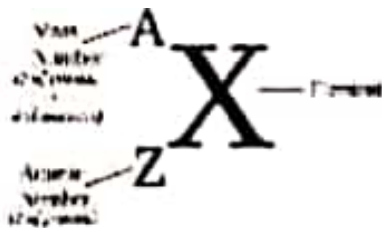
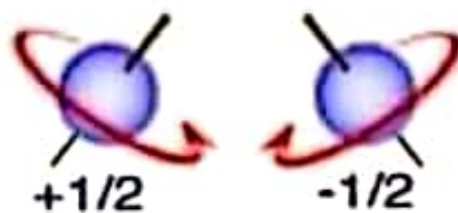

electromagnetic radiation.

- NMR spectroscopy is the most powerful tool available for **organic structure determination**.
- It is used to study a wide variety of nuclei (^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P etc).
- Most common types of NMR: proton and carbon-13
- ^1H NMR (PMR): To determine the type and number of H atoms and spatial arrangement of them in a molecule.
- ^{13}C NMR (CMR): To determine the type and number of carbon

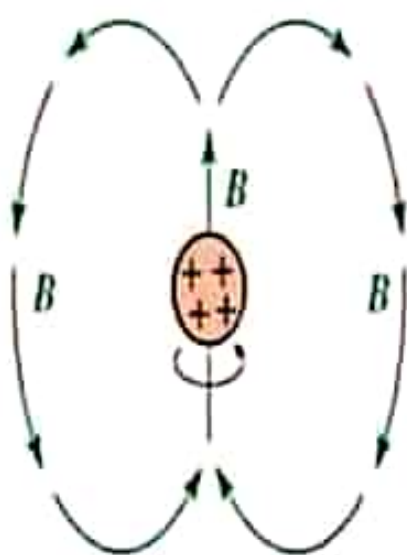


Nuclear Spin

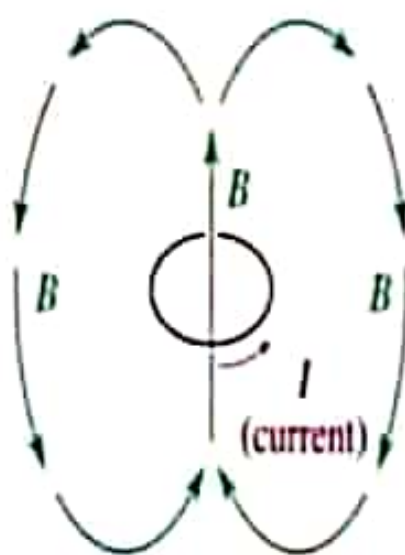
- A nucleus with an odd atomic number (no. of protons or electrons) or an odd mass number (no. of neutrons and protons in the nucleus) has a nuclear spin.
- If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$)
- If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)
- A nucleus of spin I will have $2I + 1$ possible orientations.
- A nucleus with spin $1/2$ (^1H & ^{13}C) will have 2 possible orientations.



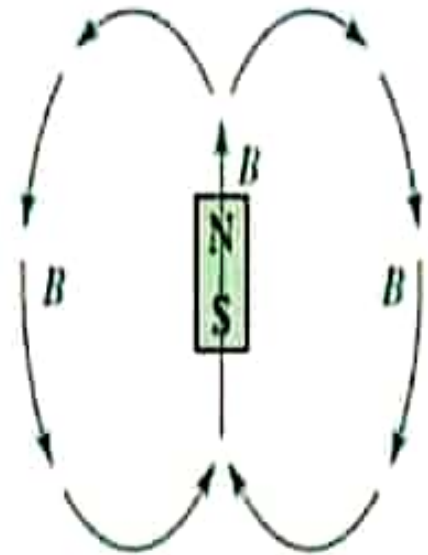
•The spinning charged nucleus generates a magnetic field.



