M.Sc. IVth Semester

Paper: CHM-404: Spectrochemical Analysis
Topic: Electron Spin Resonance (ESR) Spectroscopy

By

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ESR:

This technique is used for the species having unpaired electron (one or more), free radical, biradical, transition metal complexes and unstable paramagnetic species. ESR is shown by molecules, atoms, ions, free radicals having at least one unpaired electron. It was discovered by Zavoisky in 1944. A molecule which is ESR active observed radiation in the microwave region (0.1 cm to 100 cm) or 9000-10000 MHz (9-10 GHz). With the help of ESR spectra we can obtain the following information:

1. Local environment of the molecule
2. Electron distribution within the molecule
3. Magnitude of magnetic moment
4. Identification of free radicals
5. Determination of structure of molecules

The basic concepts of ESR are analogous to those of NMR, but it is electron spins that are excited instead of spins of atomic nuclei. Because most stable molecules have all their electron paired. ESR technique is less widely used than NMR. However, this limitations to paramagnetic species also means that the ESR technique is one of great specificity. Since ordinary chemical solvents and materials do not give rise to EPR spectra. EPR was first time observed in Kajan State University by Soviet physicist Yevgeng Zavoisky in 1944.

Theory/origin of an ESR Signal:

Every electron has a magnetic moment and spin quantum number s = 1/2 with magnetic components $m_s = +1/2$ and $m_s = -1/2$. In the presence of an external magnetic field with Bo, the electrons magnetic moment align itself either parallel ($m_s = -1/2$) or antiparallel ($m_s = +1/2$) to the field. Each alignment has a specific energy due to Zeeman effect: $E = m_s g_e \mu_B B_o$. The parallel alignment corresponds to the lower energy state and the separation between it and the upper state is $\Delta E = g_e \mu_B B_o$; where g_e is the electrons so called g factor or spectroscopic splitting factor or gyromagnetic ratio and also the Lande g factor. μ_B is the bohr magneton. This equation implies that the splitting of the energy level is directly proportional to the magnetic fields strength as shown in below figure.

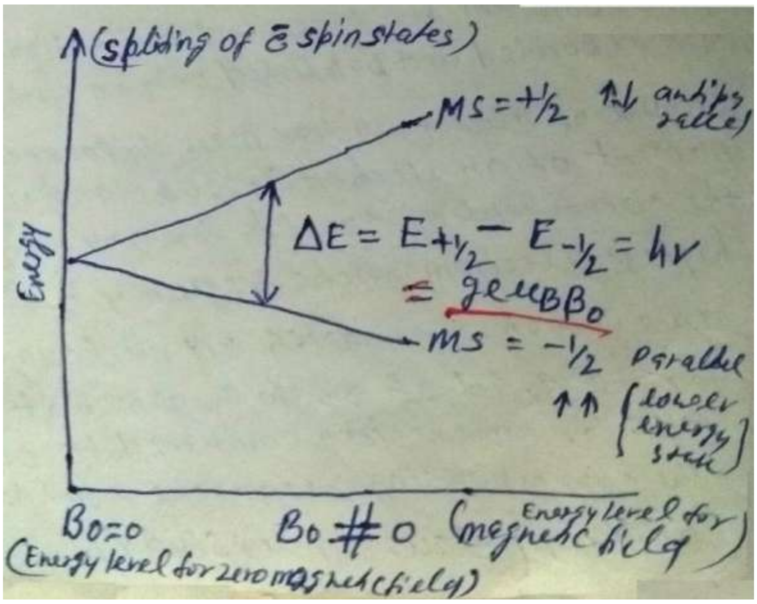


Fig.: Splitting of the energy level.

An unpaired electron can move between the two energy levels by either absorbing or emitting electron magnetic radiation of energy $\varepsilon = h\nu$ such that the resonance condition.

$\varepsilon = \Delta E$ is obeyed substituting in $\varepsilon = h\nu$ and $\Delta E = g_e\mu_B B_o$ leads to the fundamental equation of ESR spectroscopy.

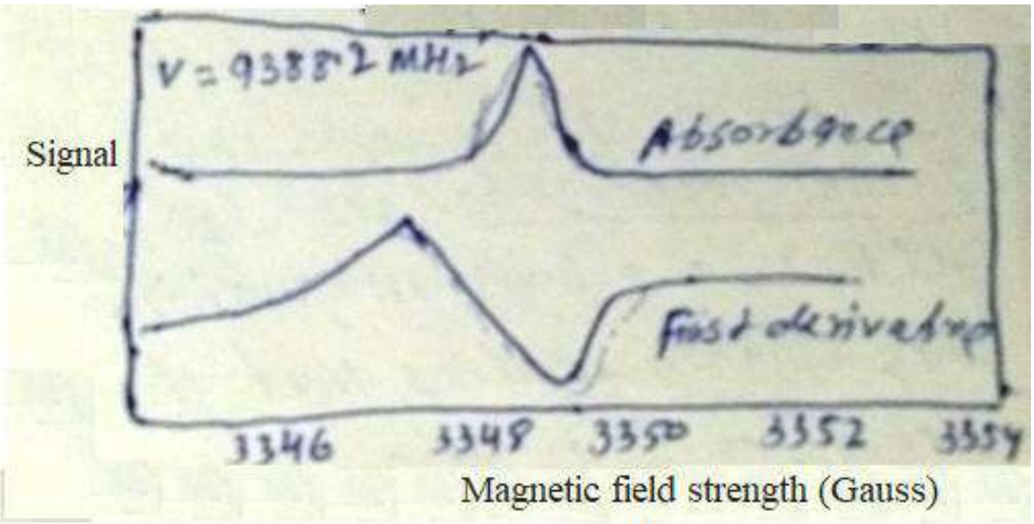
$$\boxed{h\nu = g_e\mu_B B_o}$$

Experimentally, this equation permits a large combination of frequency and magnetic field values, but great majority of EPR measurements are made with microwaves in 9000-10000 MHz (9-10 GHz) region with field corresponding to about 3500 gauss (0.35 Tesla).

ESR spectra can be generated by either varying the photo frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency which is kept fixed. A collection of paramagnetic centres such as free radicals is exposed to microwave at a fixed frequency.

By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened (enlarged or expanded) until it matches the energy of the microwaves as represented by the double arrow in the above diagram. At this point the unpaired electron can moves between their two spin states. Since there are more electrons in the lower state due to the Maxwell Boltzmann distribution (see below); there is a net absorption energy and it is the absorption which monitored and converted into a spectrum.

