Electron Spin Resonance Spectroscopy

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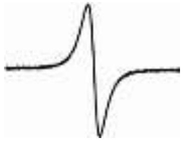


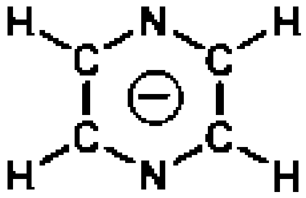
ESR Spectroscopy

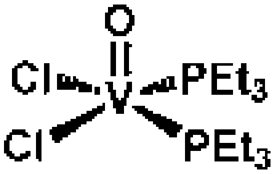
- Electron Spin Resonance Spectroscopy
- Also called EPR Spectroscopy
  - Electron Paramagnetic Resonance Spectroscopy
- Non-destructive technique

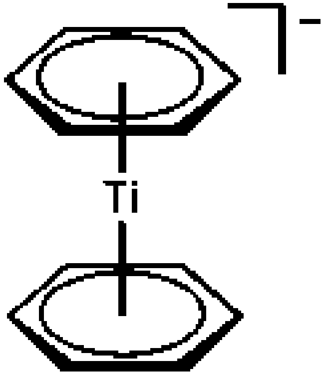
- Applications
  - Oxidation and reduction processes
  - Reaction kinetics
  - Examining the active sites of metalloproteins

What compounds can you analyze?

- Applicable for species with one or more unpaired electrons
  - Free radicals
  - Transition metal compounds
- Useful for unstable paramagnetic compounds generated *in situ*
  - Electrochemical oxidation or reduction







Types of substances with unpaired electrons (ESR active species)

- Atoms having an odd number of electrons.
- Ions having partly filled inner electron shells.
- Molecule that carry angular momentum of electronic origin.
- Free radicals having unpaired electrons.
- Molecule with paired electrons and zero magnetic field

-Diamagnetic

- Molecules with unpaired electrons and magnetic moment- **Paramagnetic**

PARAMAGNETIC.

Stable paramagnetic substances

- Studied easily by ESR
- e.g.
  - Simple molecules like N O_2, NO
  - Ions of transition metals rare earth elements

Unstable paramagnetic substances

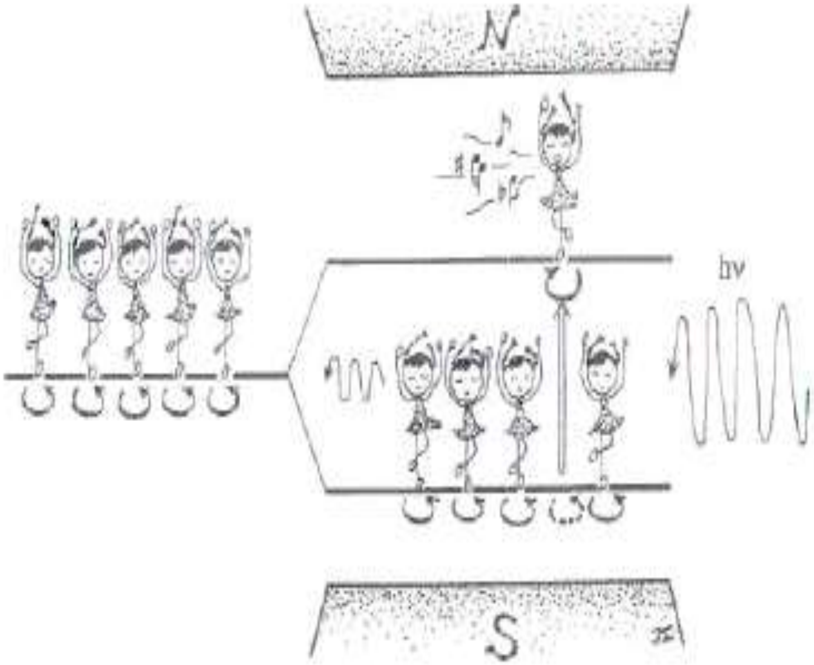
- Can be produced as
  - Intermediates in a chemical reaction
  - By irradiation of stable molecules with a beam of nuclear particles or with U.V. or X-Ray radiation.
- Called as free radical or radical ions

Energy Transitions

- ESR measures the transition between the electron spin energy levels
  - Transition induced by the appropriate frequency radiation
- Required frequency of radiation dependent upon strength of magnetic field
  - Common field strength 0.34 and 1.24 T
  - 9.5 and 35 GHz
  - Microwave region

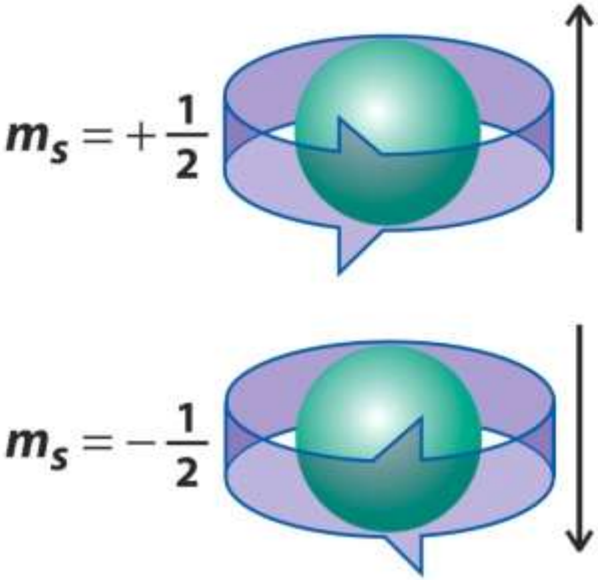
Basic Principle of ESR

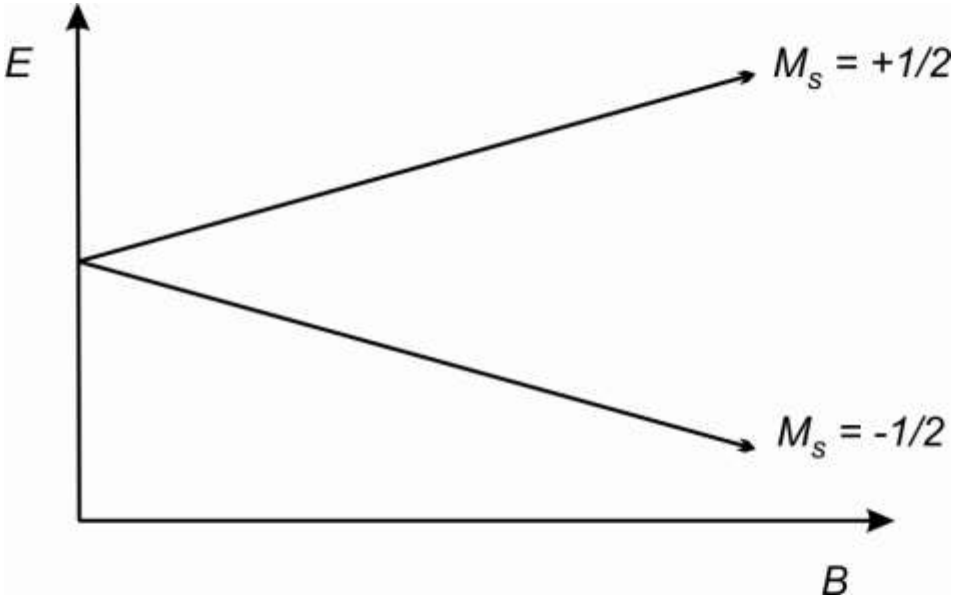
Basic Principle Of ESR...............



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 and relaxes into the ground state by emitting phonons .

What causes the energy levels?





Resulting energy levels of an electron in a magnetic field

- When an electron is placed within an applied magnetic field, B_0, the two possible spin states of the electron have different energies (Zeeman effect)

- The lower energy state occurs when the magnetic moment of the electron is aligned with the magnetic field.

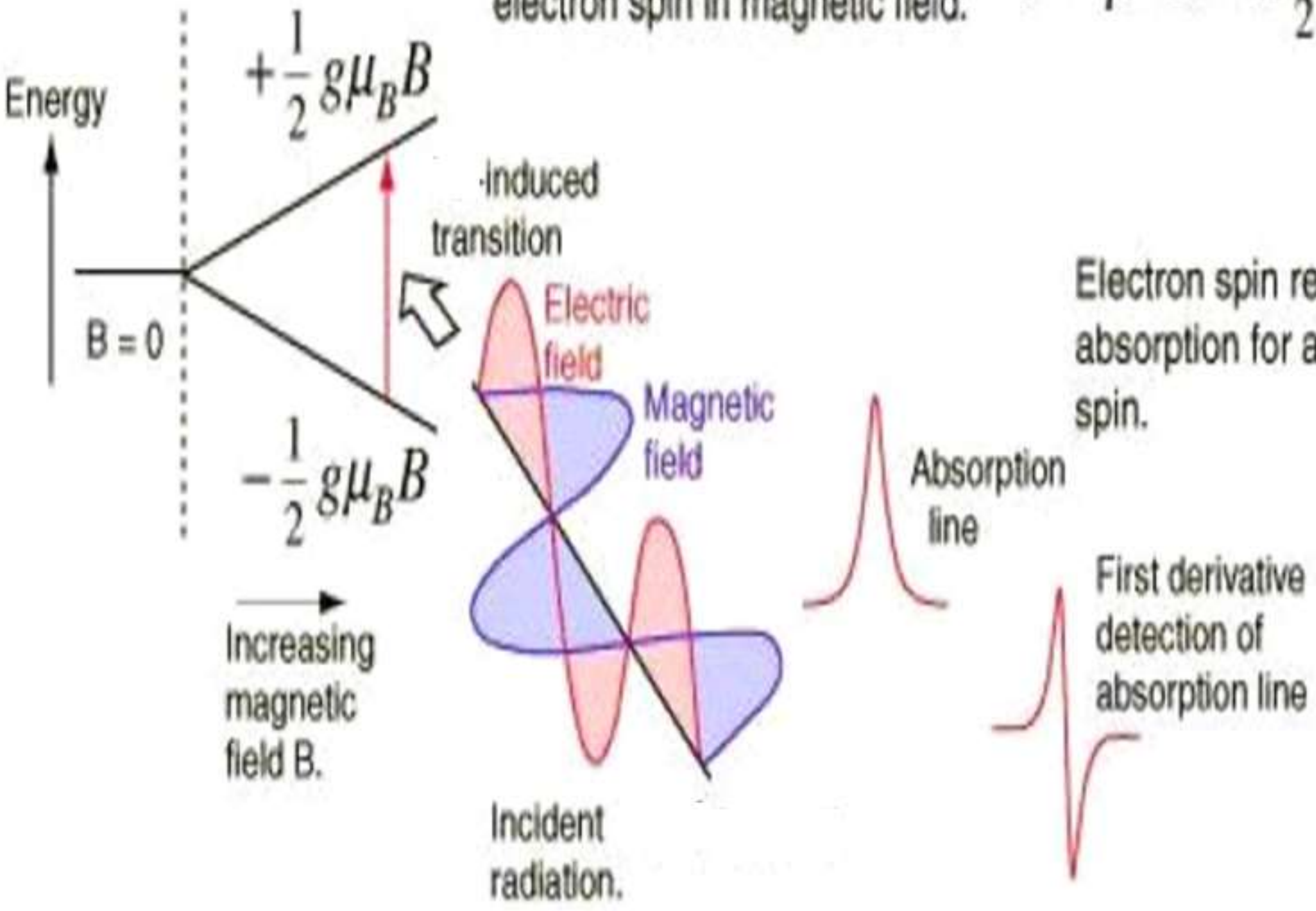
- The two states are labeled by the projection of the electron spin, M_s, on the direction of the magnetic field, where $M_s = -1/2$ is parallel and $M_s = +1/2$ is anti parallel state

The energy differences studied in EPR spectroscopy are due to the interaction of *unpaired electrons* in the sample with an external magnetic field produced by the EPR spectrometer. This effect is called Zeeman Effect.
A strong magnetic field B is applied to a material containing paramagnetic species.