spinning proton

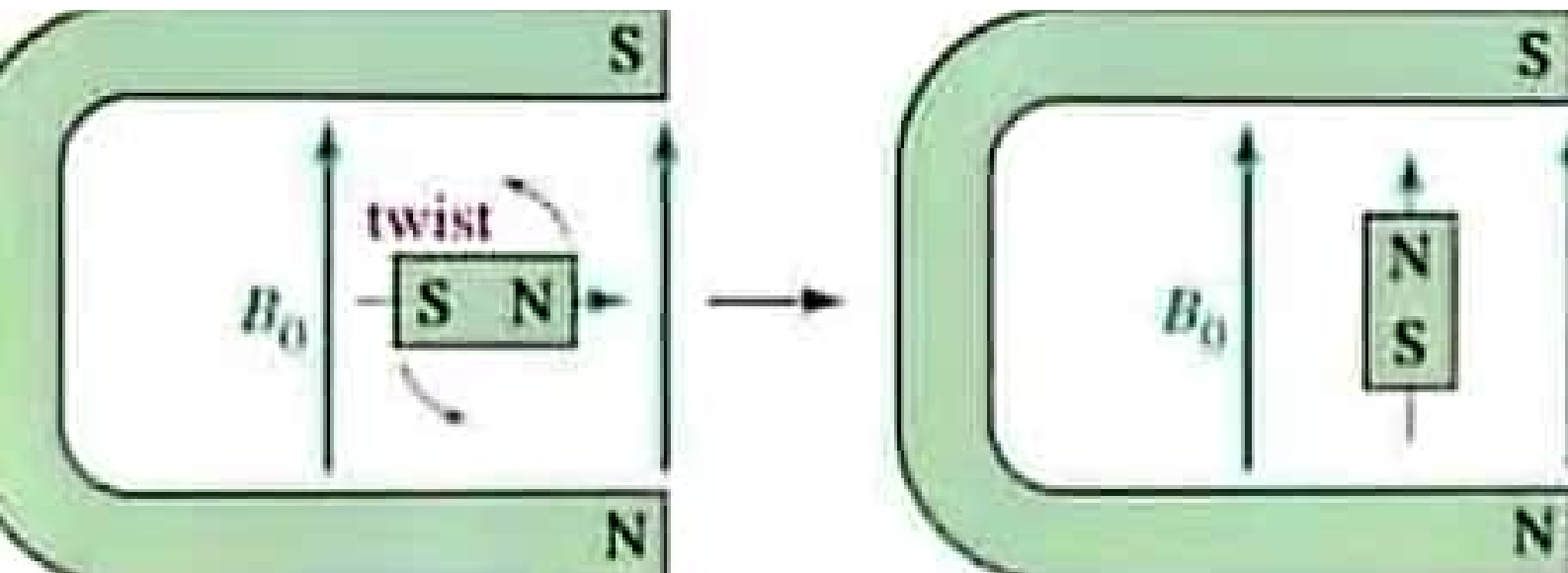


loop of current

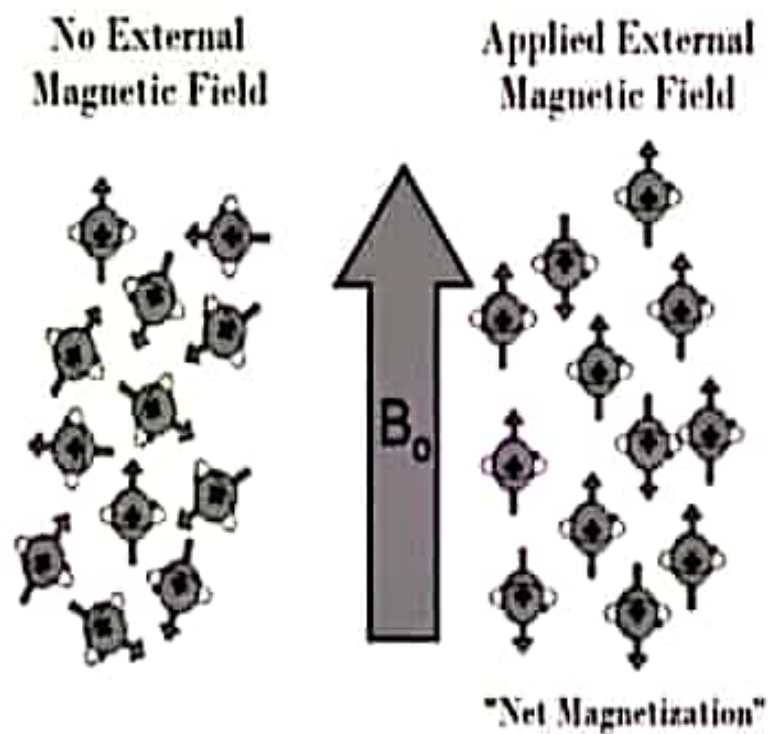


bar magnet





The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.



Two Energy

A photon with the right amount is absorbed and cause the spinning p



B_0

$$+\frac{1}{2} \text{ (or } \alpha \text{)}$$

$$-\frac{1}{2} \text{ (or } \beta \text{)}$$

Spin Energy States

strength.

$$\Delta E = h\nu = \frac{\gamma \hbar B_0}{2\pi}$$

- Gyromagnetic ratio, γ , is a constant for each nucleus.

