ESR SPECTROSCOPY

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- Electron spin resonance is a branch of absorption spectroscopy in which radiation having a frequency in the microwave region is absorbed by paramagnetic substances induces transitions between magnetic energy levels of electrons with unpaired spins. The magnetic energy splitting is done by applying a static magnetic field.
- The Electron spin resonance (ESR) is also called by other names such as “electron paramagnetic resonance” (EPR) and “electron Magnetic resonance” (EMR).
- ESR has limited applications because it is observed primarily in systems containing unpaired electrons. Thus, the systems which can be investigated by ESR spectroscopy are organic or inorganic free radicals and ions of transition metals which contain unpaired d or f- electrons.
- One of the most important uses of ESR technique lies in the detection of extremely short-lived free radical intermediates in chemical reaction.

Comparison between NMR and ESR

- NMR Spectroscopy deals with nuclear spin resonance and ESR Spectroscopy deals with electron spin resonance.
- The energy difference (ΔE) between two energy levels in ESR is greater and that in NMR.
- In NMR spectroscopy the absorption is caused by radiation of radiowave frequency and in ESR spectroscopy the absorption is caused by radiation of microwave frequency.
- In ESR spectroscopy, the condition is that the substance must have at least one unpaired electron and in NMR spectroscopy the condition is the nucleus should have a definite nucleus spin value.

The ESR experiment is generally carried out at a fixed frequency. Two common frequencies are used in ESR. They are X-band and Q-band.

- **X-band**: Frequency ranges about 9500 MHz, where field strength about 3400 gauss is employed.
- **Q-band**: Frequency ranges about 35000 MHz, where a field strength about 12500 gauss is employed.

Types of substances with unpaired electron

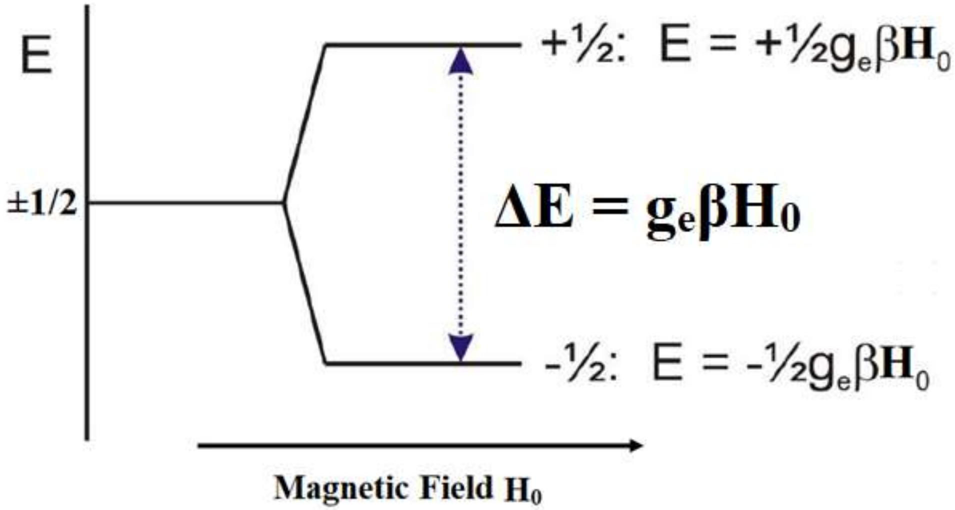
- **Stable paramagnetic substances**

These include stable substances which can be studied very easily by ESR. The examples are simple molecules like NO, O_2, and NO_2, and ions of transition metals and rare Earth elements.

- **Unstable paramagnetic substances**

These can be produced either as intermediate in chemical reaction or by a radiation of stable molecules with a beam of nuclear particles or with X-ray radiation. The substances so produced are also called free radicals or radical ions. These can be studied by ESR provided the lifetimes of such radicals are greater than 10^{-6} second. If the life times are less than 10^{-6} second, they should be produced at low temperature was in the solid state called Matrix technique, because this increases their life-times.

Theory of ESR spectroscopy



$$\Delta E = h\upsilon = g_e\beta H_0$$

Where, h = Planck’s constant (6.626×10^{-34} m^2kgs^{-1})

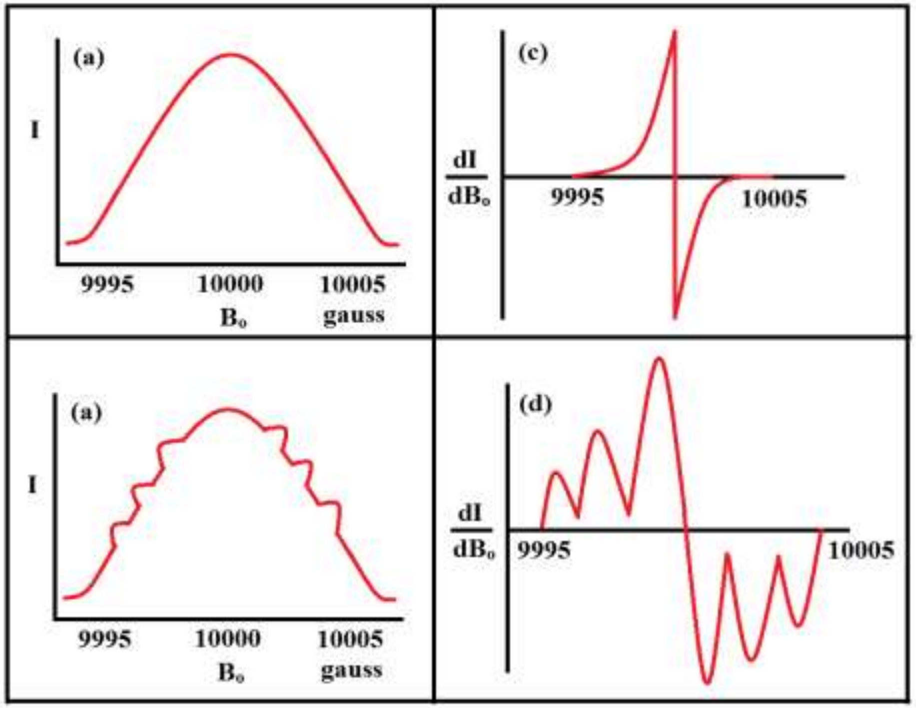
υ = Frequency of radiation

g_e = Spectroscopic splitting factor

β = Bohr Magneton ($9.274 \times 10^{-24} JT^{-1}$)

H_0 = Magnetic field strength

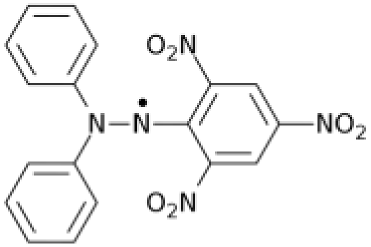
Presentation of the spectrum



In (a) a single absorption peak with no fine structure is represented. (b) is the derivative curve that corresponds to (a). The derivative curve crosses the abscissa at a maximum in the absorption curve. (c) is the absorption peak with shoulders. Curve (d) is the derivative curve of (c). The shoulders in (c) never pass through maxima and as a result the absorption peaks in (d), corresponding to these shoulders do not cross the abscissa. The number of peaks and shoulders in the absorption curve can be determined from the number of minima (or) maxima in the derivative curve.

Standard used in ESR

- In order to calculate the number of electrons an unknown sample, comparison is made with a standard sample having a known number of unpaired electrons and possessing the same line shape as unknown. The most widely used standard is 1,1-phenyl-1,2-picrylhydrazyl free radical (DPPH) whose structure is shown.



- DPPH is a chemically stable material having the splitting factor g=2.0036, DPPH contains 1.53×10^{21} unpaired electrons per gram.
- DPPH cannot be employed as an internal standard for other free radicals because there is only slight variation in the g-values and the unknown substances cannot be distinguished from the standard substance.
- In the 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 and its g value is 1.4.

In the ESR spectrometer, the standard substance is placed along with the unknown in the same chamber of a dual-cavity cell. The ESR spectrum will show two signals with a field separation of ΔH. The g-value for the unknown is given by,

$$g\beta H = h\upsilon$$

$$g = h\upsilon/\beta H$$

The fundamental equation for the standard and unknown is written as

$$h\upsilon= g_s\beta H_s \text{ -------(1)}$$

$$h\upsilon= g_u\beta H_u \text{ -------(2)}$$

(2)/(1) -------- $g_uH_u/ g_sH_s = 1$

Add and subtract H_u

$$g_uH_u/ g_sH_s = 1 + H_u -H_u$$

On simplifying we get

$$\mathbf{g_u=g_s[1-\Delta H/H_u]}$$

Where H is the resonance frequency. ΔH is positive if the unknown has its center at higher field. In a powdered sample, magnetic susceptibility measurements lead only to an average g-value, whereas ESR measurements can give the individual components of the g-tensor.

Factors affecting g value

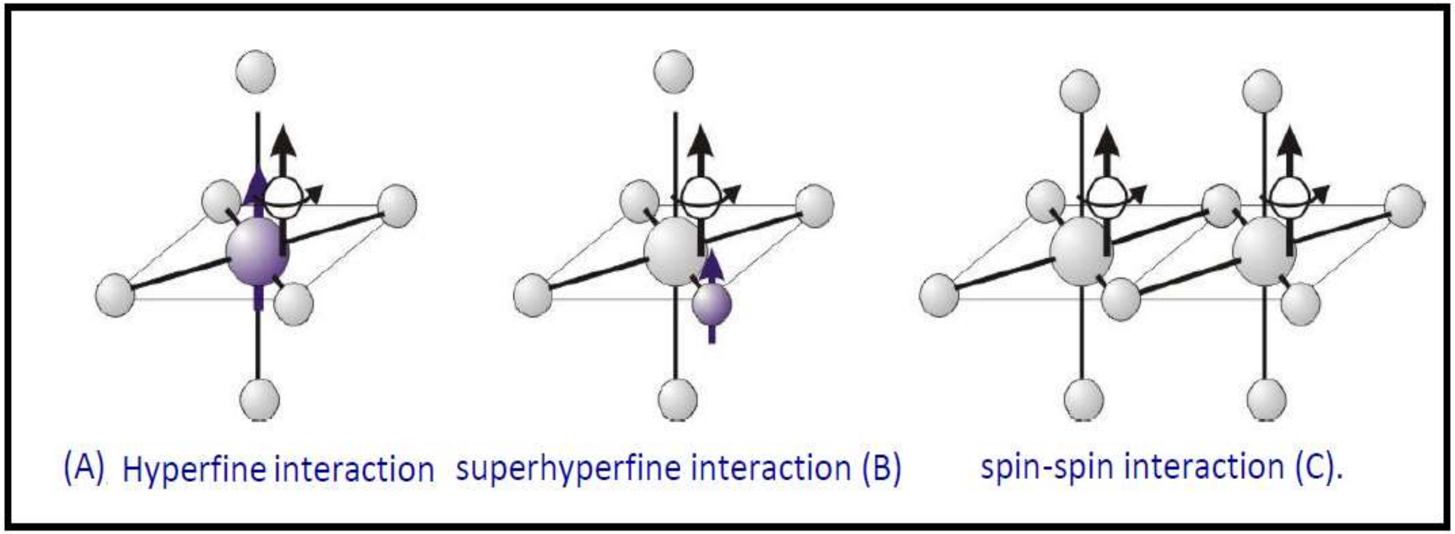
- The value of g is not constant but it is a tensor quantity. For a free electron its value is 2.0023 but this value is slightly modified for electrons in molecules.
- Virtually all free radicals and some ionic crystals have almost same value of g as for free electrons, but this value is modified by ± 0.03.
- In some ionic crystals, the values of g vary from 0.2 to 0.8.
- The value of g depends upon the orientation of molecule having the unpaired electron with respect to applied magnetic field.
- In the case of a gas or solution, the molecules have free motion and value of g is an averaged over all orientation. But in the case of crystals, the movement of electrons is not free.
- However, in the case of paramagnetic ion or radical situated in a perfectly cubic crystal, the value of g is same in all directions, i.e., the value of g does not depend upon the orientation of the crystal.
- On the other hand the value of paramagnetic ion or radical situated in a crystal of low geometry depends upon the orientation of the crystal.
- There are three axes in crystal. The values of long x, y, and z axes are denoted by g_x, g_y and g_z respectively. In the case of tetragonal site, the values of g_x, g_y are equal to referred to as g perpendicular. This value is generally attained when external magnetic field is perpendicular to z-axis. The value of g_z is obtained when the magnetic field parallel to z-axis. The value of g_z is denoted by g is parallel.

