

PHYSICAL CHEMISTRY

SECTION-B

NMR SPECTROSCOPY

General Introduction:- Interaction of EMR with matter.

Electrical field component \perp magnetic field component

↑
dual nature
↓

e^- , p^+

$$|\vec{E}| = c |\vec{B}|$$

elec. field mag. field

NMR :- Radiowaves used which is low E thus magnetic component interact

E-M. spectrum :-

Radio wave Micro Waves IR Visible UV X-Ray γ -Ray

—————→

E inc. (as $E = h\nu$)
thus $\nu \rightarrow$ inc. ($\lambda \rightarrow$ dec)

factors on which spectrum depend:-

- ① Bohr freq. condition
- ② Selection Rule
- ③ Boltzmann population Ratio.

SPECTROSCOPY :- It may be defined as the interaction and interpretation of EMR, absorption, scattered or emitted by atoms, molecule or other chemical species.

It deals with the transition induced in a chemical species by its interaction with photons of electromagnetic radiations (EMR).

Spectroscopic techniques are generally employed to measure

the E difference b/w various molecular E levels and to determine the atomic and molecular structure.

for NMR to occur $\Rightarrow \boxed{I \neq 0}$ $I \rightarrow$ nuclear spin

$$\Rightarrow E_t = \frac{nh^2}{8mL^2} \quad E_n = BJ(I+1)$$

(Translational E) (rotational E)

$$E_v = \left(n + \frac{1}{2}\right) h\nu$$

(vibrational E)

PRINCIPLE OF NMR :-

The nucleus of H-atom behaves as a spinning bar magnet bcoz it posses both magnetic and electric field.

The nucleus of H-atom generates a magnetic field.

NMR involve interaction b/w an oscillating magnetic field of EMR and magnetic E of H-nucleus when these are placed in an external static magnetic field. The sample absorbs magnetic field in EMR in radio wave region at different frequencies since absorption depends upon type of protons (p^+) or certain nuclei contained in the sample.

When the magnetic field is applied the nucleus began to precess about its own axis of spin with angular frequency ' ω ' called Larmor freq. Since the nucleus has a charge, the precession generates an oscillating electric field of the same freq.

If radio freq. waves of this freq. are supplied to precess p^+ , the energy can be absorbed i.e. when the freq. of

oscillating electric field component of the incoming radiation just matches the freq. of electric field generated by the precessing nucleus, the two fields can couple and energy can be transferred from the ~~the~~ incoming radiation to the nucleus, thus causing a spin change. This is called Resonance.

The magnetic field associated with spinning nucleus is given as-

$$\mu_m = \mu_N g_N m_I$$

$$[g_N = 5.585] \Rightarrow \text{for proton}$$

g_N = Nuclear g-factor

μ_N = Nuclear magneton

$$\mu_m = \mu_N g_N \sqrt{I(I+1)}$$

$$m_I = \sqrt{I(I+1)}$$

$$\mu_N = \frac{e\hbar}{4\pi m_p}$$

m_p = mass of p^+
 $[m_p = 1.67 \times 10^{-27} \text{ kg}]$

$$\Rightarrow \mu_N = \frac{1.6 \times 10^{-19} \text{ C} \times 6.6 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 1.67 \times 10^{-27} \text{ kg}}$$

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

$$\Rightarrow \mu_B = \frac{e\hbar}{4\pi m_e}$$

$m_e = 9.1 \times 10^{-31} \text{ kg}$

$$\mu_B = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

μ_B = Bohr Magnetron.

$$\frac{\mu_N}{\mu_B} = \frac{m_e}{m_p} \approx \frac{1}{1835}$$

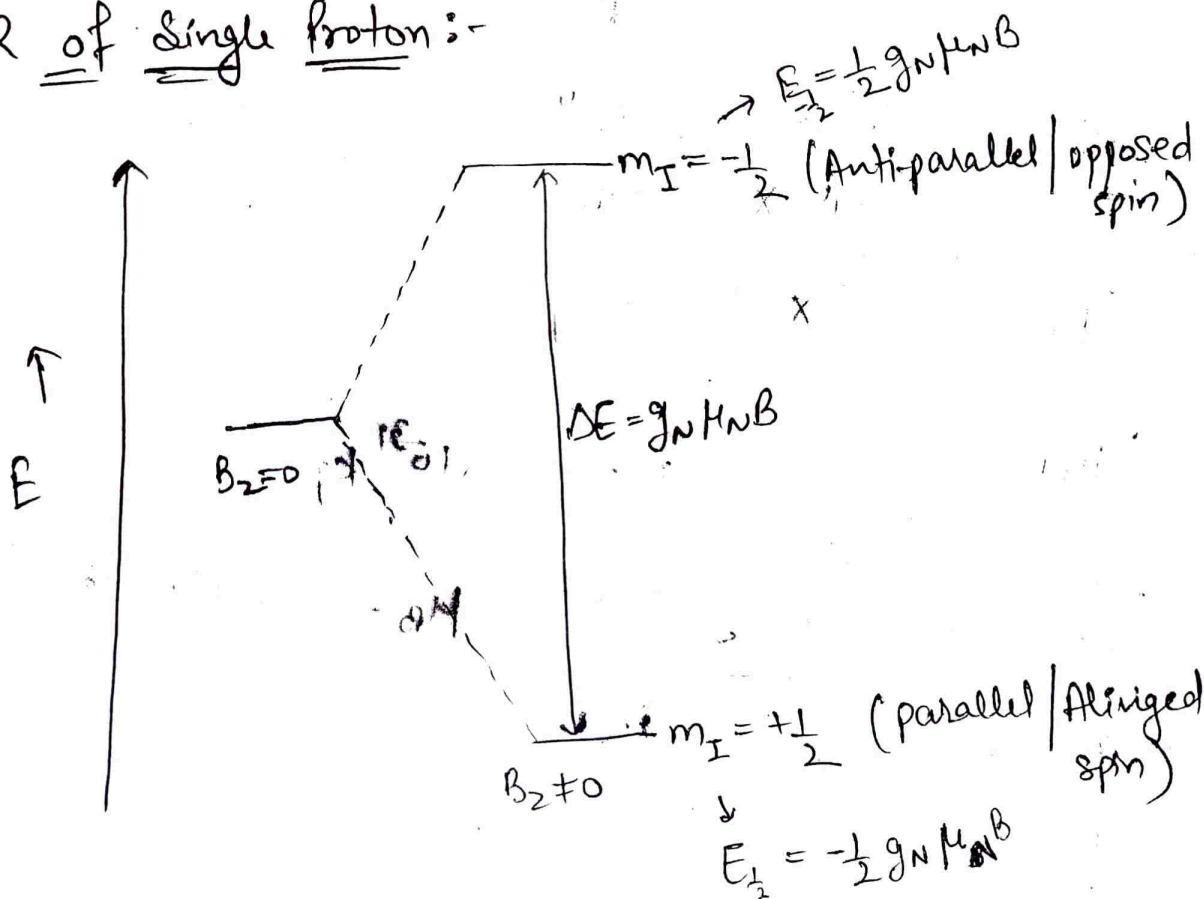
⇒ In NMR, the particular nucleus i.e. spin active nucleus having $I \neq 0$ can be easily detected by spinning magnetic bar.

E here is supplied in the form of radio waves i.e. of less energy. Due to external magnetic field nucleus possess precessional motion i.e. rotating and spinning both at the same time.

Nuclear Spin Quantum No. :-

Atomic No.	Mass No.	I	Example
odd	odd	$\frac{1}{2}$	^1_1H , $^{19}_9\text{F}$
even	even	0	$^{12}_6\text{C}$, $^{16}_8\text{O}$
odd	even	1	^3_1H , $^{14}_7\text{N}$

⇒ NMR of Single Proton :-



⇒ In the absence of external magnet field, the two component of p^+ spin have the same energy. However, in the presence of magnetic field, components may have 2 different spin. for eg. H-atom having one p^+

$$\text{i.e. } I = \frac{1}{2}$$

Two possible spin here are $\rightarrow -\frac{1}{2}$ and $+\frac{1}{2}$

In that case, nuclear E level of the p^+ splits into 2 different - different levels.

It has been observed that

$$\boxed{\omega = \gamma \times B}$$

ω = angular precessional velocity

B = applied magnetic field.

γ = Gyromagnetic ratio. (Magnetic gyre ratio)

$$\boxed{\gamma = 23567 \text{ Gauss sec}^{-1}}$$

$$\boxed{\Delta E = h\nu}$$

$$\omega = \gamma \times B_0$$

$$\omega = 2\pi\nu$$

$$\Rightarrow \boxed{\nu = \frac{\gamma B_0}{2\pi}}$$

then

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

Due to precession, the nuclei generates an oscillating electric field and the freq. with which it undergo precession is dependent on applied magnetic field (B_0) i.e more will

be the value of external magnetic field more will be the ΔE or more will be the precessional frequency.

Energy of magnetic dipole in a magnetic field is given as -

$$\boxed{E = -\mu_m B} \quad (\text{for } p^+)$$

$$\boxed{E = \mu_m B} \quad (\text{for } e^-)$$

for p^+ :- $\boxed{E = -\mu_m B}$

$$\boxed{E = -\mu_B g_N m_I B}$$

for $I = 1/2$ $m_I = +1/2$ $m_I = -1/2$

$$\boxed{E_{+1/2} = -\frac{1}{2} g_N \mu_N B}$$

$$\boxed{E_{-1/2} = \frac{1}{2} g_N \mu_N B}$$

In the presence of magnetic field, magnetic field removes degeneracy of spin component i.e. splits into two different components also called, Zeeman Splitting.

$$\Delta E = E_{-1/2} - E_{+1/2}$$

$$\boxed{\Delta E = g_N \mu_N B}$$

$$h\nu = g_N \mu_N B$$

$$\boxed{\nu = \frac{g_N \mu_N B}{h}} \quad \mu_B, g_N$$

Ques. What is the precessional freq. of p^+ at 1.4092 T

Ans. -
$$\nu = \frac{g_N \mu_N B}{h} = \frac{5.585 \times 5.05 \times 10^{-22} \text{ J T}^{-1} \times 1.4092 \text{ T}}{6.6 \times 10^{-34} \text{ J s}}$$

$$\boxed{\nu = 60 \text{ MHz}}$$

4

Ques. A typical NMR has freq. of 300 MHz. Calculate the corresponding energy in KJ mol^{-1} .

Ans. \rightarrow

$$E = h\nu$$

$$= 6.6 \times 10^{-34} \text{ J s} \times 300 \times 10^6 \text{ s}^{-1}$$

$$[\text{Hz} = \text{s}^{-1}]$$

$$= \frac{6.6 \times 10^{-34} \text{ J s} \times 300 \times 10^6 \text{ s}^{-1}}{1000} \times 6.023 \times 10^{+23} \text{ mol}^{-1}$$

$$= \text{KJ mol}^{-1}$$

Saturation:-

When a nuclei is exposed to radiation of suitable frequency, absorption takes place due to slight excess of lower E state nuclei that are present in the strong magnetic field. This excess is small and so there is always a possibility that the absorption process will equalize the no. of nuclei in the two states. This causes the absorption signal to decrease and to approach zero. Under these conditions, the spin system is said to be saturated and the process is called saturation.

\Rightarrow In order to prevent saturation, the rate of relaxation of excited nuclei to their lowest E-state must be greater than the rate at which they absorb the radio frequency energy; hence relaxation takes place which involve removal of excitation of E from upper state to restore excess energy in ground state by which nucleus in upper transition state returns to lower spin state; that is called Relaxation.

41

Relaxation Process:- It involves non-radiative transitions by which a nucleus in an upper transition state returns to the lower spin state.

In case of removal of E the nuclear spin system becomes cooler and the surrounding becomes hotter (little bit) due to the absorption of that E & this surrounding can be further used as spin or lattice called spin-spin or spin-lattice relaxation.

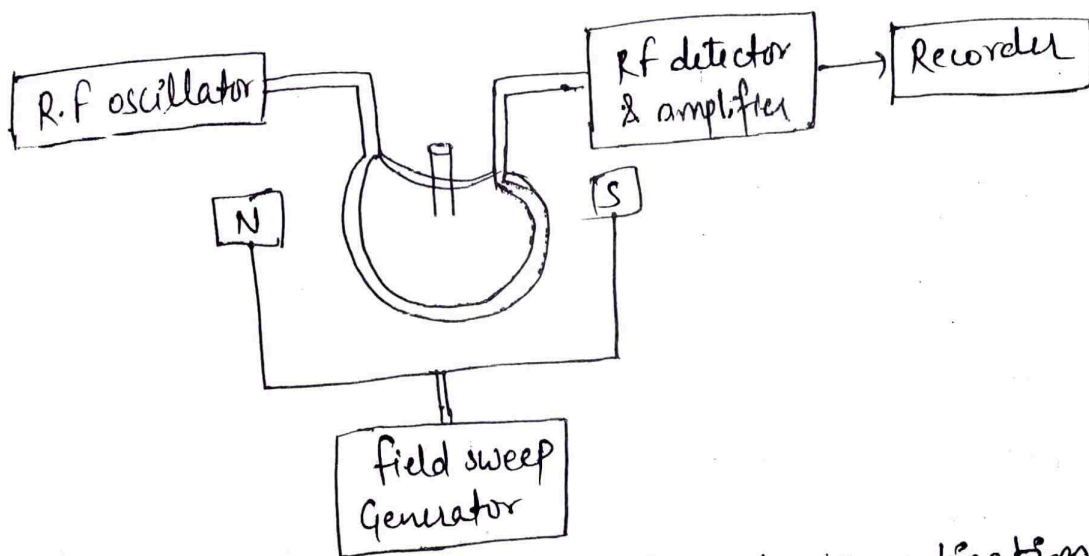
Spin-Spin Relaxation :- (Transverse Relaxation) :-

This is affected by the natural exchange of spin by 2 precessing nuclei in close proximity to one another. In each precessing nucleus there is an associated magnetic field which is the same as is required to induce a transition in the neighbouring p^+ . Then mutual exchange of spin takes place and the lifetime of an individual nucleus in the higher state is short-tened. In other words, it involve the transfer of E from one nucleus to other. There is no net loss of E .

Spin-Lattice Relaxation:-

It involve the transfer of energy from nucleus in higher state to lattice. The term lattice refers to the framework of molecules containing the precessing nuclei. All these molecules undergoes translational, rotational and vibrational motion and possess mag properties giving rise to small mag field on the lattice. A properly oriented small magnetic field induces a transition in a particular precessing magnet from an upper state to lower state. The E from this transition is transferred to the components of the lattice as additional translational and vibrational energy, the total E remains unaltered. This maintains the excess of nuclei in lower E state.

Instrumentation of NMR:-



In NMR instrumentation, the sample under investigation is taken in a glass tube which is placed b/w the pole faces of the magnet, a radio frequency (RF) source is made to fall on the sample. A signal is detected if nuclei in sample resonates with the source, E is transferred from the source to through coil to the nuclei finally the output is detected after amplification (if needed) and is recorded.

① Magnet:- The accuracy and the quality of NMR instrument depends upon strength of magnet, resolution increases with an inc in the field strength. The strength of mag. field should be very high.

② Field Sweep Generator:- A set of Helmholtz coils located parallel to the magnet faces permits alteration of the applied field over a small range. By varying a direct current through these coils the effective field can be changed.

③ Transmitter (RF source):-

A suitable oscillator having a fixed RF so that it is just sufficient to make resonate the particular nucleus.

④ Sample holder and probe :- It is a device for holding the sample tube in a fixed spot in the field.

⑤ Detector, Amplifier and Recorder:- The sample is detected and recorded as NMR spectrum as a plot of detected signals against magnetic field at constant oscillator freq.

→ We are having two types of Fourier Transformation (F.T). In F.T NMR the sample is irradiated periodically with brief, highly intense pulses of RF radiations following which free induction decay signal - a characteristic RF emission signal stimulated by irradiation is recorded as a $f \times t$ of time.

Continuous Wave (CW) NMR:- In CW NMR, the sample is ~~contin~~ continuously irradiated with a freq. while the mag. field is varied and the spectrum is obtained.

≠ Chemical Shift :-

The difference in the absorption position of a particular p^+ from the absorption position of a reference p^+ is known as Chemical shift of that p^+ .

When a molecule is placed in a mag. field its e^- are caused to circulate and thus they produce 2^{nd} mag. field i.e. induced mag. field. It can either oppose or reinforce the applied field at the p^+ .

If the induced field opposes the applied field, the p^+ is said to be shielded, while if the induced field reinforces the applied field the p^+ has a higher field strength and such a p^+ is said to be deshielded.

- ⇒ Shielding shifts the absorption upfield and de-shielding shifts the absorption downfield to obtain an effective field strength required for absorption.
- ⇒ Thus, shift compared with std. reference in the position of NMR absorption which arises due to shielding or deshielding of p^+ by e^- is called chemical shift.

p^+ with same chemical shifts are called equivalent p^+ s.
 p^+ with diff. chemical shifts are called non-equivalent p^+ s.

⇒ Measurement of Chemical Shift :- (CS)

C.S is dimensionless and is measured in Hz as well as in ppm. C.S is a difference b/w magnitude of magnetic field at which free nuclei and molecular nuclei resonates and can be given as -

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\text{operating freq. in. megacycles}} \quad (\nu_{\text{ref}} = \nu_{\text{reference}})$$

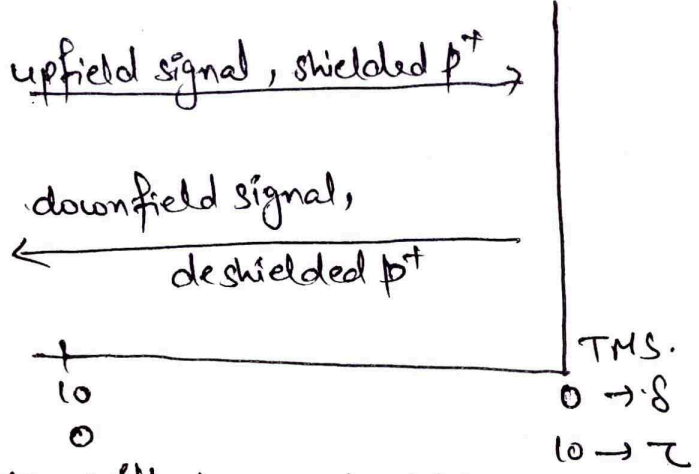
C.S is described by 2 different scales δ -scale and τ -scale. On the δ -scale, position of TMS (tetramethyl silane) signal is taken as zero ppm and values lies b/w 0-10 ppm. Hence, a small numerical value of δ indicates small downfield shift while large value indicates a large downfield shift.

On τ -scale, position of TMS signal is assigned as value of 10 ppm. So, small value of τ represents a low field absorption and higher value indicates a high field absorption.

$$\tau = 10 - \delta$$

Any p^+ or set of p^+ s which absorbs at a field lower than TMS is given a +ve value for δ .

→ Greater is the deshielding of p^+ larger is the value of δ .



δ dec with inc. shielding. However exact magnitude of δ depends upon various other factors like nature of substituent, solvent concⁿ, H-bonding etc.

⇒ Factors Affecting C.S:-

- 1) Inductive effect - Greater is electro-negativity of an atom, greater is the deshielding caused to the p^+ and hence more is the value of δ . Lesser is the e^- density circulating around the p^+ lesser is the induced field and lesser will be the applied field required to overcome shielding effect.
- 2) H-bonding - The more H-bonding that takes place the more de-shielded a p^+ becomes.
- 3) Temperature - The resonance position of most signals is little affected by temp. although $-OH$, $>NH$ & $-SH$ p^+ resonates at higher field & higher temp. Bcoz the degree of H-bonding is reduced.
- 4) Anisotropic Effect (space Effect):-

Ques. A compd. show the p^{T} NMR peak at 240 Hz downfield from the TMS peak in a spectrometer separating at 60 MHz. What is the c/s in δ -scale relative to TMS?

$$\Rightarrow \delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\text{operating freq.}} = \frac{240 \text{ Hz}}{60 \times 10^6 \text{ Hz}} = 4 \times 10^{-6} \Rightarrow 4 \text{ ppm}$$

$$\tau = 10^{-4} \Rightarrow 6 \text{ ppm.}$$

\Rightarrow Why TMS is used as a reference?

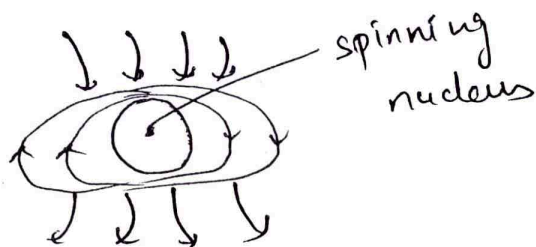
\Rightarrow ① It is chemically inert and miscible with large range of solvents.

② It is highly volatile and can be easily removed to get back the sample.

③ TMS has 12 magnetically equivalent p^{T} s and gives an intense signal.

④ Electronegativity of Si is very low (1.8) as compared to C (2.5) as a result of this shielding of equivalent p^{T} s in TMS is more than almost all org. protons. Consequently with reference to TMS signal almost all other signals appear in downfield direction.

Origin of Shielding Constant :



Diamagnetic shielding about the nucleus.

↑ ↑ ↑ ↑ B_0 (applied mag. field)

→ H-nuclei in a molecule are surrounded by the electronic charge which shields the nucleus from the influence of the applied field, so to overcome the shielding effect α to bring the p^+ to resonance, greater external field is required. Evidently, greater the e^- -density around the p^+ greater will be the induced α^o mag field (local diamag. effect) which opposes the applied field. Hence, greater ext. field will cause absorption.

→ the extent of shielding is shown in terms of shielding parameter, α , when absorption occurs the field B felt by the p^+ is represented as -

$$B = B_0 (1 - \alpha)$$

$B_0 =$ applied mag field strength

Greater the value of α , greater will be the value of applied field strength which has to be applied to get the effective field required for absorption and vice versa.

Also, $\nu = \frac{\gamma}{2\pi} B$

$$\Rightarrow \nu = \frac{\gamma}{2\pi} B_0 (1 - \alpha)$$

⇒ If shielding shift the absorption upfield in the molecule when there is a spherical distribution of e^- around the p^+ shielding is known as +ve shielding.

While if 2^o field produced by circulating e^- re-inforces the applied field the position of resonance moves downfield.

This is known as -ve shielding.

→ Also, the diamag. & paramagnetic effects from the neighbouring atoms & also effects ^{from} the inter-atomic currents, results in the p^+ absorption shift.

If the induced mag. field due to the circulation of π - e^- is oriented opp. direction of applied field → shield thus diamag.

While if it is in the direction of applied field in the π region of p^+ → deshielded → paramag.

Spin-Spin Coupling:-

The interaction b/w the spins of neighbouring mag. nuclei in a molecule may cause the splitting of NMR signal in the spectrum. This is called spin-spin coupling. It occurs through bonds (not space), by means of slight unpairing of the bonding e^- . The spin of the nearby nucleus affects the mag. environment of the nucleus, we are observing and the signal is not a simple singlet but a multiplet. This is called a splitting of signal.

→ Chemically equivalent p^+ do not show spin-spin coupling due to interaction among themselves.

Cause of Splitting:- The splitting of signal can be determined by the environment of the absorbing p^+ wrt the neighbouring p^+ .

Bcoz of diff spin states (either \uparrow or \downarrow) and the resultant mag. moments of the neighbouring p^+ , the actual mag. field experienced by the given p^+ may be modified in a no. of ways & absorption signals may be splitted into diff peaks thus it is the spin-spin coupling of the absorbing and neighbouring p^+ which is responsible for the splitting of peaks

→ Two p^+ which undergoes coupling must be suitably distanced from each other i.e. ~~not~~ ^{neither} too far nor too close.

→ The multiplicity of peak of gr. of equivalent H is determined by the neighbouring p^+ . In general, if an equivalent H interact or couple with adjacent H or adjacent C than the resonance peak is splitted into $(n+1)$ peaks.

→ Low resolution NMR spectra doesn't show spin-spin splitting but high resolution NMR spectra can easily represent spin-spin splitting

for ex. $\text{CH}_3\text{CH}_2\text{OH}$

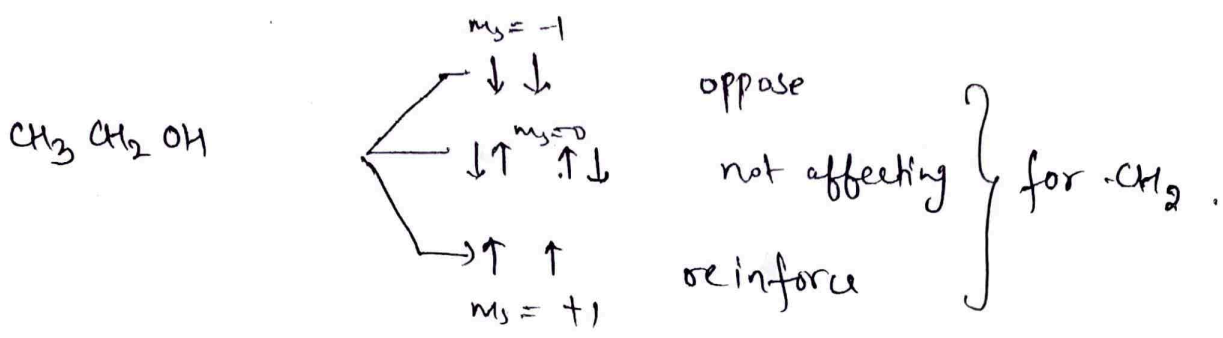
Low resolution NMR \Rightarrow 3 peaks (3:2:1)

High resolution (acrotic) \Rightarrow $\text{CH}_2 \rightarrow$ quartet $\overset{\text{CH}_3}{\text{CH}_2} \rightarrow$ triplet OH \rightarrow singlet

(pure) \Rightarrow $\text{CH}_3 \rightarrow$ triplet OH \rightarrow triplet

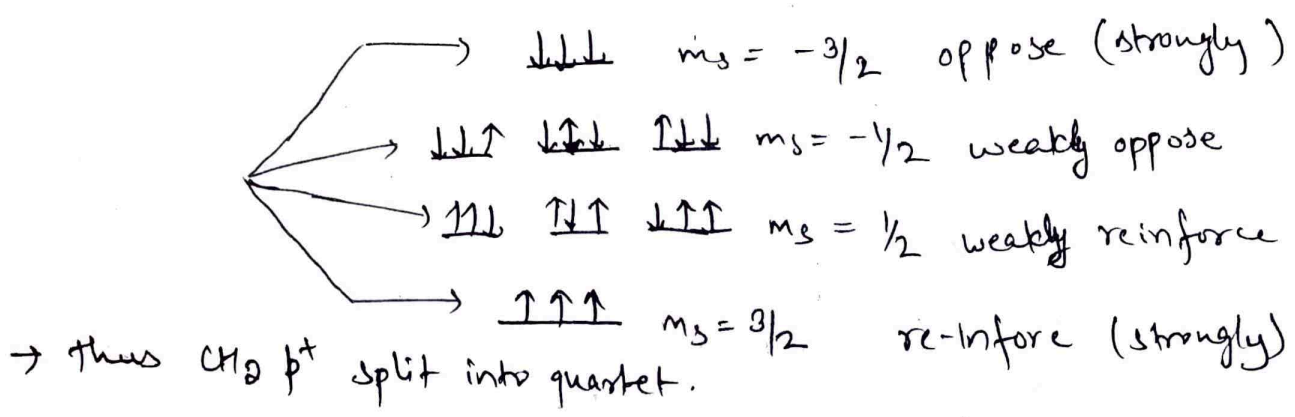
$\text{CH}_2 \rightarrow$ doublet of quartet

→ for example, let us consider the high resolution p^+ NMR spectrum of acidified ethanol. Let us designate the p^+ of CH_2 as a and b. There are four possible ways in which these p^+ can align themselves relative to a given p^+ in CH_3 gr.



Out of these four alignments 2nd & 3rd alignment are energetically equivalent thus CH₃ p⁺ peak will split into a triplet with intensity ratio 1:2:1.

Likewise when CH₃ p⁺ are related to H of CH₂ gp. it can align themselves in 8 different ways.



In acidified ethanol the hydroxylic p⁺ undergoes a fast exchange with other alcoholic p⁺s, so that it does not interact with CH₂ gp. Therefore we can see that methyl p⁺ splits the CH₂ line into a quartet with intensity ratio 1:3:3:1.

Therefore, even the high resolution NMR spectra of acidified ethanol represents -

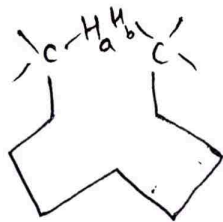
OH - singlet CH₂ - quartet CH₃ - triplet.

⇒ In contrast to acidified ethanol, bcoz of the absence of H⁺ catalyst there is no p⁺ exchange in pure ethanol, thus, due to spin-spin splitting CH₃ line is splitted into a triplet, -CH₂ line into a doublet of quartet i.e. multiplet. and OH into a triplet.

⇒ Nuclear Overhauser Effect :- (NOE)

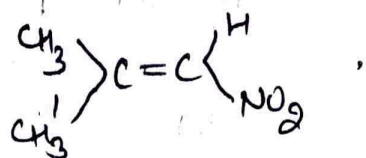
This is the technique by which intensity of NMR signal can be increased significantly by saturation of some of the nearby nuclei within a molecule. N.O.E is only noticeable over short dis. (gen. 0.2-0.4 nm). NOE tells whether 2 p^r are in close proximity within the molecule or not.

Consider a hypothetical molecule in which 2 p^r are in close proximity

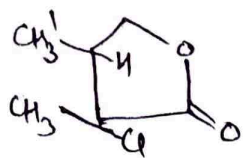


In such a compd., if we double irradiate H_b than this p^r gets stimulated and the stimulation is transferred through space to the relaxation mech^m of H_a. Thus due to inc in spin-lattice relaxation of H_a, its signal will appear more intense by 15-50%. Thus, if the intensity of absorption of H_a signal is increased by double irradiating H_b than the p^r H_a and H_b must be in a close proximity in a molecule.

2nd most imp. advantage for using this technique is describing cis or trans confi. in a molecule like



On double irradiating CH₃' there would be no effect on signal of H i.e. trans methyl doesn't make more effect on H whereas on double irradiating CH₃ gp. i.e. cis to H-atom, intensity of H inc. \therefore In compd. like -



on irradiating CH_3^1 p^+ intensity of doublet signal would inc. through lattice relaxation.

Ques. A PMR spectrometer operates at 300 MHz. Calculate the mag. field.

$$\Rightarrow B_0 = \frac{g_N M_N}{\hbar} = 7.05 \text{ T}$$

Ques. Calculate the ratio of population of lower & upper E levels for the p^+ spins which are in thermal eqm at room Temp. & subjected to a mag. field intensity of 1T in NMR spectrometer.

$$\Rightarrow \frac{N_\beta}{N_\alpha} = e^{-\Delta E / KT} \quad N_\beta \Rightarrow \text{upper}$$

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E / KT} \quad N_\alpha \Rightarrow \text{lower population}$$

$$\Delta E = g_N M_N B$$

$$\therefore \frac{N_\alpha}{N_\beta} = e^{g_N M_N B / KT} = 1 + \frac{g_N M_N B}{KT}$$

$$= 1 + \frac{5.585 \times 5.05 \times 10^{-27} \text{ JT}^{-1} \times 1 \text{ T}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 298 \text{ K}}$$

$$= 1 + 6.86 \times 10^{-6} \approx 1$$

ie saturation occur.

PHYSICAL CHEMISTRY
SECTION - B

11

ESR
(e⁻ Spin Resonance)

Discovered by Zavoisky in 1944.

⇒ ESR spectroscopy is an absorption spectroscopy which involves the absorption of radiation in microwave region by a substance containing one or more unpaired e⁻. The substance with one or more unpaired e⁻ are paramag. in nature. Hence, this spectroscopy is also known as EPR (e⁻ paramag resonance).

There are 2 types of substance containing unpaired e⁻.

- ① Stable Paramag Substance
- ② Unstable Paramag Substance

(SPS)

⇒ Stable Paramag Substance :- These includes the simple molecules like NO, O₂, NO₂, ions of transition metals and their complexes like [Fe(CN)₆]³⁻. Such substance are called S.P.S. and can be easily studied by ESR.

⇒ Unstable Paramag Substance (UPS) :- these are gen. FR or radical ions & are formed as an int. in a chemical rxn or irradiation of a substance with UV or X-ray

Q. Which of the following will show ESR spectrum (unpaired)

H ✓ (1s ¹)	O ₂ ✓	[Fe(CN) ₆] ³⁻ ✓	CuSO ₄ ✓
H ₂ x (1s ²)	O ₂ ⁻ ✓	[Ni(CN) ₄] ²⁻ x	[NiCl ₄] ²⁻ ✓
Cl ✓ (3p ⁵)	O ₂ ⁺ ✓	[Cr(H ₂ O) ₆] ³⁺ ✓	
Na ⁺ x	O ₂ ²⁻ x	ZnCl ₂ x	
Cu ⁺ ✓ (4s ⁰)			
Cu ²⁺ x (3d ⁹)			

O₂ → n_{2px}¹ = n_{2py}¹

Principle of ESR :-

It is similar to NMR except that e^- spin is involved in ESR instead of nuclear spin. ie is involved in NMR. An unpaired e^- has a spin like a p^+ and this spin has an associated mag. moment. Every e^- has a mag. moment & spin quantum no. $s = 1/2$ with mag component $m_s = \pm 1/2$. In the presence of external mag. field with strength B_0 , the e^- mag. moment align itself either parallel or anti-parallel to the field. e^- possess a spin S with value $1/2$ the mag. moment associated with this spin

$$\mu = -g_e \mu_B \vec{S}$$

g_e = Lande's g-factor

μ_B = Bohr magneton

$$\mu_B = \frac{eh}{4\pi m_e}$$

E associated with this e^- spin S in the mag. field B_0

$$E = -\mu B_0$$

$$E = g_e \mu_B \vec{S} B_0$$

$$E =$$

The component spin S along the field direction

$$E_{m_s} = g_e \mu_B B_0 m_s$$

$$m_s = \pm \frac{1}{2}$$

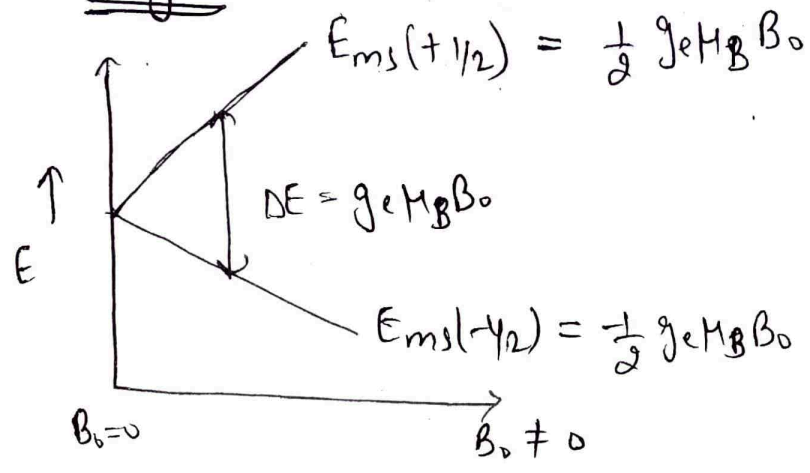
$$E_{+1/2} = \frac{1}{2} g_e \mu_B B_0$$

$$E_{m_s(-1/2)} = \frac{1}{2} g_e \mu_B B_0$$

The parallel alignment corresponds to lower E state and the separation b/w its & upper state is given by $e\hbar^2$ -

$$\Delta E = g_e \mu_B B_0$$

⇒ E-level diagram:-



An unpaired e⁻ can move b/w the 2 E-level by absorbing EMR of E hν, such that the resonance condition, ΔE is obeyed. and the fundamental eqⁿ of ESR spectroscopy

$$\Delta E = g_e \mu_B B_0 = h\nu$$

$g_e = 2.0023$ (for free e⁻)

$$\mu_B = \frac{eh}{4\pi m_e} = \frac{1.6 \times 10^{-19} \times 6.06 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31}}$$

$\mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1}$

B₀ = ext. mag field

Ques. → Calculate the ESR freq. of unpair e⁻ in mag field of 3000 Gauss.

$$1 \text{ T} = 10^4 \text{ Gauss}$$

⇒ $1 \text{ T} = 10^4 \text{ Gauss}$

$3000 \text{ Gauss} = \frac{3000}{10^4} = 0.3 \text{ T}$

$h\nu = g_e \mu_B B_0$

$$\nu = \frac{g_e \mu_B B_0}{h} = \frac{2.0023 \times 9.27 \times 10^{-24} \text{ J T}^{-1} \times 0.3 \text{ T}}{6.06 \times 10^{-34} \text{ J}}$$

$\nu = 8.34 \times 10^9 \text{ Hz}$
 $= 8.34 \text{ GHz}$

Ques. In ESR spectrophotometer, freq. of free e^- is 9.5 GHz . Calculate B_0 at which spectrophotometer is operated.

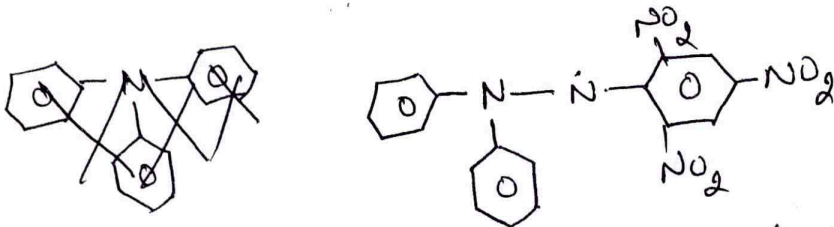
$\Rightarrow g_e \mu_B B_0 = h\nu$

$$B_0 = \frac{6.6 \times 10^{-34} \times 9.5 \times 10^9 \text{ Hz}}{2.0023 \times 9.27 \times 10^{-24}}$$

$B_0 = 0.34 \text{ T.}$

Reference Material :- in ESR spectroscopy

DPPH (diphenylhydrazide) diphenyl picryl hydrazide.



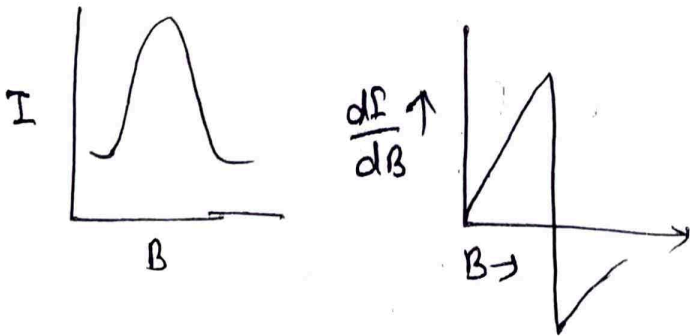
Ques. Why DPPH is used as reference material?

\Rightarrow It is stable FR.

g_e value for DPPH is approx. equal to free e^- (2.0036)

Ques. Why ESR spectra is plotted in 1st derivative mode?

\Rightarrow In ESR spectra can be represented by plotting intensity against the field as NMR.



The spectra is very broad & we can't clearly define the maxima. Hence it is better to give ESR spectra in 1st derivative mode.

Ques Why absorption spectra of ESR is broad as compared to NMR?

⇒ By uncertainty principle -

$$\Delta E \cdot \Delta t = \frac{h}{4\pi}$$

where $\Delta E = h\nu$, then

$$h \Delta \nu \cdot \Delta t = \frac{h}{4\pi}$$

$$\Delta \nu \cdot \Delta t = \frac{1}{4\pi}$$

It can be explained on the basis of uncertainty principle. Line width i.e. $\Delta \nu$ is related to life time of excited state i.e. Δt , by Heisenberg uncertainty principle, by this

$$\Delta \nu \cdot \Delta t = \frac{1}{4\pi} = \text{const}$$

In ESR, size of e^- is small, hence it can relax more easily, may be the very small relaxation time, hence, line width of spectral line is large & the signal will be broad.

On the other hand, in NMR, p^+ has larger size, therefore there will be long relaxation time i.e. Δt is high & hence $\Delta \nu$ is small & signal will be sharp.

Ques - Using uncertainty principle, calculate Δt of an E-state which gives rise to line width ($\Delta \nu$).