As an example of how $h\nu = g_e\mu_B B_o$ can be used. Consider the case of a free electron which has $g_e = 2.0023$ and the simulated spectrum shown at the right in two different forms. For the microwave frequency of 9388.2 MHz; the predicated resonance position is a magnetic field about $B_o = h\nu/g_e\mu_B = 0.3350$ Tesla or 3350 Gauss as shown. The two forms of the same spectrum are presented in the figure. Most spectra are recorded and published only on first derivatives. Because of electron-nuclear mass differences the magnetic moment of an electron is substantially larger than the corresponding quantity for any nucleus, so that a much higher magnetic frequency is needed to bring about a spin resonance with an electron than with a nucleus at identical magnetic field strength. For example, for the field of 3350 Gauss as shown in figure below, spin resonance occurs near 9388.2 MHz for an electron compared to only about 14.3 MHz for ^1H nuclei (for NMR, the corresponding resonance equation is $h\nu = g_N\mu_N B_o$, where g_N and μ_N depend on the nucleus under study).



When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two different spin states, $m_s = \pm 1/2$. The alignment can either be along the direction (parallel) to the magnetic field which corresponds to the lower energy states $m_s = -1/2$ or opposite (antiparallel) to the direction of the applied magnetic field $m_s = +1/2$. The two alignments have different energies and this difference in energy lifts ‘the degeneracy of the electron spin states. The energy difference is given by

$$\Delta E = E_{+1/2} - E_{-1/2} = h\nu = g_m\mu_B B$$

Where, h = planks constant (6.624×10^{-34} J-sec)

μ_B = Bohr magneton (9.274×10^{-24} JT^{-1})

B = strength of the magnetic field in Tesla

g = g factor (unit less)

ν = frequency of the radiation

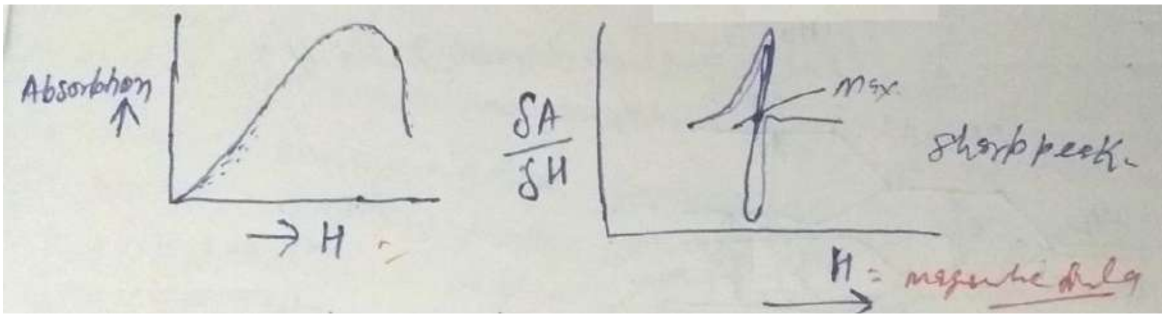
$$B = \frac{eh}{4\pi mc}$$

Presentation of ESR spectra:

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

$$g = 2.0023$$

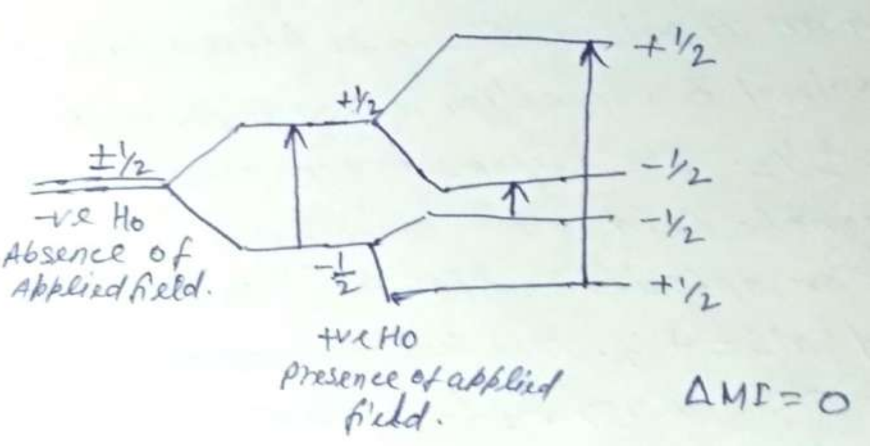
$\mu_B = 9.274\times10^{-21}$ erg/gauss



In the first representation we observed a broad peak which is less informative, that's we plot δA/δH vs H and obtained sharp peak informative.

Hyperfine splitting:

When a nuclei having I (nuclear spin quantum number) active characteristics (I greater than zero) is present it will show definite nuclear spin and there will be an interaction between nuclear spin and electron spin thus the ESR peak given by electron (unpaired) is splitted (proton and magnetically active nuclei), this is called hyperfine splitting and interaction is called hyperfine interaction.



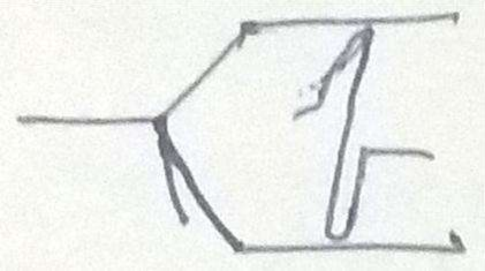
Selection Rule:

$\Delta MS = \pm1$
$\Delta MI = 0$

Hyperfine splitting means
= +1/2 to +1/2
-1/2 to -1/2
For each I, state of nuclear spin = -I to +I

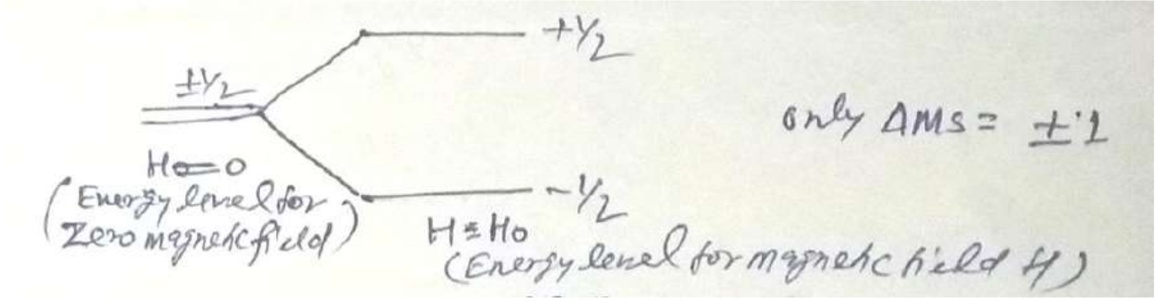
For e.g. if I = 1/2, then MI = +1/2, -1/2
I = 1, then MI = +1, 0, -1
I = 3/2, then MI = +3/2, +1/2, -1/2, -3/2
I = 5/2, then MI = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2

