

**B.Sc. Semester-VI
Paper CC-XIV
Organic Chemistry-V**



III. Nuclear Magnetic Resonance Spectroscopy



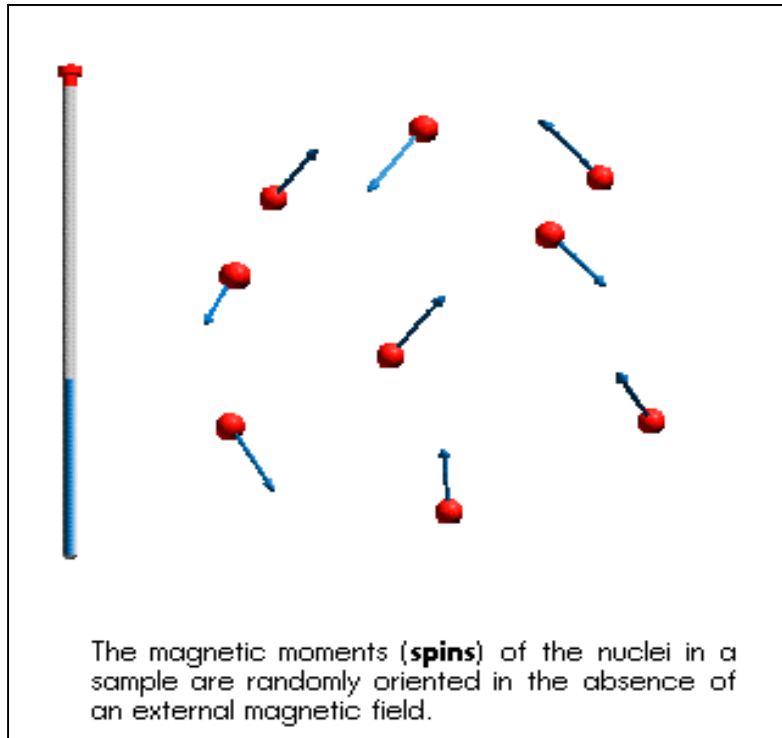
Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi



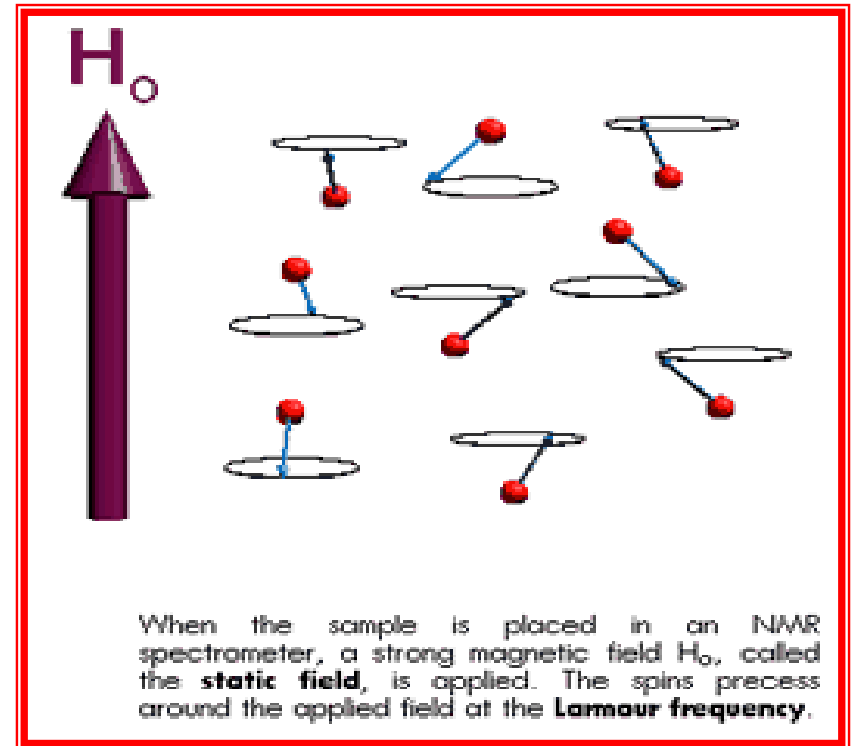
**Nuclear Magnetic Resonance
Spectrometer**

