STUDY MATERIAL

Dumkal College
Basantapur Dumkal

Topic: Organic spectroscopy : NMR spectroscopy

Course Code: CHEMHT-10

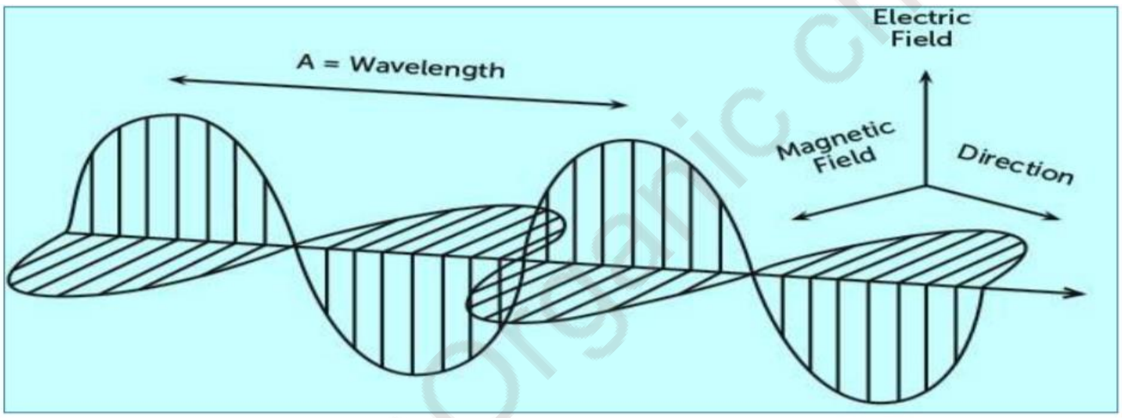
Semester: IV (Hons)

Name of the Teacher: Md Muttakin Sarkar

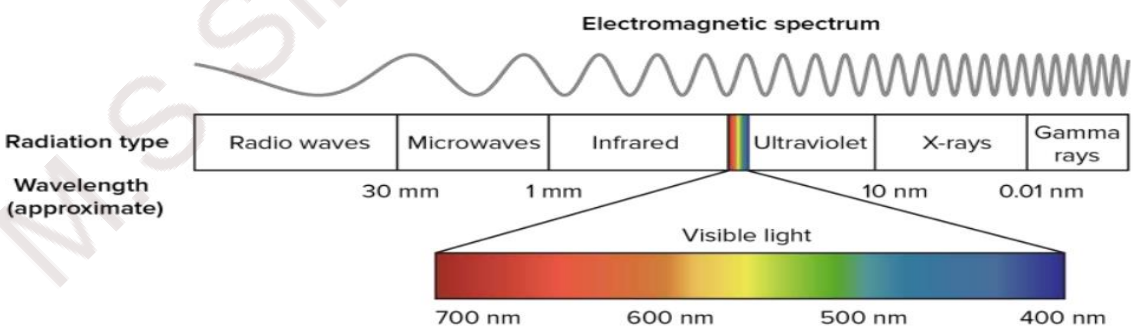
Name of the Department: Chemistry

NMR Spectroscopy

Spectroscopy is the study of interaction of electromagnetic radiation with the matter (compounds). Electromagnetic radiation is the sum of perpendicularly oscillating magnetic field vector and electric field vector which propagate through space containing energy of wide range of frequencies or wave lengths called electromagnetic spectra.



Propagation of electromagnetic radiation (alternating electric and magnetic forces)



Electromagnetic spectrum

$E = h\nu$ $\nu = c/\lambda$ $E = hc/\lambda$

Higher the frequency, higher the energy and **lower the frequency, lesser the energy**

Longer the wavelength, lesser the energy and **shorter the wavelength, higher the energy**

Spectroscopic techniques have been successfully used to determine the structure and functional groups of the organic compounds.

Spectroscopic techniques, purpose of study and their applications

Sl. No.	Name of the technique	Radiation used	Wave Length	Purpose of study	Application
1	X-Ray diffraction	X-rays	0.01 - 10nm	*Inter-atomic distance*	skeletal structure
2	UV-Visible spectroscopy	UV-visible radiations	10 - 700 nm	*electronic transitions*	conjugation
3	IR spectroscopy	IR radiation	700 nm - 1mm	*bending and stretching vibrations of covalent bonds*	functional groups
4	Microwave spectroscopy	Microwaves	1 mm-30 mm	*rotational transitions*	rotational transitions of molecules
5	**NMR spectroscopy (^{1}H NMR)**	**Radiowaves**	> 1 mm	***nuclear spin transitions***	**Number of different types of hydrogens in a molecule**

Nuclear Magnetic Resonance (or NMR) is concerned with the magnetic properties of certain atomic nuclei. Microwave frequency of electromagnetic radiation is employed here. Typically, the nucleus of the hydrogen atom-the proton (1H NMR) and that of the carbon-13 isotope (13C NMR) of carbon. Studying 1H NMR spectroscopy enables us to know the different types of hydrogen present in the organic molecule.

Nuclear spin

We know that sub-atomic particles (electron, proton, neutron) can be imagined as spinning on their axes.

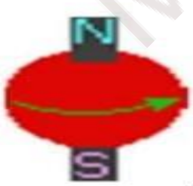
***protons and neutrons** have orbital angular momentum* ℓ *and spin* **s**

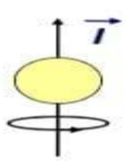
total angular momentum: $\vec{j} = \vec{\ell} + \vec{s}$

total nuclear spin: $I = \sum j$

$$I = |j_1 + j_2 + \cdots j_n|, |j_1 + j_2 + \cdots j_n| - 1, \cdots, |j_1 - j_2 - \cdots - j_n|$$ quantum mechanics

Spin angular momentum is characterized by nuclear spin quantum number (I).





- Nucleus rotates about its axis (spin)
- Nuclei with spin have angular momentum (p) or spin

1) total magnitude

$$\hbar\sqrt{I(I+1)}$$

1) quantized, spin quantum number I

2) $2I + 1$ states: $I, I-1, I-2, \ldots, -I$

$I=1/2$: $-1/2, 1/2$

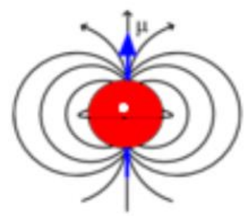
3) identical energies in <u>absence</u> of external magnetic field

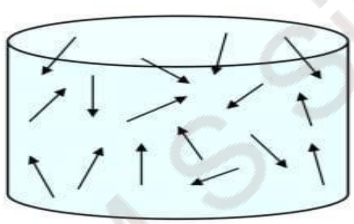
mass number	number of protons	number of neutrons	spin (I)	example
even	even	even	0	^{16}O
	odd	odd	integer (1,2,...)	^{2}H
odd	even	odd	half-integer ($^{1}/_{2}$, $^{3}/_{2}$, ...)	^{13}C
	odd	even	half-integer ($^{1}/_{2}$, $^{3}/_{2}$, ...)	^{15}N

When I = 0 ,then the nucleus is NMR inactive and I > 0 then the nucleus is NMR active.

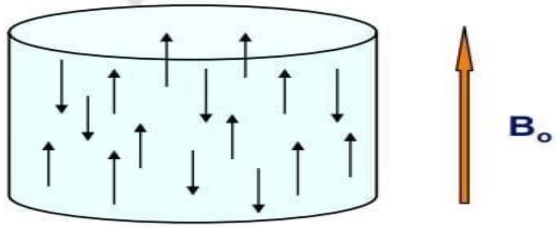
Principle of NMR spectroscopy

Any charged particle under motion generates magnetic field of its own. The proton behaves as a tiny spinning bar magnet.



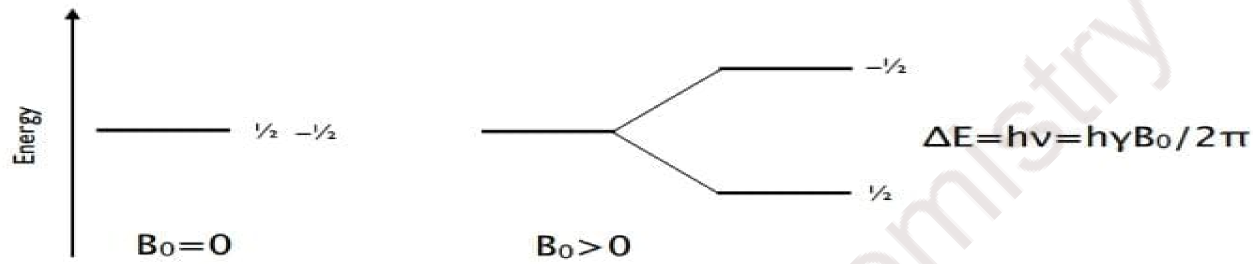


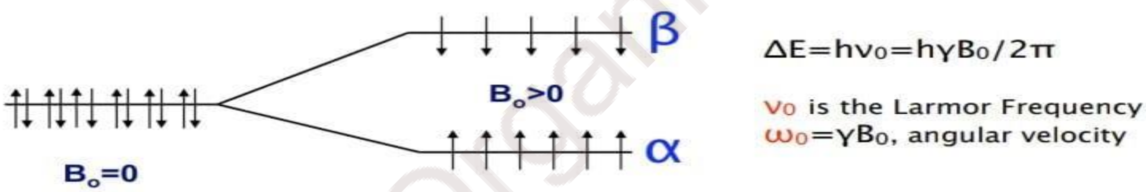
In the ground state all nuclear spins are disordered, and there is no energy difference between them. They are degenerate.

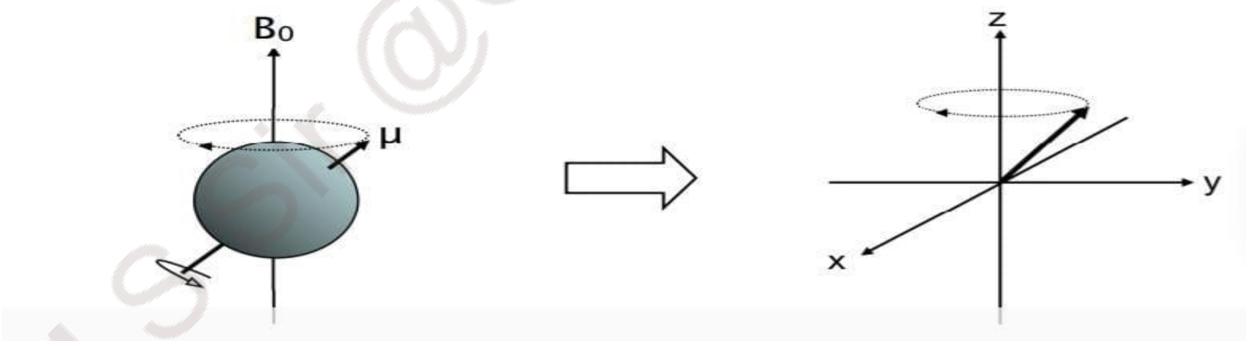


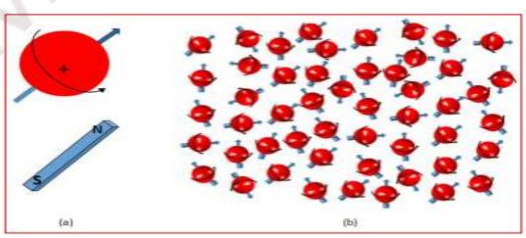
Since they have a magnetic moment, when we apply a strong external magnetic field (Bo), they orient either against or with it:
There is always a small excess of nuclei (population excess) aligned with the field than pointing against it.

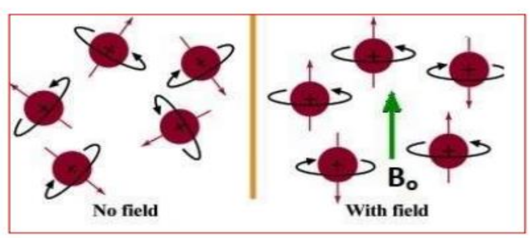
A proton can have two allowed spin states -1/2 and +1/2. Consequently in an external magnetic field B_o, the protons can only adopt two orientations with respect to an external magnetic field i.e.,
1) aligned with the external magnetic field B_o (+1/2, the lower energy state)
2) opposed to the external magnetic field B_o (-1/2, the higher energy state)

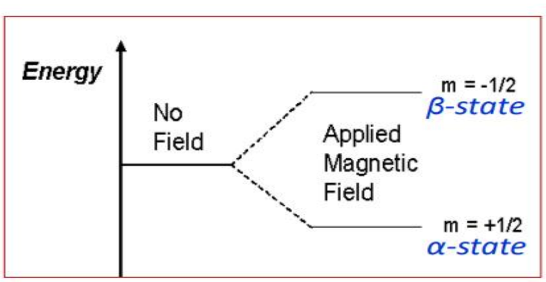

Energy
½ −½
B₀=0
B₀>0
−½
½
ΔE=hν=hγB₀/2π

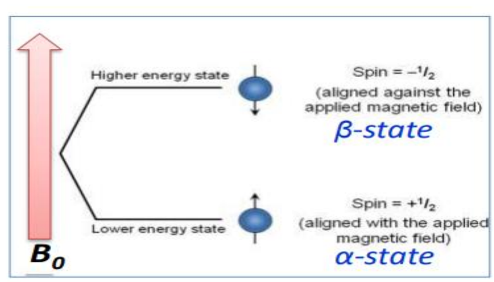

β
α
Bo=0
Bo>0
ΔE=hν₀=hγB₀/2π
ν₀ is the Larmor Frequency
ω₀=γB₀, angular velocity


B₀
μ
z
y
x


N
S
(a)
(b)