Deviation of the value of ‘g’

- The deviation of ‘g’ from $g_e = 2.0036$ depends on the ability of the applied magnetic flux density to induce local currents in the free radical and, therefore, its value gives some information about electronic structure.
- However, in the case of transition metal ions and their complexes, there is considerable interaction between the spin and the orbital motion of the electron which prevents complete quenching of the orbital contribution. Transition metal complexes containing d-shells less than half-filled, **($g<g_e$)** while for shells more than half-filled, **($g>g_e$)**.
- Also, the g-value is anisotropic, i.e. its magnitude depends upon the direction of measurement. The anisotropy in g-value is shown by systems in the solid state where conditions of restricted motion exist.
- Consider, for instance, an octahedral complex wherein two diametrically opposed ligands are pulled or pushed symmetrically while the remaining four ligands remain undisturbed. This is a case of axial symmetry.
- If the magnetic field is applied along the z-direction, the g-value is designated as g_{ll}. If the field is applied perpendicular to the z-axis, the g-value is designated as g_1.

Nuclear hyperfine splitting in isotropic systems

In EPR there are three types of interaction that can occur. The first two types are due to the interaction between an unpaired electron and a magnetic nucleus. Interaction of unpaired electron with nuclear magnetic moment is termed **nuclear hyperfine interaction**. Usually called hyperfine if it results from the nucleus where the unpaired electron originates (A) and **super-hyperfine** if it is from a neighbouring nucleus (B). The third type is the interaction between two unpaired electrons on different atoms normally within a molecule, which is termed **spin-spin interaction (C)**.



- The hyperfine splitting in ESR spectrum is caused by the interactions between the spinning electrons and adjacent spinning magnetic nuclei. When a single electron interacts with one nucleus, the number of splitting will be equal to 2I+1, where I is the spin quantum number of the nucleus. In general, if a single electron interacts magnetically with n equivalent nuclei, the electron signal is split up into a (2nI+1) multiplet. This splitting in an isotropic system is due to nuclear spin – electron spin coupling arising mainly from Fermi contact term.

The energy level is given by,

$$\mathbf{E = g\beta H_o M_S + A M_S M_I}$$

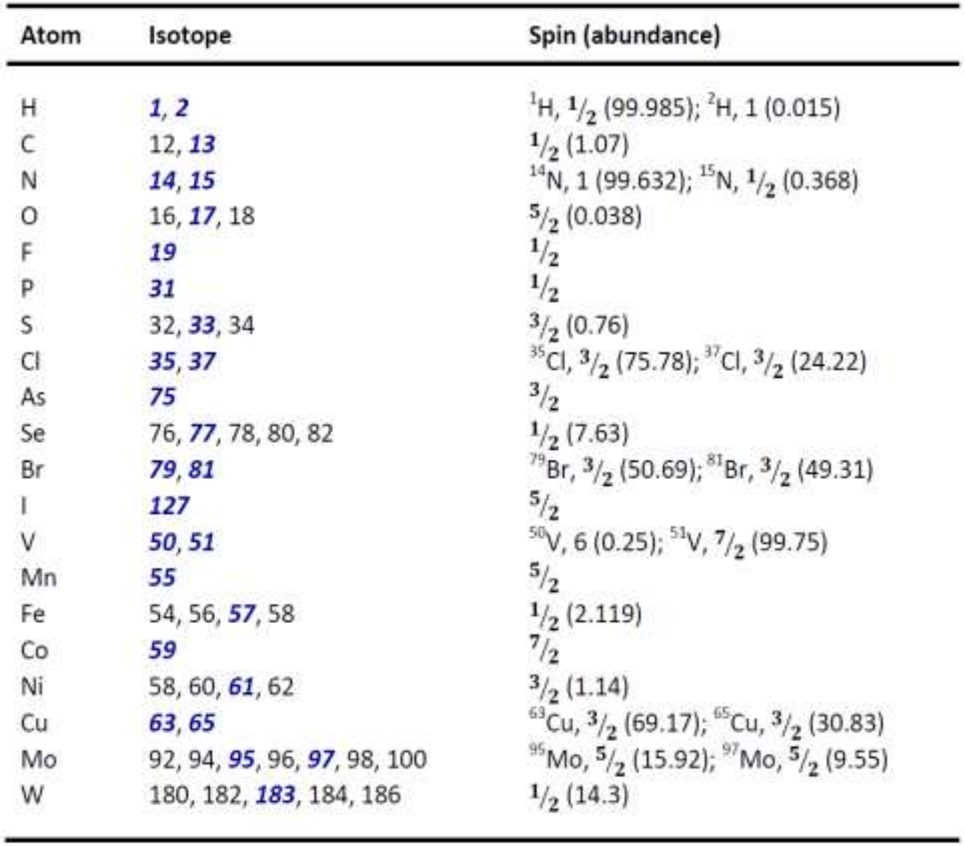
A = Hyperfine coupling constant

M_S = Spin quantum number (electron)

M_I = Spin quantum number (nucleus)

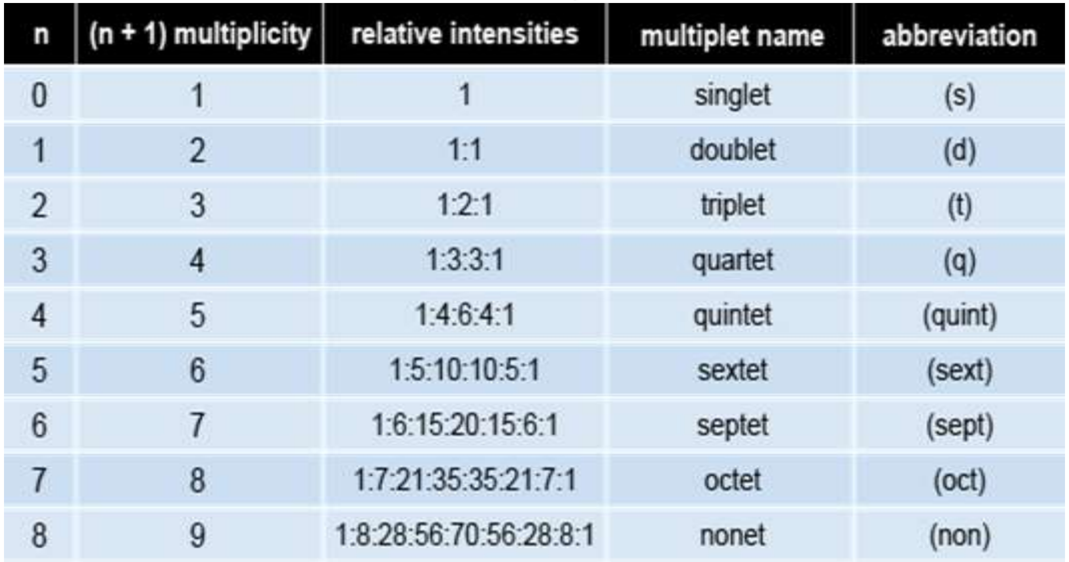
The selection rule for hyperfine transitions is

$$\mathbf{\Delta M_S = \pm 1; \Delta M_I = 0}$$



Atom	Isotope	Spin (abundance)
H	***1***, ***2***	^{1}H, $^{1}/_{2}$ (99.985); ^{2}H, 1 (0.015)
C	12, ***13***	$^{1}/_{2}$ (1.07)
N	***14***, ***15***	^{14}N, 1 (99.632); ^{15}N, $^{1}/_{2}$ (0.368)
O	16, ***17***, 18	$^{5}/_{2}$ (0.038)
F	***19***	$^{1}/_{2}$
P	***31***	$^{1}/_{2}$
S	32, ***33***, 34	$^{3}/_{2}$ (0.76)
Cl	***35***, ***37***	^{35}Cl, $^{3}/_{2}$ (75.78); ^{37}Cl, $^{3}/_{2}$ (24.22)
As	***75***	$^{3}/_{2}$
Se	76, ***77***, 78, 80, 82	$^{1}/_{2}$ (7.63)
Br	***79***, ***81***	^{79}Br, $^{3}/_{2}$ (50.69); ^{81}Br, $^{3}/_{2}$ (49.31)
I	***127***	$^{5}/_{2}$
V	***50***, ***51***	^{50}V, 6 (0.25); ^{51}V, $^{7}/_{2}$ (99.75)
Mn	***55***	$^{5}/_{2}$
Fe	54, 56, ***57***, 58	$^{1}/_{2}$ (2.119)
Co	***59***	$^{7}/_{2}$
Ni	58, 60, ***61***, 62	$^{3}/_{2}$ (1.14)
Cu	***63***, ***65***	^{63}Cu, $^{3}/_{2}$ (69.17); ^{65}Cu, $^{3}/_{2}$ (30.83)
Mo	92, 94, ***95***, 96, ***97***, 98, 100	^{95}Mo, $^{5}/_{2}$ (15.92); ^{97}Mo, $^{5}/_{2}$ (9.55)
W	180, 182, ***183***, 184, 186	$^{1}/_{2}$ (14.3)