(i) 0.1 cm^{-1} (NMR) (ii) 60 MHz

⇒ (i) $\Delta \nu = 0.1 \text{ cm}^{-1}$

$$\Delta t = \frac{1}{4\pi \cdot \Delta \nu} = \frac{1}{4 \times 3.14 \times 0.1 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm s}^{-1}}$$

$$\Delta t = 265 \times 10^{-11} \text{ s}$$

c (used to convert unit)

$$\begin{aligned}
 \text{(ii)} \quad \Delta\nu &= 60 \text{ MHz} \\
 &= 60 \times 10^6 \text{ Hz} \\
 &= 60 \times 10^6 \text{ s}^{-1}
 \end{aligned}$$

$$\Delta t = \frac{1}{4 \times 3.14 \times 60 \times 10^6 \text{ s}^{-1}} = 1.3 \times 10^{-9} \text{ sec}$$

Ques. Calculate the natural line width ($\Delta\nu$) in cm^{-1} of a spectral line which results when a quantum system have excited state of life time of 0.1 ns.

$$\Rightarrow \Delta t = 0.1 \text{ ns} = 0.1 \times 10^{-9} \text{ s} = 10^{-10} \text{ sec}$$

$$\Delta\nu = \frac{1}{4\pi \cdot \Delta t \cdot c} = \frac{1}{4 \times 3.14 \times 10^{-10} \text{ s} \times 3 \times 10^{10} \text{ cm s}^{-1}}$$

$$\Rightarrow 2.65 \times 10^{-2} \text{ cm}^{-1}$$

Ques. The NMR spectra occurs in RF region ($\approx 14 \text{ MHz}$) whereas ESR occur in microwave region ($> 9000 \text{ MHz}$). Why?

$$\Rightarrow \frac{(h\nu)_{\text{ESR}}}{g_e \mu_B B_0}$$

$$\frac{(h\nu)_{\text{NMR}}}{g_N \mu_N B_0}$$

$$\frac{\nu_{\text{ESR}}}{\nu_{\text{NMR}}} = \frac{g_e \mu_B}{g_N \mu_N}$$

Basic eqⁿ of ESR \Rightarrow

$$(h\nu)_{\text{ESR}} = g_e \mu_B B_0$$

and of NMR $\Rightarrow (h\nu)_{\text{NMR}} = g_N \mu_N B_0$

→ one of the difference in these spectroscopy is due to g-factor

$g_e = 2.0023$ $g_N = 5.585$

→ 2nd or major diff is due to mass of e^- or p^+ .

$$\frac{(h\nu)_{ESR}}{(h\nu)_{NMR}} = \frac{g_e M B_0}{g_N M_N B_0}$$

$$\frac{\nu_{ESR}}{\nu_{NMR}} = \frac{g_e M_B}{g_N M_N} = \frac{g_e \frac{eh}{4\pi m_e}}{g_N \frac{eh}{4\pi m_p}}$$

$$\frac{\nu_{ESR}}{\nu_{NMR}} = \frac{g_e m_p}{g_N \cdot m_e} = \frac{2.0}{5.5} \times 1837$$

$$\approx 660$$

$$\nu_{ESR} = \nu_{NMR} \times 660$$
$$\approx 14 \text{ MHz} \times 660$$

$$\nu_{ESR} \approx 9240 \text{ MHz}$$

Hyperfine Coupling :-

When an unpaired e^- in a molecule is delocalised over the whole it may interact with many nuclei possessing mag. moment in the molecule to cause further splitting of e^- resonance line. This type of mag. interaction b/w e^- spin & nuclear spin ($I \neq 0$), in the same molecule is called hyperfine coupling & the splitting of individual resonance lines into component lines is called hyperfine splitting.

This coupling splits the ESR signal into a multiplet which are called as hyperfine structures.

No. of signals in ESR :-

Rule 1:- When an unpaired e^- spin couples with a nucleus with spin I , the absorption signal of e^- is splitted into a multiplet with $(2I+1)$ lines.

Calculate the no. of ESR signals in

$$\begin{aligned} \text{1) } H^{\cdot} \quad 2I+1 &= 2 \times \frac{1}{2} + 1 & I = \frac{1}{2} \text{ for } H \\ &\Rightarrow 2. \end{aligned}$$

Rule 2:- In gen, when absorption signal of an unpaired e^- is splitted by an equivalent nuclei, then no. of lines is given by $(2nI+1)$

$$\begin{aligned} \text{for eg } \dot{C}H_3 \quad (2nI+1) \\ &= 2 \times 3 \times \frac{1}{2} + 1 = 4 \quad (n=3) \end{aligned}$$

Rule 3:- When splitting is caused by both, a set of n equivalent nuclei with nuclear spin I_1 and a set of m equivalent nuclei with nuclear spin I_2 ; then no. of signals is given by $(2nI_1+1)(2mI_2+1)$.

for eg
 $CH_3\dot{C}H_2$

$$\begin{aligned} &(2nI_1+1)(2mI_2+1) \\ &(2 \times 3 \times \frac{1}{2} + 1)(2 \times 2 \times \frac{1}{2} + 1) = 12. \end{aligned}$$

Que. Calculate the no. of ESR lines in following radicals

1) $\dot{C}F_2H$ $(2nI_1 + 1) \overbrace{(2mI_2 + 1)}^3 = (2 \times \frac{1}{2} \times 2 + 1) (2 \times \frac{1}{2} + 1) = 6$

ii) $^{13}C\dot{H}_3$ $(2 \times \frac{1}{2} + 1) (2 \times 3 \times \frac{1}{2} + 1) = 8$

3) $CF_3\dot{D}$ $(2 \times \frac{1}{2} \times 2 + 1) (2 \times 1 + 1) = 9$

4) $\dot{C}ClH_2$ $(2 \times \frac{3}{2} + 1) (2 \times 2 \times \frac{1}{2} + 1) = 12$

5) $^{13}CF_2\dot{H}$ $(2 \times \frac{1}{2} + 1) (2 \times 2 \times \frac{1}{2} + 1) (2 \times \frac{1}{2} + 1) = 12$

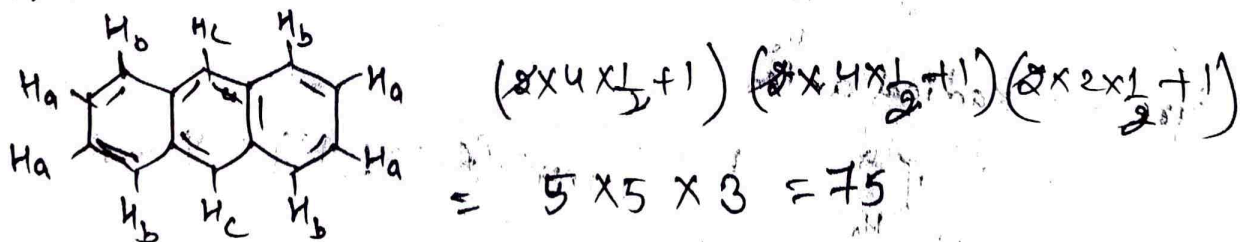
6) Isopropyl radical $(\dot{C}H-CH_3)$ $\Rightarrow (2 \times \frac{1}{2} + 1) (2 \times 6 \times \frac{1}{2} + 1) = 14$

7) Benzene radical anion $(2 \times 6 \times \frac{1}{2} + 1) = 7$

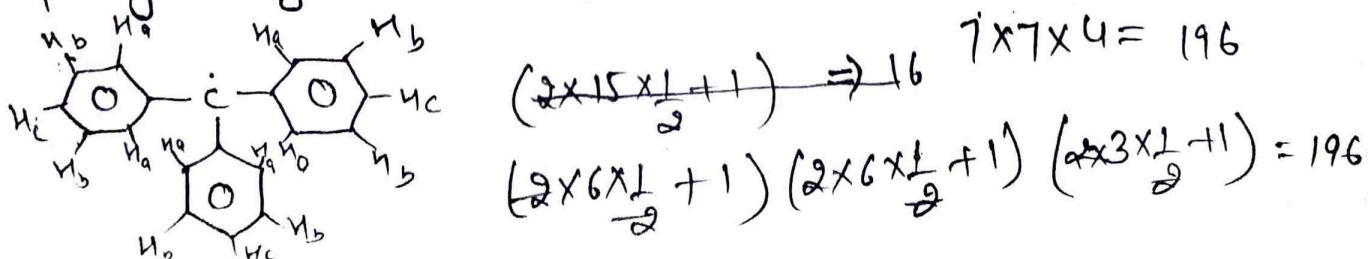
I $H = 1/2$ $F = 1/2$ $^{13}C = 1/2$ $D = 1$ $^{35}Cl = 3/2$

8) Naphthalene radical anion $(2 \times 4 \times \frac{1}{2} + 1) (2 \times 4 \times \frac{1}{2} + 1) = 25$

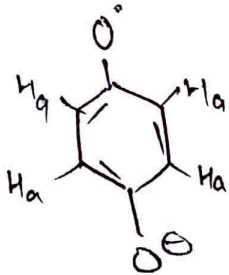
9) Anthracene radical anion



10) Triphenylmethyl radical :-



11) 1,4-benzo semiquinone [radical anion]



$$(\cancel{2 \times 2 \times \frac{1}{2} + 1}) (\cancel{2 \times 2 \times \frac{1}{2} + 1})$$

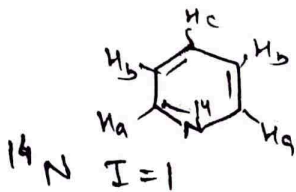
$$= \cancel{3 \times 3} \Rightarrow 9$$

$$(2 \times 4 \times \frac{1}{2} + 1) = 5$$

(All 4 equivalent
 cuz of resonance
 involvement of radical &
 anion)

12) pyridine radical anion

15 N $I = 1/2$

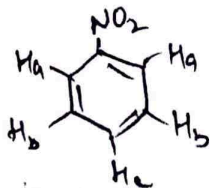


14 N $I = 1$

$$(2 \times 1 + 1) (2 \times 2 \times \frac{1}{2} + 1) (2 \times 2 \times \frac{1}{2} + 1) (2 \times \frac{1}{2} + 1)$$

$$3 \times 3 \times 3 \times 2 = 54$$

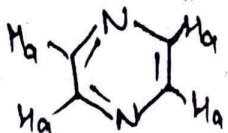
13) Nitrobenzene radical anion



$$(\cancel{2 \times 2 \times \frac{1}{2} + 1}) (2 \times 2 \times \frac{1}{2} + 1) (2 \times \frac{1}{2} \times 1) (2 \times 1 + 1)$$

$$3 \times 3 \times 2 \times 3 = 18 \times 3 = 54$$

14) Pyrazine Radical anion



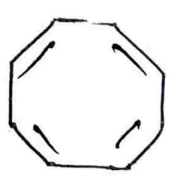
$I(N) = 1$
 $(2 \times 2 \times 1 + 1) (2 \times 4 \times \frac{1}{2} + 1) = 9 \times 5$

15) Deuterated methyl radical



$$(2 \times 3 \times 1 + 1) \Rightarrow 7$$

⑥ Cyclooctatriene radical anion:-



$$(2 \times 8 \times \frac{1}{2} + 1) = 9$$

⑦ Trimethyl radical:-

$$\dot{C}Cl_3 = (2 \times \frac{3}{2} \times 3 + 1) = 10$$

Ques:- $\dot{C}Cl_3$ show 10 lines in ESR spectra. Calculate the spin of Cl nucleus-

$$\Rightarrow (2 \times 3 \times I + 1) = 10$$

$$6I = 9$$

$$I = 3/2$$

Hyperfine st. and their dividing:-

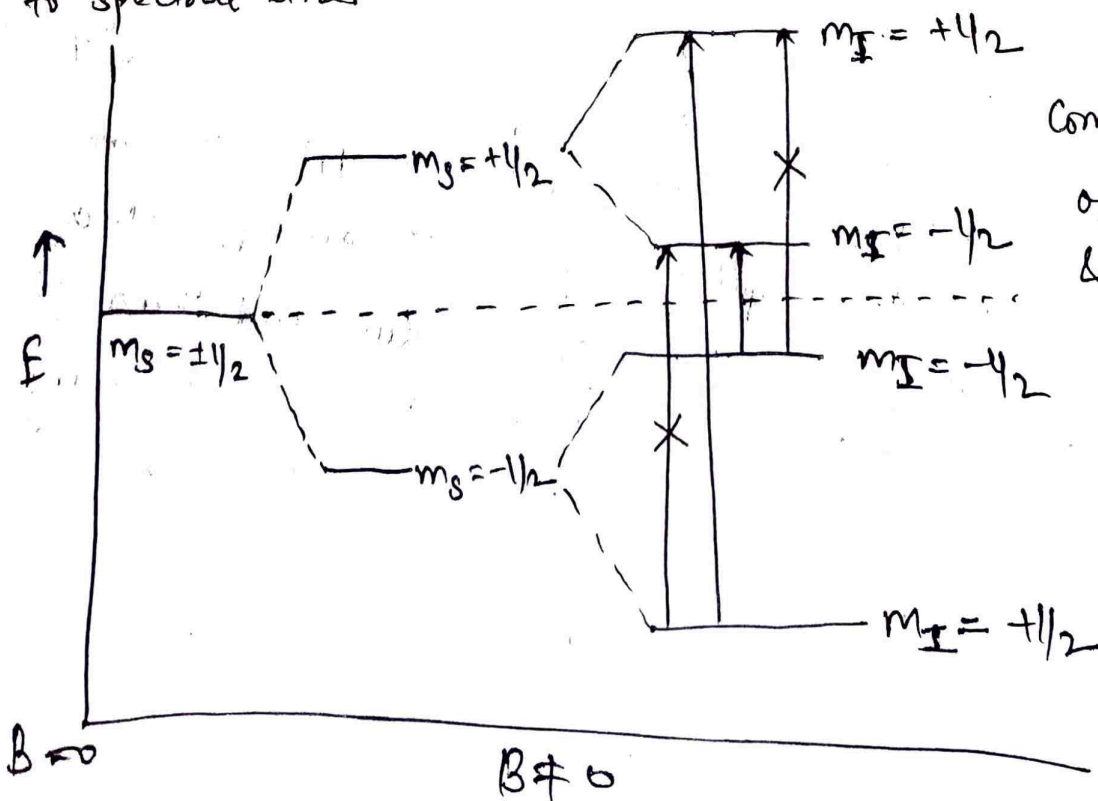
The sepⁿ b/w lines is usually of the order 10^3 to 10^4 T and that is about approx. 50 MHz which is approx. 10^6 times larger than nuclei-nuclei coupling' bcoz an e^- can approach a nucleus much more closer than other nucleus and thus interact more strongly with it. The biggest factor influencing the magnitude of e^- -nucleus coupling is the amt. of time which e^- spent in the vicinity of nuclei.