Now if radiation is supplied to sample of frequency such that energy of each quantum is equal to the difference in energy between the electron state resonance occurs. For a given magnetic field the spin can be made to flip to opposite direction when they absorb radiation at a corresponding resonant frequency. These spin flips can be considered as transition between states that become separated in energy when the magnetic field is applied.

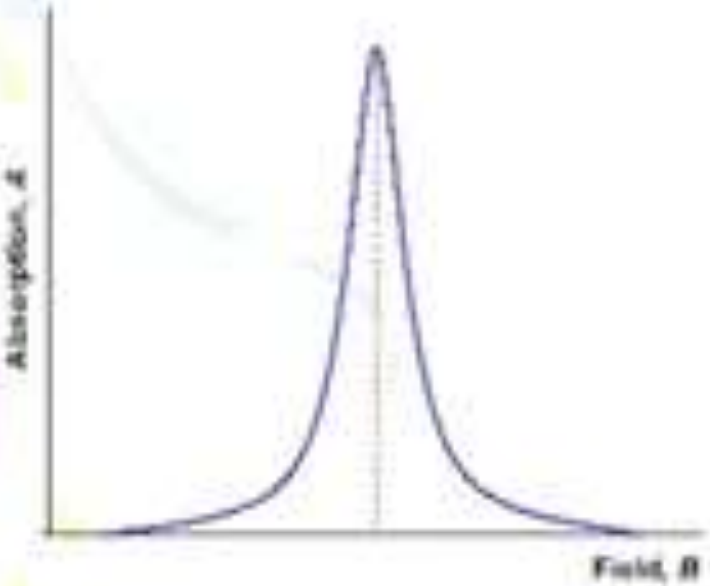
↓

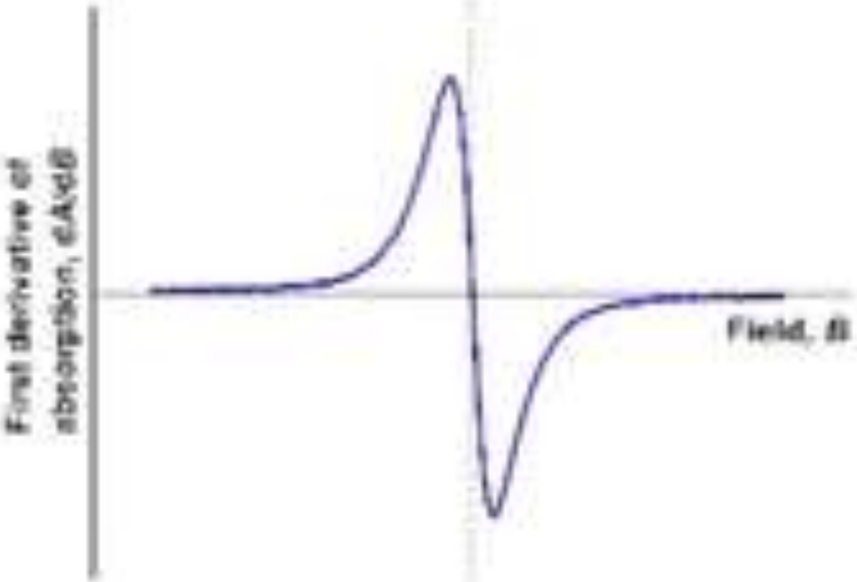
Magnetic potential energy of electron spin in magnetic field: $U = \mu \cdot B = \pm \frac{1}{2} g\mu_B B$



Electron spin resonance absorption for a single spin.

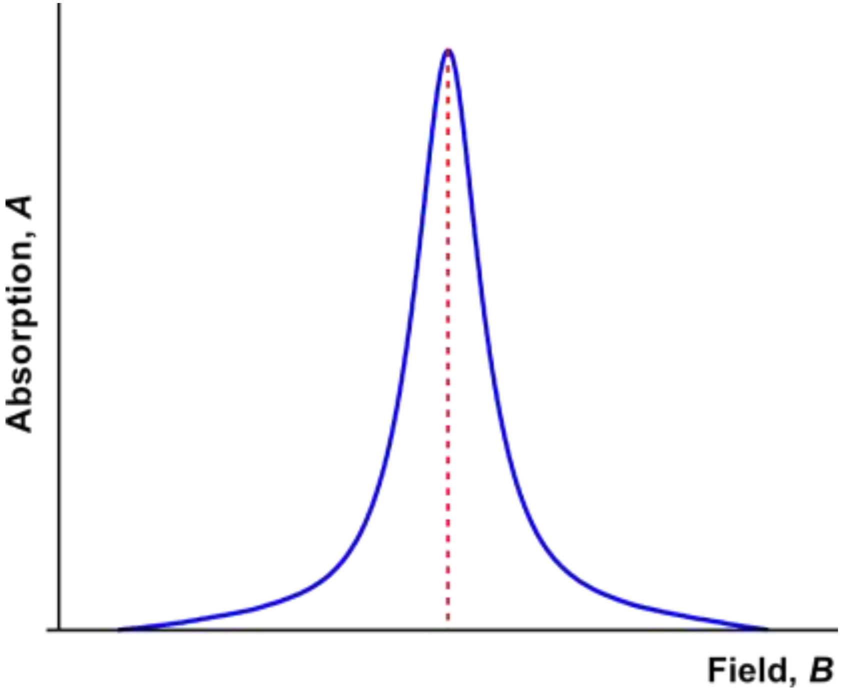
- Due to many reasons the absorption lines are very broad.
- To get finer information ∂A/∂H is plotted against H to get the first derivative curve. When phase-sensitive detection is used, the signal is the first derivative of the absorption intensity

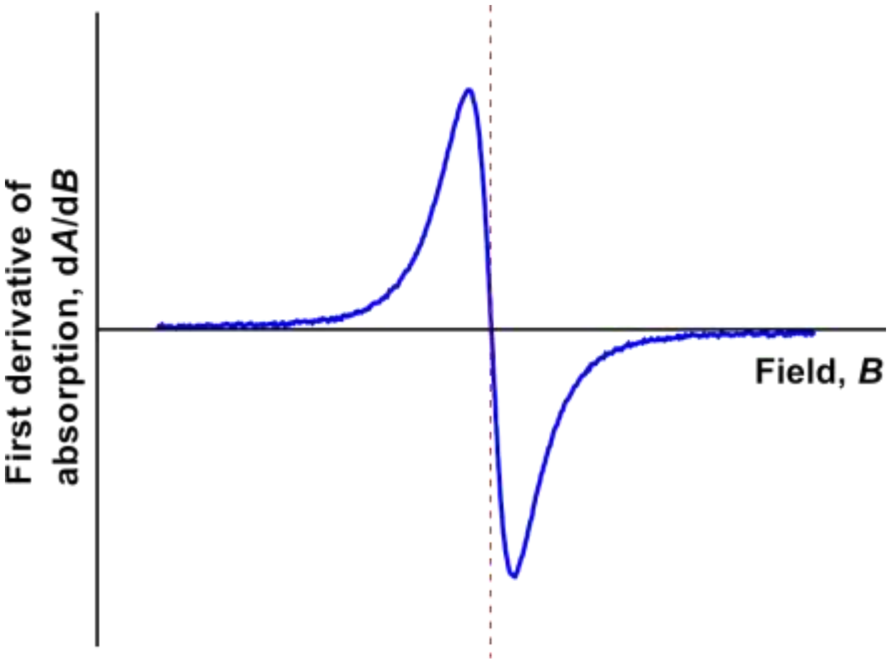




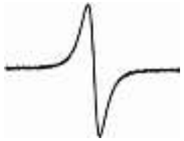
Spectra

Phase-Sensitive detectors are used in EPR





When phase-sensitive detection is used, the signal is the first derivative of the absorption intensity



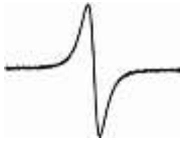
How ESR is different?

- According to uncertainty principle

$$\Delta E . \Delta t \approx h/4\pi$$

Since $\Delta E = h \Delta v$

$$\Delta v = 1/4\pi . \Delta t$$



Describing the energy levels

- Based upon the spin of an electron and its associated magnetic moment
- For a molecule with one unpaired electron
  - In the presence of a magnetic field, the two electron spin energy levels are:

$$E = g\mu_B B_0 M_S$$

g = proportionality factor

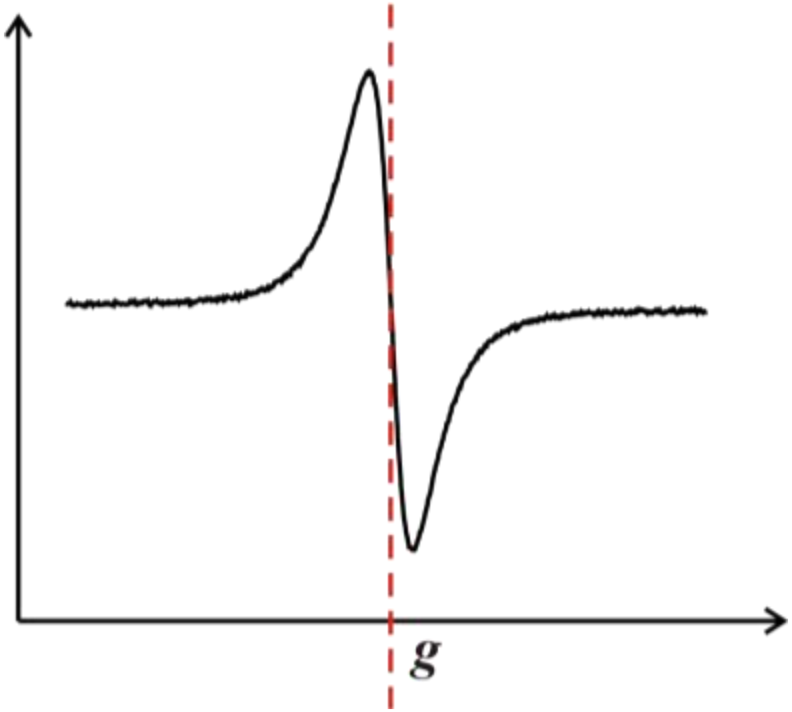
μ_B = Bohr magneton

M_S = electron spin quantum number (+½ or -½)

B_0 = Magnetic field

Proportionality Factor

- Measured from the center of the signal
- For a free electron
  - 2.00232
- For organic radicals
  - Typically close to free-electron value
  - 1.99-2.01



- For transition metal compounds
  - Large variations due to spin-orbit coupling and zero-field splitting
  - 1.4-3.0

Proportionality Factor

$MoO(SCN)_5^{2-}$	**1.935**
$VO(acac)_2$	**1.968**
e^-	**2.0023**
CH_3	**2.0026**
$C_{14}H_{10}$ (anthracene) cation	**2.0028**
$C_{14}H_{10}$ (anthracene) anion	**2.0029**
$Cu(acac)_2$	**2.13**

Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood: Chichester, 1993.

g Value and the factors affecting it

g is the tensor quantity and it is the measure of intrinsic magnetic moment of electron. It is unitless

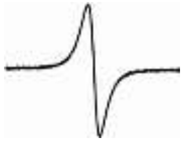
Its also called as

Zeeman splitting factor

Spectroscopic splitting factor

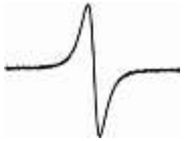
Lande’s splitting factor

Gyromagnetic ratio



Factors affecting g

- The value of g is not constant but it depends upon the type of species containing unpaired electrons.
- Orientation of molecule—anisotropy (electronic moments are aligned in parallel or antiparallel direction in presence of magnetic field).



Determination of g- values

1.Experimental method –

$$E = g\beta H_{ms} \qquad \text{----(1)}$$

$$E = h\nu \qquad \text{------(2)}$$

$$h\nu = g\beta H_{ms}$$

therefore $g = h\nu / \beta H_{ms}$

2.Alternative method -

In this method a reference material is used like the organic salt DPPH (diphenyl-picryl-hydrazyl, $(C_6H_5)_2N\text{-}NC_6H_2(NO_2)_3$), (free radical) which has a very strong and narrow line, with a g factor very close to the value for free electrons i:e 2.0036.

