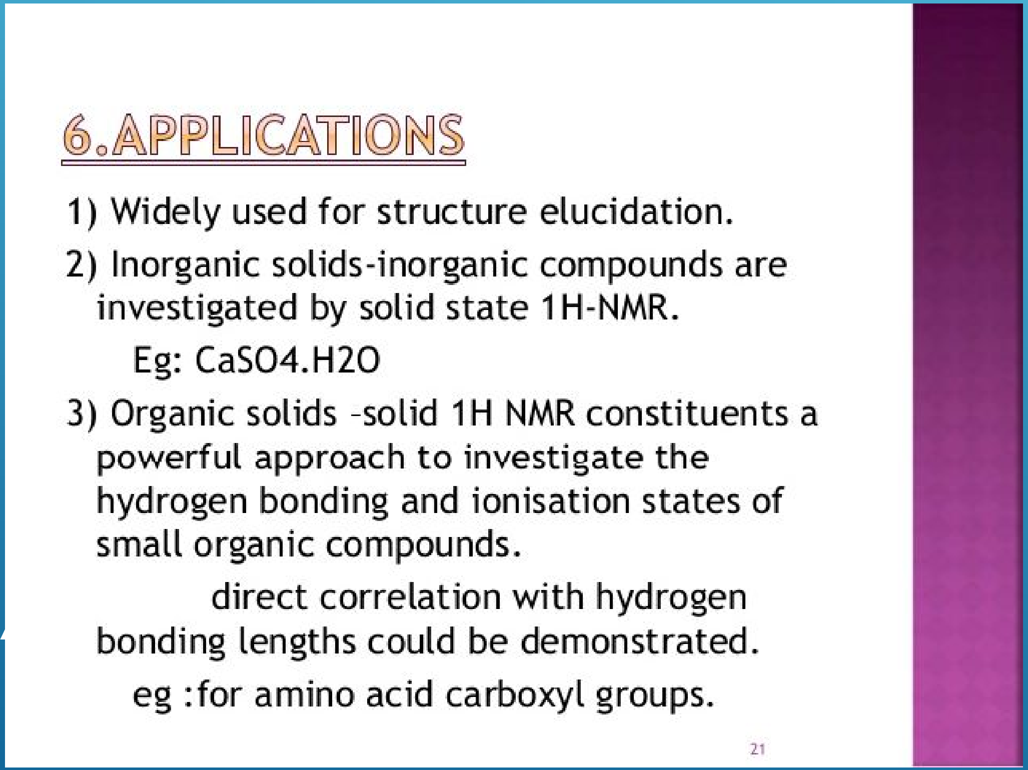


Chemical shifts for various types of protons with TMS as standard reference

primary	RCH3	0.9
secondary	R2CH2	1.3
Tertiary	R3CH	1.5
Allylic	C=C-CH3	1.7
Vinylic	C=C-H	4.6-5.9
Aromatic	Ar-H	6-8.5
Ester	R-OOR	2-2.2
Aldehyde	R-CHO	9-10
Alcohol	R-OH	3.4-4
Amide	R-NH2	1-5
Ether	R-O-R	3.3-4
Phenolic	Ar-OH	4-12
Fluoride	R-F	4-4.5
Chloride	R-Cl	3-4



- Triplet = δ-1.7,3H (CH_3)
- Quartet= δ-3.4, 2H (CH_2)



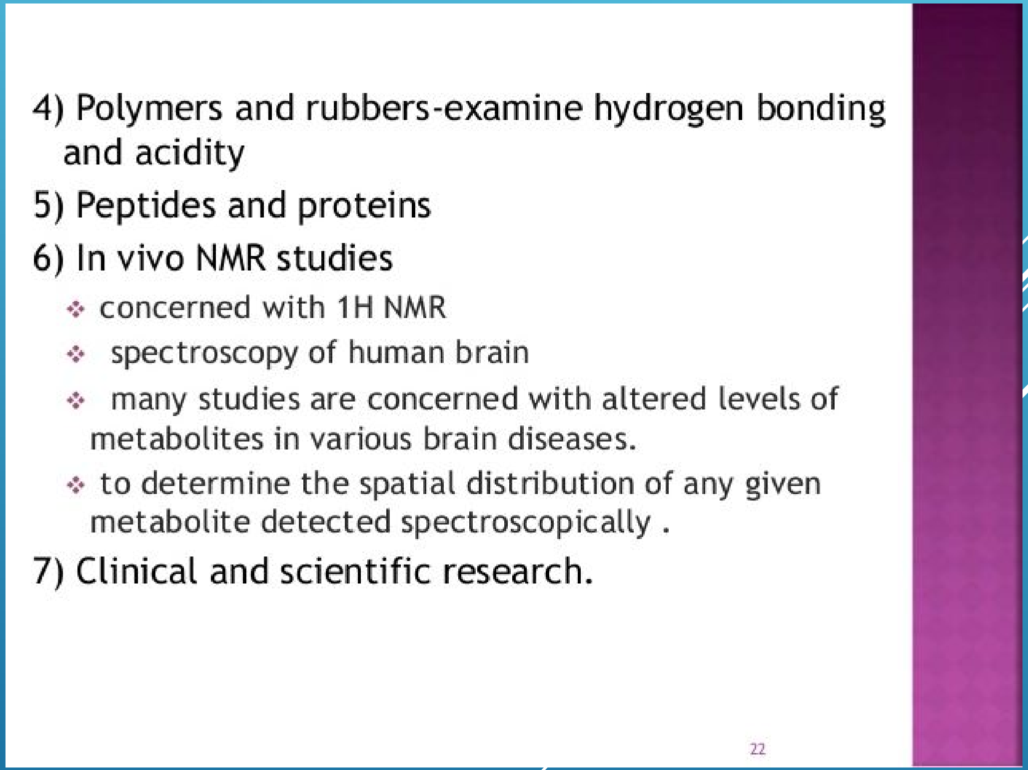
6.APPLICATIONS

1) Widely used for structure elucidation.
2) Inorganic solids-inorganic compounds are investigated by solid state 1H-NMR.

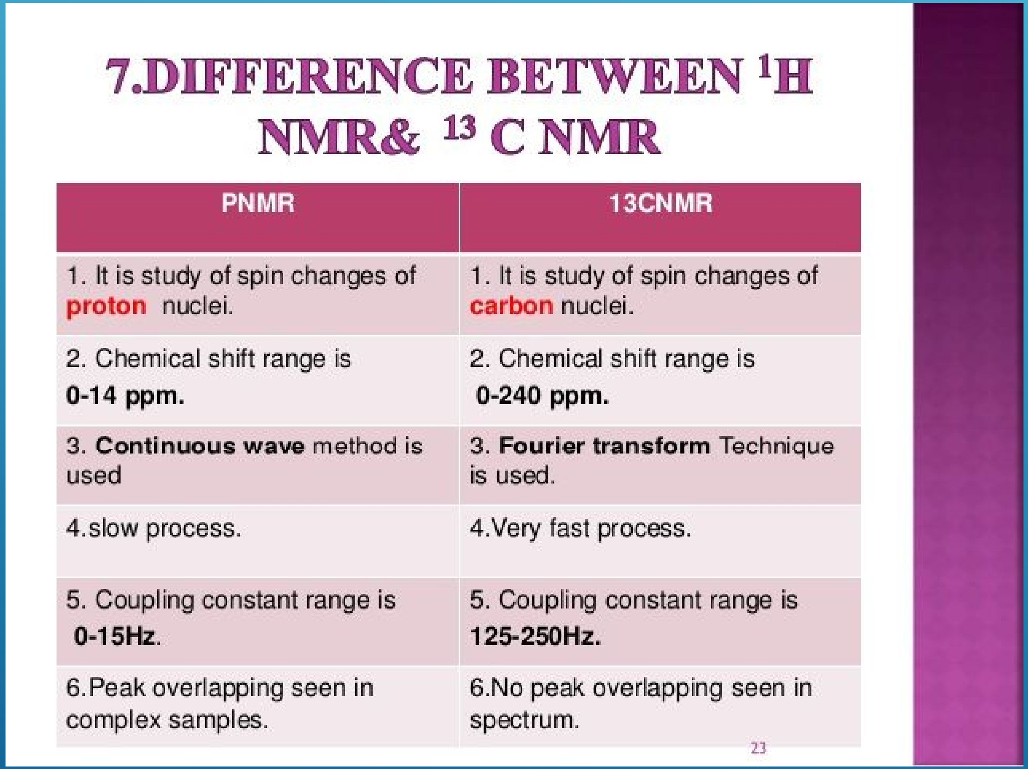
   Eg: $CaSO_4.H_2O$
3) Organic solids –solid 1H NMR constituents a powerful approach to investigate the hydrogen bonding and ionisation states of small organic compounds.

