Laboratory and Rotating frames

- The coordinate system that we used for the previous example (*laboratory frame*) is really pathetic. The whole system is spinning at ω_o, which makes any kind of analysis impossible.

- Again, an out-of-date example. It would be like trying to read the label of a record spinning in a turn-table…

- The solution is to take a coordinate system that moves at ω_o. This is like jumping on top of the long play to read the label. What we effectively do is remove the effect of **B_o**. If we take magnetization on the **<xy>** plane:

**Laboratory Frame**   **Rotating Frame**
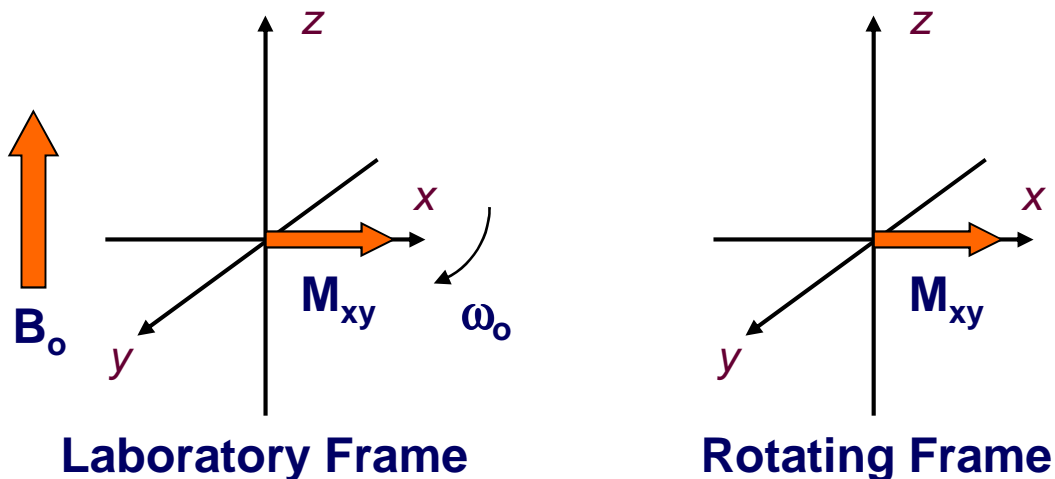
- In this coordinate system, **M_{xy}** does not move if we are at the resonant condition (the ω of **B_1** is exactly the frequency of the nuclei, ω_o). If we are slightly off-resonance, the movement of the vectors is still slow with respect to ω_o.

Chemical shifts

- If each type of nucleus has its characteristic ω_o at a certain magnetic field, why is NMR useful?

- Depending on the *chemical environment* we have variations on the magnetic field that the nuclei feels, even for the same type of nuclei. It affects the local magnetic field.

$$B_{eff} = B_o - B_{loc} \quad --- \quad B_{eff} = B_o(1 - \sigma)$$

- σ is the *magnetic shielding* of the nucleus. Factors that affect it include neighboring atoms and groups, etc., etc. The polarization of the bonds to the observed nuclei are important as well.

- As a crude example, ethanol looks like this:

HO-CH$_2$-CH$_3$

low field — ω_o — high field
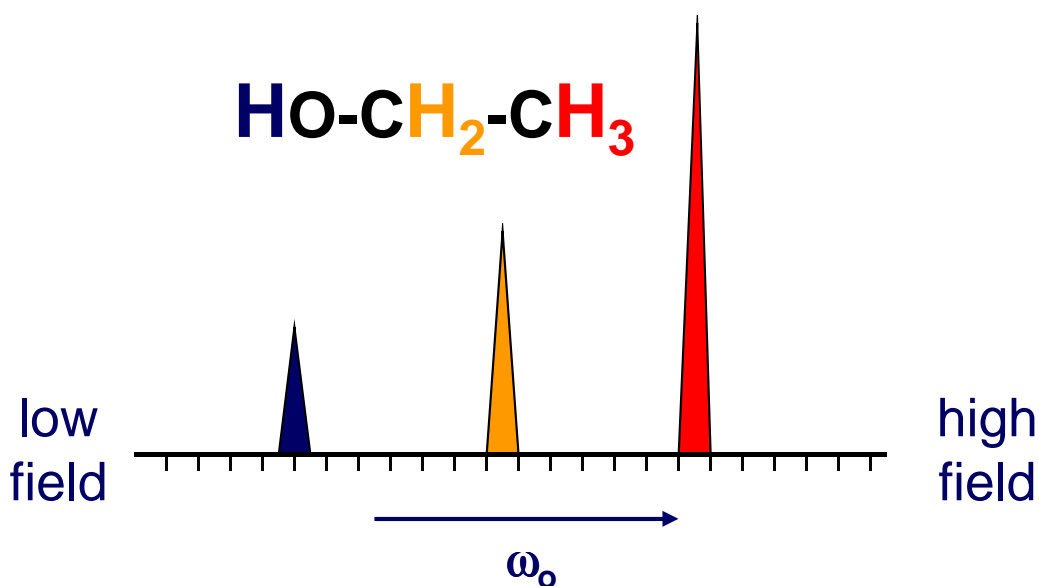
The NMR scale (δ, ppm)

- We can use the frequency scale as it is. The problem is that since B_{loc} is a lot smaller than B_o, the range is very small (hundreds of Hz) and the absolute value is very big (MHz).

- We use a relative scale, and refer all signals in the spectrum to the signal of a particular compound.

$$\delta = \frac{\omega - \omega_{ref}}{\omega_{ref}}$$ **ppm (parts per million)**

- The good thing is that since it is a relative scale, the δ in a 100 MHz magnet (2.35 T) is the same as that obtained for the same sample in a 600 MHz magnet (14.1 T).
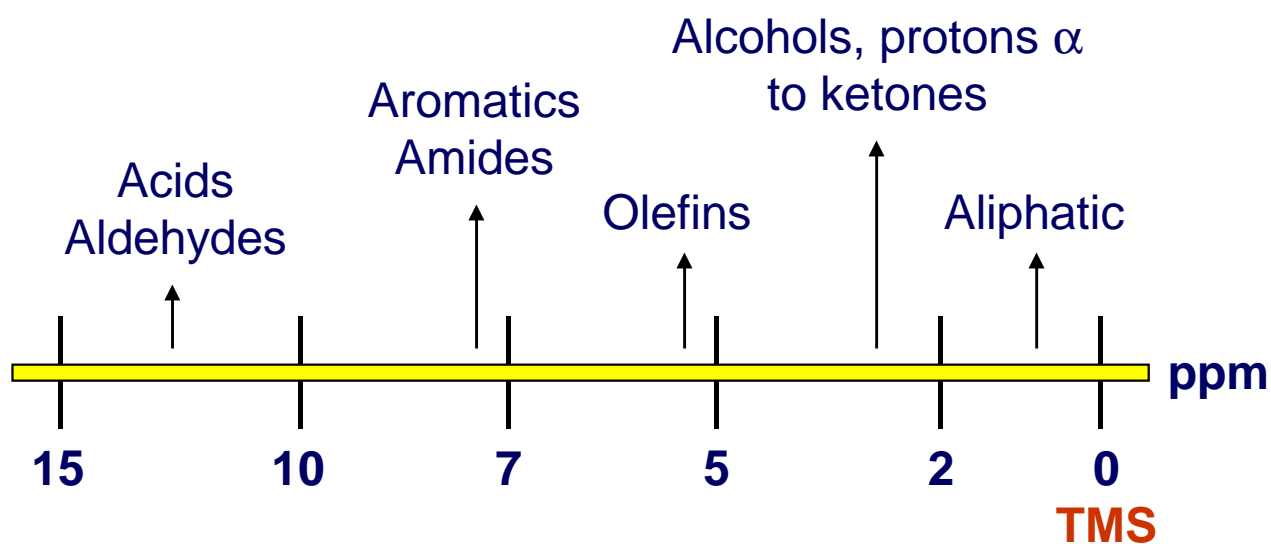
- *Tetramethyl silane* (**TMS**) is used as reference because it is soluble in most organic solvents, inert, volatile, and has 12 equivalent ^{1}Hs and 4 equivalent ^{13}Cs:

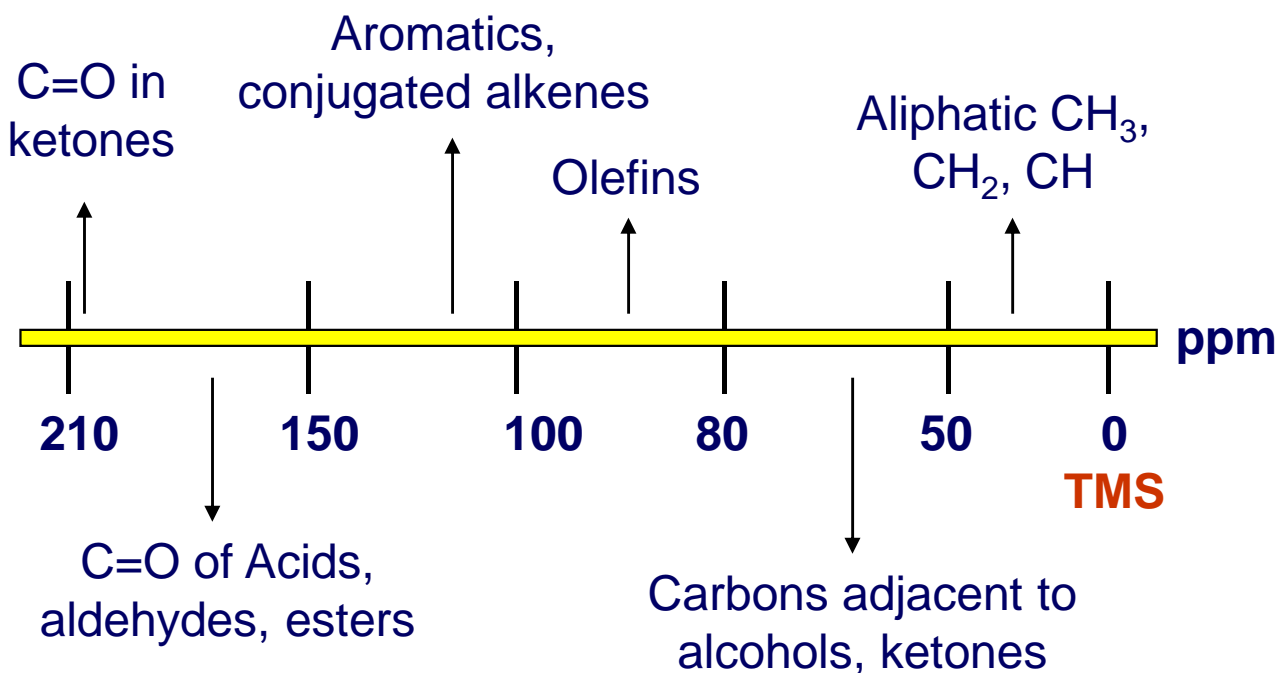$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$$
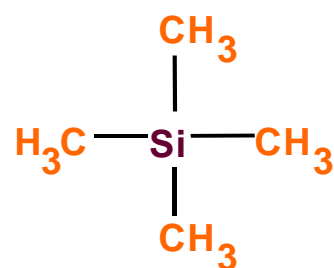
- Other references can be used, such as the residual solvent peak, dioxane for ^{13}C, etc. What reference we use is not critical, because the instrument (software/hardware) is calibrated internaly. Don't use them if you don't need to...

# Scales for different nuclei

- For protons, ~ 15 ppm:

Alcohols, protons α
to ketones

Aromatics
Amides

Acids
Aldehydes

Olefins

Aliphatic

| 15 | 10 | 7 | 5 | 2 | 0 |

ppm

TMS

- For carbon, ~ 220 ppm:

Aromatics,
conjugated alkenes

C=O in
ketones

Olefins

Aliphatic CH_3,
CH_2, CH

| 210 | 150 | 100 | 80 | 50 | 0 |

ppm

TMS

C=O of Acids,
aldehydes, esters

Carbons adjacent to
alcohols, ketones

Chemical shift in the rotating frame

- We will consider only magnetization in the **<xy>** plane. We start with a signal with an ω_o equal to the ω of **B$_1$**. After some time passes, nothing changes…
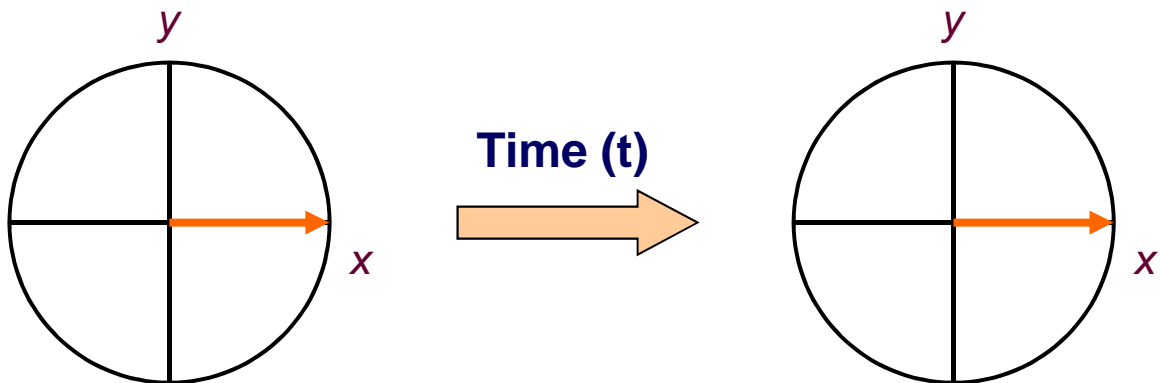

- Now, if we are slightly off-resonance ($\omega - \omega_o \neq 0$), the **M$_{xy}$** vector will evolve with time. The angle will be proportional to the evolution time and $\omega - \omega_o$ (that's why we use radians…)
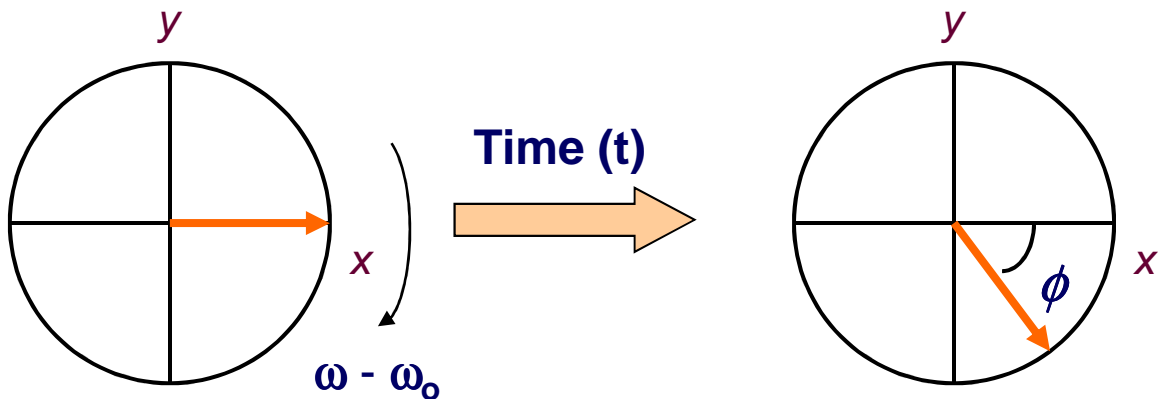

$$\phi = (\omega - \omega_o) * t$$

Coupling Constants

- The energy levels of a nucleus will be affected by the spin state of nuclei nearby. The two nuclei that show this are said to be **coupled** to each other. This manifests in particular in cases were we have through bond connectivity:

^{1}H

^{13}C

one-bond

^{1}H ^{1}H

three-bond
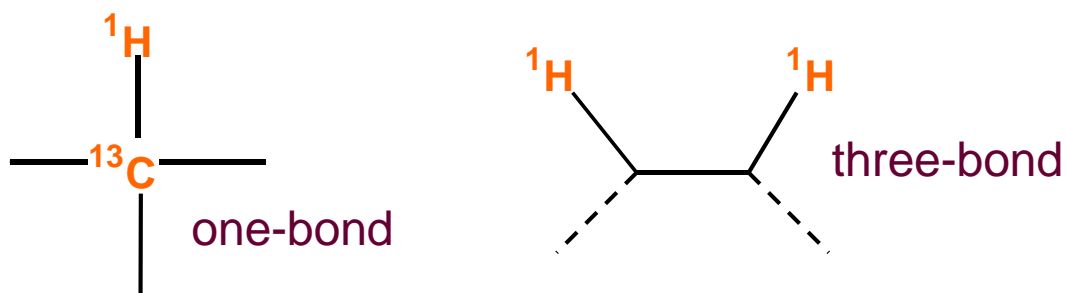
- Energy diagrams. Each spin now has two energy 'sub-levels' depending on the state of the spin it is coupled to:

$\beta_I\beta_S$

I

S

$\alpha_I\beta_S$

S

$\beta_I\alpha_S$

I

$\alpha_I\alpha_S$

J (Hz)

I   **S**
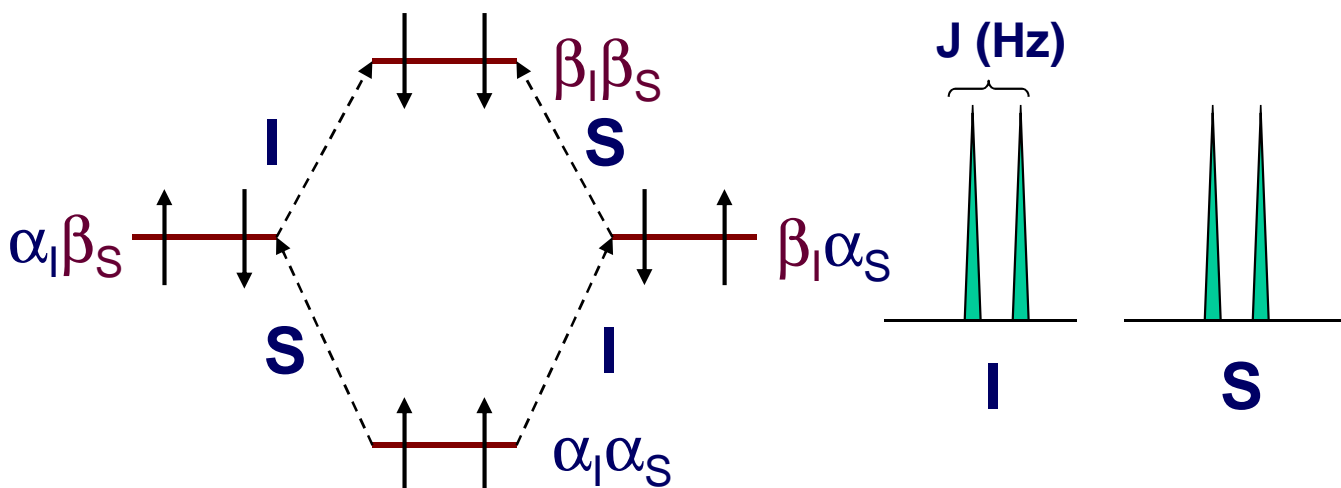
- The magnitude of the separation is called **coupling constant** (**J**) and has units of Hz.

- Coupling patterns are crucial to identify spin systems in a molecule and to the determination of its chemical structure.

Couplings in the rotating frame

- We will consider an ensemble of spins **I** coupled to another spin **S** that is exactly at the resonant condition (ω of B_1 is ω_o), and again, only what goes on in the **<xy>** plane.

- The situation is analogous to what happened with chemical shift. In this case, since there are two new energy levels for the spin, we get two counter-rotating vectors. Their evolution will depend on the magnitude of **J**, not ω_o:

$$\phi = \pi * t * J$$
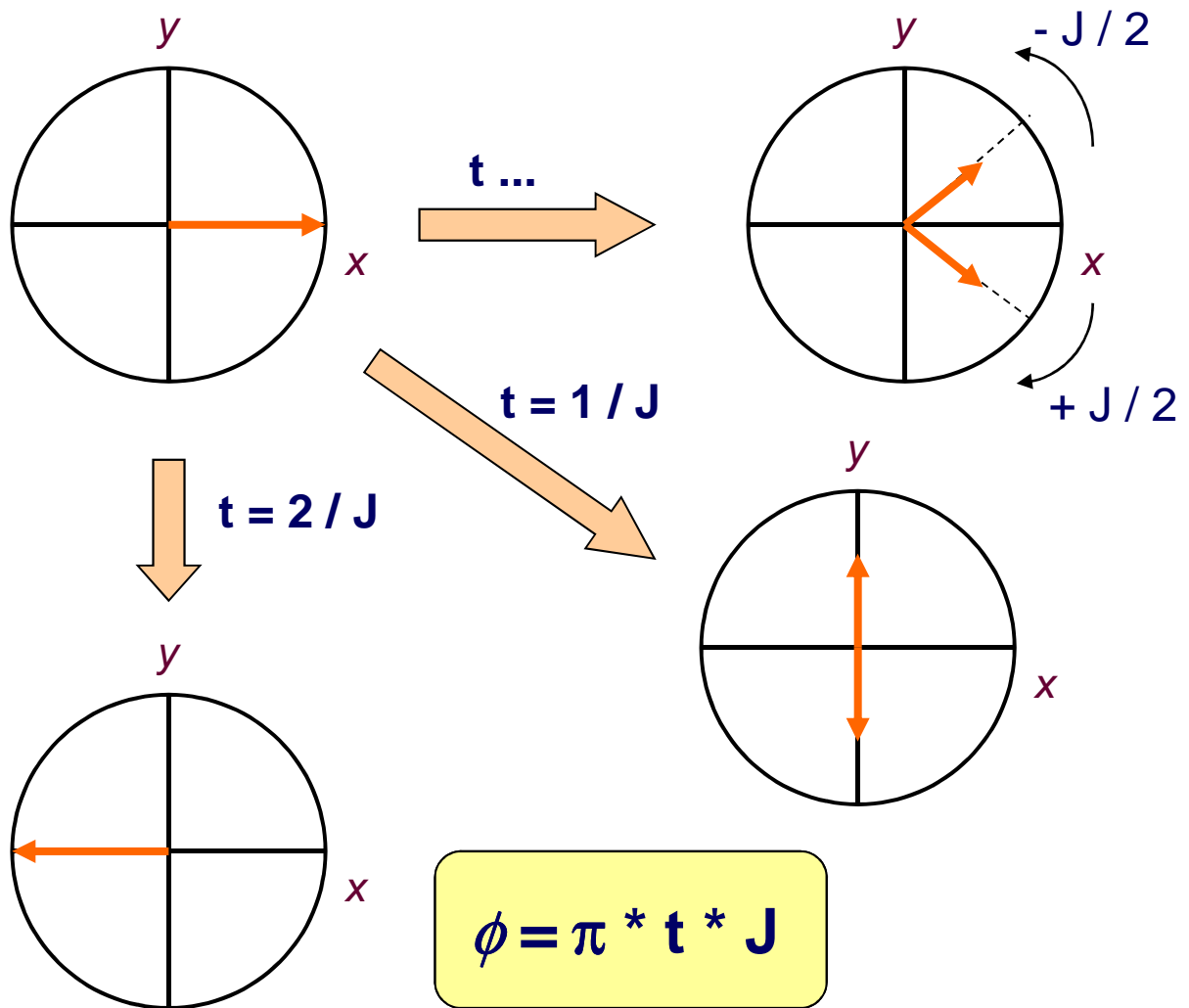
NMR Instrumentation

- An NMR machine is basically a big and expensive FM radio.
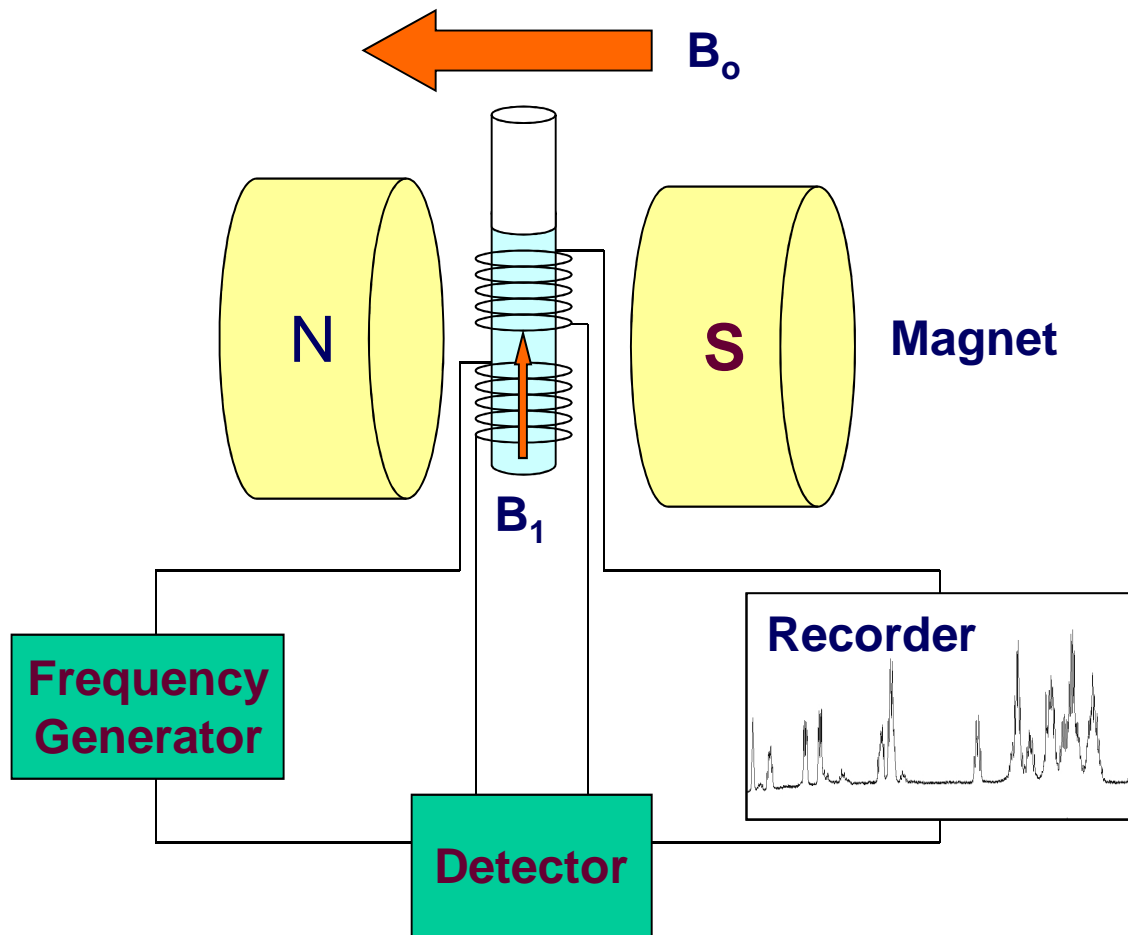
- *Magnet* - Normally superconducting. Some electromagnets and permanent magnets (EM-360, EM-390) still around.

- *Frequency generator* - Creates the alternating current (at ω_o) that induces B_1. Continuous wave or pulsed.

- *Detector* - Subtracts the base frequency (a constant frequency very close to ω_o) to the output frequency. It is lower frequency and much easier to deal with.

- *Recorder* - XY plotter, oscilloscope, computer, etc., etc.

Continuous Wave excitation

- It's pretty *de mode*, and is only useful to obtain 1D spectra.

- The idea behind it is the same as in UV. We scan the frequencies continuously (or sweep the magnetic field, which has the same effect - $\omega = \gamma\, B$), and record successively how the different components of M_o generate M_{xy} at different frequencies (or magnetic fields).
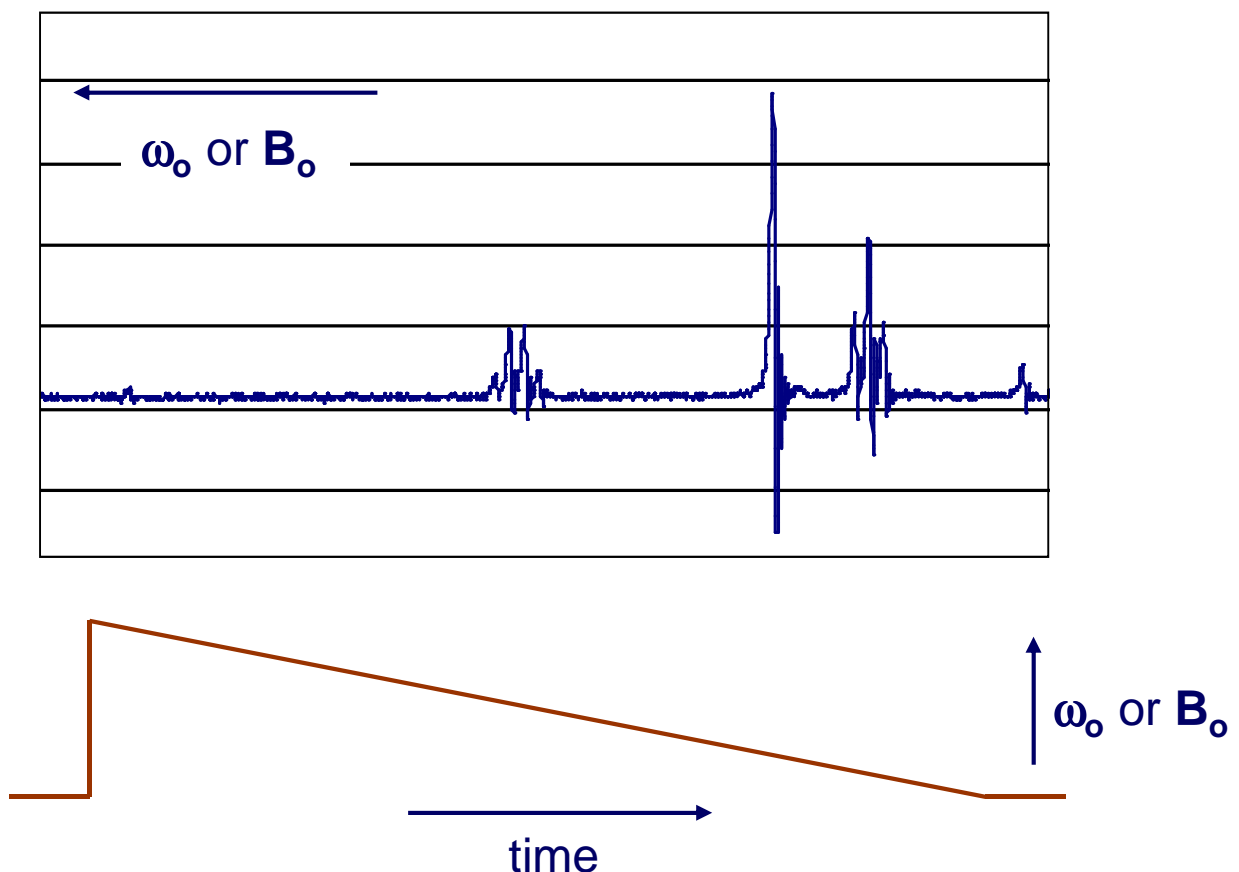
- We get a time domain effect in the frequency spectrum (the famous ***ringing***) because we cannot sweep slow enough.

Fourier Transform - Pulsed excitation

- The way every NMR instrument works today.

- The idea behind it is pretty simple. We have two ways of tuning a piano. One involves going key by key on the keyboard and recording each sound (or frequency). The other, kind of brutal for the piano, is to hit it with a sledge hammer and record all sounds at once.

- We then need something that has all frequencies at once. A short **pulse** of radiofrequency has these characteristics.

- To explain it, we use another black box mathematical tool, the **Fourier transform**: It is a transformation of information in the time domain to the frequency domain (and *vice versa*).
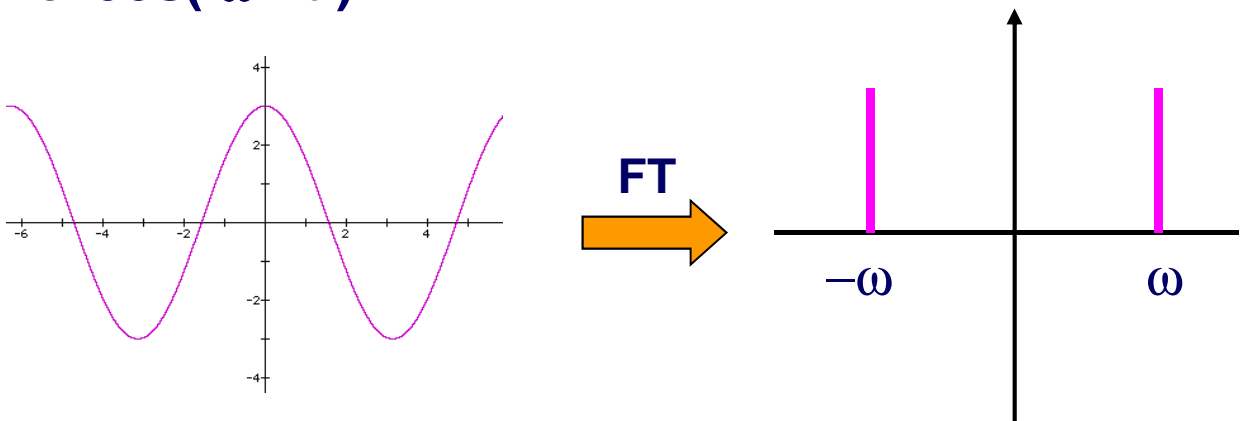
$$\mathbf{S}(\omega) = \int_{-\infty}^{\infty} \mathbf{S}(t) \, e^{-i\omega t} \, dt$$

$$\mathbf{S}(t) = {}^1/_2 \, \pi \int_{-\infty}^{\infty} \mathbf{S}(\omega) \, e^{i\omega t} \, dt$$

- If our data in the time domain is periodical, it basically gives us its frequency components. Extremely useful in NMR, where all the signals are periodical.
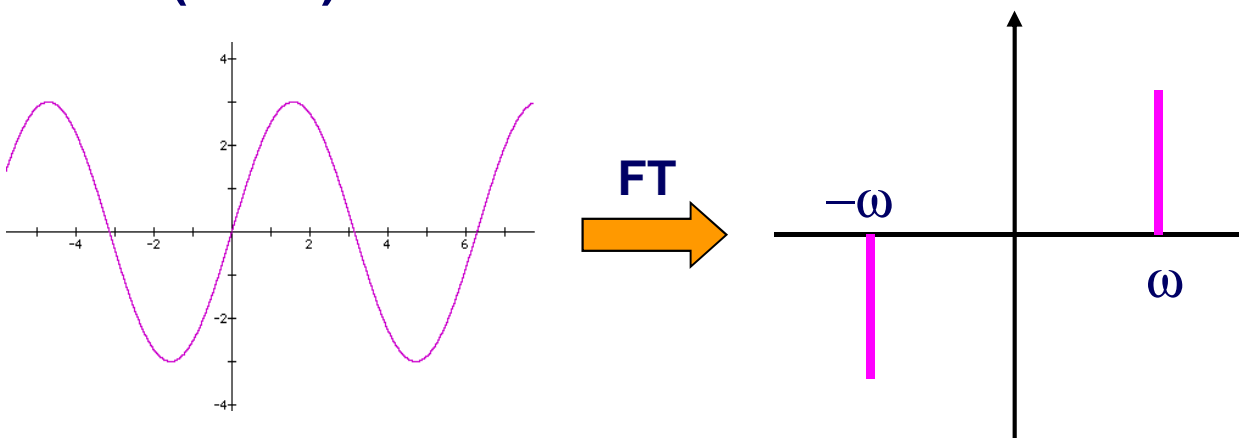
Fourier Transform of simple waves

- We can explain (or see) some properties of the FT with simple mathematical functions:

- For **cos(ω * t)**

- For **sin(ω * t)**

- The cosines are said to give *absorptive* lines, while sines give *dispersive* lines. We'll refer to these particularly when talking about the *phase of the spectrum*. It is also important to remember this to understand *quadrature detection*.
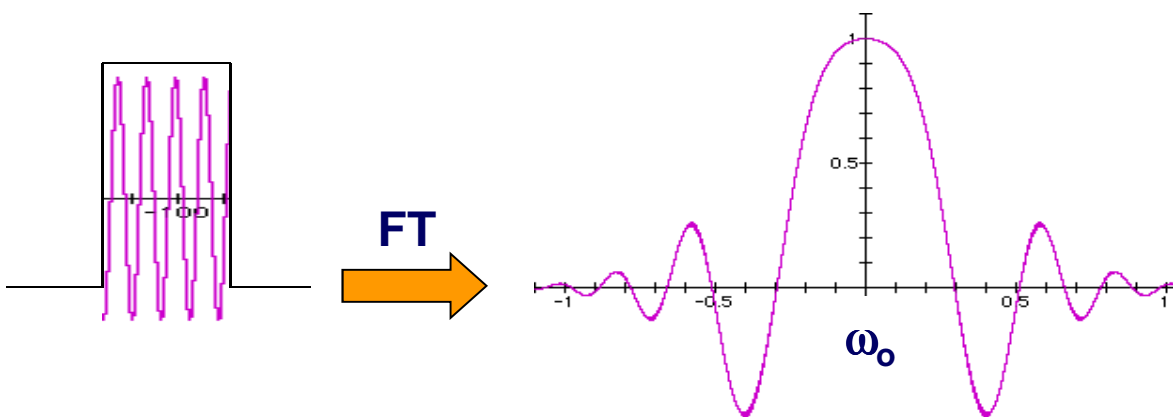
Back to pulses

- Now that we 'master' the FT, we can see how pulses work. A radiofrequency pulse is a combination of a wave (cosine) of frequency ω_o and a step function:

t_p
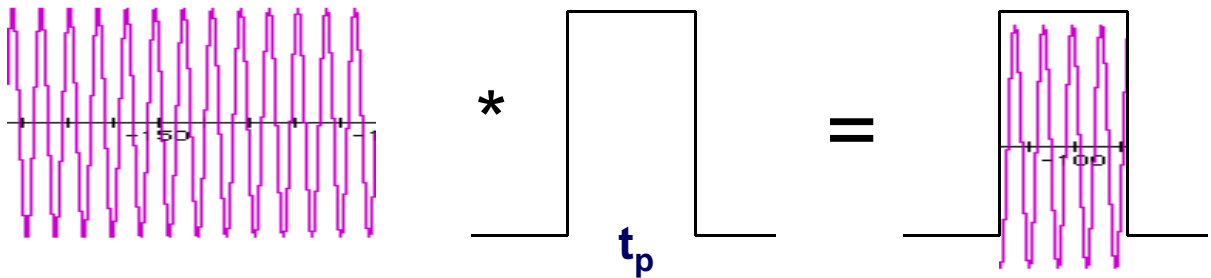
|	
FT: 1 at $\omega_o = \pm 1$	**FT:** $\dfrac{\sin(t_p\omega)}{t_p\omega}$ **or sinc($t_p\omega$)**

- This is the time domain shape of the pulse. To see the frequencies it really carry, we have to analyze it with FT:

FT

ω_o

- The result is a signal centered at ω_o which covers a wide range of frequencies in both directions. Depending on the pulse width, we have wider (shorter t_p) or narrower (longer t_p) ranges. Remember that $f \propto 1/t$.

Pulse widths and tip angles

- The pulse width is not only associated with the frequency range (or sweep width), but it also indicates how long the excitation field B_1 is on. Therefore, it is the time for which we will have a torque acting on the bulk magnetization M_o:
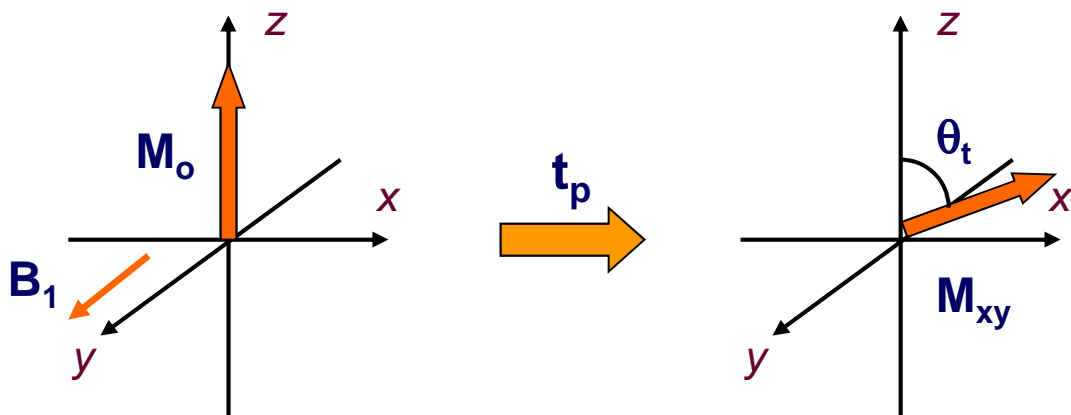

$$\theta_t = \gamma * t_p * B_1$$

- As the pulse width for a certain flip angle will depend on the instrument (B_1), we will therefore refer to them in terms of the rotation we want to obtain of the magnetization. Thus, we will have $\pi / 4$ (**45**), $\pi / 2$ (**90**), π (**180**), etc., etc., pulses.

Some useful pulses

- The most commonly used pulse is the $\pi / 2$, because it puts as much magnetization as possible in the **<xy>** plane (more signal can be detected by the instrument):
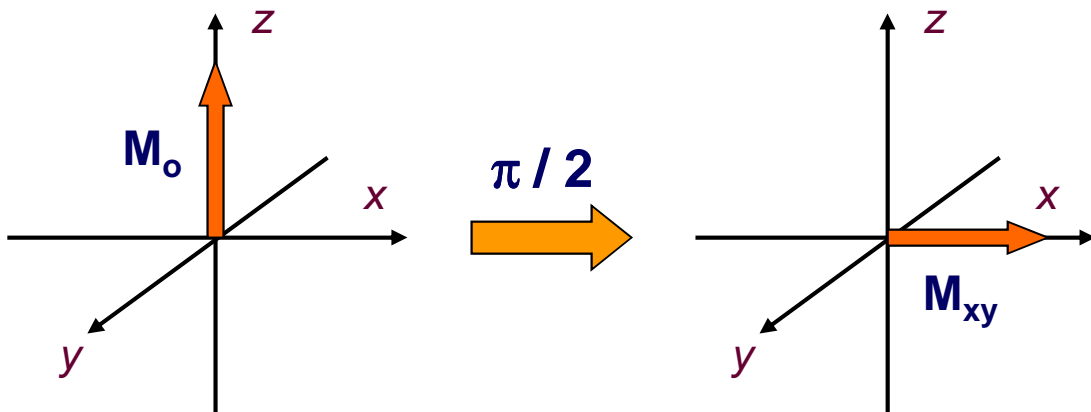

- Also important is the π pulse, which has the effect of inverting the populations of the spin system...
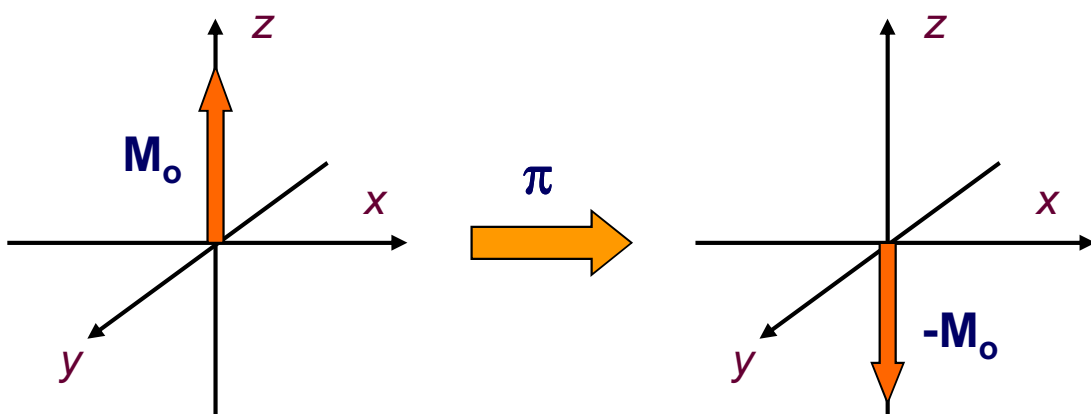
- With control of the spectrometer we can basically obtain any pulse width we want and flip angle we want.

Free Induction Decay (FID)

- We forgot about the sample a bit. We are interested in the signal that appears in the receiver coil after putting the bulk magnetization in the **<xy>** plane ($\pi / 2$ pulse).

- We said earlier that the sample will go back to equilibrium (**z**) precessing. In the rotating frame, the frequency of this precession is $\omega - \omega_o$. The relaxation of $\mathbf{M_o}$ in the **<xy>** plane is exponential (more next class). Therefore, the receiver coil detects a decaying cosinusoidal signal (single spin type):

$\omega = \omega_o$

$\omega - \omega_o > 0$

$\mathbf{M_{xy}}$

time

$\mathbf{M_{xy}}$

time
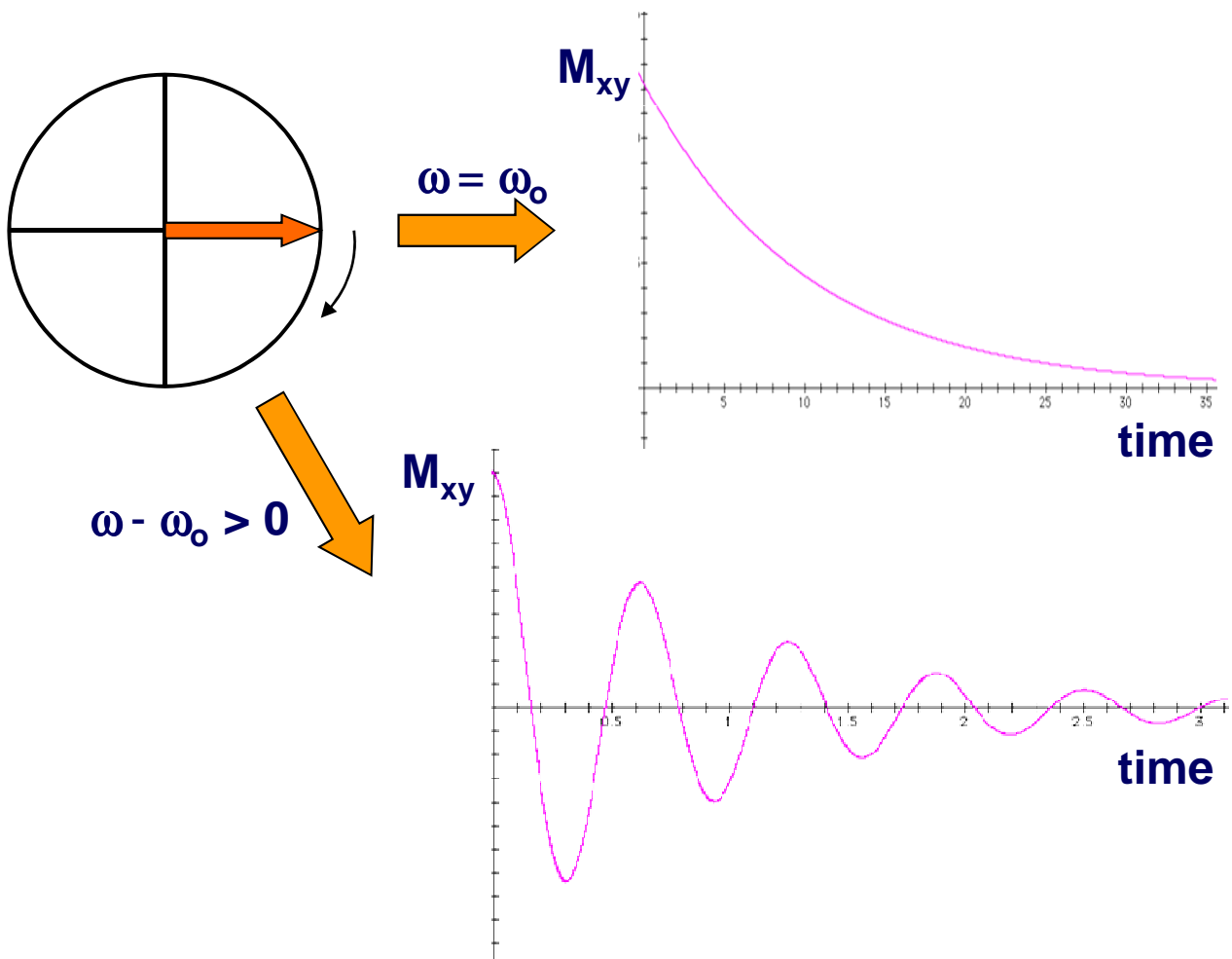
FID (continued)

- In a real sample we have hundreds of spin systems, all with frequencies different to that of **B₁** (or ***carrier frequency***). Since we used a pulse and excited all frequencies in our sample at once, we will se a combination of all of them in the receiver coil, called the ***Free Induction Decay*** (or ***FID***):
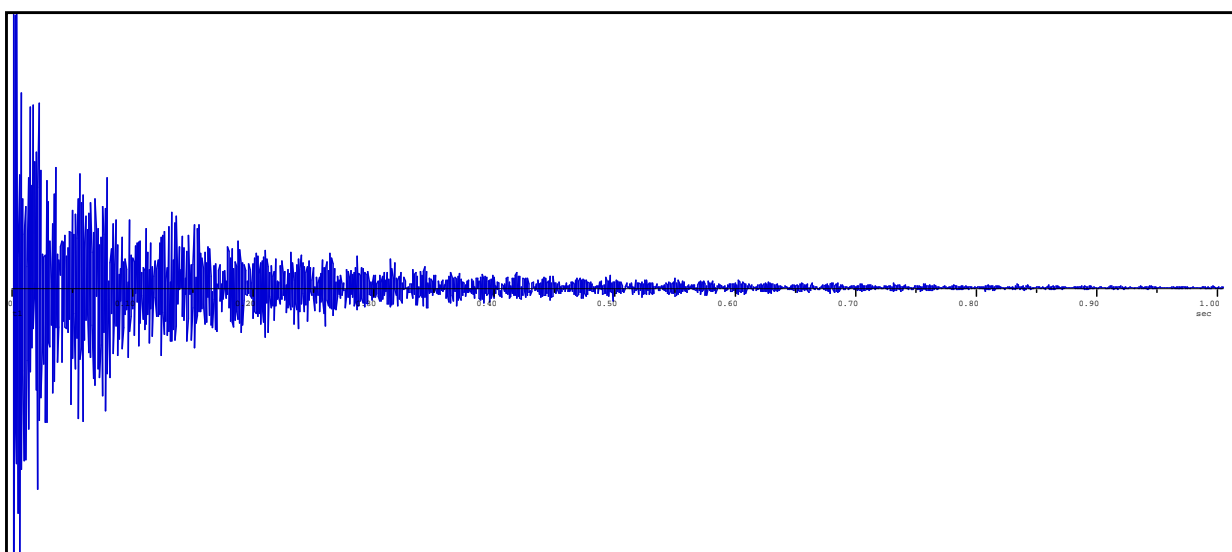
- The FT of this signal gives us the NMR spectrum: