



The number of pulses is selected such that the pulse angle  $\theta$  is equal to 90°/n. At the end, a 90° pulse is achieved. Typical value for Tr is 2 µs. An example is shown in Fig. 10.30 for the following alkenyl ester:



33. Write the general range in which carbonyl carbon of the following compounds absorb in CMR spectra.

Acid, halides, Acid amides, Esters and Carboxylic acids. *Hint*: See Section 7 and Table 8.1.

34. Write the decreasing order of chemical shift of the carbonyl carbon of the following: CH<sub>3</sub>COI, CH<sub>3</sub>COCl, CH<sub>3</sub>COBr

*Hint*: See Section 12.

35. Why are the carbonyl carbons of the carbonyl group containing compounds very much deshielded? Explain.

Hint: See Section 9 and 12.

36. In 2-butanone, the carbonyl carbon absorbs at 207 ppm, whereas in but-1-ene-3 one, the carbonyl carbon resonates at 194 ppm. Why? *Hint*: See Section 12. The positive charge on carbonyl carbon gets reduced due to resonance, in

the unsaturated ketone.

- Can we classify C-13 shifts of hydrocarbons on the basis of their hybridisation? Give the approximate range of the three categories. *Hint*: See Section 15.
- 38. How many peaks does a monosubstituted benzene ring show in its (proton decoupled) CMR spectrum? Explain. What will be the intensity of the ipso C signal compared to others? *Hint*: See Section 4, monosubstituted benzene.
- 39. How many peaks do we see in the proton-decoupled CMR spectrum of ethyl benzene? What will be the intensity of the ipso C signal compared to others? *Hint*: See Section 4, ethyl benzene (Fig.).
- 40. How many signals do we see in the proton-decoupled CMR spectrum of acetophenone? What is the intensity of ipso C signal compared to others? *Hint*: See section 4, acetophenone (Fig.).
- 41. Can we distinguish three isomeric symmetrically disubstituted benzenes on the basis of their proton-decoupled CMR spectra?

Hint: Yes, we can. See Section 4.

42. How will you distinguish the three disubstituted dibromobenzenes on the basis of their protondecoupled CMR spectra.

Hint: See Intext Exercise 4.

- 43. Whereas benzene shows only one signal in its proton-decoupled CMR spectrum, replacement of a carbon in benzene by nitrogen produces three signals in its CMR spectrum. Why? *Hint*: Compare Benzene with Pyridine. See Section 5, heteroaromatics.
- 44. How many signals are expected in the CMR spectrum of indole? *Hint*: Eight. Because all the carbons are non-equivalent. See Section 5.
- 45. How many signals are expected in the CMR spectrum of iso-quinoline?*Hint*: All 9 carbons are different in this molecule. So, they give rise to their own signals. See Section 6.

equal to the rate of tumbling of the molecule. And its amplitude is proportional to magnet strength i.e.  $r_{\rm H}$  and to  $r^{-3}$ , the distance between  ${}^{13}\text{C}$  and  ${}^{1}\text{H}$ ,  $\gamma_{\rm CH}$  being 1.1 Å. Only if the frequency exactly matches the larmor frequency for the  ${}^{13}\text{C}$  nucleus that is equal to  $Y_{\rm C}$ .  $B_0/2\pi$ , then this would stimulate the  ${}^{13}\text{C}$  nuclei to relax from the  $\beta$ -spin state to the  $\alpha$ -spin state. The energy involved is coupled to rotational motion of the sample molecule and is therefore released as thermal energy. The rate of these stimulated transitions is proportional to  $r^{-6}$ , the distance between  ${}^{13}\text{C}$  and  ${}^{1}\text{H}$  in C—H bond. In fact, the dipole-dipole interaction is responsible for NOE that is also proportional to  $r^{-6}$ .

The rate of dipolar relaxation  $R_1^{DD} (1/T_1)^{DD}$  after theoretical consideration has been shown to be dependent upon correlation time  $\tau_C$  as well :

$$R_{1}^{DD} = y_{H}^{2} y_{C}^{2} h^{2} r^{-6} \tau_{C} \qquad \dots (A)$$

where h is the Planck's constant,  $\tau_C$  is the time that characterizes reorientation of a molecule in liquid. This is essentially the average tumbling time of a molecule required to change its orientation relative to the direction of B<sub>0</sub>. Molecules that are small have small  $\tau_C$  as they tumble rapidly. On the other hand, larger molecules tumble slowly and consequently have a long  $\tau_C$ .



Fig. 11.3. The sinusoidal  ${\rm B}_{\rm eff}$  versus time in dipolar-dipolar relaxation.

Evidently, it is clear from equation, the dipolar-dipolar interaction rate is dependent to  $r^{-6}$ , and should therefore, drop off rapidly with distance. That is why, this is the major mechanism for relaxation for <sup>13</sup>C nuclei attached to protons (CH<sub>3</sub>, CH<sub>2</sub>, CH). If the <sup>13</sup>C nuclei are not attached to protons directly, this mechanism would not be efficient for relaxation of such nuclei and therefore such carbons are expected to have longer relaxation times. This also means that such carbons will also contribute weaker signals in routine CMR spectra wherein we do not use relaxation delays of the orders of 5XT<sub>1</sub>, a time consuming process as explained earlier.

The equation has got a great significance as it can give us information regarding the internuclear distances, r as well as molecular dynamics in the liquid state.

The fractional dipolar relaxation rate is related to NOE as follows :

Dipolar relaxation = 
$$\frac{ni}{Y_H / 2Y_C} \times 100$$
  
=  $\frac{n_i}{1.988} \times 100$  as  $\frac{Y_H}{2Y_C} = 1.988$ 

n<sub>i</sub> is the NOE factor for a specific <sup>13</sup>C nucleus  $Y_H/2 Y_C = max$  value of NOE = 1.988

The quaternary carbons can be characterized by the fact that they have about 10X to 20X longer  $T_1s$  compared to protonated carbons. This can be understood in terms of the inverse sixth power relation of

## 13.12 HMQC

The heteronuclear multiple quantum correlation (HMQC) spectrum is actually a variant of the 2D HSQC, whose pulse sequence is shown in Fig. 13.34a.



Fig. 13.34a. Pulse-sequence in HMQC.

## Example: HMQC spectrum of 3-heptanone

The HMQC spectrum of 3-heptanone is shown in Fig. 13.34b.

The most intense <sup>1</sup>H peaks appear at 0.78 ppm (H–7), 0.93 ppm (H–1) and 2.30 ppm (H–2 and H– 4). The contour-threshold in this experiment was set high in order to minimize the <sup>12</sup>C–<sup>1</sup>H artifacts so that only the most intense peaks are seen. These are the triplets due to H–1, H–7 and H–4, only the



Fig. 13.34b. HMQC for 3-Heptanone.