⇒ Drawing of hyperfine st. :-

Consider the hyperfine st. resulting from the splitting of an ESR signal. Consider the eg of H^+ having one p^+ and one e^- . The 2 E-levels of free e^- in an applied mag field having spin $m_s = -1/2$ align with the field and $m_s = +1/2$ align opp. to the field. Each of 2 E-levels of e^- in H-atom is splitted into 2 E-levels by interaction with nuclear spin of p^+ i.e. $m_I = \pm 1/2$ where m_I is the nuclear spin angular momentum quantum no. Thus corresponds to 2 E-states $m_s = -1/2$ & $m_s = +1/2$, four diff. E-levels are obtained but the selection rule in ESR are Δm_I must be zero & $\Delta m_s = \pm 1$.

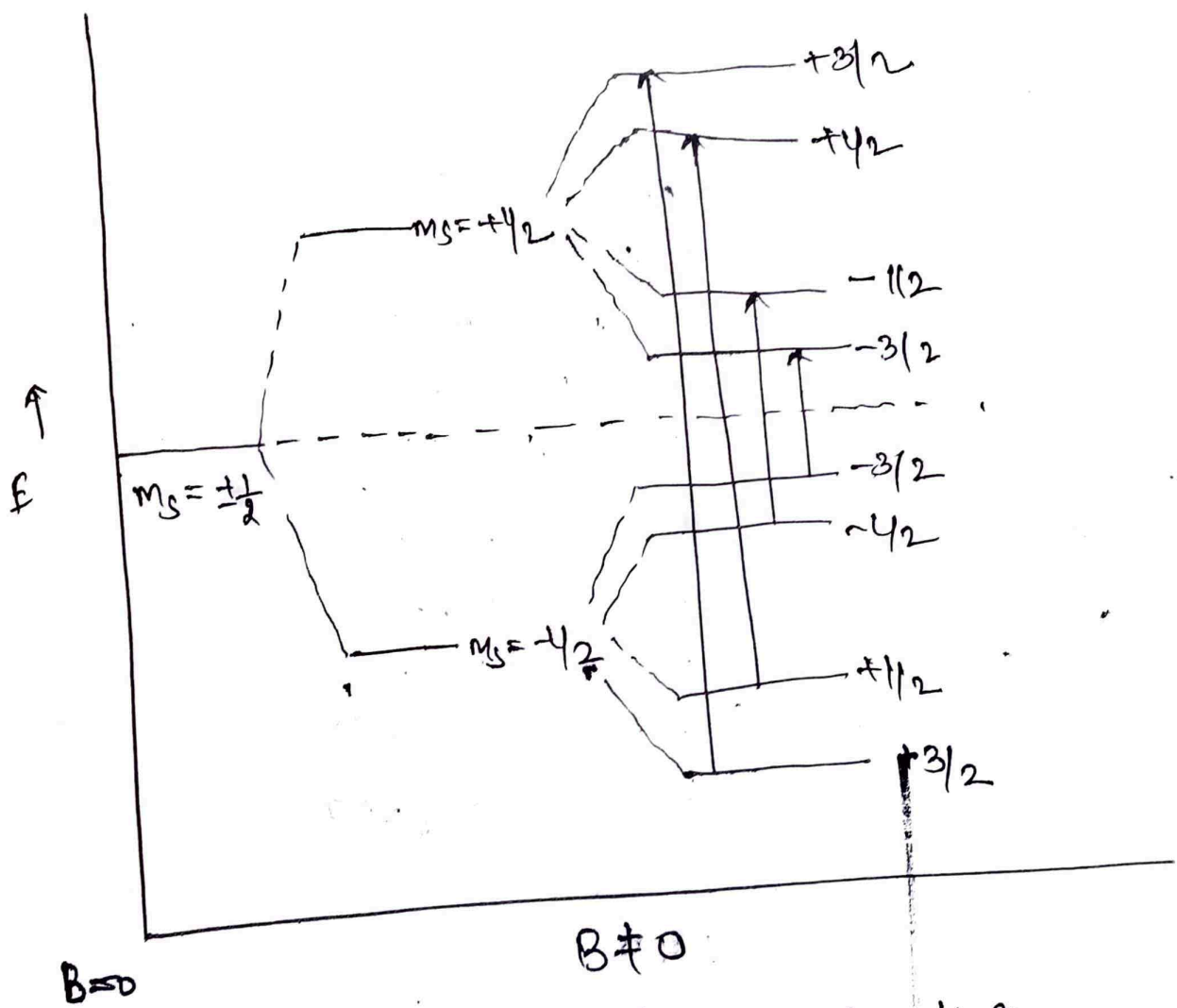
$$\Delta m_I = 0 \text{ \& \ } \Delta m_s = \pm 1$$

It allow us to decide which level of transition will give rise to spectral line.



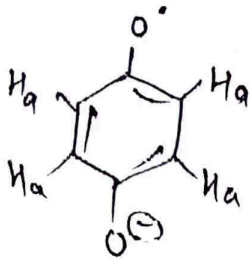
Combined effect
of applied field
& nuclear spin
of p^+ .

$^1\text{CH}_3$ $3p^1 \Rightarrow$ 4 ways of arrangement thus split in 4 level
 ($\uparrow\uparrow\uparrow$, $\downarrow\downarrow\downarrow$, $\uparrow\uparrow\downarrow$, $\downarrow\downarrow\uparrow$)



Thus $^1\text{CH}_3$ give 4 lines $\Rightarrow (2 \times 3 \times \frac{1}{2} + 1) \Rightarrow 4$ lines.

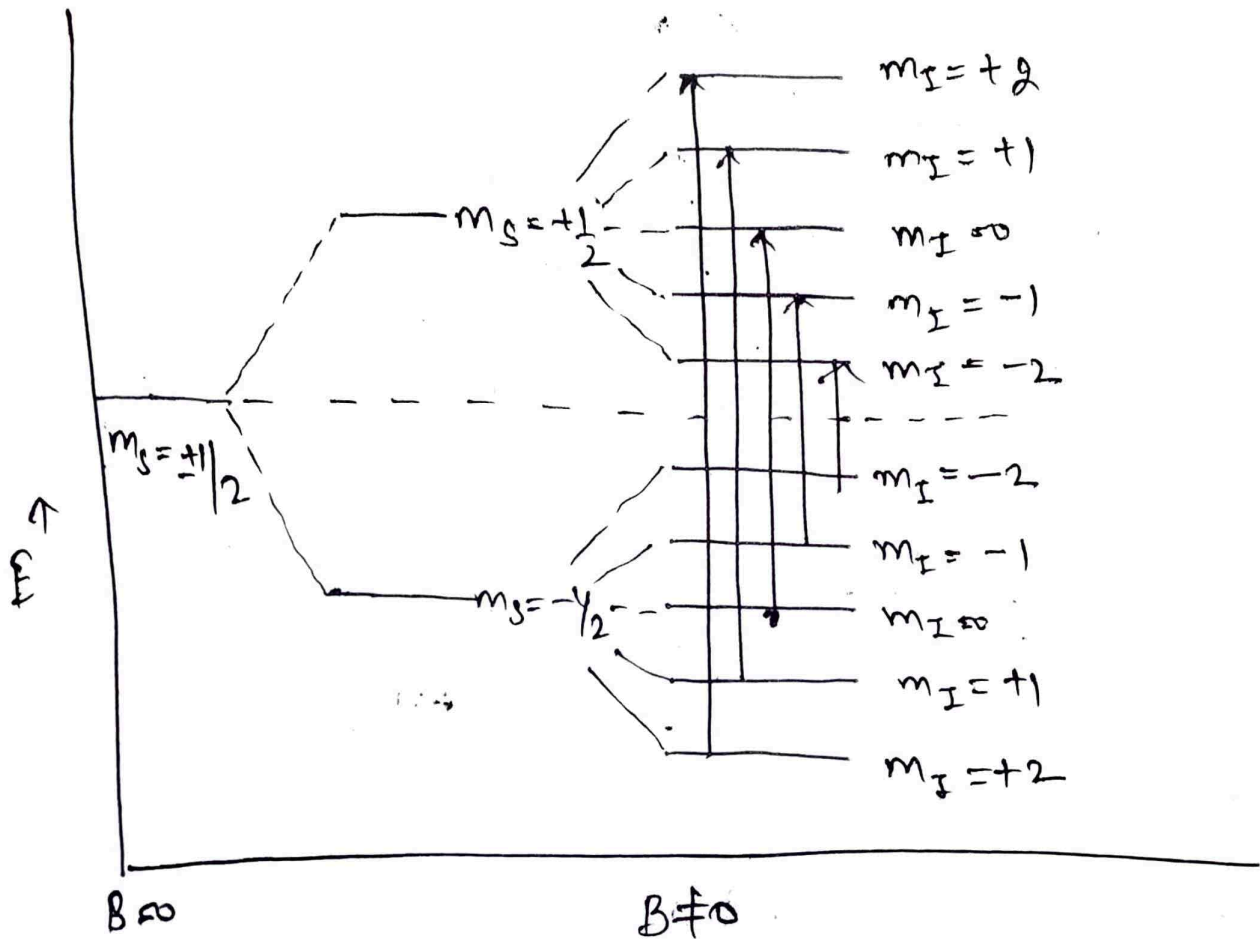
⇒ 1,4-benzoquinone radical :-



$$(2 \times 4 \times \frac{1}{2} + 1) \Rightarrow 5$$

$$2 = +\frac{1}{2} \Rightarrow \uparrow \uparrow \uparrow \uparrow = +2 \quad \text{and} \quad 2 = -\frac{1}{2} \Rightarrow \downarrow \downarrow \downarrow \downarrow = -2$$

Thus +2 to -2



Thus Give 5 lines

⇒ CD_3

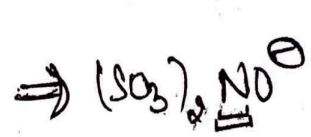
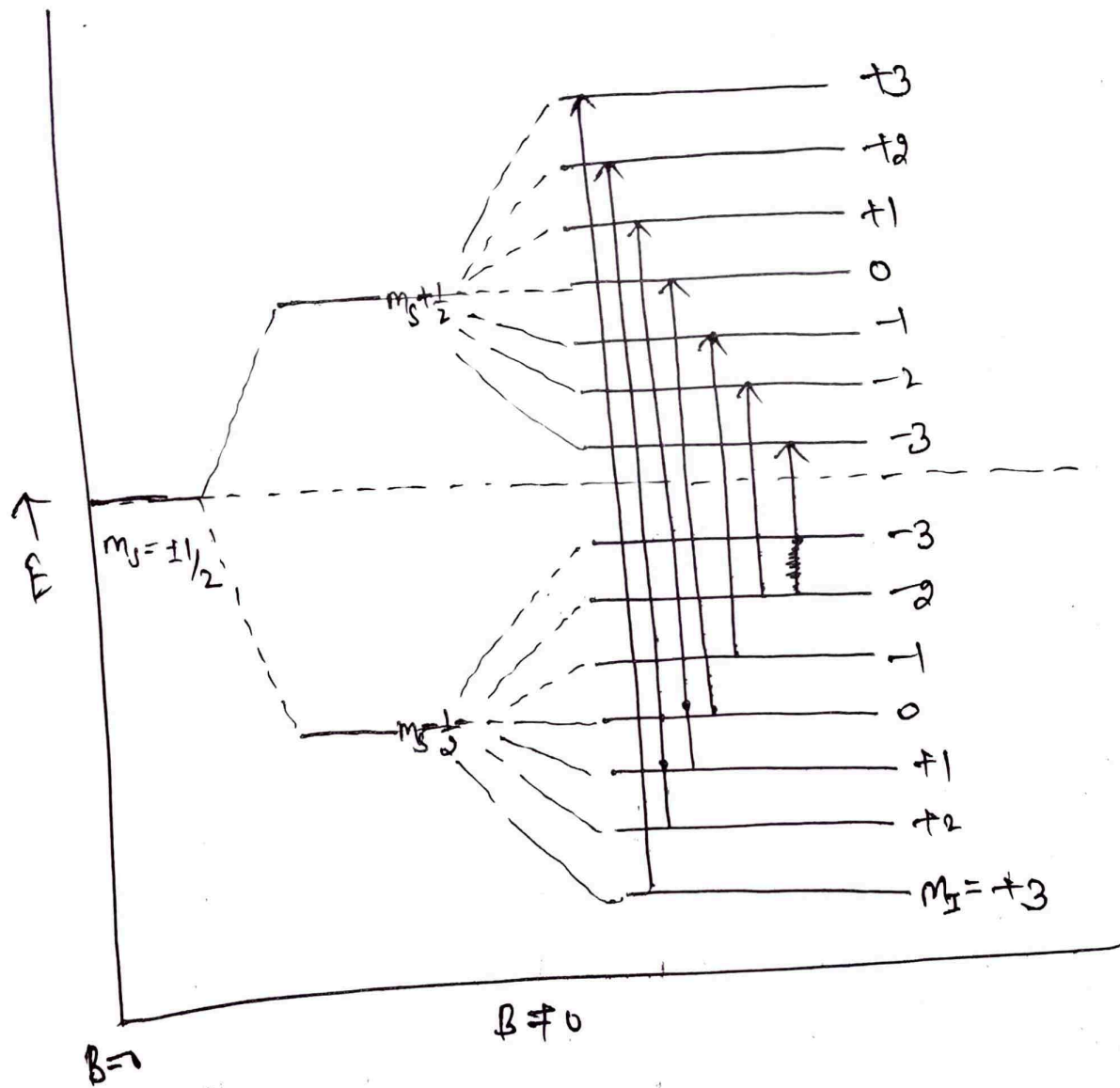
$$\uparrow \uparrow \uparrow = +3$$

$$\downarrow \downarrow \downarrow = -3$$

(because $I = 1$ for D)

Thus Give ^{splitting} lines from +3 to -3.

