NMR SPECTROMETER

Purcell and Block in 1946 independently developed an experimental technique for studying nuclear magnetic resonance. The sample usually a liquid or a solid to be investigated, is taken in the tube placed between the poles of an electromagnet of strength B. The field of the magnet is varied from 0 to 1.0 T. The radio -frequency oscillator sends a preset frequency ν in the coil located between the magnetic poles. Another coil around the sample tube, called receiver coil, picks up the signal from the sample, carries it to the receiver and is amplified. The amplified signal then goes to a cathode ray oscillography indicator or recorder. The field strength is gradually increased, and the radiation is absorbed only when the right-hand side of equation (7) is satisfied for a given frequency. At this stage the strength of the oscillating field equals the transition frequency. In other words, the sample is in resonance with the applied frequency and absorption takes place. The recorder at this point shows a peak. When the field strength is further increased the peak disappears as there is no absorption. Another peak will result only when the correspondence is reached again.

THE CHEMICAL SHIFT

NMR spectra can distinguish protons in different environments. The environment surrounding the nucleus has a little but definite measurable effect on the field experienced by the proton. This effect is extremely useful in elucidating the structure of the molecules and the nature of the chemical bonds. Protons, whether in hydrogen atoms or molecules, are surrounded by electronic charge cloud. The applied magnetic field induces in an electronic current in the molecule in a direction which opposes the applied field. The induced field is directly proportional to the applied field B and so can be represented by σB where σ is the *screening constant* of the order of 10^{-6}. The effective magnetic field B_{eff} experienced by a nucleus is given by

$$B_{eff}=B(1-\sigma)$$

Thus, in presence of the extra nuclear environment, the resonance condition (equation 12) has to be modified as

$$h\nu= g_N\mu_N B_Z (1-\sigma) \quad\quad\quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (13)$$

A positive value of σ means that the nucleus is shielded by the electronic environment whereas a negative value of σ corresponds to deshielding of the nucleus. In shielding $B_{eff} < B_Z$ hence B_Z must be increased to bring the nucleus in resonance and in deshielding $B_{eff} > B_Z$ resulting in the resonance at lower field. So due to shielding (or deshielding) identical nucleus having different chemical environments resonante at different values of the applied field. These values being characteristic can be used to identify various types of environments in which the nucleus is present. Since the shift in the position of resonance is due to the difference in chemical environments, it is called chemical shift and is denoted by δ. This is expressed relative to some standard substance $(CH_3)_4Si$ tetramethyl silane (TMS), usually chosen as reference.

$$\delta = \frac{B_{sample} - B_{ref}}{B_{ref}} \times 10^6$$

………………………..(14)

This is multiplied by 10^6 to express it as parts per million (ppm).

The advantages of using tetramethyl silane (TMS) are:

   (i) It gives a single sharp peak, as all the twelve nuclei are equivalent.

   (ii) Its resonance peak occurs at very field, and

   (iii) It dissolves without reaction in many systems and hence can be readily recovered from most sample after use.

sen for ues are positive.

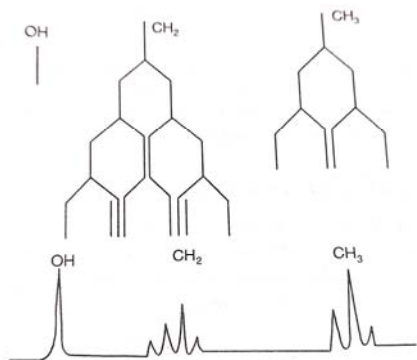NMR spectrum for ethanol at high resolution is shown in figure 3.

Figure 3: NMR spectrum of ethanol

Here the peak for CH_2 group splits into four lines (fine structure) and the peak for CH_3 splits into three lines following the n+1 rule. This fine structure is due to the interactions of the nuclear spins of one set of equivalent protons with another set. This is known as spin -spin splitting. The absorption line of CH_3 group is first split into two by the two orientations of one of the methylene (CH_2) protons; each line is further split due to the interaction of the second methylene proton. The absorption line of CH_3 is thus split into three lines of intensities 1:2:1. Similarly, the absorption line of methylene protons is split into four lines due to the three protons of the neighbouring methyl group. The intensities of these lines are 1:3:3:1. However, it should be

noted that a hydroxyl proton does not show splitting as it undergoes chemical exchange rapidly with protons in other molecules.

PMR spectrum of CH₃OH: The extent of shielding will be constant for a given atom in isolation, but will vary in a molecule because of different chemical environments. Consider, for an example, the molecule CH_3OH.It has three identical C—H bonds and one O—H bond. The chemical environments of hydrogen atoms in C—H bonds and O—H bond are different. Since oxygen is more electronegative than carbon, the electron density on H in O—H bond will be less than that on H in the C—H bond. In other words, it can be said that the hydrogen atom in C—H bond is more shielded than the hydrogen atom in O—H bond, i.e

$$\sigma_{CH} > \sigma_{OH}$$

Thus from the equation, $B_{eff} = B(1-\sigma)$ or $B_{observed} = B_{applied}(1-\sigma)$, it follows that

$$B_{applied}(1-\sigma_{CH}) < B_{applied}(1-\sigma_{OH}) \quad [\text{since}, \sigma \text{ is positive}]$$

$$\text{So}, (B_{observed})_{CH} < B_{observed})_{OH}$$

that is, the actual field seen by the meyhyl protons will be lesser than that seen by the hydroxyl proton.

Now, the spacing between the two nuclear levels in the presence of a magnetic field as given by the Eq.

$$\Delta E = E_\beta - E_\alpha$$

$$= \frac{1}{2}|g_N|\mu_N B_{observed} - \left(- \frac{1}{2}|g_N|\mu_N B_{observed}\right)$$

$$= |g_N|\mu_N B_{observed}$$

$$= \gamma \frac{h}{2\pi} B_{observed}$$

$$= \gamma \frac{h}{2\pi} (1-\sigma)B_{applied}$$

$$\dots\dots\dots\dots\dots\dots\dots(14)$$

$$\text{Since}, (B_{observed})_{OH} > B_{observed})_{CH}$$

it follows that for a given applied field, the energy levels of O—H proton will be more widely spaced than those of C—H protons. The effect of a steadily increasing magnetic field on the energy levels of —CH₃ and —OH protons is shown in Figure 4.

Since most of NMR spectrometers are operated by using a constant frequency oscillator (usually at 60MHz) and varying the external magnetic field, it is obvious from Figure 4 that the hydroxyl proton will be thrown into resonance earlier than the methyl protons as the external magnetic field is steadily increased. This means that the PMR signal of hydroxyl proton will be observed at the low end field and that of methyl protons at the high end field (Figure 4). The area under the signal of methyl protons will be three times larger than that under the hydroxyl proton, since in the former has three identical protons. It may be recalled that neither oxygen nor carbon will exhibit any absorption s both of them are magnetic inactive nuclei.
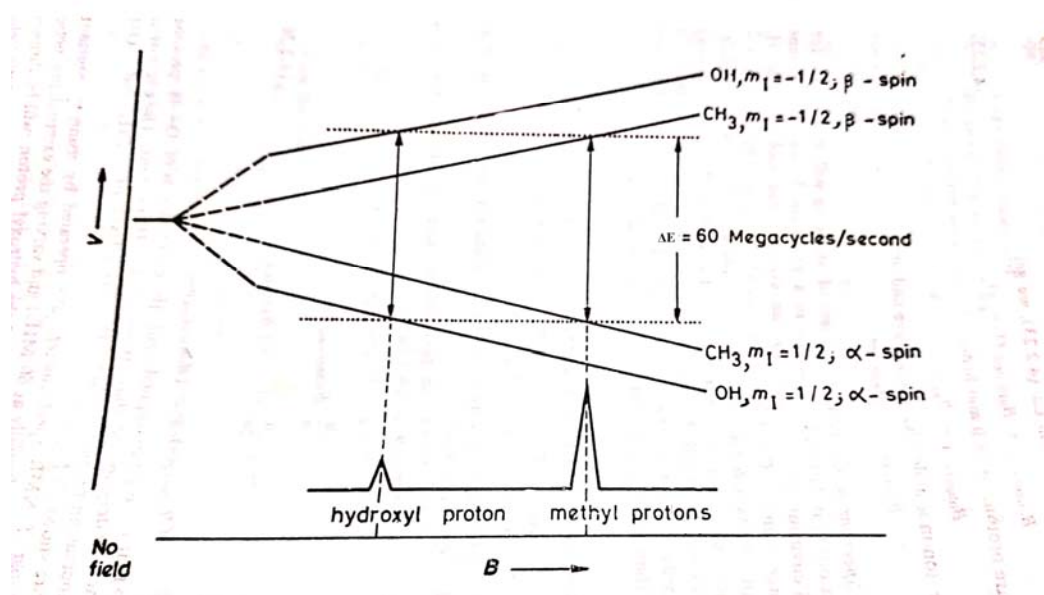

Figure 4: Variation of potential energy of methyl and hydroxyl protons of CH₃OH in presence of varying external magnetic field.