Properties of DPPH

- It is not an internal standard for free radicals.
- It contains 1.53×10^{21} unpaired electrons per gram
- DPPH shows the dependence of the resonant magnetic field on the microwave frequency.

  The width of the resonant peak also provide valuable information regarding the local environment of the electron.
- In case of free radicals , an internal standard is a trace of Cr (III) entrapped in a tiny chip of ruby crystal cemented permanently to the sample cell. This standard shows a strong resonance & its g value is 1.4

Technique to measure g –

In this method the field separation between centre of unknown spectrum & that of reference substance whose g-value is accurately known. First of all ESR spectrum of DPPH is obtained & then same magnetic field is applied to sample & its ESR spectrum is obtained. For this standard substance is placed along with unknown in same chamber of dual cavity cell. The ESR spectrum will show two signals with field separation of ΔH.

The centre of ESR spectrum for sample may be obtained before or after the DPPH centre & therefore value of ΔH may be positive or negative.

Shifting of g value in transition metal complexes

In transition metals shifting takes place due to orbital degeneracy and spin orbital coupling

When the metal orbitals containing unpaired electrons mix with empty ligand orbitals then there is negative shift whereas when it mixes with filled ligand orbitals then there is positive shift.

Relaxation And Saturation

If the number of electrons in both energy levels become equal then further no absorption of radiation occur & no resonance signal would be observed. This is known as Saturation.

Saturation Condition.

§ No further absorption.
§ No further resonance.
§ No further signal.
§ Broadening in signal.

In order to maintain steady state conditions there must be some mechanism known as **relaxation**.

By this electrons that have been exited to higher energy level can lose energy and return to lower level.In absence of relaxation saturation occurs in which continuous absorption of energy by electron present in lower state leads to equal population in both state – **Saturation Condition.**

Relaxation occurs by two mechanisms

SPIN LATTICE RELAXATION

- Interactions between an electron in an excited energetic level and surroundings

SPIN SPIN RELAXATION

- Spinning electron in upper level transfer it's energy to an electron in lower level that is electron exchange spin state.

- Relaxation time decreases.

·Relaxation time should be sufficiently rapid to prevent saturation of upper energetic level at the same time sufficiently slow to yield narrow spectral peaks.

·Ratio of numer of electrons in upper energy level to those in lower energy level is given by BOLTZMANN LAW. $n1/n2 = \exp - DE / kT = \exp - g\mu_B B / kT$

Hyperfine Interactions

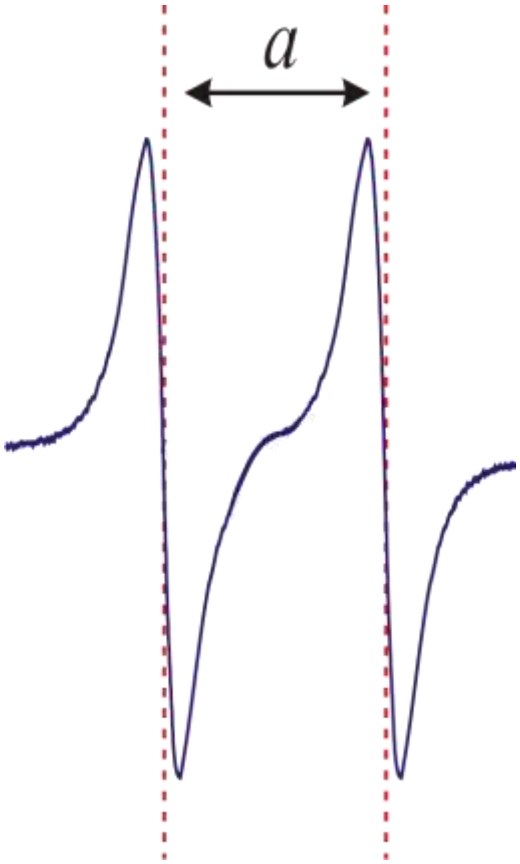
- EPR signal is ‘split’ by neighboring nuclei
  - Called hyperfine interactions
- Can be used to provide information
  - Number and identity of nuclei
  - Distance from unpaired electron
- Interactions with neighboring nuclei

$$E = g\mu_B B_0 M_S + a M_s m_I$$

a = hyperfine coupling constant

m_I = nuclear spin quantum number

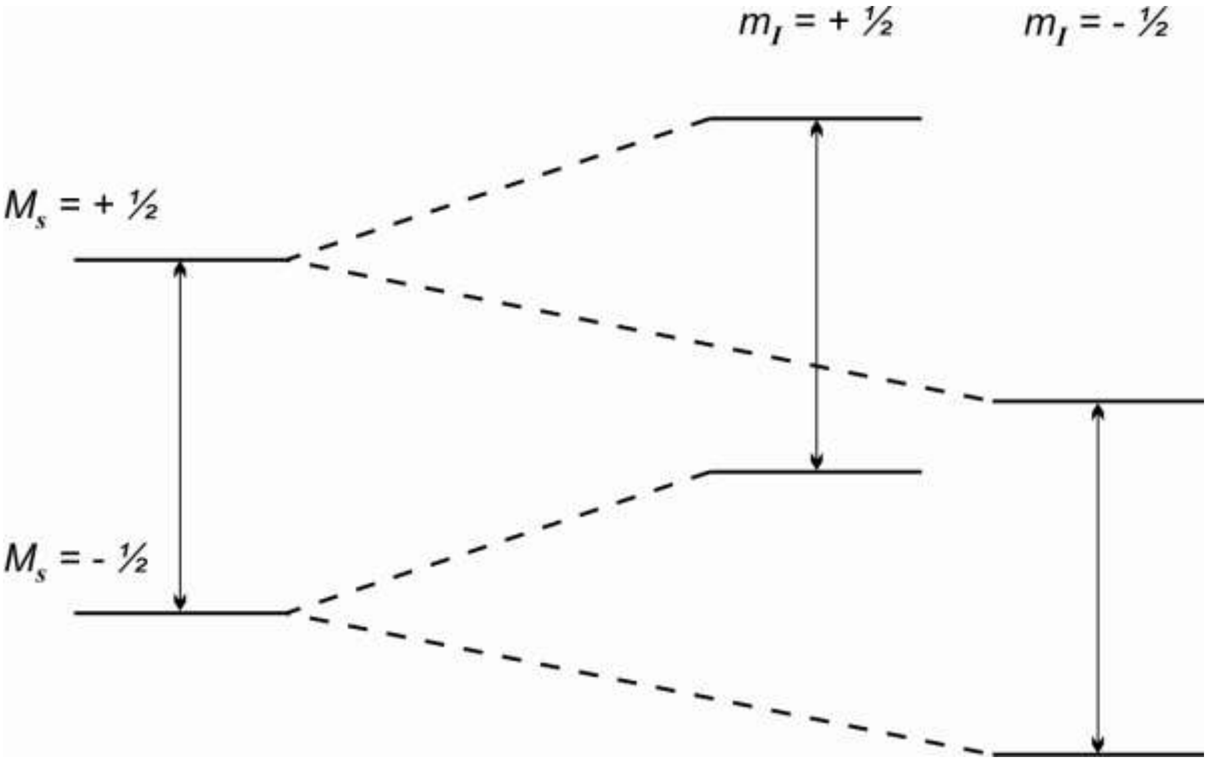
- Measured as the distance between the centers of two signals



Which nuclei will interact?

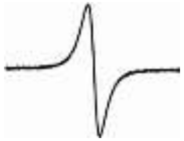
- Selection rules same as for NMR
- Every isotope of every element has a ground state nuclear spin quantum number, I
  - has value of $n/2$, n is an integer
- Isotopes with even atomic number and even mass number have $I = 0$, and have no EPR spectra
  - ^{12}C, ^{28}Si, ^{56}Fe, …
- Isotopes with odd atomic number and even mass number have n even
  - ^{2}H, ^{10}B, ^{14}N, …
- Isotopes with odd mass number have n odd
  - ^{1}H, ^{13}C, ^{19}F, ^{55}Mn, …

Hyperfine Interactions



Interaction with a single nucleus of spin ½

Ebsworth, E. A. V.; Rankin, David W. H.; Cradock, Stephen *Structural Methods in Inorganic Chemistry*; CRC Press: Boca Raton, 1987.



Hyperfine Interactions

- Coupling patterns same as in NMR
- More common to see coupling to nuclei with spins greater than ½
- The number of lines:

$$2NI + 1$$

N = number of equivalent nuclei

I = spin

- Only determines the number of lines--not the intensities

Hyperfine Interactions

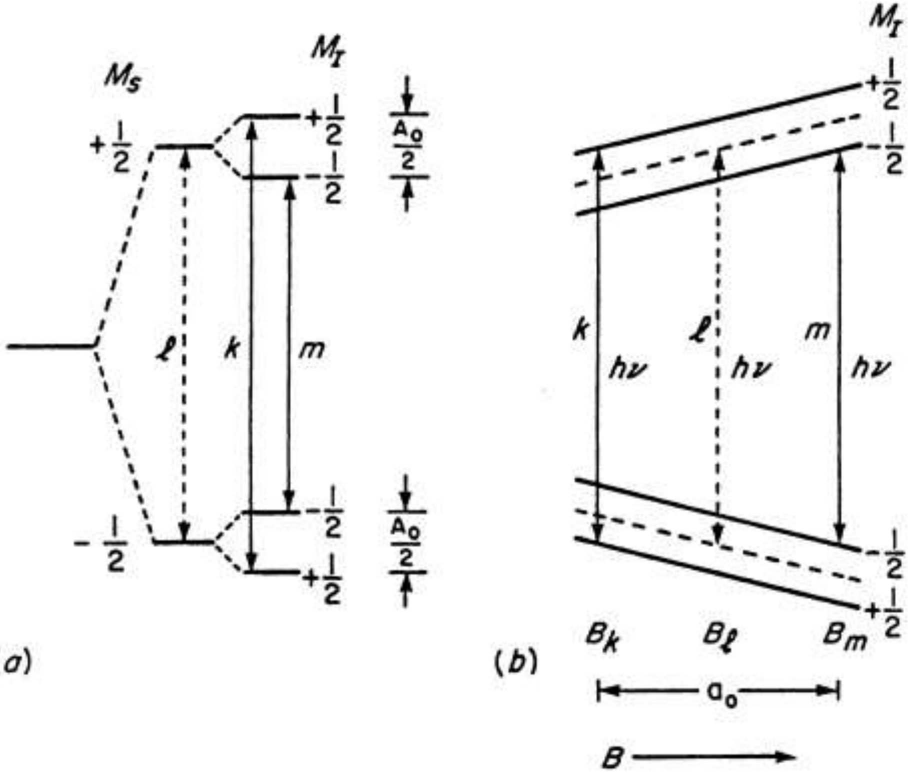
- Relative intensities determined by the number of interacting nuclei

- If only one nucleus interacting
  - All lines have equal intensity

- If multiple nuclei interacting
  - Distributions derived based upon spin
  - For spin ½ (most common), intensities follow binomial distribution

