

Figure 3.4 : Experimental setup for transmission Mössbauer spectroscopy.

a velocity v along the gamma-ray propagation direction is shifted by a first-order linear Doppler effect

$$E_D = v/c E_{\gamma}$$

The typical experimental setup for Mössbauer spectroscopy in transmission geometry is shown on Fig. 3.3(2). The source is mounted on a loudspeaker-like electromechanical system which is excited by a signal generator to a periodic movement in a constant acceleration mode. The gamma-rays are counted by a gamma detector. The result is stored in a multichannel analyser synchronised by the signal generator.

The spectrum is typically presented as the relative transmission (in percent) vs. the velocity (in mm/s), which can easily be converted to energy by using eq. (1).

I. Hyperfine interactions

The interaction between the nuclear charge and magnetic moment on one side and electronic charges and moments of the absorber atom itself and on surrounding atoms on the other side are known as hyperfine interactions. These interactions influence the nuclear levels (and thus also the transition energies) in a characteristic way and allow to obtain valuable informations about the absorber atom and its surrounding.

Three main hyperfine interactions can be distinguished:

- i) electric monopole interaction, detectable as a line shift (isomer shift)
- ii) electric quadrupole interaction, detectable as a line splitting (quadrupole splitting)
- iii) magnetic dipole interaction, detectable as a line splitting (nuclear Zeeman effect).

II.1. Isomer shift

The electric (Coulomb) interaction between the nuclear charge, distributed over a finite nuclear radius R , and the charges of all surrounding electrons furnishes an additional energy to all nuclear levels. Because R is different in the ground and excited states, the energy shift is also different. Therefore the transition energy is also shifted by an amount depending on the electron density within the volume of the nucleus. Thus, the shift is a measure of the number of electrons on an atom, i.e. of its oxydation state, its co-

Anchor

m

nucleus of the same isotope in the absorber, which is usually our sample (Fig. 1). Typical gamma energies lie in the range 5 ... 200 keV. Emission and absorption lines are extremely narrow (10^{-5} ... 10^{-17} eV).

The recoil energy transferred to the nucleus by the absorption or emission process (conservation of energy and momentum) lies in the range 10^{-1} ... 10^{-4} eV. Emission lines are shifted to lower energies, absorption lines to higher energies by an amount equal to the recoil energy. As this energy is several orders of magnitude greater than the line width, absorption and emission lines are generally out of resonance. From this follows that only recoil-free absorption/emission processes (i.e. without excitation of phonons in the source or the absorber) contribute to the Mössbauer effect. In this case, the recoil energy is absorbed by the crystal lattice as a whole and not by a single atom. This implies that Mössbauer spectroscopy is limited to solid samples. Some isotopes with particularly high gamma energies (^{121}Sb : $E = 37.15$ keV, ^{125}Te : $E = 35.46$ keV) require that source and absorber be cooled to liquid helium temperature to increase the fraction of recoil-free absorption/emission processes.

of γ radiation by Nucleus Radioactive

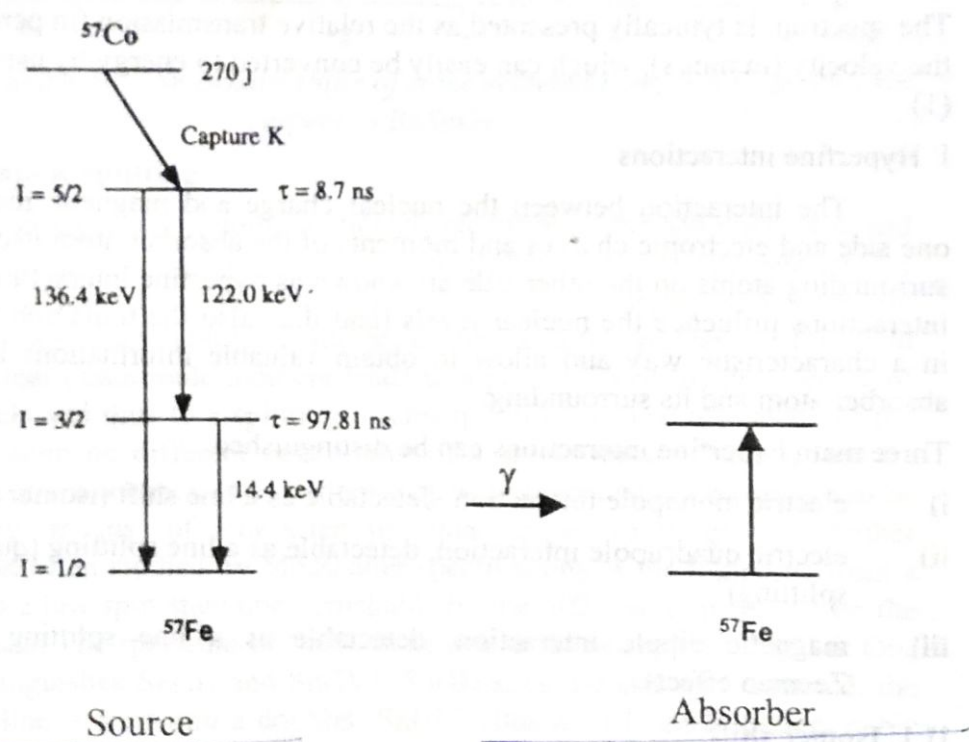


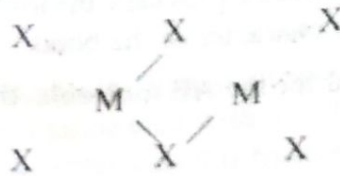
Figure 3.3: Resonant absorption of gamma radiation by ^{57}Fe . The mother isotope is ^{57}Co , which transforms to ^{57}Fe by K capture. Transition to the nuclear ground state of ^{57}Fe produces the 14.4 keV gamma radiation used for Mössbauer spectroscopy.

The extremely narrow spectral lines cannot be resolved by gamma detectors. Instead, the energy of the gamma-rays from the source is slightly varied by the Doppler effect. The energy of gamma-rays emitted from a nucleus moving with



p-type bonding. A possible explanation for the large asymmetry parameter observed is that the bonding orbitals have about 15 percent of character.

Structural information: A number of group III halides of the type MX_3 , (for example, $AlBr_3$) have been studied by the NQR technique. The basic halogen spectrum consists of three resonance lines: two are closely spaced together and are far above the third. The fact that different resonance frequencies are observed for the same nuclei indicates that they are not chemically equivalent. This is supported by the x-ray data that these halides exist as dimers and there are two types of halogen atoms corresponding to the bridge and end positions



The small difference of one set of resonance frequencies is thought to be due to a slight difference of the crystalline field around the chemically equivalent set of atoms.

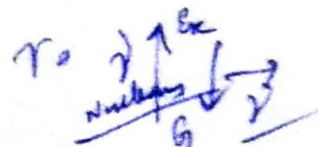
Study of charge-transfer compounds Charge-transfer compounds are believed to be formed when equimolar CBr_4 and p-xylene are brought together. The same is true for mixtures of CCl_4 and p-xylene and Br_2 and benzene. Hooper has studied the frozen solutions of these mixtures and found that the resonance frequencies of the halogens are not appreciably different from those in the pure molecular state. The conclusion therefore is that there is a lack of "charge transfer" of these compounds in the ground state.

3.4 Mossbauer spectroscopy

Mössbauer spectroscopy is a means to study the various steps of a synthesis or a charge/discharge process of electrode materials, *in situ* by using specific test cells or *ex situ* by extracting the material from the cell at a given point of the charge/discharge curve. It allows to study the bulk (in transmission geometry) as well as the surface alone (in scattering geometry). Each absorber atom contributes to the absorption spectrum independently from all other atoms. There is thus no restriction concerning a domain size like in x-ray diffraction. The technique allows therefore the study of nanostructured materials. Mössbauer spectroscopy is further very useful because it can give information not only on static properties (such as crystal structure, magnetic properties, valence state, bonding) but also on dynamic properties (such as diffusion, mechanic vibrations of nanoparticles, superparamagnetic relaxation, electron hopping, etc).

