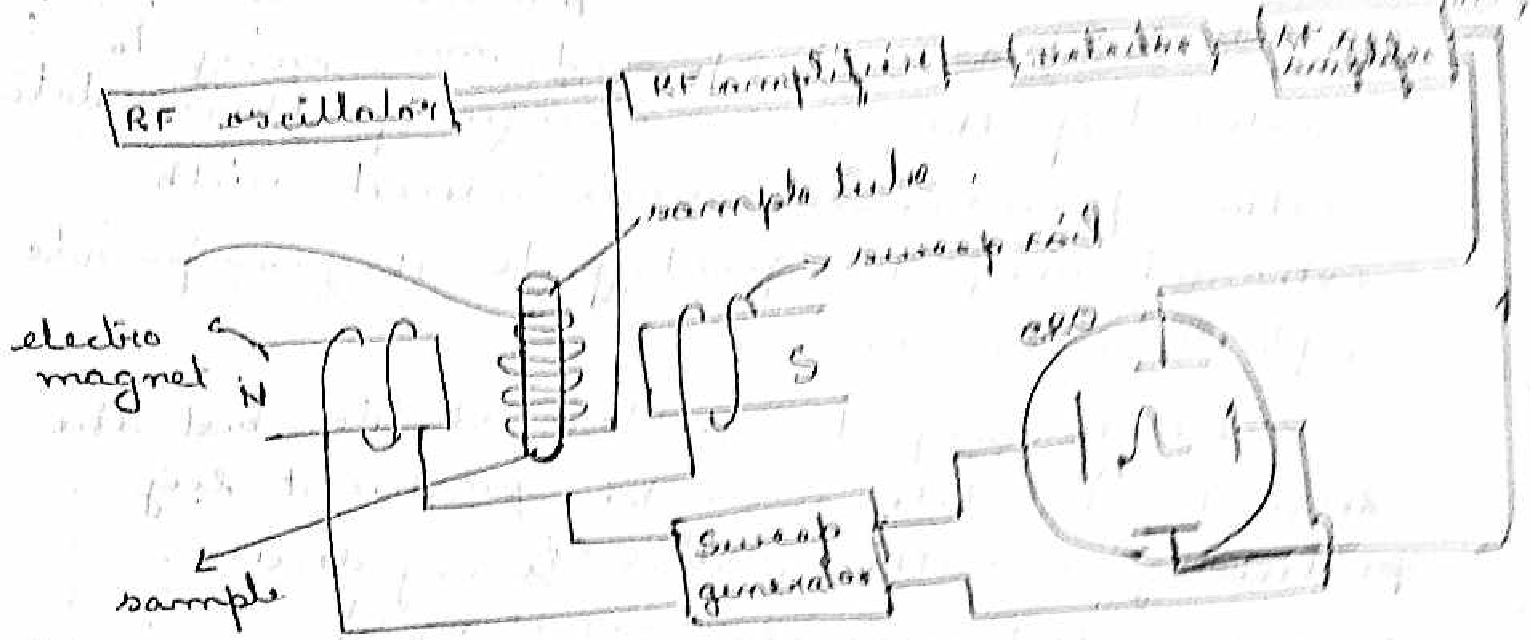
## Instrumentation : of NMR spectroscopy




General Block diagram of NMR

NMR spectrometer basically consists of a powerful magnet, radio frequency oscillator, suitable detectors, sweep generator, AF amplifier and recorder, CRO. The block diagram of NMR spectrometer is shown in above figure.

**Magnet :-**

Permanents (or) electro magnets can be used. The most important features of magnet is that the field should be highly homogeneous that is strength and the direction of magnetic field should not vary from point to point. Further magnetic field should be highly order of 10,000 to 20,000 gauss. Magnetic field should be constant over long periods of time / for which the electro magnet is energized by a highly stable DC power supply.

Permanent magnets can provide stable fields and are cheap and are easy to construct if they are carefully Thermostated. Further permanent magnets interact with external magnetic ~~field~~ effects. They can provide upto 4000 gauss.

Electromagnets are less stable but the desired stability can be produced by producing ancillary stabilising device. Recently electromagnets consisting of super conducting solenoid operating in liquid helium crystals have been developed and are highly stable

Sample holder

Sample should be held in a holder which should be chemically inert, durable and transparent to RF radiation. generally glass tubes are employed which are sturdy, practical and cheap. They are generally about 8.5 cm long and approximately 0.3 cm in diameter.

Radio frequency generator

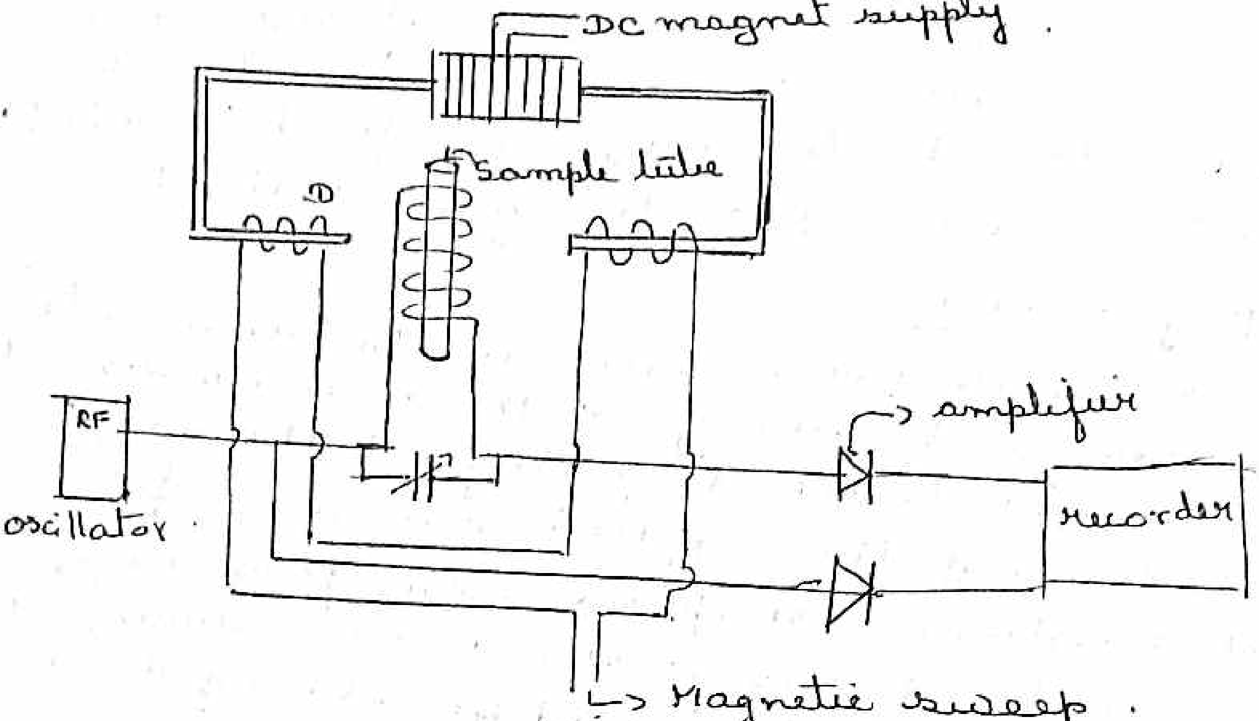
The RF radiation are generated from the radio frequency oscillator, capable of producing several MHz. The coil of oscillator is wound around the sample holder. To achieve maximum interaction of radiation with the sample, the axis of the coil is perpendicular to the magnetic field. Crystal control oscillator provides good stability.