The hyperfine effect

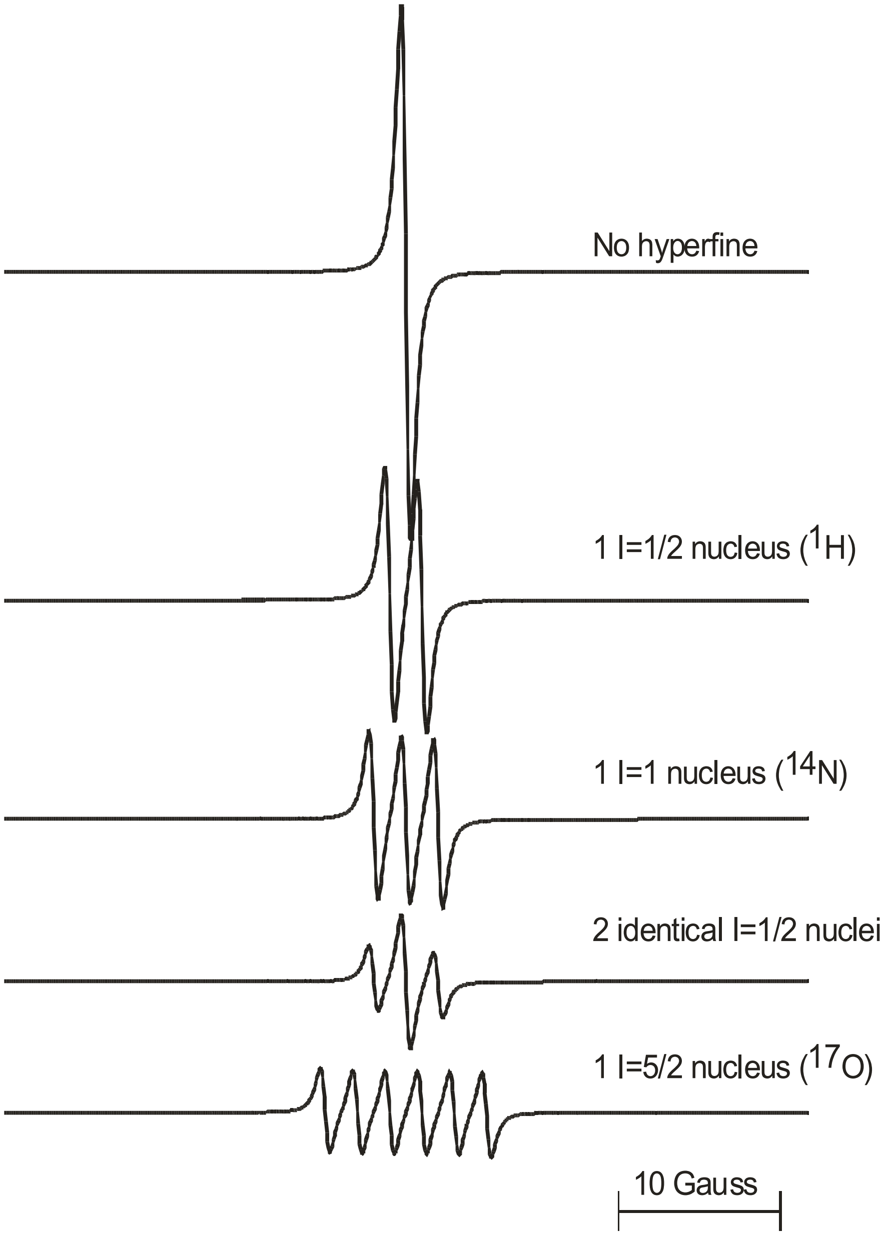
- The magnetic field experienced by the unpaired electron is affected by nearby nuclei with non-zero nuclear spin



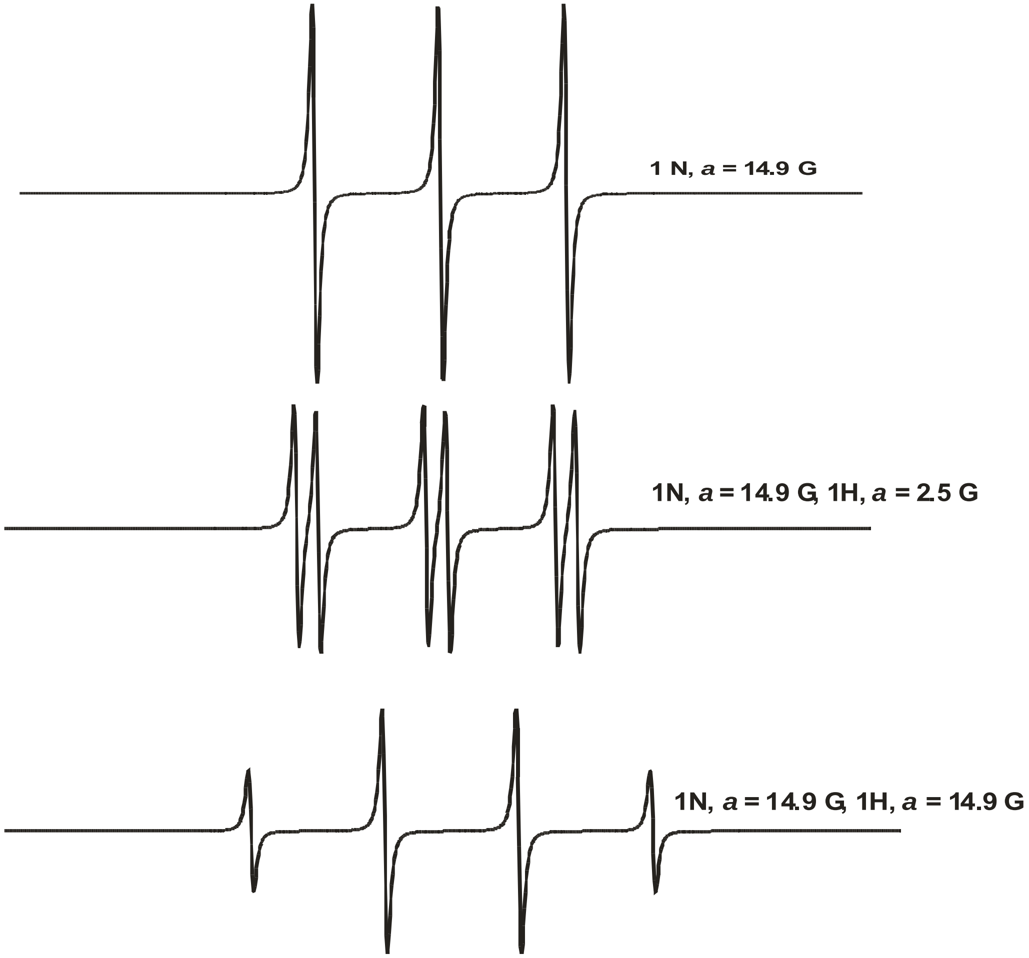
Weil, Bolton, and Wertz, 1994, “Electron Paramagnetic Resonance”, New York: Wiley Interscience.

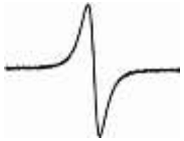
Hyperfine splitting of EPR spectra

- The magnitude of the splitting and the number of lines depend upon:
  - The nuclear spin of the interacting nucleus
    - # of lines = $2n(I + \frac{1}{2})$ so $I = \frac{1}{2}$ gives 2 lines, etc.
  - The nuclear gyromagnetic ratio
  - The magnitude of the interaction between the electronic spin and the nuclear spin
    - Magnitude of the splitting typically decreases greatly with increasing numbers of bonds between the nucleus and unpaired electron


No hyperfine
1 I=1/2 nucleus (^{1}H)
1 I=1 nucleus (^{14}N)
2 identical I=1/2 nuclei
1 I=5/2 nucleus (^{17}O)
10 Gauss

Hyperfine splittings are additive

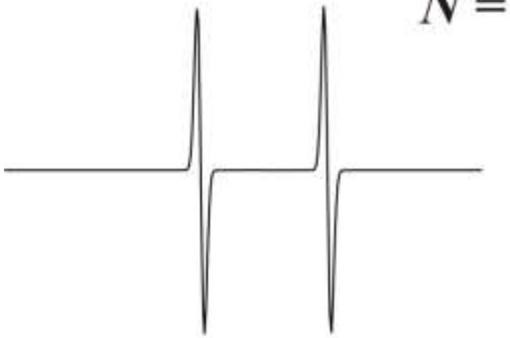




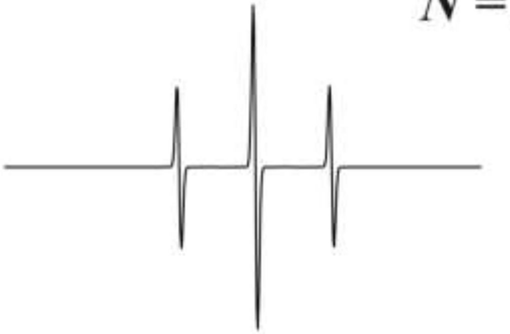
Relative Intensities for $I = \frac{1}{2}$

N	Relative Intensities
0	1
1	1 : 1
2	1 : 2 : 1
3	1 : 3 : 3 : 1
4	1 : 4 : 6 : 4 : 1
5	1 : 5 : 10 : 10 : 5 : 1
6	1 : 6 : 15 : 20 : 15 : 6 : 1