$$\gamma = \mu / p$$

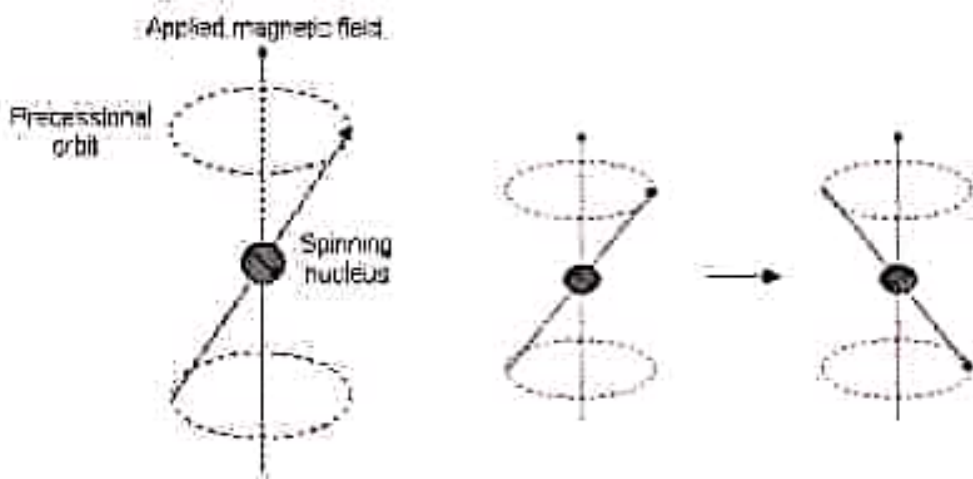
μ -dipole moment
 p -angular momentum

- In a 14,092 gauss field, a 60 MHz photon is required to flip a proton.
- A nucleus is in *resonance* when it

Nucleus or Particle	Gyromagnetic Ratio (γ) in MHz/Tesla
^1H	42.58
^3He	-32.43
^{13}C	10.71
^{19}F	40.05
^{23}Na	11.26
^{31}P	17.24
electron	-27,204

Larmor Precession

Spinning particle precesses about the external magnetic field axis at an angular frequency known as **Larmor frequency**. $f_0 = \gamma B_0$

