# The Basics of Fourier Transform NMR Spectroscopy

CHM-5235, October 2009

*Despite its inception in the laboratories of physicists, it is in the chemical laboratory that NMR spectroscopy has found greatest use and, it may be argued, has provided the foundations on which modern organic chemistry has developed. Modern NMR is now a highly developed, yet still evolving, subject that all organic chemists need to understand, and appreciate the potential of, if they are be effective in and able to progress their current research.*

*Timothy Claridge*

## Recommended textbooks:

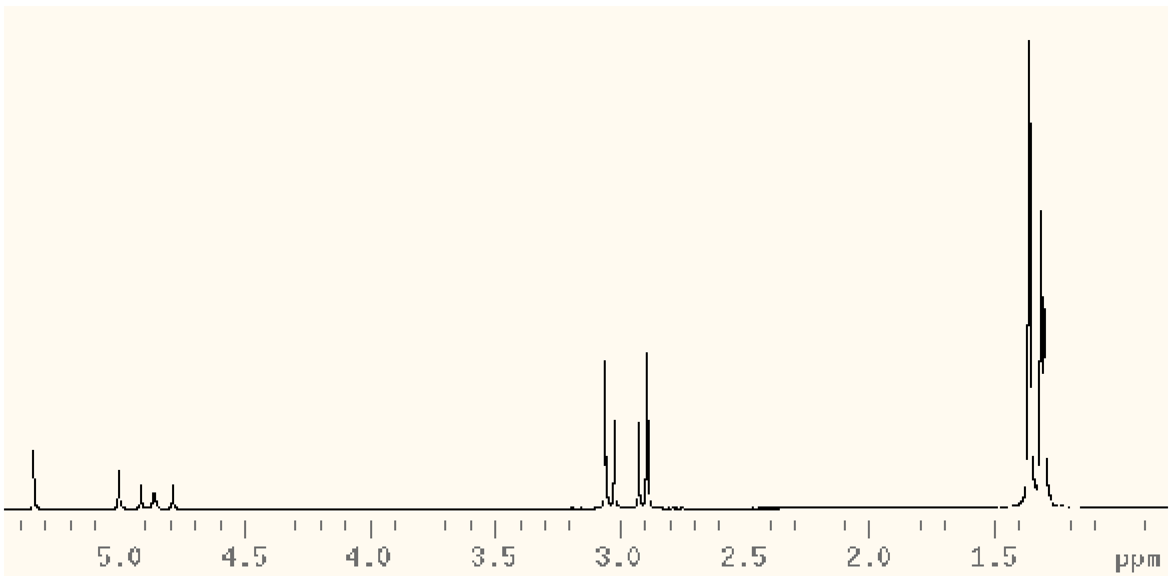

T. D. W. Claridge, "*High-Resolution NMR Techniques in Organic Chemistry*", Pergamon, 1999.

J. K. M. Sanders and B. K. Hunter, "*Modern NMR Spectroscopy*" Oxford University Press, 1993.

A. E. Derome, "*Modern NMR Techniques for Chemistry Research*" Pergamon, 1995.

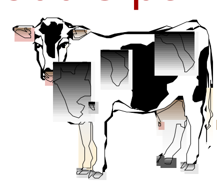
# Continuous wave (CW) *vs.* Fourier Transform (FT) NMR

In CW-NMR the resonance condition $\nu = \gamma B_0/2\pi$ is matched for one frequency at a time, by sweeping the field $B_0$.



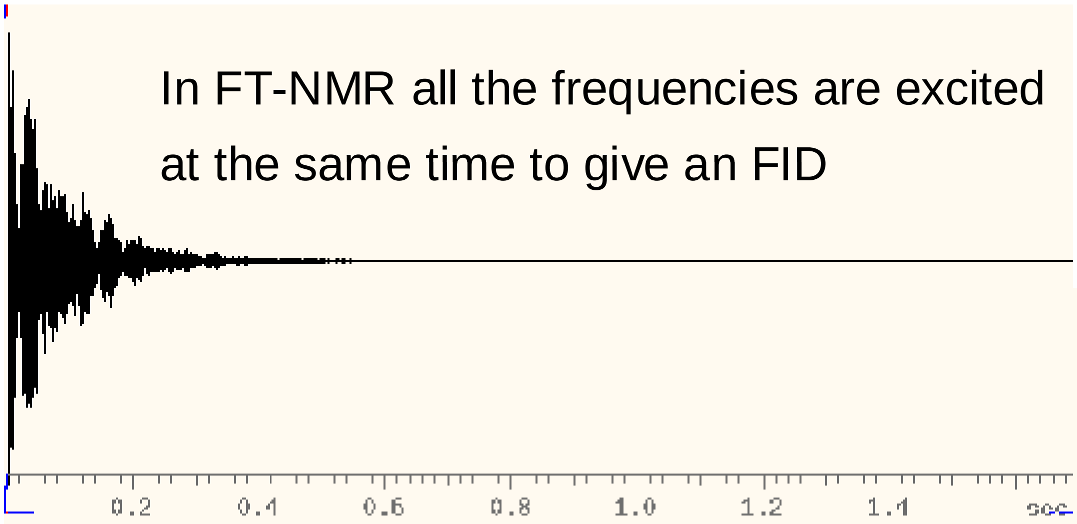

The uncertainty principle says that one has to spent one second per each Hz of the sweep width in order to measure the frequency with a precision of 1 Hz.
( $\Delta E * \Delta t \geq h$, $h * \Delta\nu * \Delta t \geq h$ )

A 15 ppm sweep width at 300 MHz takes 4500 s per scan for a poor resolution of 1Hz !

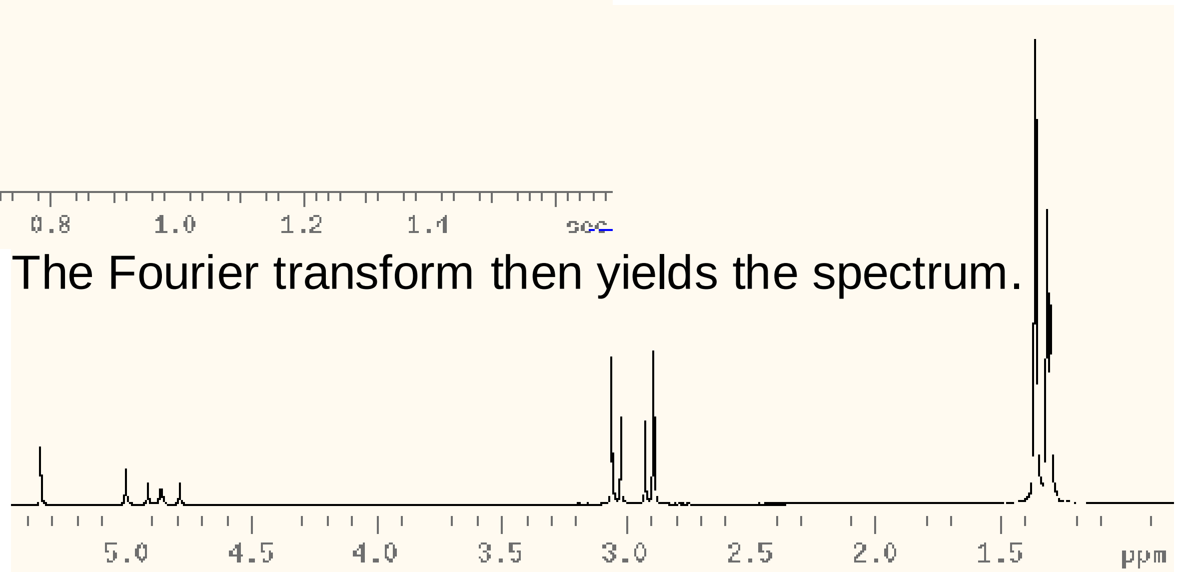


# Continuous wave (CW) *vs.* Fourier Transform (FT) NMR

In FT-NMR all the frequencies are excited at the same time to give an FID




The Fourier transform then yields the spectrum.




A 15 ppm sweep width at 300 MHz takes **1 s** per scan for a poor resolution of 1Hz !

# Advantages of FT over CW:

- Faster - no sweeping, all the frequencies at once.

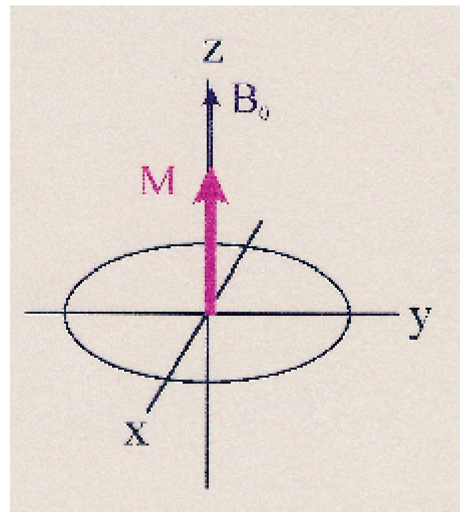
- The possibility of multiple scanning, to improve the signal to noise ratio.

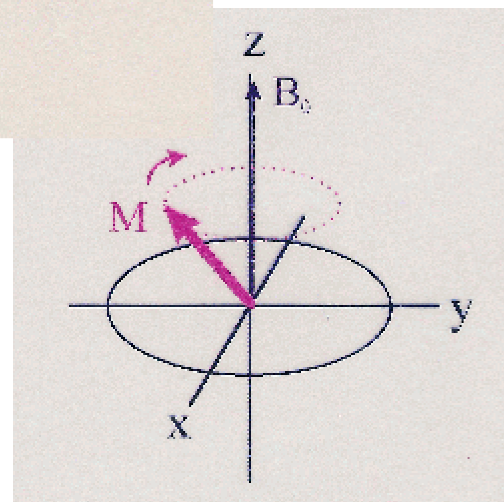
- The possibility of spin-engineering -manipulation of the spins through pulses and delays reveals more information (2D NMR).

# Magnetization

- The Bulk Magnetization M is the sum of the magnetization of the individual spins. M is oriented parallel to $B_0$, which defines the z axis (a).

- When misaligned from $B_0$, M precesses about it at an angular velocity $\omega_0 = \gamma B_{eff}$. (b).




One can measure $B_{eff}$ by measuring the frequency of the current induced by M in a coil.

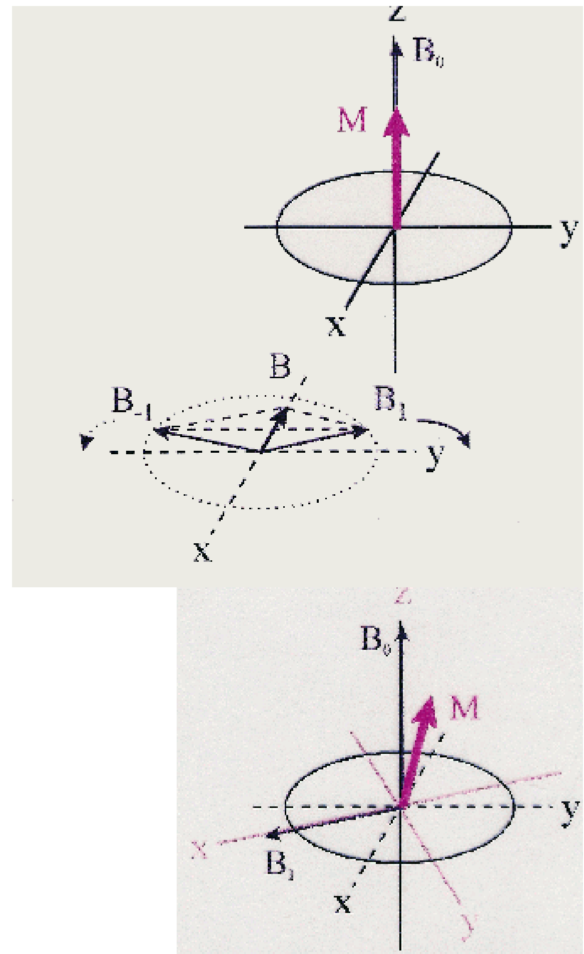
# Perturbation

- M can be tilted away from $B_0$ by precession about a field $B_1$, perpendicular to M.

- $B_1$ has to rotate at $\omega_0 = \gamma B_0$, in order to have a constant pull.

- A rotating $B_1$ can be generated (together with $B_{-1}$ rotating in the opposite direction) by an alternating current (AC).

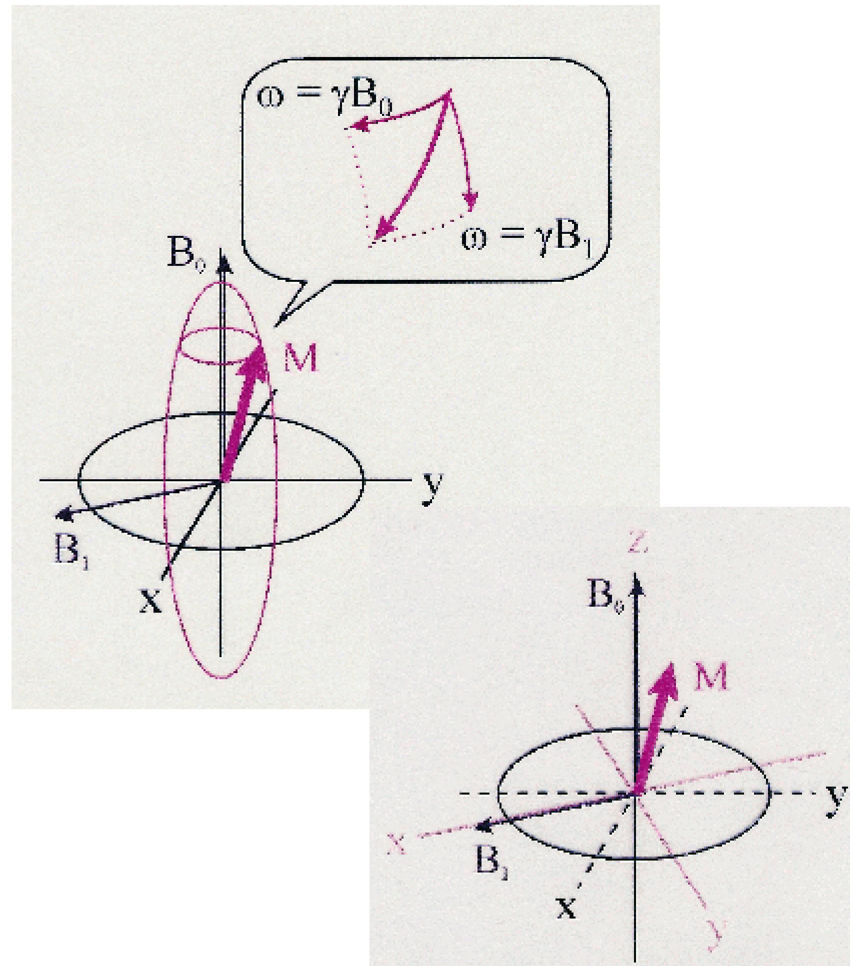
- Only $B_1$ which rotates in the same direction as M has an effect on M.



- In the laboratory frame, M rotates simultaneously about two axes, $B_0$ and $B_1$.

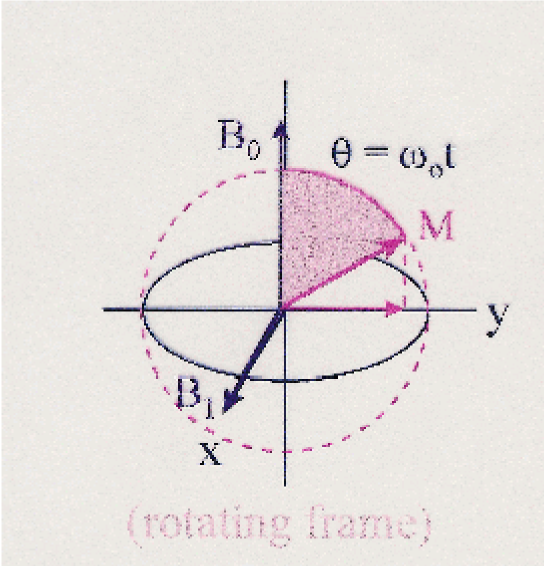
- The rotating frame of reference has z defined by $B_0$ and x defined by $B_1$.