Theory of NMR Spectrometry

Orientation of nuclei in a magnetic field

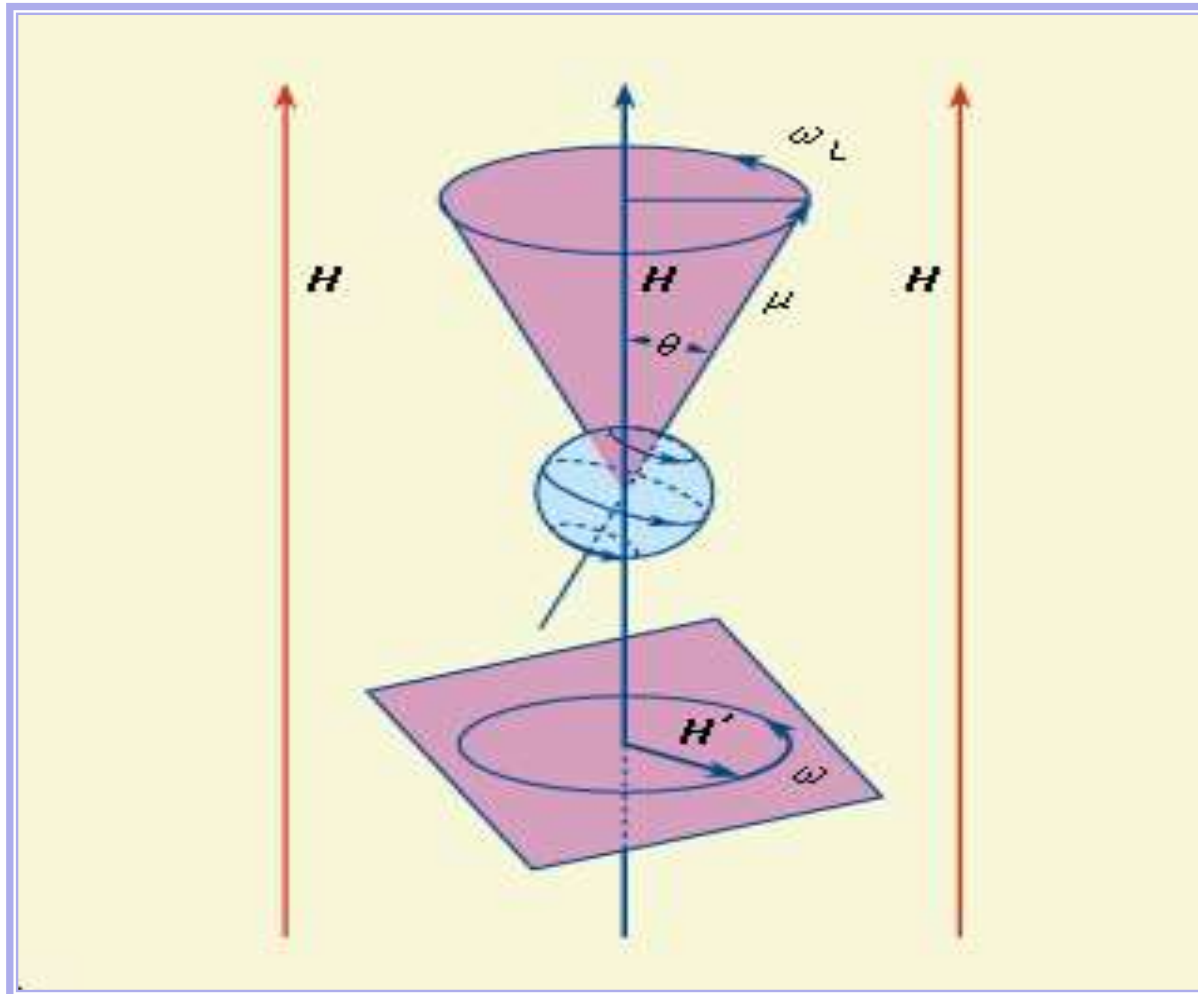


Random orientation



**In presence of a magnetic field
Magnetic moments precess and
Orient with or against the field**

Precession



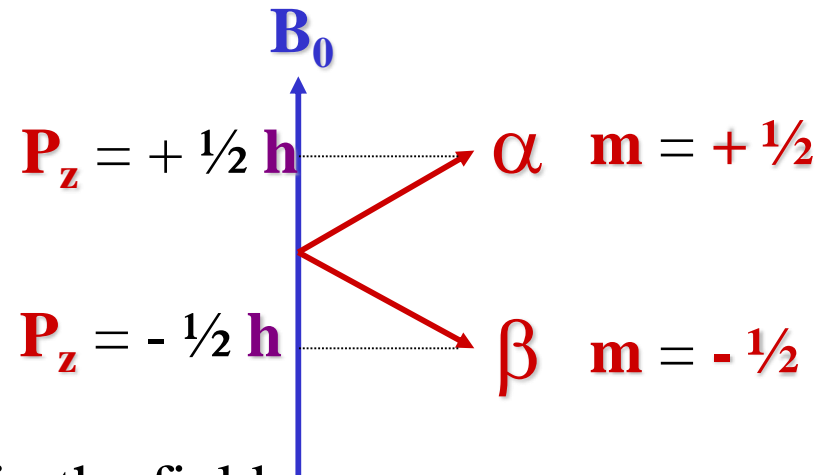
Directional Quantization

If a nucleus with angular momentum \mathbf{P} and Magnetic Moment $\boldsymbol{\mu}$ is placed in a magnetic field \mathbf{B}_0 ,

