Toppersnotes
Unleash the topper in you

CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - II

PHYSICAL **CHEMISTRY**

SIERRA INNOVATIONS

Index

Spectroscopy :-

→ An Instrumental Technique Through $\bar{c}$ we determine the structure of Org & Inorg. Cmpd generally by ~~using~~ interactn of EMR $\bar{c}$ Matter (sample)

EMR :

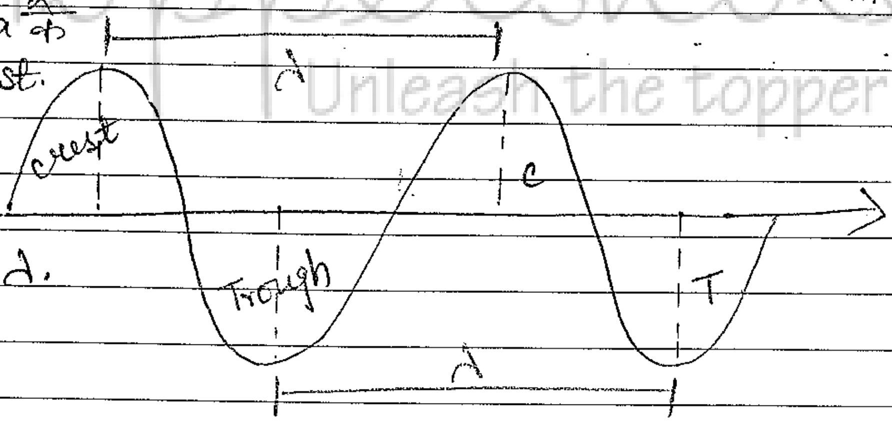
$$\boxed{E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}}$$ $$\boxed{\bar{\nu} = \frac{1}{\lambda}}$$

$h \rightarrow$ Plank's Const $(6.6 \times 10^{-34}\ \underline{JS})$

$\lambda \rightarrow$ Wave length (m, cm, Å, nm, pm)

$\nu \rightarrow$ freq. (Unit :- Hz or Cps or sec^{-1}) एक ही बात है ये तीनो का matlb.

2 maxima के बीच की dist. or 2 minima के बीच की dist. c/o λ.



$\bar{\nu} \rightarrow$ wave no. (m^{-1}, cm^{-1}, $Å^{-1}$, nm^{-1}, pm^{-1})
or Kaiser*

$*\ \boxed{1\,cm^{-1} = 1\ Kaiser}$

$\boxed{h \rightarrow 6.6 \times 10^{-34}\ JS}$

$C = 3 \times 10^{8}\ m\,s^{-1}$

$C = 3 \times 10^{10}\ cm\,s^{-1}$

$\frac{1\ \text{Joule}}{1.6 \times 10^{-19}\ \text{Coulomb}}$ eV

$\boxed{\frac{\text{Joule}}{\text{Coulomb}} = \text{Volt}}$

1 Joule → 1×10^{7} erg

1 Joule → $\frac{1}{4.18}$ Cal.

1 Joule → $\frac{1}{hc}\ cm^{-1}$

1 Joule → $\frac{1}{h}$ Hz

क ख ग सिम ई

★ $\boxed{1\ \text{Cal} > 1\ \text{Joule} > 1\ \text{erg} > 1\ \text{eV} > 1\ cm^{-1} > 1\ Hz}$

Q. Determine the Energy of a radiatn have freq. $2 \times 10^{3}\ cm^{-1}\ (\bar{\nu})$, in Joule, erg, Cal.

$2 \times 10^{3} \times hc$ Joule

$E = hc\bar{\nu}$

$E = 6.6 \times 10^{-34}\ \cancel{JS} \times 3 \times 10^{10}\ \cancel{cm}\ \cancel{s^{-1}} \times 2 \times 10^{3}\ \cancel{cm^{-1}}$

$E = 39.6 \times 10^{-21}$ Joule.

$E = 39.6 \times 10^{-21} \times 1 \times 10^{7}$ erg

$E = 39.6 \times 10^{-14}$ erg

$E = 39.6 \times 10^{-21} \times \frac{1}{4.18}$ Cal.

$E = 9.47 \times 10^{-21}$ Cal

Range of EMR :- A R m I V U X γ rays.

Audiowaves < Radio waves < micro waves < IR < vis < U.V. < X-rays < γ-rays

→

↑ing Order of E (or) ν (or) $\bar{\nu}$
↓ing Order of λ

EMR Region	Spectroscopic Tech:
① Radiowaves	NMR, NQR spectro.
② microwaves	ESR, Rot. spectro.
③ IR	vib. spectro., Rot-vib spectro.
④ Visible	visible spectro (colourimetry), Raman Spectro
⑤ UV	electronic spectro (U-V vis spectro) ~~Raman~~ spectro.
⑥ X-ray	X-ray techniques used in Crystallography
⑦ γ-rays	Mossbeaus Spectro.

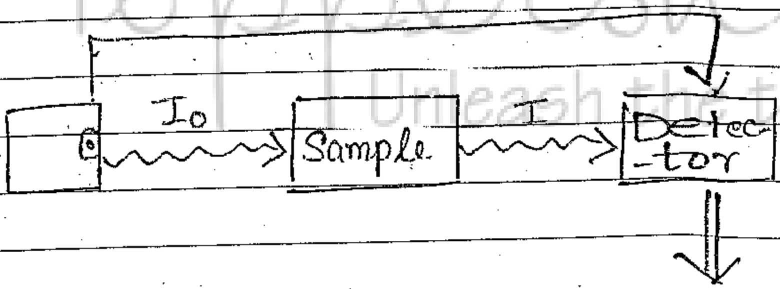
Interactn of EMR $\bar{c}$ Matter :—

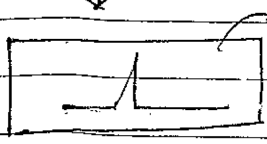
→ All absorption spectro. follow Beer-lambert's law.
i,e

$$\boxed{A = \varepsilon c l = \log \frac{1}{T} = \log \frac{I_0}{I}}$$

$$\boxed{T = \frac{I}{I_0}}$$

T → Transmittance
A → Absorbance.
c → conc.
l → length
I_0 → Intensity of Incident radiatn.
I → —— " transmitted — " —





signal of absorbed radiatn

Absorbance के liye interactn जरूरी है तभी signal aega.

→ For Absorbtn spectrum :—

* $\boxed{A > 0}$ (zero) or (OR) $\boxed{I_0 > I}$ (OR) $\boxed{T < 1}$

ν
I_0

Sample

Interaction

Intensities में relation → Absorption

$\boxed{A > 0}$ $\boxed{I_0 > I}$ $\boxed{T < 1}$

⇓

Absorption Spectro.

Freq में relation दिखता यहाँ → Scattering

Rayleigh

$\boxed{\nu_0 = \nu_s}$

incident freq. = scattered freq.

Raman

$\boxed{\nu_0 \neq \nu_s}$

Molecular Energy:-

→ Acc. to Born Oppenheimer approxm, the Energy in a mc (gaseous or liq. state) is of following type:

① Electronic Energy (E_e)
② Vibrational E (E_v)
③ Rotational E (E_r) or (E_j)
④ Translational E (E_t)

(All are Independent of each other)

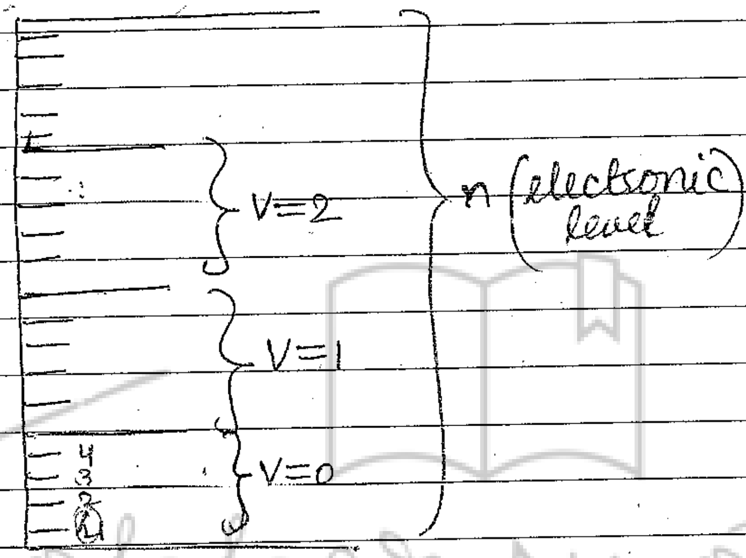
→ And acc. to them the Total E of mc is the sum of these Energies & these are Independent of each other

$$\boxed{E_{Total} = E_e + E_v + E_r + E_t}$$

$$\boxed{E_e \gg E_v \gg E_r \gg E_t}$$

→ The For E_t is Not quantised due to molecular collision factor so the total quantised Energy is as:-

$$\boxed{E_{total} = E_e + E_r + E_v}$$



☆ Energy levels are discrete (fixed).

☆ ↑ Uncertainity ज्यादा → mtlb lifetime of ES कम ↓ & Vice-Versa.

Uncertainity in Energy

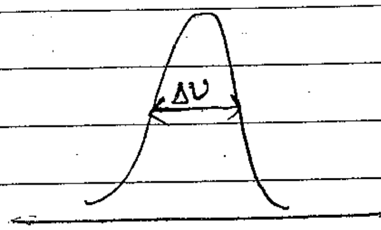
$$\boxed{\Delta E \times \Delta t = \frac{h}{2\pi}}$$

Lifetime

$$\boxed{\Delta \nu \times \Delta t = \frac{1}{2\pi}}$$

$$\boxed{\Delta \nu = \frac{1}{2\pi \Delta t}}$$

$\Delta \nu$ → Natural line width



Nuclear Magnetic Resonance

NMR :-

$\boxed{\text{Region} \rightarrow \text{Radiowave}}$

- नीचे से ऊपर जाना ⟶ c/o Reso.
- ऊपर से नीचे जाना ⟶ c/o Relaxation.

$\boxed{\text{Nuclei}}$
magnetic hona chahie
& tbi hoga जब $\boxed{I \neq 0}$
वही NMR denge.

Magnetic
- $\boxed{I \neq 0}$
Nuclear spin (I)
- NMR Active.

Non-Magnetic
$\boxed{I = 0}$
- NMR Inactive Nuclei.

⟶ Nuclei whose nuclear spin $\boxed{I > 0}$, can give NMR in suitable mag. field.

* ⟶ Nuclei whose $\boxed{\text{atomic no.}}$ & $\boxed{\text{mass no.}}$ both are $\boxed{\text{even}}$ have $\boxed{I = 0}$ & they are NMR ~~Act~~ Inactive.

eg: He^{4}, C^{12}, Ne^{20}, Mg^{24}, S^{32}, O^{16} ⟶ Mass no.
(atomic & mass no Even है इसलिए)
∴ NMR Inactive.

Proton Atomic No.	(neutron + Proton) Mass No.	Nuclear Spin (I)
even	even	I=0 He^4, C^{12} etc..... ^{20}Ne, ^{24}Mg, ^{32}S, ^{16}O
even	odd	$I = 1/2, 3/2, 5/2, 7/2$ ......
odd	odd	eg: N^{15}, P^{31}, B^{11}, H^1, ^{13}C, ^{19}F etc....

Atomic no.	Mass no.	(I)	(Eg)
odd	even	$I = 1, 2, 3, 4 \ldots$	^{2}H, ^{14}N, $^{10}B \ldots$

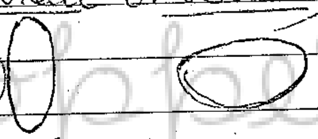
magnetic
Nuclei

Quadrupole (electron environment Asym hona chahie)

$\boxed{I \geq 1 \text{ or } I > 1/2}$

^{9}H, ^{11}B, ^{14}N, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br etc....

★ Non-spherical shape (either prolate or oblate)
(egg shape or disc shape)



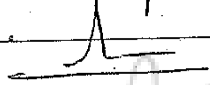
$\boxed{\text{Quadrupole Moment} \neq 0}$

Non-Quadrupole.

$\boxed{I < 1 \text{ or } I = 1/2}$

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

They give sharp signal in NMR.



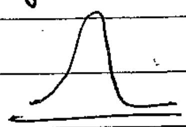
Quadrupole moment = 0

Spherical shape nuclei.

(electronic env. sym hota h.)

Quadrupole nuclei solid hona chahie, (liq या Gas नहीं) तभी signal dega

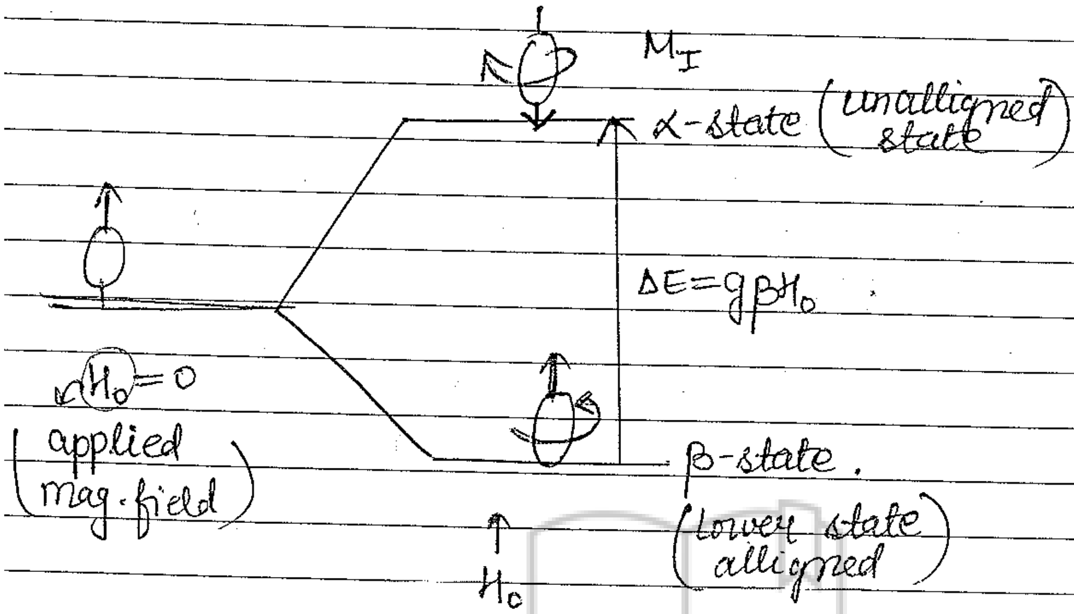
They give Broad signal in NMR



★ In case of Quadrupole Nuclei, due to less relaxation time (Δt), the NMR signal will be broad & sometimes it will not appear.

signal width ← $\boxed{\Delta\nu = \dfrac{1}{2\pi \Delta t}}$ $\Delta t \rightarrow$ lifetime or relaxation time.

Nuclear Transition :-



$\boxed{H_0 \uparrow \rightarrow \Delta E \uparrow}$

(App. mag. field) (Seperation of Energy levels)

$\boxed{\Delta E = g\beta H_0}$

→ The applied M.F. ↑es then the seperatn b/w 2 states ↑

$$\boxed{\Delta E = h\nu = g\beta H_0}$$

Reso. freq.

$$\boxed{\nu = \frac{g\beta H_0}{h}}$$

where g → Nuclear g-factor (or) gyroscopic ratio.
→ Unitless

$\boxed{g = 5.585 \text{ for } H_2 \text{ nuclie}}$

β → Nuclear Bohr magneton.

$$\boxed{\beta = \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27}\ J/Tesla}$$

m_p → (Mass of proton)

$\boxed{1\ \text{Gauss} = 10^{-4}\ \text{Tesla}}$ (T)

$$\boxed{\nu = \frac{g\beta H_0}{h}}$$

★ { freq. (ν) → Hz or MHz में होगा
Applied M.F → Tesla or Gauss में होगा।
(H_0) }

Q. Any spectrometer operates at 1 Tesla, the NMR freq of ^{19}F is 40.06 MHz. Cal the magneto-gyric ratio (γ) of the Nuclei ?

$$\boxed{\gamma\hbar = g\beta} \qquad \left(\hbar = \frac{h}{2\pi}\right)$$

$$\nu = \frac{g\beta H_0}{h} = \frac{\gamma\hbar H_0}{h} = \frac{\gamma H_0}{2\pi}$$

$$\cancel{40.06} = \frac{\gamma \cdot 1}{2\pi} \qquad \boxed{\gamma = \frac{2\pi\nu}{H_0} = \frac{\omega}{H_0}}$$

$$\gamma = \frac{2 \times 3.14 \times 40.06 \times 10^6\ s^{-1}}{1\,T}$$ MHz to Hz

$$\gamma = \qquad T^{-1}s^{-1}$$

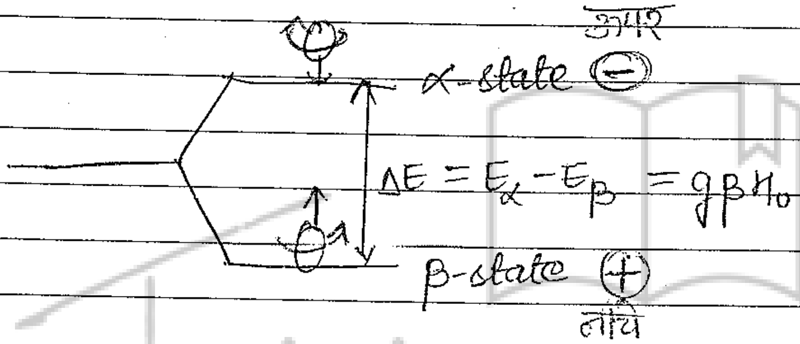
Q. Cal Nuclear 'g' factor for ^{19}F Nuclei ~~have a magnetic~~ operates at 1 Tesla & the reso freq is 40.06 MHz.
($\beta = 5.05 \times 10^{-27}\ JT^{-1}$)