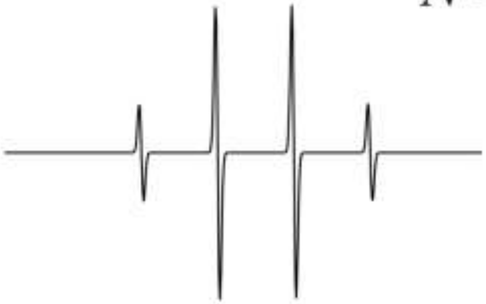
Relative Intensities for $I = ½$



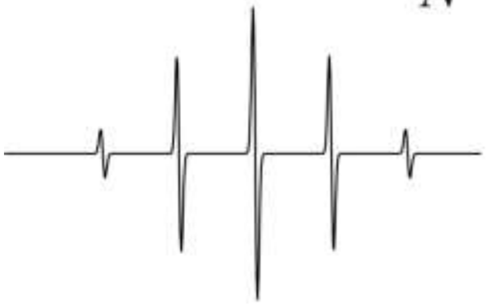
$N = 1$



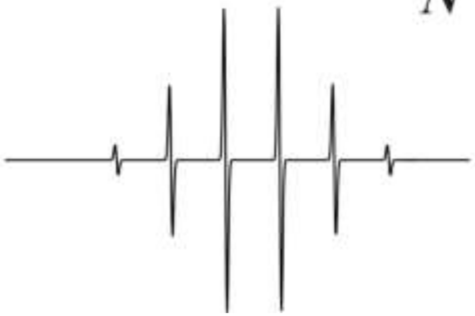
$N = 2$



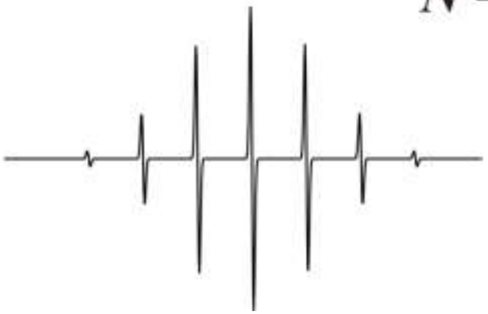
$N = 3$



$N = 4$



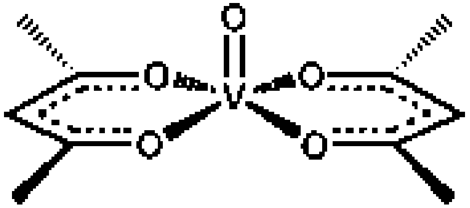
$N = 5$



$N = 6$

Hyperfine Interactions

- Example:
  - $VO(acac)_2$
  - Interaction with vanadium nucleus

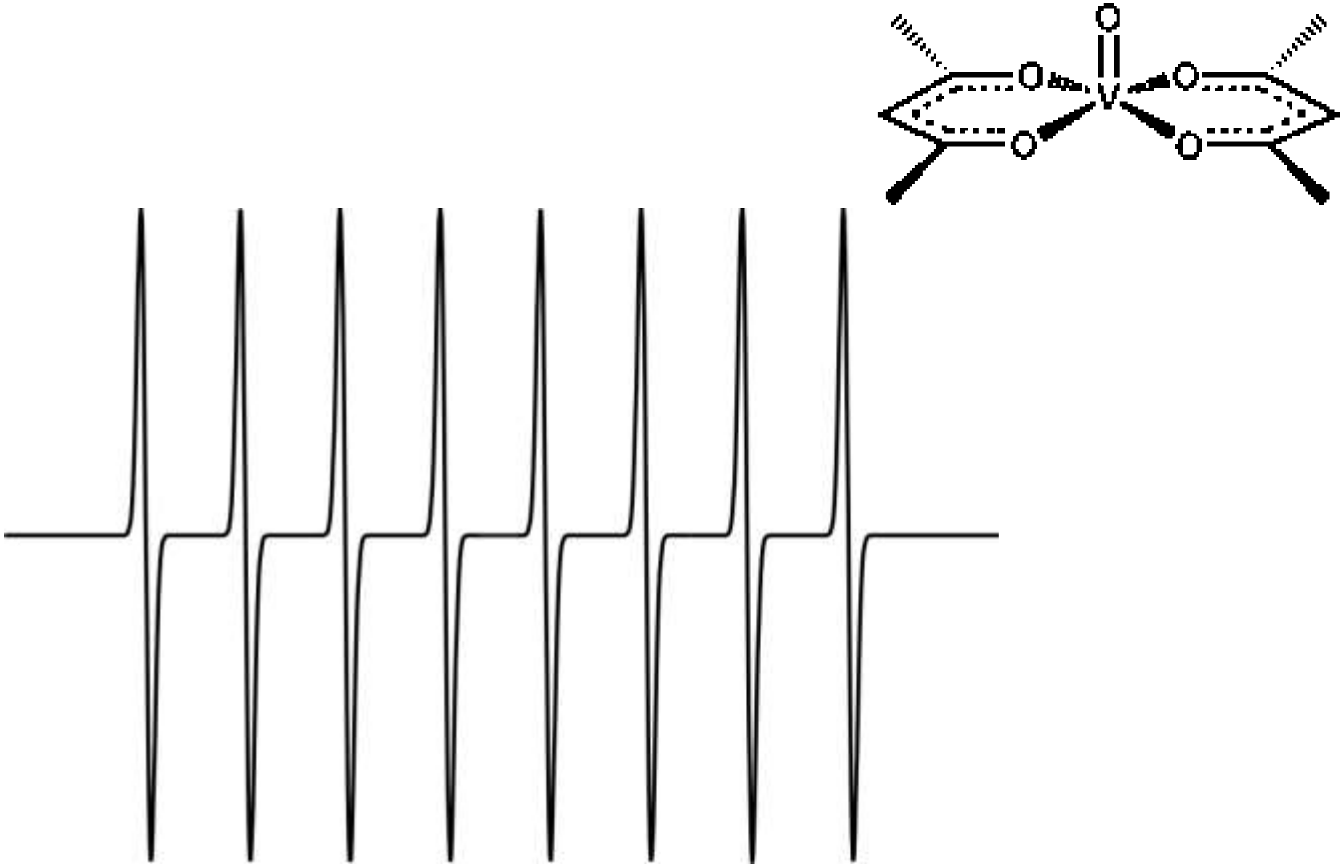


  - For vanadium, $I = 7/2$
  - So,

$$2NI + 1 = 2(1)(7/2) + 1 = 8$$

  - You would expect to see 8 lines of equal intensity

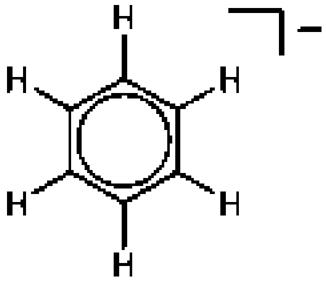
Hyperfine Interactions



EPR spectrum of vanadyl acetylacetonate

Hyperfine Interactions

- Example:
  - Radical anion of benzene $[C_6H_6]^-$

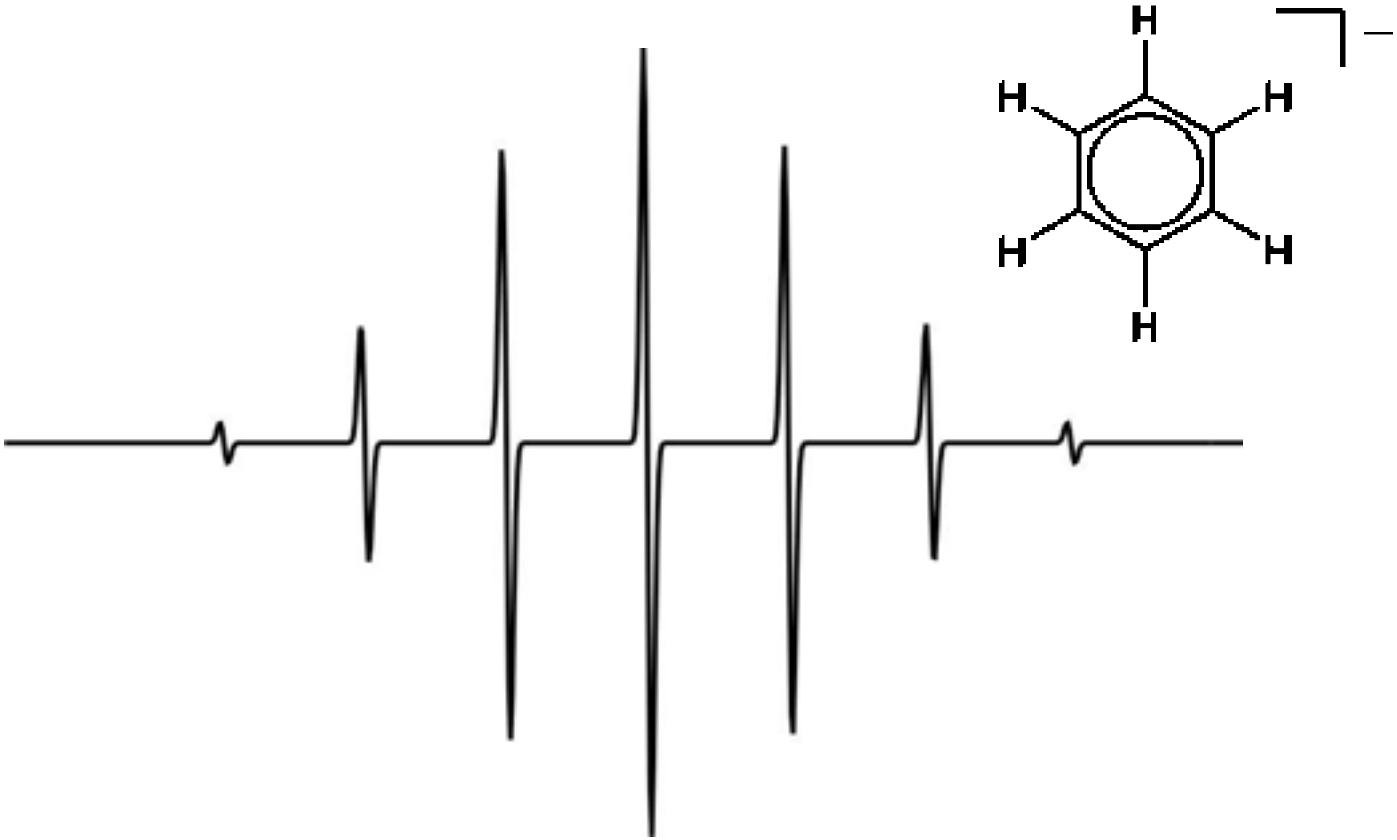


  - Electron is delocalized over all six carbon atoms
    - Exhibits coupling to six equivalent hydrogen atoms
  - So,

$$2NI + 1 = 2(6)(1/2) + 1 = 7$$

  - So spectrum should be seven lines with relative intensities 1:6:15:20:15:6:1

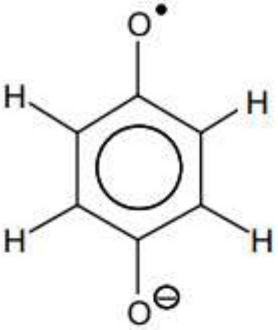
Hyperfine Interactions



EPR spectrum of benzene radical anion

ESR of 1,4 Benzosemiquinone radical anion

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$



1 : 4 : 6 : 4 : 1,

ESR spectrum of Naphthalene

It has two sets of equivalent protons

α=4
β=4

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$

ESR Spectrum of Anthracene

It has three sets of equivalent protons

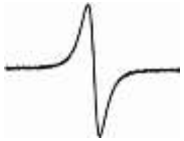
α=4

β=4

ϒ= 2

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$

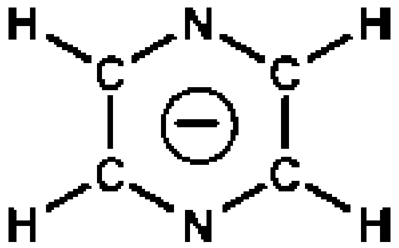
$$2NI + 1 = 2(2)(1/2) + 1 = 3$$



Hyperfine Interactions

- Coupling to several sets of nuclei
  - First couple to the nearest set of nuclei
    - Largest ***a*** value
  - Split each of those lines by the coupling to the next closest nuclei
    - Next largest ***a*** value
  - Continue 2-3 bonds away from location of unpaired electron

Hyperfine Interactions



- Example:
  - Pyrazine anion
  - Electron delocalized over ring
    - Exhibits coupling to two equivalent N (I = 1)

$$2NI + 1 = 2(2)(1) + 1 = 5$$

    - Then couples to four equivalent H (I = ½)

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$

  - So spectrum should be a quintet with intensities 1:2:3:2:1 and each of those lines should be split into quintets with intensities 1:4:6:4:1

Zero-field splitting (zfs)

Just like the spin of nucleus affects the spin of electron causing hyperfine lines in the similar manner the spin of unpaired electron of the same or adjacent atom affects the ESR spectrum i;e **when two unpaired electrons of the same atom or on the adjacent atom of diatomic molecule the spinning motion of these electrons influence each other & causes zero field splitting which results in ESR spectrum.**

