

Electron-Spin-Resonance Spectroscopy

(ESR)

Introduction →

The electron spin resonance spectroscopy is called also electron paramagnetic resonance. or electron magnetic resonance. (EMR)

It is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by paramagnetic substance.

It's uses ∴ is atoms with unpaired electrons free radicals, ions, triplet state molecules or molecular fragments & complexes with unpaired d & f electrons.

ESR helps in the study of the intermediates, the extent of delocalisation of the unpaired e^- bond angles, the relative energies of unpaired e^- etc.

The ESR technique was developed by Zavoiskis in 1944 & it is similar to NMR Spectroscopy only exception is the absence of chemical shift phenomenon in ESR spectrum.

It detects the change in electron configuration. Substance containing one or more unpaired e^- then it is ESR active.

→

Condition of ESR Spectroscopy

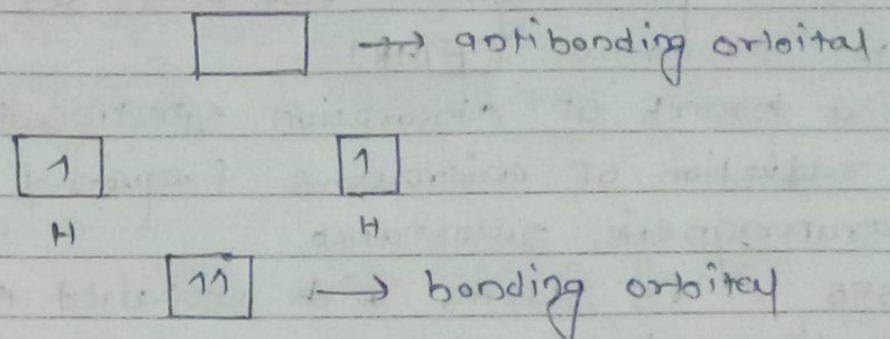
1) It having unpaired e^-

2) having spin $S = \frac{1}{2}$

$\text{OH}^\bullet$ FSP active

ex $\rightarrow$

molecular orbital of H_2



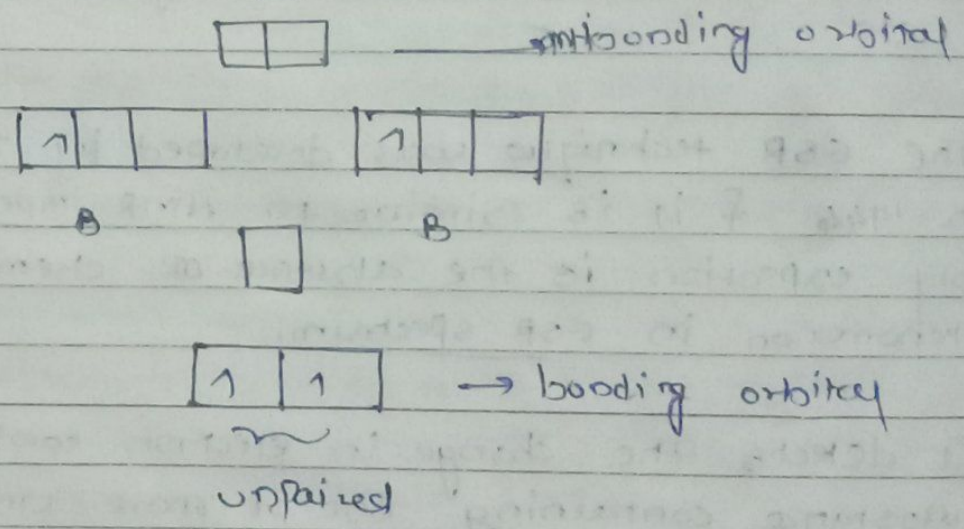
So H_2 is CPP inactive.

2) B_2

electronic configuration $\rightarrow$

$\text{B}_1 \rightarrow 1s^2, 2s^2, 2p^1$

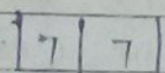
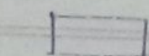
$\text{B}_2 \rightarrow 1s^2, 2s^2, 2p^1$



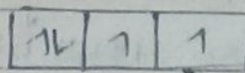
B_2 is CPP active.

3) O_2

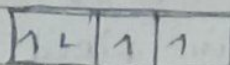
$1s^2, 2s^2, 2p^4$



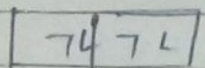
→ unpaired e⁻



0



0



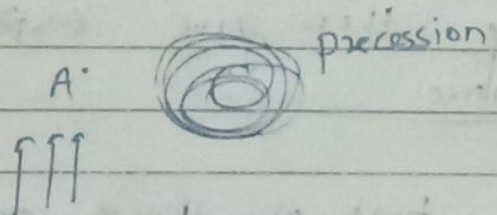
So ESR is active.

Basic principle

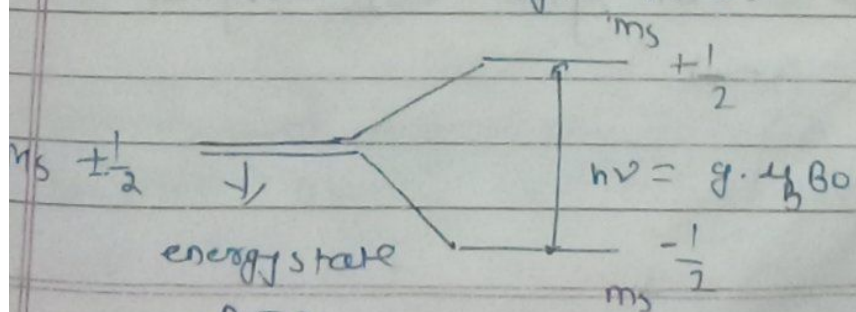
The unpaired electrons are excited to a high energy state under the magnetic field by the absorption of microwave.

The excited electron changes its direction of spin & relaxes into the ground state by emitting ~~photons~~ its energy.

microwave absorption is measured as a function of the magnetic field by ESR spectroscopy.



B_0 (external magnetic field)



$m_s \rightarrow \vec{e}$ spin in comp

(A) having one e^- taking in external magnetic field then the e^- are precession (circle) then the energy level is $+\frac{1}{2}$ or $-\frac{1}{2}$ then applying the external magnetic field then level of electron are split in two state ($+\frac{1}{2}$, $-\frac{1}{2}$)

where,

$m_s \rightarrow$ spin of e^-

$g \rightarrow$ Lande Splitting factor for free e^- then

$$g = 2.0023$$

$\mu_B =$ Bohr's magneton

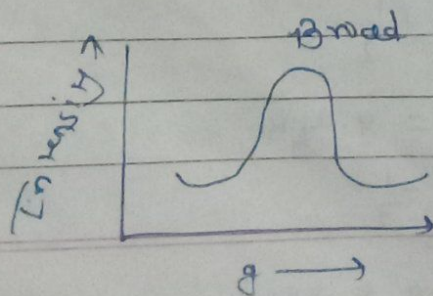
$B_0 =$ applied magnetic field.

e^- Precession then apply microwave frequency then precession electron absorb this frequency. consider,

e^- Precession generate 60 Hz frequency microwave frequency also apply = 60 Hz frequency

when frequency of both e^- Precession & microwave frequency are equal then e^- absorb microwave frequency then give ESR signal. called as Resonance.

when frequency of both of these are high or less then does not give ESR signal.



participle of e^- in ESR so Relaxation of e^- time is less so give broad spectra.

So spectra of ESR study is its derivatives. f gives the spectra is,

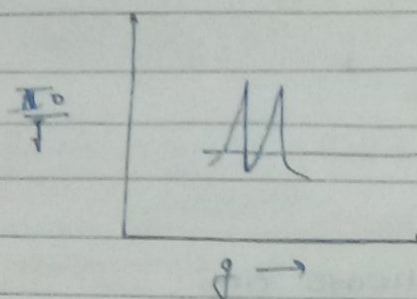


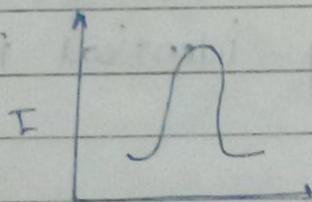
Fig- spectra of ESR

Hypofine Structure of ESR is isotopic system.

