5.22 NMR Spectrum at more than one Radio-Frequency

It may be noted that the chemical shift positions for the various sets of protons are field dependant. If we work the spectra of a particular compound at different radio-frequencies, then it has been found that the value of coupling constant (measured in cps) remains the same whatever the applied field. Scanning at different radio-frequencies tells clearly whether a particular signal is a multiplet or a few singlets. Let us consider a case in which a doublet is observed and is being suspected as two singlets. For this, the spectrum of the same compound is re-run at a higher radio-frequency. Now the signal will appear at a different field strength but if the distance between the two peaks (coupling constant J) remains the same, then it is necessarily a doublet. If the distance between the two peaks increase by working at a higher radio-frequency, the formation of two singlets can be safely declared. Sometime, it happens that at a certain radio-frequency, the two signals in the *nmr* spectrum overlap and thus, the analysis becomes difficult. This technique helps in simplifying such a complex spectrum. The multiplets can be pulled apart by scanning the spectrum of the same compound at a higher radio-frequency. Thus, the complex spectrum is improved*. For example, in the *nmr* spectrum of 4-chlorobutyric acid ($ClC^4H_2C^3H_2C^2H_2C^1OOH$) at 60 mega cycles sec^{-1}, the quintet for the central methylene and the triplet for C_2-methylene overlap and thus complexity arises. But the signals get apart by working the spectrum at 200 mega cycles sec^{-1}. At 200 mega cycles sec^{-1}, two distinct signals (quintet and triplet) are observed with different chemical shifts.

5.23 Deuterium Exchange Reactions

It has been found that if a few drops of deuterium oxide are added in the sample, the D_2O exchanges with the labile protons such as —OH, —NH, —SH and also with the reactive methylene protons flanked by the carbonyl groups. The mechanism involves the same course as is seen in **proton exchange reactions.**

When a little D_2O is added to ROH, then due to rapid exchange, ROH becomes ROD.

$$ROH + D_2O \rightleftharpoons R{-}OD + H{-}OD$$

Thus, the signal for —OH proton normally observed in ROH will be missing in the PMR spectrum and instead, a signal for proton in H—OD will appear. Similarly, if a little D_2O is added to RCOOH, then due to rapid exchange, it becomes RCOOD.

$$RCOOH + D_2O \rightleftharpoons RCOOD + H{-}OD$$

Clearly, the signal for the proton in RCOOH (in the PMR spectrum) which normally appears (in the absence of D_2O) at a negative tau value will be missing or diminished and a signal for proton corresponding to H—OD appears instead. This technique which is employed for detecting the presence of OH, NH groups etc. is called **deuteration.** For the deuterium exchange technique, two spectra are run.

(*i*) One with the sample dissolved in a solvent other than D_2O.

(*ii*) Second spectrum with the sample dissolved in the same solvent and containing a few drops of D_2O.

On comparing the two spectra, if the peak areas are seen to diminish then the sample may contain —OH, —NH, —SH group in which deuterium exchange is possible.

5.24 C^{13}–nmr Spectroscopy

C^{13}-nuclear magnetic resonance is a relatively new technique. There are considerable differences between the H^1 *nmr* and C^{13} *nmr* spectra both in the mode of recording as well as appearance.

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* The degree of improvement of the spectrum depends upon the differences in chemical shift and also upon the coupling constants involved.

The spin quantum number, I for C^{12} is equal to zero. It is, therefore, non-magnetic and does not give any *nmr* signal. C^{13} has a spin quantum number equal to ½ and its nuclear magnetic resonance can be observed in a magnetic field of 23,500 gauss at 25.2 mega cycles per second. It may be noted that with the same magnetic field, H^1 *nmr* is observed at 100 mega cycles per second. The natural abundance of C–13 isotope is only 1.11%. The low abundance further reduces the sensitivity of absorption. Although the low abundance had been a major obstacle for the advent of C^{13} *nmr*, we now know that the nature's choice had been a very fortunate one. Since with higher abundance, probably, neither proton nor C^{13} *nmr* would ever have even become a meaningful technique for the organic chemist because of the great complexity of spectra that would result from heteronuclear and homonuclear spin-spin coupling. H^1 *nmr* spectrum is normally obtained by sweeping either the excitation frequency or the field through the region of nuclear precession frequencies. The inefficiency of this method is clear from the fact that only one line can be observed at a given point in time. The problem arises when C^{13} with intrinsically narrow lines covering a wide absorption range are studied. It is, therefore, advantageous to excite the whole band of frequencies simultaneously. It is done by using a strong pulse of radio-frequency covering a large band of frequencies which is capable of exciting all resonances of interest at once. At the end of the pulse period, the nuclei will precess freely with their characteristic frequencies reflecting with the chemical environment.

Each C^{13} resonance in organic molecule is spin coupled not only to the directly attached proton but also to the proton(s) which is (are) two to four bonds away. The value of the coupling constant also differs accordingly. The value of the coupling constant is over 125 cps for the C^{13} absorption when it couples with the proton directly attached to it ($J_{C—H} > 125$ cps). The value of coupling constant is nearly 20 cps when the coupling proton is two to four bonds away. C^{13} *nmr* spectra, therefore, appear as multiplets with unresolved long range couplings. Each signal appears as a broad peak. The complexity in the spectrum further increases by the overlap of multiplets due to the large number of one bond C—H couplings.

Development of a proton decoupling technique was most significant in simplifying C^{13} *nmr* spectra. In this technique, a single H^1 decoupling frequency as the centre of a finite excitation band is utilised. It is called **proton noise decoupling.** This single frequency is modulated by a pseudo random noise generator yielding effective excitations throughout a preset band width. The band width can be set broad enough to cover all protons in a sample.

Chemical Shift in C^{13} *nmr*. For almost all organic molecules, complete C^{13} spectra appear between low field carbonyl carbons and high field methyl carbons in the range 0 to 200 ppm (δ value). TMS is the common internal reference which is used for C^{13} *nmr*. One of the advantages of using CMR* in organic chemistry is that many of the functional groups containing carbons are directly observable. The CMR spectrum detects:

(*i*) the total number of protons

(*ii*) the total number of carbon atoms and also

(*iii*) the presence of carbonyl group in the organic compound.

Medium induced and concentration dependant chemical shifts are negligible in C^{13} *nmr* because the nuclei studied are buried in the molecular framework. Unlike protons which are in the periphery of a molecule, C^{13} chemical shifts are, however, extremely sensitive to substitution and molecular geometry. It may be noted that highly substituted carbon atoms resonate at lower field. Carbon atoms separated by several bonds strongly influence each other if these are spatially close (NOE).

The state of hybridisation is the dominating factor determining the chemical shift of a carbon atom. sp^3 hybrid carbon atoms absorb upfield while sp^2 carbon atoms absorb at lower field strength.

$$sp^3 > sp > sp^2$$

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* CMR means C^{13} *nmr*

The carbonyl carbon has been the most investigated of all carbon atoms by CMR. The resonance of carbonyl carbons of all aliphatic ketones absorb farthest downfield with δ value equal to 200 ppm. The esters and lactones appear between 160–180 δ.

In an unsaturated framework, delocalisation of charge across the π electron system produces large effect on the value of the chemical shift. In aromatic compounds, the electron donating substituents *viz.* —NH_2, —OH delocalise their lone electron pairs into the π system, thus, increasing the charge density at the ortho and the para carbons. Substituents with lone pairs, thus, shield ortho and para carbons while the electron attracting groups have a deshielding influence. Carbonyl carbons are particularly important in describing the position of chemical shift. The carbonyl carbon bears a partial positive charge and hence resonate at the lower field (higher δ value). In the case of conjugated carbonyls, the positive charge can be delocalised and as a result of it, the carbonyl carbon resonates upfield.

5.25 F^{19} – nmr

Fluorine with mass number 19 is the naturally occurring isotope. Like ^1H, we know that it has $I = \frac{1}{}$ Except for th