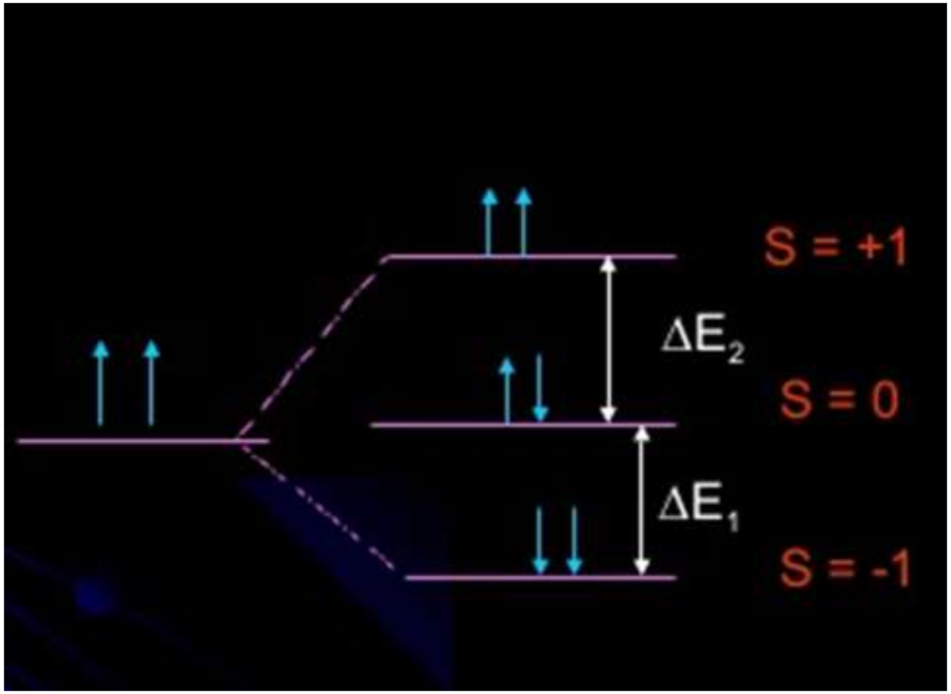
For such substance value of $S = 1$

$M_s = +1, 0\ -1$

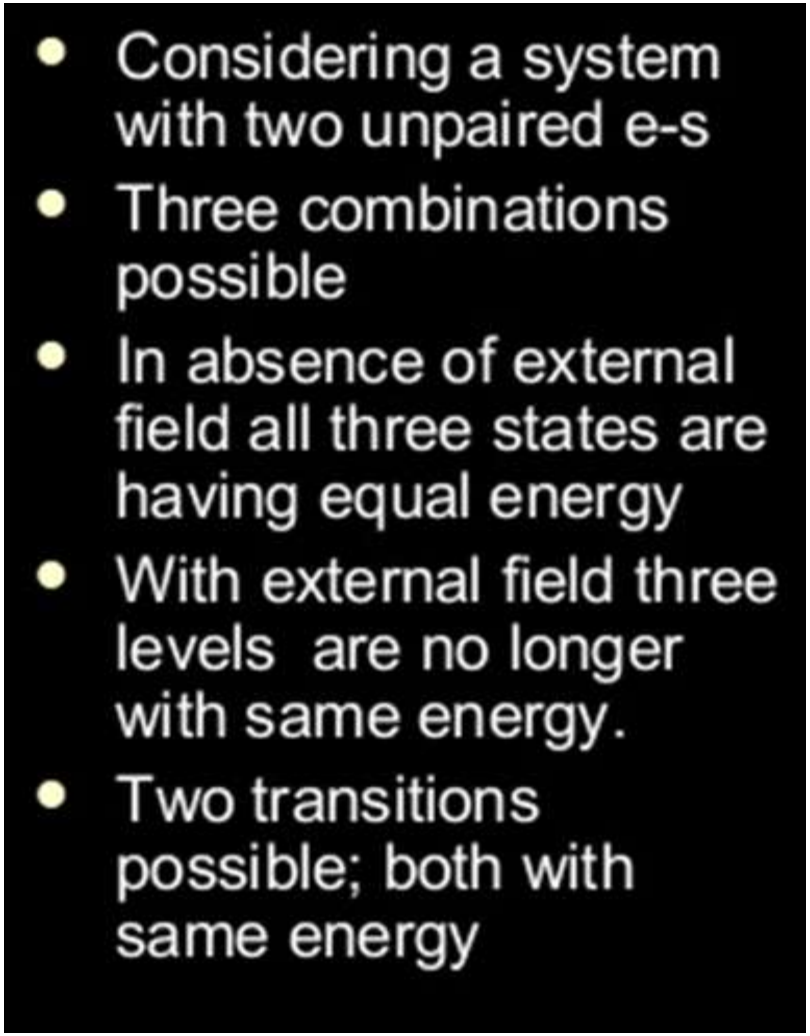
In the absence of magnetic field the three values of M_s are degenerated but when the magnetic field is applied to it then it get splits up into three energy levels.

It is the removal spin microstate degeneracy for systems with $S > 1/2$ in the absence of an applied field. That is, the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution.

ZERO FIELD SPLITTING



Splitting even in the absence of magnetic field



- Considering a system with two unpaired e-s
- Three combinations possible
- In absence of external field all three states are having equal energy
- With external field three levels are no longer with same energy.
- Two transitions possible; both with same energy

Zero-field splitting :-

- The splitting of spin levels even in the absence of magnetic field is called zero–field splitting.
- Occurs mainly in in transition metal complexes where there are more than one unpaired electrons.
- Removes the degeneracy of transitions and more transitions are observed than expected , in the presence of external magnetic field.
- Fine structure in ESR spectrum is obtained.

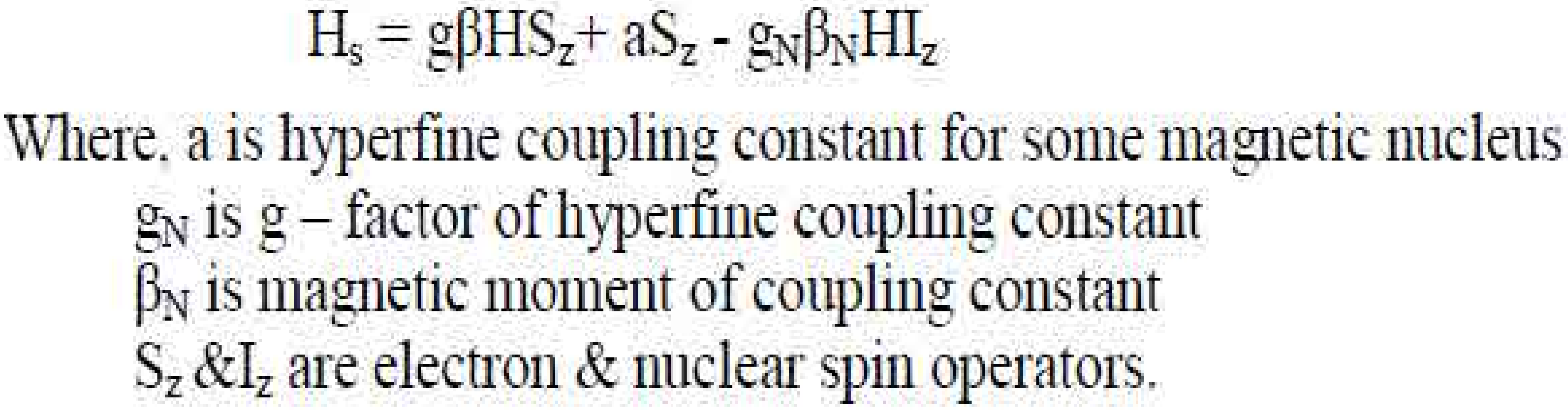
- Rhombic zfs (the “*E*” zfsparameter) splits the Kramer’s doublets.
- Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic *properties*. For example, magnetic hardness is related to the magnetoanisotropy.
- At the molecular level, understanding zfs is essential for rational design of single-molecule magnets since the energy barrier separating the +ms and –ms microstates is equal to |S2*D*|,where D is the energies of spin microstates .
- Orbital angular momentum can be of primary contributor to zfs, and can make the zfs quite large (≈1-10 cm-1)compared to spin-dipolar contributions (≈10-3 - 10-1 cm-1). There are two scenarios in which orbital angular momentum manifests itself in zfs: in-state orbital angular momentum (*e.g.*, orbital T states in *O*h symmetry), and out-of state orbital angular momentum (*e.g.*, spin-orbit mixing of certain excited states into the ground state).
- In-state orbital angular momentum can give rise to very large zfs.
- Spin-Orbit Coupling Splits spin multiplet by mixing with orbital multiplet. "ZFS" large,
- Out-of state orbital angular momentum can also give rise to zfs, but not alone and the degeneracy is retained.
- Spin-Orbit Coupling **does not** remove degeneracy of spin multiplet (D = 0) Any distortion that removes the degeneracy of t1g will work. Thus, the spin-orbit coupling plus the distortion combine as perturbations to allow the ground state “feel” the excited state splitting. The result is zero-field splitting.

Kramer's Degeneracy

- **As the number of unpaired electron increases from 0 to 2, zfs occurs which give rise to fine structure in ESR spectrum.**
- **If even number of unpaired electron then Ms=0**

Spin Hamiltonian

Energy levels have been represented in terms of Hamiltonian, as electron spin resonance (ESR) is concerned with electron & nuclear spin, the scheme of energy levels is called as spin



$$H_s = g\beta HS_z + aS_z - g_N\beta_N HI_z$$

Where, a is hyperfine coupling constant for some magnetic nucleus

g_N is g – factor of hyperfine coupling constant

β_N is magnetic moment of coupling constant

S_z & I_z are electron & nuclear spin operators.

1st term in the equation represents energy of interaction of magnetic moment of odd electrons with field.

2nd term indicates the interaction between the moments of electrons & magnetic nucleus & is responsible for nucleus hyperfine structure.

3rd & last term is small in value & can be neglected as it represents the energy of magnetic nucleus in the field.

In case of free radicals ,g-factor slightly depart from the free spin value of 2.0023,therefore Hamiltonian is quite adequate for free radicals in solution. Interpretation of ESR spectra is difficult for free radical due to coulomb repulsion between d or f electrons & spin spin orbit coupling combine to give g-factor for electrons & resonance lines depart widely from 2.0023.

Spin orbit couping couples the spin angular momentum of unpaired electrons with their orbital angular momentum.

Ions & complexes of transition metals & rare earth metals contain unpaired electrons in d & f orbitals therefore can be studied by ESR.

Spin densities & Mc Conell Relationship

Hyperfine splitting is observed in case of those nucleus where unpaired electron has some s-character at the nucleus & the numerical value of the splitting indicates the amount of s-character possessed by the nucleus.

But there is no mechanism by which unpaired spin density could appear at the ring protons, because there is nodal plane in the plane of the molecule. Mc.Conell (1956) proposed a mechanism for the appearance of hyperfine structure from ring protons in π-radical systems due to configuration interaction. According to wave mechanics , the unpaired electron in the π – orbital polarizes the electrons in the covalent C-H bond. As a result, a small unpaired spin density takes place at the proton.

The Mc.Conell relation is

$$a=Q\rho$$

where, a=Hyperfine splitting from the proton, & is proportional to unpaired π spin density ρ, on the adjacent carbon atom.

Q is constant.

Example - The value of Q is taken as 22.5 gauss from the spectrum of benzene negative ion. Charge density is 1/6 at each carbon atom & proton hyperfine splitting is 3.75 gauss.

This relationship allows the unpaired spin density distribution on the carbon skeleton of a free radical to be obtained from the experimental proton splitting constant.

Study of ESR gives detailed information about the structure of the compound as –

- It shows the site of unpaired electron(s) - The total area covered by either the absorption or derivative is proportional to the number of unpaired electrons in the sample.

- The number of line components decide the number & type of nuclei present in the vicinity of the odd electron.

- Hyperfine splitting shows interaction between the electron spin & the nuclear spin of the adjacent magnetic nuclei.

- Zero field splitting shows the number of unpaired electrons on the adjacent atom.

Applications

A. *Applications of ESR spectra:*

- It decides the site of unpaired electrons.
- The number of line components decide about the number and type of nuclei present in the neighborhood of the odd electron.
- If the electric field is not spherical then the ESR spectrum is anisotropic,ie the rotation of the sample shifts the ESR spectrum.
- From this the g value can be measured by comparing the position of the line with that of standard substance.
- Determination of type of nuclei which are responsible for splitting pattern by comparing the relative intensities.

Applications of ESR spectroscopy:

❑ Study of Free radicals

- Even in very low concentrations also we can study the free radicals by using ESR spectroscopy.
- Structure of organic and inorganic free radicals can be identified.
- Investigation of molecules in the triplet state.
- Spin label gives the information about polarity of its environment.

❑ Structural Determination

- In certain cases ESR provides the information about the shape of the radicals.

