* How is this maintained even after the nuclear transition from the lower to higher energy state in the light of second postulate of the theory of electromagnetic radiation ?

Ans. As the collection of nuclei continuously absorbs radio frequency radiation the excess of nuclei originally present in the lower energy state may diminish. Accordingly the intensity of the absorption signal may diminish and may under certain circumstance vanish entirely.

saturation

Such a phenomena is known as saturation. When the nuclear population in the two spin states are exactly equal and again fortunately for us under normal condition.
But under normal condition saturation does not take place. Therefore, there must be some processes which are responsible for the return of the nuclei from the upper state to the lower state to maintain the original excess of nuclei always in the lower energy state.

* How do the nuclei in the higher energy state return to the lower energy state ?

Ans. The various radiationless transitions by which a nucleus in the higher energy state returns to the lower energy state are called relaxation processes. The two must important relaxation processes are – i) spin-spin relaxation
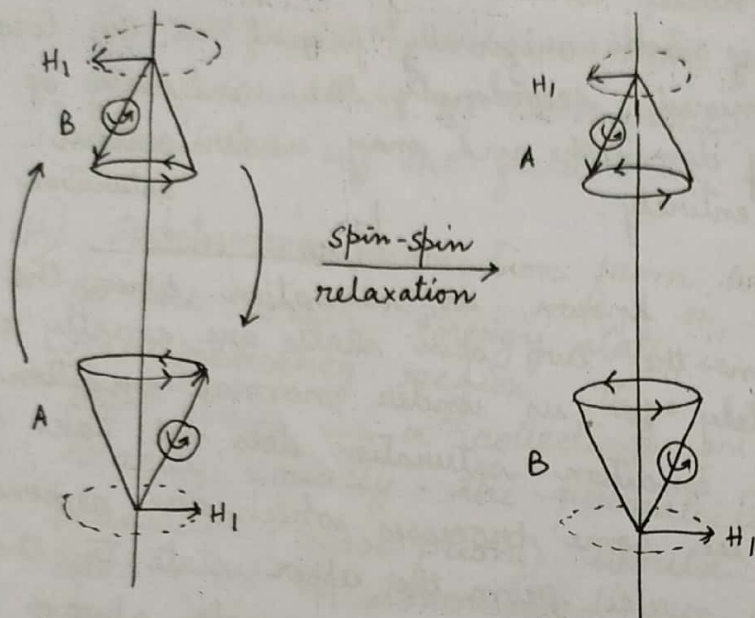ii) spin-lattice relaxation

i) Spin-spin relaxation (transverse relaxation)
Spin-spin relaxation is effected by the mutual exchange of spins by two precessing nuclei in close proximity to each other. Associated

* protons of organic compound.

with each precessing nucleus there is a magnetic vector component rotating in a plane perpendicular to the main magnetic field. If two nuclei are in close proximity, this rotating magnetic field is exactly what is required to induce a transition in the neighbouring nucleus.

Spin-spin relaxation

Although spin-spin relaxation shortens the life time of an individual nucleus in the higher energy state. It does not contribute to the maintanance of the required excess of nuclei in lower energy state, which is necessary condition for NMR.

ii) **Spin-lattice relaxation** (Longitudinal relaxation)

The required excess of nuclei in the lower energy state is maintained by spin-lattice relaxation.

The term lattice refers to the framework of molecules containing the precessing nuclei. All of these molecules are undergoing translational, rotational and vibrational motion and have magnetic properties. Hence a variety of small magnetic fields are present in the lattice, so a particular small magnetic

field property oriented in the lattice can induce a transition in a particular precessing nuclear magnet from an upper state to a lower state. The energy from a this transition is transferred to the component of lattice as additional, translational, rotational, vibrationa energy which is ultimately transformed into thermal energy. Thus a nucleus returns to the lower state from an upper state by a radiationless transitional process which maintains an excess of nuclei in the lower energy state and ensures the condition necessary for the observation of nuclear magnetic resonance phenomenan

Half life of the spin-lattice relaxation is designated by T_1 and that of spin-spin relaxation (T_2). If T_1 & T_2 are small, the life time of an excited nucleus is short. A short lived excitation gives broad signal, while an extended excitation results in sharp spectral lines.
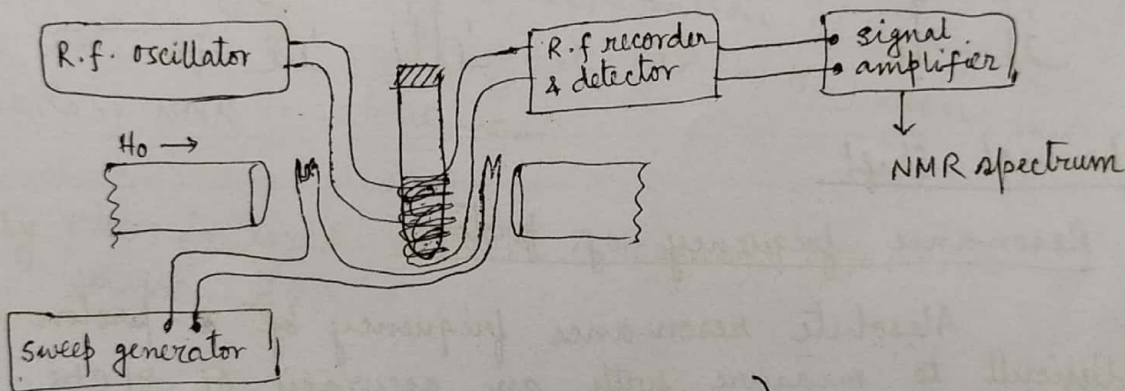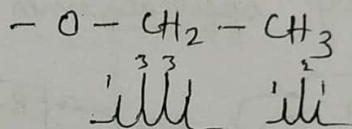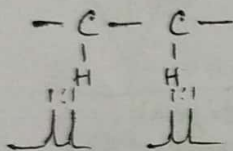

Fig:- Continuous wave (c.w)
Mode of Instrument operation

protons of organic compound.

Since the effective mag. fields experienced by different protons in a particular compound are different, the precessional frequencies of these protons are also different from that of the r.f oscillator these protons are brought into resonance condition through succession by slowly changing the magnetic field from low field to high field keeping r.f oscillator unchanged.

Computer Averaging Of Transient (CAT)

chemical shift → nature of protons

Spin - spin coupling → multiplicity of proton signal

↓

Environment of the proton

$$-\overset{|}{\underset{H}{C}} - \overset{|}{\underset{H}{C}} -$$

$$\Perp \quad \Perp$$

$$- O - CH_2 - CH_3$$
$$\quad\quad 3 \quad\; 3$$

$$\Perp \quad \Perp$$
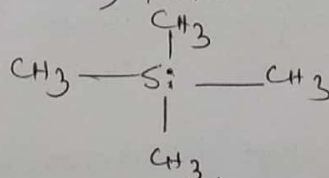
Chemical Shift

Resonance frequency of protons

Absolute resonance frequency of a proton is difficult to measure with an accuracy of ±1 cps. However relative proton resonance frequencies can be readily determined with an accuracy of ±1 cps.

what is meant by chemical shift or relative resonance frequency of a proton?

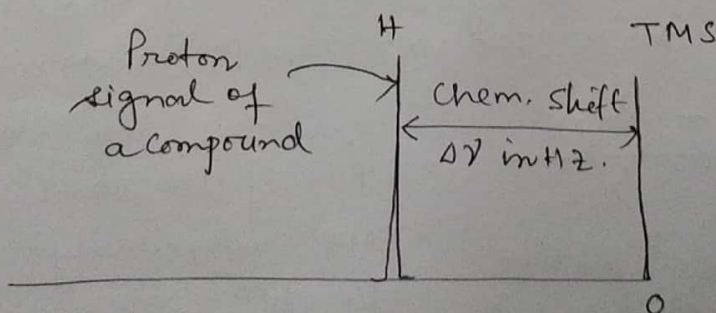What is meant by chemical shift or relative resonance frequency of a proton?

For a field strength of 1.4T, protons have a precessional frequency of ≈ 60 MHz. The precessional frequency of all protons in the same external magnetic field is not same, and it depends on a number of factors.

It has been found that different precessional frequency values of different proton depends on the chemical environment. As the shift in frequency depends on chemical environment, this give rise to the term chemical shift.

To measure the precessional frequency of a group of nuclei in absolute frequency units is not difficult but is rarely required. More commonly the differences in frequency are measured w.r.to some reference group of nuclei.

For protons and ^{13}C, the universally accepted reference is tetramethyl silane, TMS.

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$$

Separation of resonance frequencies of nuclei (Proton/Protons) in different structural environments from that of an arbitarily choosen standard is termed the chemical shift or relative resonance frequency.

Proton signal of a compound — H — TMS

Chem. shift
$\Delta\gamma$ in Hz.

0

Resonance frequency of the protons of TMS used as internal standard is arbitarily taken as zero and the chem. shift of a proton of an organic compound is given by the separation of a signal from that of the TMS signal ($\Delta\gamma$ in Hz) run in a particular NMR instrument.

⦿ why TMS is used as an internal ~~Ste~~ reference compound?

The reasons are as follows:

(i) It is chemically inert. → (operating equally through space).

(ii) It is magnetically isotropic in nature.

(iii) It is highly volatile (b.P = 27°c) so that precious sample can be recovered.

(iv) It is miscible with most organic compound (Solvent).

(v) It gives a sharp spectral line.

(vi) The protons of the reference compound resonance at a higher field than most other protons of organic compound.

chemical shift or relative resonance frequency may be expressed in 3-different units.

(i) in cps or Hz

(ii) in δ_{ppm}

(iii) in $\gamma = (10 - \delta)$

(i) when chemical shifts of protons are expressed in cps or Hz. One should have to mention not only the internal reference compound but also the instrument in which the spectrum was run. This unit is field dependent.
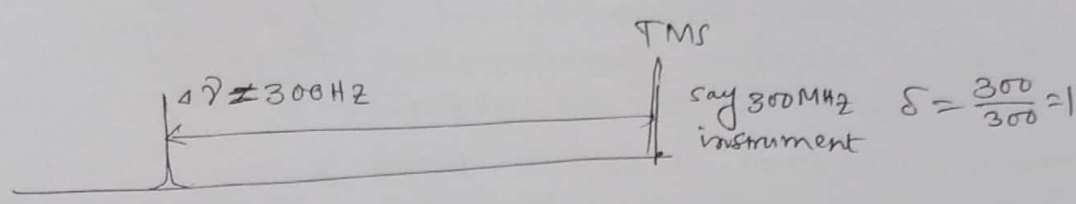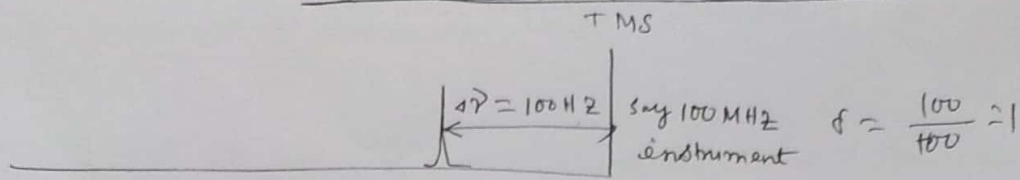
(ii) δ unit: chemical shift positions are normally expressed in δ (delta) units, which are defined as ~~proto~~ proportional differences, in parts per million (PPm) from reference standard. It is dimensionless and independent of field strength. So that a signal with a δ value = 4.6 derived from a 60 MHz spectrum (1.4 T ∝ instrument) will be found at exactly the same value, δ 4.6, on a 100 MHz or on a 600 MHz (14.1T) instrument.

$$\delta_x = \frac{\gamma_x - \gamma_{TMS}}{\gamma_o}$$

δ_x is the chemical shift (in ppm)

γ_x & γ_{TMS} are frequencies (in Hz) of the signals of x & TMS, respectively & γ_o is the operating frequency of the instrument (in MHz)

NMR spectra

TMS

$\Delta \mathcal{V} = 100 Hz$ say 100 MHz instrument $\delta = \dfrac{100}{100} \simeq 1$

TMS

$\Delta \mathcal{V} = 300 Hz$ say 300 MHz instrument $\delta = \dfrac{300}{300} \simeq 1$
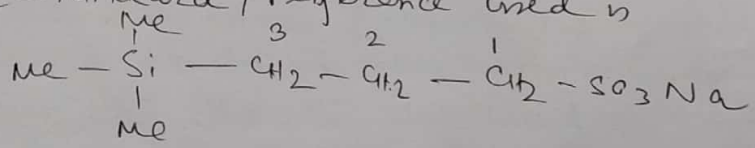
The higher the δ value, the lower the field at which proton resonates & lower δ value, higher the field at which proton resonates.

(iii) <u>τ units</u> : chemical shift may also be expressed in terms of τ. ~~when expressed in terms~~ of To correspond with low field values on the left and high on the right, a scale of units from 0 to 10, also running from left to right, was proposed, thus running counter to the δ scale, so that $\delta = 10 - \tau$. They are only ~~words~~ found in order spectra and are not used at all in current practice.

Those compounds which are soluble only in water NMR spectrum of those compounds are to be run in D_2O. where TMS cannot be used as reference because TMS is insoluble in D_2O. In such cases the internal standard/reference used is

$$Me - \underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}} - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_2 - SO_3Na$$

sodium salt of
3 - (trimethyl silyl) - propanesulfonic acid.

⓿ By international convention, an NMR spectrum is always plotted with TMS on the right hand side, at low frequency, and with high frequency on the left-hand side.

downfield
Hs high?
upfield
lower
Hs
TMS
Hs