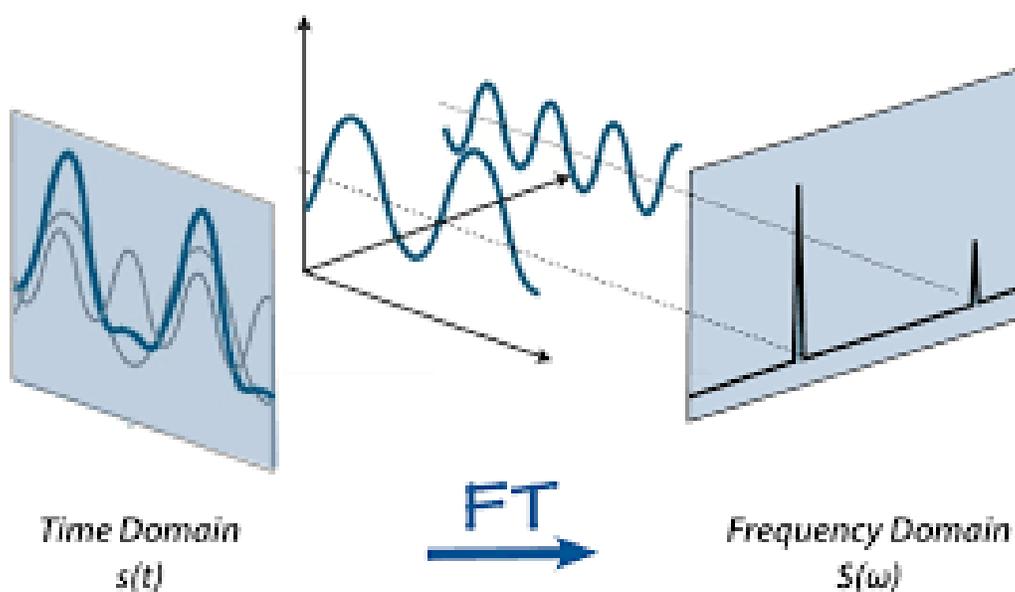


BASICS OF FOURIER TRANSFORM IN NMR



Target audience Chemistry Post Graduate students

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CW NMR spectrometers record the spectra by recording either with field sweep or frequency sweep ie

- Keeping the magnetic field constant and varying the frequency
- Or keeping the frequency constant and varying the magnetic field (more Convenient)

The CW method was the basis of all NMR till 1960 but now has been entirely superseded by the pulsed method

In the pulsed method all the frequencies are excited at the same time using a pulse to give an FID

ADVANTAGES OF FT NMR/PULSED TECHNIQUE

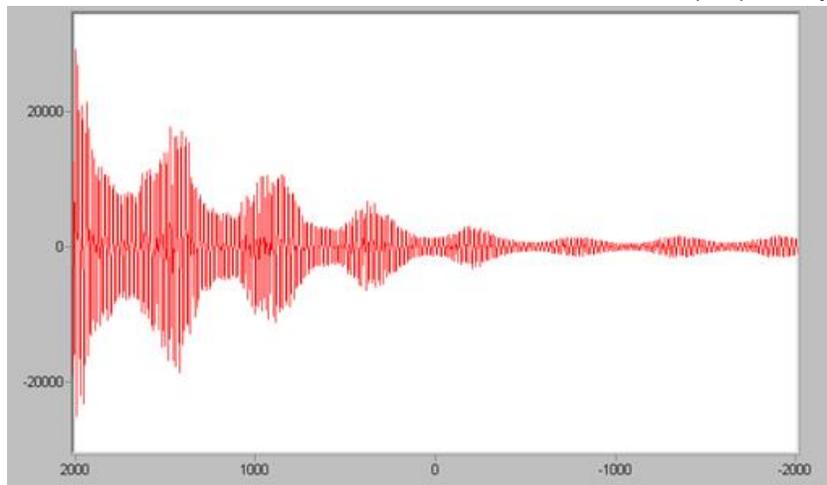
- FT NMR is much faster than CW NMR (secs instead of minutes)
- Is much more sensitive, thus can even be used for those nuclides which are found in low abundance
- FT NMR can be obtained with less than 5mg of compound

- The signals stand out clearly with almost no electronic background noise

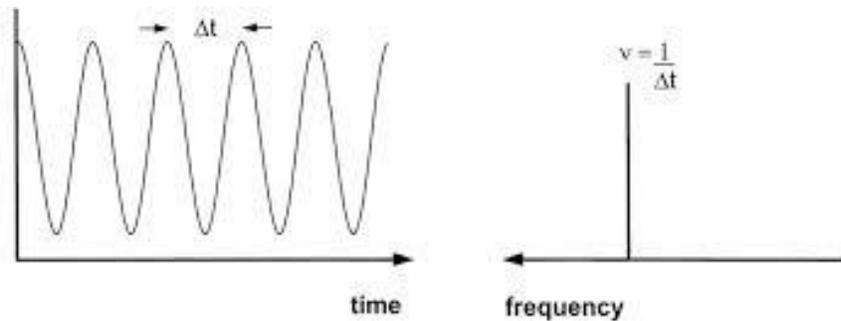
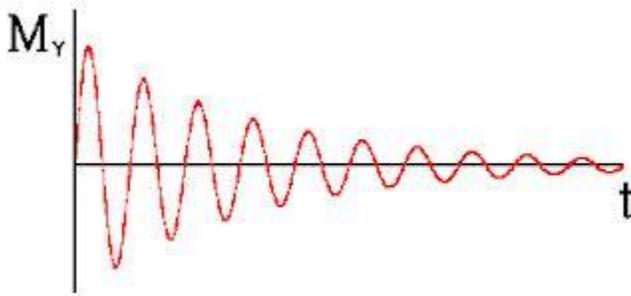
An alternative approach is the pulse method, a powerful but short burst of energy, called a **pulse** is used to excite all the magnetic nuclei in the molecule simultaneously. In PMR all the H nuclei are induced to undergo resonance at the same time. An instrument with a 2.1 tesla magnetic field uses a short (1-10 μ sec) burst of 90MHz energy to accomplish this. The source is turned on and off very quickly to generate a pulse. The pulse actually contains a range of frequencies centered about the fundamental frequency. This range of frequencies is great enough to excite all distinct types of hydrogens in the molecule at once with this single burst of energy.

When the pulse is discontinued, the excited nuclei begin to lose their excitation energy and return to their original spin state, or **relax**. As each excited nucleus relaxes, it emits electromagnetic radiation. since the molecule contains many different nuclei, many different frequencies of electromagnetic radiation are emitted simultaneously. This emission is called a **free induction decay (FID) signal**. The intensity of FID decays with time as all of the nuclei eventually lose their excitation. The FID is a superimposed combination of all the frequencies emitted and can be quite complex. Individual frequencies are extracted using a computer and a

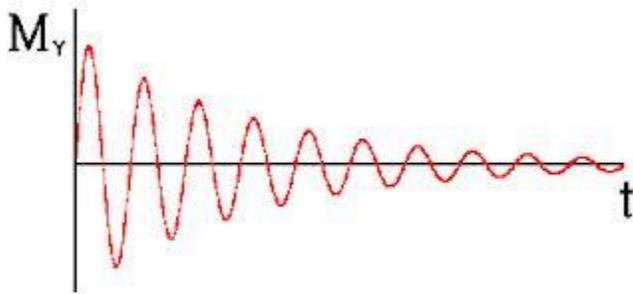
mathematical method called a Fourier Transform(FT) analysis.



A molecule like acetone which has only one type of hydrogen gives an FID curve composed of a single sinusoidal wave. The signal decays exponentially with time as the nuclei relax and their signal diminishes. Since the horizontal axis on this signal is time, the FID is sometimes called a **time –domain signal**. If the signal did not decay in intensity, it would appear as a sine (or cosine) wave of constant intensity. The frequency of this wave can be calculated from its measured wavelength λ (difference between the maxima).



The determined frequency is not the exact frequency emitted by the methyl hydrogens. The observed FID is actually an interference signal between the radiofrequency source (300 MHz in this case) and the frequency emitted by the excited nucleus, where the wavelength is given by



In other words, this signal represents the difference in the two frequencies. Since the frequency of the pulse is known, the exact frequency can be readily calculated. However, there is no need to calculate it since the chemical shift can be directly calculated and can be reduced to ppm

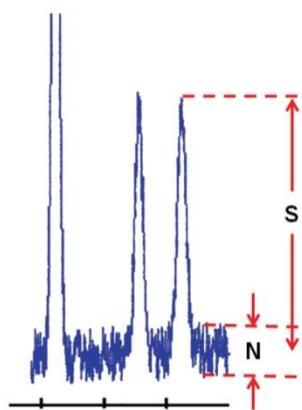
Acetone is the chemical shift of the protons of acetone from the position of the pulse, and not from TMS. If we know TMS (the position of TMS from the pulse), the actual

chemical shift of this peak can be calculated by subtracting chemical shift of TMS from acetone

This peak can now be plotted as a chemical shift on a standard NMR spectrum chart. The peak for acetone appears at 2.1 ppm. Thus a time domain signal has been converted to a frequency domain signal.

A complex molecule e.g. Ethyl phenyl acetate has many types of hydrogens and the FID is the superimposition of many different frequencies, each of which could have a different decay rate. A mathematical method called a **Fourier Transform**, however, separates each of the individual components of this signal and convert them to frequencies. The Fourier transform breaks the FID into its separate sine or cosine wave components. This procedure is too complex to be carried out by eye or hand, it requires a computer. Modern FT NMR instruments have computers built into them.

Noise is random electronic signals that are usually visible as fluctuations of the baseline in the signal. Since noise is random, its intensity does not increase as many iterations of the spectrum are added together. The signal to noise ratio improves as a function of the square root of the number of scans n

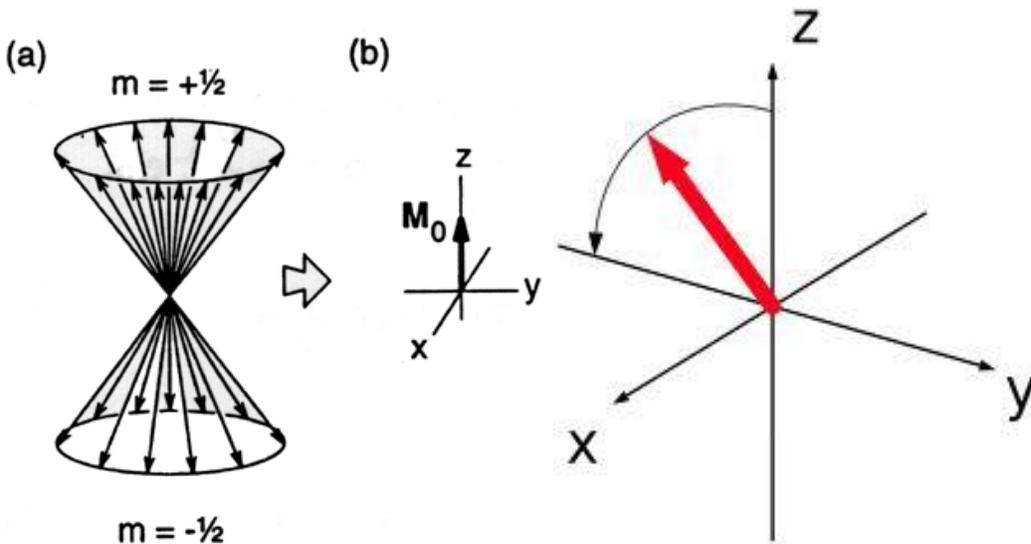


$$S/N = f \ n$$

Pulsed FT-NMR is therefore especially suitable for the examination of nuclei that are not very abundant in nature, nuclei are not strongly magnetic, or very dilute samples.

PULSE ANGLE, SPINS AND MAGNETIZATION VECTORS

Let us consider a sample containing only one nuclear species eg protons in a chloroform sample



The moments precess with the Larmor frequency ω_L on the surface of a double cone and as a result of the difference in populations there is macroscopic magnetization M_0 along the field direction.

To induce NMR transitions the radiofrequency pulse is applied to the sample along the direction of the X axis.

The magnetic vector of this electromagnetic radiation is then able to interact with the nuclear dipoles and therefore with M_0 . The linear alternate g magnetic field along the X direction will be represented by two vectors with the same magnitude $B_1(r)$ and $B_1(l)$. Along the X axis its max value will be $2B_1$. Of the two rotating magnetic field components only the one which has the same direction of rotation as the precessing nuclear dipoles can interact with them (and thus with M_0). Under its influence M_0 is tipped away from the Z axis.

However, as the plane rotates with the Larmor frequency ω_L , the complicated motion of M_0 is difficult to represent in a diagram. If instead of fixed coordinate system, we use a rotating coordinate system $X'Y'Z'$ which rotates with the same frequency as B_1 .

As B_1 is normally taken along the X' axis, the effect of B_1 is to turn the vector M_0 about the X' axis i.e. in the $Y'Z'$ plane.

The angle θ is referred as the pulse angle $\theta = \sqrt{1} B_1 T_p$

This θ can be increased by either –The amplitude of the pulse component (B_1) of the rf pulse having frequency $\omega = \omega_L$ or by increasing the pulse duration T_p . Normally a 90° X' and a 180° X' pulse is used.

From the vector diagrams it can be seen that the transverse magnetization $M_{Y'}$ is greatest after a $90^\circ X'$ Pulse and is zero for 0° or 180° .

The transverse component $M_{Y'}$ is crucial for the observation of an NMR signal, since the receiver coil is oriented with its axis along the Y direction

The condition of the spin system after 180° pulse is that the populations of N_α and N_β have been exactly reversed by the experiment so that there are now more nuclei in the upper than the lower energy level. By a $90^\circ X$ pulse more number of particles are tilted towards the Y axis. The nuclear dipoles no longer precess with their axes in a uniform random distribution over the surface of the double cone but instead they are bunched together towards the Y axis. This condition is referred to as PHASE COHERENCE.

RELAXATION

At the instant when the pulse is switched off the vector M_0 is deflected from the equilibrium position through an angle θ . At the instant time t it has the coordinates M_X , M_Y and M_Z in the stationary coordinate system.

The spin system now reverts to its equilibrium state by relaxation with M_Z growing back to its original value M_0 while M_X and M_Y approach zero. F. Bloch mathematically analysed relaxation and assumed that the relaxation process were first order and could be described by two different relaxation times T_1 and T_2 . (using a rotating coordinate system $X'Y'z$)

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} = \frac{M_0 - M_z}{T_1}$$

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \quad \frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

Longitudinal Relaxation T_1

Transverse Relaxation T_2

T_1 is the spin-Lattice or Longitudinal relaxation time and T_2 is the spin spin or transverse relaxation time

The magnetization $M_{Y'}$ is the sum of the Y' components of all the individual spins. The evolution of this transverse magnetization after the pulse is determined by the Bloch equation (The time constant T_2 – spin-spin or transverse magnetization time determines how rapidly the transverse magnetization components $M_{X'}$ and $M_{Y'}$ decay.

As the precessing nuclear spins which are bunched together gradually lose their phase coherence i.e. the fanning out process continues M_y' becomes smaller and with it the induced signal in the receiver coil.

The energy of the spin system is not altered by spin-spin relaxation as the level populations are not affected. Only the phase coherence between the bunched precessing nuclear spins is lost. This type of relaxation is therefore sometimes referred to as an entropy process.

The precessing magnetization which oscillates at the Larmor frequency eventually decays due to the action of relaxation. This signal is therefore called as the free induction decay or FID

REPRESENTING THE FID

If our pulse acquisition experiment has used a 90° pulse about Y, rather than about X the equilibrium magnetization would have been rotated onto the X axis and the evolution of the X and Y components are given by

$$M_x = M_0 \cos \Omega t$$

$$M_y = M_0 \sin \Omega t$$

The precession of the magnetization gives rise to a current in the Rf coil which, after various manipulations by the Rf electronics in the spectrometer results in a signal voltage which can be digitized and the result stored in computer memory.

The spectrometer is capable of detecting simultaneously both the x and the y components of the magnetization denoted by S_x and S_y . As these signals are proportional to M_x and M_y

$$S_x = S_0 \cos \Omega t \quad S_y = S_0 \sin \Omega t$$

As the magnetization and hence the signal will decay over time assuming that the signal decays exponentially

$$S_x = S_0 \cos \Omega t \exp(-t/T_2) \quad S_y = S_0 \sin \Omega t \exp(-t/T_2)$$

Where T_2 is a time constant which characterizes the decay. The shorter T_2 , the more rapid the decay.

Rather than dealing with the X and Y components separately, it is convenient to bring them together as a complex signal, with the X component becoming the real part and the Y component the imaginary part. The complex signal is written as $S(t)$ to remind us that it is a function of time

$$S(t) = S_x + iS_y$$

$$S_t = S_0 \Omega t \exp(-t/T_2) + I [S_0 \sin \Omega t \exp(-t/T_2)]$$

$$= S_0 (\cos \Omega t + I \sin \Omega t) \exp(-t/T_2)$$

$$= S_0 \exp(I \Omega t) \exp(-t/T_2)$$

Since $R = 1/T_2$ ($R =$ First order rate const)

Thus the time domain signal can be written as

$$S_t = S_0 \exp(I \Omega t) \exp(-R t)$$

As R increases the decay becomes more rapid and so the corresponding line becomes broader.

If there are several resonances present, then the complex time-domain signal is a sum of terms

$$S(t) = S_0 \exp(I \Omega_1 t) \exp(-t/T_2(1)) + S_0 \exp(I \Omega_2 t) \exp(-t/T_2(2))$$

INEPT

Insensitive Nuclei Enhanced By Polarization Transfer- is a signal enhancement method used in NMR spectroscopy which involves the transfer of nuclear spin polarization from spins with large Boltzmann population differences to nuclear spins of interest with low Boltzmann population differences. INEPT uses J coupling for the polarization transfer in contrast to NOE which arises from dipolar cross-relaxation. The sensitivity of the NMR signal depends on the gyromagnetic ratio (γ) of the nucleus. In general, the signal intensity produced from a nucleus with the gyromagnetic ratio of γ is proportional to γ^3 because the magnetic moment, the Boltzmann populations and the nuclear precession all increase in proportion to the gyromagnetic ratio γ . eg gyromagnetic ratio of ^{13}C is 4 times lower than the proton so the signal intensity it produces will be 64 times lower than that of the proton.

INADEQUATE

The probability of any one C atom being ^{13}C is about 0.01%. Thus the probability that any two adjacent carbon atoms will both be ^{13}C atoms is $0.01 \times 0.01 = 0.0001$ ie 1 in 10,000. This seemingly impossible task is accomplished with the aid of double quantum filtering. The double quantum filtering removes all single spin transitions, which in this case corresponds to all isolated ^{13}C atoms. Only those transitions from systems with two spins (AB and AX systems) are detected.

The Inadequate spectrum is run slightly differently from a COSY (expected that both F1 and F2 would be carbon axis). Here F2 is the Carbon axis while F1 is the sum of the chemical shifts of the coupled nuclei which evolve during T1.

Reference Books

- 1.Spectroscopy by Pavia,Lampman,Kriz & Vyvyan
- 2.Spectrometric Identification of Organic Compounds
- 3.Organic Spectroscopy William Kemp