$$\nu = \frac{g\beta H_0}{h} \Rightarrow 40.06 \times 10^6\ s^{-1} = \frac{g \times 5.05 \times 10^{-27}\ JT^{-1} \times 1\,T}{6.6 \times 10^{-34}\ Js}$$

$$g = \frac{h\nu}{\beta H_0} = \frac{6.6\times10^{-34}\,\cancel{Js} \times 40.06\times10^{8}\,\cancel{s^{-1}}}{5.05\times10^{-27}\,\cancel{JT^{-1}} \times 1\cancel{T}}$$

$$g = \frac{264.396}{5.05}\times 10 = \underline{523.5}$$

Energy of Zeeman Level :-



$$E_{m_I} = -m_I\, g\beta H_0$$

Imp.

- Acc. to Boltzmann, the population in lower zeeman level is slightly higher than upper zeeman level i,e

(lower level Populatn) $\boxed{N_\beta > N_\alpha}$ (higher level populatn) & it is necessary for Nuclear reso. or transition.

$$\boxed{\text{Excess population} \Rightarrow \frac{N_\alpha}{N_\beta} = e^{-\frac{\Delta E}{KT}}}$$

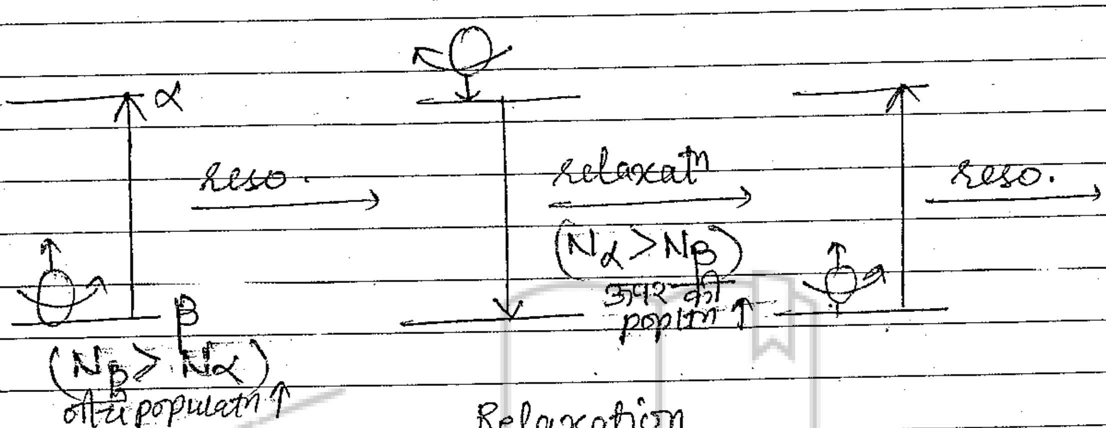
$$\boxed{\Delta E = g\beta H_0}$$

$$\boxed{\frac{N_\alpha}{N_\beta} \simeq 1 - \frac{\gamma H_0 h}{2\pi KT}}$$

$$\boxed{\Delta E = g\beta H_0 = \frac{\gamma H_0 h}{2\pi}}$$

★ $\boxed{\hbar \equiv 1.05 \times 10^{-34}\ \text{Js}}$ (8-1 को Hz बोलते हैं।)

i,e For Resonance ; $\boxed{\frac{N_\alpha}{N_\beta} < 1}$



Relaxation

Spin-spin relaxation	Spin-lattice
→ Denoted by T_2	Denoted by T_1.
→ It determines the natural line width in spectrum.	Lattice can define all kinds of aggregate atom or mc in the sol^n (solute or solvent mc).
→ Transfer of E to the processing Proton sample's proton जो signal दे रहे हैं (nuclei)	→ Transfer of E from E.S. proton to the surrounding lattice.

mathematical Relatn & Conditn for NMR:—

① Reso. freq

$$\boxed{\nu = \frac{g\beta H_0}{h} = \frac{\gamma H_0}{2\pi} = \frac{\omega}{2\pi}}$$