Example: (1) O_2^{16}, I = 0, 2nI + 1 = 2×1×0 + 1 = 1 peak

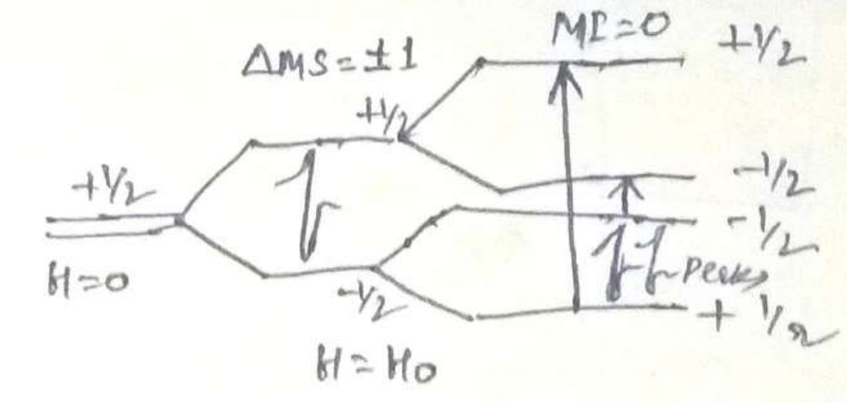


(2) Nitrogen, if I = 0

2nI + 1 = 2×0×1/2+1 = 1 line



If I = 1/2

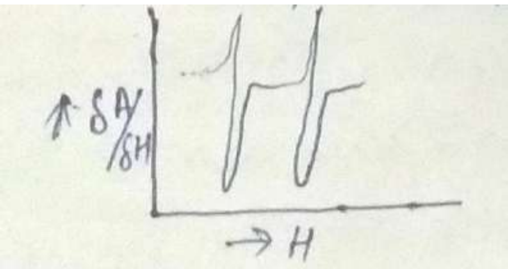


ΔMI = 0,	ΔMS = ± 1,
+1/2 to +1/2 = 0	-1/2 to +1/2 = 1
-1/2 to -1/2 = 0	+1/2 to -1/2 = -1

2nI + 1 = 2×1×1/2+1 = 2 lines

Q. (a) Give the ESR spectra of H atom

H = 1 e^- and I = 1/2, 2nI + 1 = 2×1×1/2+1 = 2 lines



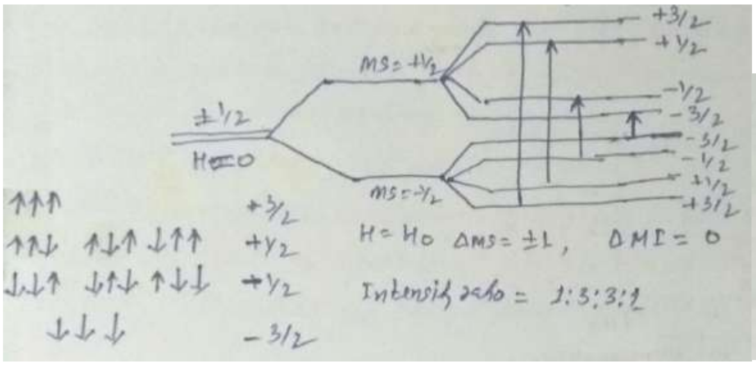
(b) Give the ESR spectra of $CH_3^{\bullet}$

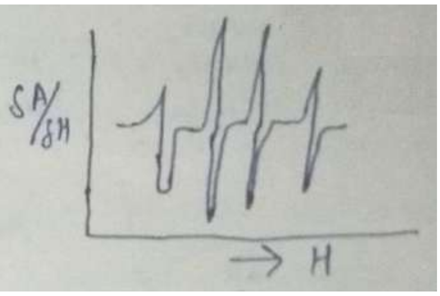
I = 1/2, 2nI + 1 = 2×3×1/2+1 = 4 lines

(c) Give the ESR spectra of $CH_3^{\bullet}$

I = 1/2, 2nI + 1 = 2×3×1/2+1 = 4 lines

One H = 1/2 = I
if I = 3/2 = +3/2, +1/2, -1/2, -3/2
if 3H = 1/2×3 = 3/2
MI = +3/2 to +3/2 = 0
+1/2 to +1/2 = 0
-1/2 to -1/2 = 0
-3/2 to -3/2 = 0





Hyperfine Interaction: The resonance frequency of an electron depends upon the magnetic field at the electron. Previously the applied magnetic field was assumed to be the field at the electron. Actually the electron is affected by both the applied magnetic field, H_o and any local fields due to the magnetic fields of nuclei or other effects H_{local}, so that equation: $\Delta E = h\nu = g\mu_B H$ may be written as

$$h\nu = g\mu_B(H_o + H_{local})$$

Which will cause transition between these energy levels. In distinction to other types of spectroscopy, in which the energy levels are essentially fixed, in ESR spectroscopy the splitting in energy levels and therefore, the frequency capable of causing transitions between these levels is a function of the magnetic field strength H.

The effect of the magnetic moments of nuclei on the ESR spectrum is called hyperfine interaction and leads to a splitting of the ESR line (hyperfine structure). Consider a hydrogen atom composed of an unpaired electron associated with a proton. Since the proton is a charged spinning particle with a nuclear spin I of 1/2, it has a magnetic moment and the electron will be affected by the magnetic field of the proton as well as that of the applied magnetic field.

The relative orientation of the nuclear magnetic moment and the electron magnetic moment causes a splitting of the original two levels to four levels (see figure below). Only two transitions are found between these states, so that transitions occur only between I = +1/2 or I = -1/2 states (i.e. the selection rule for the transition is ΔMI = 0). The result is a splitting of the original line into a doublet.

The magnitude of the splitting usually given in gauss is called the hyperfine coupling constant, a. For the hydrogen atom aH is about 508 gauss.