3.5 Principle of Mössbauer spectroscopy

The technique is also known as "recoil-free resonant absorption of gamma radiation". The source is a radioactive material containing the desired mother isotope. Its decay populates the excited nuclear state of the Mössbauer isotope which, in turn, emits the gamma radiation used for spectroscopy by transition to its nuclear ground state. This radiation can then be absorbed by a



$$eQq_{\text{mol}} = (1 - s + d - \dagger - x) eQq_{\text{atom}}$$

Table 4-1 Kowns the eQq_{mol} and eQq_{atom} values for some halogen compounds bone. For example eQq_{mol} of chlorine in KCl is almost zero, indicating that the molecule must be essentially ionic.

APPLICATIONS

Nature of chemical bond NQR is most frequently employed to investigate the electronic structure of molecules. As Eqs. (2-15) and (2-16) show, a comparison of a nuclear quadrupole coupling constant in the atomic and molecular state for the same nucleus provides information regarding the extent of hybridization and the ionic character of the bond.

† If ψ in the bonding orbital for the AB molecule, then

$$\psi = a\phi_A + b\phi_B$$

and the ionic character I is defined as $I = a^2 - b^2$, if A is more electronegative than B.

Unfortunately there are usually too many unknowns involved, and it is not often possible to deduce the exact nature of bonding simply from the NQR data alone. Thus the same data are interpreted differently by different scientists. Here we shall discuss a more clear-cut example—the bonding in H₂S. The electronic configuration of sulfur is [Ne]3s²p⁴ and because HSH in H₂S is nearly 90° it had been assumed for many years that pure *p* orbitals of sulfur were involved in the bonding. However, the NQR measurement of H₂S showed a large asymmetry parameter of $\eta = 0.60$ for sulfur². In an asymmetric molecule the EFG along the three axes can be written as

$$eQq_{zz} = \left(\frac{N_v + N_s}{2} - N_z \right) eQq_{\text{atom}}$$

$$eQq_{vv} = \left(\frac{N_z + N_s}{2} - N_{zv} \right) eQq_{\text{atom}}$$

$$eQq_{ss} = \left(\frac{N_z + N_v}{2} - N_s \right) eQq_{\text{atom}}$$

where N_z , N_v and N_s are the effective electron populations of the P_z , P_v and p_s orbitals of the atom. Hence η can be written as

$$\eta = \frac{q_{zz} - q_{vv}}{q_{ss}} = \frac{3(N_v - N_z)}{N_z + N_v - 2N_s} = -0.60$$

If we let the p_s orbital contain the lone pair, we have $N_s = 2$ and $1.33 N_v = N_z + 1$. It is clear that N_z cannot be equal to N_v and therefore we do not have pur

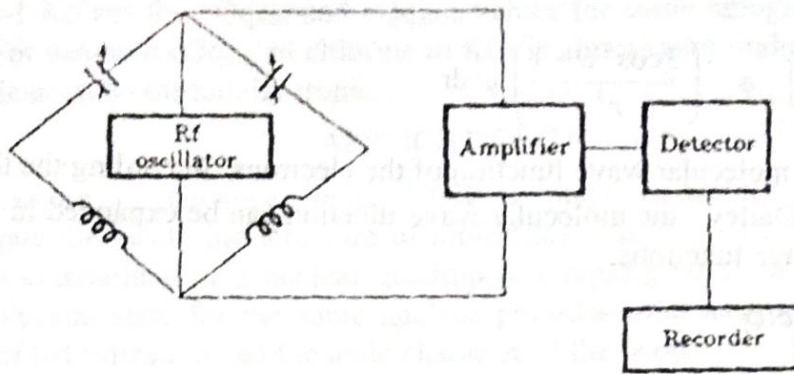


Fig.3.2

NQR spectra can be obtained only for solids. In liquids and gases, at normal pressure, collision between molecules changes the axis of rotation continuously, and consequently the EFG at the nucleus will be averaged to zero. Because of this indication, NQR does not have the same range of applications as NMR (fig.2.3).

3.3 Theory NQR in atoms:

In an atom the EFG at the nucleus is due to the electrons in the various valence shells. Closed shells have spherical symmetry and do not contribute to the field gradient \uparrow . The same is true for electrons in the orbitals. Thus only the p and d electrons in the valence shells contribute to the EFG. For an atom having one valence electron, the EFG, q_{atom} , is given by

$$q_{\text{atom}} = e \int \phi^* \left(\frac{3 \cos^2 \theta - 1}{r^2} \right) \phi \, dr$$

$$\psi = \phi$$

where ϕ is the electronic wave function and θ the angle between the fixed z axis in space and the radius vector r (from the nucleus to the electron). ϕ can be separated into the angular and radial parts with the result that

$$q_{\text{atom}} = \frac{2le}{2l+3} \left(\frac{1}{r^2} \right)_{\text{av}}$$

where l is the orbital angular momentum of the electron and $(1/r^2)_{\text{av}}$ is the average distance between the nucleus and the electron.

The quantity of prime interest is, of course, the EFG, since it tells us about the electronic structure of the atom. Nuclear quadrupole coupling constants of a number of atoms have been measured by the atomic-beam technique, and the EFGs for atoms of known quadrupole moment Q have been evaluated. They agree quite well with the calculated values.

Nuclear quadrupole coupling in molecules

In a molecule the EFG at a particular nucleus due to the valence electrons is given by

$$q_{\text{atom}} = \int \psi^* \left(\frac{3 \cos^2 \theta - 1}{r^3} \right) \psi \, dr$$

where ψ is the molecular wave function of the electrons. According to the theory of Townes and Dailey,² the molecular wave function can be expanded in terms of the atomic wave functions.

$$\psi = \sum_i a_i \phi_i$$

They showed that the dominant contributions of EFG at a nucleus are due to the p-type valence electrons associated with the chemical bonding as well as p-type long-pair electrons. Contributions due to other charges in the molecule and the various polarization effects on the inner shells are all negligible. In a molecule, the electronic structure near a nucleus depends on the hybridization of the bonding orbital and the ionic character of the bond. The equation relating the nuclear quadrupole constants

Table 3-1, Nuclear quadrupole coupling constants of Cl^{35} , Br^{79} , and I^{127} and some of their compounds†

| Molecule | eQq_{mol} (MHz) | Molecule | eQq_{mol} (MHz) |
|------------------------|--------------------------|------------------------|--------------------------|
| Cl (atomic) | -109.7 | Br (atomic) | 769.7 |
| BrCl | -103.6 | BrCl | 876.8 |
| ICl | -82.5 | LiBr | 37.2 |
| FCI | -142.9 | NaBr | 58 |
| KCl | 0.04 | KBr | 10.2 |
| RbCl | 0.77 | CH_2Br | 528.9 |
| CaCl | 3 | I (atomic) | -2292.8 |
| CH_2Cl | -74.7 | NaI | -259.9 |
| | | KI | -60 |

† Values taken, with permission, from C. H. Townes and A.L. Schawlow, "Microwave Spectroscopy," McGraw Hill Book Company, New York, 1955.

of a halogen atom to that measured in an isolated atom eQq_{atom} is given by

$$eQq_{\text{mol}} = [1 - s + d - i(1 - s - d)] eQq_{\text{atom}}$$

where s and d denote the amount of r and a character of a bonding orbital and i is the ionic character of the bond. † When there is also x bond present, Eq. below is modified to give

Where E is proportional to a function $f(\xi)$ of the angle. Frequently q is simply replaced by q so that

$$E = eQqf(\xi)$$

The energy levels for a nucleus having spin I corresponding to this are given by

$$E = eQq \left[\frac{3M_I^2 - I(I+1)}{4I(2I-1)} \right]$$

where eQq is the nuclear quadrupole coupling constant. Figure 4-2 shows the splitting of the nuclear quadrupole energy levels for a nucleus having $I = \frac{3}{2}$. Because of the M_I^2 term in only one line is observed. The resonance condition is

$$\Delta E = h\nu = \frac{1}{2} eQq$$

For most nuclei, ν is in the megahertz range and for this reason nuclear quadrupole resonance (NQR like NMR is branch of r-i spectroscopy)

$$3 q_{zz} \neq q_{vv} \neq q_{ss}$$

This is the most complex case. The energy of interaction is given by

$$E = \frac{eQq}{4I(2I-1)} [3M_I^2 - I(I+1)] \left(1 + \frac{\eta^2}{3} \right)^{\frac{1}{2}}$$

Where η , the asymmetry parameter, is given by

$$\eta = \frac{q_{zz} - q_{vv}}{q_{zz}}$$

The M_I degeneracy of the energy levels is removed for nuclei having integral spins if $\eta \neq 0$. For half-integral spins the M_I degeneracy is unaffected whether η is zero or not. Figure 4-3 shows the splitting of the quadrupole energy levels for $I = 1$. An example of $\eta \neq 0$ is the chlorine nucleus in $\text{CH}_2 = \text{CHCl}$.