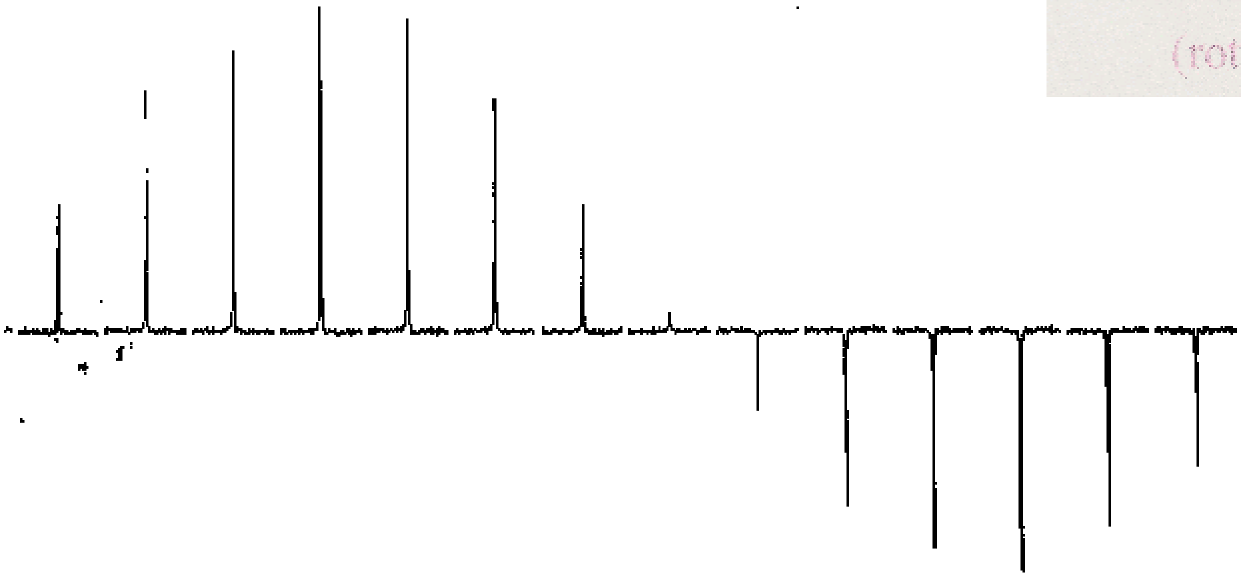
- In the rotating frame of reference M rotates only about $B_1$.



- The intensity of the signal is proportional to the projection of M into the xy plane: $M_y = M \cos(\gamma B_1 t)$.

- A plot of the signal intensity versus t (pw) yields pw90.



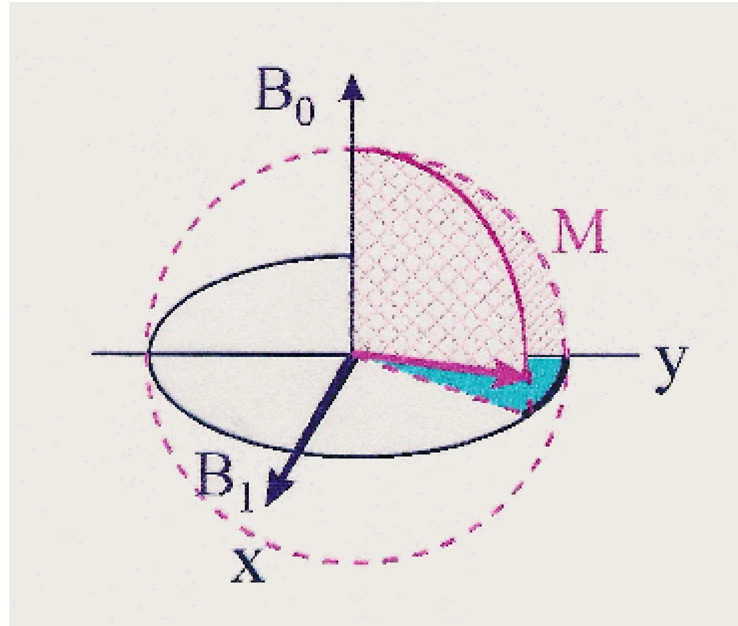



➢For a real sample, with more than one signal, $B_1$ precesses with $\omega_0 = \gamma B_0$ while M precesses with $\omega = \gamma B_{eff}$. Consequences:

➢ A phase error: $\theta = (\omega_0 - \omega)\, t = 2\pi\Delta\nu\, t$ For $\Delta\nu = 10^3$ Hz (3.33 ppm at 300 Mhz) $3.6 = 2\pi 10^{-2}$ rad $= 2\pi 10^3\, t \quad t =$ 10 $\mu$s.

➢ An amplitude error - the intensity diminishes as $(\omega_0 - \omega)$ increases.

➢ A shorter pulse excites a wider range of frequencies.



# Detection

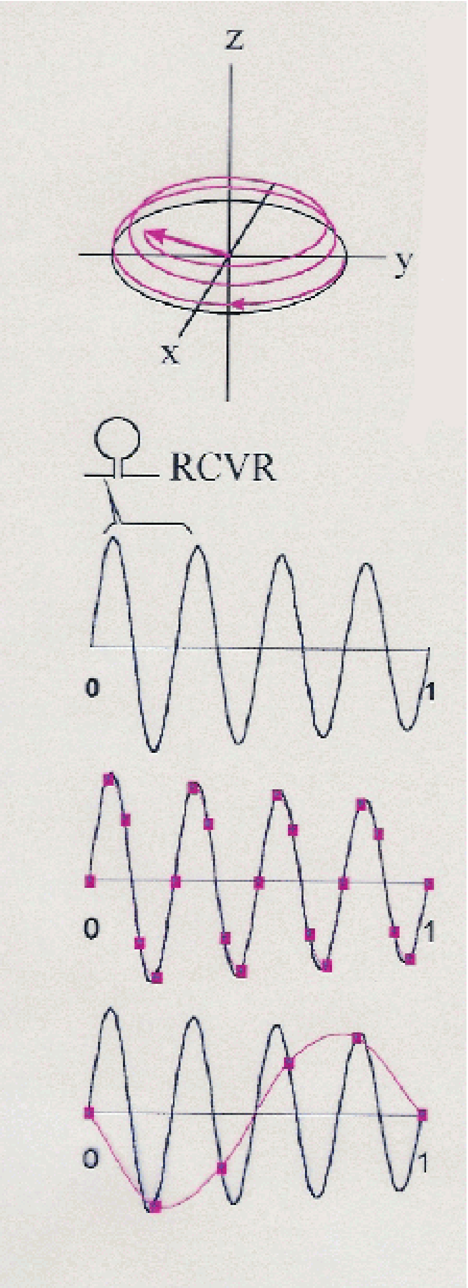
In the rotating frame, after the pulse, M is on y and relaxes back to z in the zy plane.

In the laboratory frame, M precesses at $\omega_0$, while relaxing back to z. The projection of M in the xy plane induces in the receiver coil a current (which oscillates at the Larmor frequency) called FID:

- Free (of the pulse)
- Induction (induces a current in the receiver)
- Decay (decays due to relaxation).

The FID is sampled by an ADC (analog to digital converter). The sampling rate (1/DW) has to be at least twice $\nu$, otherwise a false frequency is obtained.

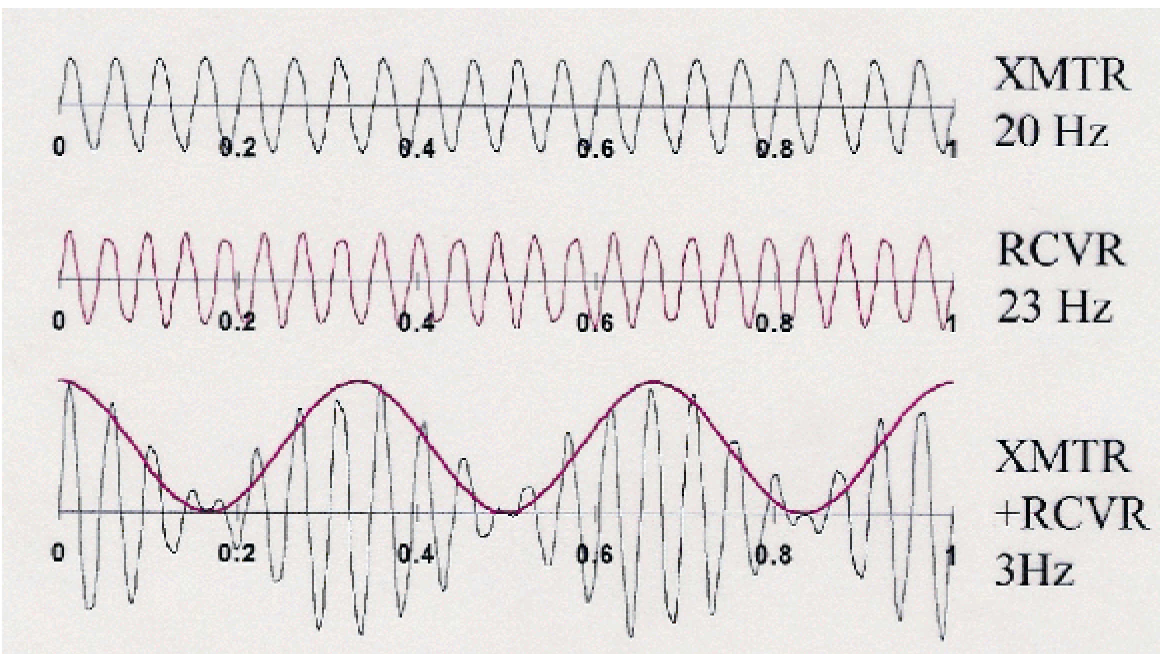
The spectral window (sw) is the range of frequencies which can be measured correctly.  1/DW=2sw . np=at/DW=2sw*at .