The angular momentum takes an orientation along \mathbf{B}_0 such that it is an **integral** or **half integral** of h (Planck constant)

m is the magnetic or **directional quantum number** it can take values:

$$m = I, I-1, \dots, -I$$

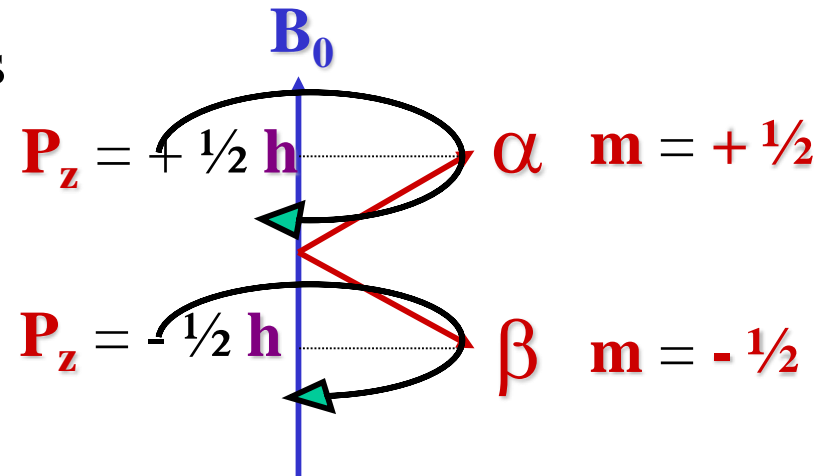


There are then $2I + 1$ orientations in the field

Directional Quantization

The Magnetic Moment $\mu = m \gamma h$ precesses around the z-axis (magnetic field B_0)

$$\nu_L = \gamma B_0 / 2\pi$$



The **Energy** of a magnetic dipole in the magnetic field B_0 is:

$$E = - \mu B_0 \quad \text{Where } \mu = m \gamma h$$

For a nuclei with $(2I+1)$ orientations the energy of the individual states (Zeeman levels) is:

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

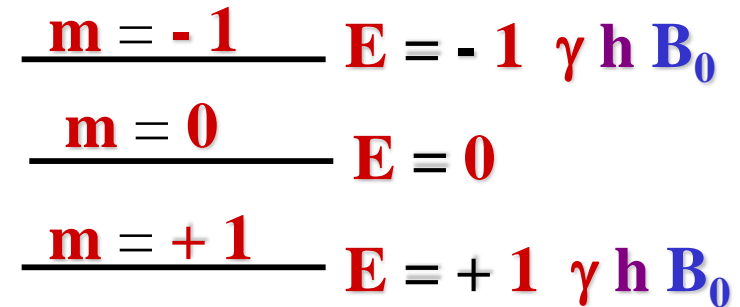
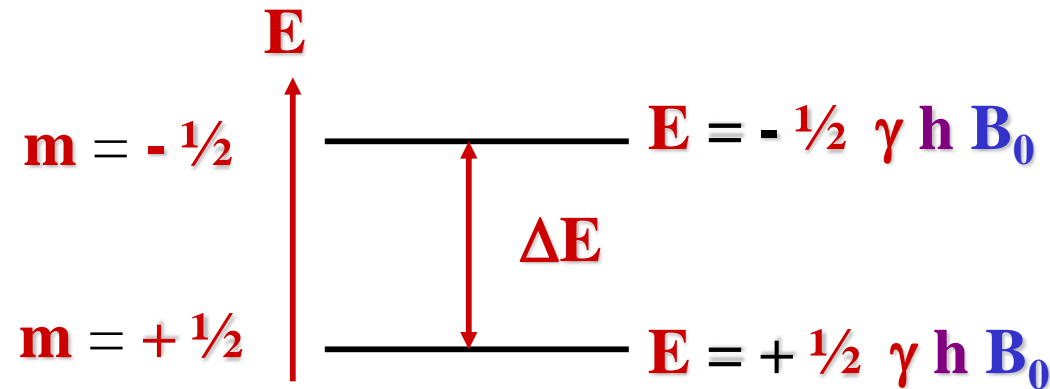
Energy Level and Resonant Transitions

For spin $\mathbf{I} = 1/2$ the energy gap between the 2 levels is:

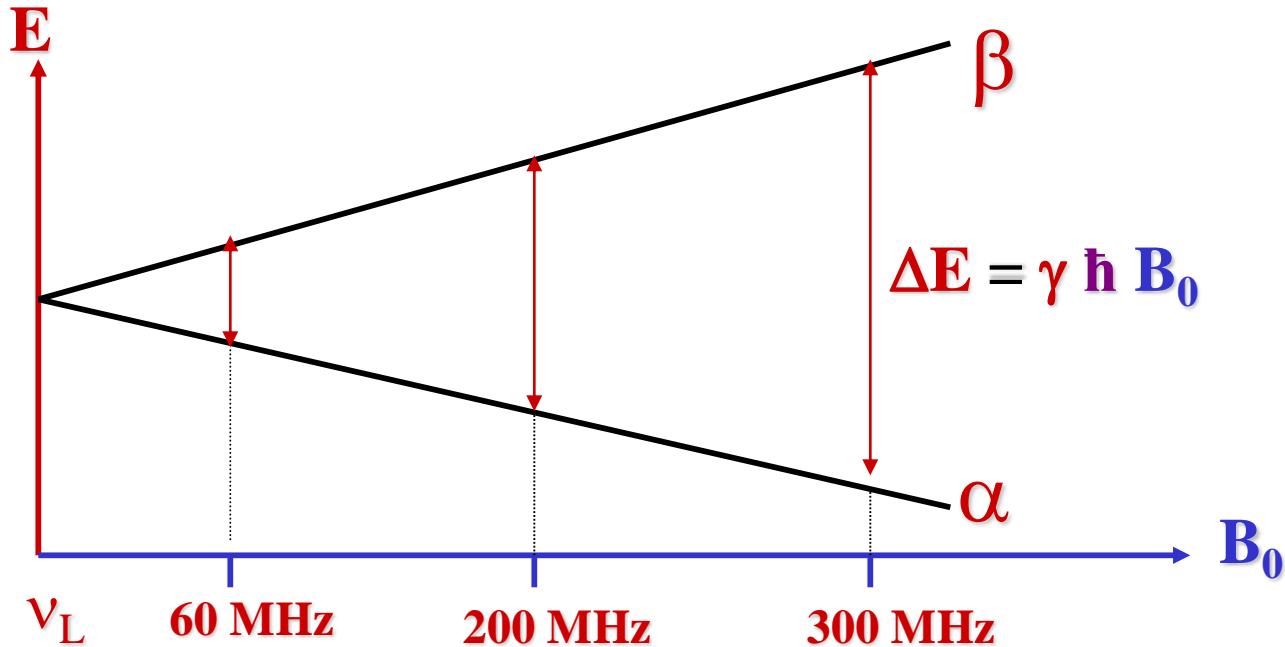
$$\Delta E = \gamma \hbar B_0 = h \nu$$

$$\nu = \gamma B_0 / 2\pi$$

For spin $\mathbf{I} = 1$



Energy vs Field Strength



Boltzmann Equation

$$\frac{N_{\beta}}{N_{\alpha}} = e^{(\Delta E/kT)} \sim 1 - \Delta E/kT$$

Where $k=1.3805 \times 10^{-23} \text{ J K}^{-1}$
T is the temperature

e.g. with $B_0=1.4 \text{ T}$ ($\nu_L=60 \text{ MHz}$)

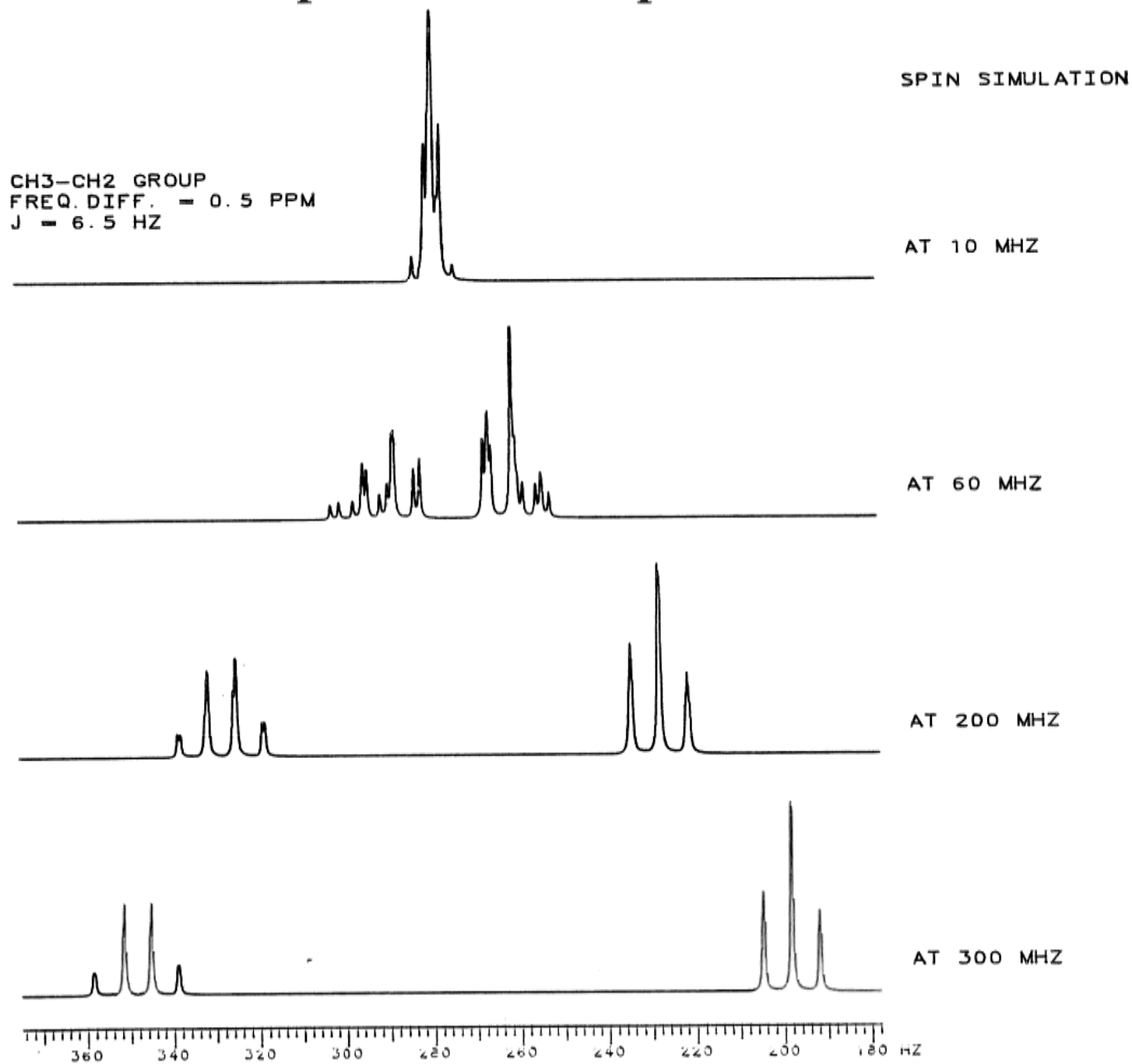
$\Delta E_H \sim 2.4 \text{ J/mol}$ At $T=300\text{K}$