3.2 Experimental techniques

Unlike the NMR experiment where an external magnetic field is required to remove the M_I degeneracy, the electric field required in an NQR experiment is provided by the electrons in the molecule. This means that the transition frequencies are fixed by the electronic structure of the molecule, and we observe the resonance by varying the frequency instead of the field. Figure shows the schematic diagram of an NQR spectrometer. Power from a r-f oscillator is supplied to a previously balanced bridge circuit. At resonance, energy is absorbed by the sample in the inductive coil and this causes an imbalance in the circuit. The resultant output voltage is then amplified and recorded. Spectra obtained this way are often called the pure quadrupole resonance spectra since the electric quadrupole constant eQq can also be obtained from the fine structure of the rotational spectra.



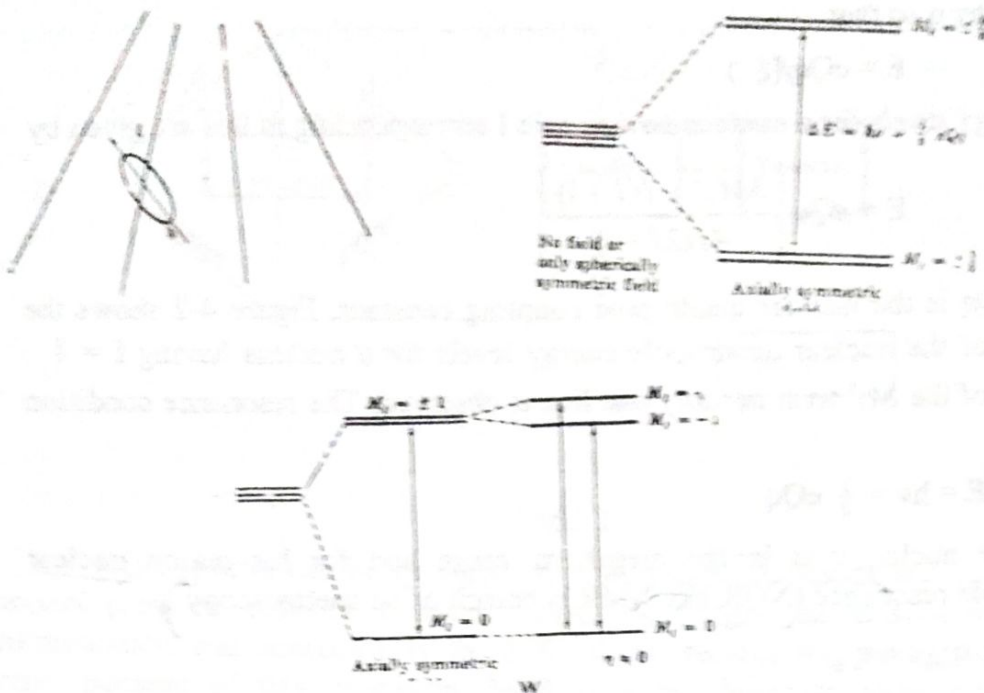


Fig.3.1

This corresponds to the special symmetry of the field gradient; all orientations of the quadrupole moment with the field have the same energy; consequently the degeneracy corresponding to M_1 is not removed, and no resonance can occur. An example of this is the chloride ion Cl^- . The closed-shell structure has a spherical symmetry and EFG at the nucleus along the three axes are the same?

$$2. q_{zz} = q_{xx} = q_{yy}$$

This corresponds to the axial symmetry along the z axis. For example, in the FCl molecules, the EFG at the chlorine nucleus along the $\text{F}-\text{Cl}$ bond, defined as the z axis, is different from those along the x and y axes. According to the Laplace equation,

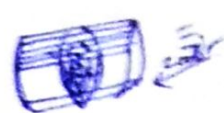
$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

We have

$$q_{xx} = -2q_{zz} = -q_{yy}$$

For axial symmetry. Since any two of the field gradients are determined by the third, it is only necessary to use one parameter to define the field in homogeneity. The standard convention is to choose q and the energy of interaction between the quadrupole and the field gradient is given by

$$E = eQq_{zz} f(\xi)$$



$$eQq_{zz} \times \frac{E}{\Delta E} = \frac{eQq_{zz}}{\Delta E} \times E$$

3.1 Introduction to NQR

Nuclei having spin $I > 1/2$ have a non-spherical distribution of charge density and therefore possess an electric quadrupole moment Q . Q is a measure of the deviation of the nuclear charge from spherical symmetry and is given by

$$Q = \int \rho r^2 (3 \cos^2 \theta - 1) dr \quad (3-1)$$

Where ρ is the nuclear charge density, r is the distance from the origin to the element dr , and θ is the angle between r and the spin axis. (If the nucleus possessing a quadrupole moment is placed in an inhomogeneous electric field, the potential energy of the quadrupole will vary depending on the orientation of the quadrupole moment with the field.)

Analogous to the NMR case, quantum mechanics imposes the restriction that there can be only certain orientations of the spin axis in space.

† Electric quadrupole moment is sometimes simply expressed as Q .

In any inhomogeneous electric field, the interaction is between the nuclear quadrupole moment and the electric field gradient (EFG) q at the nucleus. In the Cartesian co-ordinates we define the EFGs along the x, y, and z axes as

$$q_{zz} = \frac{\partial^2 V}{\partial x^2}$$

$$q_{yy} = \frac{\partial^2 V}{\partial y^2}$$

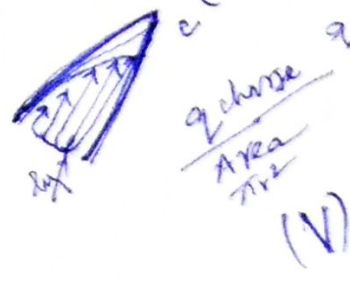
$$q_{xx} = \frac{\partial^2 V}{\partial z^2}$$

Where V is the potential the nucleus due to some electric charge. In atoms and molecules the EFG at a nucleus arise, as a result of the surrounding electrons. Depending on the particular symmetry and electronic configuration, we can have any one of the following three situations.

1. $q_{zz} = q_{yy} = q_{xx}$

$$Q = \sum_{i=1}^n q_i$$

$$Q = \int \rho r^2 (3 \cos^2 \theta - 1) dr$$



$$q = \frac{\partial E}{\partial x} = \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} \right)$$

$$E = \left(\frac{\partial V}{\partial r} \right) \frac{\partial}{\partial r}$$

$$\frac{dE}{dx} = \frac{\partial E}{\partial x} \quad (x, y, z)$$

SCHFL

excited to a higher singlet state. The lifetimes of the triplet state are fairly long (of the order of seconds), the reason being that the transition from the triplet to the singlet state is spin-symmetry-forbidden. (The selection rule is $\Delta S = 0$.) These triplet molecules are paramagnetic, and if a high enough concentration is maintained, we might expect that ESR experiments can be performed. The hamiltonian operator for the triplet molecule can be written in a similar way to that for the doublet state:

$$\mathfrak{H} = \mathfrak{H}_{zeeman} + \mathfrak{H}_{dip} + \mathfrak{H}_{vs}$$

SUMMARY:

Nuclear Magnetic Resonance (NMR) is a branch of spectroscopy in which radio frequency wave induce transitions between magnetic energy levels of nuclei of a molecule. Electron Spin Resonance spectroscopy having frequency in the microwave region is absorbed by paramagnetic substances.

SELF - ASSESSMENT QUESTIONS:

1. Without the magnetic field, the spin states of nuclei are _____ (degenerate).
2. The range of nuclear quadrupole interactions is such that the transition frequencies can occur anywhere between _____ KHz to _____ MHz making detection by a single spectrometer very difficult.