Hypofine structure →

ESR spectrum:

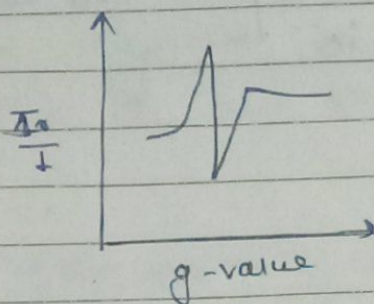
ESR spectrum is a plot of intensity of signal against the g -values of unpaired electron for a free e^- .



$g \rightarrow$ simple ESR signal

Simple ESR signal is always very broad compare to NMR signal bc relaxation time of e^- in ESR is less.

ESR signal are always recorded in the derivatized form.



Parameters

- 1) number of signal always one.
- 2) position of signal g -value.
- 3) multiplicity of signal intensity of multiplet
- 4) Hyperfine splitting constant of signal.

Hyperfine structure of ESR

Hyperfine structure :- It is caused by the interaction of electron spins with the magnetic nuclei in the sample.

isotropic system $\rightarrow$ is the property of molecules & materials of having identical physical properties in all directions.

As a result of this interaction the ESR signal peak splits into several lines.

The selection rule for hyperfine transition is,

$$\Delta m_s = \pm 1 \quad \Delta m_I = 0$$

Isotropic system is a quantum mechanical interaction that depends on the electron spin density in the immediate vicinity of the nucleus.

This interaction is ^(near) orientation independent hence known as isotropic hyperfine interaction.

Some example $\rightarrow$

main formula $\rightarrow 2nI + 1$

where,

$n \rightarrow$ number of spin Nbr of nucleus ion/wave

$I \rightarrow$ interact ~~quantity~~ with an unpaired e^- spin of e^- _{nuclear spin (I)}

$s \rightarrow$ spin quantum no.

EPR spectrum due to single proton (H-atom)

hydrogen atom has one proton & one electron
with $s = \frac{1}{2}$ & $I = \frac{1}{2}$