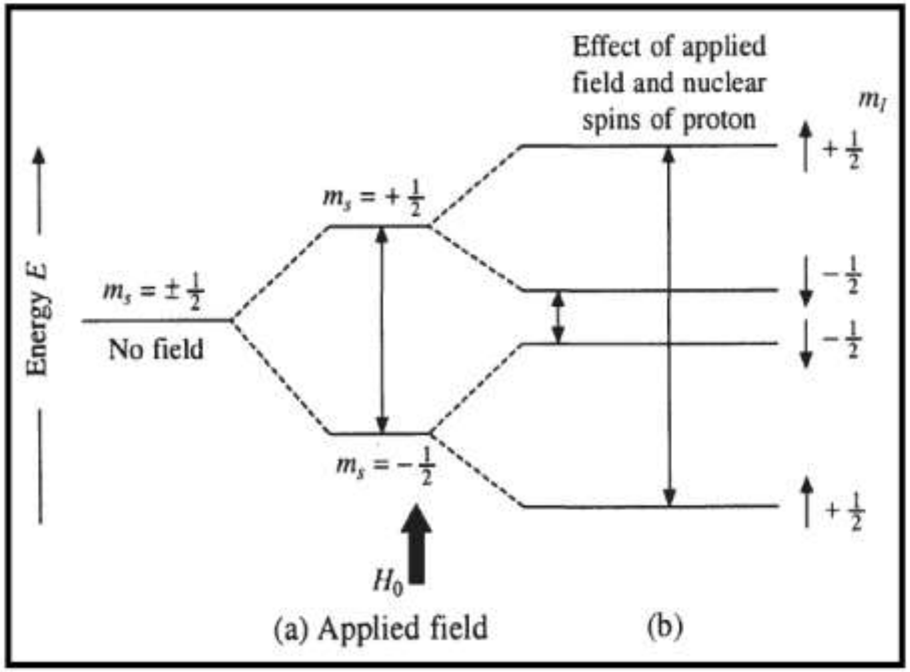
No. of protons	**No. of neutrons**	**Nuclear spin I**	**Examples**
even	**even**	**0**	**C^{12}, O^{16}, S^{32}**
Odd	**even**	**1/2, 3/2, 5/2**	**H^{1}, F^{19}, P^{31}, B^{11}**
even	**odd**	**1/2, 3/2, 5/2**	**C^{13}, I^{127}**
odd	**odd**	**1, 2, 3…**	**H^{2}, N^{14}**

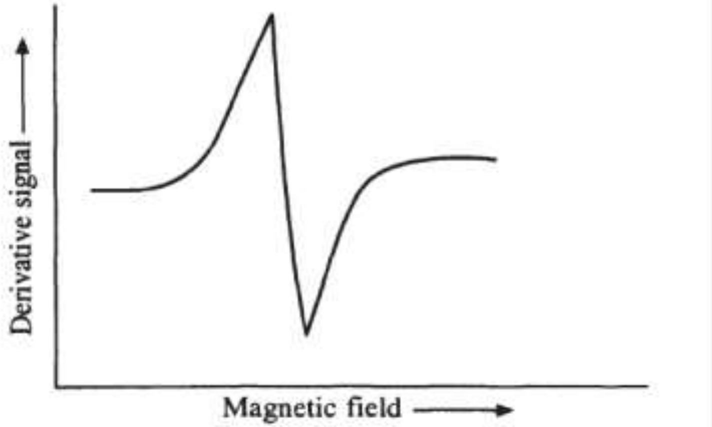


n	(n + 1) multiplicity	relative intensities	multiplet name	abbreviation
0	1	1	singlet	(s)
1	2	1:1	doublet	(d)
2	3	1:2:1	triplet	(t)
3	4	1:3:3:1	quartet	(q)
4	5	1:4:6:4:1	quintet	(quint)
5	6	1:5:10:10:5:1	sextet	(sext)
6	7	1:6:15:20:15:6:1	septet	(sept)
7	8	1:7:21:35:35:21:7:1	octet	(oct)
8	9	1:8:28:56:70:56:28:8:1	nonet	(non)

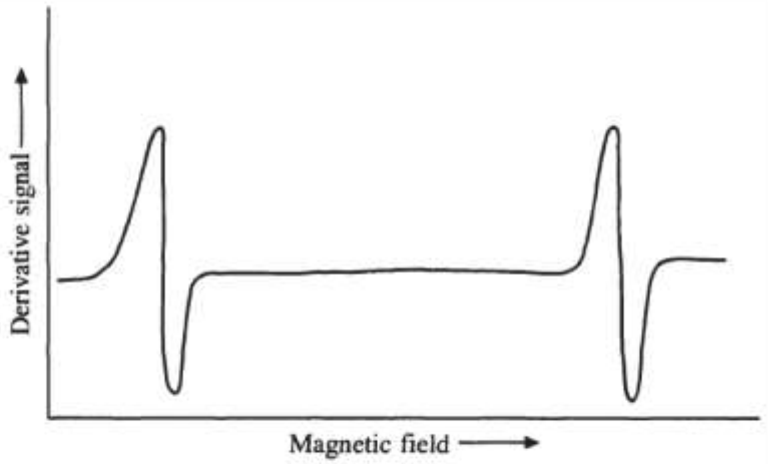
Examples

(i) Hydrogen atom



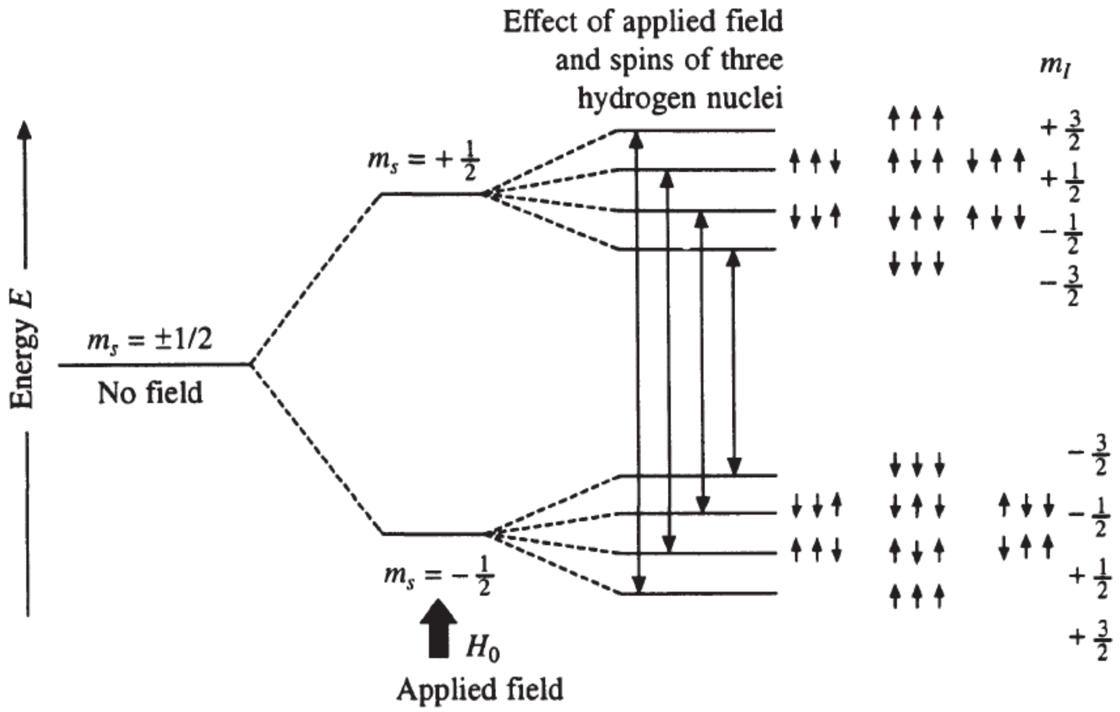


First derivative ESR spectrum of a free electron

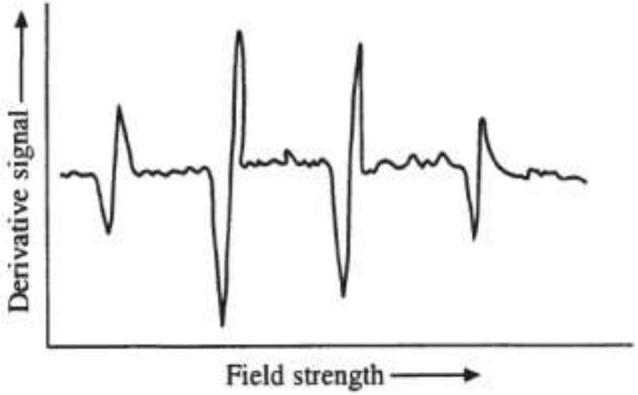


First derivative ESR spectrum of hydrogen atom

(ii) Methyl radical

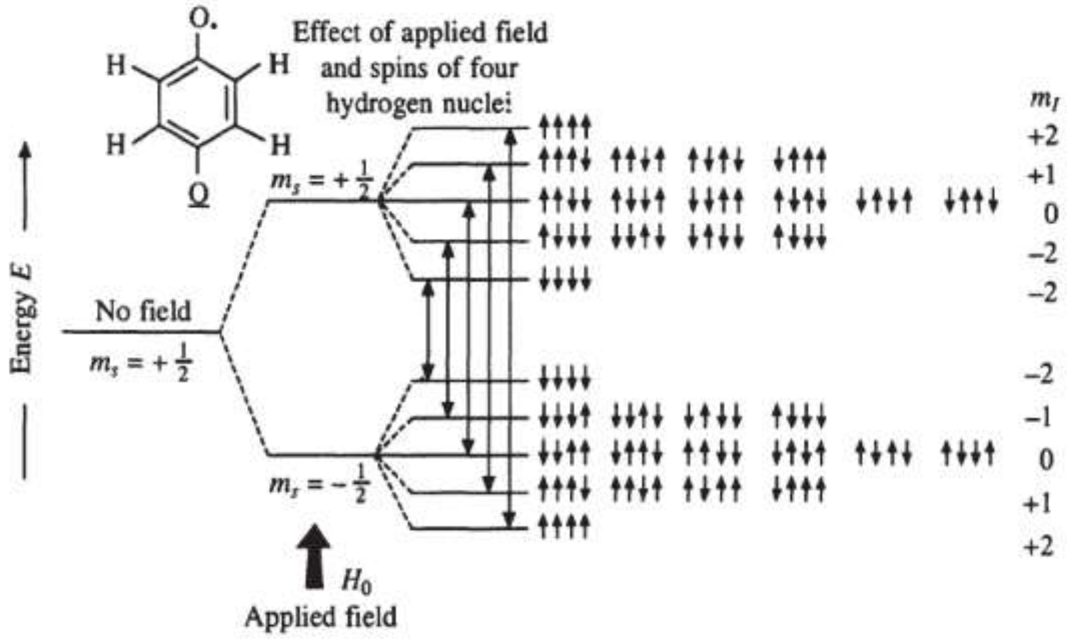


Energy level diagram illustrating coupling between the spins of the unpaired electron and hydrogen nuclei in methyl radical

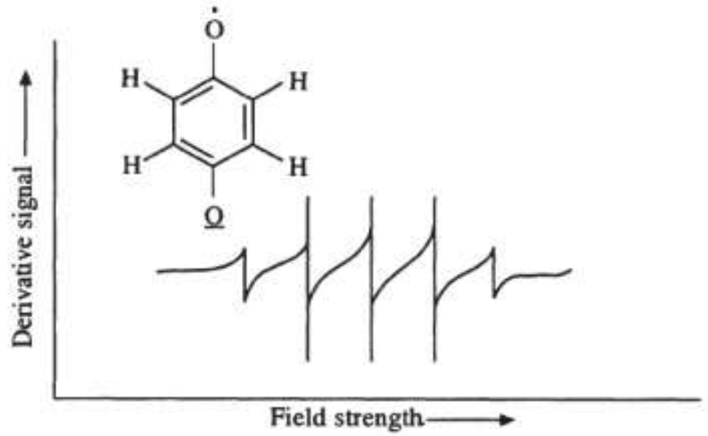


First derivative ESR spectrum of methyl radical

(iii) 1,4-benzosemiquinone

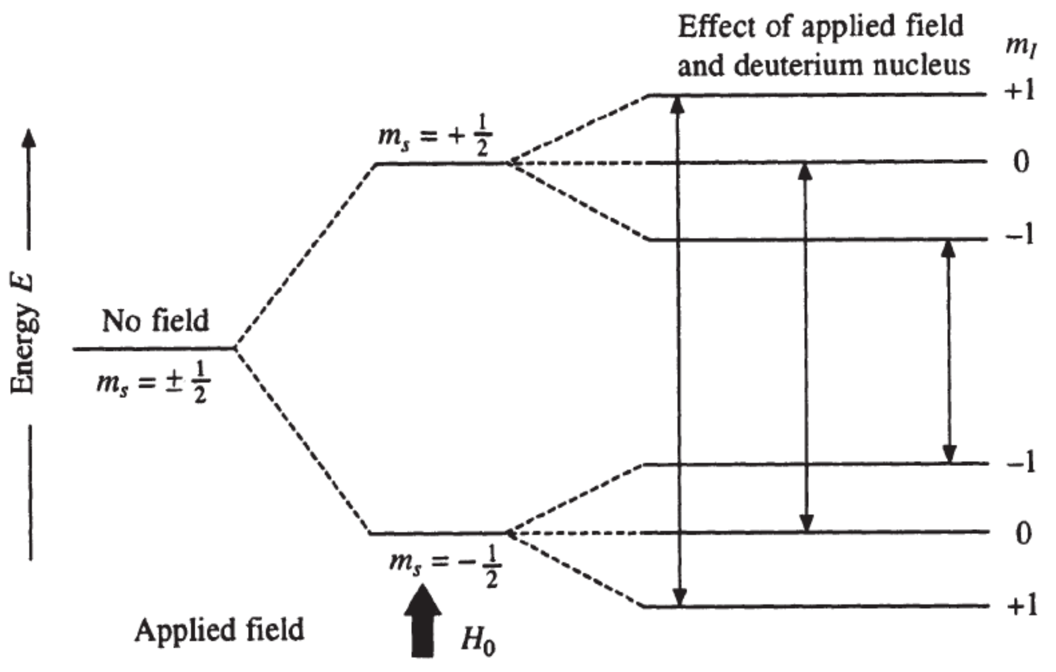


Energy level diagram illustrating coupling between the unpaired electron and the four protons in 1,4-benzosemiquinone

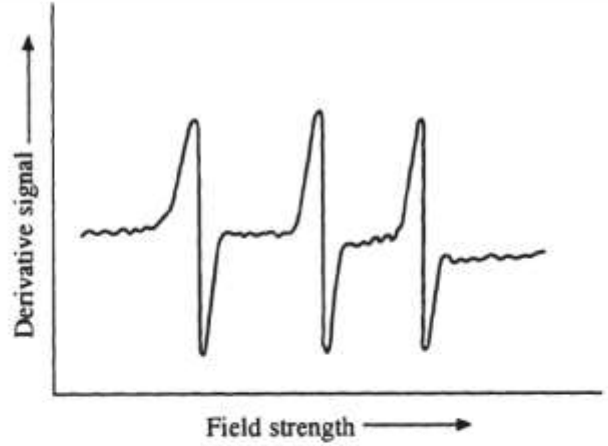


(b) first derivative ESR spectrum of 1,4-benzosemiquinone

(iv) Deuterium atom

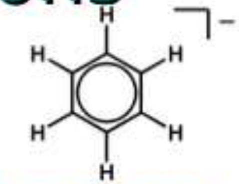


Energy level diagram illustrating coupling between the unpaired electron and deuterium nucleus



First derivative ESR spectrum of deuterium atom

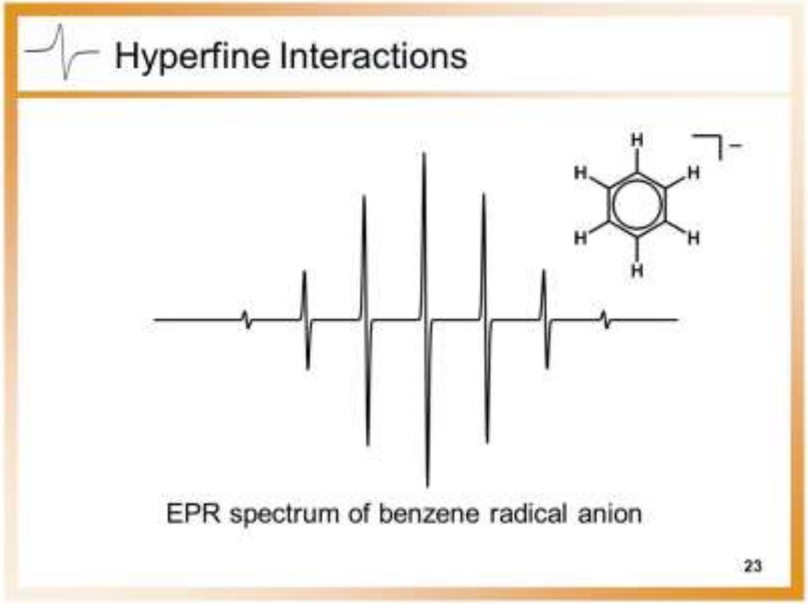
Hyperfine Interactions



- **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

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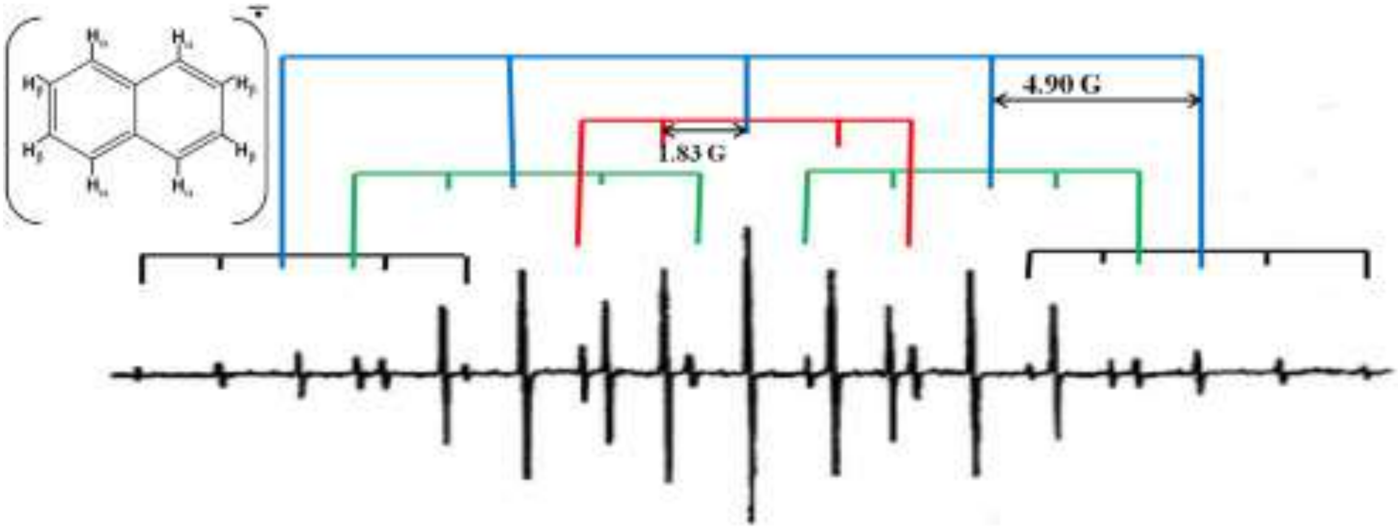
Naphthalene anion

One of the first aromatic organic radical anions studied by ESR spectroscopy was the naphthalene anion, the spectrum of which is shown in Figure.

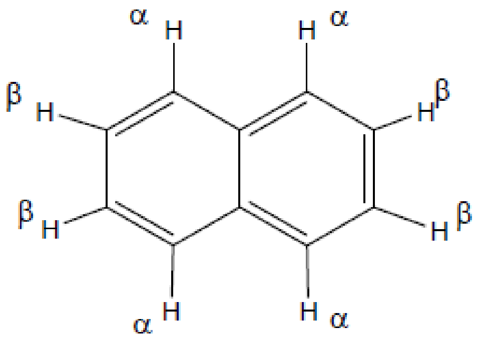
This **radical anion consists** of one unpaired electron interacting with two sets (α and β) of four equivalent protons each.

The ESR spectrum would thus show, i.e., $(2nI_1 + 1) \times (2nI_2 + 1) = (4 + 1) \times (4 + 1) = 25$ lines.

A quintet of quintets as expected for hyperfine coupling to two sets of four equivalent protons.



(ii) **Nephthaline (radical anion)**



Aα = 4.90

Aβ = 1.89

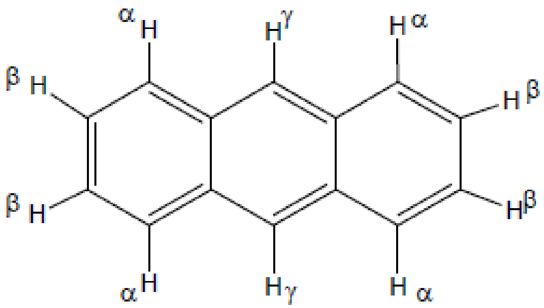
First splitting = 2nI + 1

n = Hα hydrogen = 2×4×1/2+1 = 5

Hβ hydrogen = 2×4×1/2+1 = 5

Total lines = 5×5 = 25 lines

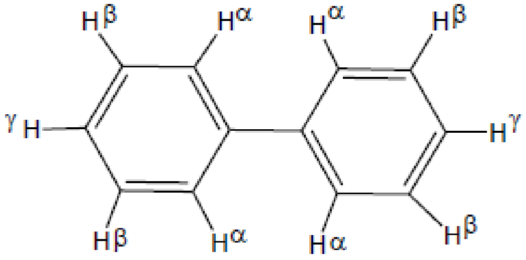
(iii) **Anthracene radical anion**



Total lines = (2nI+1) (2nI+1) (2nI+1)

= 75 lines

(iv) **Total lines and ESR in biphenyls radical anion**

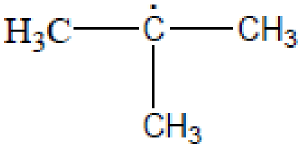


2γ> Hα > Hβ

(2×2×1/2+1)×(2×4×1/2+1)×(2×4×1/2+1) =

3×5×5 = 75 lines

(v) ESR lines and butyl radicals



$H_3C-\dot{C}(CH_3)-CH_3$

Total lines = 2×9×1/2+1 = 10 lines

(vi) ESR lines for $^{13}CH_3^{\cdot}$

Total lines = (2×1×1/2+1) (2×3×1/2+1) = 2×4 = 8 lines

(vii) ESR lines in $CD_3^{\cdot}$

I = 1, Total lines = (2×3×1+1) = 7 lines

(viii) $CF_2H^{\cdot}$

I = 1/2, Total lines = (2×2×1/2+1) (2×1×1/2+1) = 2×3 = 6 lines

$^{13}CF_2H^{\cdot}$

Total lines = (2×1×1/2+1) (2×2×1/2+1) (2×1×1/2+1) = 2×3×2 = 12 lines

(ix) $CH_3CH_2^{\cdot}$

Total lines = (2×2×1/2+1) (2×3×1/2+1) = 3×4 = 12 lines

Anisotropy in hyperfine coupling

- ESR spectra can be obtained for neutral free radicals in the gas phase and for radicals or ions in the liquid/solid phase.
- Spectra in the gas phase are complicated because excited rotational states are populated. Simple spectra were obtained for the halogen atoms in the gas phase.
- Six lines were obtained for ‘F’ and twelve lines for ‘Cl’ and ‘Br’.
- Rotational states in condensed media are non-quantized and orbital contributions are largely quenched.
- Therefore a complication not arises in the case of ESR spectra obtained on samples in solution or in solid state. When the absorbing species is rotated rapidly in all directions and has a spherical symmetry, then the g-value and hyperfine coupling constant is isotropic.
- The energy of the transition ‘E’ is given by

$$\mathbf{E = h\upsilon = g\beta H_o + AM_I}$$

- When a radical is rigidly held in solid matrix or in a crystal, the electron may be subjected to magnetic anisotropies and this lead to anisotropy in the hyperfine coupling constant and g-value. The energy of the transition ‘E’ is rewritten to take account of anisotropy in both ‘g’ and ‘A’ is

$$\mathbf{E = h\upsilon = (1/3g_{ll}+2/3g_{l})\ \beta H_o + AM_I + [1/3\ (g_{ll}-g_{l})\ \beta H_o + BM_I]\ [3cos^2\Theta-1]}$$

Where, Θ = angle between the direction of magnetic field and z-axis

A = Isotropic coupling constant

B = Anisotropic coupling constant

- In a powdered sample the crystals are randomly oriented and wide range of angles are present. The spectra of such samples are usually broad.
- In these cases where the anisotropic contribution is important, the magnitude of the coupling constant depends on the direction of the external field. Example (NO_2 in an Argon matrix).
- The spectrum contains three lines from the ‘N’ hyperfine interaction with variable width indicating anisotropy in both ‘g’ and the hyperfine splitting.

Double resonance in ESR

The concept of double irradiation in ESR spectroscopy is exactly parallel to that in NMR, i.e. observation of a spectrum at one frequency while simultaneously irradiating at another. The two possibilities for double resonance in ESR spectroscopy are

- ENDOR and
- (ii) ELDOR.

(i) ENDOR (Electron Nuclear Double Resonance)

- In ENDOR technique, a microwave frequency suitable for electron spin resonance and a radio frequency suitable for nuclear spin resonance are simultaneously required.
- In an ENDOR experiment, the sample is irradiated with a fairly intense microwave radiation to reach microwave saturation (i.e. an ESR transition $\Delta m_S = \pm 1$ is saturated) and at the same time the radio frequency is swept slowly upwards so that an NMR transition $\Delta m_I = \pm 1$ occurs. This causes partial desaturation of the ESR transition ($\Delta m_S = \pm 1$) which results in the observation of an ENDOR signal in the ESR spectrum.
- Thus, the ENDOR can be considered as a special variety of NMR where the unpaired electron serves as the detector. The ENDOR technique is used for improving the effective resolution of an ESR spectrum.

The following are the main applications of the ENDOR technique:

(a) There is broadening of ESR signals due to large variety of nuclear energy levels. Thus, the spectral structures which contain important physical and chemical information are masked. In such cases the ENDOR technique is useful for revealing the desired information. For example, nuclear couplings are much easier to observe in ENDOR spectra than that in usual ESR spectra.

(b) If hyperfine structures are resolved but more precise values of coupling constants are desired, then these are more accurately measured from the sharper spectral lines given by ENDOR.

(c) In cases where an unpaired electron is coupled with a nucleus having a spin number $I \geq 1$, the ESR signal is split into $2I + 1$ lines. This splitting gives a complex spectrum if resolved or a very broad signal if unresolved. In such cases, the ENDOR spectrum is much simpler because whatever the spin number of the coupled nucleus, its resonance is split only into a doublet by coupling with the single electron. Thus, the ENDOR method is also used for measuring quadrupole coupling constants in a system with spin number $I \geq 1$.

(ii) ELDOR (Electron-Electron Double Resonance)

- In ELDOR technique, the sample is irradiated simultaneously with two microwave frequencies. One of these frequencies is used to observe an ESR signal at some point of the spectrum while the other is swept through other parts of the spectrum. Thus, the ESR signal height is displayed as a function of the difference of the two microwave frequencies. This technique is used for resolving overlapping multi-radical spectra and for studying relaxation mechanisms. The ELDOR method has been used for very precise measurements of the coupling constants of DPPH.

Zero field splitting

- When a metal ion is placed in a crystalline field, the degeneracy is resolved for d-orbitals due to electrostatic interactions. The spin degeneracy will remain until a magnetic field is applied. When the species contains more than one unpaired electron the spin degeneracy can also be resolved by the crystal field. The spin level may be split even in the absence of magnetic field. This phenomenon is known as zero field splitting.

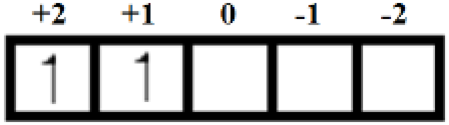
- Transition metal having more than one unpaired electron, that shows zero field splitting. For example (V^{3+} and Ni^{2+} - d^2 configuration) the system having two unpaired electrons, which arranged according to Hund's rule of maximum multiplicity,

$S = S_1 + S_2$

$S = 1/2 + 1/2 = 1$

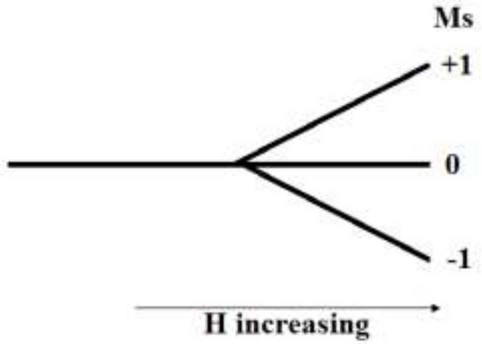
Spin multiplicity $2S+1 = 3$

$m_S = +1, 0, -1$

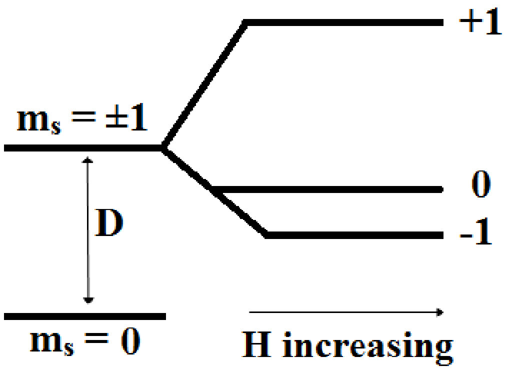


- If only exchange and electrostatic interactions existed in the molecule, three configurations $m_S = +1, 0, -1$ would be degenerate in the absence of a magnetic field. The magnetic field would remove this degeneracy and a single transition would be observed for the case $S = 1/2$.

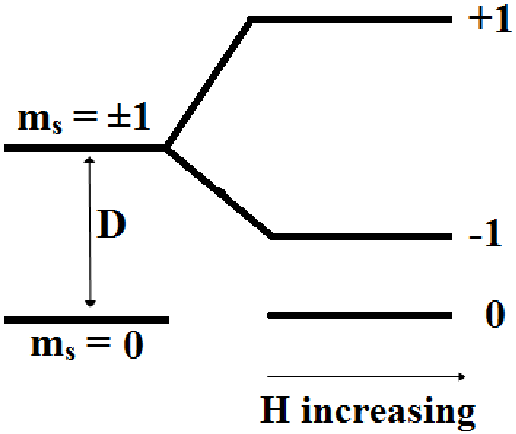
However magnetic dipole-dipole interaction between the two unpaired electrons removes the degeneracy of the m_S components of S = 1 even in the absence of an external field. This removal of degeneracy in the absence of the field is called zero field splitting.



When the magnetic field is applied, the levels are split so that two $m_S = \pm1$ transitions can be detected. Two peaks are observed for the ESR spectrum of the triplet state. Two of these are the $m_S = \pm1$ transitions. The third is $m_S = 0$ transition which becomes allowed only when the zero field splitting is small compared to the microwave frequency.



When zero field splitting is very large, the m_S values becomes valid quantum numbers and the energies for the $\Delta m_S = \pm1$ allowed transitions becomes too large to be observed in the microwave region; accordingly no spectrum is seen.

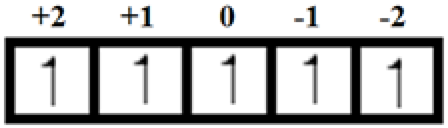


Kramer’s degeneracy

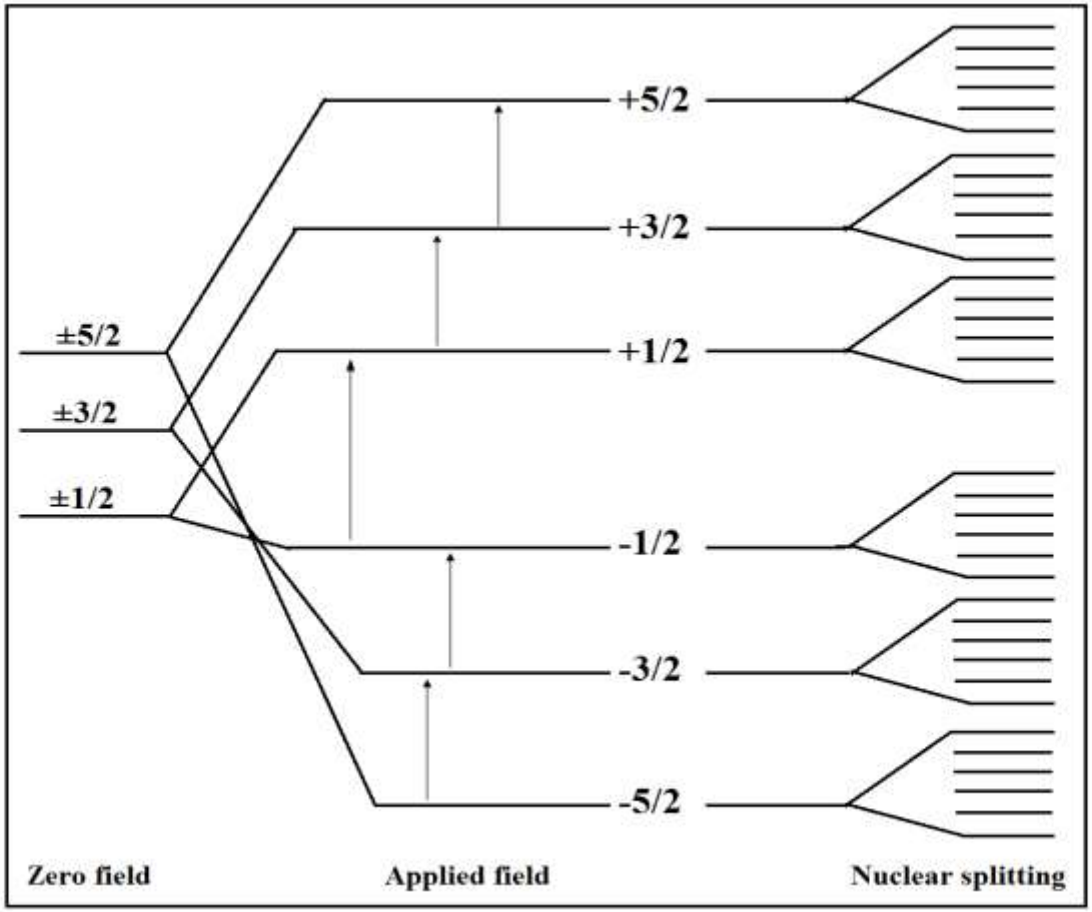
- When the species contains odd number of unpaired electrons, the spin degeneracy of each level remains doubly degenerate. This is known as Kramer’s degeneracy. For an even number of unpaired electrons the spin degeneracy may be removed entirely by the crystal field. For example, In Mn^{2+} (d^5-configuration) because of the presence of odd number of unpaired electrons Kramer’s degeneracy must exist. The zero field splitting produces three doubly degenerate spin states i.e. $m_S = \pm 5/2, \pm 3/2$ and $\pm 1/2$.