$$N_{\beta} = .9999904 N_{\alpha}$$

with $B_0=7.05 \text{ T}$ ($\nu_L=300 \text{ MHz}$)

$$N_{\beta} = .99995 N_{\alpha}$$

Field dependence of a spectra



Spin Quantum Number

ELEMENT	# Protons	# Neutrons	I (Spin Quantum Number)
^1H	1	0	1/2
^2H	1	1	1
^3H	1	2	1/2
^4He	2	2	0
^3He	2	1	1/2
^6Li	3	3	1
^7Li	3	4	3/2
^{10}B	5	5	3
^{11}B	5	6	3/2
^{12}C	6	6	0
^{13}C	6	7	1/2
^{14}N	7	7	1
^{15}N	7	8	1/2

Even mass:

protons & # Neutrons **Both Even** : $I=0$ (^4He , ^{12}C ...)

Protons & # Neutrons **Both Odd** : $I=1, 2, \dots$ (Integer)

Odd mass:

protons **odd** & # Neutrons **Even** : $I=1/2, 3/2, \dots$ (Half-integer)

protons **even** & # Neutrons **odd** : $I=1/2, 3/2, \dots$ (Half-integer)

Important Elements in NMR Spectrometry

There are 4 important elements in Org. Chemistry: (frequency at 2.35T)

- H : Best NMR element
 - ^1H , $I = 1/2$ (sharp lines), $a = 99.98\%$, high frequency ($\nu = 100$ MHz)
 - ^2H , $I = 1$ (broad lines), $a = 0.02\%$, $\nu = 15.4$ MHz, $Q = 0.038$
- C :
 - ^{12}C , $I = 0$ (no signal in NMR)
 - ^{13}C , $I = 1/2$ (sharp lines), $a = 1.1\%$, $\nu = 25.3$ MHz
- N :
 - ^{14}N , $I = 1$ (broad lines), $a = 99.6\%$, $\nu = 7.2$ MHz, $Q = 1.0$
 - ^{15}N , $I = 1/2$ (sharp lines), $a = 0.4\%$, $\nu = 10.1$ MHz
- O :
 - ^{16}O , $I = 0$ (no signal in NMR)
 - ^{17}O , $I = 5/2$ (broad lines), $a = 0.04\%$, $\nu = 13.5$ MHz, $Q = -0.037$

Important Elements in NMR Spectrometry

•N :

– ^{14}N , $I = 1$ (broad lines), $a = 99.6\%$, $\nu = 7.2 \text{ MHz}$ $Q=1.0$

– ^{15}N , $I = 1/2$ (sharp lines), $a = 0.4\%$, $\nu = 10.1 \text{ MHz}$ $Q=0$

Although N-14 has large natural abundance, the presence of quadrupole moment and very low frequency make it impractical for NMR studies.

The presence of quadrupole moment in that abundant element **alter the shape of nearby protons and carbons**

N-15 is a better candidate but the **low abundance & low frequency** render it's observation **extremely difficult**.

Important Elements in NMR Spectrometry

- Halogens: ^{19}F , Cl, Br, I
- ^{31}P , S
- B, ^{29}Si
- Na
- Co, Cd, W, Pt, Hg...

Relaxation Effects

T₁ : Spin-Lattice Relaxation: reestablish population equilibrium along Z
Convert Spin Energy to thermal energy => spin transition from upper to lower state

T₂ : Spin-Spin Relaxation: Dephase nuclear dipole in the XY plane

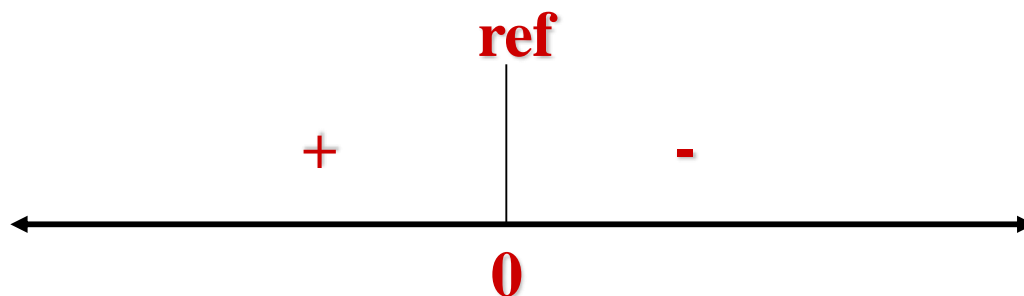
There are 5 mechanism for **T₁ Relaxation**

1. **Dipole-Dipole** : most important => intramolecular interaction between nearby nuclei. Depends on **intensity of magnetic moment** and on **distance between nuclei**
2. **Spin-Rotation**
3. **Anisotropy**
4. **Scalar coupling**
5. **Quadrupolar Relaxation (very large)**