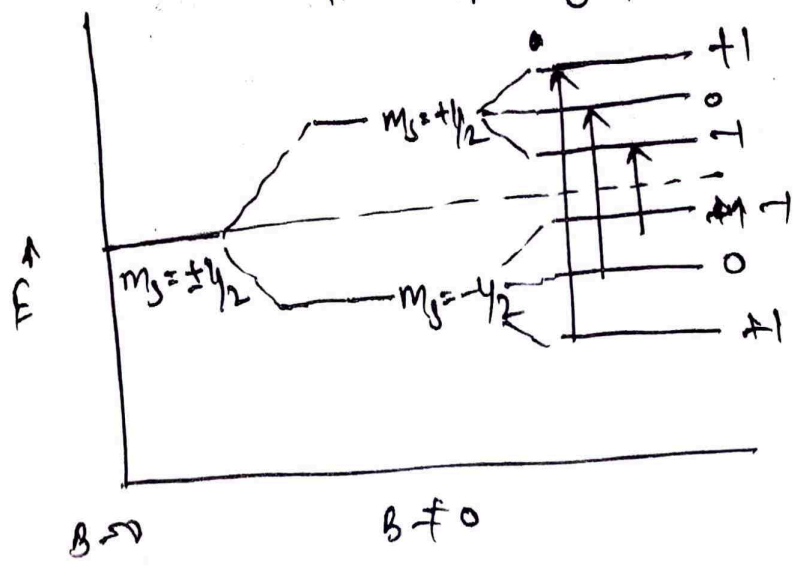
$$[2I+1 = 2 \times 3 \times 1 + 1 = 7 \text{ lines}]$$



for N = 1, I = 1
 thus splitting from -1 to +1

(~~10 + 3 = 13~~ unpaired)

~~1111~~



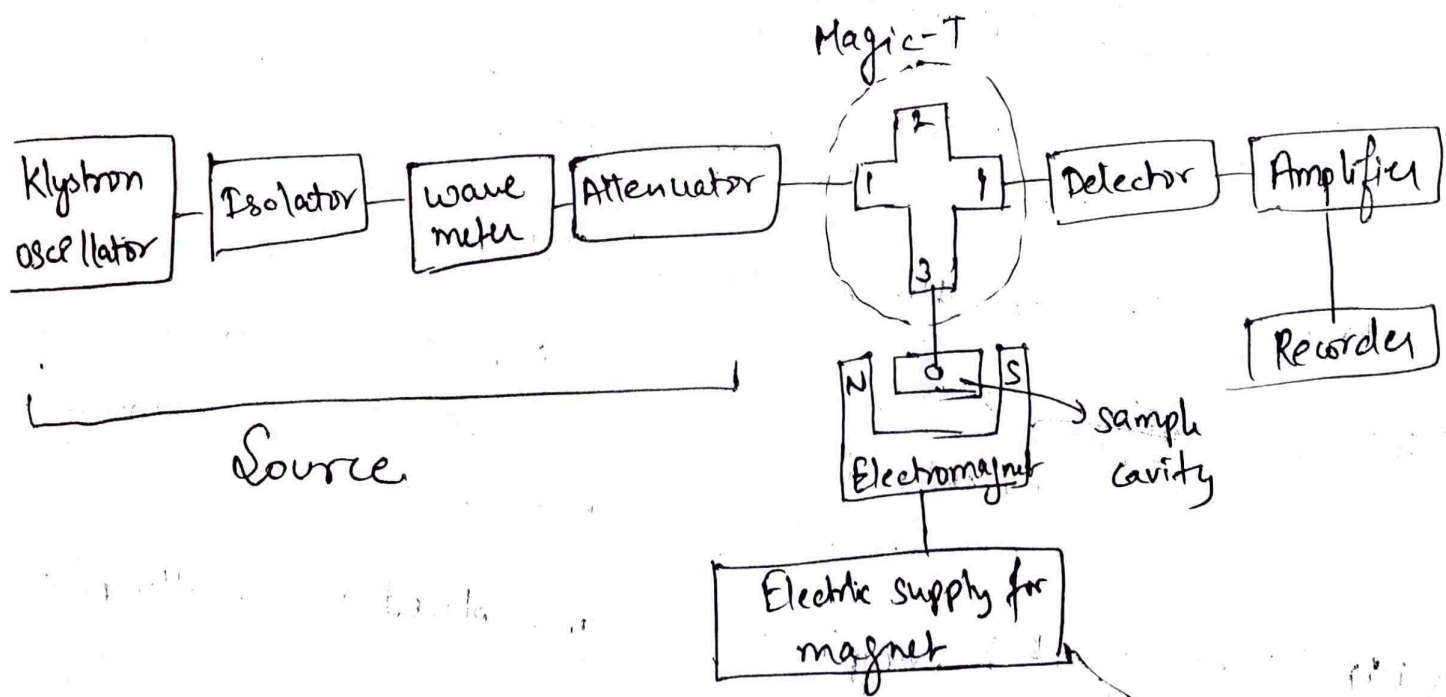
\Rightarrow 3 lines produced

⇒ Difference b/w NMR and ESR :-

NMR	ESR
<ul style="list-style-type: none"> In NMR nuclear spin is involved The nuclear g-factor has value $g_N = 5.585$ In NMR, nuclear magneton is involved where $\mu_N = \frac{eh}{4\pi m_p}$ It is observed in radio-freq. region It has sharp line width. In this, interaction occur b/w the 2 nuclei & hence spin-spin splitting due to nuclei occur. It is plotted b/w I vs B In this, coupling constant (J) is used 	<ul style="list-style-type: none"> In ESR, e^- spin is involved The Lande-g-factor has value of $g_e = 2.0023$ In ESR, Bohr magneton is involved have value $\mu_e = \frac{eh}{4\pi m_e}$ It is observed in microwave region It has broad line width In this, interaction b/w nuclear spin & e^- spin occur. It is plotted b/w dI/dB vs B. In this hyperfine coupling constant (A) is used

⇒ Instrumentation of ESR :-

The sample whose ESR is to be recorded is kept in the resonant cavity. The klystron tube is operated to produce monochromatic radiation of freq, 9.5×10^9 9500 MHz. This tube is an electronic oscillator in which a beam of e^- s is pulsed b/w a cathode & a reflector. The oscillating output is transmitted to a wave guide by a loop of wire which sets up a fluctuating mag. field in the guide. The wave guide transmits the microwave radiation to the sample which is positioned b/w the poles of a permanent magnet. Helmholtz coils provide a means for varying the field over the small range in which resonance occurs.



Working :-

Source 1- (1) Klystron Oscillator → It is a vacuum tube which can produce microwave oscillation.

(2) Isolator - It is a strip of ferrite material which minimise vibrations in the freq. of microwave produced by Klystron.

(3) Wave meter - It is used to measure the freq. of microwave produced by Klystron.

(4) Attenuator - It is used to adjust the microwave power incident on the sample.

↳ Circular or Magic-T :-

Arm 1 - Microwave radiations enters through arm 1.

Arm 3 - Connected to resonant cavity or sample.

Arm 2 - It is a terminating load and absorb any power which might be reflected from detector arm.

Arm 4 - It is directly attached to detector.

↳ (i) Sample Cavity :- It is a heart of an ESR spectrometer and gen. the instruments have dual resonant or sample cavity one for sample & other for reference.

↳ (ii) Electromagnet :- Sample cavities are placed in b/w the poles of electromagnet.

↳ (i) Crystal Detector :- Si & W detectors are use in ESR spectrophotometer that converts microwave power to direct current output.

(ii) Amplifier :- It is used to amplify the signal if it is weak.

(iii) Recorder :- It is used to record the signal. The signal is recorded and plotted.

Basics of Me-Connell Eqⁿ :-

→ Electron nucleus coupling constants are much higher than nucleus-nucleus coupling const. bcoz an e^- can approach nucleus more closely as compared to nucleus approach an another nucleus.

→ e^- mag dipole is about 1000 times larger than that of nucleus & its value for H-atom is -

$$A = 0.05 \cdot \text{where } A \text{ is the hyperfine}$$

coupling const.

→ The coupling const for most of the org molecules with unpaired spin are smaller than that of H-atom bcoz an unpaired e^- in a molecule is never confined to just one nucleus & seldom given even to one bond, but can move to several bonds with relative ease spending only a part of its time at any one of the nucleus.

→ In another way, we look at this in terms of e^- density. In H-atom, the e^- density is one. e^- is on one atom & now to a good approximation the magnitude of coupling constant is directly related to e^- density acc to Me-Connell eqⁿ -

$$A \propto f$$

$A \rightarrow$ hyperfine coupling const

$f \rightarrow e^-$ density

$$A = Rf$$

$R \rightarrow$ proportionality const. & is the intrinsic coupling for unit density.

thus

$$0.05 = R \times 1$$

$$\Rightarrow R = 0.05$$

Let us consider the case of $\dot{C}H_3$ spectrum & A is $2.3 \times 10^{-3} T$

thus

$$f = \frac{A}{R} = \frac{2.3 \times 10^{-3}}{0.05} \approx 4.6 \% \text{ (for H-atom)}$$

for 3-H atom = $3 \times 4.6 = 14\%$

$$100 - 14 = 86\%$$

i.e. the free radical spend 14% of its times on all 3 H-atom & remaining 86% time on C-atom.

\rightarrow In the spectrum of \dot{C}_6H_6 $A = 0.38 \times 10^{-3} T$

$$f = \frac{0.38 \times 10^{-3}}{0.05} = 7.6 \times 10^{-3}$$

for 6 H-atom, $6 \times 7.6 \times 10^{-3} \approx 5\%$

i.e. a FR spends a total of 5% of its times on all 6-H-atom & remaining 95% on all the C-atoms.

g-value :- In ESR spectrum, the lines positions are denoted in terms of g-value which is expressed as a fun of microwave freq. (ν) & external mag. field (B) at resonance.

$$g_e = \frac{h\nu}{\mu_e B}$$

$g_e =$ Lande's g-factor

→ for a free e^- , g -value is 2.0023 due to relativistic correction whereas, g -value for free radicals in atoms, molecules & crystals depends on their electronic st.

→ The value of g is not constant & is a tensor quantity. This quantity specifies the strength of interaction of a given e^- with the applied mag. field. It is a spectroscopic gauge of the ~~interact~~ magnitude of magnetic moment of e^- under study.

$$\mu_c = -g_e \mu_B \sqrt{S(S+1)}$$

The quantum mechanical expression for Lande's splitting factor is given by -

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Acc. to R-S coupling (Russell Saunder's coupling) -
 $J = L + S$.

For a free e^- $S = 1/2$, $L = 0$ thus $J = 1/2$.

This implies $g = 2.0$.

• All FR and some ionic crystals e^- is not localised in a particular orbital but it can move freely over the whole molecules orbital. So that spin-orbit coupling of the parent atom is small & orbital degeneracy is quenched.

In transition-metal systems, the e^- is localised in a particular orbital around the atom, so the parent nucleus has large

spin-orbit coupling const. and accessible orbital degeneracy & hence magnetic moment contains additional contribution & g-value differs from 2.

Applications of ESR :-

Study of FR :-

One of the existing use of ESR spectroscopy is the study of F.R intermediates in org. rxn. for eg in oxidation of hydroquinone in alkaline solⁿ with the help of oxygen, the formⁿ of semiquinone F.R has been proved by ESR spectroscopy with 5 lines in its spectra.

Org. & Inorg. radicals can be detected in electrochemical systems & in materials exposed to UV light.

In many cases the rxn^s to make the radicals & the subsequent rxn^s of radicals are of interest. While in other cases, EPR (ESR) is used to provide information on a radical's geometry and the orbital of unpaired e⁻.

Rxn velocity & Mechⁿs

A large no. of org. rxn^s proceeds through F.R mechⁿ. Such rxn^s can be studied by ESR and a direct measure of variation of radical concⁿ with time, during these rxn^s would be valuable term for their speed & mechⁿ.

Effect of Ionisation on Matter :-

Polymers are generally made more suitable for certain purposes by irradiation with X-rays or γ -rays. This is because free radicals are formed during the initial bond breaking by radiation which is easily studied by ESR. If lifetime is greater than 10^{-6} sec & subsequently these radicals react with one another to form the chain b/w them.