$$L = 0;\ s = 5 \times \tfrac{1}{2} = 5/2$$

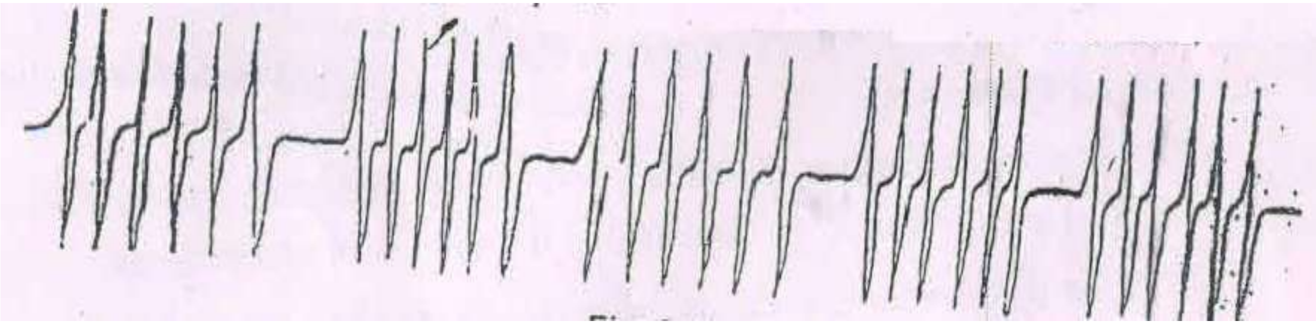
$$2S+1 = 2 \times 5/2 + 1 = 6$$



- The ground state term symbol is 6S. The splitting of the 6s state of an octahedral Mn(II) complex is shown below. Each of these is split into two singlets by the applied field producing six levels. As a result five transitions are expected. The spectrum is further complicated by the hyperfine splitting due to manganese nucleus (I = 5/2). Thus 5 peaks each split into six hyperfine components are expected. This would rise to thirty peaks in the spectrum.



±5/2
±3/2
±1/2
+5/2
+3/2
+1/2
-1/2
-3/2
-5/2
Zero field
Applied field
Nuclear splitting



EPR spectra of transition metal complexes

EPR spectra of transition metal complexes is complicated because

- They have several degenerate orbitals and unpaired electrons.
- There is anisotropy in g-factors.
- There exist zero field splitting.
- In a complex the orbitals do not interact equally with ligands and the energy levels are split into two or more groups. For example, in a octahedral complex there are 3t_{2g} lower levels and two e_g upper levels.

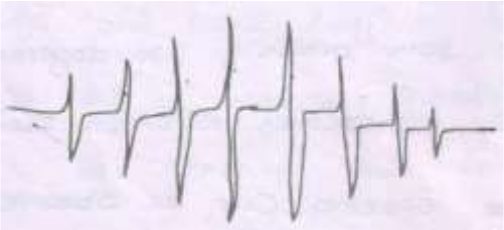
For octahedral first row transition metal complexes, the crystal field energy is greater than the spin orbit interaction energy. For understanding the EPR spectrum the following points must be considered.

- Number of d-electrons in the metal.
- To identify whether it is a low spin or high spin complex.
- Effect of Jahn-teller distortion.
- Zero field splitting and Kramer’s degeneracy.

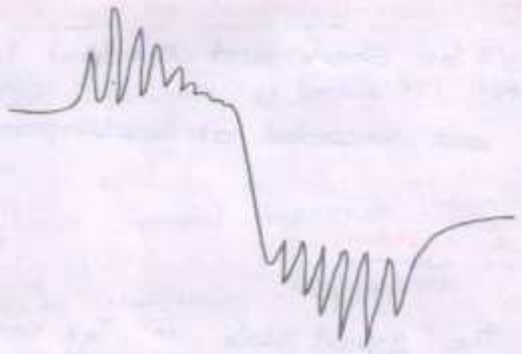
For heavier atoms due to zero field splitting it is difficult to observe and interpret the EPR spectrum. For example, second and third row transition metal complexes.

d^1 system

- In an octahedral field, the ground state is t_{2g} and in tetrahedral field, the ground state is e_g. **There is a large spin-orbit coupling which leads to a short spin relaxation time for the electron and will results in broad absorption lines.** Therefore the complexes are studied at liquid helium temperature. For example,
- The EPR spectrum of $[VO(glycolate)_2]^{2-}$ in water (V, I=7/2) shows eight equispaced lines, since the system is isotropic. There is only one g value.



- For vanadyl complex of d,l-tartrate at room temperature, two sets of spectral lines are observed. One with $g_{11}>g_e$ and another with $g_1<g_e$.



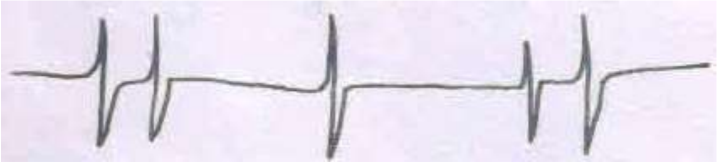
In frozen solutions peaks at three different places are observed, since it is anisotropic with three g values of g_{xx}, g_{yy} and g_{zz}.

d^5 low spin S=1/2

Low spin ferric haemoglobin (Fe^{3+}) has large deviations from octahedral symmetry. These deviations cause an orbitally singlet state to have lowest energy and well remove from orbitally non degenerate excited states. This increase electron relaxation time and hence the spectra can be observed at higher temperature. There exists large anisotropy in g values. They arise due to the interaction of iron d-orbital with a nitrogen π-orbital from the coordinated histidine group, which ties the globin to the heme unit.

d^5 high spin S=1/2

- **For an undistorted octahedral iron (III) complex, the zero field splitting is very small**. Therefore there are only three transitions, two of them are doublet and another one is a singlet.



- In iron (III) complexes with **small tetragonal distortions the zero field splitting is very small**. The g values are very close to 2.00 because of small amount of spin-orbit coupling. Therefore EPR spectrum is observed at room temperature.
- In some iron (III) complexes the zero field splitting is very large and hence only one transition between +1/2 and -1/2 states will be observed. Therefore only one peak is observed in EPR spectrum.

For example, Na[Fe(EDTA)].$4H_2O$ complex shows one isotropic transition at g=4.27 and two anisotropic transition ate g=9.64 and 1.10

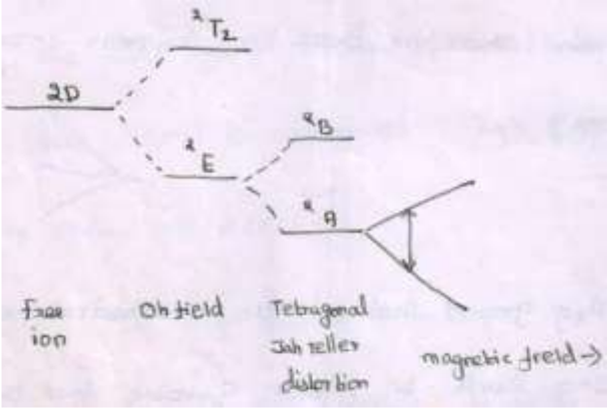
d^7 high spin S=3/2

- The ground state for an octahedral high spin complex is T_{1g}. Due to large spin-orbit coupling; EPR measurements are possible only at low temperature. At low temperature only the low lying doublet spin state is populated. Therefore only one signal is observed. $[CoF_6]^{4-}$ - gives a sharp peak at 20 K.
- In tetrahedral symmetry, A_2 ground state is closer in energy with excited T_2 states. Due to more spin-orbit coupling, broader lines are observed for Co(II).

d^7 low spin S=3/2

- For low spin complexes S=1/2, the ^2E state becomes lowest in energy. In ^2E state, there is no spin-orbit coupling. There are no nearby doublet states. Therefore electron spin life times are long leading to narrow EPR lines at liquid nitrogen and room temperatures.
- The EPR spectra of O_2 adducts of Co(III) complexes show that the unpaired electron resides mainly on O_2. There is also metal hyperfine coupling. The extent of electron transfer from Co(III) to O_2 has been estimated from the anisotropic cobalt hyperfine coupling constant.
- For an octahedral high spin d^7 Co(II) ion, there are three lines in the EPR spectra due to zero field splitting. The ground state is T_{1g}. Jahn-Teller splitting will give $m_s = \pm 3/2$ and $\pm 1/2$ levels. Therefore three lines appear from $\Delta m_s = \pm 1$ transitions.

- **d^8 system**
- Ni(II) has A_{2g} ground state in an octahedral field. Spin-orbit coupling leads to greater g value than that for a free electron and splits A_{2g} configuration. This is because of the zero field splitting and it is very anisotropic. Therefore EPR spectra of Ni(II) octahedral complexes are difficult to detect.
- The Ni(II) square planar complexes are diamagnetic in nature. Therefore EPR spectra are not recorded for them. They are used to dilute the spins of copper (II) complexes.
- **d^9 system**
- The ground state of an octahedral d^9 system is E_g. Since there is large Jahn-Teller distortion, the spectrum is recorded at room temperature.
- In tetragonal complexes the ground state is ^2A which will give sharp EPR lines. The square planar complex has the same symmetry as tetragonally distorted octahedron. So there are two resonances with g_{11} and g_1.
- For example, Cu(II) tetraphenyl phorphine complex consists of four groups of parallel resonances, three are seen at low field.

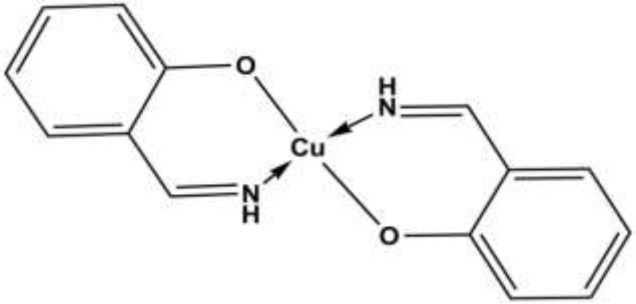


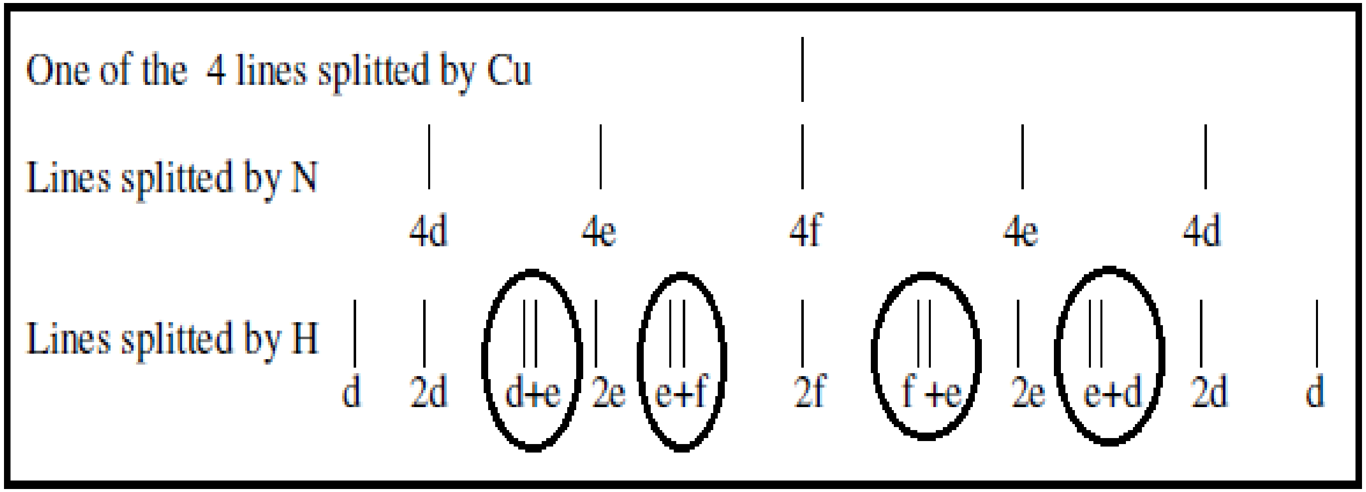
(i) EPR spectrum of Bis salicylaldiminecopper(II) complex

- Bis salicylaldiminecopper(II) complex : CuL_2 ; L = Salicylaldimine = C_6H_4 CHO = NH

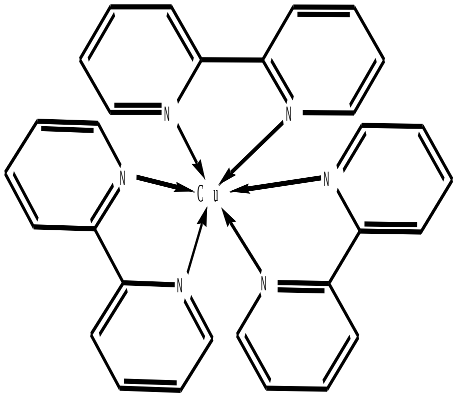
  {Bi dentate ligand with O & N as donors) [I : Cu = 3/2 ; N = 1 ; H = ½]

- The spectrum was obtained on a solid and is not isotropic. Four main group of lines result from coupling of the ^{63}Cu nucleus (I = 3/2) with the electron. But, due to overlapping, we get 44 lines as 4 set each consisting of 11 lines. The intensity of lines in each set is in the ratio 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1.



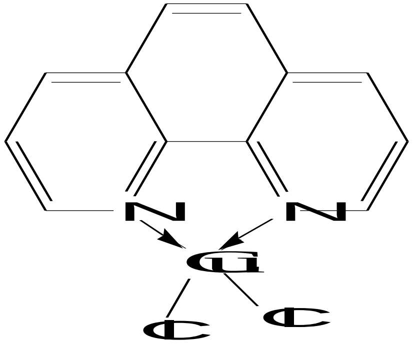


(ii) EPR spectrum of $[Cu(bpy)_3]^{2+}$



- When one electron couples with ^{63}Cu (For Cu, I = 3/2) four lines of equal intensity are obtained. 2nI+1 = 2(1)(3/2) +1 = 3 + 1 = 4.
- Each bipyridyl ligand contains 2 N atoms. The electron on Cu also couples with these 6 N atoms to give 13 lines each. (for N, I = 1), 2nI+1 = 2 (6) (1) +1 = 13.
- **Total lines = 4 x 13 = 52 lines are obtained.**

(iii) EPR spectrum of $[Cu(Phen)Cl_2]$,



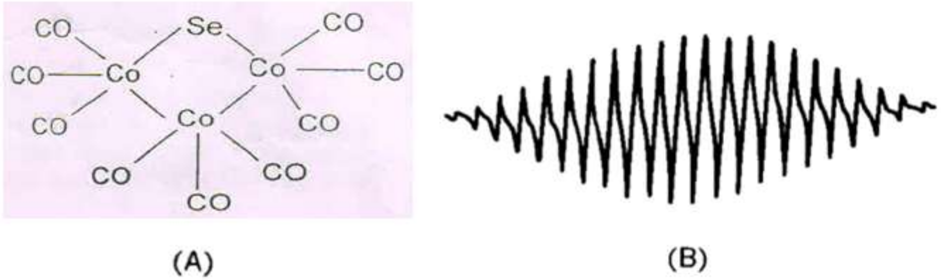
- When one electron couples with ^{63}Cu (I, Cu = 3/2) four lines of equal intensity are obtained, 2nI+1 = 2(1)(3/2) +1 = 3 + 1 = 4.
- 1,10-phenanthroline ligand contains 2 N atoms. The electron on Cu also couples with these 2 N atoms to give 13 lines each, 2nI+1 = 2 (2) (1) +1 = 5.
- Total = 4 x 5 = 20 lines are obtained.
- If ^{35}Cl, I = 3/2, also interact, this will further split the spectrum into 7 lines (2nI+1 = 2(2)(3/2)+1 = 7).
- **Total 4 x 5 x 7 = 120 lines are expected.**

(iv) EPR spectrum of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+}$

- The EPR spectrum of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+}$ consists of 15 lines. There are four possibilities.
- Two Co(III) is connected by O_2 bridge. In this case a **single line** is expected.
- Co(III) and Co(IV) are connected by means of peroxo bridge O_2. In this case **8 lines** are expected. I = 7/2 for Co.
- Two equivalent Co atoms owing to equal interaction of one unpaired electron with both cobalt atoms. Therefore **15 lines** are expected (2 x 2 x 7/2 + 1).
- Interactions of electrons with both Co atoms but more with one than with other. In this case **64 lines** are expected.
- Among the four possibilities, **(i) and (ii) are most probable**. An ^{17}O hyperfine result would be required to determine the importance of structure (i).

(v) EPR spectrum of $Co_3(CO)_9Se$

- The EPR spectrum of this complex is given below. The 22-line spectrum indicates that the one unpaired electron in this system is completely delocalized over the three cobalt atoms. (I Co = 7/2). 2x3(7/2)+1=22.
- The intensity ratio is 1:3:6:10:15:21:28:36:42:46:48:48:46:42:36:28:21:15:10:6:3:1. This in effect gives rise to an oxidation state of +2/3 for each cobalt atom. For Se, I = 0, hence it does not give hyperfine splitting.

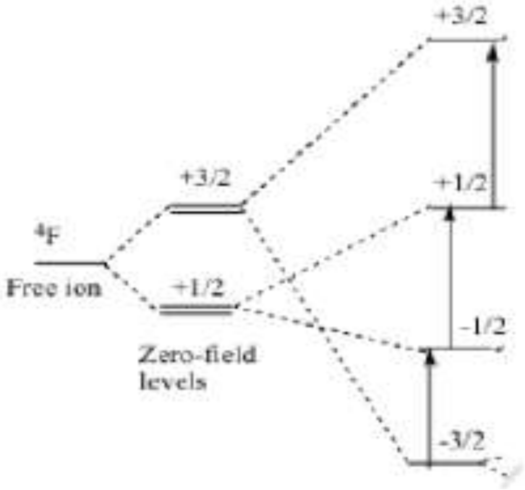


(A) Basic molecular geometry of the $Co_3(CO)_9Se$ complex.

(B) The EPR spectrum of a single crystal of $FeCo_2(CO)Se$ doped with about 0.5% of paramagnetic $Co_3(CO)Se$.

(vi) EPR spectrum of $Co_3(CO)_9Rh$

- Three ESR transitions are expected, but the electrons also couple with 3 Co atoms.
- For Co, I = 7/2, 2nI+1 = 2(3)(7/2)+1= 22).
- Rh (I=1/2) also couple and hence each line will be further split into a doublet, total 44 lines would be obtained.



(vii) EPR spectrum of $[CoF_6]^{4-}$

- $[CoF_6]^{4-}$, the unpaired electrons can also couple with 6 F ligands which are directly attached to give super hyperfine splitting, 2nI+1 = 2 x 6 (1/2) + 1= 7.
- Hence 3 x 8 x 7 = 168 lines are expected.
- Theoretically, $[CoF_6]^{3-}$ is expected to give 168 lines spectrum.

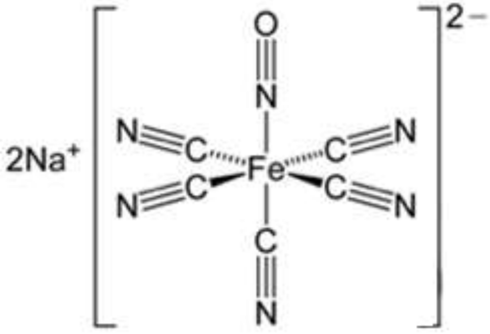
(viii) EPR spectrum of $[CrF_6]^{3-}$

- An unpaired electron on a Cr^{3+} couples to the Cr nucleus giving rise to an 8-line splitting pattern, $2I+1 = 2(7/2)+1= 8$.
- The unpaired electrons can also couple with 6 F ligands which are directly attached to give super hyperfine splitting, $2nI+1 = 2x6(1/2)+1= 7$.
- **So in $[CrF_6]^{3-}$, 3 x 8 x 7 = 168 lines are expected.**

(ix) EPR spectrum of $[VO(H_2O)_6]^{2+}$

- V(IV) has a $3d^1$ electron configuration and hence one unpaired electron. For vanadium, I = 7/2 (almost 100% abundant).
- The unpaired electron couples only to ^{51}V (^{16}O has I = 0), expected to give eight line pattern. But two overlapping eight-line patterns are obtained.
- This arises from the fact that one of the axes in the complex is different to the other two, resulting in the tetragonal spectrum, with a parallel and perpendicular component.
- For VO^{2+}, $g\parallel = 2.0023 - 8k\lambda/\Delta Ex2\text{-}y2$; $g= 2.0023 - 2k'\lambda/\Delta Exz, yz$
- Since λ is positive, both g_s are less than the free electron value: typical ranges are $1.97 > g\parallel > 1.93$ and $2.0 > g1> 1.96$.
- Many measurements are made on solution, when only the average g-value is obtained; this is usually reported as g_{iso}.

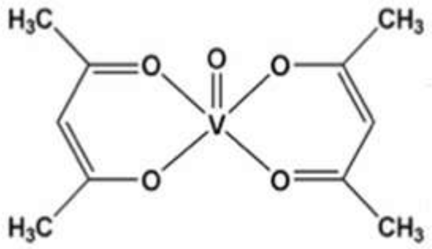
(x) EPR spectrum of $[Fe(CN)_5NO]^{3-}$

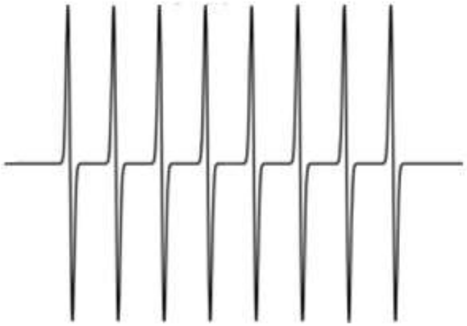


- The ESR spectrum of a solution of $[Fe(CN)_5NO]^{3-}$ consists of three equally-spaced hyperfine lines, while that of $[Mn(CN)_5NO]^{2-}$ has six hyperfine lines.
- Shows unpaired electron interacting with N (^{14}N, I=1) of NO ligand. (Fe is 98% I=0, and ~2% ^{57}Fe, I=1/2)
- The spectrum of $[Mn(CN)_5NO]^{2-}$ has six lines, showing electron interacting with ^{55}Mn nucleus (100%, I=5/2), but not with NO ligand.
- Consider NO as neutral (with one "extra" electron) or as NO^+ (isoelectronic with CN^-)
- So $[Fe(CN)_5NO]^{3-}$ is either an Fe(II) (d^6) complex with NO or an Fe(I) (d^7) complex with NO^+.
- Either way, there are 7 valence electrons. Six will occupy the t_{2g} orbitals and the seventh will be in an e_g orbital directed towards the ligands (i.e. towards the N in NO).
- $[Mn(CN)_5NO]^{2-}$ is either a Mn(III) (d^4) complex with NO, or a Mn(II) (d^5) complex with NO^+.
- Either way, there are 5 valence electrons. These will occupy the t_{2g} orbitals, and the unpaired electron will therefore be associated with the metal center.

(xi) EPR spectra of $VO(acac)_2$

- For vanadium, I = 7/2 (99.75% abundant). The unpaired electron couples only to V (O has I = 0), expected to give eight-line pattern. (2nI + 1 = 2(1)(7/2)+1=8), 8 lines of equal intensity are expected. (A = 120 G, g = 1.971)

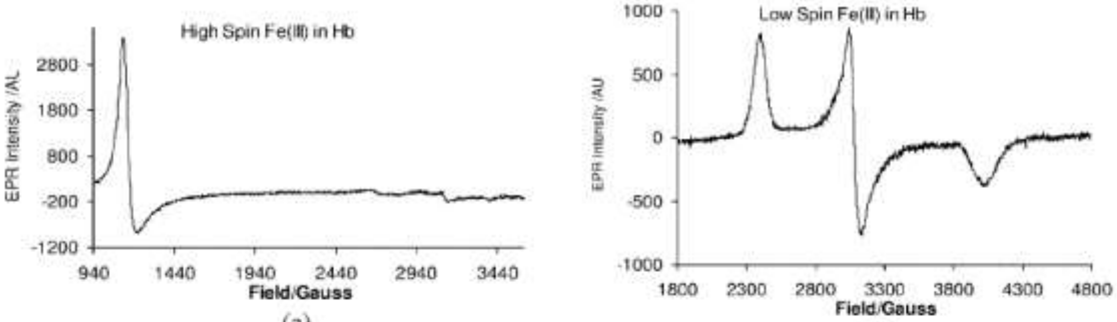




- At 298K, the EPR spectrum corresponds to an isotropic system and this is because the molecules are tumbling rapidly in solution and an average orientation is observed.
- On cooling to 77 K, the spectrum splits into two superimposed 8-line patterns.
- The two g values of 1.985 and 1.942 correspond to $g\parallel$ and g_1. The value at 298 K (g = 1.971) is in between the values of $g\parallel$ and g_1.

Iron proteins

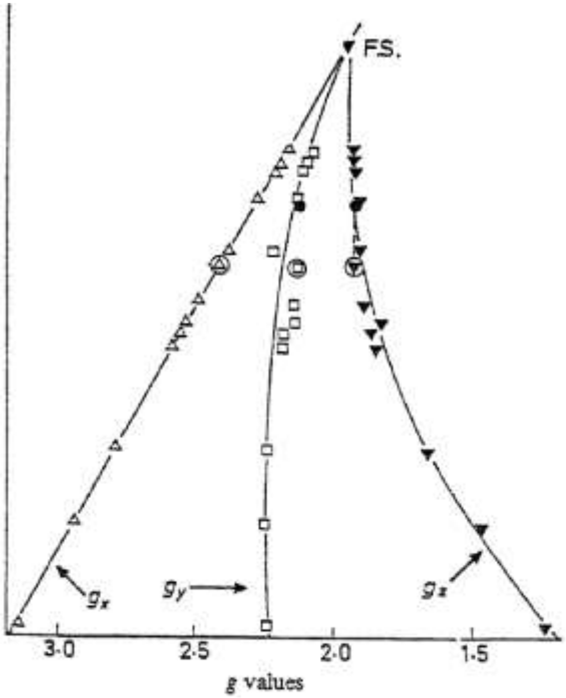
- Figure 1 show typical EPR spectra for Fe(III) derivatives of haemoglobin in high and low spin spectroscopic states. The X-band spectrum for high spin state shows strong features at $g = 6$ and a complimentary weak absorption at close to free spin, $g = 2$. High spin Fe(III) may also show up at $g = 4.3$ due to quantum mechanical mixed states.
- For the low spin form three lines can be observed at *g*-values of 2.82, 2.20, and 1.67, all of which arise from the same transition in axial symmetry exhibiting *gx*, *gy*, and *gz* orthogonal character of a tensor.
- As the ligand at the sixth coordination position changes, including pH effects, the symmetry of the central metal iron also changes creating distortions from rhombic to axial symmetry. This is a consequence of Jahn–Teller effect.



(a) (b)

Fig. 1. First derivative X-band EPR spectrum for methaemoglobin showing (a) high spin features of Fe^{III} at $g = 6$, low field, (b) low spin Fe^{II} features at $g = 2.855, 2.226$, and 1.794, mid-field.

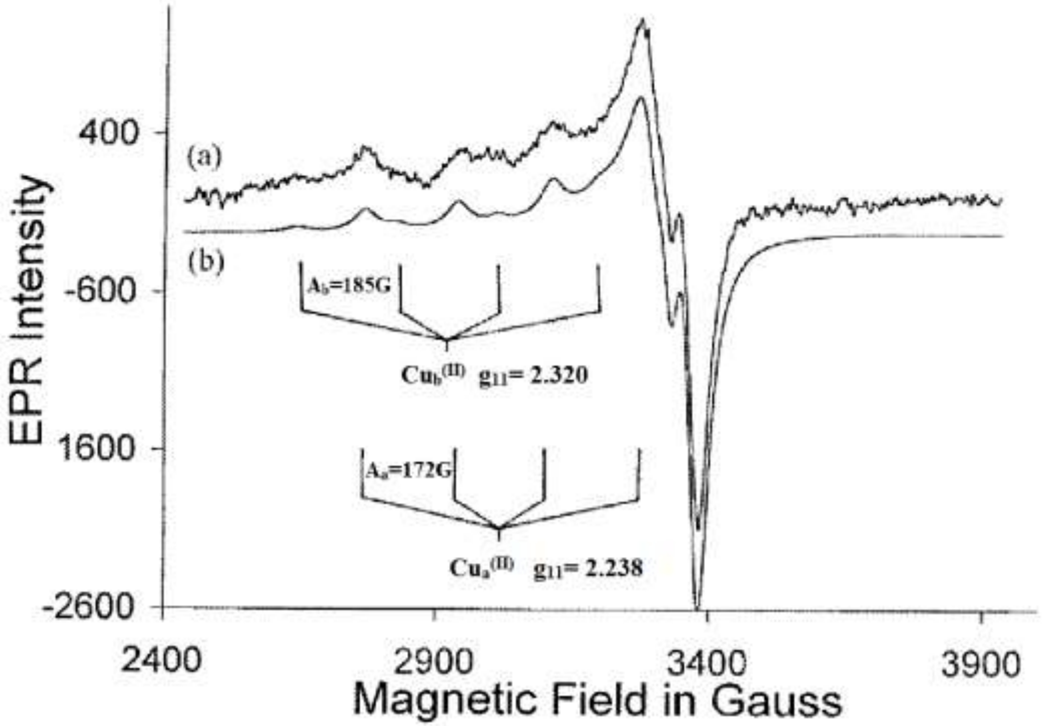
- If the *g*-values of low spin Fe(III) spectra were plotted to display *gx* in a linear format, the *gy* and *gz* have been shown to follow a trend as shown in Fig.2. The convergence point of all *g*-values is at ‘free spin’. This therefore is a display of EPR spectroscopic parameters as geometry changes from axial to rhombic symmetry.



Trends in the *g*-values for a range of low spin Fe(III) complexes showing convergence of *g*-values to ‘free spin’.

Copper proteins

The Cu(II),d^9 species contain an odd number of electrons to give a spin s = 1/2 and therefore EPR transitions. With a magnetic moment M_I = 3/2, Cu(II) gives a spectrum comprising a quartet of lines. Major parameters for copper in proteins are the parallel and perpendicular features arising from an axial type spectrum defined by g// and g⊥ and A// and A⊥. Typical spectra for Cu(II)II at 77 K are shown in figure.



It is important to note differences in EPR parameters of the two copper species indicating different Cu(II) centres by virtue of respective ligand environments. Some works have identified copper centres as type 1, type 2 and type 3.

- The type 1 has an intense blue coloration and a high extinction coefficient in its electronic absorption spectrum.
- The type 2 has a weaker absorption spectrum and higher hyperfine splitting constants (*A*-values) in its EPR spectrum than type 1.
- Type 3 comprises pairs of copper so close there is antiferromagnetic coupling and therefore not detectable by EPR spectroscopy.

However, since all the others such as ^{63}Cu (abundance 69%), have well defined hyperfine splitting, the absence of any splitting is a good signature for Fe(III) in biological conditions. The quartet of lines arising from $s = 1/2$, $M_I = 3/2$, is generally only resolved for the parallel features which come at low magnetic fields (high *g*-values), leaving the perpendicular feature unresolved with an intense peak representative of a combination of the *x* and *y* components.

Thank you