☐ **Reaction Velocities and Mechanisms**

☐ **Study of inorganic compounds**

☐ **Study of catalysts**

☐ **Determination of oxidation state of a metal.**

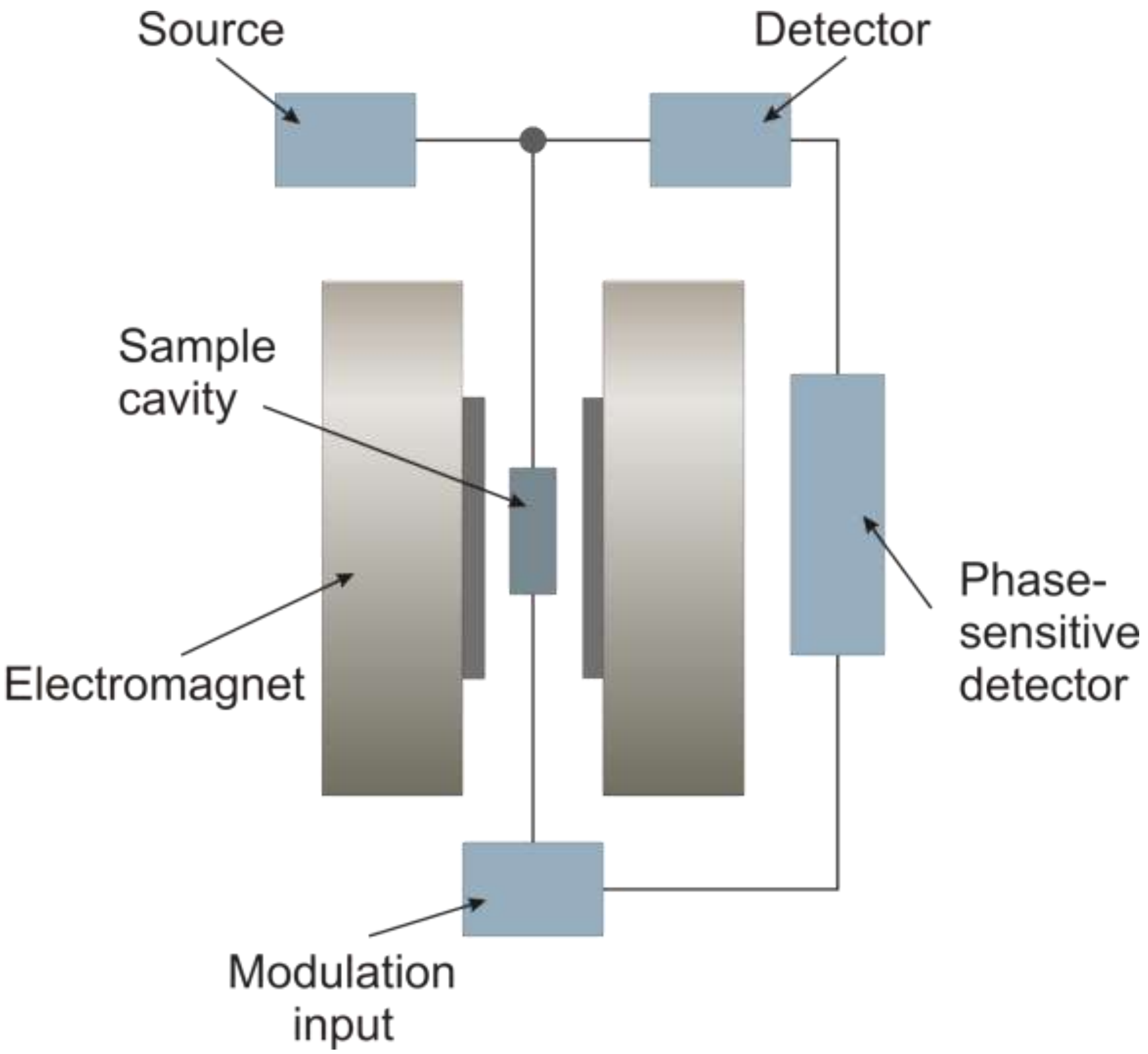
☐ ***Analytical applications:***

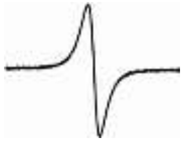
- Determination of Mn^{2+}
- Determination of vanadium.
- Determination of poly nuclear hydrocarbon.

☐ ***Biological applications*:**

- The presence of free radicals in healthy and diseased conditions.
- Functioning of most of the oxidative enzymes can be conformed.

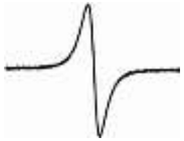
How does the spectrometer work?





Instrumentation

- Source
- Circulator or Magic -T
- Sample Cavity
- Magnet System
- Crystal Detector
- Auto amplifier and Phase sensitive Detector
- Oscilloscope and Pen Recorder



Source:

- **Klystron**

- It is a vacuum tube which can produce microwave oscillations centered on a small range of frequency
- The frequency of the monochromatic radiation is determined by the voltage applied to Klystron.

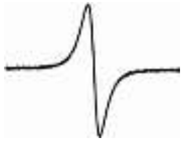
Isolator:

- It is a non reciprocal device which minimizes vibrations in the frequency of microwaves produced by Klystron oscillator.
- The variations occur in the frequency due to the backward reflections in the region between the Klystron and circulator.
- Isolator is a strip of ferrite material.

Wave meter

- It is fixed in between the isolator and attenuator to know the frequency of microwaves produced by Klystron oscillator.

- Usually it is calibrated in frequency units instead of wavelength.

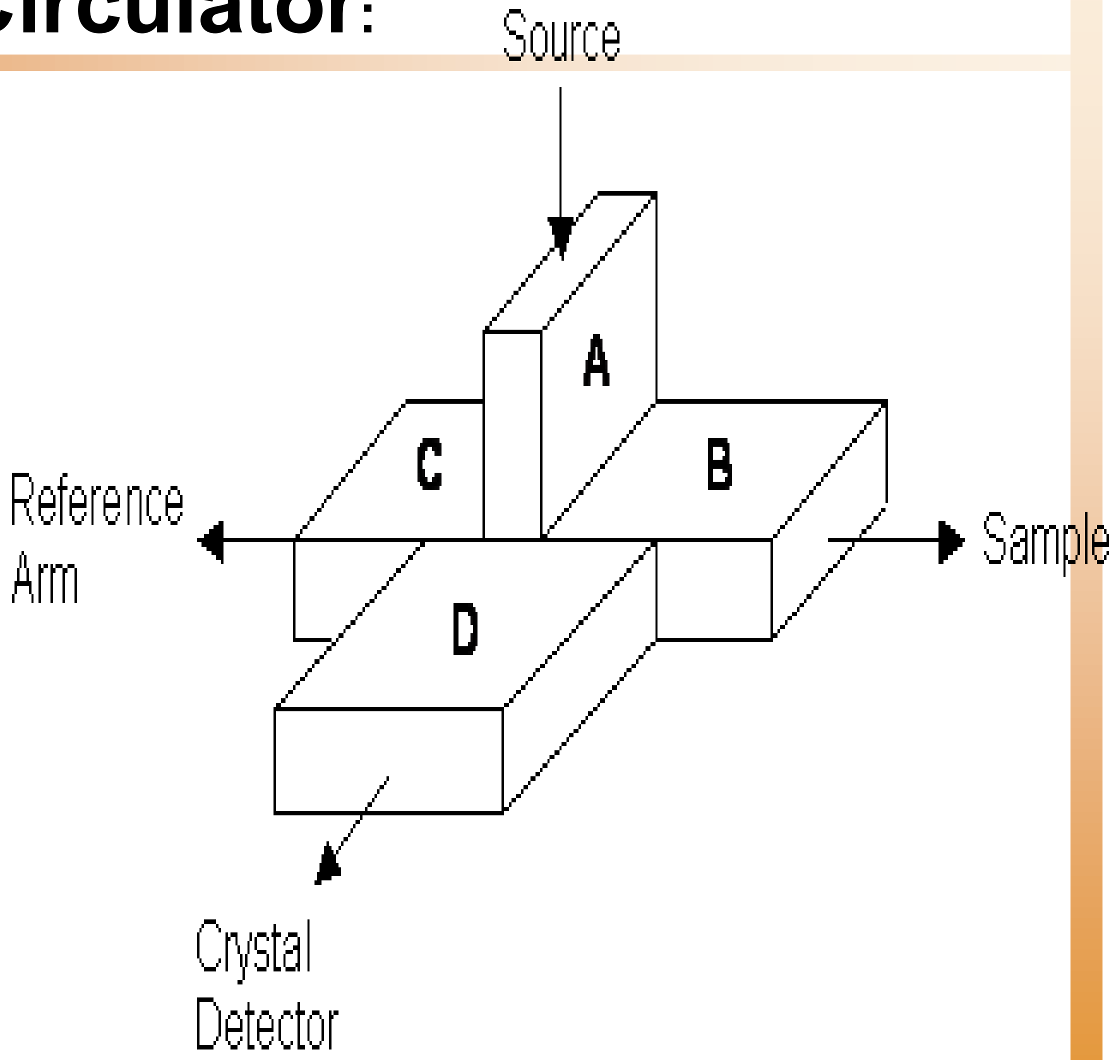


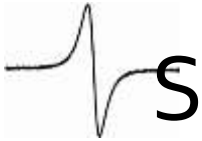
Attenuator:

- Attenuator is used to adjust the level of the microwave power incident upon the sample.
- It processes an absorption element and corresponds to a neutral filter in light absorption measurement.

Magic T or Circulator:

- Microwave radiations finally enter to the circulator through a wave guide by a loop wire which couples with oscillating magnetic field and setting a corresponding field.





Sample Cavity:

- This resonant cavity which contains the sample is called the heart of ESR.
- It is constructed in such a way to maximize the applied magnetic filed along the sample dimension.
- In most ESR spectrometer dual sample cavities are used for simultaneous observation of sample and reference materials.

Magnet System:

- The sample cavity is placed between the pole pieces of an electromagnet
- This provides a homogenous magnetic field and can be varied from zero to 500 gauss.
- The stability of the field is achieved by energizing the magnet with a highly regulated power supply.

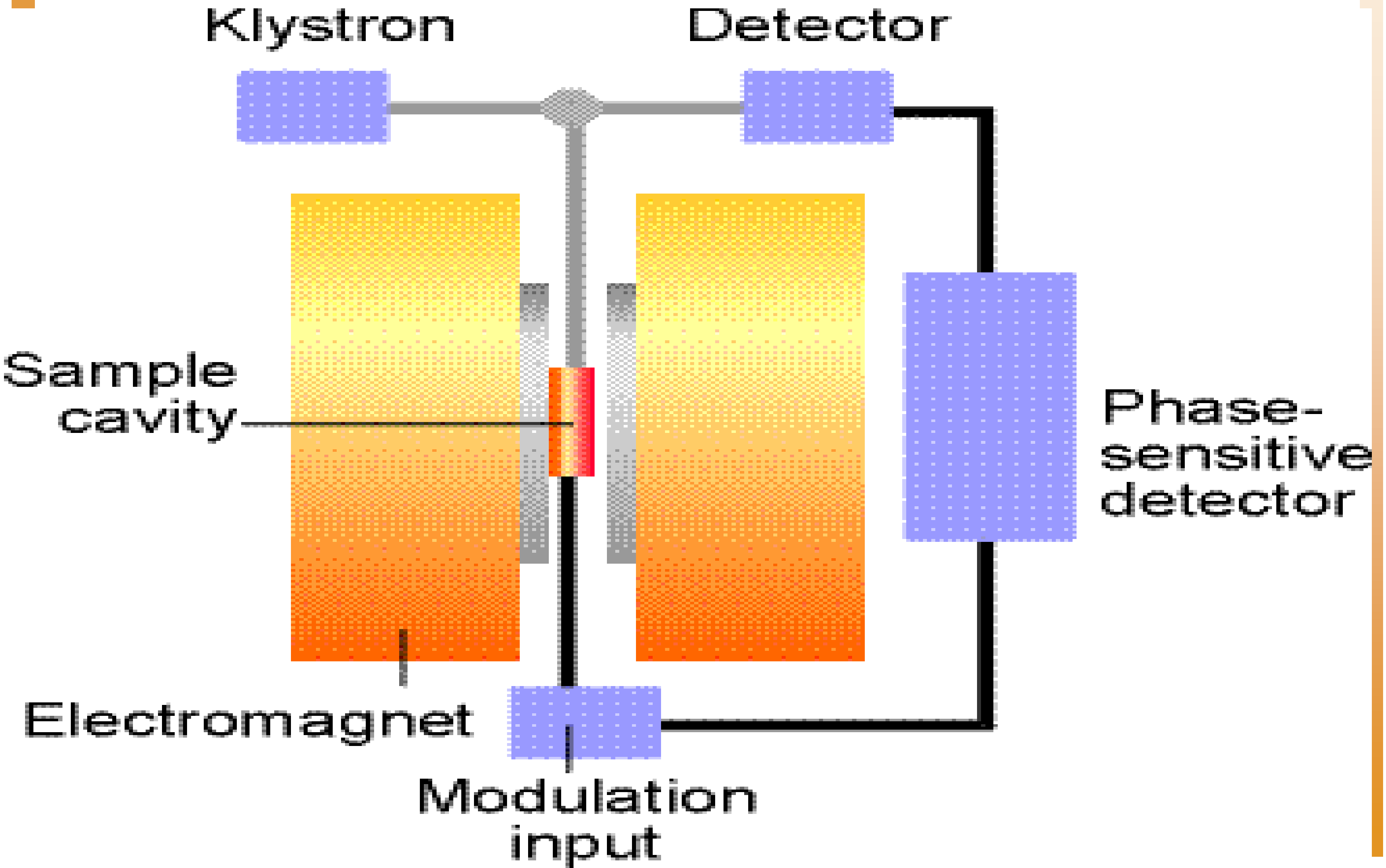
Crystal Detectors:

- The most commonly used detector is a silicon crystal which acts as a microwave rectifier.
- This converts microwave power into a direct current input.