Analytical Applications:-

ESR spectroscopy is used for the determination of various transition metal ions such as Mn^{2+} , V^{4+} , Cu^{2+} , Cr^{3+} , Fe^{3+} etc. For eg. ESR spectra of solⁿ of Mn^{2+} ion (d⁵) exhibit 6-lines in its spectra with $I = 5/2$. Thus Mn^{2+} ion can be measured & detected readily even when present in traces.

Biological system:-

Most of the oxidative enzyme function via one e^- redox rxn involving the production of either enzyme bound free radical or by a change in the valence state transition metal ion. This has been confirmed by ESR studies. ESR has studied the presence of free radicals in healthy & diseased tissues.

(B)

NQR (Nuclear Quadrupole Resonance)

DATE: 17/20
PAGE No

NQR spectroscopy was discovered by H. G. Dehmelt in 1950. It is resonance phenomenon related to NMR. All nuclei with spin quantum no. $I \geq 1$ possess in addⁿ to magnetic moment an electric quadrupole moment (eQ).

→ Transition b/w these levels are observed in RF region of electromagnetic spectrum. These transition known as NQR transition.

Quadrupole Nuclei: - Nuclear Quadrupole moment deals with unsymm. distribution of electric charge of spinning nuclei.

All nuclei have integral & half integral nuclear spin.

($I = 1, 2, \dots$ or $1/2, 3/2, \dots$ resp) possess nuclear electric quadrupole moment designated as eQ or Q .

where e is electronic charge & Q is quadrupole moment.

These nuclei are referred to as quadrupole nuclei. If the nucleus is spherical ($I = 0, 1/2$) or e^- environment around the nucleus is spherical, all nuclear orientations are equivalent & the corresponding energy states are degenerate.

Quadrupole Moment: - Quantum mechanical considerations of the distribution of nuclear charge shows that nuclei do not have permanent electric dipole moments but can have electric quadrupole moment when their electric charges are not spherically symm.

this is usually the case when $I \geq 1$, the Quadrupole moment is measure of the deviation of nuclear charge distribution from spherical symm.

Q express as:-

$$Q = \frac{1}{e} \int \rho(r^2) (3\cos^2\theta - 1) d\tau = Z(3z^2 - r^2) A \nu$$

$e \Rightarrow$ fundamental charge.

$\rho \Rightarrow$ nuclear charge density.

$r \Rightarrow$ distance from centre of gravity of charge to element of vol. $d\tau$.

$\theta \Rightarrow$ angle b/w r & spin axis z .

$Z \Rightarrow$ atomic no.

$A \nu \Rightarrow$ Average taken over nuclear state.

$m \Rightarrow$ magnetic quantum no.

\Rightarrow Prolate (egg shape; $Q > 0$) charge distribution with its axis parallel to z -axis give rise to ve Quadrupole moment.

\Rightarrow oblate :- ($Q < 0$) distribution gives a ve Q. moment. Hence a ve value of Q shows that nucleus is a prolate spheroid elongated along spin axis while a ve value indicates that nucleus is oblate spheroid flattened along the spin axis.

Q is zero for spherical nuclei for $I=0, \text{ or } \frac{1}{2}$.

Electric field gradient & coupling constant:-
 Quadrupole nuclei possess nuclear electric quadrupole moment which interact with electric field gradient (q) created at the nuclei by symm. distribution of charge arising from the extra nuclear e^- or non bonding e^- . The EFG ' q ' determines the extent of splitting of quadrupole E-level, hence splitting is related to product of quadrupole moment eQ or Q and EFG i.e. Qq or eQq is called nuclear quadrupole coupling constant. The energy difference b/w various level & hence the frequency of transition will depend upon both the field gradient (q) Quadrupole moment of nucleus & this is constant for a given isotope.

Theory of NQR:- the nuclei having integral and half integral spin ($I=1, 3/2, 2, 5/2$) possess nucleus electric quadrupole moment which interact with EFG created at nuclei by the unsymmetrical distribution of charge arising from extra nuclear e^- or bonding e^- in the molecule of which nuclei forms a part.

The NQR energy level for both integral & half integral spin ($I \geq 1$) are given by.

$$E_m = \frac{e^2 Qq}{4I(2I-1)} [3m_I^2 - I(I+1)]$$

$$= A [3m_I^2 - I(I+1)] \text{ where } A \text{ is}$$

$$A = \frac{e^2 Qq}{4I(2I-1)}$$

where $m_I = -I, -I+1, \dots, +I$.

Q or $eQ =$ Nuclear Quadrupole moment

$$q = efb.$$

$e^2 Qq =$ nuclear Quadrupole coupling const.

$m_I =$ Component of I along axis of quantisation along z -axis.

The Efb is tensor quantity having a components defined as follows:-

$$q_{xx} = -\frac{\partial E_x}{\partial x} = \frac{\partial^2 V}{\partial x^2}$$

$$q_{xy} = -\frac{\partial E_x}{\partial y} = \frac{\partial^2 V}{\partial x \partial y}$$

$$q_{zz} = -\frac{\partial E_z}{\partial z} = \frac{\partial^2 V}{\partial z^2}$$

It is supposed that nucleus is centred at origin of an arbitrarily oriented coordinate system x, y, z . The time averaged electrostatic pot. V is produced at nucleus by all charges outside it.

$$\vec{E} = E_x \vec{i} + E_y \vec{j} + E_z \vec{k}$$

$\vec{i}, \vec{j}, \vec{k} \rightarrow$ unit vectors which specify the directions of x, y, z .

the components of electric field are related to electrostatic pot. by relation.

$$E_x = -\frac{\partial V}{\partial x}, \quad E_y = -\frac{\partial V}{\partial y}, \quad E_z = -\frac{\partial V}{\partial z}$$

$$\therefore E = - \left[\frac{\partial V}{\partial x} \hat{i} + \frac{\partial V}{\partial y} \hat{j} + \frac{\partial V}{\partial z} \hat{k} \right]$$

the field gradient component written as:-

$$\begin{bmatrix} q_{xx} & q_{xy} & q_{xz} \\ q_{yx} & q_{yy} & q_{yz} \\ q_{zx} & q_{zy} & q_{zz} \end{bmatrix}$$

they are found to symm. matrix with $q_{ij} = q_{ji}$ so that, $q_{xy} = q_{yx}$, $q_{xz} = q_{zx}$, $q_{yz} = q_{zy}$.

thus the electric field gradient tensor can be represented as:-

$$\begin{vmatrix} q_{xx} & q_{xy} & q_{xz} \\ q_{xy} & q_{yy} & q_{yz} \\ q_{xz} & q_{yz} & q_{zz} \end{vmatrix}$$

It will obey Laplace eqⁿ.

$$q_{xx} + q_{yy} + q_{zz} = 0 \quad \text{--- } \textcircled{A}$$

$$\therefore \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \quad \Rightarrow \quad \nabla^2 V = 0$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

its cross component $q_{ij} = 0$
EFG components in this system are designated:-

q_{xx}, q_{yy}, q_{zz}
 in principle axis system,
 $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$ — (B)

from (A); the sum of EFG Component is zero. It follows therefore that only two parameters are needed specify the EFG tensor.

The asymm. parameter (η) is defined as:-

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \quad \text{--- (C)}$$

from (A) (B) & (C)

parameter lies b/w 0 & 1

$0 < \eta < 1$
 when $\eta = 0$, we speak of a case of axial symm. around the z-axis

$q_{xx} = q_{yy} = -\frac{1}{2} q_{zz}$
 The field gradient is said to be spherical if $q_{xx} = q_{yy}$

In this case, there is no interaction of nuclear Quadrupole moment (Q) with electronic charge distribution. The field gradient is said to be non-symm. if $q_{xx} \neq q_{yy} \neq q_{zz}$.

Features OF NQR:-

- ① NQR is observed with nuclei $I \geq 1$. when $I < 1$, the nuclei do not possess EQ so that there is no quadrupole interaction with electric field gradient (q).
- ② NQR is observed only in solid state. In liq. & gaseous state, bcz of very fast molecular collision resulting in fast tumbling motion, the axis of orientation changes. Continuously, so that EFG (q) approaches to zero. Thus, there is no NQR interaction. Hence NQR observed in solids.
- ③ Most important quantities in NQR are: EQq, q, η where η is a measure of non symmetry of electric field gradient (EFG).
- ④ the detailed mechⁿ by which radio freq. field produces transition b/w quadrupole E-level is approx same as in NMR. Hence, most of factors affecting line width, intensities & saturation are operable. But the major diff. b/w NMR & NQR is that an external MF is used to established spacing of Zeeman levels in NMR while in NQR spacing arises through molecular electric field. & hence. This is reason why no magnet is needed in NQR spectroscopy.
- ⑤ the setⁿ of SWE for quadrupole nucleus having both the integral & half integral

$I \geq 1$ gives a following expression for NQR energy levels.

$$E_{m_I} = \frac{e^2 Q q}{4I(2I-1)} [3m_I^2 - I(I+1)]$$

or $E_{m_I} = A [3m_I^2 - I(I+1)]$

NQR energy level involves m_I^2 term which are surely degenerate. selection rule for that is

$$\Delta m_I = \pm 1$$

Splitting in NQR spectra ✓

① $^{14}\text{N} (I=1)$
7

$m_I = \pm 1, 0, \pm 1$

But $m_I = -1, 0, +1$ are degenerate $I=0, \pm 1$

$$E_{m_I} = \frac{e^2 Q q}{4I(2I-1)} [3m_I^2 - I(I+1)]$$

$E_0 = -\frac{2}{4} e^2 Q q$ [$m_I=0, I=1$]

$E_{\pm 1} = \frac{1}{4} e^2 Q q$ [$m_I = \pm 1, -1$ are of same E]

Selection rule. $\Delta m_I = \pm 1$ which give $\nu = \pm 1$

$\nu(0 \rightarrow \pm 1) = \frac{E_{\pm 1} - E_0}{h} = \frac{3}{4h} e^2 Q q$

(2) ${}_{17}^{36}\text{Cl} (I=2)$

$m_I = -2, -1, 0, +1, +2$

But $m_I = 0, \pm 1, \pm 2$

$E_{m_I} = \frac{e^2 Q_2}{4I(2I-1)} (3m_I^2 - I(I+1))$

$E_0 = \frac{e^2 Q_2}{24} (-6)$

$E_{\pm 1} = \frac{e^2 Q_2}{24} [3-6] = -\frac{3}{24} e^2 Q_2$

$E_{\pm 2} = \frac{e^2 Q_2}{4(2)(2 \times 2 - 1)} [3 \times 2 \times 2 - 2(2+1)]$

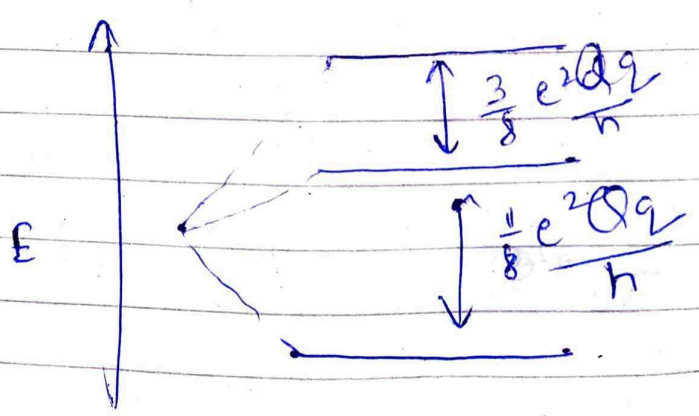
$= \frac{e^2 Q_2}{24} [12-6]$

$= \frac{6 e^2 Q_2}{24}$

selection rule:-

$\Delta V (0 \rightarrow \pm 1) = \frac{3}{24} \frac{e^2 Q_2}{h} = \frac{1}{8} \frac{e^2 Q_2}{h}$

$\Delta V (\pm 1 \rightarrow \pm 2) = \frac{3}{24} \frac{e^2 Q_2}{h} = \frac{3}{8} \frac{e^2 Q_2}{h}$



2

27
13 Ad

$$(\pm = \frac{5}{2})$$

$$m_I = \pm 5/2, \pm 3/2, \pm 1/2$$

$$E_{\pm 5/2} = \frac{e^2 Q q}{40} \left[3 \times \frac{25}{4} - \frac{5}{2} \left(\frac{5}{2} + 1 \right) \right]$$

$$= \frac{e^2 Q q}{40} \left[\frac{75}{4} - \frac{35}{4} \right] = \frac{40}{40 \times 4} e^2 Q q$$

$$E_{\pm 3/2} = \frac{e^2 Q q}{40} \left[3 \times \frac{9}{4} - \frac{5}{2} \left[\frac{5}{2} + 1 \right] \right]$$

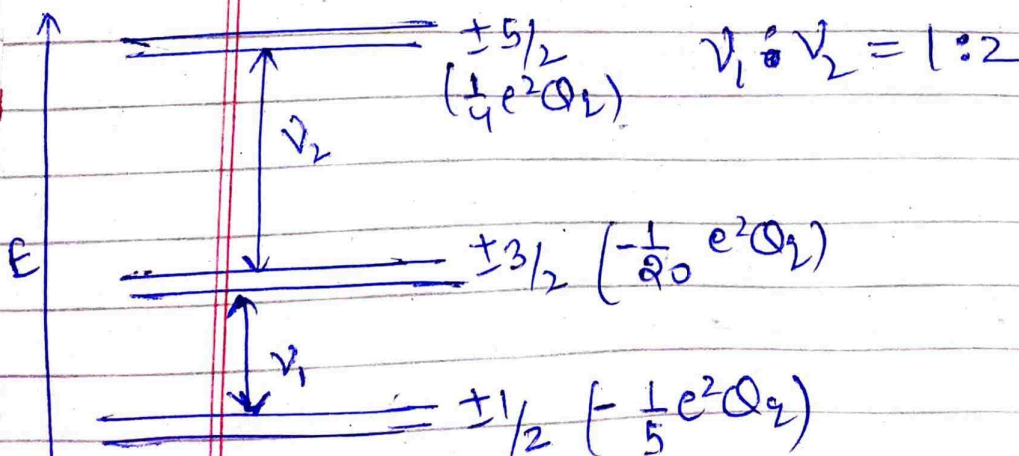
$$= \frac{e^2 Q q}{40} \left[\frac{27}{4} - \frac{35}{4} \right] = -\frac{8}{4 \times 40} e^2 Q q$$

$$E_{\pm 1/2} = \frac{e^2 Q q}{40} \left[3 \times \frac{1}{4} - \frac{35}{4} \right] = -\frac{32}{40 \times 4} e^2 Q q$$

