Electron Spin Resonance Spectroscopy

Electromagnetic Resonance

Electron para magnetic

Instrumentation of ESR Spectroscopy

A typical ESR Spectrometer consists of following componants.

1. **Electro magnet :**

A linear magnetic field is generated by a powerful electromagnetic Modulation - coils, located on the sides of the resonant cavity, modulate the magnetic field.

2. **Source of Microwave Radiation :**

(In most of the ESR Spectrometers, the wral source is a klystron oscillator that normally operate at 9500 MHz and produces monochromatic microwave radiation) is transmitted into the sample

(The wave meter or the frequency meter meanuse the microwave frequency)

(The radalion is transmitted into the sample cavity.

by means of a wave guide) (made of brass or copper tubing.)

3. Sample Cavity:

(The sample cavity or resonant cavity is placed between the poles of an electromagnet.) (The cavities currently in use are the cylindrical or rectangular type.) (The cavities can be designed so that the sample can be irradiated or photolysed in situ.) For studying anisotropic effects in solid samples, rotatable cavity is generally employed. Since (paramagnetic species are often unstable, one should be very careful in the preparation of samples.) Generally a single crystal of a diamagnetic host containing a low concentration of an oriented radical as a substituent impurity is the most useful sample.)

f. Choice of the solvent:

(ESR spectra can be obtained for gases, powders, crystals and frozen solutions. The best frozen solution results are obtained when the solvent) (eg. Methyl cyclohexane) freeze to-from a glass, solvent of high dielectric constant, (water and alcohol should be avoided because they absorb in microwaves region) These solvents can only be used when the sample has a strong absorbance and is containing in a narrow sample tube. (Solvents like toluene, glycerol, nujol, triethanol amine are also employed to dissolve the sample). (concentration of the sample should be about $10^{-6} M$) when structu... determination and quantitativ... analysis are to be carried out.)

5. Crystal Detectors:

(commonly used detector i... a silicon crystal which ac... as a microwaves rectifi...

. This converts microwaver power into a direct true current output. (phase sensitive detectors are used to reduce the noise level.)

6. Auto amplifier:

(After detection by the crystal detector) the singgnal undergoes narrow-band amplifier.)

7. Recorder or an Oscilloscope:

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

principle:

A single unpaired election possesses a spin quantum number of $\frac{1}{2}$ and may exist in either of the two degenerate energy state, namely $+\frac{1}{2}$ or $-\frac{1}{2}$. when a magnetic field is applied. The degenerated is lifted and the transition from the low energy state $(m_s = \frac{1}{2})$ to the high energy state $(m_s = +\frac{1}{2})$ can be achieved by absorption of

radition in the microwave region. The energy (E of the transition is given by

$$\Delta G = hv = g\beta H_o \text{ where}$$

h = plank's constant
v = frequency of microwave radiation
β = The Bohr magneton
e = electronic charge
m = mass of an electron
c = velocity of light
g = 2.0023. The Lande splitting factors.

As in the nmr, the energy requirement for a transition is dependent upon the strength of the applied magnetic field. It as 3.4 Kilogause field is applied. the frequency of the radiation used for excitation is 9.5 GHz. The Bohr magnetion is about 1000 tries larger than the nuclear magneton. Hence (the spin magnetic moment of the Therefore the energy difference between the upper state and the lower state is greater in the case of electrons than in the case of protons when expose to the same magnetic field.

field (Gauss)
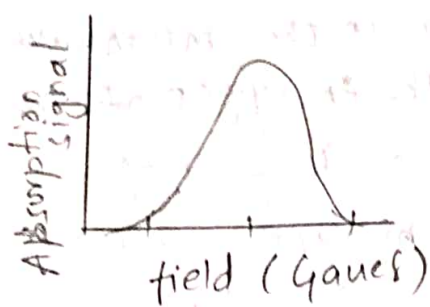
(a)

ESR Absorption Spectrum

$\frac{ds}{dH}$ — field
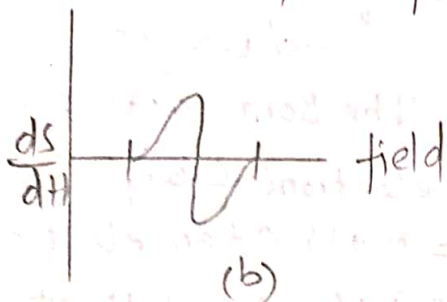
(b)

ESR Derivative Spectrum

The esr spectrum of a free electron consists of a single absorption peak as shown fig (a). But the resonance spectrum lines are always recorded as a first derivates spectrum fig (b).

An electron spin resonance spectum provides two kinds of Information.

1. The position of absorption

2. The magnetic interaction of the unpaired electron. with its neighbouring nuclei with I>0.

The position of the single is indicated by the g value. for free electrons. The g value is 2.0023. Departure from

This value is attributed to interaction with the orbital angular momentum by neighbouring groups. Hence the g value is dependent upon the chemical enviorment. For example,

If an electron in a molecular is free to move about due to complete delocalization, Then the g value is very close to the value of free electron. On the other hand, if its momonent is restriced and completely localized. Then the value of g differes considerably from 2.0023 Liquids, because of molecular collisions, generally passes a single g value Indicates randomization of the interactions with neighbouring molecules, But in paramagnetic solids, the g may be have different value along the coordinates axis x, y, and z.

To measure the g value of free or radical, the sample and a refrence compound with known g value (DPPH – Diphenylpicrylhydrazyl radical). are taken in two separate sample tubes and placed in a duel sample cavity of the esr instrumentation.

The esr spectrum is then recorded. The Spectrum will show two signals with a field spectraction of ΔH. The g value for the unknown substence is given by :

$$g = g_{ref} (1 - \Delta H / H)$$

Here H is the resonance frequency.

Hyperfine Splitting :

(The esr signal is due to the transition of the electron from the spin state $m_s = -\frac{1}{2}$ to the spin state $m_s = +\frac{1}{2}$) These spin states interact with the magnetic moments of nuclei, with which the unpaired electrons may be partially or wholly associated. This interaction may lead to further splitting of resonance signals into several lines.)

(for example, In hydrogen atom the electrons is associated with the nuclei with $I = \frac{1}{2}$) (In the presence of an external magnetic field, the lower energy state ($m_s = -\frac{1}{2}$) is either associated with the $m_I = +\frac{1}{2}$ or with the nuclei $m_I = -\frac{1}{2}$)
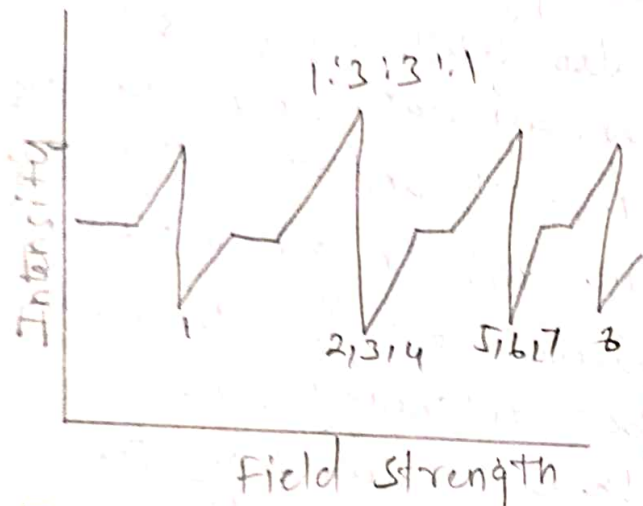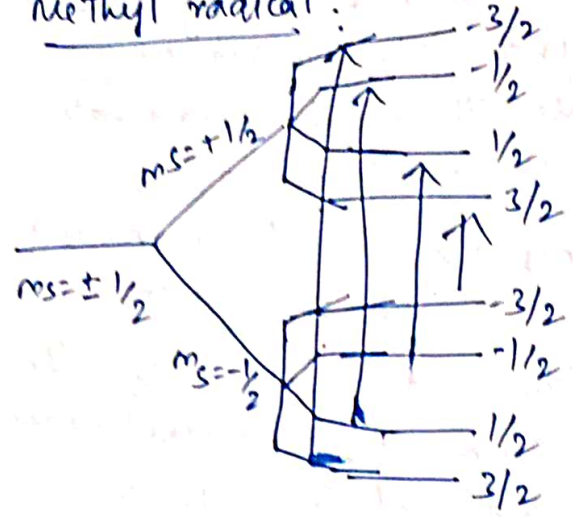
Thus (the lower energy state is splitte into two-sub-energy state) (the - sub-energy state $= -\frac{1}{2}$ with $m_s = \frac{1}{2}$)

$m_I = +\frac{1}{2}$ has a lower energy then the sub-energy state with $m_s = -\frac{1}{2}$, $m_I = -\frac{1}{2}$. (In the same manner, the higher energy state ($m_s = +\frac{1}{2}$) is also splitte into two sub-energy state; one with $m_s = +\frac{1}{2}$ $m_I = -\frac{1}{2}$ and other with $m_s = +\frac{1}{2}$ $m_I = +\frac{1}{2}$). In general, If the nuclear spin is I, there will be $2I+1$ energy levels for each value of m_s. The selection rule for the allowed esr transition is $\Delta m_I = 0$ and $\Delta m_s = \pm 1$.)
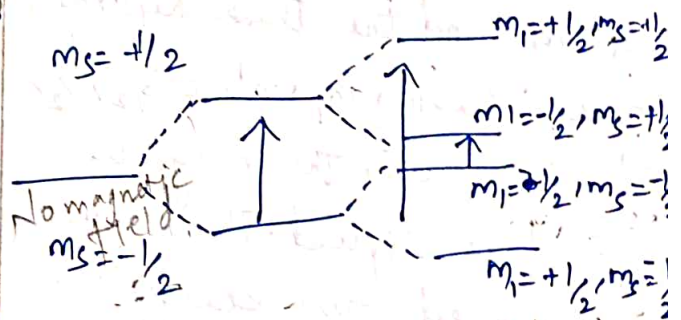
Hyperfine splitting for Hydrogen atom.

methyl radical.

$ms=+\frac{1}{2}$ ·$\frac{3}{2}$

·$\frac{1}{2}$

$\frac{1}{2}$

$ms=\pm\frac{1}{2}$ ·$\frac{3}{2}$

·$\frac{3}{2}$

$m_s=-\frac{1}{2}$ ·$\frac{1}{2}$

·$\frac{1}{2}$

·$\frac{3}{2}$

1:3:3:1

2,3,4   5,6,7   8

Field Strength

In methyl radical, there is an interaction between the single unpaired electrons of carbon atom and the three hydrogen nuclei having m_1 value $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. when the magnetic field is applied. The degeneracy is removed. two energy level will be obtained. one having $ms=-\frac{1}{2}$ and the other having $ms=+\frac{1}{2}$. The interaction b/w each of these electrons spin state and nucleus state spin states results is. Obeying the selection rule ($\Delta ms=\pm1$ & $\Delta m_1=0$) four

transtions occure giving four peaks. in the esr spectrum. the relative intensity ratio of the four peaks is 1:3:3:1.
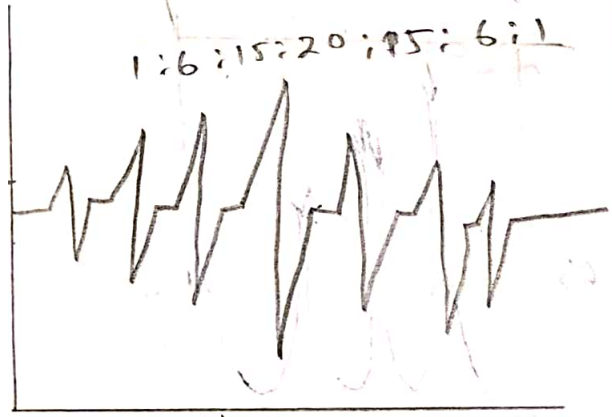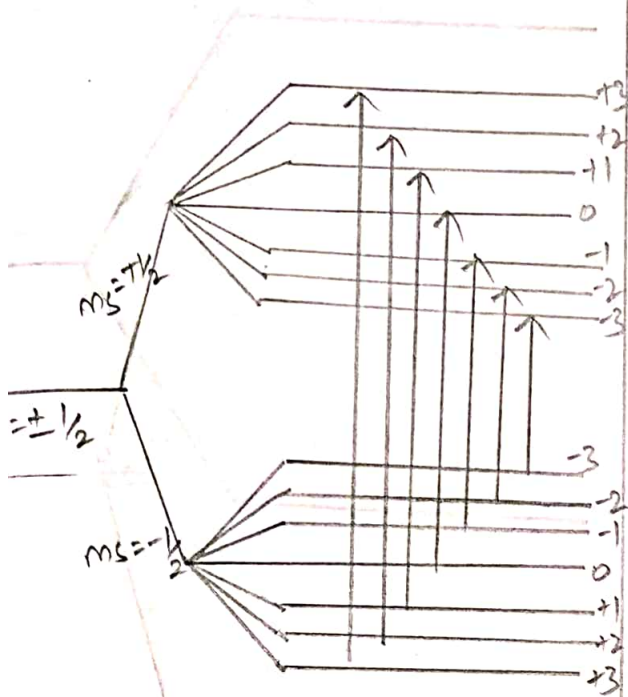
ECR Spectroscopy gives useful information about the shape of radicals. for example, myethyl radicals can have anyone of the following two structure.

1. The planner structure corresponds to sp^2 hybrization to carbon
2. The tetrahedral structure correrponds to sp_3 hybrizat

if the csr spectrum of meth radical shows the enacted fou lines with a splitting separtio of 25 Hz then the mgethyl radical has planner Structure

If the esr spectrum of shows four spectral lines with splitting separation of 41 Hz, then the methyl radical may have the tetrahedral shape with sp3 hybrization, But experiment results show that clts radical has a planner structure..
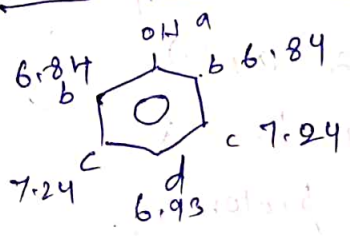
phthalene anion $(C_{10}H_8)^-$

iv) In naphthalene an odd electron is delocalised over entire naphthalene ring.
Naphthalines contains two different sets of four equvilant protons. There is are four α and β hydrogen. There for naphthyl anion, altogether 25 lines are obtained.

$1 : 6 : 15 : 20 : 15 : 6 : 1$

field strength

NMR spectra for phenol.

OH a
6.84 b   b 6.84
c 7.24
7.24 c
6.93 d

Equivalent protons = 4 (a, b, c, d)
Number of protons = a = 1
b = 2
c = 2
d = 1

i) when the absorption spectrum is splitte by 'n' equvilant nuclei of I then $(2nI+1)$ lines result

ii) when the absorption spectrum is splite by two sets of non-equvilant nuclei of spins I and I: then $(2nI+1)(2n'I'+1)$ lines result

iii) If an odd electrone is delocalised over two sets of non equvilent protons, the number of lines expected is the product of number expected for each set $(2nI+1)(2n'I'+1)$.

OH Hydroxyl :
No spiliting of or by the hydroxyl OH proton.

The six hydrogen of phenol occupy 4 different chemical enviorment, so spectra should show 4 principle peaks.

a protons :
& OH protons have no spiliting.
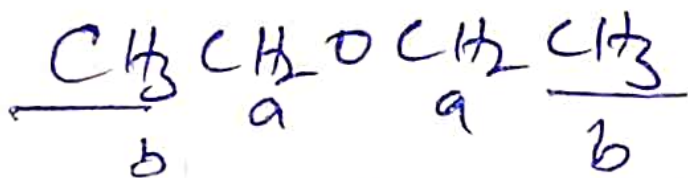& Singlet

b) protons

doublet = (1:1)

iii) c protons

triblelet — (1:2:1)

iv) d protons

triblelet — (1:2:1)

NMR spectra for diethyl ether:

$$\underset{b}{CH_3}\ \underset{a}{CH_2}\ O\ \underset{a}{CH_2}\ \underset{b}{CH_3}$$

Equavalent number of protons = 2 (a, b)

No. of signals = 2

number of protons=

$a = 4$ } ratio 4:6
$b = 6$ ~~3:3~~