   direct correlation with hydrogen bonding lengths could be demonstrated.

   eg :for amino acid carboxyl groups.

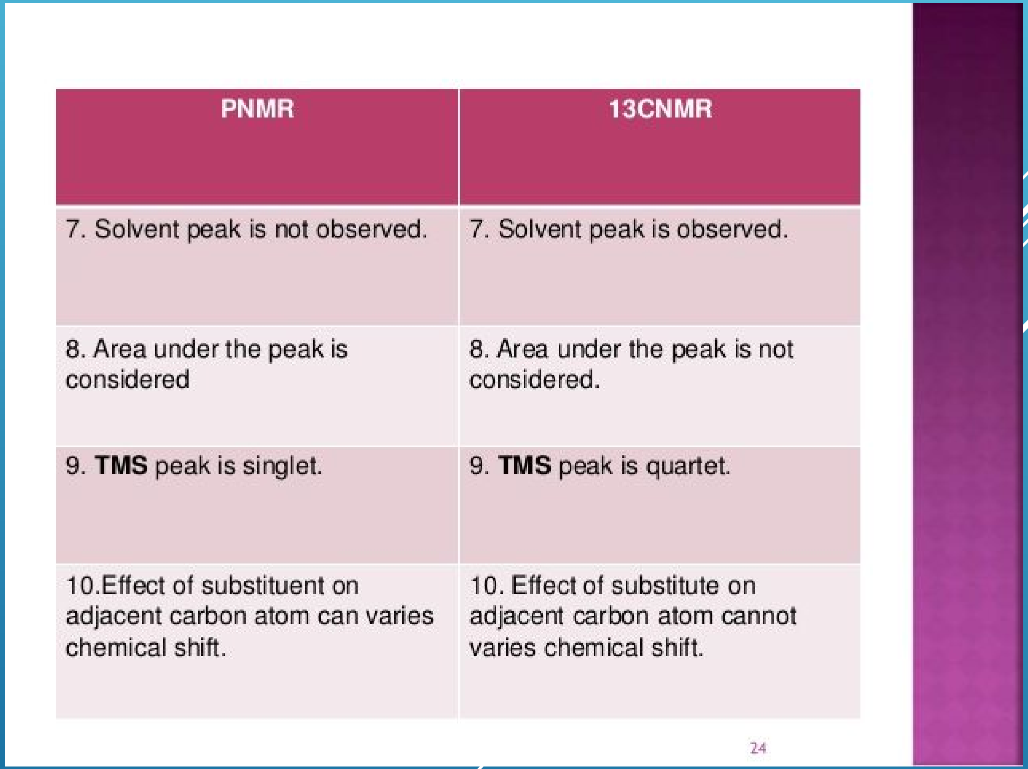


4) Polymers and rubbers-examine hydrogen bonding and acidity
5) Peptides and proteins
6) In vivo NMR studies
   - concerned with 1H NMR
   - spectroscopy of human brain
   - many studies are concerned with altered levels of metabolites in various brain diseases.
   - to determine the spatial distribution of any given metabolite detected spectroscopically .
7) Clinical and scientific research.