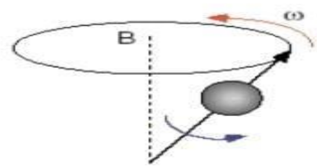

No field
With field
Bo


Energy
No Field
Applied Magnetic Field
m = -1/2
β-state
m = +1/2
α-state

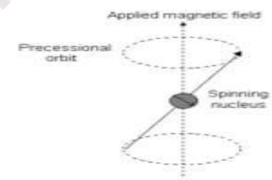

Higher energy state
Lower energy state
Spin = −1/2
(aligned against the applied magnetic field)
β-state
Spin = +1/2
(aligned with the applied magnetic field)
α-state
B₀

Larmour frequency

- **Precession**: The circular movement of the magnetic moment in the presence of the applied field.
- **Larmour frequency** : The angular frequency of the precessionis related to the external magnetic field strength B_0, by the gyromagnetic ratio γ :

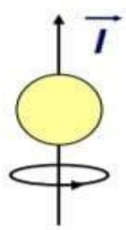


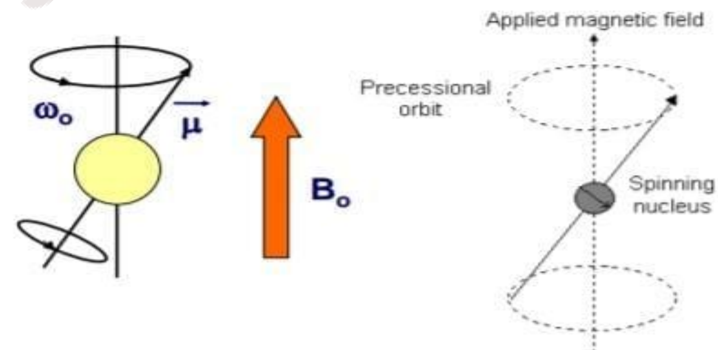
$$\omega_0 = \gamma B_0$$



Precession or ***Larmor*** frequency: $\omega = 2\pi\nu \Rightarrow \omega_o = \gamma B_o$ (radians)

angular momentum (I)





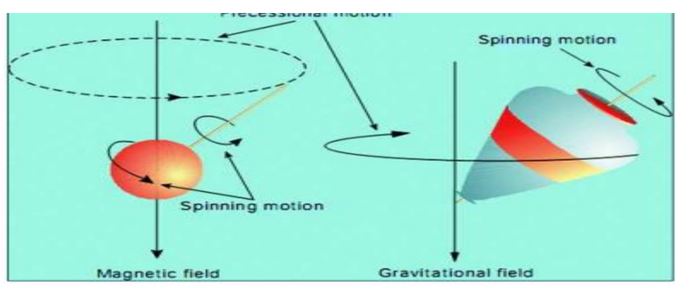
Simply, the nuclei spins about its axis creating a magnetic moment $\vec{\mu}$

Maxwell: Magnetic field $\equiv$ Moving charge

Apply a large external field (B_o) and $\vec{\mu}$ will precess about B_o at its Larmor (ω) frequency.

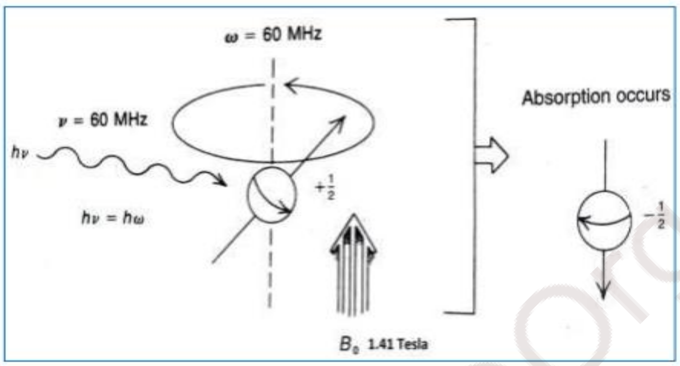
Important: This is the same frequency obtained from the energy transition between quantum states