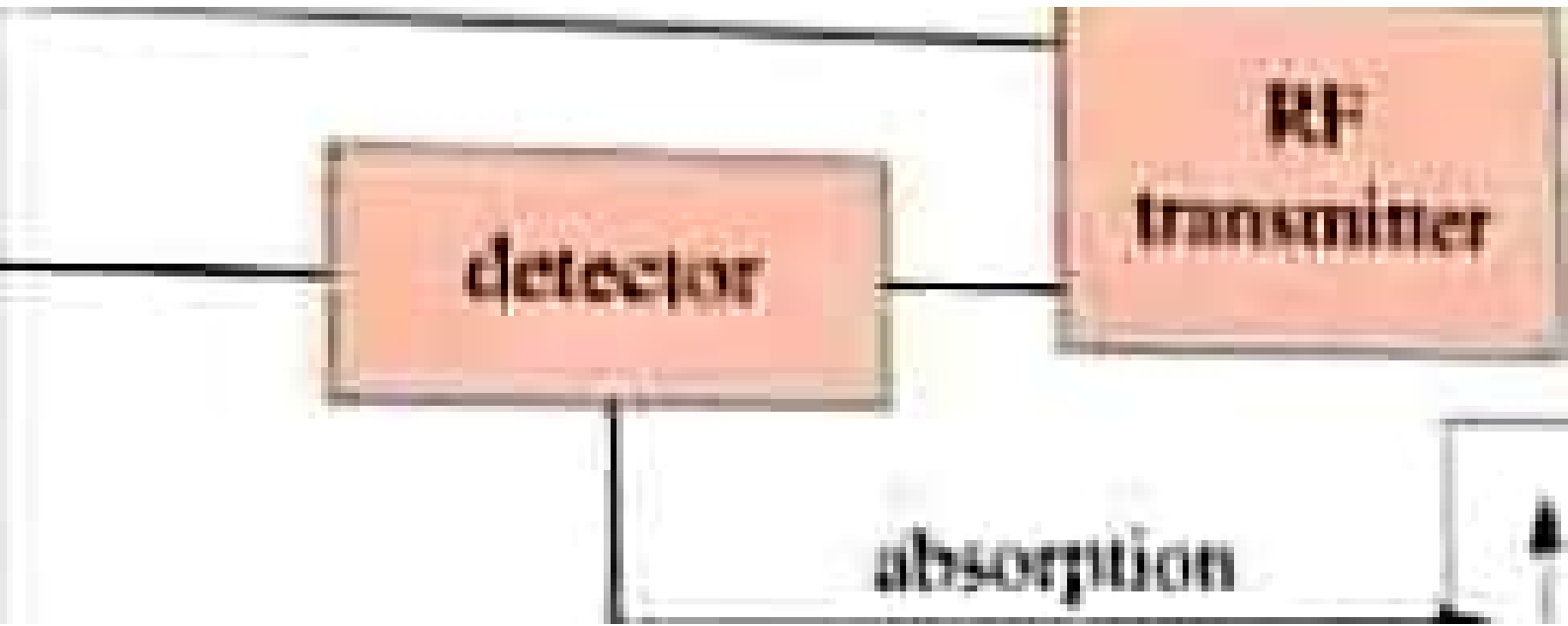


video playback (1).mp4



video playback (5).mp4

© NURLISA HIDAYATI'S PAGE



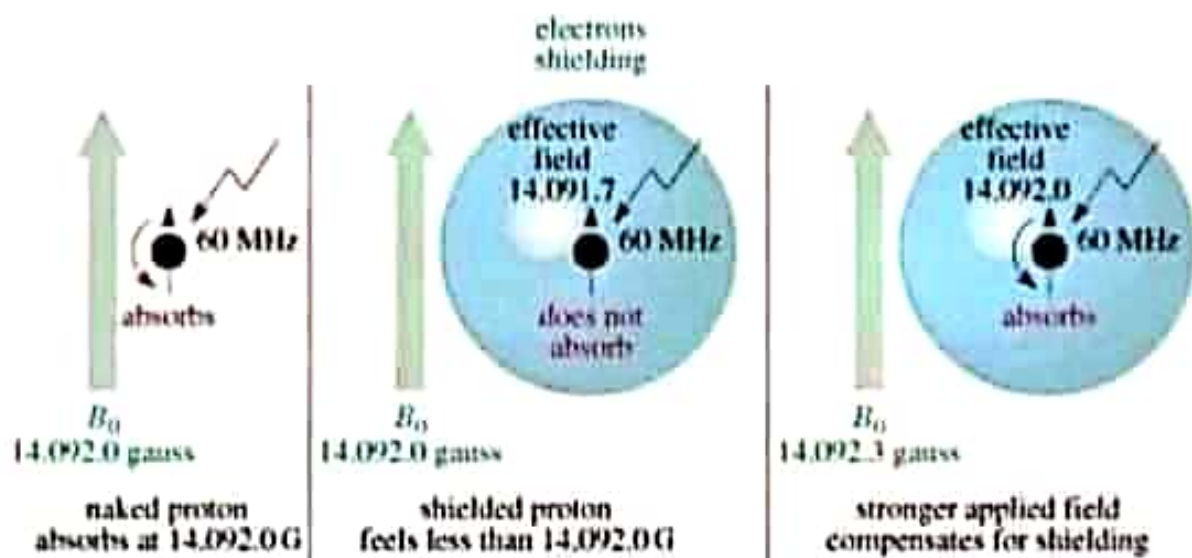
^1H NMR

Magnetic Shielding:

- If all protons absorb the same amount of energy in a given magnetic field, not much information can be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.

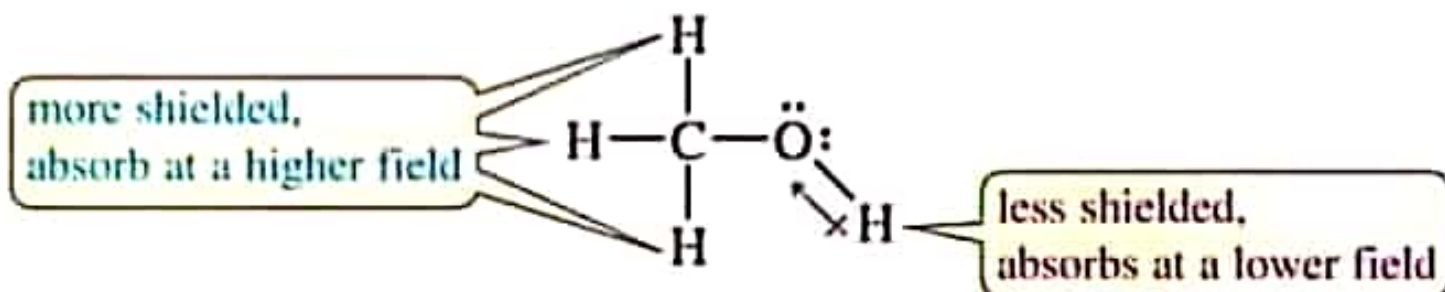
Shielded Protons

- Magnetic field strength must be increased for a shielded proton to flip at the same frequency.