(precessional freq.) $\boxed{\omega = 2\pi\nu = \gamma H_0}$ (ω → Larmor freq. Precessional freq)

(2) Selection Rule : $\boxed{\Delta m_I = \pm 1}$

(3) Nuclear g factor $g = 5.585$ (for H nuclei)

$$\beta = \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27}\ JT^{-1}$$

(4) Magneto Gyric Ratio (γ)

$\boxed{\gamma = \frac{\mu}{I\hbar}}$ Unit $\rightarrow T^{-1}S^{-1}$ $\gamma = \frac{2\pi\nu}{H_0}$

$\mu \rightarrow$ Nuclear mag. moment. $\boxed{\mu = \gamma P}$

(momentum) $\boxed{P = \frac{h}{2\pi}\sqrt{I(I+1)}}$ Imp $\boxed{\mu = g\beta I}$

$\mu = ($गी ई ऊ$)$ — β I g

★ $\boxed{\gamma\hbar = g\beta}$

★ $\boxed{\omega = 2\pi\nu = \gamma H_0}$

Imp For 2 diff. nuclei (eg: H, ^{13}C)

$$\boxed{\frac{\nu_H}{\nu_{^{13}C}} = \frac{\gamma_H}{\gamma_{^{13}C}} = \frac{g_H}{g_{^{13}C}}}$$ if (H_0 = constant)

$$\boxed{\frac{H_0(H)}{H_0(^{13}C)} = \frac{\gamma_{^{13}C}}{\gamma_H} = \frac{g_{^{13}C}}{g_H}}$$ (if ν = const)

($\beta_N = \mu_N$ भी बोलते हैं।)

Q. The mag. Moment (μ) of ^{31}P nuclei is equals to 1.1305 β nuclear magneton. Cal the magnetogysic ratio (γ) & g-factor?

$$\beta = 5.05 \times 10^{-27}\ JT^{-1}$$

$$\gamma = \frac{\mu}{I\hbar} = \frac{1.1305\,\beta}{I\hbar}$$

$$\gamma = \frac{1.1305 \times 5.05 \times 10^{-27}\ \cancel{J}T^{-1}}{\frac{1}{2} \times 1.05 \times 10^{-34}\ \cancel{J}S}$$

$$\gamma = 10.87 \times 10^{7}\ T^{-}S^{-}$$

$$g = \frac{\mu}{\beta I} = \frac{1.1305\,\beta}{\beta I} = 1.1305 \times 2$$

$$g = \underline{2.261}$$

Q. Cal NMR freq. of Proton in a mag. field of intensity 1.4092 Tesla.

$$g_N = 5.585$$
$$\mu_N = 5.05 \times 10^{-27}\ JT^{-1}$$

$$\nu = \frac{g\beta H_0}{h} = \frac{g\mu_N H_0}{h}$$

$$\nu = \frac{5.585 \times 5.05 \times 10^{-27}\ \cancel{J}\cancel{T^{-1}} \times 1.4092\ \cancel{T}}{6.6 \times 10^{-34}\ \cancel{J}S}$$

Q. In a NMR spectrometer operates at 30.256 MHz. Cal the Mag. field required to reso. for proton nuclei & for ^{13}C nuclei. Given:-

$\mu_{(H^1)} = 2.7927\,\beta$

$\mu(^{13}C) = 0.7022\,\beta$

Sol^n

$\nu = \frac{g\beta H_0}{h}$; $(\mu = g\beta I)$

$\nu = \frac{\mu H_0}{Ih}$ $\left(g\beta = \frac{\mu}{I}\right)$. $\nu \propto g$

I

For H^1: $H_0 = \frac{\nu I h}{\mu} = \frac{30.256 \times 10^6 s^{-1} \times \frac{1}{2} \times 6.6 \times 10^{-34}\,JS}{2.7927\,\beta}$

$H_0(H^1) = \frac{30.256 \times 10^6\, s^{-1} \times \frac{1}{2} \times 6.6 \times 10^{-34}\, JS}{2.7927 \times 5.05 \times 10^{-27}\, JT^{-1}}$

$(H^1)\ H_0 = 0.71$ Tesla.

II

Here ν = constant $\frac{\mu}{I}$

$H_0 \propto \frac{1}{\mu}$ (when $\nu \to$ const)

$H_0(^{13}C) = \frac{30.256 \times 10^6\, s^{-1} \times \frac{1}{2} \times 6.6 \times 10^{-34}\, JS}{0.7022 \times 5.05 \times 10^{-27}\, JT^{-1}}$