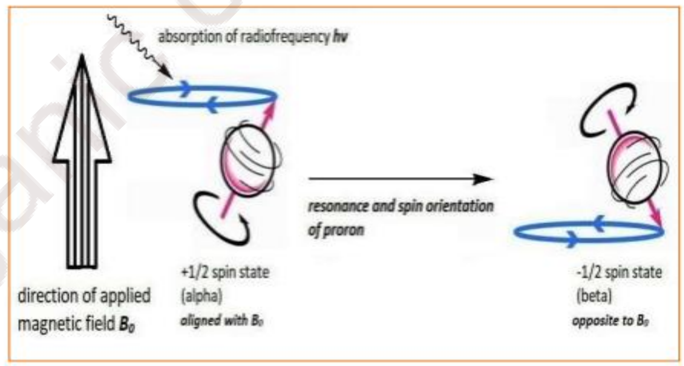
To understand the nature of nuclear spin transition , the analogy of a child's spinning top is useful. Under the influence of earth's gravitational field, the spinning top begins to precess about its axis.



The mechanism of absorption of radiofrequency (resonance)

- Since the **proton** is **positively charged**, the precession generates both **magnetic field** and **electric field** of a particular **frequency**
- If the **radiofrequency waves** (***hν***) of this **frequency** are supplied to the **precessing proton**, the **energy** can be **absorbed**
- When the **frequency** of the oscillating electric field component of a **precessing proton matches** the **frequency** of the **oscillating electric field** component of the incoming **radiofrequency**, the two fields can **couple**
- **Energy** can be **transferred** from the incoming **radiation** to the **proton**, thus causing a **spin change** (+1/2 spin state to -1/2 spin state). This condition is called ***resonance***





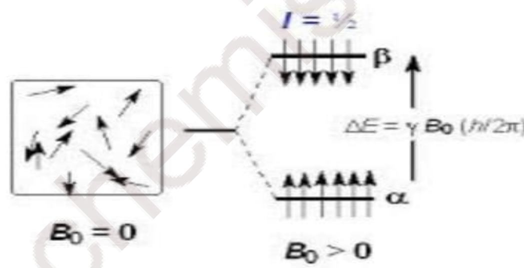
The nuclear magnetic resonance process; absorption occurs when ν = ω

Population of nuclei in spin states

- For a **proton**, if the **applied magnetic field** has a **strength** of **1.41 Tesla**, **resonance** occurs at about **60 MHz** of **radiofrequency**
- Using $\Delta E = h\nu$, the difference in energy (ΔE) between the two spin states (+1/2 and -1/2) of the proton is found to be around 2.39×10^{-5} kJ/mole
- Since this energy difference (ΔE) between the two levels is small, thermal energy resulting from room temperature is sufficient to populate both of these energy levels
- However, there is a **slight excess of protons** in the **α-spin state** (**lower energy level**)
- The **excess nuclei** are the ones that allow us to observe **resonance**
- When the radiofrequency is applied, it not only induces transitions upward (from **α-spin state** to **β-spin sate**) but also stimulates transitions downward (from **β-spin state** to **α-spin state**)
- The **population of spin states** is dependent on the **field strength** B_o
- **If the strength of applied magnetic field is increased, the energy difference between the two states also increases, which cause an increase in excess population**

Boltzmann Distribution

In the absence of an external magnetic field ($B_0 = 0$), the nuclear spin energy levels are *degenerate* ($\Delta E = 0$). When $B_0 > 0$, the nuclei are split between the nuclear spin energy levels: α and β.



Using the Boltzmann equation, the population distribution is given as:

$$N\beta / N\alpha = \exp(-\Delta E / k_B T)$$

where $k_B = 1.381 \times 10^{-23}$ J/K

T is the absolute temperature in Kelvin

Since $\Delta E = (h/2\pi)\,\gamma\, B_0$, the Boltzmann equation can be rewritten as:

$$N\beta / N\alpha = \exp(-h\,\gamma\, B_0 / 2\pi\, k_B T)$$

Reference Books

1. Kemp, W. Organic Spectroscopy, Palgrave.
2. Pavia, D. L. et al. Introduction to Spectroscopy, 5th Ed. Cengage Learning India Ed. (2015).
3. Dyer, J. Application of Absorption Spectroscopy of Organic Compounds, PHI Private Limited.