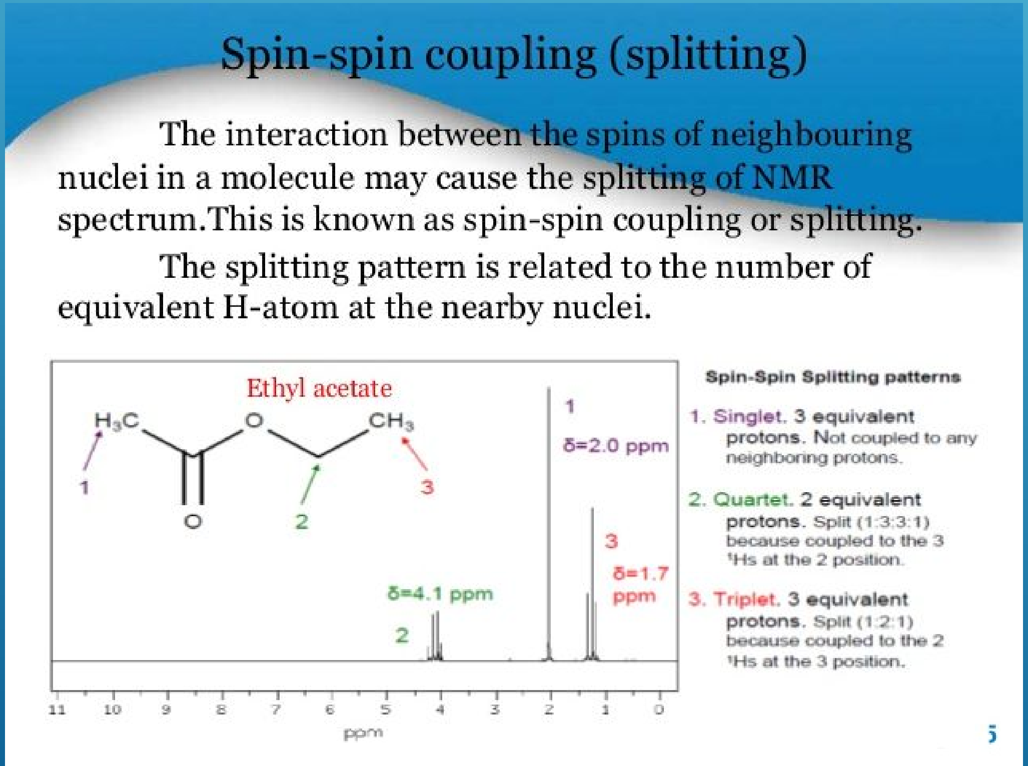


7.DIFFERENCE BETWEEN ^{1}H NMR& ^{13} C NMR

PNMR	13CNMR
1. It is study of spin changes of **proton** nuclei.	1. It is study of spin changes of **carbon** nuclei.
2. Chemical shift range is **0-14 ppm.**	2. Chemical shift range is **0-240 ppm.**
3. **Continuous wave** method is used	3. **Fourier transform** Technique is used.
4.slow process.	4.Very fast process.
5. Coupling constant range is **0-15Hz**.	5. Coupling constant range is **125-250Hz.**
6.Peak overlapping seen in complex samples.	6.No peak overlapping seen in spectrum.



PNMR	13CNMR
7. Solvent peak is not observed.	7. Solvent peak is observed.
8. Area under the peak is considered	8. Area under the peak is not considered.
9. **TMS** peak is singlet.	9. **TMS** peak is quartet.
10.Effect of substituent on adjacent carbon atom can varies chemical shift.	10. Effect of substitute on adjacent carbon atom cannot varies chemical shift.



