

2. BASIC THEORY OF NMR SPECTROSCOPY.

2.1 INTRODUCTION :

It is well known that nuclei possess mass as well as the electric charge along with intrinsic mechanical spin or angular momentum. The maximum measurable component of the angular momentum (ie. Spin quantum number I) has values which are integral or half integral multiples of $\frac{h}{2\pi}$ Where h -planck's constant depending upon atomic weight and atomic number of the atom. The atoms with both odd-odd atomic number and atomic weight has spin quantum number always of half integral multiple of $\frac{h}{2\pi}$ and the atoms with odd-even atomic number and atomic weight have spin quantum number of integral multiple of $\frac{h}{2\pi}$. The atoms with even-even atomic number and atomic weight has zero quantum number and hence have no angular momentum; such atoms can not be studied using NMR spectroscopy. This indicates that nuclei with angular momentum only can be studied using NMR spectroscopy.

If an external magnetic field (H_0) is applied to a system of nuclei with magnetic moments, these nuclear magnets will experience torques and will tend to be lined up parallel to the field. Such magnetic

field at the site of a nucleus is the applied field modified by certain effects depending upon nuclear environments and the local magnetic field is determined by number of factors including the polarization of remote parts of the sample, magnetic moments (nuclear and electronic) of neighbouring molecules the intramolecular effects due to other nuclei and electrons in the same molecule. It is due to these effects that NMR is of potential value in problems involving the investigations of molecular structure and environmental effects to structural chemists.

For spin $\frac{1}{2}$ nuclei in diamagnetic materials important parameters in NMR spectra are :-

- 1) Chemical Shift.
- 2) Indirect spin-spin coupling constant.
- 3) Direct dipole-dipole coupling constant.
- 4) Relaxation time and line width.
- 5) The anisotropy of chemical shift.

NMR spectra of nuclei with spin $\frac{1}{2}$ are in addition influenced by Quadrupole and higher rank of interactions (27). In paramagnetic species, additional factors influence the spectra in the form of shifting and/or broadening the spectral lines. For the present work, only nuclei of spin $\frac{1}{2}$ are considered hence the parameters 1 to 5 mentioned above are discussed.

2.2 Chemical Shift :

An atom or molecule in magnetic field acquires a diamagnetic moment due to induced orbital motions of the electrons; a secondary magnetic field is produced at the site of nuclei having a direction opposite to the direction of applied magnetic field. Since, the induced currents are directly proportional to the applied magnetic field, the magnitude of secondary fields is also proportional to H_0 . This induced field screens the applied field at the site of nuclei and field experienced by nuclei becomes $H_0(1-\sigma)$ where σ is dimensionless quantity known as 'screening constant'. The magnitude of Screening constant varies from 10^{-5} for protons to 10^{-2} for heavy atoms (28).

Values of σ differ for nuclei in different environments. Consequently, resonance for such nuclei occur at different applied magnetic fields at constant radio-frequency; the difference is directly proportional to the differences in σ values. This displacement of the signal for different chemical ^{environment} ~~environments~~ due to difference in the screening constant is called the chemical shift and is directly proportional to the applied magnetic field. The chemical shifts are usually expressed in terms of dimension-less parameter δ

given by the equation (2.2).

$$\delta = \frac{H - H_r}{H_r} \quad (2.2)$$

Where H -resonant field of the signal being measured at a fixed frequency and H_r -the corresponding resonant field for the second proton signal chosen as reference signal, since the proton chemical shifts are of the order of 10^{-6} , they are conveniently expressed in parts per million (p.p.m.) defined by equation (2.3)

$$\delta = \frac{\Delta \nu \text{ in Hertz}}{(\text{Spectrometer frequency in mega Hertz})} \text{ PPM.} \quad (2.3)$$

Where $\Delta \nu = \nu - \nu_r \rightarrow$ the separation between the resonance frequencies of nucleus under consideration and that of reference nucleus, generally internal reference TMS-Tetra Methyl Silane. From above discussion of chemical shift, it can also be defined in terms of the screening constants δ . If δ and δ_r are respectively the screening constant of the proton to be measured and that of reference proton then

$$\delta = (\delta - \delta_r) = \frac{(\nu - \nu_r)}{\nu_r} \times 10^6 \text{ ppm} \quad (2.4)$$

Accordingly, a positive value of δ corresponds to higher electronic screening than that of the reference protons. The chemical shifts δ , in parts per million, for a particular nucleus in different compounds measured from the same reference are the

same as for the corresponding isotopic compounds measured from the isotopically substituted reference.

In fact, chemical shift changes with the orientation of the nucleus relative to the applied magnetic field and is actually a second rank tensor with as many as nine independent components. However, due to rapid molecular motions, the NMR spectra of isotropic liquids and gases are influenced by single parameter proportional to the trace of the tensor. On the other hand, if the motion of the molecule is anisotropic, i.e., when it is dissolved in an anisotropic solvent such as liquid crystal solvent, the spectra may in addition be influenced by other elements of the chemical shift tensor. The interpretation of spectra in isotropic solvents is, therefore, considerably simple but the additional information about the chemical shift anisotropy is lost.

2.3 Indirect Spin-Spin coupling constant :

The high resolution NMR spectra often consist of more lines than are expected on the basis of chemical shift alone. This multiplicity of the lines is independent of the applied magnetic field and temperature variations. These multiplicities of lines are due to interactions between nuclear spins

via electrons. (29). In liquids, the interaction energy is given by

$$\Delta E = -\frac{h}{2\pi} J_{ij} I_{i,1j} \quad (2.5).$$

Where J_{ij} --coupling constant between nuclei i and j .
 $\alpha \times e$ measured in Hzs. For protons its magnitude is of the order of 10 Hzs. In the case of spin $\frac{1}{2}$ nuclei so coupled, the resonance of each one is split into a doublet with spacing equal to J_{ij} . The sign of the spin-spin coupling constant may be positive or negative depending upon the relative orientations of the coupling spins. If the spin orientations of the coupled nuclei are antiparallel, the coupling between them is referred to as positive whereas if they are parallel, the coupling is negative (30). The relative intensities of lines due spin-spin coupling are in the ratio of the corresponding binomial coefficients. From the values of relative line intensities of the signals obtained, information can be obtained about the number of equivalent protons giving rise to each signal. The electron-coupled spin-spin interaction usually attenuates rather rapidly with the number of chemical bonds separating the two nuclei in question.

2.4 Direct dipole-dipole coupling constant :

It arises due to the interaction of nuclear dipoles in space. The magnetic field of one dipole at the site of another is proportional to $(3\cos^2 \theta_{ij} - 1)/r_{ij}^3$, where θ_{ij} is the angle which the axis joining nuclei i and j makes with the applied magnetic field directions and r_{ij} is the distance between the two nuclei. The interaction, therefore, provides useful information on the molecular geometry. A fine structure in the NMR spectrum is obtained due to this type of interaction. For nuclei separated by $1\text{\AA}$, this interaction may be of magnitude of several KHz.

Since the nuclear spins can align parallel or antiparallel to the direction of applied magnetic field, (For $I=\frac{1}{2}$) such an interaction produces a doublet for each of the two interacting nuclei. This is known as the direct dipole-dipole interaction. This type of interaction is two times larger than the interaction due to spin-spin couplings. Direct dipole-dipole interaction depends upon the internuclear distances, it may provide useful geometrical information if it does not vanish. Due to rapid molecular motions in the liquids and gases where all θ 's are equally probable the average value of $(3\cos^2 \theta_{ij} - 1)$ is zero, resulting in loss of the information carried by this

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interaction. On the other hand, in solids both the inter and the intramolecular dipole-dipole interactions are nonvanishing which results into broad lines in their NMR spectra. The geometrical information in such cases may be derived from line width measurements but with low precision.

Experiments, where intermolecular dipolar couplings are averaged out and the intramolecular ones have non-zero values provide more precise information on molecular geometry, since it is derived from line positions which can be measured more accurately than line widths. Pioneering experiments in this direction were carried out in 1963 by Saupe and Englert (10) who suggested the use of nematic liquid crystal solvent as an anisotropic media for orienting molecules in NMR studies. This technique has since then extensively used to derive information on relative inter nuclear distances, bond order and bond angles. The technique provides a unique method for the precise determination of molecular shape in the liquid crystal solvent. In addition, this method provides information on the anisotropic contributions to the chemical shift and to the indirect spin-spin coupling constants (31-33), Such information is not obtainable from the Spectra in isotropic media.

2.5 Relaxation times and line widths :

Energy separation between two spin states of nucleus (with spin $\pm \frac{1}{2}$) in an external magnetic field H_0 is equal to $2\mu H_0$ as shown in Fig. 2.1.

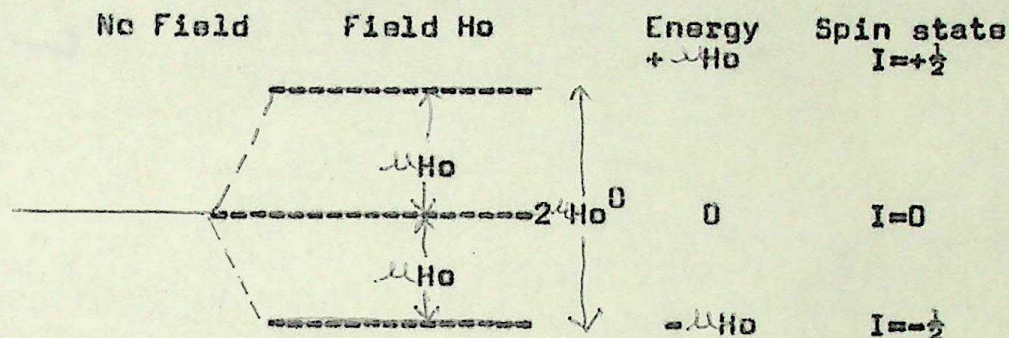


Fig. 2.1 Zeeman splittings of nuclear energy levels in a magnetic field.

This splitting of energy levels in a magnetic field is referred to as nuclear Zeeman splittings; Where μ is magnetic moment of the nucleus. If such nuclei are in thermal equilibrium at a temperature T , the lower of the two states is more populated. The distribution of spins among the possible states is sometimes discussed in terms of the concept of spin temperature T_z . The distribution of spins in different levels is governed by the Boltzmann distribution law. The relative spin populations in the two levels can be expressed approximately by $\frac{n_+}{n_-} = 1 + \frac{2\mu H_0}{kT_z}$. So that spin temperature $T_z = T$ the thermal equilibrium temperature and n_+ and n_- are the spin populations of the lower and upper states respectively. When such

nuclei are subjected to a radio-frequency field of suitable frequency being the principle of NMR, some of the nuclei in the lower energy level absorb energy and go to the higher energy level. The populations of the energy levels are now different from their equilibrium states. The population of upper level increases. It may, therefore, appear that some time when both the levels become equally populated, the absorption of energy from r.f. should cease, contrary to the general observation. This indicates that some of the nuclei in higher energy level must be giving up energy to other degrees of freedom in the system i.e. to the lattice (34). This process known as spin-lattice relaxation, occurs exponentially with characteristic time T_1 , called spin lattice relaxation time, Such a process is important as it not only helps to maintain resonance but governs its line width also.

Spins of the nuclei also transfer energy by interactions among themselves. This process is called spin-spin relaxation that occurs with a characteristic time T_2 called the spin-spin relaxation time. The local fields produced by such an interaction among magnetic neighbours have in general a static and an oscillating components. The static components add to or subtract from the external field and consequently

the fields at the sites of different nuclei are different giving rise to line broadening. The oscillating components produce spin exchanges shortening the life of a nucleus in particular spin state and broaden the resonance line.

These relaxation processes are the main cause of line broadening in NMR spectroscopy. The field inhomogeneity, the unresolved couplings, the dipolar and quadrupolar ($I=1$) relaxation times are also the additional factors causing the line broadening. To minimise the line broadening effects, nothing can be done except to adjust the homogeneity of field and concentration of the sample.

2.6 The Anisotropy of Chemical shift :

In isotropic media due to random motion of nuclei in all possible directions being equally probable the chemical shift is identical along all directions; but in anisotropic media such as liquid crystal solvents the chemical shift along the direction of magnetic field and perpendicular to magnetic field differ in magnitude giving rise to the effect called anisotropy in chemical shift. To consider this anisotropic contribution of chemical shift for liquid crystal

solvent the factor $(\sigma_{\parallel} + \sigma_{\perp})$ must be considered while analysing the spectrum. This anisotropic effect is found to be more in fluorine compounds as compared to others. The anisotropy in chemical shift, spin-spin-coupling and direct dipolar coupling should be taken into account for analysing only Fluorine compounds and for other compounds the effect is negligible.

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