Ans: (1-10)

3. Nuclear spins can be determined by ESR. a) True b) False.

UNIT QUESTIONS

1. Explain the theory of NMR spectroscopy.
2. Give the applications of NMR spectroscopy.
3. State the principle and working of ESR spectroscopy.
4. Briefly explain the theory of ESR spectroscopy.
5. Short note on applications of ESR spectroscopy.

molecule can sometimes be deduced from the sets or equivalent nuclear. In some cases, however, ESR soluble to provide useful information about the shape of the radicals. An interesting example of this is the determination of the methyl radical structure. The methyl radical can be produced in the solid state by high-energy irradiation of CH_3I matrix. It may have one of the following two structures: planar and tetrahedral. The first corresponds to a sp^2 and the second corresponds to a sp^3 hybridized carbon atom. The ESR spectrum of $\cdot\text{CH}_2$ shows the expected four lines (from the three equivalent protons) with a splitting of 25 G. Recalling McConnell's equation we write

$$a_H = Q_{CHP}$$

which is derived for planar π radicals. Using $a_H = 25$ G and $p = 1$ we obtain a value of 25 G for Q_{CH} , which is very close to the value obtained for most aromatic radicals. This would seem to suggest that methyl radical has a planar structure. However, the observed splittings are not positive proof of the planarity of $\cdot\text{CH}_2$ for we do not know on theoretical grounds just how large the proton HSC would be if $\cdot\text{CH}_2$ were not planar. On the other hand, we can make reasonable theoretical estimates of the C^{13}H_3 radical, a splitting of 41 G is obtained.⁴ If the methyl radical were tetrahedral, the unpaired electron would be in one of the sp^3 hybrid orbital. This would have 25 percent s character, \dagger and the interaction with the C^{13} nucleus, according to theoretical calculations, would give a splitting of 300 G. The much smaller splitting constant observed can only be taken to mean that the unpaired electron has very small amount of s character; that is, it is in a predominantly p_v -type orbital. Therefore, methyl radical is most likely to be planar. *n.w.*

2. Study of unstable paramagnetic species:

n.w. Many chemical reactions are known to involve the formation of paramagnetic intermediates at one stage or another, and their identification is important in mechanistic studies. Most of these radicals are unstable because of their high reactivities. In order to maintain a high enough steady concentration for ESR studies, the rapid-flow system is usually employed. The compounds whose interaction yields the paramagnetic intermediates are mixed shortly before the mixture flows through the cavity of the ESR spectrometer. The usual arrangement is to pass two jets of solutions into a mixing chamber which is directly under the cavity, and the mixed solution then flows through the cavity under hydraulic pressure. In this way a steady concentration of the radicals can be maintained. With proper adjustment of pressure, radicals of lifetimes of about 0.01 sec have been studied. Figure 6-11 shows the ESR spectrum of $\cdot\text{CH}_2 - \text{OH}$ and $\text{CH}_2 - \dot{\text{C}}\text{H} - \text{OH}$

\dagger The four sp^3 hybrid orbitals, in Cartesian coordinates, are

$$\Phi_1 = \frac{1}{2} (s + p_z - p_y + p_x)$$

$$\Phi_2 = \frac{1}{2} (s + p_z - p_x + p_y)$$

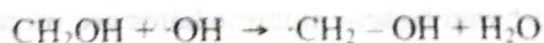
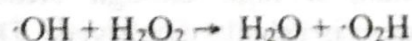
$$\Phi_3 = \frac{1}{2} (s + p_z + p_x + p_y)$$

in the plane of the molecule, that is, the wave function is zero at the nucleus. How do we then account for the observed hyperfine structure? Qualitatively, the origin of hyperfine interaction can be explained by considering the $>C-H$ of an aromatic system. A $C-H$ σ -bonding orbital is formed from the overlap of the carbon sp^2 hybrid orbital with the hydrogen $1s$ orbital and is occupied by two electrons. The unpaired electron occupies carbon $2p_z$ orbital. According to the particular manner of electroning in this orbital, two structures are possible, as shown in Fig. 6-9. whatever, the structure shown in Fig. 6-9a is slightly favored over the Fig. 6-9b because the electrons on the carbon atom have their parallel to each other so that there will be an exchange interaction between which stabilizes the system. The result is that there will be a amount of electron impairing in the $C-H$ σ -bonding orbital. Polarization of the electrons will produce some unpaired spin density by defined later) on the hydrogen atom, which accounts for the hyper structure observed. Of course this is only a very small effect as evident by the small HSC of 3.75 G (cf. HSC in hydrogen atom).

Quantitative calculations of this effect involve the use of configuration interaction and perturbation theory. A useful result is given Mc Cornell

$$a_H = Q_C$$

Where a_H is the proton HSC, p is the unpaired spin density on the carbon atom to which the proton is attached, and Q_{CH} , which is called the polarization parameter, is roughly a constant for π radicals and is usually given in the value of 25 G. The unpaired spin density is defined in for using the flow technique. These radicals were generated by mixing an acidified solution containing titanium ions ($TiCl_3$) with an acidified solution containing CH_3OH or C_2H_5OH and hydrogen peroxide. the following reactions are known to take place



in the flow system. Apparently only the hydroxyl radical is responsible for the abstraction of the hydrogen atom because of its greater reactivity. With this technique a large number of unstable aliphatic and aromatic radicals are now accessible to us, and the scope of ESR solution studies is very much widened.) n n

2.7 Applications

(1) Structural determination:) n n The ESR technique cannot be applied to elucidate molecular structure as NMR can because the information obtained from the hyperfine structure is mostly about the extent of electron delocalization and Fermi contact interaction. It does not tell us, for example, the arrangement of the atoms in the molecule although the symmetry of the

$$a = \frac{8\pi}{3} g\beta N\beta\beta N |\psi(0)|^2$$

n.n Since $\psi(0)$ is the value of ψ at the nucleus, we would expect electron-nucleus contact interaction only if ψ has a finite, nonzero value at the nucleus (see Fig.). It follows, therefore, that in order to have this contact interaction ψ must have some s character.

Applying to the hydrogen atom we obtain.

$$M_S = \frac{1}{2} \begin{cases} E_1 = \frac{1}{2} g\beta H + a(\frac{1}{2})(\frac{1}{2}) \\ E_2 = \frac{1}{2} g\beta H + a(-\frac{1}{2})(\frac{1}{2}) \end{cases}$$

$$M_S = -\frac{1}{2} \begin{cases} E_1 = -\frac{1}{2} g\beta H + a(-\frac{1}{2})(-\frac{1}{2}) \\ E_2 = -\frac{1}{2} g\beta H + a(\frac{1}{2})(-\frac{1}{2}) \end{cases}$$

The two allowed transitions are

$$E_1 - E_4 = g\beta H + \frac{a}{2}$$

$$E_2 - E_3 = g\beta H - \frac{a}{2}$$

The two resonance lines are shown in Fig. When more than one type of proton is present, the above equation can be written in the general form

$$E = g\beta H M_S + a_1 M_S \sum_{i=1}^n M_i' + a_2 M_S \sum_{i=1}^n M_i' + \dots$$

where a_1, a_2, \dots are the HSCs of proton types 1, 2, ..., and n is the number of proton for a particular type. Experimentally, HSCs are usually measured in gauss although they can also be expressed in megahertz. The conversion between gauss and megahertz is as follows:

$$a \text{ (G)} = 0.35683 \left(\frac{g_{\text{freeelectron}}}{g_{\text{radical}}} \right) a \text{ (MHz)}$$

The ESR spectrum of the hydrogen atom produced by electric discharge or trapped in solids shows the expected two-line spectrum with a separation of 506 G. This is the largest splitting for a proton since the unpaired electron is in the 1s orbital and so has 100 percent s character.