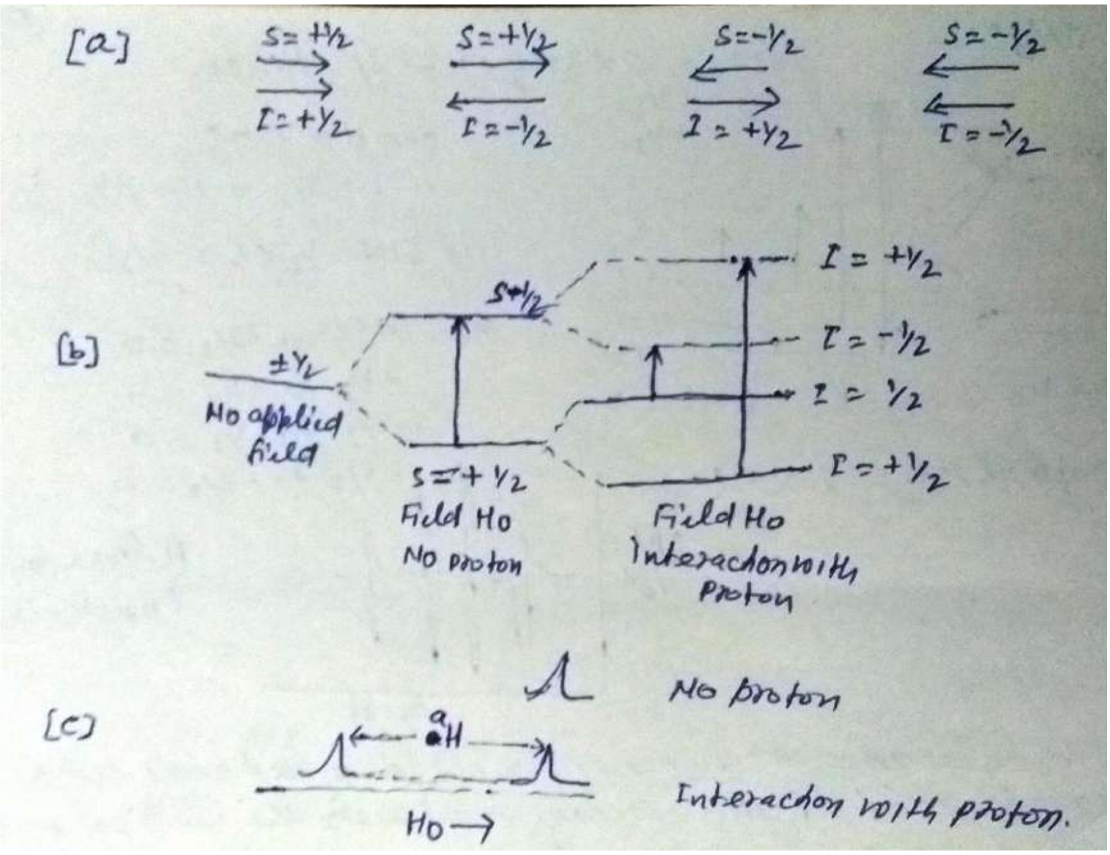


Fig.: Interaction of unpaired electron with one proton. [a] possible orientation of electron and nuclear magnetic moments. [b] splitting of energy levels. [c] splitting of spectral line.

In general, a single nucleus of spin I, will cause a splitting into (2I+1) lines, so that interaction with a single nitrogen nucleus (N^{14}, I = 1) will cause a splitting into three lines, and unpaired electron in manganese (II) (Mn^{55}, I = 5/2) interaction with the nucleus to form a six lines spectrum. Many common nuclei such as C^{12} and O^{16} have zero spin and do not interact with the electron.

For a system with the unpaired electron interacting with two equivalent protons a similar analysis shows that formation of a triplet occurs with relative intensities 1:2:1 (see figure below).

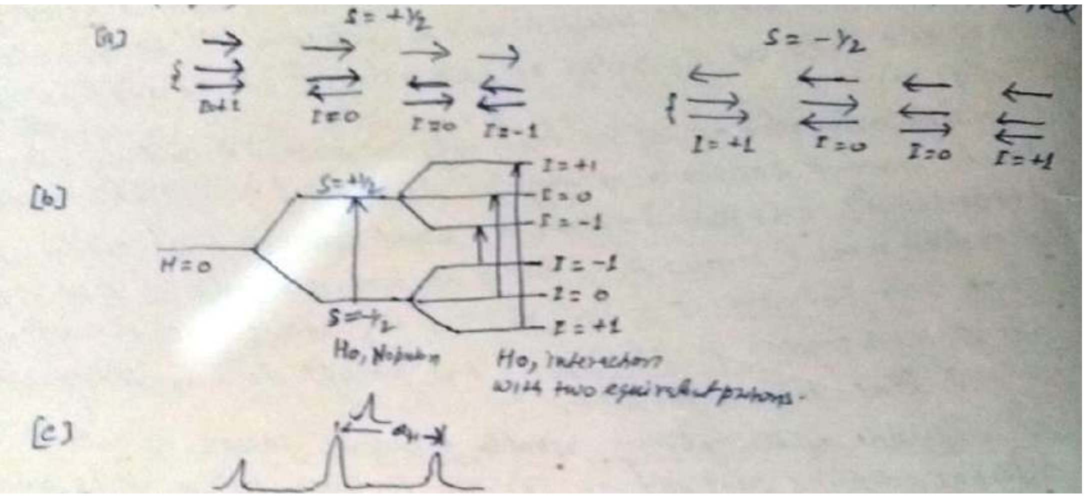


Fig.: Interaction of unpaired electron with two equivalent protons. [a] possible orientation of electron and nuclear magnetic moments. [b] splitting of energy levels. [c] splitting of spectral line.

The two protons may either both oppose or both act in the direction of the magnetic field causing the two extreme lines, or they may act opposite directions from one another, essentially cancelling their effect on the electron, resulting in the line located at the same position as the unperturbed line. Since this latter condition can occur in either of two ways, this centre line is twice as intense as the two extreme lines. Continuing an analysis in this way results in the general conclusion that n equivalent protons cause a splitting into nH lines; the relative intensities of these lines follow the binomial expansion.

For non-equivalent nuclei, each will interact with the electron with a different coupling constant to produce a hyperfine splitting. For example, if the electron interacts with one proton (H_1) with a coupling constant a_1 and another proton (H_2) with a coupling constant a_2, assuming a_1 is much larger than a_2, a doublet due to interaction of H_1, split into a doublet due to H_2 will results (H_1 and H_2 hydrogen numbering) (see figure below).

Similarly, the interaction of two equivalent hydrogens with a second pair of equivalent hydrogens results in a triplets for very different coupling constants.