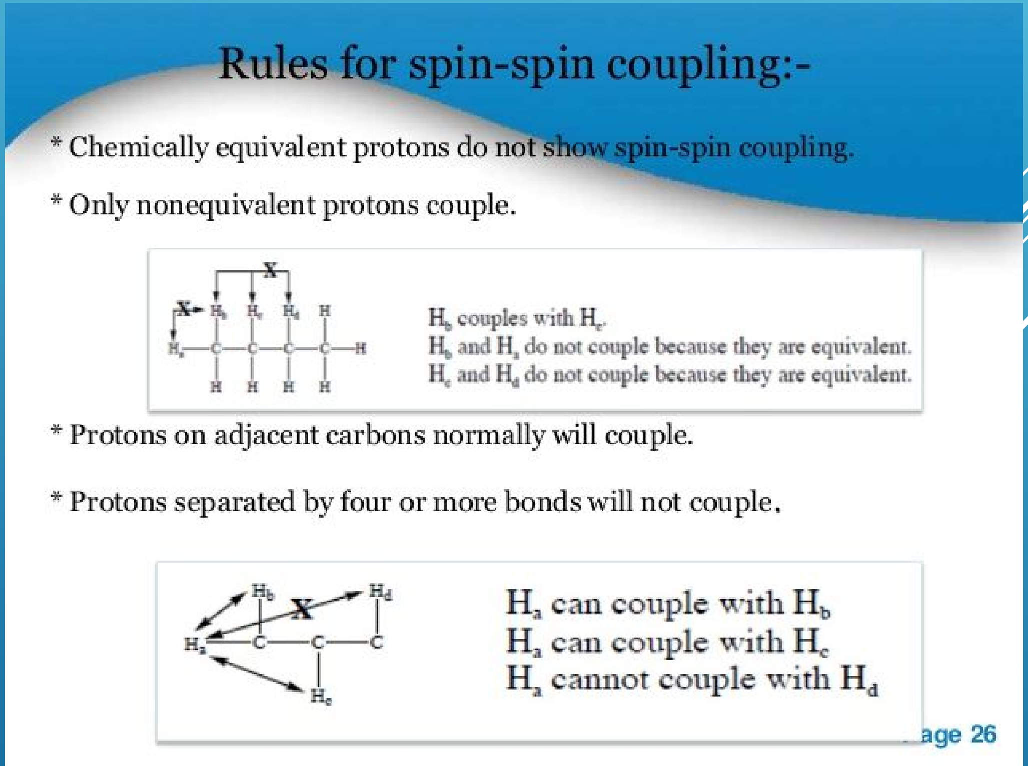
Spin-spin coupling (splitting)

The interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum.This is known as spin-spin coupling or splitting.

The splitting pattern is related to the number of equivalent H-atom at the nearby nuclei.

Spin-Spin Splitting patterns

1. Singlet. **3 equivalent protons.** Not coupled to any neighboring protons.
2. Quartet. **2 equivalent protons.** Split (1:3:3:1) because coupled to the 3 ^{1}Hs at the 2 position.
3. Triplet. **3 equivalent protons.** Split (1:2:1) because coupled to the 2 ^{1}Hs at the 3 position.



Rules for spin-spin coupling:-

* Chemically equivalent protons do not show spin-spin coupling.

* Only nonequivalent protons couple.

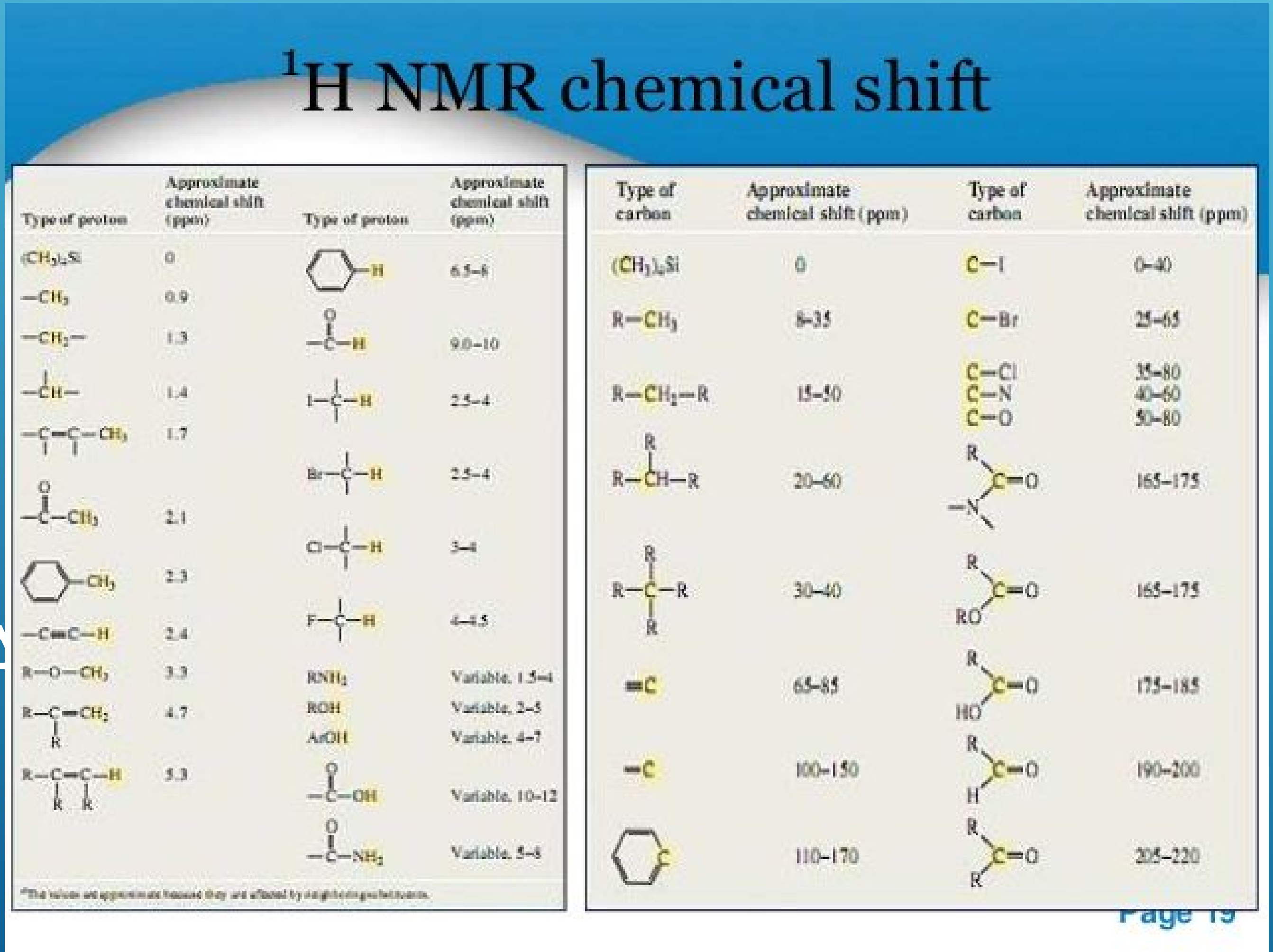
H_b couples with H_c.
H_b and H_a do not couple because they are equivalent.
H_c and H_d do not couple because they are equivalent.

* Protons on adjacent carbons normally will couple.

* Protons separated by four or more bonds will not couple.

H_a can couple with H_b
H_a can couple with H_c
H_a cannot couple with H_d

CHEMICA



^{1}H NMR chemical shift

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$-H$	6.5–8
$-CH_3$	0.9	$-\overset{O}{\overset{\|}{C}}-H$	9.0–10
$-CH_2-$	1.3	$I-\overset{\mid}{\underset{\mid}{C}}-H$	2.5–4
$-\overset{\mid}{C}H-$	1.4	$Br-\overset{\mid}{\underset{\mid}{C}}-H$	2.5–4
$-\underset{\mid}{C}=\underset{\mid}{C}-CH_3$	1.7	$Cl-\overset{\mid}{\underset{\mid}{C}}-H$	3–4
$-\overset{O}{\overset{\|}{C}}-CH_3$	2.1	$F-\overset{\mid}{\underset{\mid}{C}}-H$	4–4.5
$-CH_3$	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	$ArOH$	Variable, 4–7
$R-\underset{R}{\underset{\mid}{C}}=CH_2$	4.7	$-\overset{O}{\overset{\|}{C}}-OH$	Variable, 10–12
$R-\underset{R}{\underset{\mid}{C}}=\underset{R}{\underset{\mid}{C}}-H$	5.3	$-\overset{O}{\overset{\|}{C}}-NH_2$	Variable, 5–8

*The values are approximate because they are affected by neighboring substituents.

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
$R-\overset{R}{\overset{\mid}{C}}H-R$	20–60	R, $-N$ $C=O$	165–175
$R-\overset{R}{\overset{\mid}{\underset{R}{\underset{\mid}{C}}}}-R$	30–40	R, RO $C=O$	165–175
$\equiv C$	65–85	R, HO $C=O$	175–185
$=C$	100–150	R, H $C=O$	190–200
C	110–170	R, R $C=O$	205–220

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