H⁺

$$n = 1 \quad I = \frac{1}{2}$$

$$2nI + 1 = 2 \times 1 \times \frac{1}{2} + 1$$

$$1 + 1$$

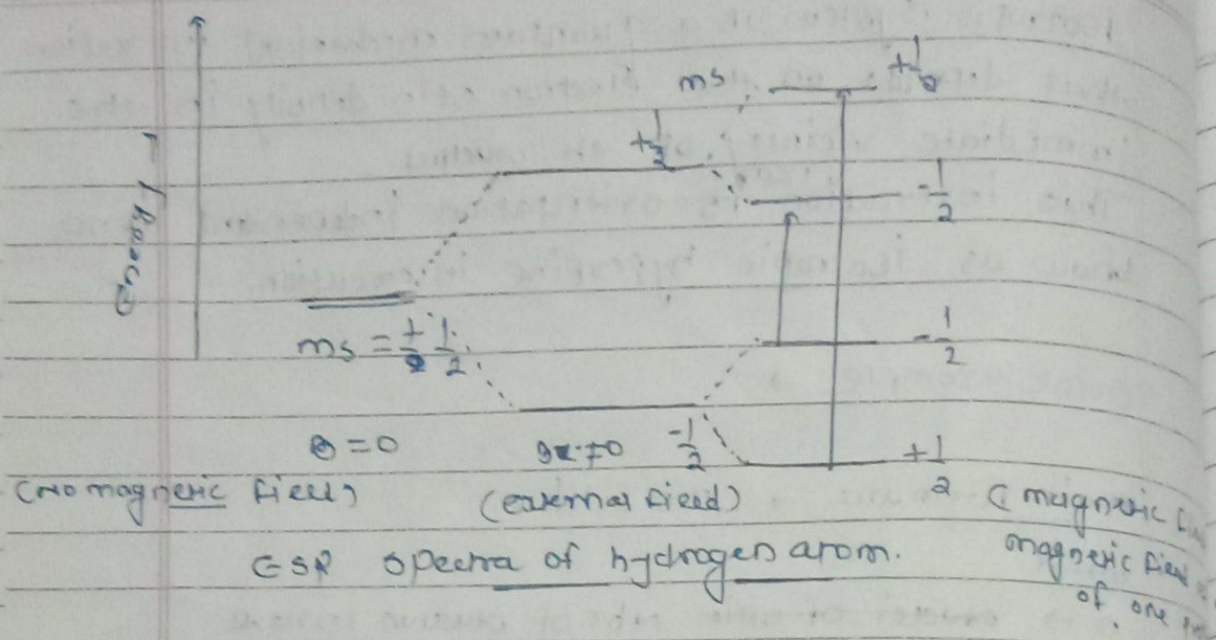
$$= 2 \text{ lines}$$

$$s = \frac{1}{2}$$

$$I = \frac{1}{2}$$

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

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



In energy level are zero when not applied external magnetic field. means the energy level ~~energy~~ are degenerate means having equal or same energy.

when apply external magnetic field then energy level are split into two energy level i.e. $-\frac{1}{2}$ & $+\frac{1}{2}$

see, $+\frac{1}{2}$ & $-\frac{1}{2}$ are interact with only one proton electronic spin interact with nuclear spin & splits into further two energy proper level i.e. $+\frac{1}{2}$ & $-\frac{1}{2}$ & given four energy

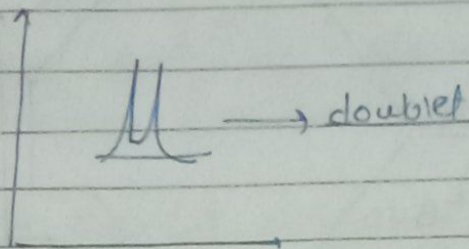
level i.e. $(+\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2})$

$$\left(-\frac{1}{2} - \frac{1}{2} = -1\right) \quad \left(\frac{1}{2} + \frac{1}{2} = 1\right)$$

ratio is 1:1 i.e. doublet.

hyperfine structure of isotropic system

Spectra of (^1H) Proton atom is,



II) GSR spectrum of CH_3



$$2I + 1$$

$$n = 3$$

$$I = \frac{1}{2}$$

$$\frac{2 \times 3 \times \frac{1}{2} + 1}{2}$$

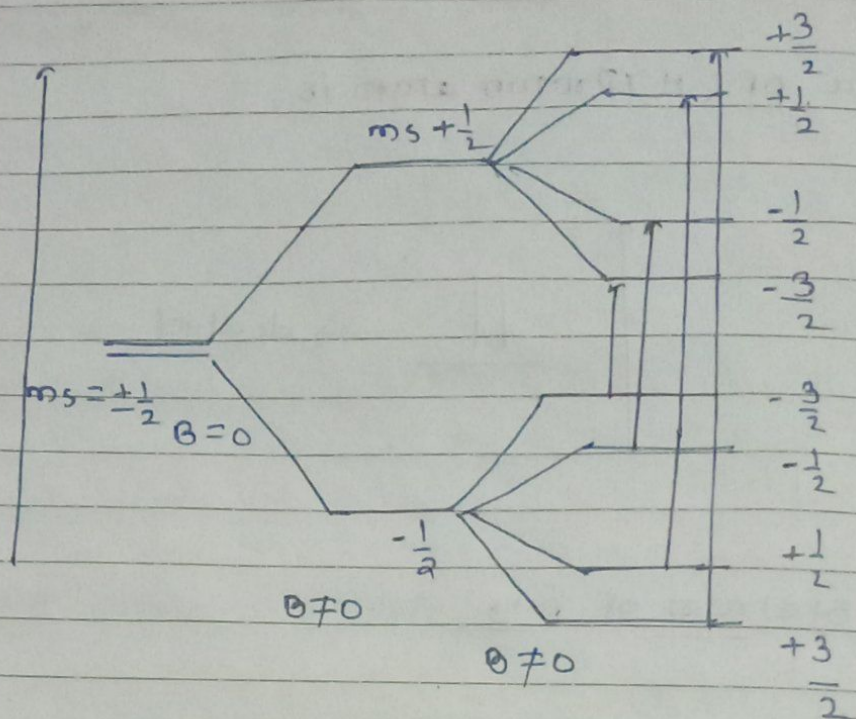
$$8 + 1$$

4 lines

$$S = \frac{1}{2} \quad I = \frac{1}{2}$$

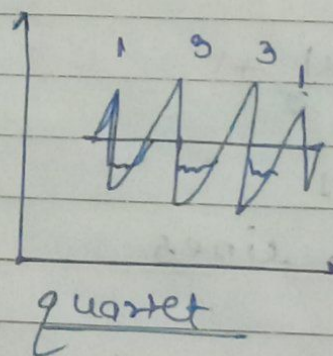
$$m_I = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