## Sweep generator

In order for a nucleus to resonate, the precession frequency of the nucleus should become equal to the frequency of the applied RF radiation. If the applied magnetic field $H_0$ is kept constant, the precession frequency is fixed. In order to bring about resonance, the frequency of RF field should be changed so that it becomes equal to the resonance frequency (frequency sweep method).

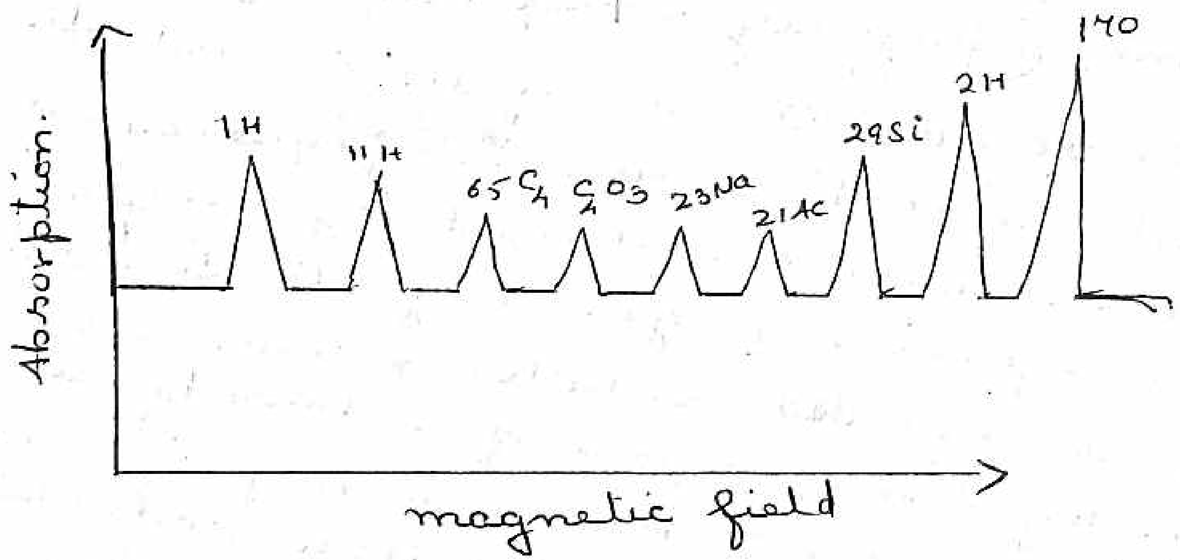
On the other hand, if the RF radiation is kept constant, the resonance frequency of the nucleus must be changed by varying $H_0$ (field sweep method). Generally, the field sweep method is regarded as better method. This is done by fixing a pair of helmholtz coils in the pole faces of the main magnet. The magnetic field induced by these coils can be varied by varying the current flowing through them. The small magnetic field generated by Helmholtz coil is in the same direction as the main field and therefore, it is added to the main field.