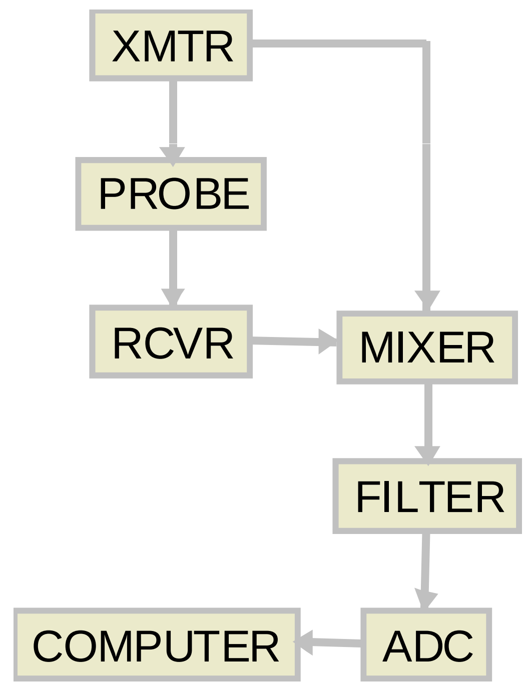


At 300 Mhz, 1/DW should be >600 MHz.  Actually the ADC is 100 kHz.

We measure the frequency difference between the transmitter and the signal, which is less than 5 kHz for H1 at 300 MHz.

The spectral window is defined by sw (in turn defined by the sampling rate, 1/DW) and tof (the frequency of the excitation pulse, which is the center of the spectral window).

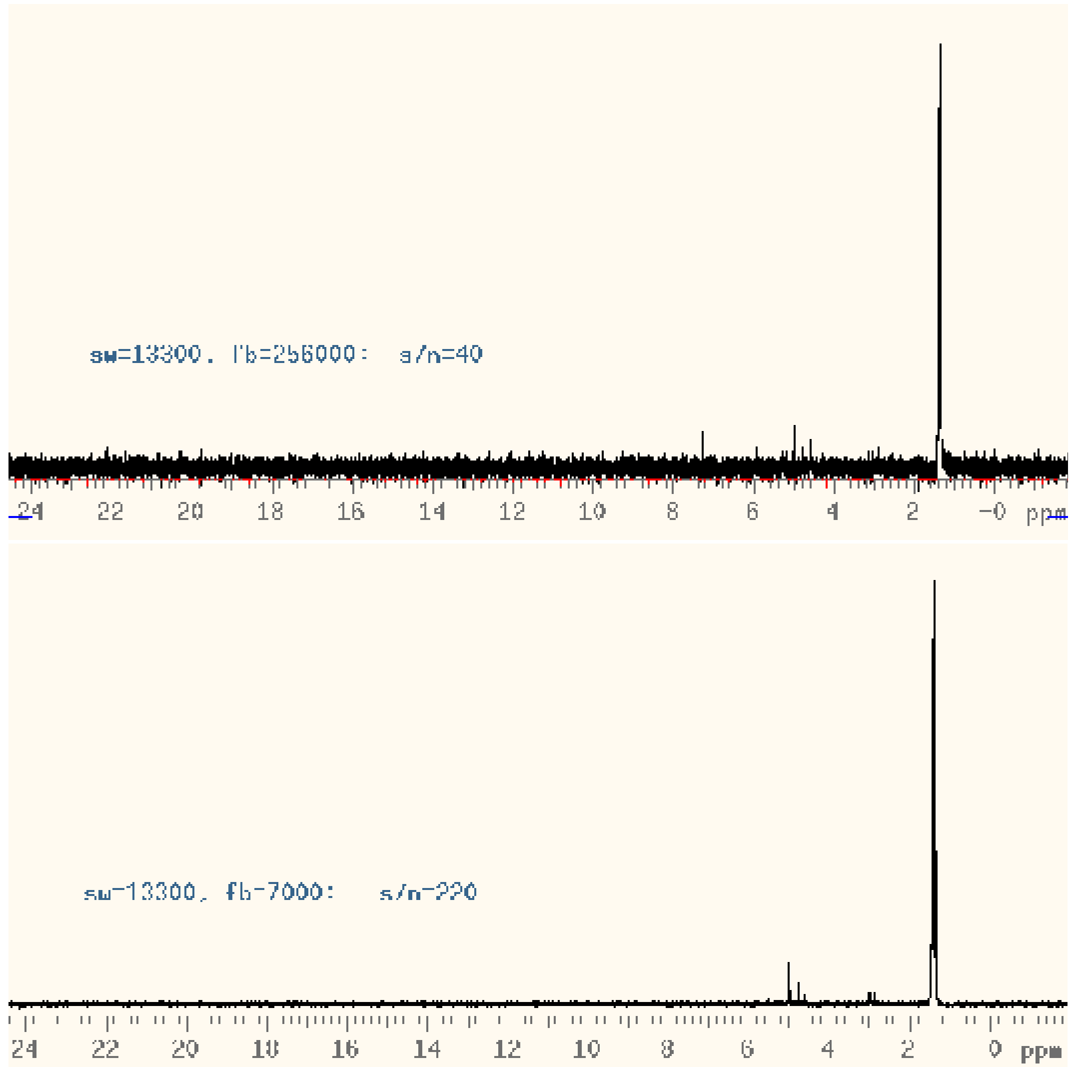


- ➢Noise from outside sw comes folded into the spectrum.

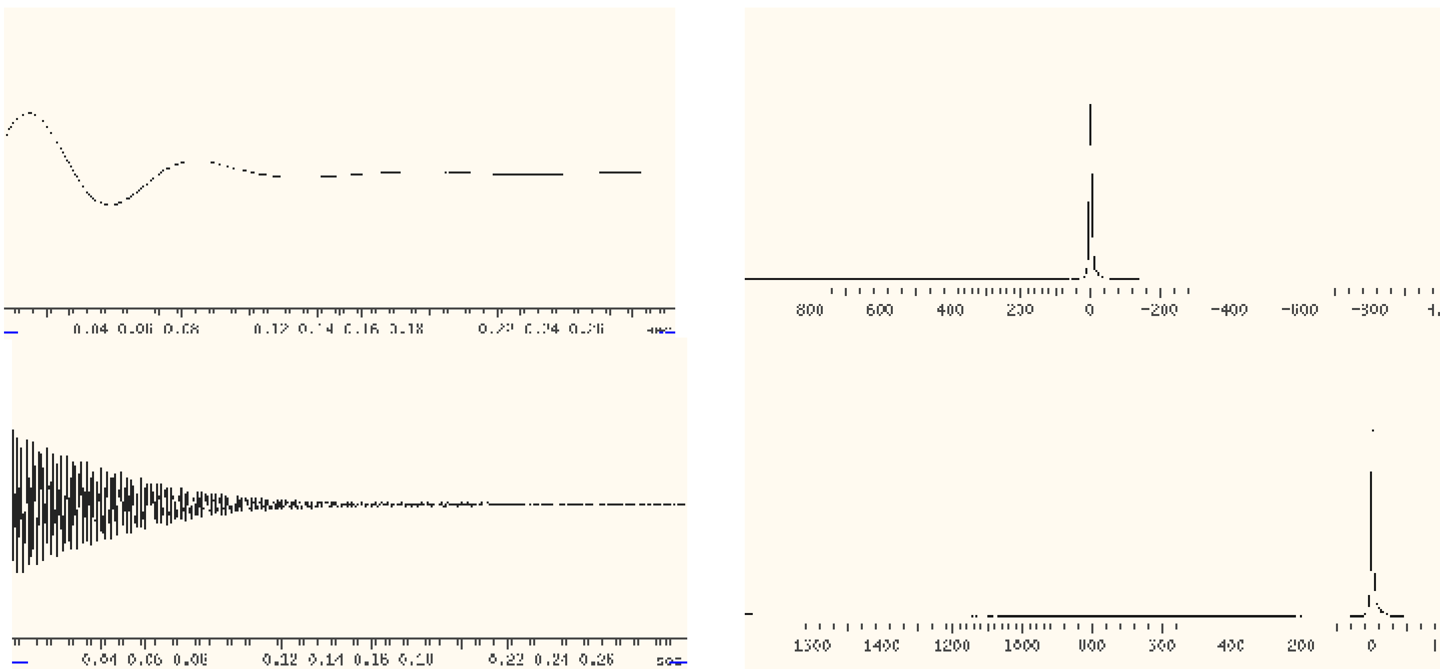
- ➢ This noise is removed by audio filters.  The filter bandwidth is controlled by fb, which is adjusted automatically when sw is changed.

- ➢ One can set fb to allow the signals outside sw to pass. Intentional folding is used in 2D NMR to reduce sw.

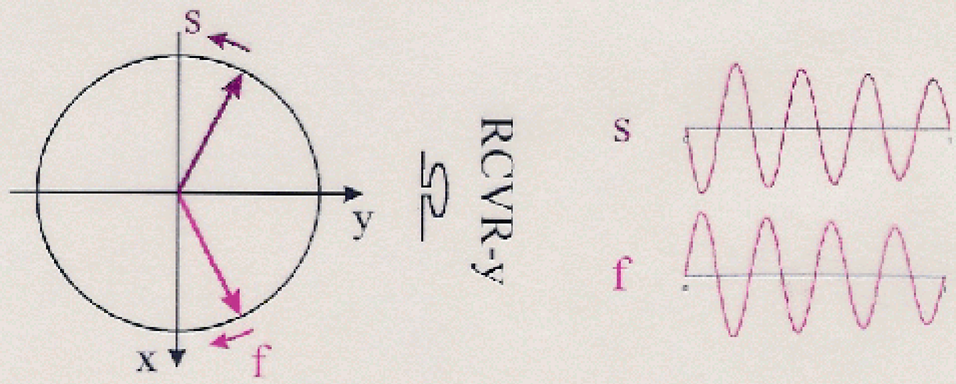


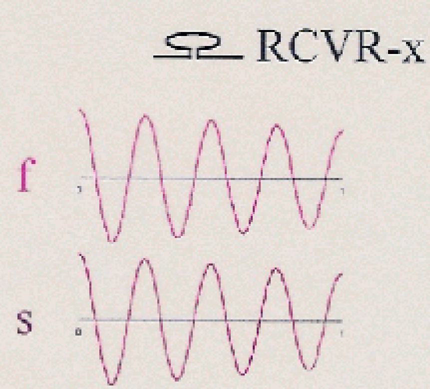
➢The spectral window is defined by sw and tof (the frequency of the pulse, which is the center of the spectral window).

➢ Because ABS(tof-ν) is detected, all the frequencies in the spectrum have to be on the same side of tof. If one could tell the sign of tof-ν (quadrature detection) the sw could be reduced to half and the s/n improved.



# Quadrature detection



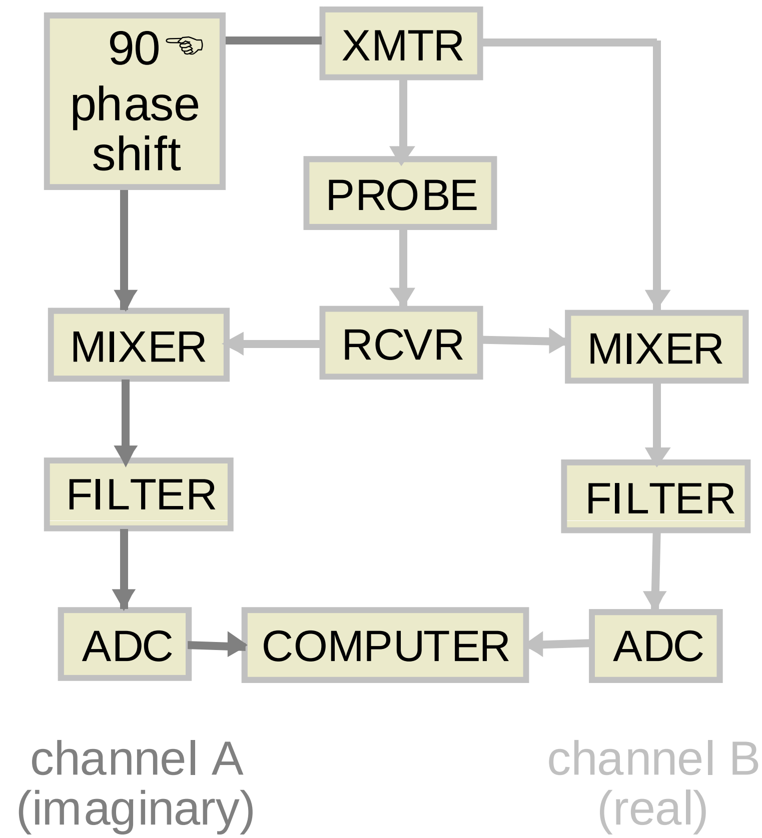




Two detectors are needed to discriminate between f - a frequency higher than the one of the XMTR and s - a frequency lower than the one of the XMTR.

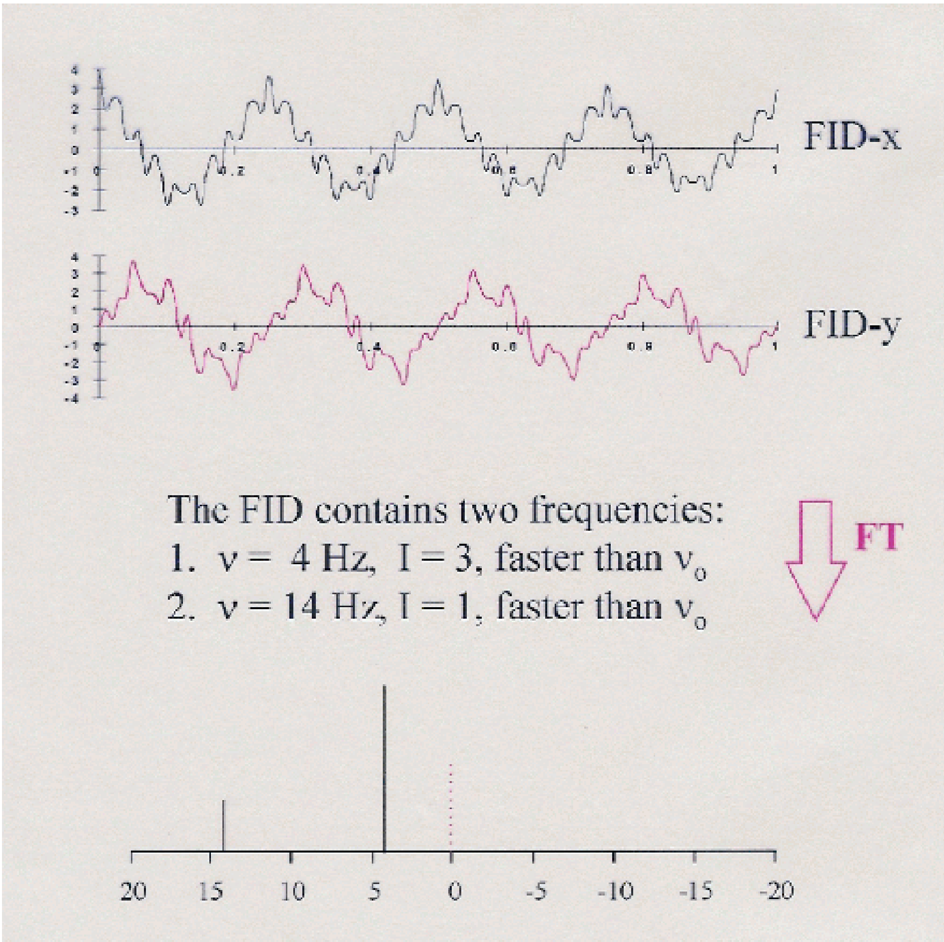
➢Physically a second detector, is realized by combining the signal with the transmitter frequency, shifted by 90.

➢ Two points are collected at a time, by the two ADC's, or one can think of it as a complex point (hence the real and imaginary FID's).

➢ With quadrature detection, sw is half, but the amount of data the same.

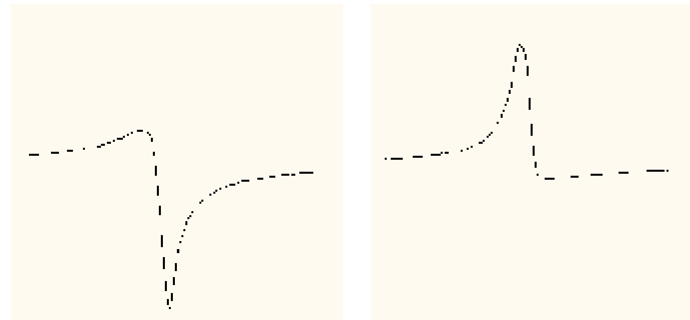


# Fourier transform



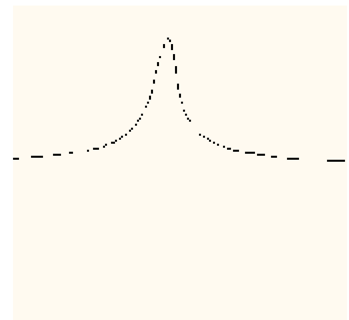

- The Cooley-Tuckey algorithm transforms an FID of np=$2^n$ points into a spectrum of fn=$2^n$ points.
- fn is always $2^n$. For np<fn, the FID is filled with zeroes up to $2^n$.

The complex Fourier transform produces two representations of the spectrum:



In the absolute value mode,

$spectrum(\omega) = (real(\omega)^2 + imaginary(\omega)^2)^{1/2}$

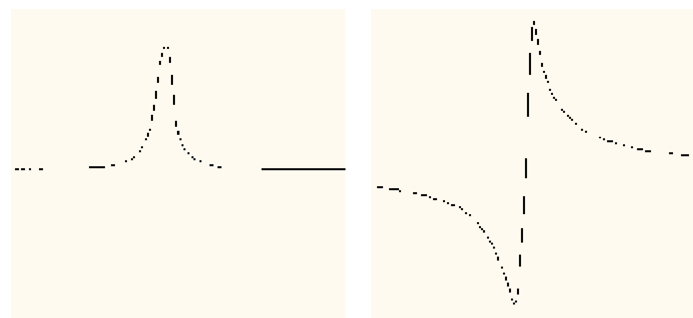


In the phase-sensitive mode,

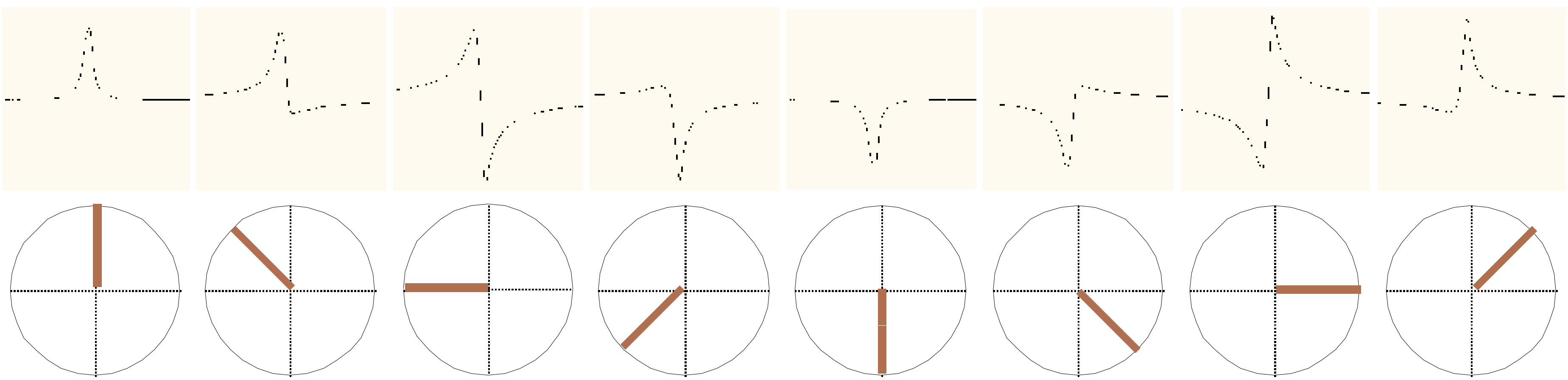
$spectrum(\omega) = real(\omega)\sin(\theta)+$

$imaginary(\omega)\cos(\theta)$

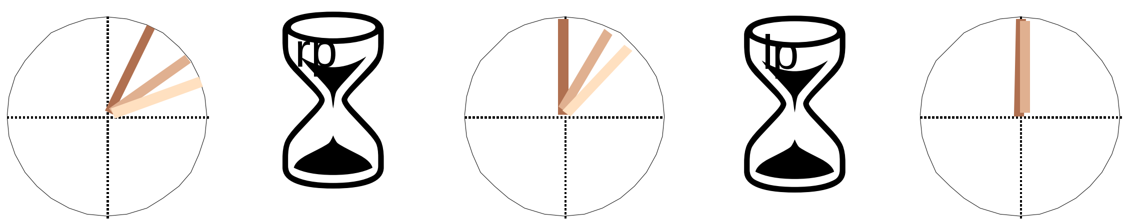
$\theta = rp + (\omega-\omega_0)\ lp$



One can think of the *real*(ω) and *imaginary*(ω) as the spectra seen by the two detectors - they are necessary 90☜dephased. The phase is given by the position of the global magnetization **M** at the beginning of the acquisition. The zero-order correction (rp) takes care of the dephasing between the transmitter and the reciever.

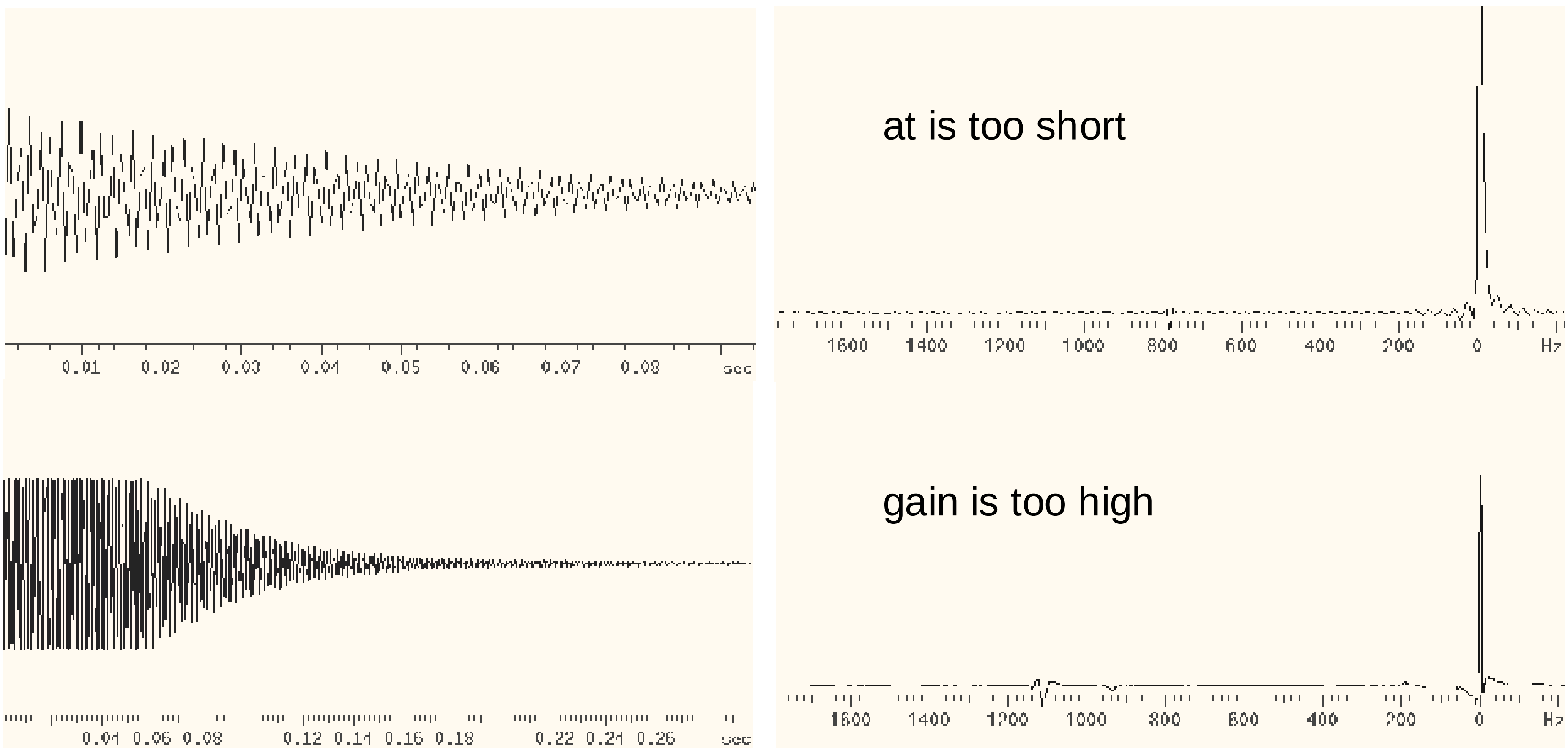


The first-order correction (lp) takes care of the dephasing of the frequencies between the middle of the pulse and the beginning of the acquisition.



A point in the FID influences all the frequencies in the spectrum.

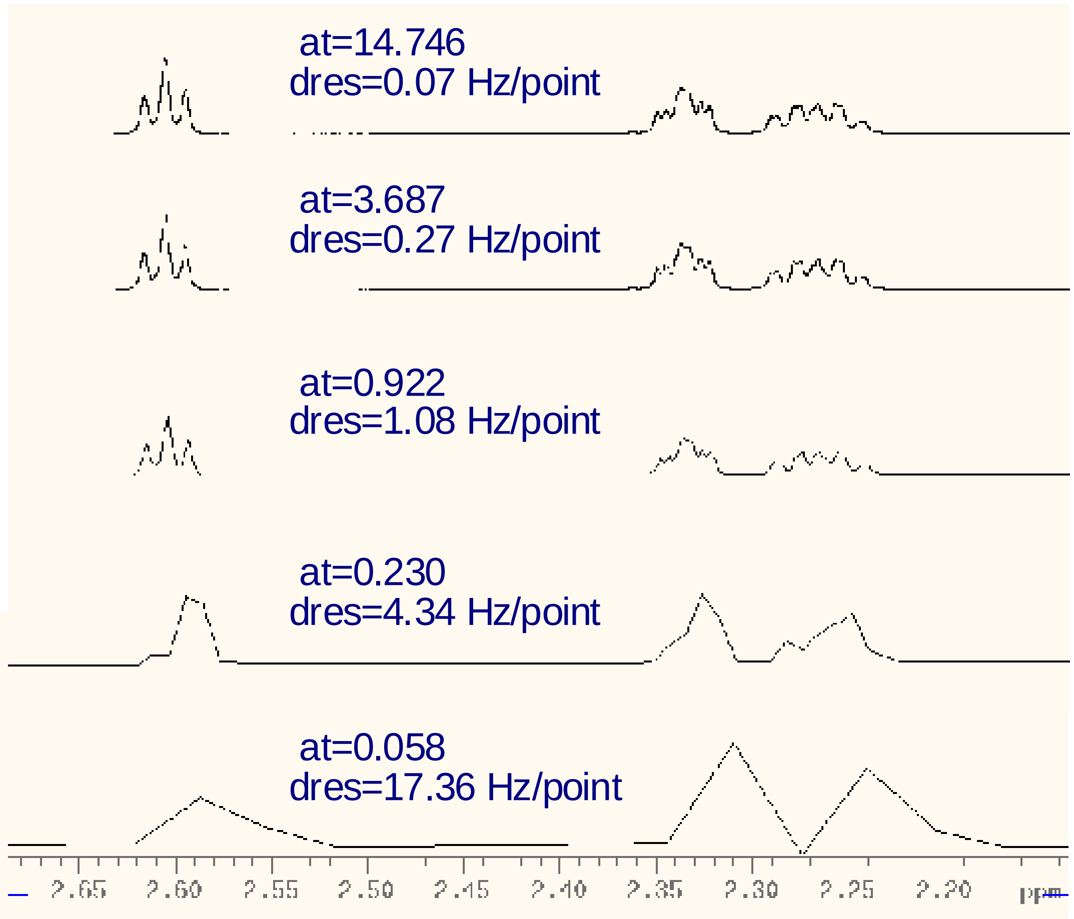
The Fourier transform of a product of functions is the convolution of the transforms of the individual functions.

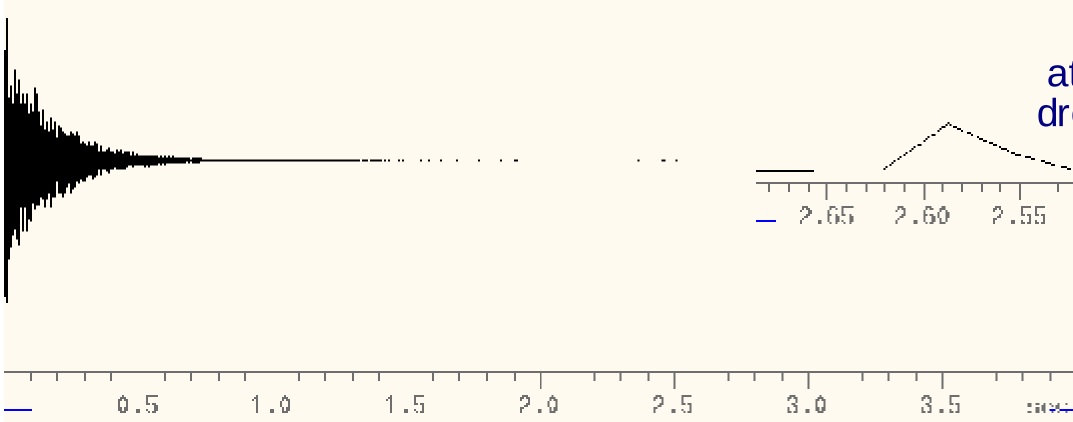


# Digital Resolution

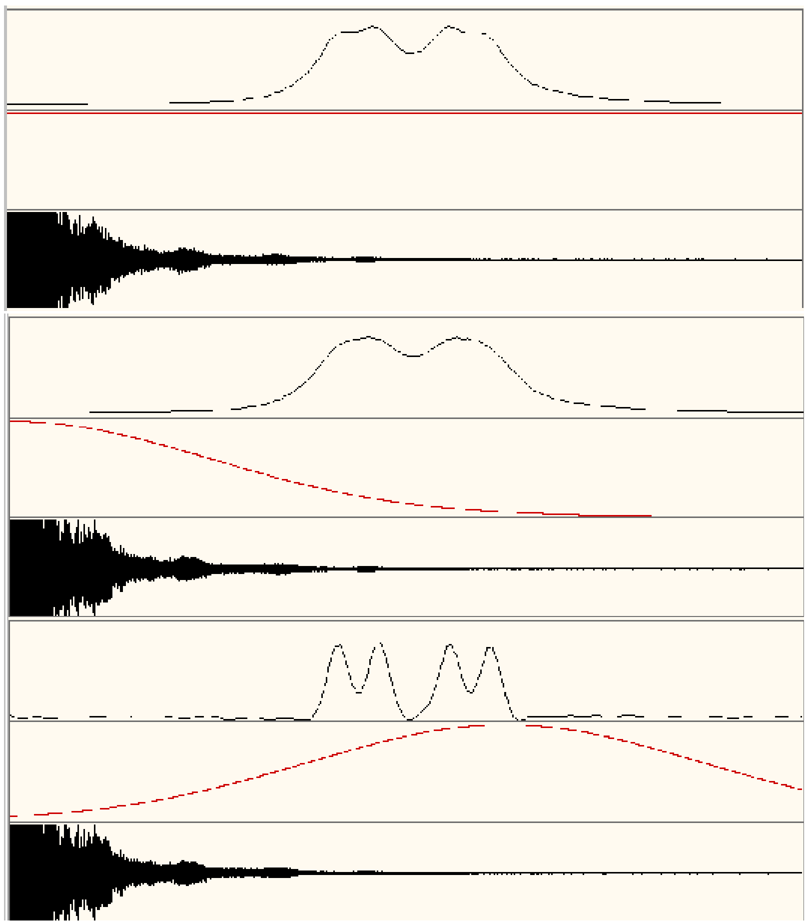
$$dres = sw/(np/2) = 2sw/(at/DT) = sw/(at*2sw) = 1/at$$

Acquiring after complete signal relaxation introduces noise in the spectrum, without improving the resolution.



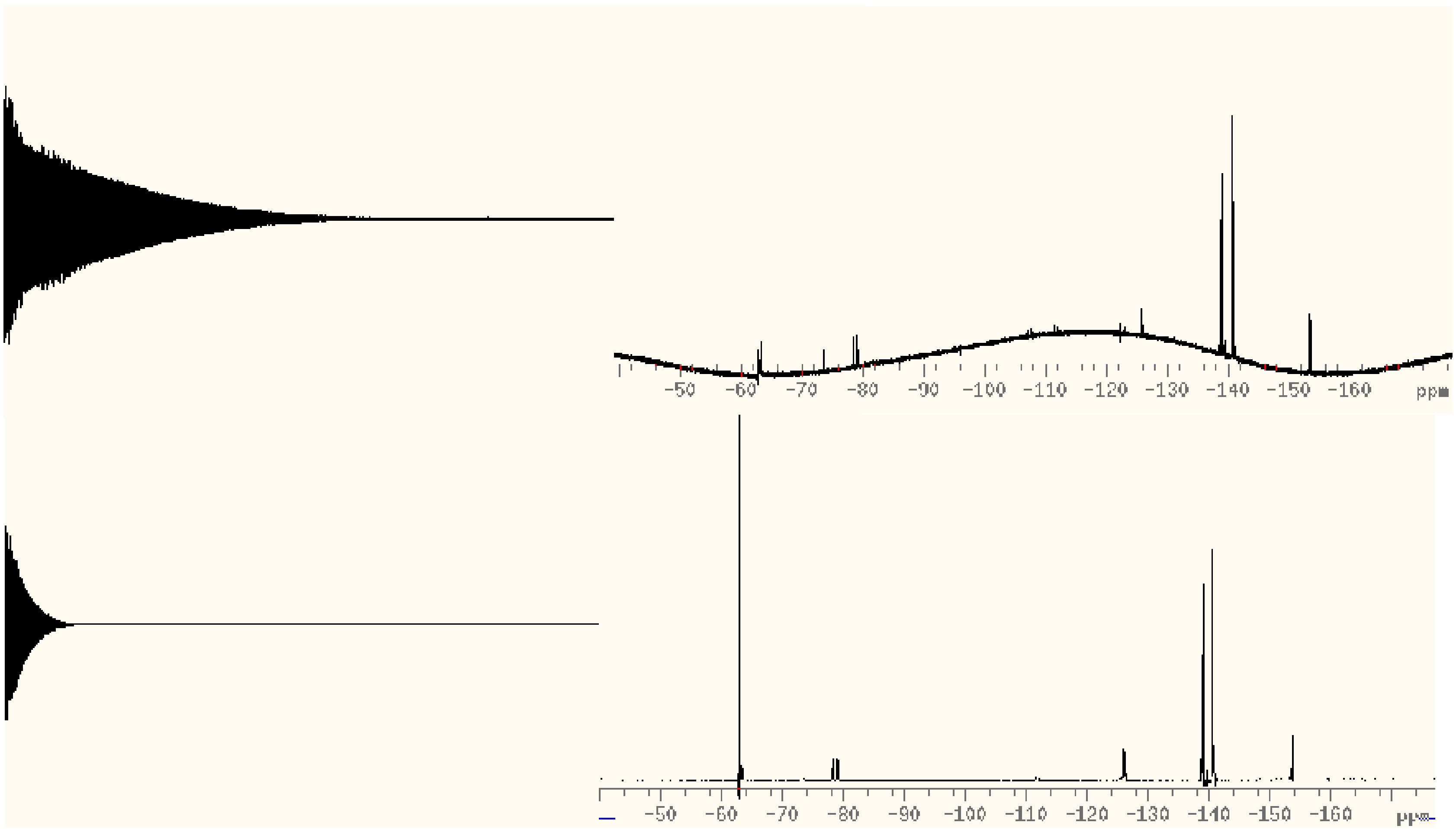
# Weighting (Apodization)



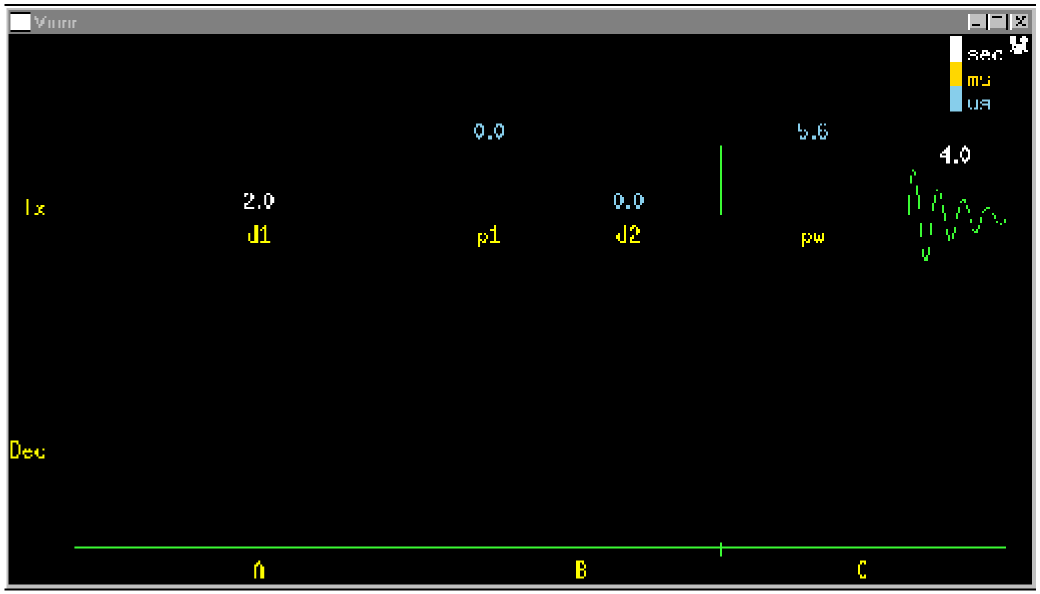
One can improve the resolution or the signal to noise ratio by multiplying the FID with a window function prior to Fourier transform. Like this one can increase the weight in the spectrum of the first part of the FID (good s/n) or of a later part (good resolution).

# Linear Prediction

One can use the good part of the FID to extract the frequencies and then extrapolate the FID backward or forward to correct for the bad part.



# s2pul




| ACQUISITION | | SAMPLE | | PROCESSING | | FLAGS | |
|---|---|---|---|---|---|---|---|
| sfrq | 499.550 | date | Oct 30 2000 | lb | not used | il | n |
| tn | H1 | solvent | CDCl3 | sb | not used | in | n |
| at | 3.999 | file | exp | gf | not used | dp | y |
| np | 70976 | DECOUPLING | | awc | not used | hs | nn |
| sw | 8873.1 | dn | H1 | lsfid | not used | SPECIAL | |
| fb | 5000 | dof | 0 | phfid | not used | temp | 25.0 |
| bs | 32 | dm | nnn | wtfile | | | |
| ss | 0 | dmm | c | proc | ft | | |
| tpwr | 57 | dmf | 15630 | fn | not used | | |
| pw | 5.5 | dpwr | 35 | math | f | | |
| p1 | 0 | | | | | | |
| d1 | 2.000 | | | werr | | | |
| d2 | 0 | | | wexp | wft | | |
| tof | 439.2 | | | wbs | | | |
| nt | 16 | | | wnt | wft | | |
| ct | 0 | | | | | | |