Oscilloscope and Pen Recorder

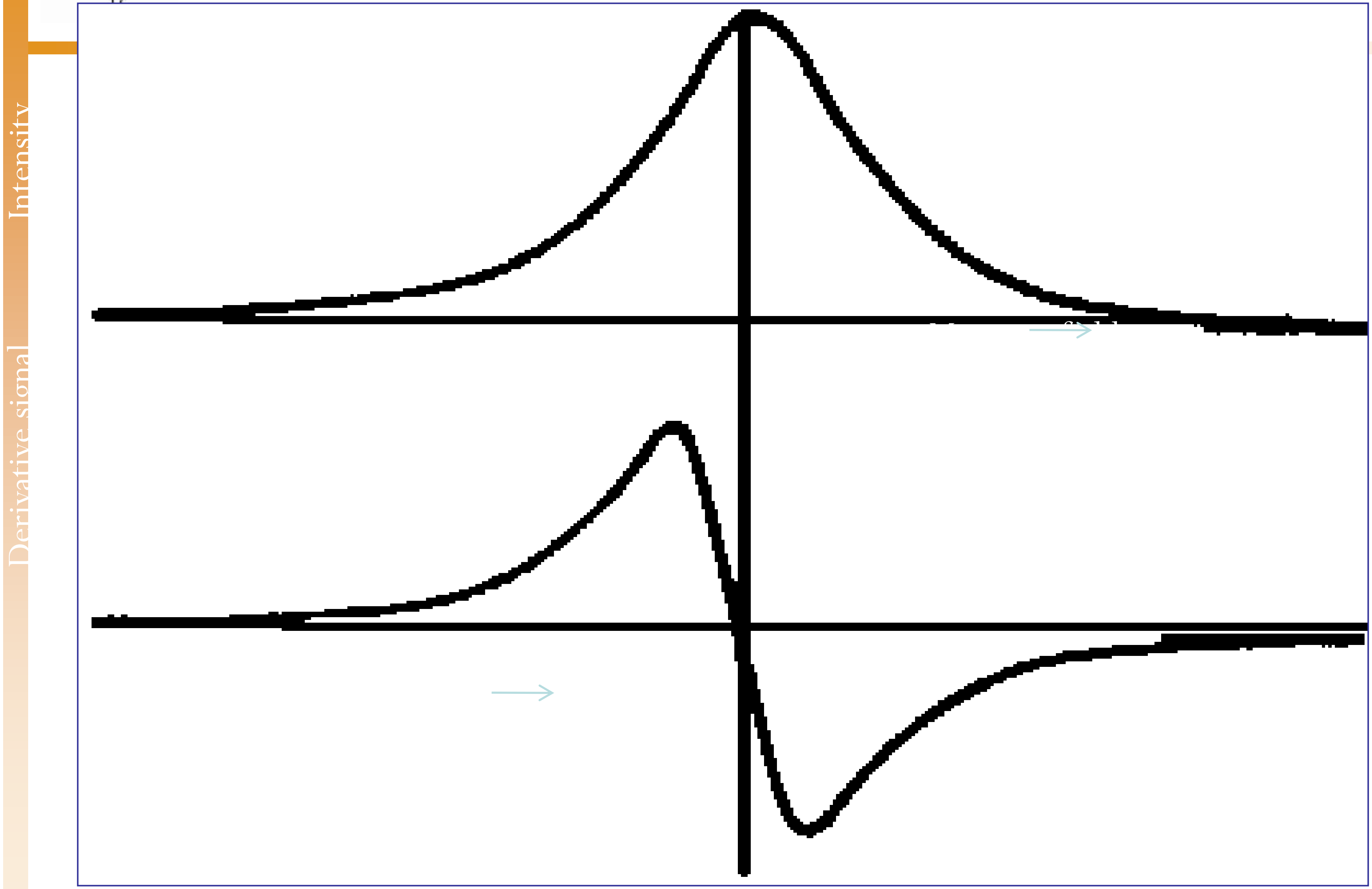
- The signal from phase sensitive detector and sweep unit is recorded by the oscilloscope or pen recorder.

ESR Spectrometer:



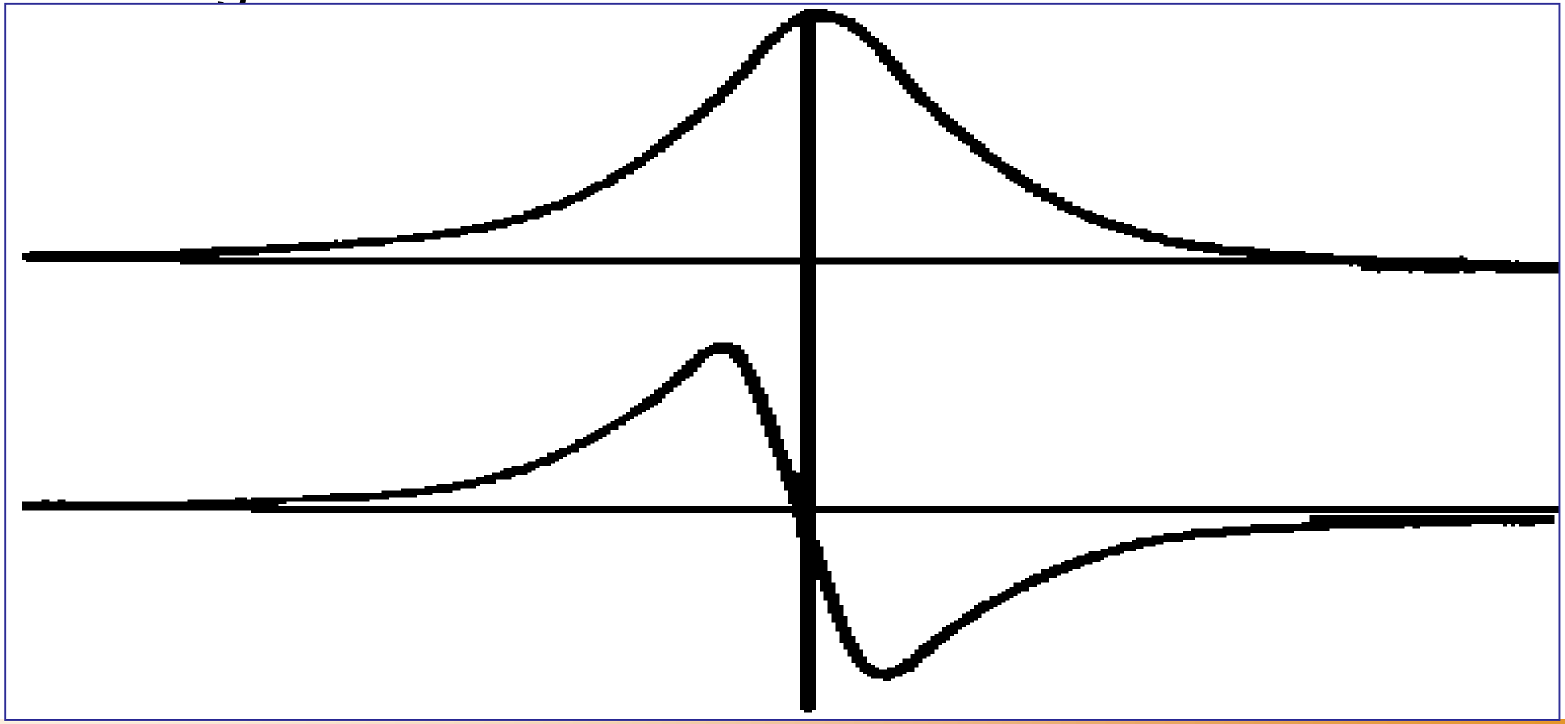
Working:

- The Klystron oscillator is set to produce microwaves.
- After passing though the isolator, wave meter and attenuator the microwaves are entered into the circulator on magic T
- Then it reaches the detector which acts as a rectifier, ie. converting the microwave power into the direct current.
- If the magnetic field around the resonating cavity having the sample is changed to the value required for the resonance, the recorder will show an absorption peak.
- If the magnetic field is swept slowly over a period of several minutes, the recorder will show the derivative of the microwave absorption spectrum against magnetic field as shown below:

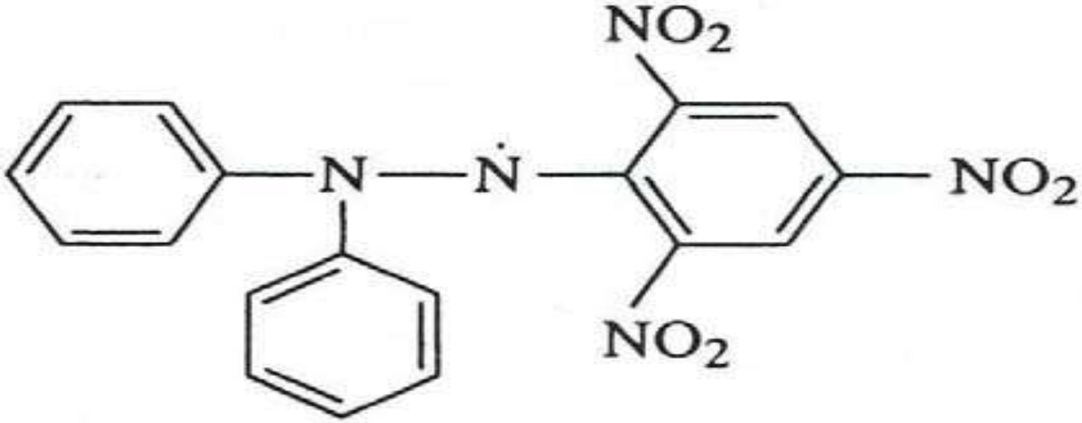

Intensity
Derivative signal

Presentation of ESR Spectrum:

- The ESR spectrum is obtained by plotting intensity against the strength of a magnetic field.
- The better way is to represent ESR spectrum as a derivative curve in which the first derivative(slope) of the absorption curve is plotted against the strength of the magnetic field



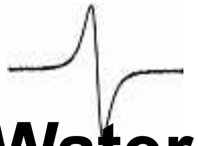
- The total area covered by either the absorption or derivative curve is proportional to the number of unpaired electrons in the sample.
- In order to find out the number of electron in an unknown sample, comparison is made with a standard sample having a known number of unpaired electrons and possessing the same line shape as the unknown.
- The most widely used standard is 1,1-diphenyl-2-picrylhydrazyl free radical(DDPH)



DPPH

Conclusions

- Analysis of paramagnetic compounds
  - Compliment to NMR
- Examination of proportionality factors
  - Indicate location of unpaired electron
    - On transition metal or adjacent ligand
- Examination of hyperfine interactions
  - Provides information on number and type of nuclei coupled to the electrons
  - Indicates the extent to which the unpaired electrons are delocalized



TO SUM UP

- Water and alcohol are not suitable solvents in ESR becoz they strongly absorb in microwave region

- In ESR transitions occur in microwave region and in NMR the transitions occur in rf region.

- The intensity of absorption line is proportional to the number of unpaired electrons in ESR spectrum.

- In NMR spectroscopy, the two different energy states are produced as a result of alignment of nuclear spin relative to the applied field whereas in ESR spectroscopy, the two different enegy states are produced due to alignment of electronic field