n.n Next, let us consider a simple organic free radical, the benzene union radical prepared by the chemical reduction of benzene with alkali metal in an intra solvent such as 1, 2-dimethoxyethane or tetrahydrofuran. A spectrum containing seven lines with relative intensities 1:6:15:20:15:6:1 and a HSC of 345 G is contained. In the simple molecular orbital approximation, the unpaired electron occupies the antibonding molecular orbital, which has a node

$$a_{\text{zeeman}} = -gN\beta N_I H + g\beta S.H$$

a_{dip} represents the classical dipole-dipole interaction between the electron and nuclear magnetic moments

$$a_{\text{dip}} = ggN\beta\beta N \left[\frac{S.I}{|r_c - r_n|} - \frac{3(S.r)(I.r)}{|r_c - r_n|^3} \right]$$

where r_c is the vector position of the electron and r_n is the vector position of the nucleus. In non viscous liquids this interaction vanishes because of rapid tumbling of the molecules just as in the NMR case. Of course the same type of interaction also exists between unpaired electrons on different molecules, and we might expect that this effect would be much larger because of the much larger magnetic moment of the electron. However, if we study only very dilute solutions of these radicals, which is often the case, such electron-electron dipolar interaction can be neglected.

a_{ac} , which is also called Fermi contact interaction, depends only on the electron "contact" with the nucleus. It has no classical counterpart and does not vanish in solution. We have^{1a}

$$a_{\text{ac}} = ggN\beta\beta N \frac{8\pi}{3} S.I \delta(r_c - r_n)$$

The most important term in Eq. (6-16) is the Dirac delta function $\delta(r_c - r_n)$, which will have a nonzero value only if the wave function of the unpaired electron in the radical has a nonvanishing value at the nucleus.

The total energy of various magnetic interactions is given by

$$E = \int \psi a \psi dr$$

where ψ contains both the space and the spin part of the wave function of the electron. the spin part of the wave function, which is denoted by α or β , gives

$$\int \alpha(g\beta S.H) \alpha dr = \frac{1}{2} g\beta H \quad \int \beta(g\beta S.H) \beta dr = \frac{1}{2} g\beta H$$

Thus in general we write

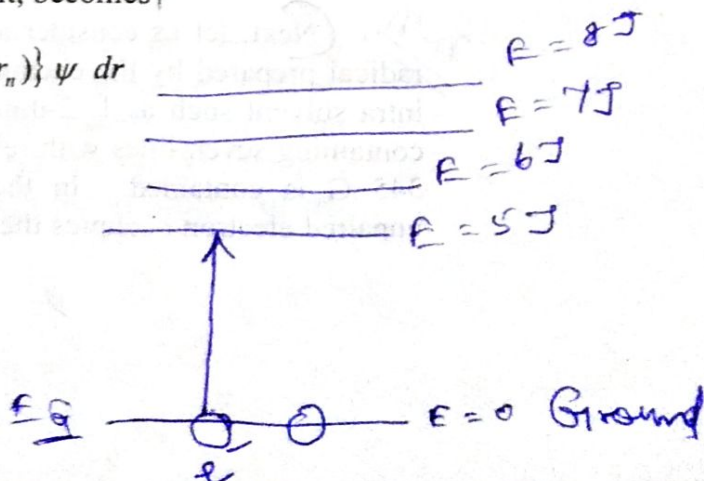
$$\int M_s (g\beta S.H) M_s dr = g\beta H M_s$$

If we consider the situation in solution then a_{dip} vanishes. The nuclear Zeeman interaction is much smaller than that for the electron and is also neglected. Equation (6-17), when written in the Paschen-Back limit, becomes†

$$E = \int \psi \left\{ g\beta S.H + ggN\beta\beta N \frac{8\pi}{3} S.I \delta(r_c - r_n) \right\} \psi dr$$

$$= g\beta H M_s + a M_I M_s$$

E is the HSC mentioned earlier and is given by



6. Triplet state molecules

In this chapter we shall discuss only the ESR aspects of 5 and 6

The next simplest case of ESR is that of a hydrogen atom. The proton has a nuclear spin I of $\frac{1}{2}$ with a resultant magnetic moment which can be aligned either parallel or antiparallel to the electron magnetic moment. This interaction further splits the electron Zeeman levels into four levels and additional transitions are now possible. The transitions are restricted by the selection rules $\Delta M_s = \pm 1$ and $\Delta M_I = 0$, so only two lines can be detected. These two lines are of equal intensity, and the separation between them gives the hyperfine structure. When two protons are present which interact equally with the electron there will be the levels and three allowed transitions. In general, for n equivalent protons† there are $n + 1$ lines; the relative intensities of the lines are proportional to the coefficients of a binomial expansion of order n , that is, $(1 + x)^n$. In Fig. resonance is achieved on varying the microwave frequency (constant magnetic field). In practice, however, because of practical convenience, ESR experiments, like NMR, are always performed by varying the field (constant frequency).

In addition to the intrinsic spin angular momentum, an electron may also possess an orbital angular momentum in atoms and molecules. The magnitude of the orbital angular momentum is given by $\sqrt{L(L+1)} \hbar$, where L is the azimuthal quantum number. There will then be two contributions to the electron magnetic moment, one due to the spin and the other due to orbital motions. The resultant magnetic moment μ_J is given by

$$\mu_J = -gJ\beta\sqrt{J(J+1)} \hbar$$

where J is the resultant angular momentum which in the Russell-Saunders coupling scheme is given by

$$J = L + S$$

and g_J may be appreciably different from 2.0023 if there is coupling between the orbital and the spin angular momentum. However, for most organic free radicals, because of the high asymmetry of the molecules, the orbital angular momentum is not conserved, and consequently we say that L is not a "good" quantum number. Hence we have $L = 0$ and $J = S$. Therefore, their g values lie very close to that of the free electron.

ESR theory is simplest for liquid solutions and it is in these systems that most of its chemical applications are found. Let us now consider the various magnetic interactions of organic radicals containing nuclei with spin I . In the presence of an external magnetic field the various magnetic interactions are represented by the hamiltonian

$$\mathcal{H} = zee \text{ man} + \text{dip} + \text{sc}$$

where $zee \text{ man}$ represents the interaction of the electron and the nucleus with the applied field

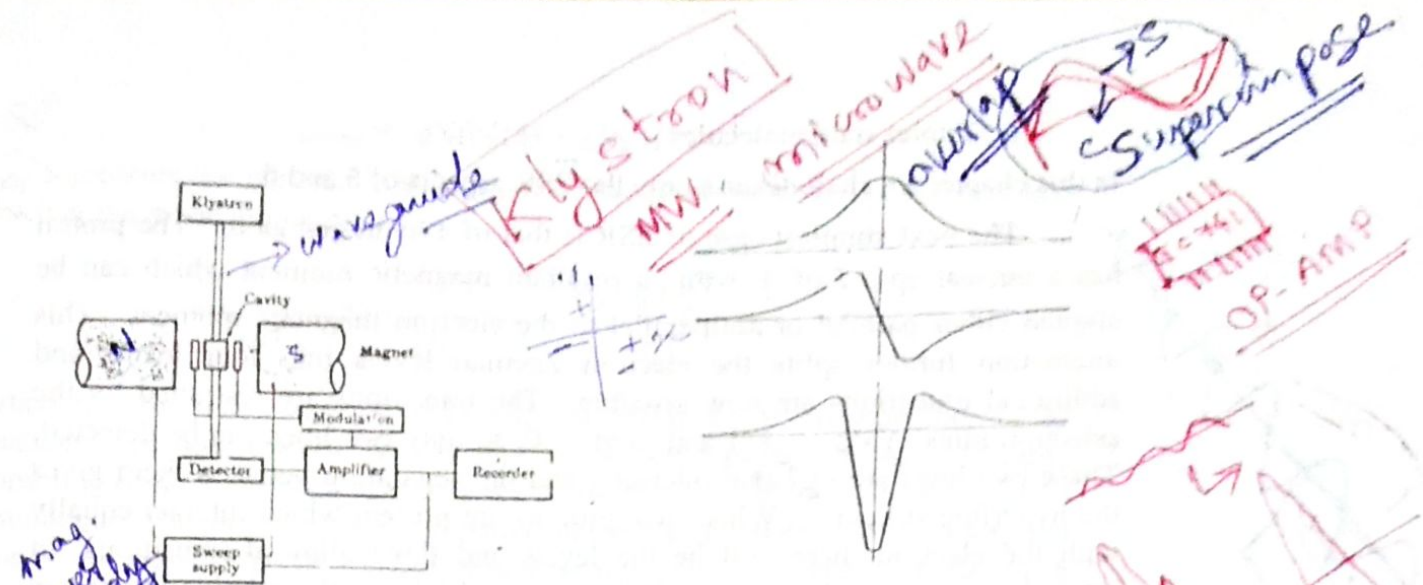


Fig.2.3

The basic features of an ESR spectrometer are (1) a source of microwave radiation, (2) a sample cell, (3) a means of transmitting the radiation energy to the sample cell, (4) a de magnetic field, (5) a detection system, and (6) a recorder or an oscilloscope. The usual source of radiation is a klystron oscillator which produces monochromatic microwave radiation. This radiation is transmitted into the sample cell by means of a waveguide, which is a copper or brass tubing of dimensions appropriate to the wavelength of radiation. The sample cell is called the cavity and is located in a homogeneous magnetic field. The transmitted radiation is detected in a rectifier crystal and the signal, after amplification, is either displayed on an oscilloscope or recorded permanently on the chart paper. (Instead of displaying the signal as the absorption curve as with NMR experiments, ESR signals are usually phase-sensitive detected and represented as the first derivatives). The absorption curve and the first and second derivatives of an ESR line are shown in Fig (2.3).

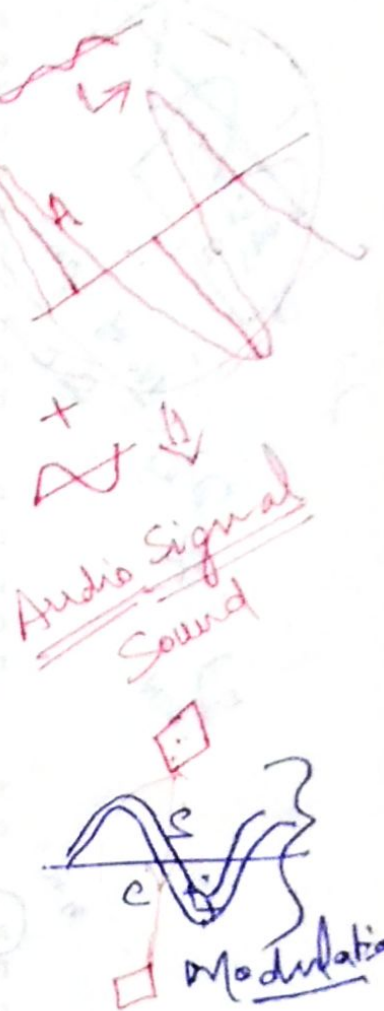
2.6 Theory

we saw the simplest example of ESR experiment, that is, the resonance of a free electron. Isolated electrons are of little interest and we are naturally more interested in situations in which we can use the electron as a probe to obtain useful information about the atoms and molecules. In most molecules electrons regularly occur in pairs with opposite spins as required by the Pauli exclusion principle; hence ESR does not have as wide an application as NMR. The same restriction, however, also makes it a unique tool in the study of paramagnetic systems. The following is a list of systems containing unpaired electrons.

1. Conduction electrons of metals
2. Semiconductors
3. Transition metal ions
4. Molecules containing odd number of electrons (NO, NO₂, ClO₂ and NF₂)
5. Radicals produced by chemical or physical means

Fe, Co, Ni

n, l, m, s
 e_1, e_2
 $s \pm 1/2$
 $s \pm 1/2$
 CW
 $s \pm 1/2$
 ACW
 longitudinal wave
 Transverse



For a spin of $\frac{1}{2}$, the electron has lower energy state of $-\frac{1}{2}g\beta H$, which corresponds to the parallel alignment of the magnetic moment to the applied field, and a higher energy state of $\frac{1}{2}g\beta H$, which corresponds to the antiparallel situation. In the absence of the field the two states corresponding to $M_s = \pm \frac{1}{2}$ have the same energy and are said to be degenerate. This degeneracy is removed when the field is applied and the splitting of the levels is shown in Fig.6-3. If electromagnetic radiation of frequency ν is present which satisfies the resonance condition transitions

$$\Delta F = h\nu = g\beta H$$

between these Zeeman levels can occur. This is the simplest case of ESR. For an assembly of unpaired electrons, the ratio of the electron population in the $M_s = \frac{1}{2}$ state, $n_{\frac{1}{2}}$, to that in the $M_s = -\frac{1}{2}$ state, $n_{-\frac{1}{2}}$, is given by

$$\frac{n_{\frac{1}{2}}}{n_{-\frac{1}{2}}} = e^{-\Delta E / kT}$$

2.5 Experimental Techniques

ESR experiments are performed by detecting the amount of energy absorbed, therefore, in order to improve the sensitivity of detection we want to have as many electrons in the lower state as possible. According to this can be achieved by either reducing the temperature or increasing the field or both. We see that as H increased so does ν , and it is the frequency that turns out to have a practical upper-limit. This results from the difficulty encountered in generating and detecting frequencies greater than 36,000 MHz . The most common experimental arrangements employ frequency either in the X-band or K-band region as shown in Table 2-1. Both of the frequencies are in the microwave region, and this is why ESR is often treated as a branch of microwave spectroscopy.

Table 2-1 The frequency, wavelength, and magnetic field values for the common ESR experiments

| Band | $\nu (MHz)$ | $\lambda (cm)$ | $H (G)$ |
|------|-------------|----------------|---------|
| X | 9,500 | 3 | 3,400 |
| K | 36,000 | 0.8 | 13,000 |

where γ is the magnetogyric ratio of the dipole, that is, the ratio of the magnetic moment to the angular momentum. The magnetic energy of interaction E is given by

$$E = -\mu_s H \cos \theta$$

where θ is the angle between the axis of the dipole and the field direction. Once again because of the restriction imposed by quantum mechanics, there can be only certain values for θ . Figure shows the vector representation of the relation between the angular momentum and its components along the axis of quantization, that is, the external magnetic field.

For an electron having spin S of $\frac{1}{2}$, there are only two possible values of θ . The projection of the spin angular momentum vector onto the axis of quantization gives $\frac{1}{2} \hbar$ and $-\frac{1}{2} \hbar$. This can be written as $M_s \hbar$ where M_s is the magnetic spin quantum number which has the values of $\pm \frac{1}{2}$. It can be easily shown that θ in this case is either $35^\circ 15'$ or $144^\circ 45'$. The same is true for the magnetic moment vector except that its direction is exactly opposite to that of the angular momentum vector.

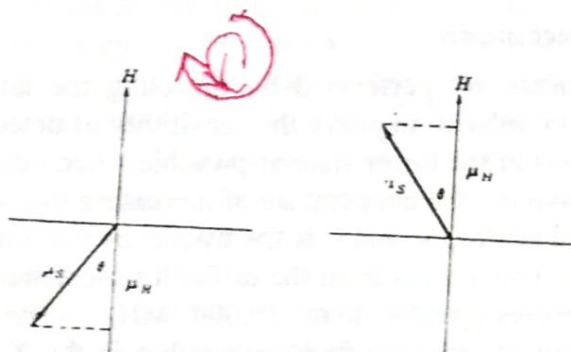


Fig.2.2

Next we derive the resonance condition for an unpaired electron. Let μ_H be the component of μ_s in the direction of the field so that

$$\cos \theta = \frac{\mu_H}{\mu_s}$$

becomes

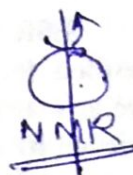
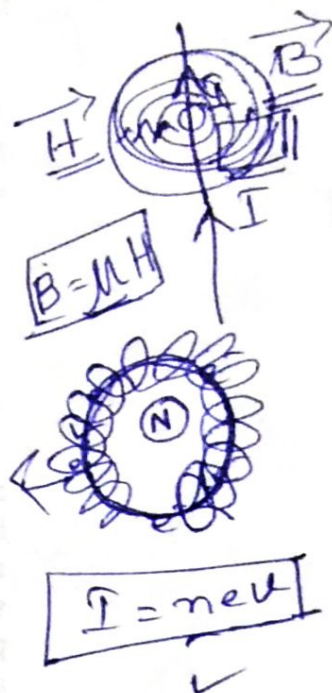
$$E = -\mu_H \cdot H$$

where μ_H is given by

$$\mu_H = -g\beta M_s$$

where β is the electronic Bohr magneton, equal to $(e/2m_e c) \hbar$ (see Appendix 3). Substituting we obtain

$$E = -g\beta M_s$$



$$\mu = \mu_N \mu_0$$

↑
Permeability

$$\therefore B = \mu H$$

$$\mu_0 = \frac{\mu}{\mu_N}$$

~~Singh~~

FTIR

3 APPT = 10 Bohr magneton



2.3 Applications

Crystal
Structural determination: Although the NMR technique is now being employed to solve various chemical and biochemical problems, structural determination still ranks foremost among these. The elucidation of molecular structure from NMR spectra is essentially the determination of two quantities, that is, chemical shift and spin-spin coupling constant. The former tells us about the nature of the functional groups and the latter about the arrangement of the atoms. Furthermore, the relative intensity of the peaks tells us about the ratio of the same atoms in different chemical environments. However, the task of analyzing spectra of large molecules can be quite complex because of the spin-spin interaction. It is indeed fortunate that naturally abundant carbon (C^{12}) and oxygen (O^{16}) do not have nuclear magnetic moments; otherwise structural studies would be limited to only very simple molecules.

Complex spectra analysis can often be aided by either chemical or physical means. We could, for example, replace some hydrogen atoms with deuteriums and compare their spectra. Since isotopic substitution has a negligible effect on the electronic structure of the molecule, the chemical shifts will remain unchanged but the coupling constants will be different because deuterons have a smaller magnetic moment. Since deuteron has a spin $I = 1$, we might expect that the resulting spectrum of the deuterated compound would be more complex. However, spin-spin interactions due to deuterons are seldom observed because of the quadrupole relaxation effect discussed earlier.

A rather interesting feature of this kind of kinetic study is that all measurements are carried out without disturbing the chemical equilibrium whatsoever.

2.4 Introduction to ESR

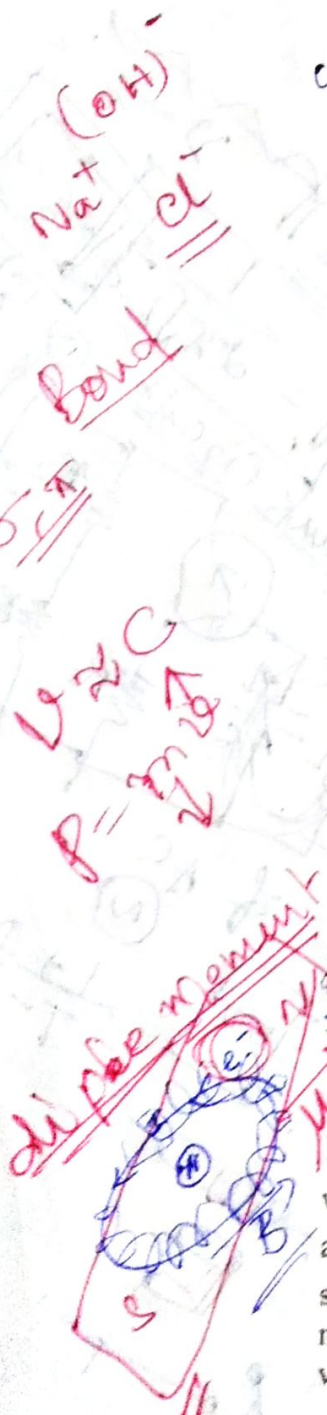
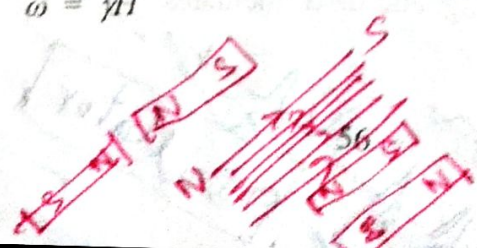
The fundamental properties of an electron are (1) mass, (2) charge, (3) spin, or intrinsic angular momentum. The spinning motion of the electron acts as a circular current and so generates a magnetic field. But the magnetic field of a circular current is equivalent to that of a magnetic dipole of moment μ_s which is given by.

$$\mu_s = -g \frac{e}{2m_e c} h \sqrt{S(S+1)}$$

where g is the g factor for free electron ($g = 2.0023$), e and m_e are the charge and mass of the electron, and $\sqrt{S(S+1)} h$ is the length or magnitude of the spin angular momentum vector. The negative sign indicates that the magnetic moment vector is in the opposite direction to that of the angular momentum vector.

When the electron is introduced into a uniform magnetic field of strength H the electron magnetic dipole will precess about the axis of the field. Analogous to the NMP case the Larmor frequency of precession ω is given by

$$\omega = \gamma H$$



6.5×10^{-24}

6.2×10^{-24}

$Na^+ (OH)^-$
Bond
 Cl^-

N^{14} , N^{15} , P^{25} , etc., but we shall concentrate only on the proton magnetic resonance in this chapter.

2.2. Experimental techniques

Detecting the amount of energy absorbed performs NMR experiments; therefore, in order to improve the sensitivity of detection, we want to have as many spins in the lower state as possible. According to nuclear magnetic moment this can be achieved by either reducing the temperature or increasing the field strength, or both. There are, of course, practical limitations to these two variables.

The basic features of an NMR spectrometer are: (1) a source of radio-frequency radiation, (2) a receiver coil, (3) a de magnetic field, and (4) a recorder or an oscilloscope. Figure 3-3 shows the schematic diagram of an NMR spectrometer (fig.2.1).