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



hyperfine splitting in ESR spectra of CH_3 radical

4 signal $\rightarrow 1:3:3:1$



In energy levels are zero. when applied external magnetic field then energy level split into two energy level i.e. $(+\frac{1}{2}, -\frac{1}{2})$ i.e.

electronic spin interacts with three protons. each energy sublevel $+\frac{1}{2}$ give four energy level & sublevel $-\frac{1}{2}$ give also four

energy level is total eight energy level & lines are four.

$$\left(-\frac{3}{2}, -\frac{3}{2}, -\frac{1}{2} \right) \quad \left(-\frac{1}{2}, -\frac{1}{2}, 1 \right)$$

$$\left(\frac{1}{2}, \frac{1}{2}, 1 \right) \quad \left(\frac{3}{2}, \frac{3}{2}, \frac{1}{2} \right) = 3$$

four lines gives quartet means ratio is 1:3:3:1

hyperfine structure as a result of the magnetic interaction between the electronic spin (S) & nuclear spin (I).

The magnitude of this interaction is given by A called isotropic hyperfine coupling constant.

The hyperfine interaction in ESR spectra is analogous to the fine structure i.e. nuclear spin-spin interaction.

The ESR signal or peaks are further split into several lines.

isotropic hyperfine splitting is depends on the magnetic of magnetic moment of nuclear & electron spins.

It is independent of applied magnetic field.

It obeys $(n+1)$ rule for $I = \frac{1}{2}$ i.e. $(2nI+1)$

3] ESR Spectrum of CH_2 :-(System with $S = 1$ $I = 1, 0, -1$)

The magnetic moment of two equivalent protons (CH_2) will split two paramagnetic e^- spin states ($M_S = \pm \frac{1}{2}$) into six sublevels characterised by the nuclear spin quantum no's $M_I = +1, 0, -1, 0, +1$

The ESR spectrum will split into three (triplet) of equal intensity ratio is 1:2:1. The two hyperfine splitting constant are equivalent $A_1 = A_2$.

$$20\frac{1}{2} + 1$$

$$n = 2$$

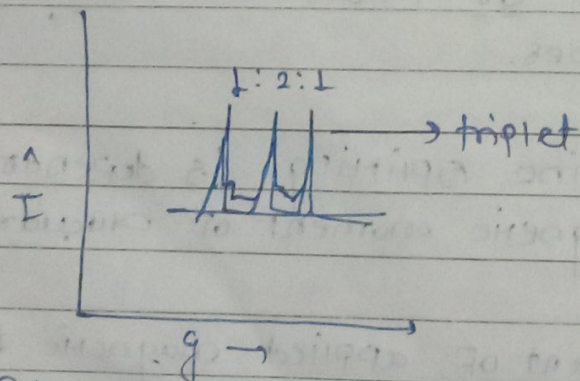
$$2 \times 2 \times \frac{1}{2} + 1$$

$$S = \text{Spin of } e^- = \frac{1}{2}$$

$$I = 1$$

$$2 \times 1 + 1$$

- 3 lines

Fig- ESR Spectrum of CH_2

EPR spectra of transition metal complexes as

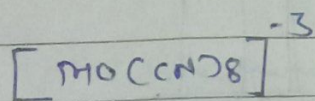
single crystal

most of the EPR studies have been carried out on transition metal compounds particularly first transition series in different valence state.

EPR spectra of coordination compound may be measured either in solution or powdered solid or in single crystals.

example of transition metal complex

- 1) EPR spectrum of the complex ion $[\text{Mo}(\text{CN})_8]^{3-}$ in solution consist of one line.



$$\text{Mo} = 4d^5 5s^1$$

$$x + x(-8) = -3$$

$$x - 8 = -3$$

$$x = -3 + 8$$

$$= 5$$

$$\text{Mo} = 4d^5 5s^1$$

$$\text{Mo} = 7 \text{ configuration}$$

when the sample is enriched (making) with Cl^{3+} , the spectrum consist of nine line.