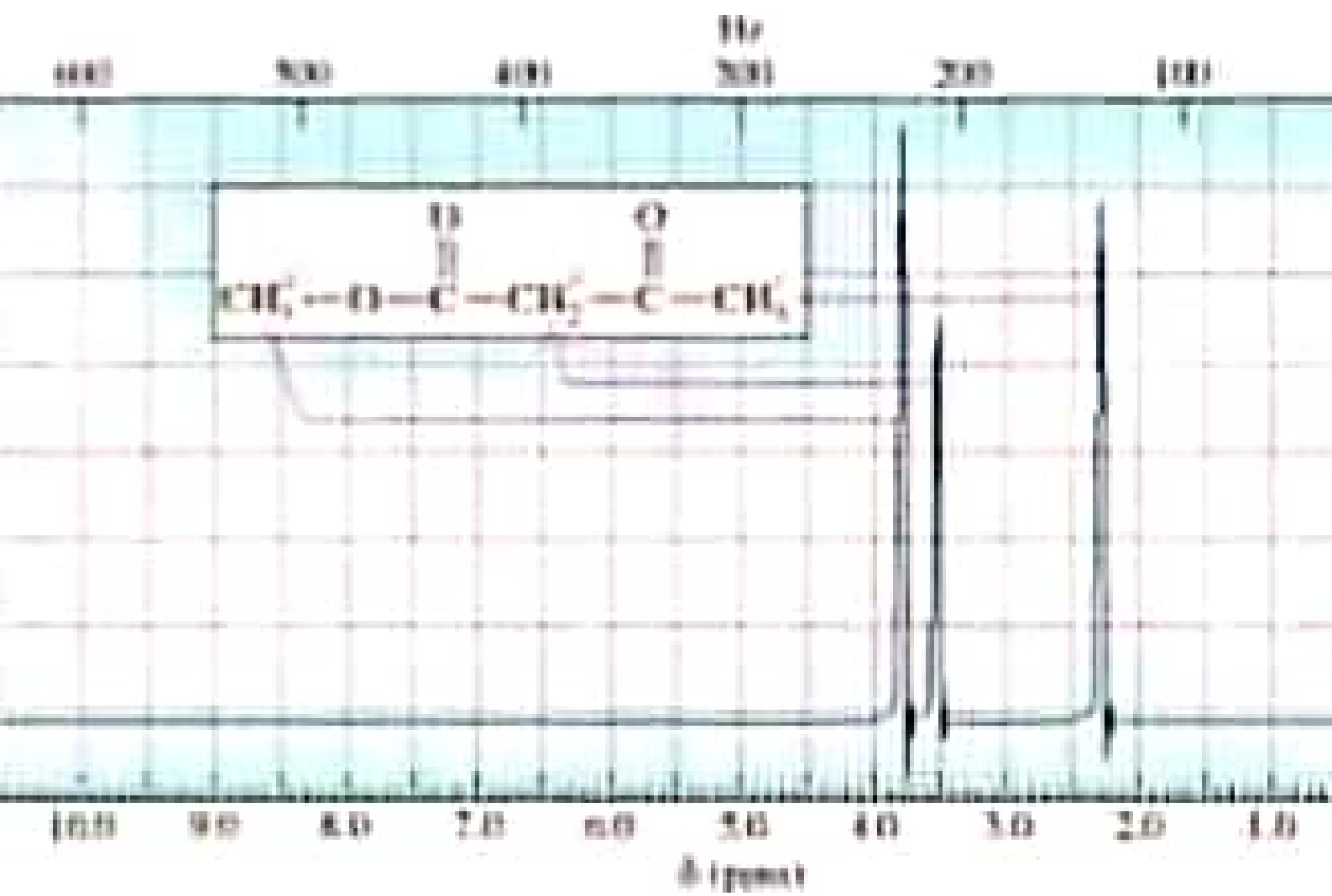
Protons in a Molecule

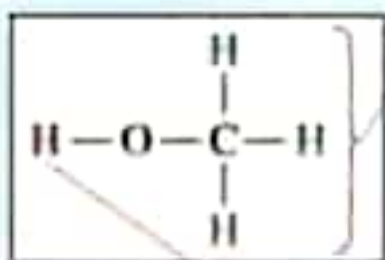
- Depending on their chemical environment, protons in a molecule are shielded by different amounts.



NMR Signals

- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms.



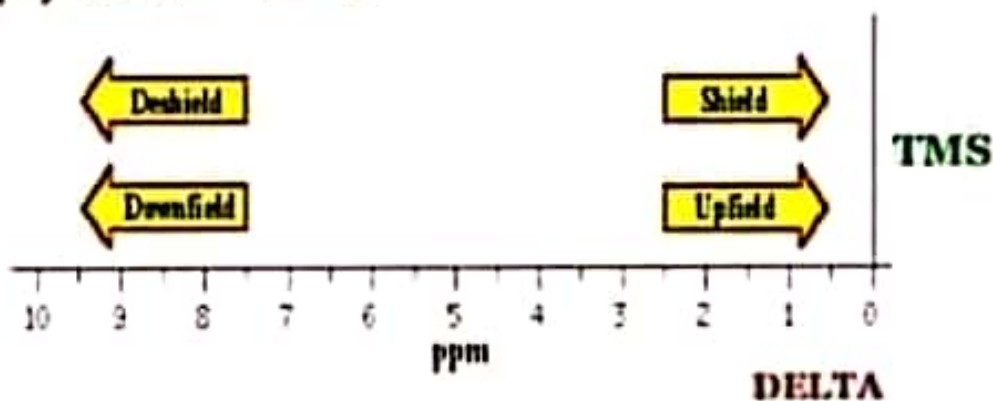


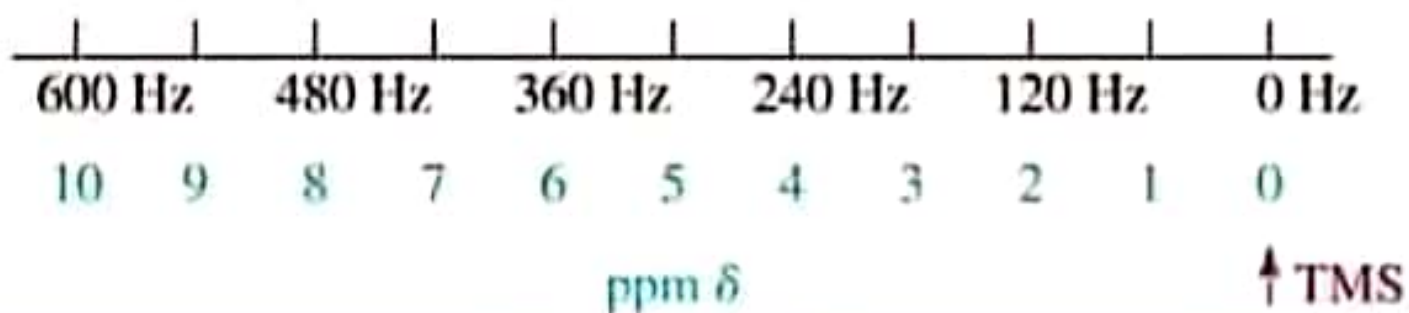
less shielded
lower field (downfield)

more shielded
higher field (upfield)

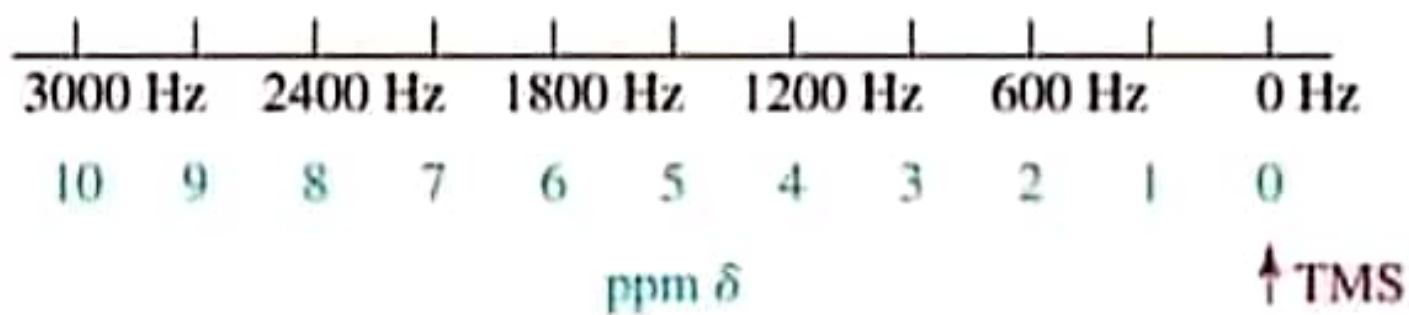
Chemical Shift

- Measured in parts per million (ppm), called the delta (δ) scale.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (MHz).
- Same value for 60, 100, or 300 MHz machine.
- **Tau (τ) value = $10 - \delta$**





60 MHz





- TMS is added to the sample.
- Since silicon is less electronegative than carbon, **TMS protons are highly shielded**. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

TABLE 13-2 Chemical Shifts of the Chloromethanes


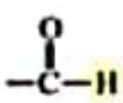
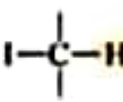
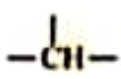
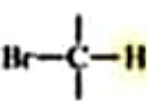
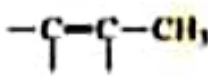
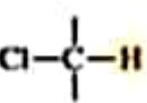
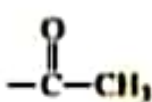
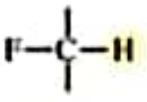
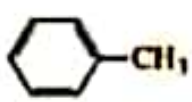
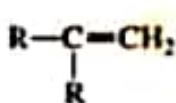
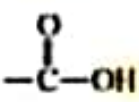
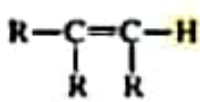
Compound	Chemical Shift	Difference
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	80.2	
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$	83.0	2.8 ppm
$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$	85.3	2.3 ppm
$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	87.2	1.9 ppm