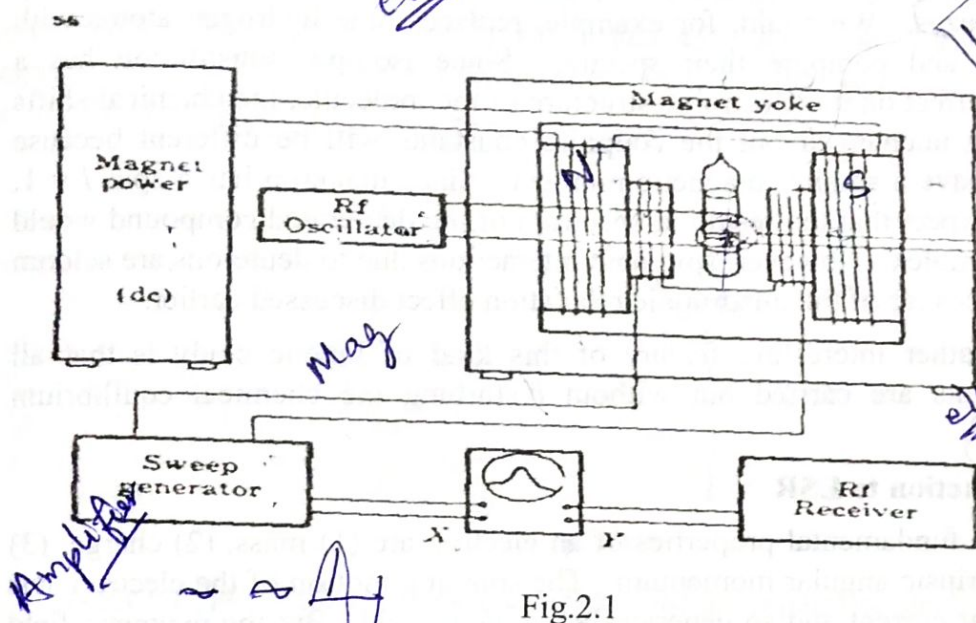
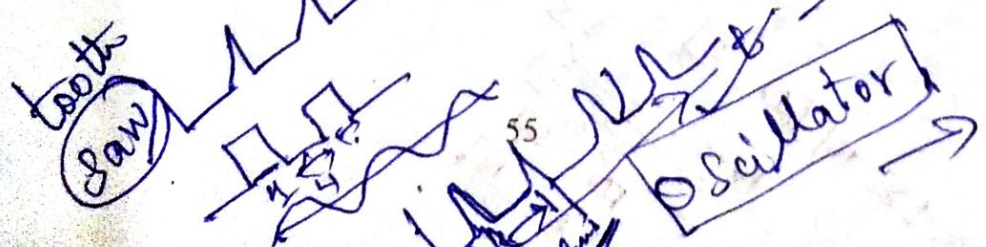
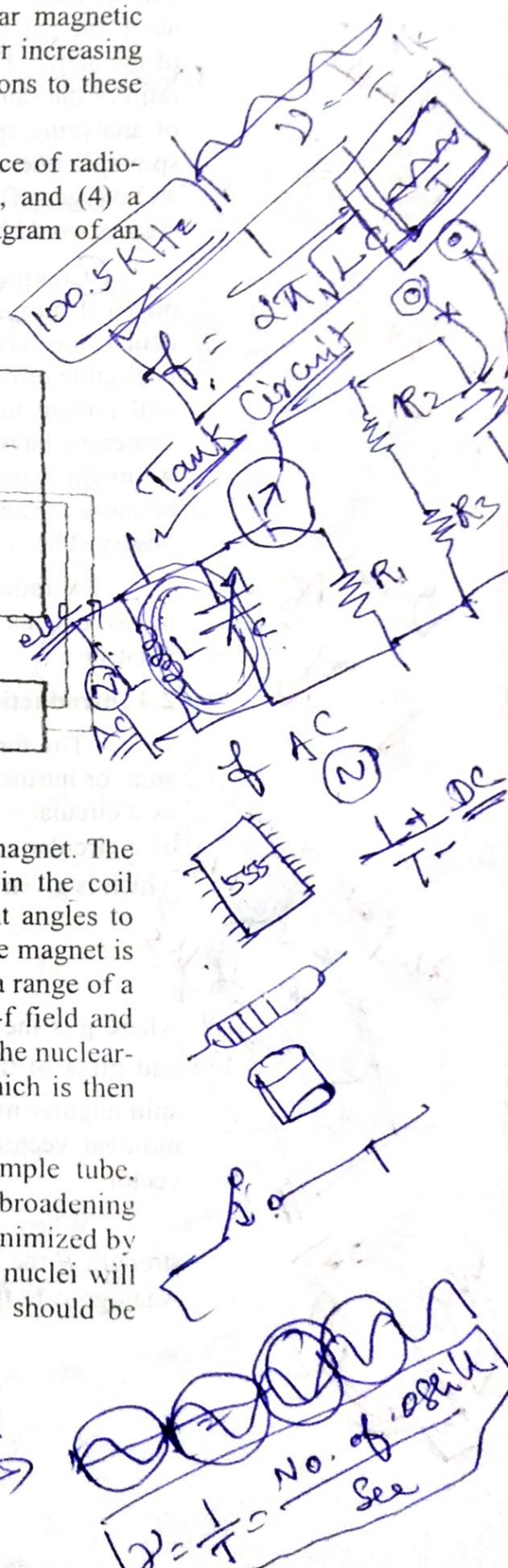


Fig.2.1

The sample tube is placed between the poles of a powerful magnet. The source of energy, that is the radio-frequency field, is generated in the coil connected to the r-f oscillator. The detector coil is placed at right angles to both the direction of the magnetic field and the transmitter coil. The magnet is provided with the sweep coils which are used to vary the field over a range of a few gauss. In a typical experiment, we fix the frequency of the r-f field and vary the magnetic field H until the resonance condition is reached. The nuclear-magnetic-moment transition induces an emf in the detector coil which is then amplified and displayed on the recorder or oscilloscope.

If the magnetic field H is not homogeneous over the sample tube, resonance will occur at apparently different magnetic field and line broadening will result because of the overlapping of lines. This effect can be minimized by spinning the sample tube with an appropriate frequency so that the nuclei will experience an average magnetic field. The frequency of spinning should be greater than the rate at which the magnetic field fluctuates.



If μ_H is the component of μ in the direction of the field, we have

$$\cos \theta = \frac{\mu_H}{\mu}$$

Equation (3-4) now becomes

$$E = -\mu_H H$$

where μ_H is given by

$$\mu_H = g_N \beta_N M_I$$

where β_N is the nuclear magneton, equal to $(e/2M_p c)h$

Substituting into the above equation we obtain

$$E = -g_N \beta_N H M_I$$

Nuclear Magnetic Resonance Spectroscopy

If electromagnetic radiation of frequency ν is present which satisfies the resonance conditions.

$$\Delta E = h\nu = g_N \beta_N H$$

transition between these Zeeman levels can occur. This is the simplest case of nuclear magnetic resonance (NMR). For a system containing an assembly of

non interacting protons, the ratio of the proton population in the $M_I = -\frac{1}{2}$ state,

$n_{-\frac{1}{2}}$, to that in the $M_I = +\frac{1}{2}$ state, $n_{+\frac{1}{2}}$, is given by Boltzmann's expression.

$$\frac{n_{-\frac{1}{2}}}{n_{+\frac{1}{2}}} = e^{-g_N \beta_N H / kt}$$

The nuclear spin I for any nucleus may be zero, a half-integer, or an integer-its value is determined by the mass number A and atomic number Z of the nucleus. The following rules are useful in determining the value of I :

1. If A is odd and Z is even or odd, I is a half-integer.
2. If A and Z are both even, I is zero.
3. If A is even and Z is odd, I is an integer.

Appendix 4 gives a list of the magnetic moments and spins of all the elements of interest in chemical spectroscopy.

If I is zero, μ is zero, and NMR experiments are not possible. Some examples of nuclei with non zero spins, for which NMR is applicable, are C^{13}

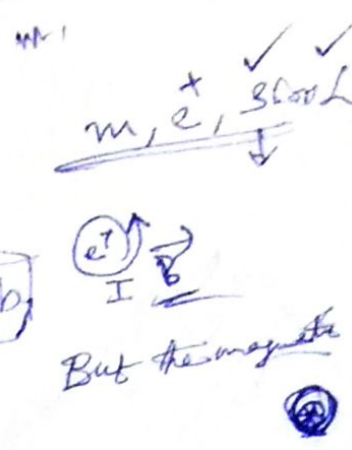
UNIT - II

2.1. Introduction to NMR

The fundamental properties of a proton are: (1) mass, (2) charge, and (3) spin or intrinsic angular momentum. The spinning motion of the proton acts like a circular current and so generates a magnetic field. But the magnetic field of a circular current is equivalent to that of a magnetic dipole of moment μ : given by (see Appendix 3)

$$\mu = gN \frac{e}{2M_p} \hbar \sqrt{I(I+1)}$$

$e = 1.8 \times 10^{-19} \text{ Coulomb}$



where gN is the nuclear g factor, M_p is the mass of the proton, e is the electronic charge, and $\sqrt{I(I+1)} \hbar$ is the length or magnitude of the spin-angular momentum vector.

When a proton is introduced into a uniform magnetic field of strength H , the nuclear magnetic dipole will precess about the axis of the field. This precession occurs because there is a tendency for the magnetic field to turn the nuclear magnetic moment around into the field direction. But this effort is opposed by the rotational inertia due to the revolution of the proton, and the consequent motion is analogous to the precession of a spinning mechanical top under the influence of gravity. The angular precession frequency ω , which is called the Larmor frequency, is given by

$$\omega = \gamma H$$

where γ , the gyromagnetic ratio, is defined by

$$\gamma = \frac{\text{magnetic moment}}{\text{angular momentum}} = \frac{\mu}{\sqrt{I(I+1)} \hbar}$$

The energy E due to this magnetic interaction is given by

where θ is the angle between the axis of the dipole and the field directed. Classically can be taken any value, so that the energy varied continuously. Quantum mechanics, however, imposes the restriction that the angular momentum is quantized in space so there are only certain allowed values for the Figure below shows the vector representation of the relation between the angular momentum and its components along the axis of quantization, that is, the external magnetic field.

For a proton having spin I of $\frac{1}{2}$ there are only two possible values of θ .

The projection of the spin angular momentum vector onto the axis of quantization gives $\frac{1}{2} \hbar$ and $-\frac{1}{2} \hbar$. This can be written as $M_r \hbar$ where M_r is the magnetic spin quantum number which has the values of $\pm \frac{1}{2}$. It can be readily shown the θ in this case is either 35.26° or 144.74° . The same is also true for the magnetic moment vector.