This can be explained on the basis that Mo(V) in $[\text{Mo}(\text{CN})_8]^{3-}$ has d^1 configuration

& only a single line is expected. but Cl^{3+} enriched (making) sample for ($\text{Cl}^{3+} \quad I = \frac{1}{2}$)

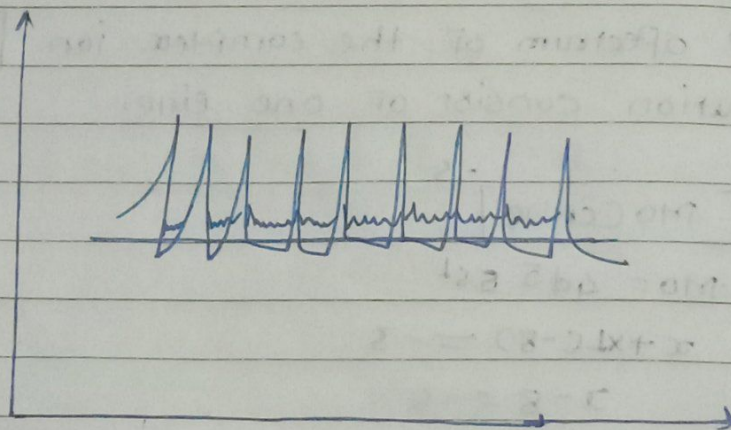
there will be $2nI+1$ nine line because
atoms in the CN groups surround the mo
atom.

$$2nI+1$$

$$n=8 \quad I=\frac{1}{2}$$

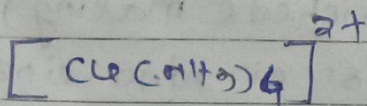
$$2 \times 8 \times \frac{1}{2} + 1$$

9 nine



presence of motion

2] GOR spectral line of $[Cu(NH_3)_6]^{2+}$



$$2 + 6 \times 1 = +2$$

$$2 + 6 = +2$$

$$2 = 6 - 2$$

$$2 = 4$$

$$Cu = 4s^2 3d^9 = Cu = 9$$

Frequency in ESR

$$\text{Cu } I = \frac{3}{2} \quad N = 1$$

$$(2nI_1 + 1) (2nI_2 + 1)$$

$$\left(\frac{2 \times 1 \times 3}{2} + 1 \right) (2 \times 4 \times 1 + 1)$$

$$(3 + 1) (8 + 1)$$

$$4 \times 9$$

$$= 36 \text{ hyperfine}$$

3) The EPR spectrum of single crystals of CoCl_2 complex of ~~5-chlorosalicylaldoxime~~ is shown.

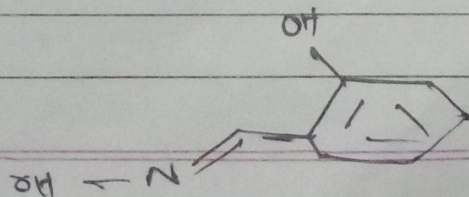
The spectrum can be divided into four groups, each consist of five lines.

within the group the spacings between the lines are equal while their intensity ratio is 1:2:3:2:1

This indicates that these lines are due to equivalent atomic nuclei.

such are the two nitrogen atom located in the immediate vicinity of metal ion.

Since the nuclear spin of the nitrogen atom nucleus ($I = 1$) these two nuclei will give rise to five lines.



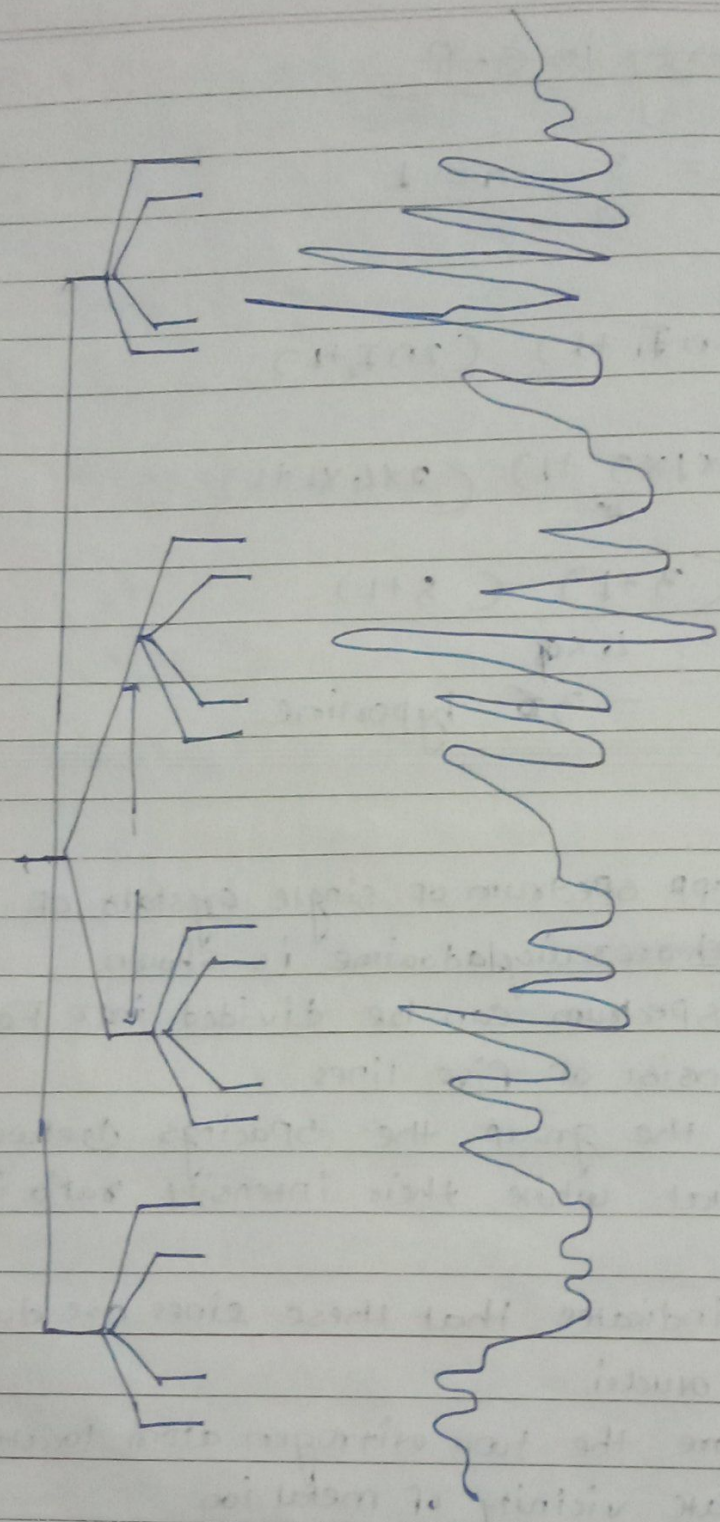
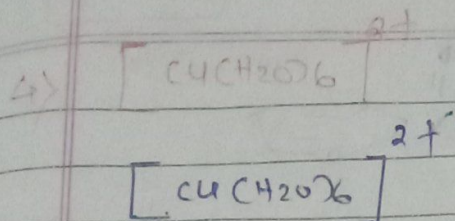
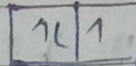


Fig → GPR spectrum of a single crystal of CuCl2 - Schottky defect

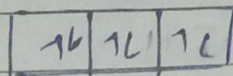


$$\text{Cu}^{2+} = 3d^9$$



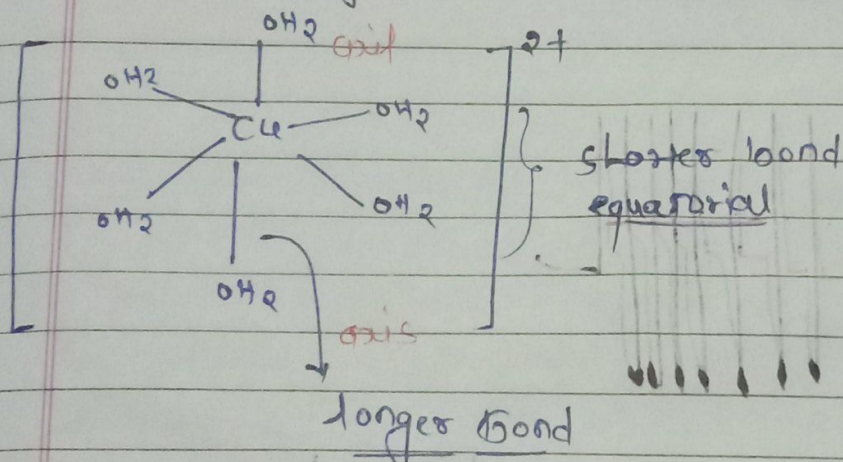
$$\text{Cu}^{2+} = 9$$

unpaired e^- is 1



John. teller distortion.

When t_{2g} is similar field & e_g is unsymmetrically field so John teller distortion is strong.



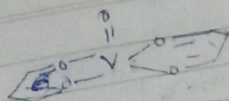
O is inactive why locs it is not magnetic active.

$$\begin{aligned}
 & 20I + 1 \quad \text{(proton equatorial)} \quad \text{(proton axial)} \\
 \text{Cu} = & \left(\frac{2 \times 1 \times 3 + 1}{2} \right) \left(\frac{2 \times 8 \times 1 + 1}{2} \right) \left(\frac{2 \times 4 \times 1 + 1}{2} \right)
 \end{aligned}$$

$$4 \times 9 \times 5$$

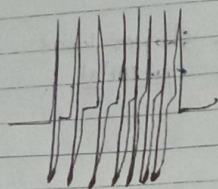
180 lines are present

5) $V(acac)_3$



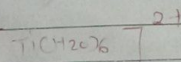
vanadyl acetylacetonate
Interaction with vanadium Oxidant.
For vanadium $T = \frac{1}{2}$

So $2nI + 1$
 $2 \times 1 \times \frac{1}{2} + 1$
 $1 + 1$
 $2 + 1$
3 lines

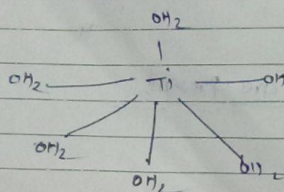


EPR spectra of vanadyl acetylacetonate

6)



$Ti = 4s^2 3d^2$
 $Ti = 2$



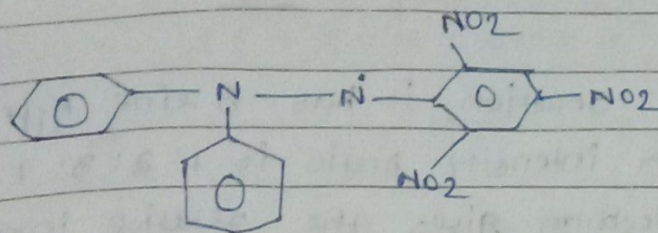
$$T = \frac{3}{2}$$

$$Ti = (2nI + 1) \quad H = (2nI + 1)$$

$$(2 \times 1 \times \frac{3}{2} + 1) \quad (2 \times 1 \times \frac{3}{2} + 1)$$

4×3
52 lines

Reference compound in ESR



DPPH

(α, α' -diphenyl- β -picrylhydrazyl) (DPPH)

In ESR the widely used standard is α, α' -Diphenyl- β -picrylhydrazyl (DPPH) Free radical.

It is chemically stable having the splitting factor $g = 2.0036$.

The ESR experiment uses a DPPH sample which has an unpaired e^- & its orbital contribution to the magnetic moment is negligible bcz the molecules moves on a highly delocalised orbit. Since, the electron is free only its spin contributes to the magnetic moment.

- DPPH has been studied with ESR because of its ability to absorb free radicals.

The etc contain three benzene ring, its important features is that it contains a single unpaired e^- whose orbital angular momentum is zero.

Typical spectrum of DPPH radical $\rightarrow$

A typical ESR spectrum is characterised by the position, intensity & shape.

DPPH is a convenient std for its component lines & reference comp in EPR.

In benzene solution, it has 5 line hyperfine pattern with intensity ratio is 1:2:3:2:1. But the spectrum gives the relative intensities 1:6 three central lines of multiplet overlap. Solid DPPH exhibits a singlet 1:6 of strong interaction between adjacent radicals in the Solid state.

EPR spectra of DPPH.