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

Location of Signals

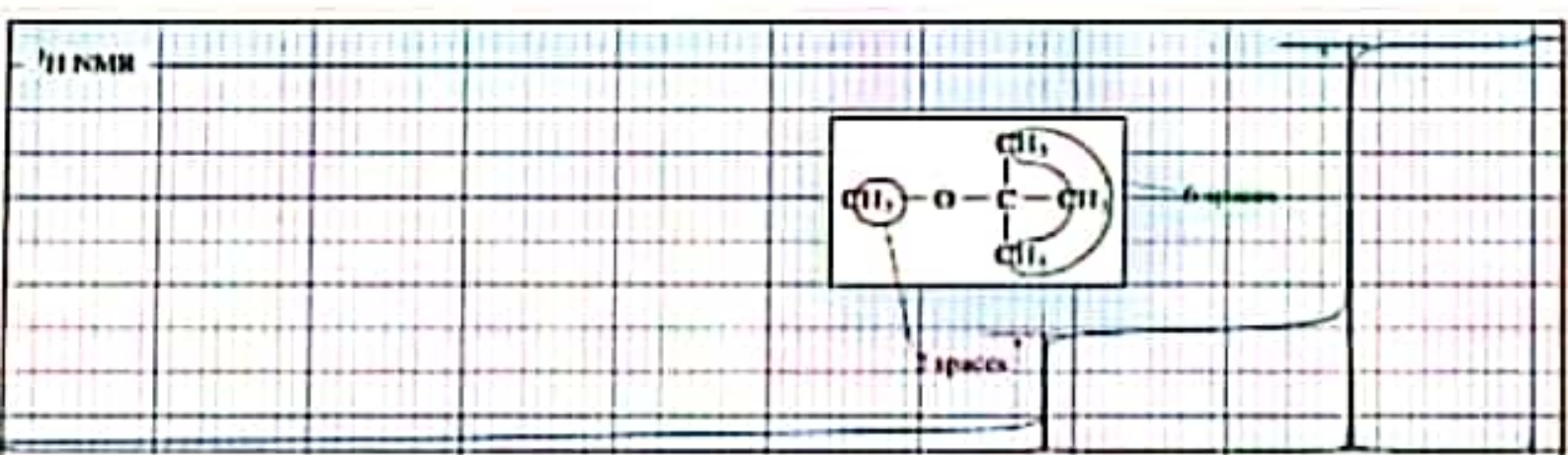
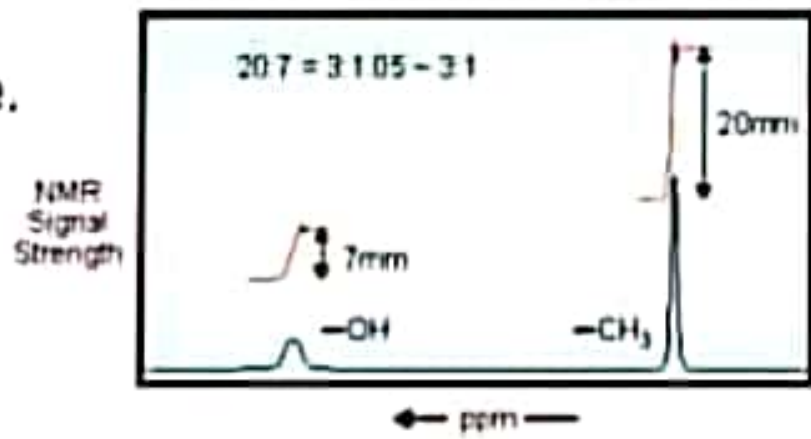
- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

PROTON CHEMICAL SHIFTS

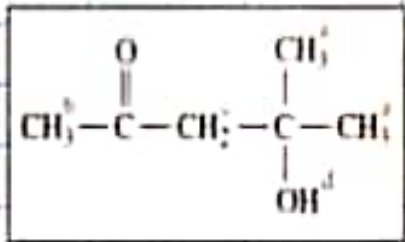
Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0		6.5-8
$-\text{CH}_3$	0.9		9.0-10
$-\text{CH}_2-$	1.3		2.5-4
	1.4		2.5-4
	1.7		3-4
	2.1		4-4.5
	2.3	RNH_2	variable, 1.5-4
$-\text{C}=\text{C}-\text{H}$	2.4	ROH	variable, 2-5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	variable, 4-7
	4.7		variable, 10-12
	5.3		

Intensity of Signals

- The area under each peak is proportional to the number of protons.
- Shown by integral trace.



¹H NMR



Spin-Spin Splitting

- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.
- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.
- All possibilities exist, so signal is split and splitting patterns (Multiplicity) results.