~~$$E_{\pm 1/2} = \frac{e^2 Q q}{40} \left[3 \times \frac{1}{4} - \frac{35}{4} \right] = -\frac{32}{40 \times 4} e^2 Q q$$~~

$$v_1 (\pm 1/2 \rightarrow \pm 3/2) = \frac{3}{20} \frac{e^2 Q q}{h}$$

$$v_2 (\pm 3/2 \rightarrow \pm 5/2) = \frac{6}{20} \frac{e^2 Q q}{h}$$



(4) Cs ($I = 7/2$)
55

$$m_I = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$$

$$E_{\pm 7/2} = \frac{e^2 Q q}{14(6)} \left[-3 \times \frac{49}{4} - \frac{7}{2} \left(\frac{7}{2} + 1 \right) \right] = \frac{84}{84 \times 4} e^2 Q q$$

$$E_{\pm 5/2} = \frac{12}{4 \times 84} e^2 Q q$$

$$E_{\pm 3/2} = \frac{e^2 Q q}{84} - \frac{36}{4}$$

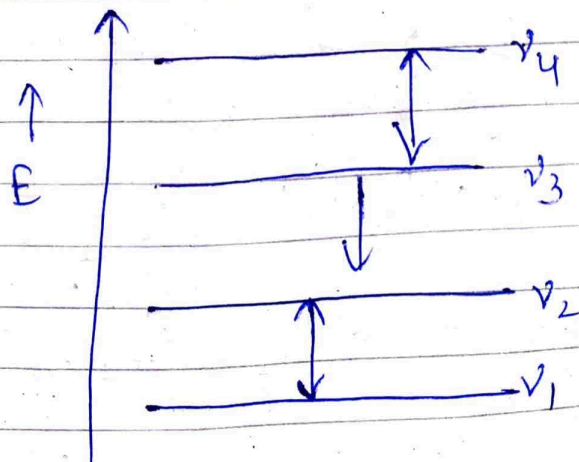
$$E_{\pm 1/2} = \frac{-60}{4 \times 84} e^2 Q q$$

$$\nu_1 (\pm 1/2 \rightarrow \pm 3/2) = \frac{1}{14} \frac{e^2 Q q}{h}$$

$$\nu_2 (\pm 3/2 \rightarrow \pm 5/2) = \frac{2}{14} \frac{e^2 Q q}{h}$$

$$\nu_3 (\pm 5/2 \rightarrow \pm 7/2) = \frac{3}{14} \frac{e^2 Q q}{h}$$

$$\boxed{\nu_1 : \nu_2 : \nu_3 = 1 : 2 : 3}$$



Que:- NQR spectra when EFG not axially symm. ($\eta \neq 0$)

Solⁿ these NQR is very complex. energy level expression has terms involving η & power of η .

for $I=1$

$$E_0 = -\frac{1}{2} e^2 Q q$$

$$E_{\pm 1} = \frac{1}{4} e^2 Q q (1 \pm \eta)$$

$$\Delta m_I = \pm 1$$

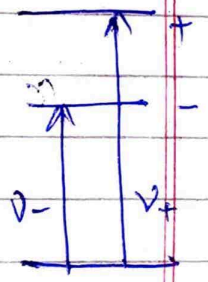
$$\nu_{(0 \rightarrow +1)} = \frac{3}{4} \frac{e^2 Q q}{h} \left[1 + \frac{1}{3} \eta \right]$$

$$\nu_{(0 \rightarrow -1)} = \frac{3}{4} \frac{e^2 Q q}{h} \left[1 - \frac{1}{3} \eta \right]$$

thus frequencies are separated by $\Delta \nu$

$$\Delta \nu = \frac{1}{2} \frac{e^2 Q q}{h} (\eta)$$

the exact measurement of two frequency yield the value of $e^2 Q q$ & η .



NQR transition for $I=1$, $\eta \neq 0$

for $I=3/2$, the two doubly degenerate energy levels are

$$E_{\pm 1/2} = -\frac{1}{4} e^2 Q q \left[1 + \frac{1}{3} \eta^2 \right]^{1/2}$$

$$E_{\pm 3/2} = +\frac{1}{4} e^2 Q q \left[1 + \frac{1}{3} \eta^2 \right]^{1/2}$$

selection Rule $\Delta m_I = \pm 1$ gives only one frequency

$$\nu(\pm 1/2 \rightarrow \pm 3/2) = \frac{1}{2} \frac{e^2 B_0}{h} \left(1 + \frac{1}{3} \eta^2 \right)^{1/2}$$

η is found to be very small thus it can be neglected & $e^2 B_0$ determined with accuracy when η is large it is possible to observe some of forbidden transitions ($\Delta m_I = \pm 2$) in addⁿ to strongly allowed transition ($\Delta m_I = \pm 1$).

Zeeman effect in NMR:-

Zeeman effect is splitting of spectral lines in presence of external MF. This effect is due to distortion of electronic orbitals in the presence of magnetic field so if we talk about Zeeman effect in NMR,

we take example $I = 3/2$, which gives only one NMR frequency in absence of Zeeman effect. when we apply external M.F. it removes the degeneracy of $\pm 1/2$ & $\pm 3/2$ energy sublevels due to Zeeman effect.

theoretically, it has been found that $-3/2$ level is raised in energy & $+3/2$ sub-level is lowered in energy.

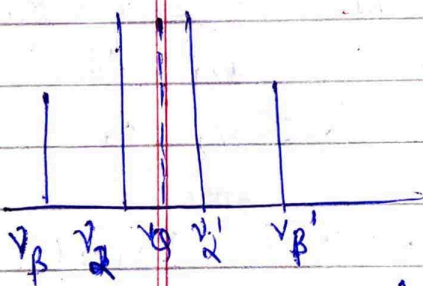
However exactly same splitting in not occur for energy level $\pm 1/2$. Actually there occurs a considerable mixing of states so that $+1/2$ sub-level pertakes the character of $-1/2$ & vice-versa & the resulting sub-levels are designated as (+) & (-) respectively.

So the Zeeman splitting for $I = 3/2$ gives 4 different NQR frequency by applying selection rule.

The application of Zeeman's freq. brings about the transition b/w sublevels, however, the transition b/w $+1/2$ to $-1/2$ is not of our interest bcoz it involves the freq. much smaller than NQR freq. So $I \pm 1/2$ or I give up to 4 different frequency.

$$\begin{array}{l} \nu_{\alpha} (+ \rightarrow +3/2) \quad \nu_{\beta} (+ \rightarrow -3/2) \\ \nu_{\alpha}' (- \rightarrow +3/2) \quad \nu_{\beta}' (- \rightarrow -3/2) \end{array}$$

The four frequency are symm. about the pure NQR freq. ν_{α} . The inner pair of line i.e. ν_{α} & ν_{α}' have equal intensity also for outer transition ν_{β} & ν_{β}' . However, exply it is found that ν_{α} & ν_{α}' are more intense than ν_{β} & ν_{β}' pair.



Hence for a given orientation of E.M.F both component α, α' & β, β' has more intensity when RF field is perpendicular to axis of EFG. Hence the intensity of two pairs depends on orientation of magnetic field. Hence both unknown quantity eQ & eQ_2 can be determined by 4 different frequencies.

Ques: Why does NH_4^{\oplus} show sharp signal whereas NH_3 show broad signal?

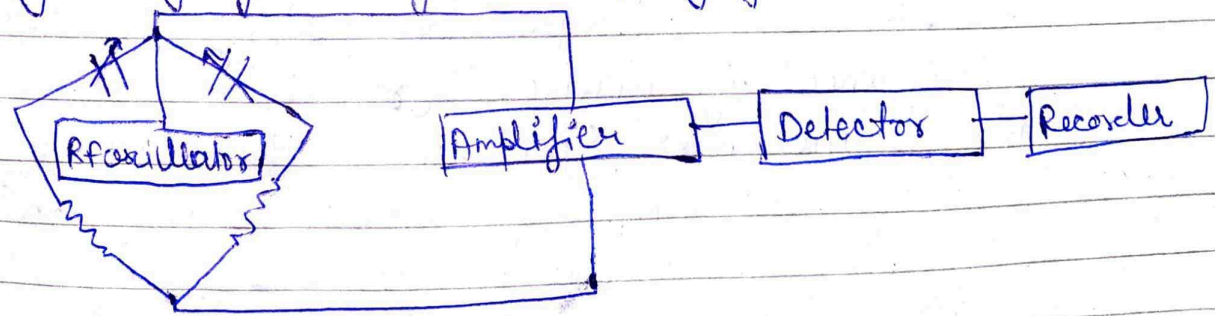
If the nucleus is spherical or the electronic environment of nucleus is spherical.

eg:

In case of NH_4^+ all nuclear orientations are equivalent & corresponding energy states are degenerate. i.e. Quadrupole moment is negligible & there is no further interaction or splitting in electronic levels. That's why signal of NH_4^+ is quite sharp. While NH_3 lone pair is present on N. Hence due to axial symmetry at a particular axis Quadrupole effect is generated & hence due to interaction of Quadrupole moment with electric field we have to study further variations in energy levels & thus we get a broad signal.

Experimental techniques of NQR:-

In NMR experiment an external MF is required to remove m_I degeneracy, the electric field required in NQR is provided by electron distribution in molecule. It means that transition frequency is fixed by the electronic structure of the molecule & we observe a resonance by varying the frequency of field.



Power from RF oscillator is supplied to a previously balanced bridge circuit. At resonance the E is absorbed by the sample.

in inductive coil & causes imbalance in circuit. The resultant output voltage is then amplified & recorded. Spectra obtained is pure NQR spectra. NQR technique provides the more accurate measurements in case of solid when the coupling constant has value of range 3 MHz to 500 MHz. However the crystalline solid should often be cooled to 77K. The strength of resonance depends

Application of NQR :-

① Structural information from NQR spectra :-
 NQR technique is used to study no. of molecules containing ^{10}B , ^{11}B , ^{35}Cl , ^{37}Cl , ^{63}Cu , ^{65}Cu , ^{79}Br , ^{81}Br , ^{14}N , ^{33}S , ^{127}I , ^{129}I etc. Since, different field gradient will exist for non-equivalent nuclei in a molecule, different set of lines are expected for each type of environment. The halogen NQR spectra of K_2PtCl_6 , K_2SeCl_6 , $(\text{NH}_4)_2\text{TeCl}_6$, $(\text{NH}_4)_2\text{SnBr}_6$ etc consist of only one line bcoz all of them possess octahedral geometry. K_2SeBr_6 exhibits a single spectrum at room temp. which becomes a doublet at dry ice temp. indicating the non-equivalence of lattice positions. The iodine NQR spectrum of solid iodine gives a large asymm. parameter η which confirms inter-molecular bonding in solid states.

Multiple lines in NQR spectrum may be due to following factors →

- Chemically non-equivalent atom in the molecule.
- Chemically equivalent atom in the molecule occupying non-equivalent position in crystalline lattice of solid.
- splitting of degeneracy of quadrupole energy-level by asymm. of field gradient.
- splitting of ~~quadrupole~~ level by magnetic nuclei in the molecule.

② Structure of Group III halides:-

the NMR spectrum of halides (MX_3 type), M-metal of group-III consist 3 resonance lines. 2 of these line are clearly spaced & far from 3rd. The different resonance frequency for same nuclei reveals that 3 halogen atoms are not chemically equivalent. This conclusion is supported by X-ray data, where in 3 halides exist as dimer & 2 metal atom are held together by halide bridges.

③ Study of CH_3Cl & chloroacetyl chloride:-

the coupling constant for ^{35}Cl in various chloromethane shows that increasing the no. of Cl atoms inc. the value of J by ≈ 3.5 MHz per Cl.

This large shift is due to an effective use of electro-veity by the entity to which a Cl- atom is bonded, through an inductive effect. In chloroacetyl chlorides, the coupling constant J_{Cl} with the effective electro-veity of group bonded to carbonyl chloride.

④ Study of charge transfer compounds:-

Charge transfer compounds are formed probably when equimolar amount of p-xylene and CCl_4 are brought together. These compounds are also formed b/w CCl_4 & p-xylene, Br_2 & benzene.

Hooper studied the frozen solⁿ of these mixtures and reported that the resonance frequencies of halogen are not appreciably different from their in pure molecular state.

⑤ Nature of chemical bond:-

NQR is mainly used for investigating the electronic structure of molecule. The extent of hybridisation & ionic character can be known by comparing the nuclear quadrupole coupling constant. In atomic & molecule state for the same nucleus.

Consider bonding in H_2S . The angle H-S-H is nearly 90° . It was assumed that pure p-orbitals were involved in bonding but NQR results in large asymmetry parameter w/ $\eta = 0.60$ for sulphur. Thus there is no pure p-type bonding. However, large asymmetry parameter indicates the involvement of orbitals having 15% d-character.