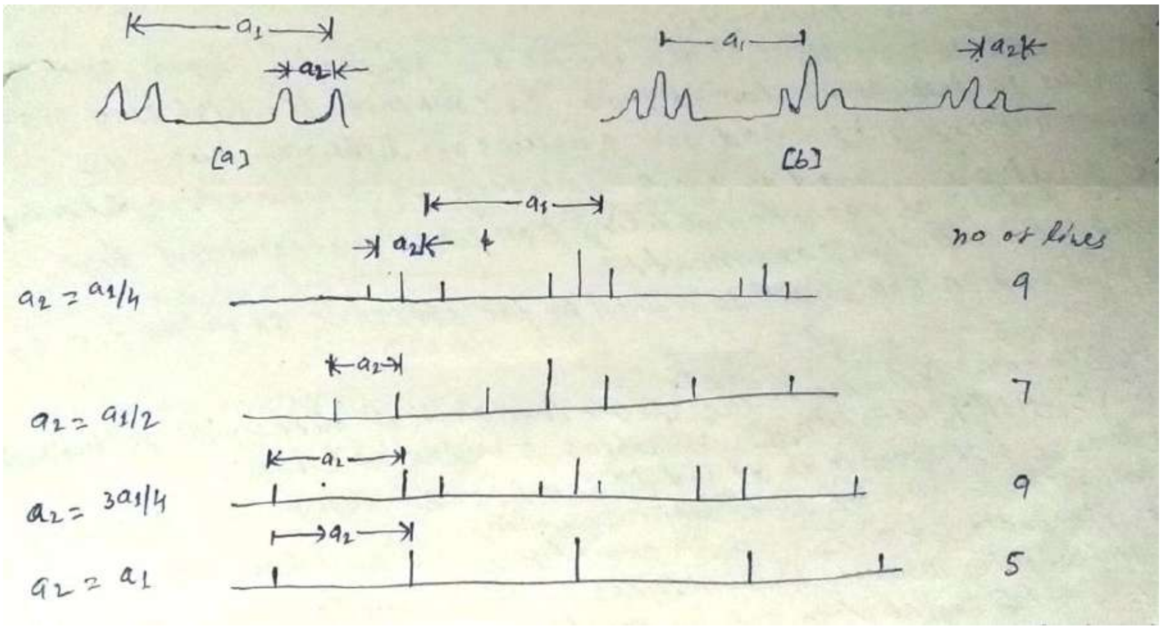


Fig.: A spectra due to interaction of unpaired electron with [a] two non-equivalent protons; [b] two non-equivalent sets of two equivalent protons; [c] variation of spectra for interaction of two sets of equivalent pairs of protons for different values of the coupling constants a_1 and a_2.

g-Value or factor affection g value: g-value in ESR is similar to chemical shift in NMR. For a free electron g = 2.0023. Transition metal complexes have extremely variable g values but broadly speaking less than 2.00 indicates the complex is electron poor often associated with higher oxidation states while greater than 2.00 is electron rich.

For example, in low spin Fe^{3+} the spectra one generally sharp and the g-value is close to 2.00. In contrast, the high spin (with 5 unpaired electrons) is broad and g-values are between 4.0-4.5. The g-value is affected by total electronic angular momentum, the orbital angular momentum and the spin angular momentum of the metal centre. The line pattern observed is temperature dependent. So the nature of magnetic coupling can been determined by temperature dependent measurement. The position of an ESR signal is defined by the effective g value i.e. by $g = \frac{h\nu}{\mu_B B}$.

A very common reference is the stable free radical diphenylpicrylhydrazyl $(C_6H_5)_2NN^{\bullet}\{C_6H_2(NO_2)_3\}$ for which g value = 2.0036. g values of ESR spectra of d^n and f^n complexes can differ greatly from 2.00, because of spin-orbit coupling. The effective g for an electron in a d^n complex will depend upon how much orbital angular momentum contributes to the magnetic moment and whether this orbital contribution acts in parallel or is opposed to the spin angular momentum.

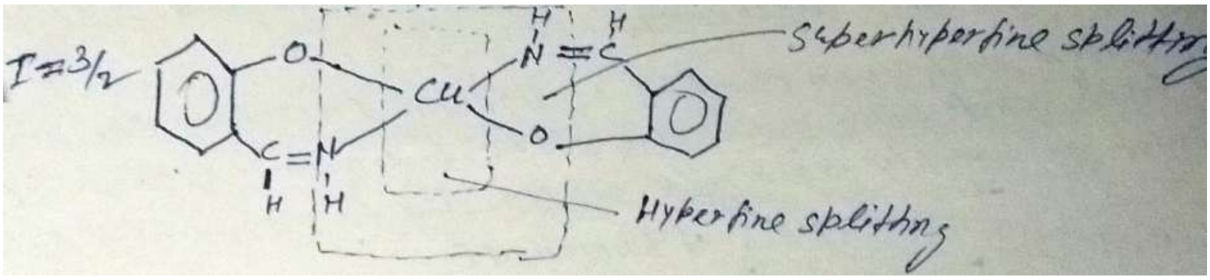
Example: V^{4+} (d^1) $g < 2.00$ (typically 1.9)
Cu^{2+} (d^9) $g > 2.00$ (typically 2.2)
Mn^{2+} (d^5) $g = 2.00$

Super hyperfine splitting

When nuclei and electron spin interacts then super hyperfine splitting takes place if further I active nuclei is present then hyperfine peaks are further splitted and this type of splitting is called super hyperfine splitting.

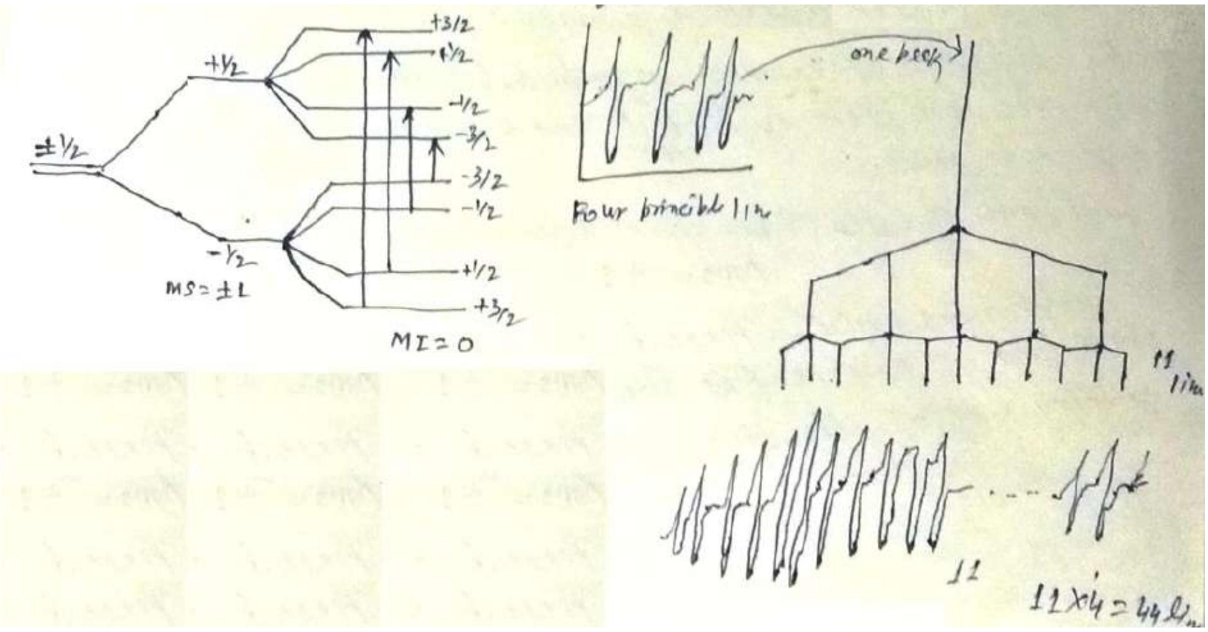
Example: Give the ESR spectrum of *bis* salicyaldehyde Cu(II).

I = 3/2



For this complex Cu is in Cu^{II} state thus there is d^9 configuration hence there is one unpaired electron.

For Cu^{II} (I = 3/2), thus they will be hyperfine splitting and four peaks will be obtained and since N is also I active (magnetically active) so it will further interacts called superfine splitting and each peak will be splitted give five signals. Hydrogen will further split each in three peaks, thus from one principle peak there should be 15 peaks but only 11 peaks are observed, it is due to overlapping between some peaks.



Cu has one unpaired electron = 2×1×3/2+1 = 4

N = 2×1×1+1 = 3

But 2N = 2×2×1+1 = 5

For 2H = 2×2×1/2+1 = 3

5×3 = 15 lines

No. of peaks	Ratio	No. of peaks	Ratio
2	1:1	5	1:4:6:4:1
3	1:2:1	6	1:5:10:10:5:1
4	1:3:3:1	7	1:6:15:20:15:6:1

Zero field splitting and Kremer degeneracy

Zero field splitting is observed when system has d block element having more than one unpaired electron. When metal ion with two or more unpaired electrons is incorporated in the ligand field then the degeneracy of spin state is destroyed and it is taking place in absence of external magnetic field thus it is called zero field splitting and Kremer degeneracy.

For a system with even number of unpaired electrons the lowest energy level must take zero spin state and other higher state will exist as doubly degenerate sates due to zero field splitting.

	± 3	If 6 unpaired electrons
+2, +1, 0, -1, -2	± 2	If 4 unpaired electrons (doubly degenerate)
+1, 0, -1	± 1	If 2 unpaired electrons (doubly degenerate)
	0	single degenerate

for odd number of electrons (unpaired) all spin states exist as double degenerate state:

$7e^- = \pm 7/2$, $5e^- = \pm 5/2$, $3e^- = \pm 3/2$, $1e^- = \pm 1/2$

The existence of double degenerate spin state due to zero field splitting is called Kremer degeneracy. By the application of external magnetic field, the degeneracy of doubly degenerate spin state is lifted and we will obtain singly degenerate state.
Selection rule, this step (into Kremer degeneracy) is $\Delta M_S = \pm 1$
If further active nuclei are present then hyperfine splitting will take place and we observe fine lines.
Selection rule, this step $\Delta M_I = 0$

Give the ESR lines:

(i) $\mathrm{HO\dot{C}H{-}COOH}$

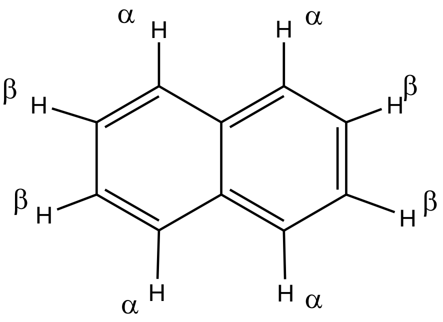
ACH > A(COH)

H-O-CH-COOH

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

= (2×1×1/2+1) (2×1×1/2+1) = 2×2 = 4 lines

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



Aα = 4.90

Aβ = 1.89

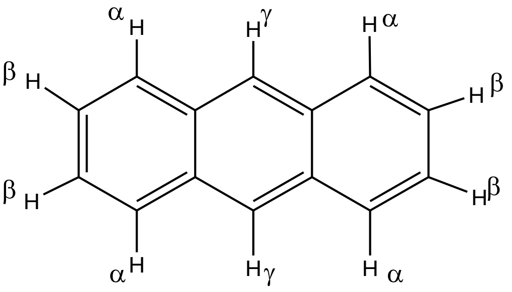
First splitting = 2nI + 1

n = Hα hydrogen = 2×4×1/2+1 = 5

Hβ hydrogen = 2×4×1/2+1 = 5

Total lines = 5×5 = 25 lines

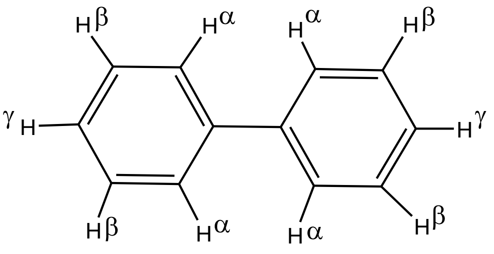
(iii) **Anthracene radical anion**



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

= 75 lines

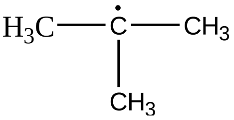
(iv) **Total lines and ESR in biphenyls radical anion**



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



$$H_3C-\underset{CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_3$$

Total lines = 2×9×1/2+1 = 10 lines

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

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

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

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

(viii) $CF_2H^{\bullet}$

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

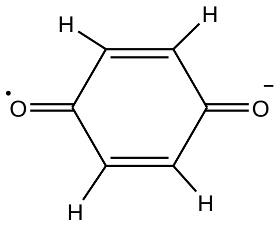
$^{13}CF_2H^{\bullet}$

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

(ix) $CH_3CH_2^{\bullet}$

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

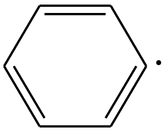
(x) Benzoquinone radical anions



Total lines = (2×4×1/2+1) = 5 lines

One unpaired electron interacts with H equivalent hydrogen atoms.

(xi) Benzene radical



Total lines = (2×6×1/2+1) = 7 lines

Instrumentation

An understanding of ESR instruments requires a general knowledge of the operation of microwave and other spectrometer components. A brief description of these will be given and the design of a typical commercial instruments; the Varian V-4502 spectrometer are described.

Spectrometer components

Klystrons (source): The source of the radiation ν is a klystron tube operating in the X-band (3 cm) region at about 9 G. The klystron can be turnover the range of about ± 0.5 gauss by a control which varies the dimensions of a resonant cavity inside the tube. The output frequency is also a function of a resonator and reflector voltages fed to the klystron by a power supply. It is generally stabilized against temperature fluctuations by immersion in an oil bath or by a feed-back Automatic Frequency Control (AFC) circuit. The power output of klystrons used in ESR spectrometer is generally about 300 milliwatts.

Wave Guide: A microwave radiation is conveyed to the sample and crystal by a wave guide, a hallow rectangular brass tube 0.9 inch x 0.4 inch.

Attenuators: The power propagated down the wave guide can be continuously decreased by interseting a variable attenuator consisting of a piece of resistive material into the wave guide. By the use of this attenuators, the power at the sample may be varied from the full power of the klystron to one attenuated by a factor of 100 or more.

Cavities: The sample is contained in a resonant cavity in which a standing wave is setup. The cavity is analogous to a tuned circuit (e.g. a parallel L-C combination) used at low frequencies. A measure of quality of the cavity is its “Q” or “Q-factor” which is defined as

$$\mathrm{Q} = \frac{\text{Energy stored in cavity}}{\text{Energy lost}}$$

The sensitivity of a spectrometer is directly proportional to the value of Q. Two frequently used cavities are the rectangular TE102 cavity and the cylindrical TE011 cavity. Since the component of interest is the magnetic field; which interacts with the sample to cause spin resonance, the sample is placed where the intensity of the magnetic field is at its highest. The electric field, however, also interacts with the sample and if the sample has a high dielectric constant (i.e. lossy) the Q of the cavity may be drastically decreased.

Crystal detectors: The detector of the microwave radiations is usually a silicon crystal detector (which converts AC radiation to DC). An appreciable amount of noise is generated in a crystal detector; the magnitude of this noise is decreases with increasing frequency of the output signals. Therefore, the signal is usually modulated at a high frequency (6 k to 100 k) to decrease this source of noise.

Magic T’s Bridge: Microwave bridges (which are analogous to impedance bridges in conventional circuits) can be of the “magic-T” variety.

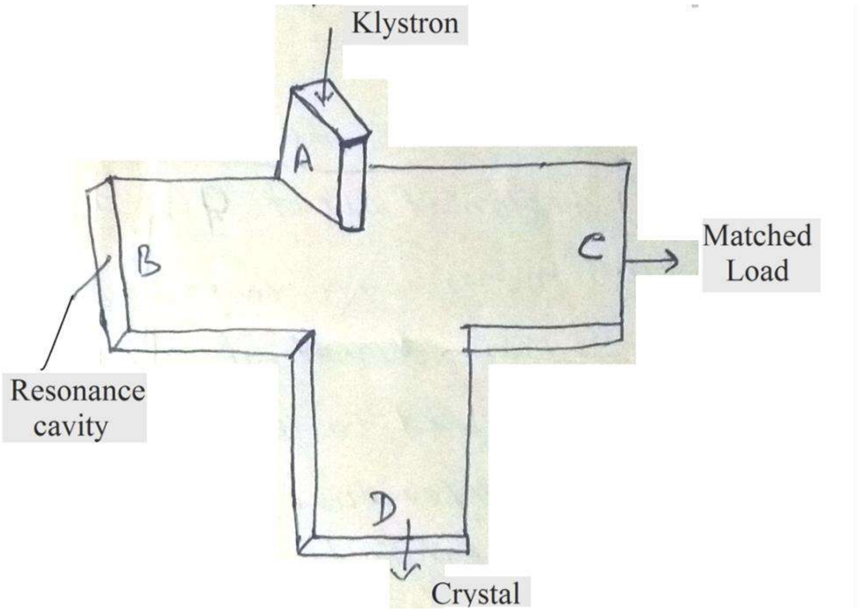


Fig.: Magic 'T' bridge.

Power entering arm A will divide between arms B and C if the impedances of B and C are the same, so that no power will enter in arm D. Under these conditions the bridge is said to be balanced. If the impedance of arm B changes, say because a resonant cavity coupled to the end arm B changes its Q because of the occurance of ESR absorption by a sample in it. The bridge becomes unbalanced and some microwave power enters into arm D containing the crystal detectors. In this way the ESR absorption occurs as an increase of a small signal rather than as a decrease in a large one.

Magnets: An electromagnet capable of producing field of at least 5000 gauss is required for ESR. The homogeneity of the field for solution studies should be about 50 milligauss over the ESR sample region. The ESR spectrum is recorded by slowly varying the magnetic field through the resonance conditions by sweeping the current supplied to the magnet by the power supply. This sweep is generally accomplished with a variable speed motor drive. Both the magnet and power supply may required water cooling.

Modulation Coils: The modulation of the signal at a frequency constant with good signal to noise (S/N) ratios in the crystal detector is accomplished by a small alternating variation of the magnetic field. The variation is produced by supplying an a.c. signal to modulation coils oriented with respect to the sample in the same direction as the magnetic field. For low frequency modulations (400 cycle per second or less) the coils can be mounted outside the cavity and even on the magnet pole pieces. High modulated frequencies (1 KV or more) cannot penetrate metal effectively and either the modulation coils must be mounted inside the resonant cavity or cavities constructed of a non-metallic materials (e.g. quartz with a thin silvered plating) must be employed.

Display devices: A cathode ray oscilloscope is used to adjust the spectrometer and sometimes to observe the signal.

Block diagram of ESR spectrometer:

The most widely used commercial ESR spectrometers are probably those made by Varian Associates. A simplified block diagram of the Varian V-4502 spectrometer is shown below:

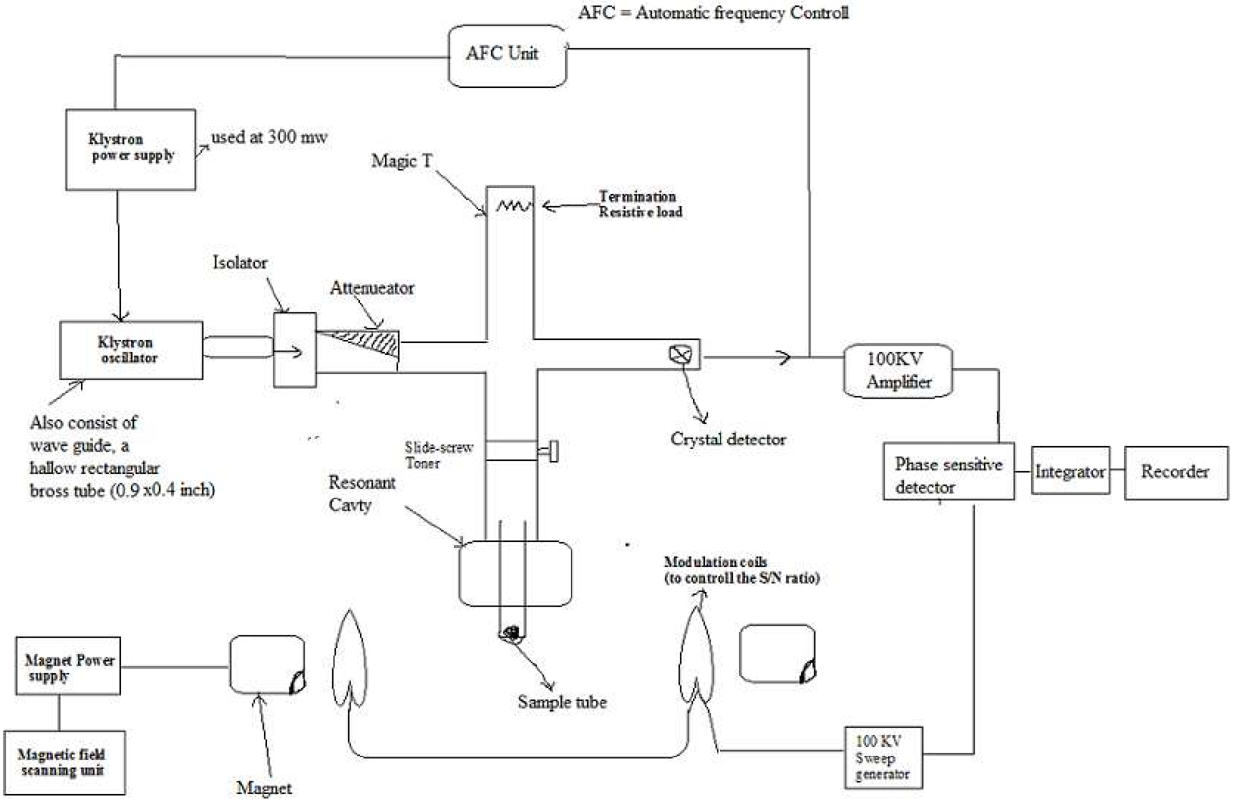


Fig.: Block diagram of a reflection ESR spectrometer incorporating 100 kV modulators and phase sensitive detector. The Varian Associates V-4502 spectrometer.

Although X-band is common, ESR spectrometers are available commercially in several frequency ranges. As particular matter, wave guides cannot be too big or too small (1 cm is a bit small and 10 cm a bit large). The most common choice called X-band microwaves has length (l) in the range 3.0-3.3 cm (n ~ 9-10 GHz); in the middle of X-band, the free electron resonance is found at 3390 gauss.

Designation	n (GHz)	l (cm)	$B_{electron}$ (Tesla)
S	3.0	10.0	0.107
X	9.5	3.15	0.339
K	23	1.30	0.82
Q	35	0.86	1.25
W	95	0.315	3.3

Application of ESR

The scope of application of ESR spectrometry to analysis is somewhat limited by the requirement that the substance being analyzed contains unpaired electrons. A few methods for transition metals and free radicals have been reported. The widest use for ESR in organic chemistry has been in the analysis of free radicals produced by chemical reaction or irradiations. These studies were usually associated with kinetic measurements or involved only qualitative identification of radicals. However, non-paramagnetic organic substances can be determined by a technique which converts them qualitatively or at a constant yield into free radicals which are then observed by ESR spectrometry. Techniques for producing free radicals include pyrolysis, adsorption on alumina or zeolites, photolytic methods and reductions or oxidations by chemical or electrolytic means. Classes of components which might be studied by this kind of techniques include aromatic hydrocarbons, ketones, quinoline, amines and phenols.

Analysis of Metals:

Analysis of vanadium in petroleum oils: Vanadium (IV) found in the ppm range in petroleum oils, leads to corrosions effects in combustion engines and furnaces using petroleum oils fuels and alters the catalytic cracking of the petroleum during processing. The analysis of Vanadium by ESR spectroscopy in such sample has been investigated by several groups and has been shown to be a rapid and convenient method of analysis. Vanadium (IV) yields an eight-line spectrum due to the interaction of an unpaired 3d electrons with a nucleus ($I = 7/2$). In highly viscous media, due to the anisotropy of the g-value; splitting into a greater number of lines occurs. A typical analysis involved using identical precession bore tubes of 3 mm. i.d. and using vandylitioporphyrine (I) dissolved in heavy oil distillate as a standard. The intensity measurements were made by measuring the peak to peak height on the first derivatives recording of a given hyperfine line. Peak height measurement rather than double integration can be used as long as lines widths and shapes remain constant. Quantities of Vanadium in the 0.1 to 50 ppm range were determined with results checking to within ± 20% in most cases with analysis performed by alternate method. No other constituents of oils interfered.

Organic Analysis

Analysis of polynuclear hydrocarbons: The determination of anthracene, perylene, dimethylanthracene and naphthalene by conversion to radical cations and determination by ESR spectrometry. When benzene or carbon disulphide solutions of these hydrocarbons are treated with an activated silica-alumina catalyst, they are quantitatively converted to the radicals and adsorbed on the surface of the catalyst. The procedure involved adding the polynuclear hydrocarbon sample in benzene or carbon disulphide and activated catalyst to 6 mm. Uniform pore tubes and measuring the peak heights. The standard deviation of a series of measurements of samples in the 10 μg range was about 5%. Benzene, naphthalene and other hydrocarbons which do not form radicals at the catalyst surface did not interfere.

Others Applications

EPR spectroscopy is used in various branches of science, such as chemistry and physics for the detection and the identification of free radicals and paramagnetic centres. EPR is sensitive, specific method for studying both radicals formed in chemical reaction and the reactions themselves. For example, when frozen water (solid H_2O) is decomposed by exposure to high energy radiation, radical such as H, OH and HO_2 are produced. Such radicals can be identical and studied by EPR. Organic and inorganic radicals can be detected in electrochemical system and in materials exposed to UV-light. In many cases, the reactions to make the radicals and the subsequent reaction of the radicals are of interest; while in other cases EPR is used to provide information on a radicals geometry and the orbital of the unpaired electrons.

Medical and biological applications of EPR also exist. Although radicals are very reactive and so do not normally occur in high concentrations in biology. Special reagents have been developed to spin-label molecules. These reagents are particularly useful in biological system. Specially designed non-reactive radicals molecules can attach to specific sites in a biological cells and EPR spectra can then give information on the environment of these so called spin-label or spin-probe.

EPR spectroscopy can only be applied to system in which the balance between radical decay and radical formation keeps the free-radical concentrations above the detection limit of the spectrometer used. This can be particularly severe problem in studying reactions in liquid. An alternative approach is to slow down reaction by studying samples held at cryogenic (freezing mixture) temperature, such as 77 K (liquid nitrogen) or 4.2 K (liquid helium). An example of this work is the study of the radical reactions in single crystals of amino acids exposed to X-ray; work that sometimes lead to activation energy and rate constants for radicals reactions.

EPR also have been used by archaeologist for the dating of teeth. Radiation damage over long periods of times creates free radicals in tooth enamel, which can then be examined by EPR and after proper calibration dated. Alternatively material extracted from the teeth of people during dental procedures can be used to quantity their cumulative exposure to ionizing radiation. People exposed to radiation from the chemobyl disaster have been examined by this method.

Radiation-sterilized foods have been examined with EPR spectroscopy, the aim being to develop methods to determine, if the particular food sample has been irradiated and to what dose. Because of its high sensitivity, EPR is used recently to measure the quantity of energy used locally during a mechanochemical milling process.