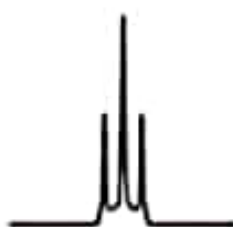
Common NMR peaks



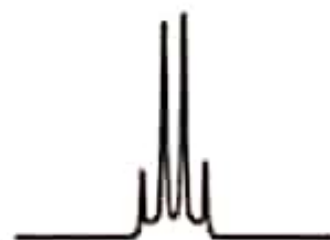
Singlet



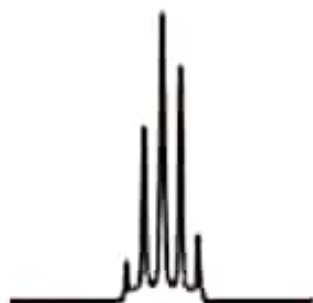
Doublet



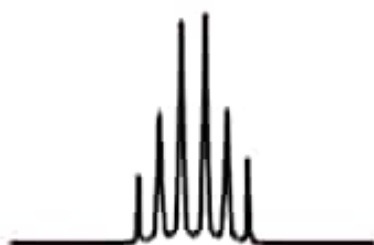
Triplet



Quartet



Quintet



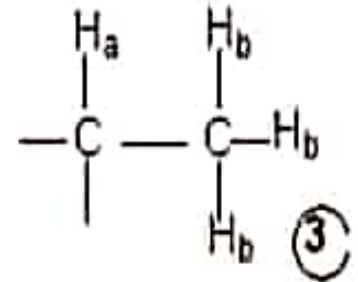
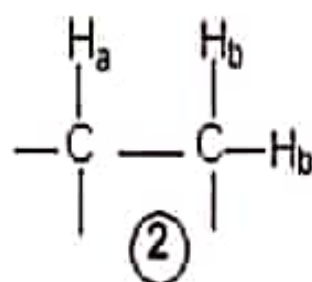
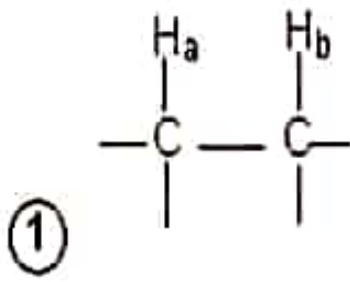
Sextet



Septet

Relative Peak Intensities of Symmetric Multiplets

<i>Number of Equivalent Protons Causing Splitting</i>	<i>Number of Peaks (multiplicity)</i>	<i>Area Ratios (Pascal's triangle)</i>
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1



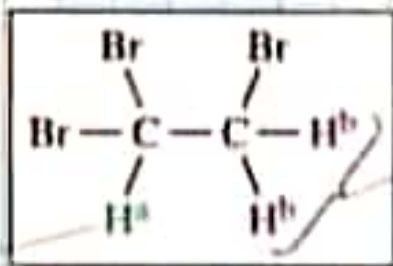
Spin orientations due to H_b



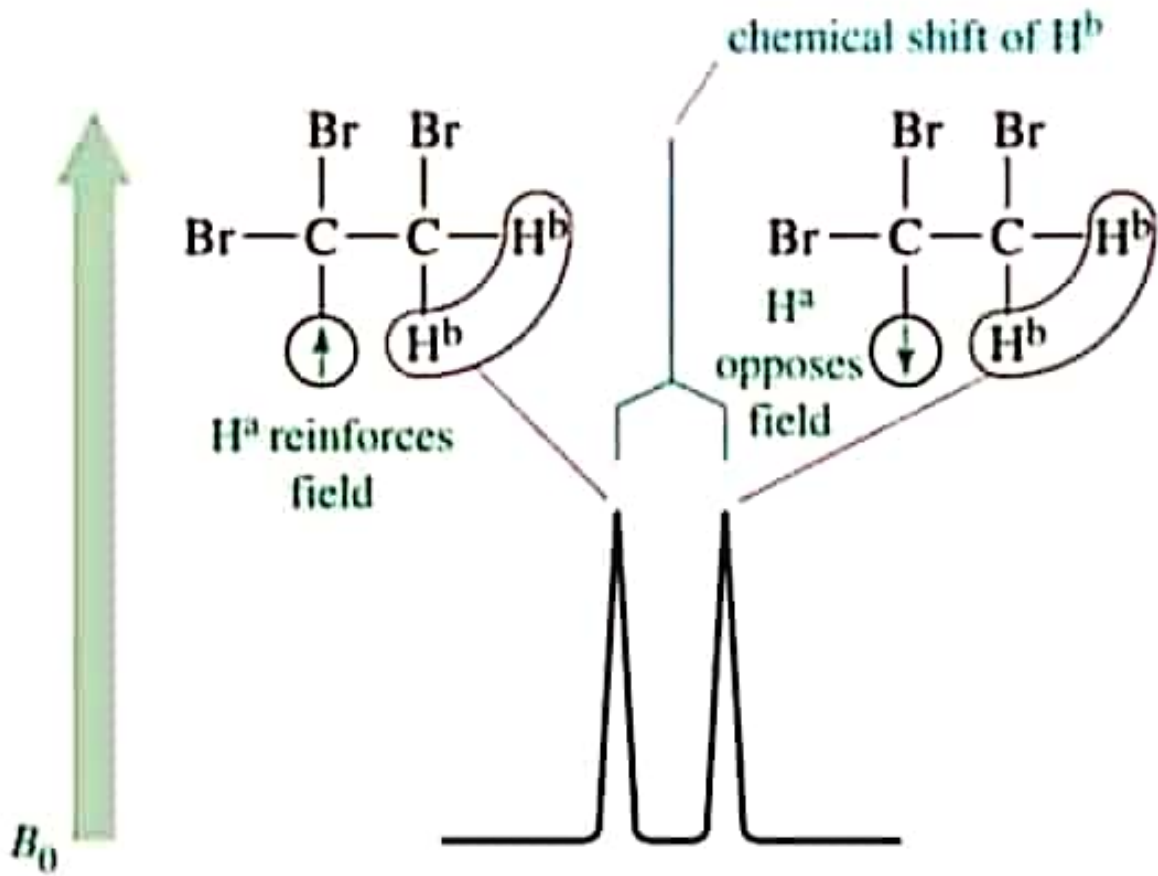
energy states splitting pattern two doublet

three triplet

four quartet



Doublet: 1 Adjacent Proton



Triplet: 2 Adjacent Protons