## NMR spectrometer (single coil) (continuous wave)

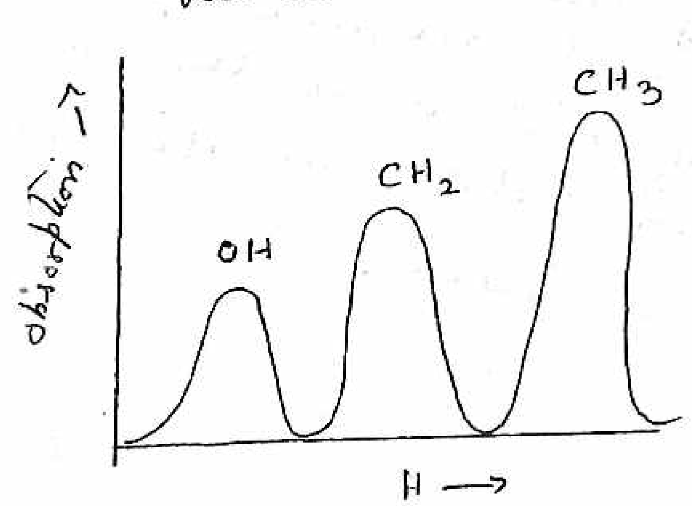



## working

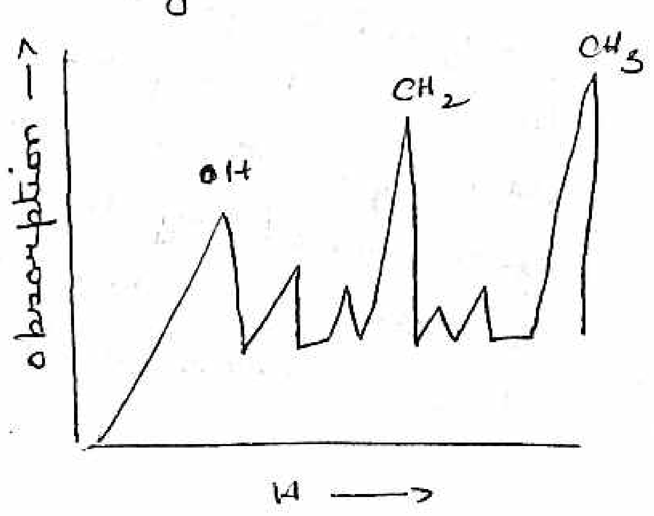
write it on your own



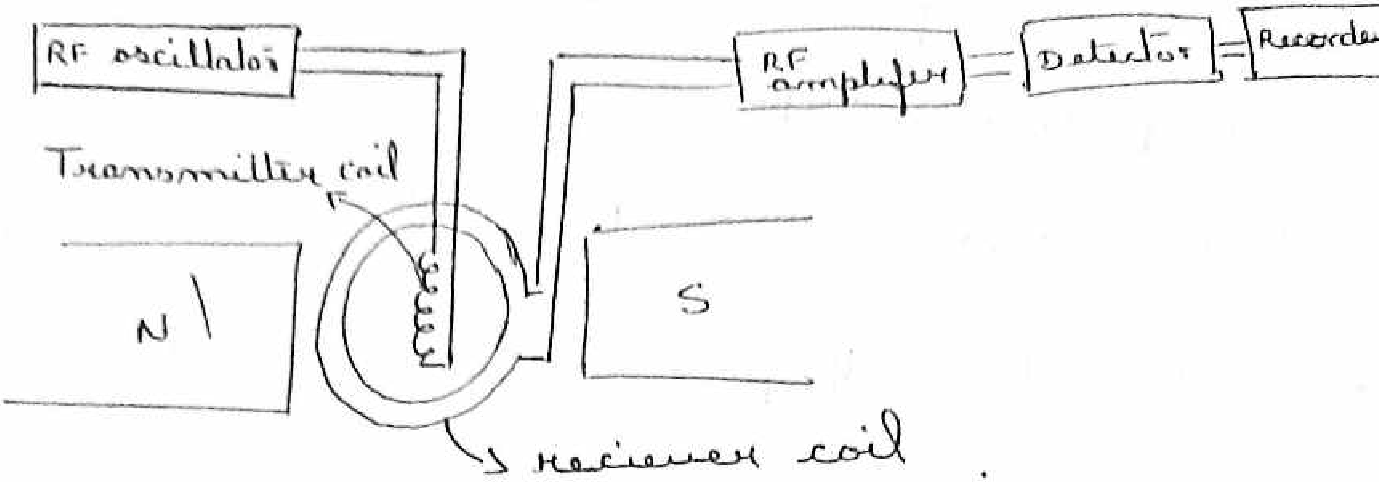

Low resolution




high resolution.

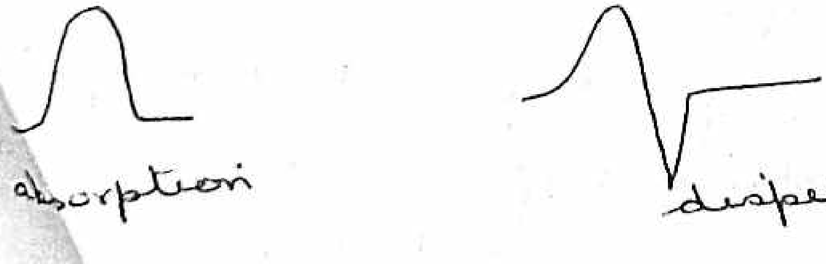


## Double coil NMR



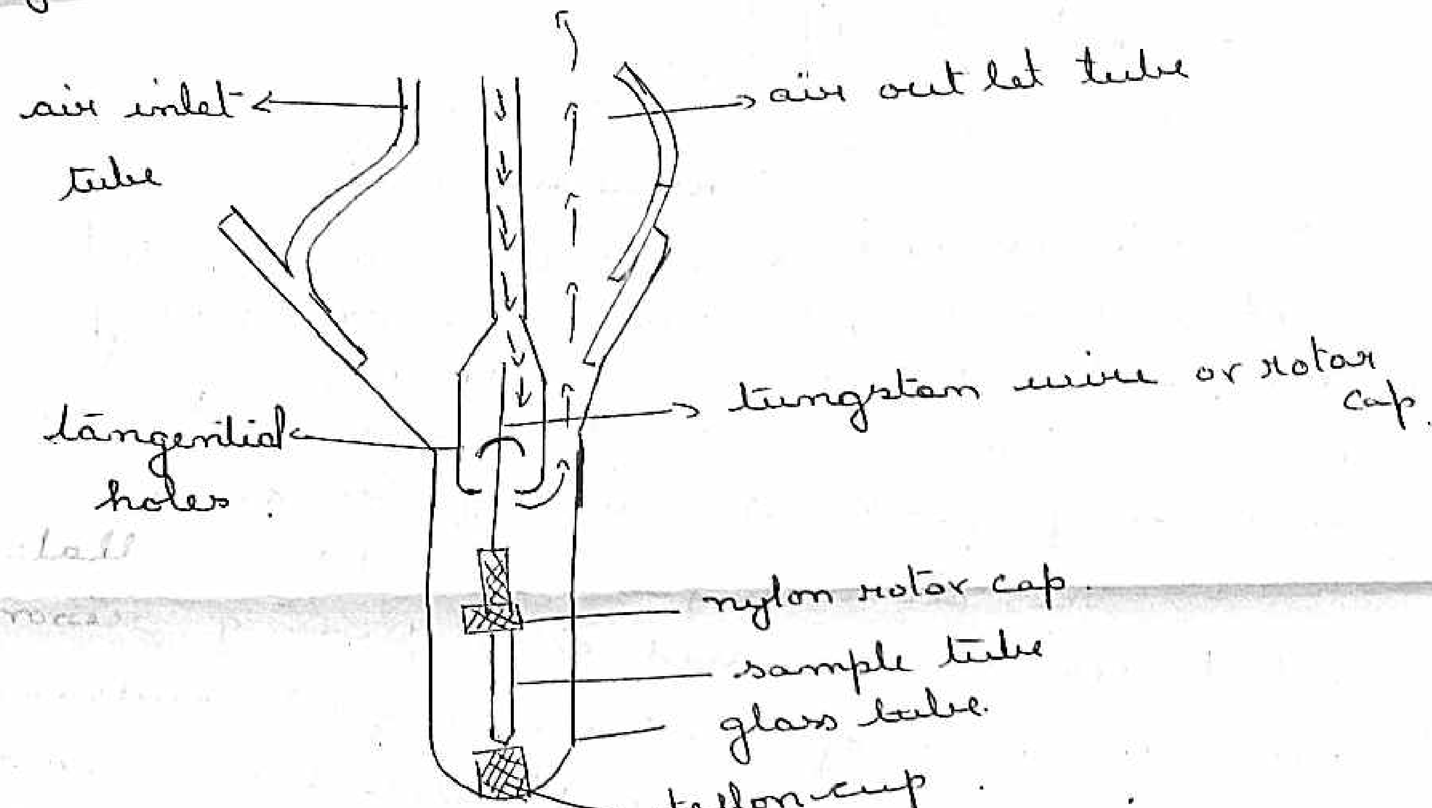

In this method two coils are seperately used one coil for transmission of RF power. other coil used for Receving the signal Two coils are right angle to each other and both are perpendicular to magnetic field.

The current from the RF oscillator is fed to the transmitted coil during resonance, the precission of nuclear magnets induces a signal voltage in a ⊥$^{er}$ direction. This is picked by the reciever coil and sent to the amplifier. The double coil method has good noise factor.




After detection signal contain only AF component which is further amplified using AF ampeifiers. The amplified signals are fed to y-plates of the CRO. A reference voltage from sweep generator is applied to the x-plates. The curve may be of dispersive type.

<u>High resolution NMR spectrometer</u>: [Pulsed wave NMR]




spectrometer which can resolve the internal chemical shift of proton are considered to be high resolution types. All high resolution spectrometer modification are either bridge type or crossed coil type.

A magnetic field of high homogenity is required to obtain high resolution of order one part $10^7$. The time stability of RF oscillator on the magnetic field should be of higher order.

In addition to that, the other requirements, are amplifier, ~~add~~ detectors and recorders should be distortion free and must have good performance in the working range of frequency.

(20)

magnets

Both permanent and electromagnet are used. Since the field of both magnet depends on temperature, temperature control is essential for maintaining constant field.

sample

Sample should be pure liquids or the components may be dissolved in a suitable liquid. Sample may be filled into cylindrical tube or spherical like

sampling and spinning

liquid sample gives short NMR signal while solid only lines spectra the reasons is that in liquid sample the nuclei are in continuous motion and thus are exposed to average field

The effective homogenity can be increased by providing a rapid motion of the substance. The sample is rotated about vertical axis of speed greater than 10 rps (rotating per second).

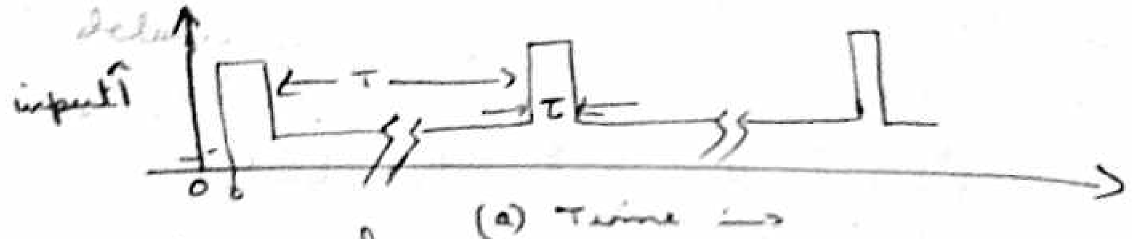
## Air-jet driven device

The above arrangement are designed for the 0.5mm glass sample tube.

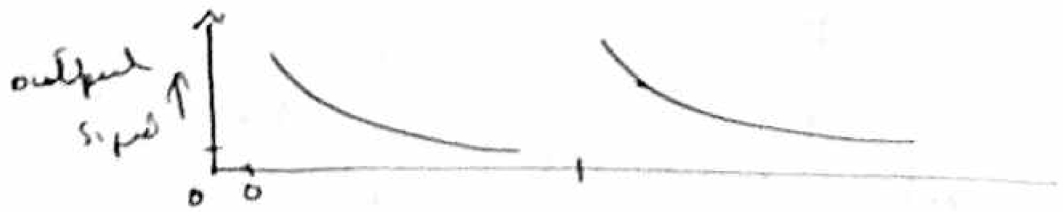
Sample spinning sometime help side bands to appear. If the spinning rate is increased side bands move away from the resonance band in that way various signals are identified.

## FT NMR

(a) input signal

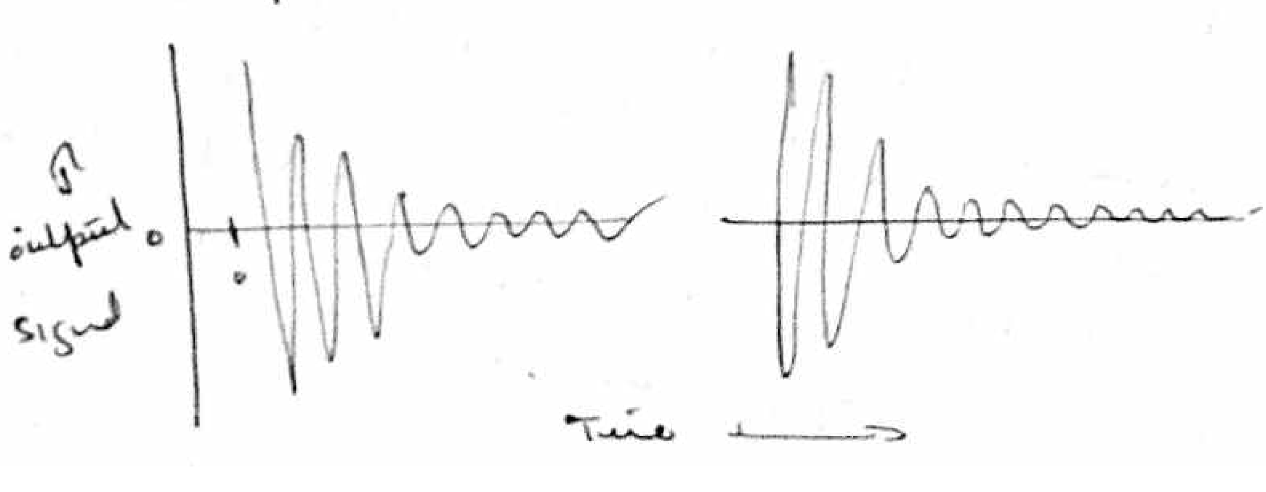



(b) output signal



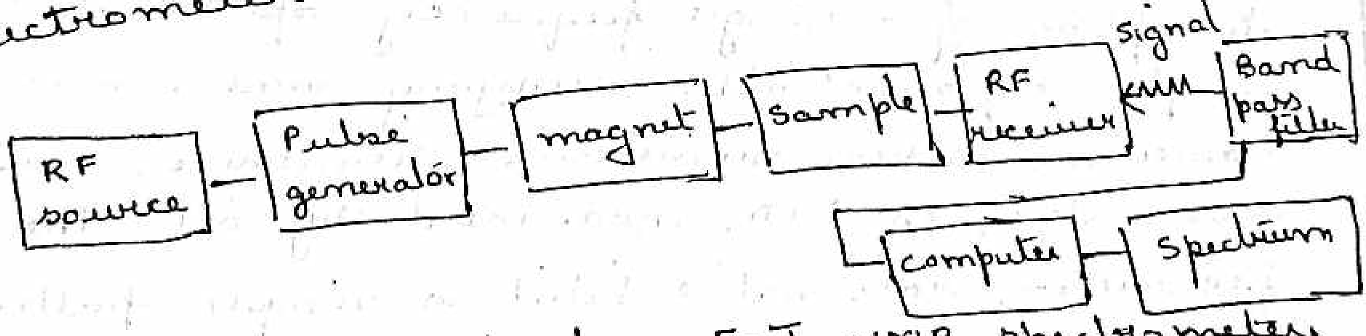

(b) output signal for a single nucleus.

(c) Free-induction decay signal when several types of nuclei are present.



FTNMR [spectroscopy - H - Kaur]

Fourier transform NMR has resulted in a dramatic increase in the sensitivity of NMR measurements. This is possible by exciting all possible resonances simultaneously. The sample is subjected to a high power short duration pulse of radiofrequency (RF) radiation. This pulse of radiation contains a broad band of frequencies and causes all the spin-active nuclei to resonate all at once at their larmor frequencies. Just following the pulse, the sample radiates a signal called free induction decay (FID), which is modulated by all the frequencies of the nuclei excited by the pulse. The signal detected as the nuclei return to equilibrium [intensity as a function of time] is recorded, digitized and stored as an array of numbers in a computer. Fourier transformation of the data affords a conventional (intensity as a function of frequency) representation of interferogram. FTNMR spectrum resembles the spectrum obtained from a continuous wave (CW) spectrometer.




Basic components of an F-T. NMR spectrometer stages involved are

1. <u>sample stimulation</u>:

(i) Power of the RF Pulse:

The intensity of the signal detected in pulsed NMR experiment is a sinusoidal function of the power of the RF pulse used for excitation. By employing suitable RF power and pulse width, the magnetization can be made to rotate by 90° pulse. The magnitude of this magnetization decreases with time as the individual nuclei move out of phase owing to field in homogenities and relaxation processes. Resulting signal is known as free induction decay (FID).

(ii) <u>Pulse</u> duration and Recycling Time:

Here all precessional frequencies within the effective band width of the pulses are excited. The extent of this distribution in the frequency domain is inversely proportional to the duration of the pulse in the time domain. The broader the spectral region, the shorter is the pulse.

2. <u>Detector</u>:

It detects the decay of magnetization (FID) with respect to time. The FID corresponding to absorption of a single frequency spectrum is a simple exponentially decaying sine wave. However, when numerous frequencies are associated, the FID, modulated by all the frequencies, does not exhibit a simple pattern but consist of a set of interfering wave forms along with noise. Since FID is related to time, it is called time domain spectrum.

Rate of exponential decay of signal in FID is related to the relaxation time ($T_1$) of the nuclei

The acquisition time (resolution) must be 3 or 4 times $T_2$ the transverse relaxation time.

3. Digitization (Rate of data sampling). FID is digitized by employing an analogue to digital converter (ADC) and collected as an array of integers in a computer. The interval ($\Delta t$) between points at which the FID is sampled shows the maximum frequency that can be measured in the FID. The detected spectral width $S_\omega$ of FTNMR experiment is given by

$$S_\omega = \frac{1}{2 \times \Delta t}$$

For large spectral widths, the rate of digitization should be fast.

4. Signal to Noise ratio (S/N).

S/N ratio depends on

(i) strength of applied magnetic field $[\propto H_0^{3/2}]$

(ii) design of the probe, mainly length & geometry of receiver coil.

$$\frac{S}{N} = \frac{\text{average signal amplitude}}{\text{Root mean square (RMS) noise}}.$$

where RMS noise $= \dfrac{\text{average peak to peak noise}}{2.5}$

5. signal to noise enhancement techniques is required.

**Fourier Transformation**

FT is the mathematical operation required to convert a time domain spectrum into a frequency domain spectrum (or viceversa). The following equation pertain to the transformation of frequency and time domains.

$$F(\nu) = \int_{-\infty}^{+\infty} f(t)\, e^{-i(2\pi\nu)t}\, dt.$$

$$f(t) = \int_{-\infty}^{+\infty} F(\nu)\, e^{i(2\pi\nu)t}\, 2\pi\, d\nu$$

where $F(\nu)$ and $f(t)$ are the frequency and time Domain spectra respectively.

Fourier transformation of an exponentially decaying signal produces a lorentzian line shape. If the time constant for exponential decay is $T_2$, then the lorentzian line will have a width at half-height ($\omega_{1/2}$) in hertz. That is $W_{1/2} = \dfrac{1}{\pi T_2}$

x — x