Chemical Shift in NMR

Since it is not easy to report and measure **Absolute Frequency**,

Relative scale referencing is usually adopted in NMR



$$\delta \text{ (ppm)} = \frac{\nu - \nu_{\text{ref}} \text{ (Hz)}}{\nu_{\text{ref}} \text{ (MHz)}} \cdot 10^6 = \frac{\Delta\nu \text{ (Hz)}}{\nu_{\text{ref}} \text{ (MHz)}} \cdot 10^6$$

In ^1H , ^2H , ^{13}C , ^{29}Si : ref. is **TMS**

In ^{77}Se : ref. is **(Me) $_4$ Se**

In ^{119}Sn : ref. is **(Me) $_4$ Sn**

In ^{15}N : ref. is **Nitromethane**



Chemical shift in NMR

1. Chemical shift (δ) \rightarrow ppm
Structural information

$$\delta \text{ (ppm)} = \frac{\nu_{\text{PEAK}} - \nu_{\text{REF}} \text{ (Hz)}}{\text{Freq of the nuclei (MHz)}} = \text{ppm}$$

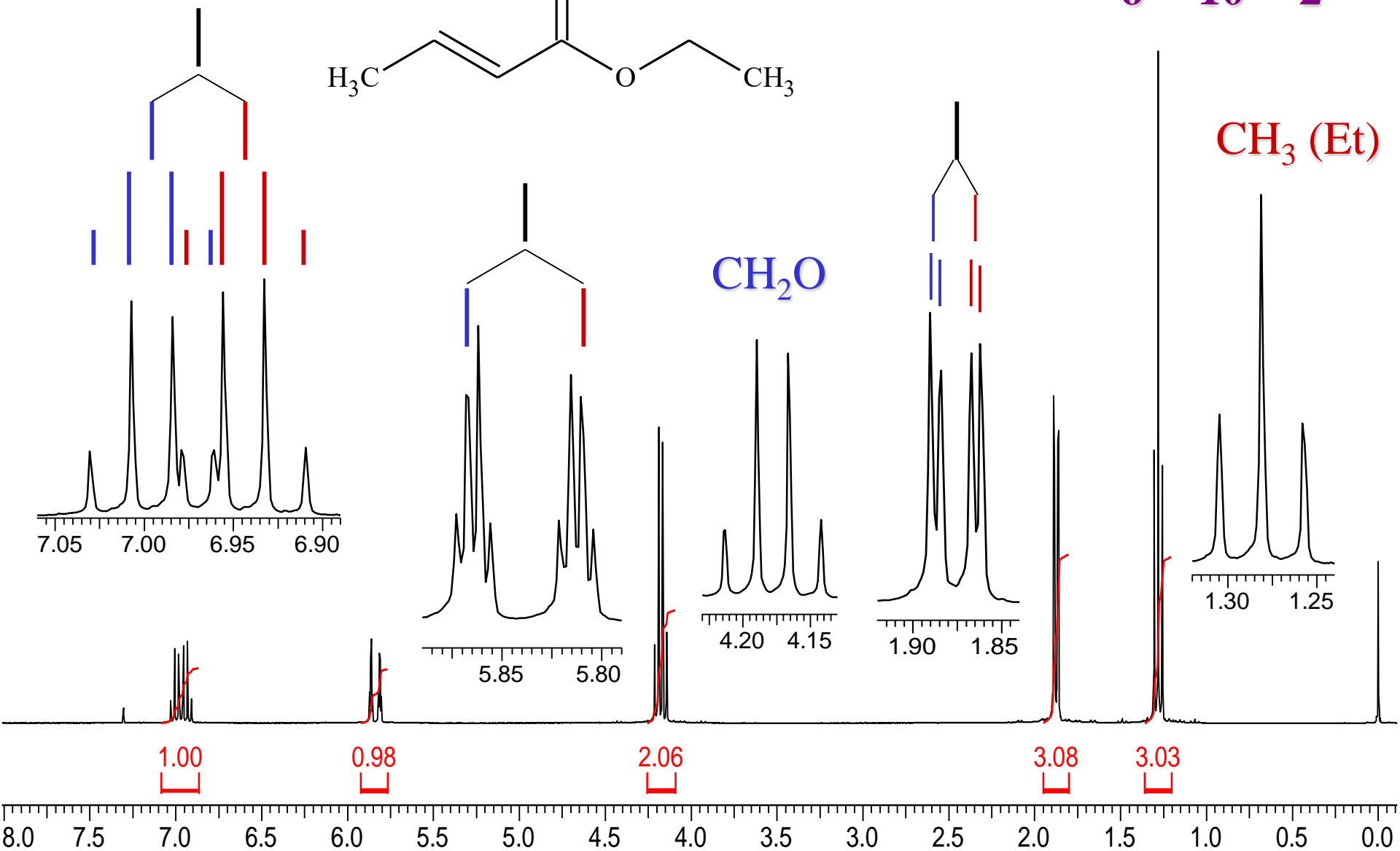
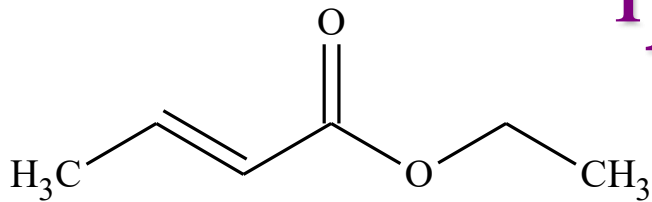
e.g. at 200 MHz:

If **R-CH(OR)₂** appear at **1,000 Hz** from **TMS (0)**
It's chemical shift is:

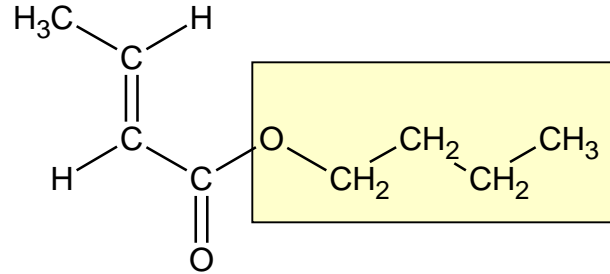
$$\delta = 1,000 \text{ Hz} / 200 \text{ MHz} = 5 \text{ ppm}$$

δ is dimensionless (independent from the applied field)
 δ changes with the applied field

$^1\text{H NMR}$: $\text{C}_6\text{H}_{10}\text{O}_2$



$^1\text{H NMR}:\text{C}_8\text{H}_{14}\text{O}_2$



triplet

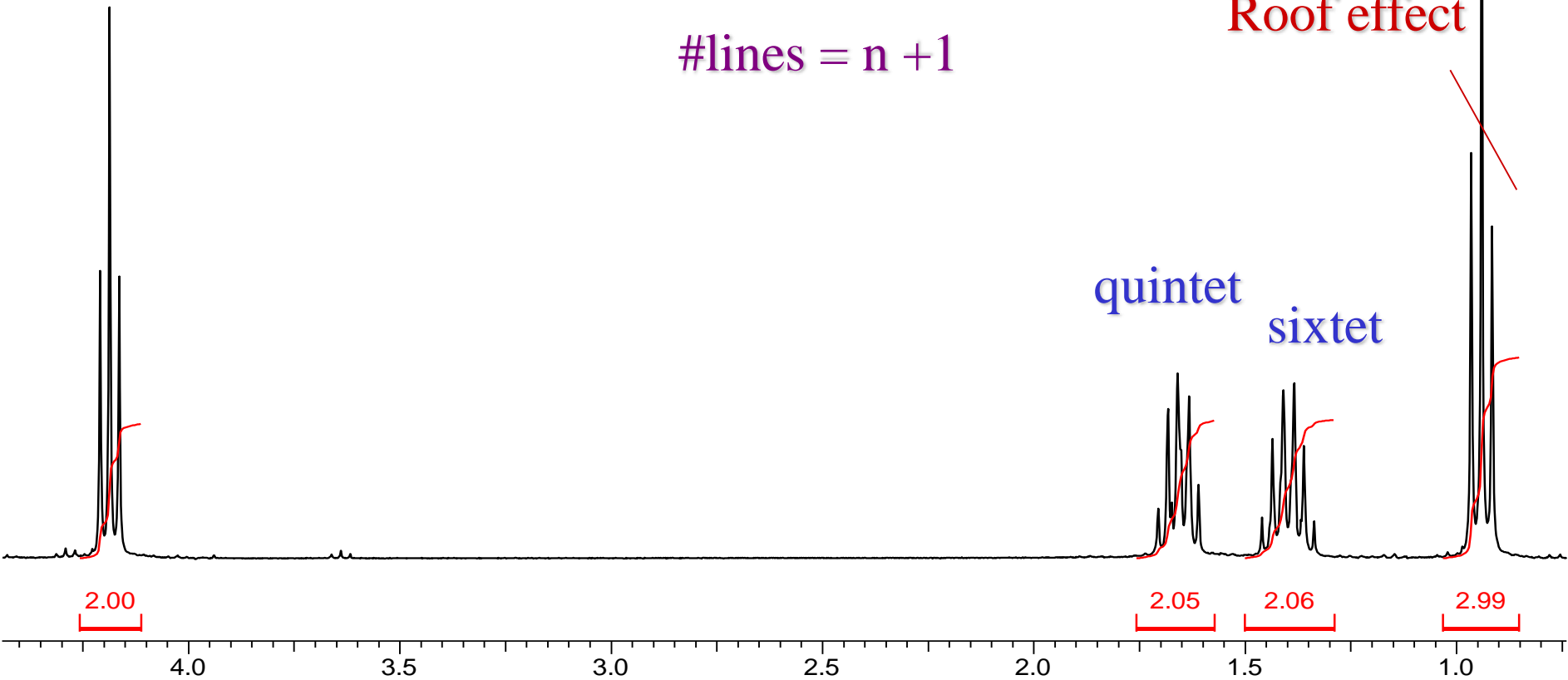
triplet

Roof effect

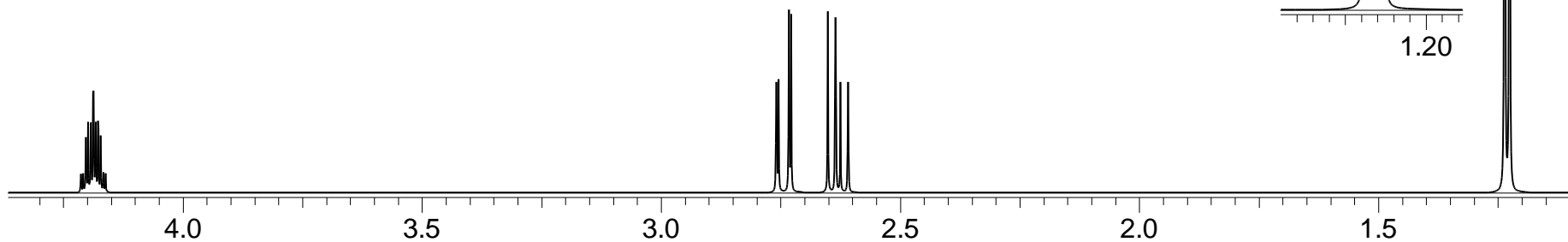
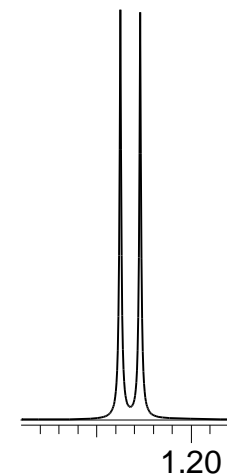
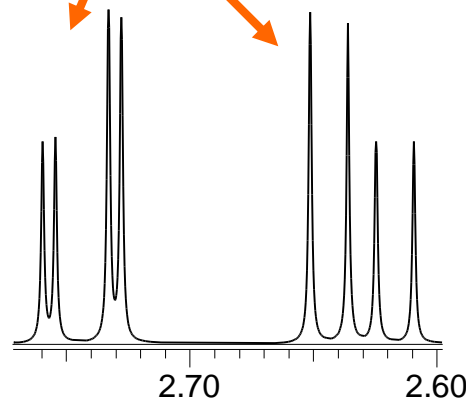
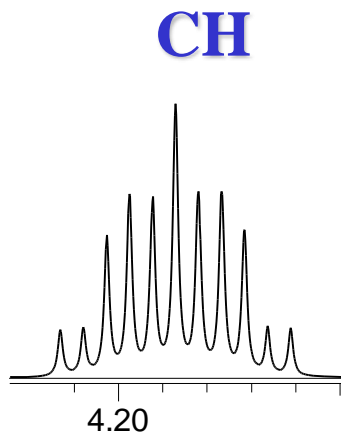
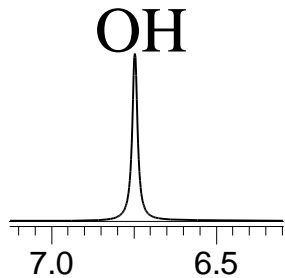
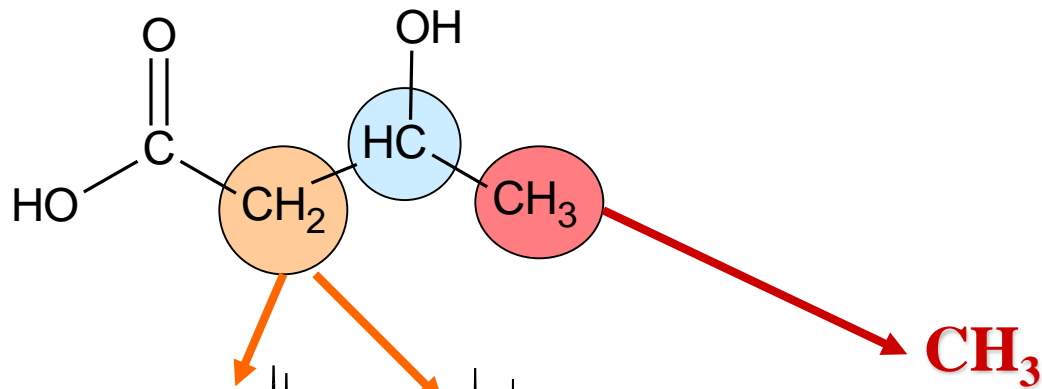
#lines = n + 1

quintet

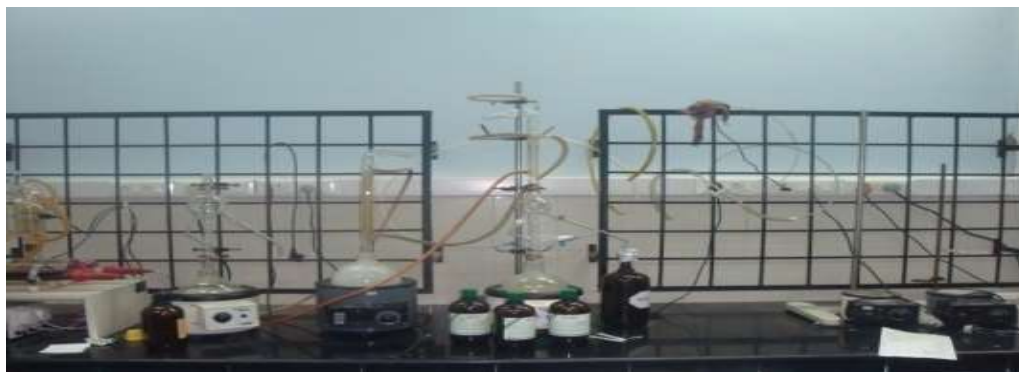
sixtet



$^1\text{H NMR} : \text{C}_4\text{H}_8\text{O}_3$



Thank You



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi