NMR Spectroscopy: Principles and Applications

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Fourier Transform

Lecture 3

Fourier Transform in NMR

The measured (or detected) signal in modern NMR is in time domain. This is a major difference compared to other kinds of spectroscopy.

The time domain signal is of limited value except in very simple cases. In realistic situations it is essential to present a spectrum i.e. frequency vs intensity plot and Fourier transform elegantly does this conversion from the time domain signal or FID.

Fourier Transform in NMR

time
domain

time

Fourier
transform

$$S(\omega) = \int\limits_{-\infty}^{\infty} S(t)e^{-i\omega t}\,dt$$

$$S(\upsilon) = \int\limits_{-\infty}^{\infty} S(t)e^{-i2\pi\upsilon t}\,dt$$

frequency
domain

frequency
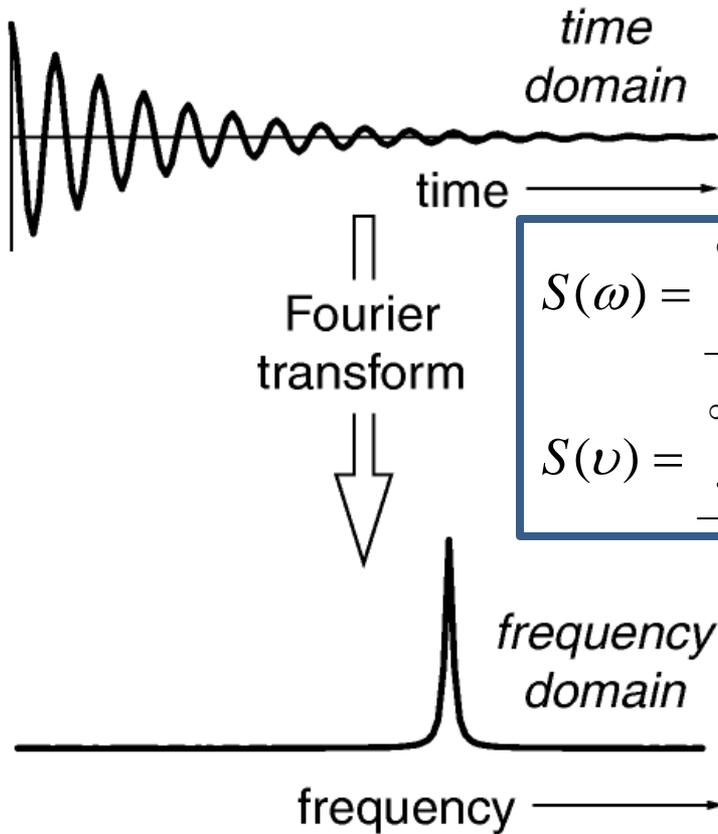
Mathematically, the Fourier transform of a time domain signal can be expressed as an integral of the product of the time domain signal and a sinusoidal signal. The result can be expressed in either rad/sec or in Hz units.

Fourier Transform in NMR

Let us try to understand FT qualitatively with a specific case. Consider a single FID for analysis. We multiply this FID with 3 trial cosine signals of (a) 15Hz, (b) 17Hz, and (c) 30Hz. We take the product signals compute area under these and plot them as a function of the reference cosine wave frequency.
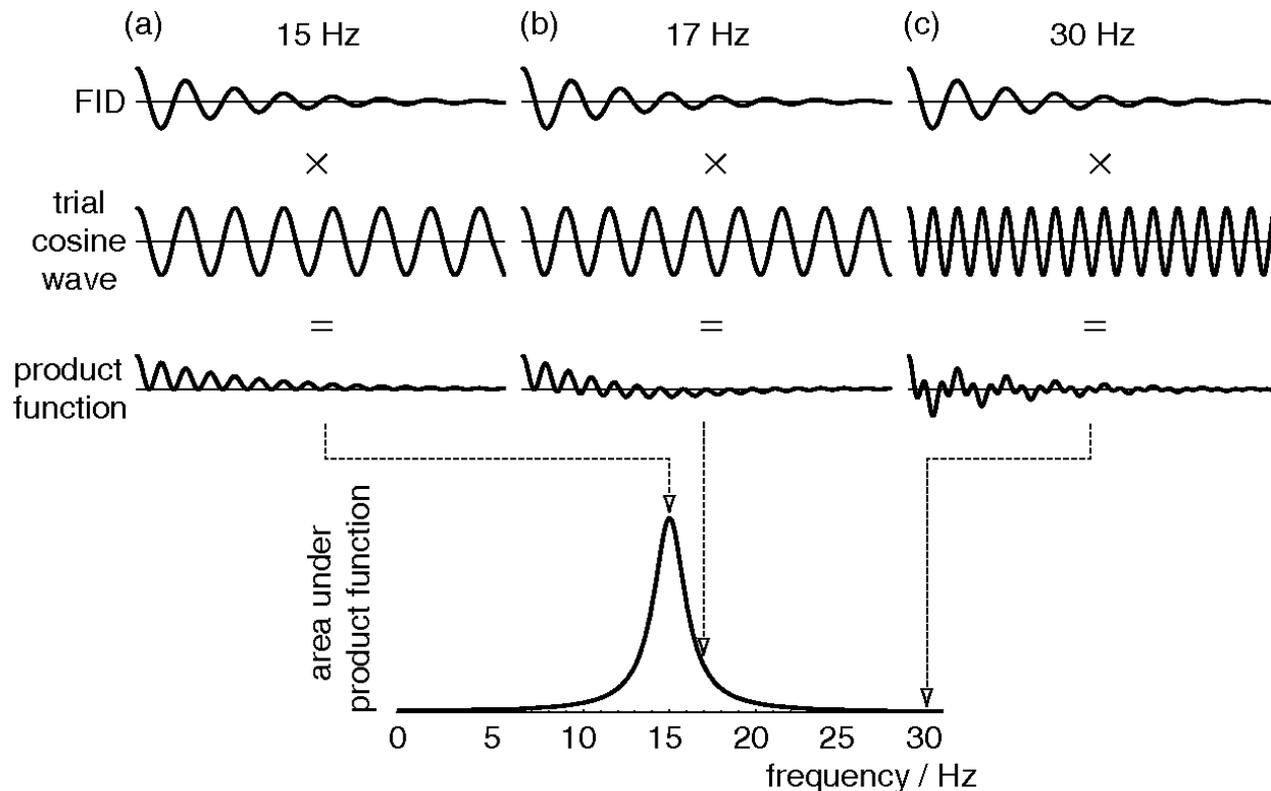
Fourier Transform in NMR

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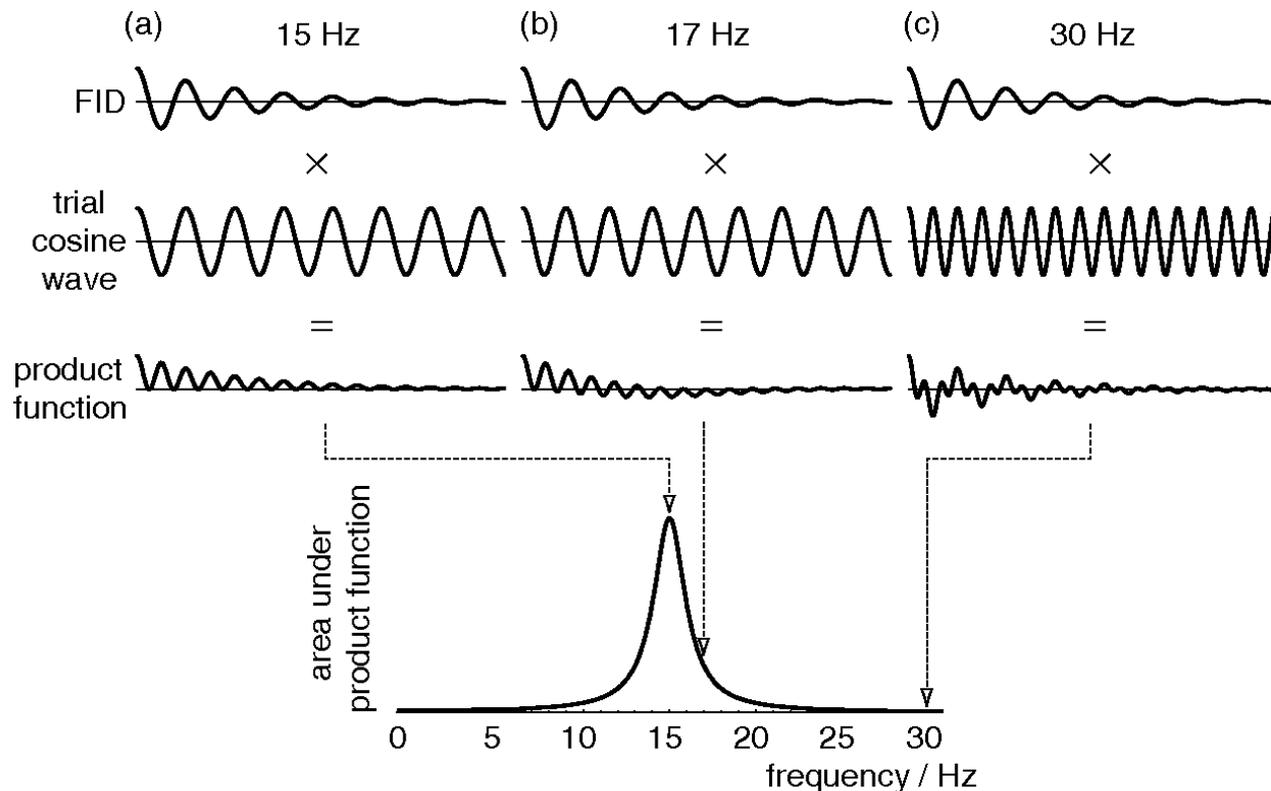
Fourier Transform in NMR

In (a) the product is always positive and the area is shown by the arrow. In (b) the signal is positive for most but less than that of (a) and so the area is less than (a). In (c) the product signal oscillates rapidly and the area under the product signal is zero. The spectrum is plotted as area under the product signal vs the reference cosine wave frequency.

Fourier Transform in NMR
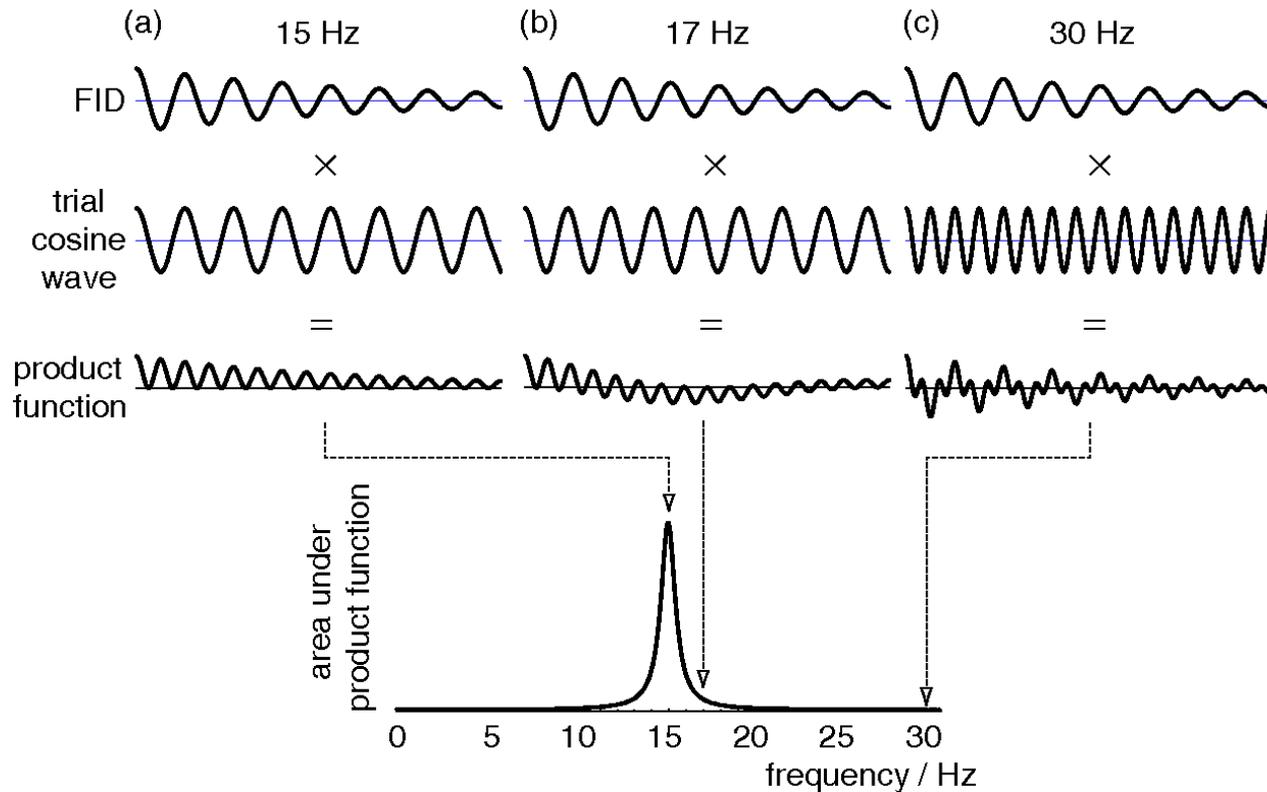
Same analysis as before but the FID has a slower decay. The resulting spectrum is narrower than the one before. These analyses illustrate the FID is at a frequency of 15 Hz.

Fourier Transform in NMR
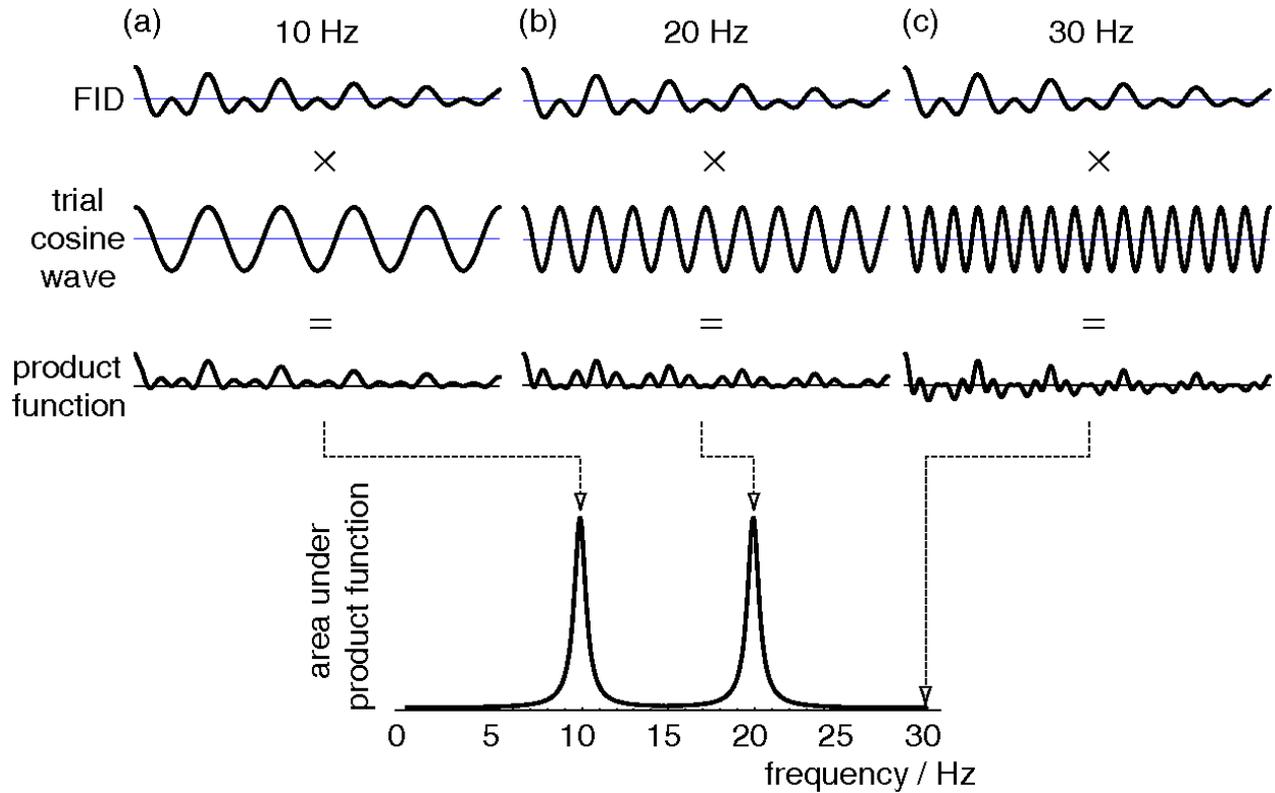
The same analysis can be performed even if the FID arises from more than one resonance.

Fourier Transform in NMR

Thus FT is a procedure in which the intensity at a frequency f Hz is calculated as the area under the product of the FID and a cosine wave at that frequency f. Since there is no signal before time t=0 the FT integral can be written as

$$S(\omega) = \int\limits_{0}^{\infty} S(t)e^{-i\omega t}\,dt$$

$$S(\upsilon) = \int\limits_{0}^{\infty} S(t)e^{-i2\pi\upsilon t}\,dt$$

In any spectrometer the FID is not detected as a continues signal (a) but as a discrete set of N digital points - i^{th} point at time t_i (b) and then the spectrum is computed as

$$S(\upsilon) = \sum\limits_{i=1}^{i=N} S_{FID}(t)e^{-i2\pi\upsilon t_i}$$

(a)

(b)

time
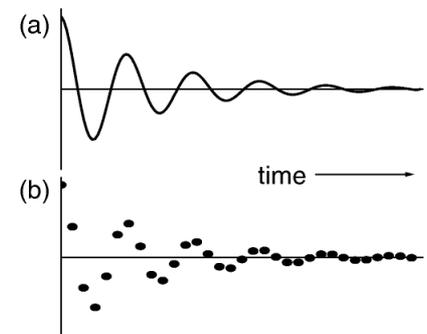
FID

Let's look at the simple 1D – pulse-acquire experiment
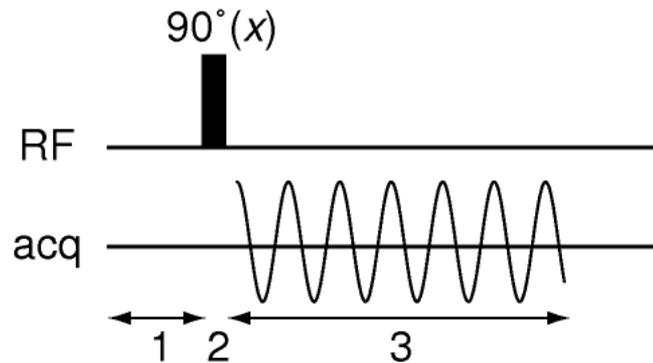
The $90^o(x)$ pulse rotate M_0 to $-y$ axis. The x and y component of the magnetizations are then given as

$$M_x = M_0 \sin \Omega t \qquad M_y = -M_0 \cos \Omega t$$

Instead, if we use $90^o(y)$ pulse then M_0 will go to x-axis and then the x and y components are

$$M_x = M_0 \cos \Omega t \qquad M_y = M_0 \sin \Omega t$$
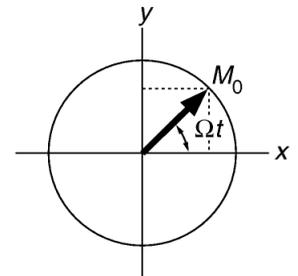
FID

The precession of the magnetization in the xy-plane induces a voltage (signal S) in a coil which will be written as

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

We should also take in to account that the signal decay over time and "model" this decay as an exponential decay

$$S_x = S_0 \cos \Omega t \times e^{-\frac{t}{T_2}} \qquad S_y = S_0 \sin \Omega t \times e^{-\frac{t}{T_2}}$$

T_2 is a time constant characterizing the decay. Combining $S_x(t)$ and $S_y(t)$

$$S(t) = S_x + iS_y = S_0 (\cos \Omega t + i \sin \Omega t) \exp\left(-\frac{t}{T_2} \right)$$

$$S(t) = S_0 \exp(i\Omega t) \exp\left(-\frac{t}{T_2} \right)$$

FID

Thus the time domain signal is represented as a complex function with a decay constant T_2 means that the vector S_0 rotates in the xy plane while its length shrinks as time goes by. The x and y components of this rotating vector is the real and imaginary part of the signal.

$$S(t) = S_0 \exp(i\Omega t)\exp\left(-\frac{t}{T_2}\right)$$

Sometimes it is convenient to define a rate constant R in s^{-1} or Hz unit as

$$R = \frac{1}{T_2}$$

Then the signal can be written as

$$S(t) = S_0 \exp(i\Omega t)\exp(-Rt)$$
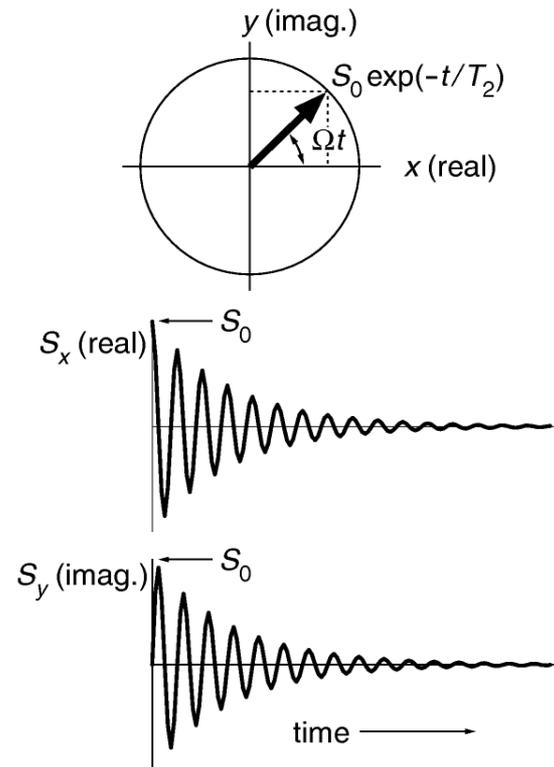
FT of Complex FID

Let us Fourier transform the complex FID S(t).

$$S(\omega) = \int_0^{\infty} S(t)e^{-i\omega t}\,dt = \int_0^{\infty} S_0 \exp(i\Omega t)\exp(-Rt)e^{-i\omega t}\,dt$$

$$S(\omega) = \int_0^{\infty} S_0 e^{[-i(\omega-\Omega)-R]t}\,dt$$

$$= S_0 \left. \frac{e^{[-i(\omega-\Omega)-R]t}}{[-i(\omega-\Omega)-R]} \right|_0^{\infty}$$

$$= -\frac{S_0}{[-i(\omega-\Omega)-R]} = \frac{S_0}{[i(\omega-\Omega)+R]}$$

$$= \frac{S_0}{[i(\omega-\Omega)+R]} \frac{[-i(\omega-\Omega)+R]}{[-i(\omega-\Omega)+R]} = \frac{S_0[-i(\omega-\Omega)+R}{(\omega-\Omega)^2+R^2}$$

FT of Complex FID

S(ω) can be expressed in terms of real and imaginary parts as

$$S(\omega) = \frac{S_0[-i(\omega-\Omega)+R]}{(\omega-\Omega)^2+R^2}$$

$$S(\omega) = \frac{S_0 R}{(\omega-\Omega)^2+R^2} + i\frac{-S_0(\omega-\Omega)}{(\omega-\Omega)^2+R^2}$$

Real Part   Imaginary Part

*The real part is called **absorption mode Lorentzian lineshape** and the imaginary part is called **dispersion mode Lorentzian lineshape**.*

Lineshape

For convenience, let us set $S_0=1$ without loss of generality. Then the real and imaginary part of the spectrum are

$$S(\omega) = \frac{R}{(\omega-\Omega)^2+R^2} + i\frac{-(\omega-\Omega)}{(\omega-\Omega)^2+R^2} = A(\omega)+iD(\omega)$$

Then at $\omega=\Omega$ we have the real part $A(\omega=\Omega)$ is just $1/R$ and the imaginary part $D(\omega=\Omega)$ is zero. The maximum height of the peak in the absorption shape is $1/R$ as in (a) and the dispersion curve goes through zero at that same point in frequency (b).
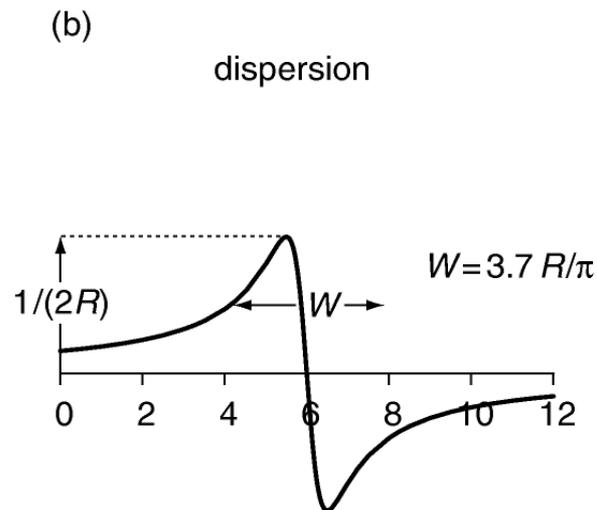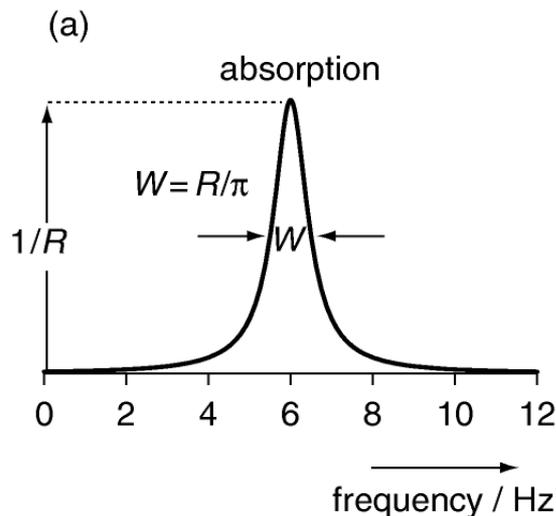
T$_2$ from Lineshape

The rate constant R=1/T$_2$ characterizing the decay of FID can be obtained from the absorption lineshape

$$A(\omega = \Omega) = \frac{R}{(\omega - \Omega)^2 + R^2} = \frac{1}{R}$$

Let us focus on the points when the height is half of maximum

$$A\left(\omega_{1/2}\right) = \frac{R}{(\omega_{1/2} - \Omega)^2 + R^2} = \frac{1}{2R}$$

$$\left(\omega_{1/2} - \Omega\right)^2 = R^2$$

$$\left(\omega_{1/2} - \Omega\right) = \pm R$$

$$\omega_{1/2} \Rightarrow (\Omega + R) \text{ and } (\Omega - R)$$

T$_2$ from Lineshape

Thus the width at the ½ height of the absorption shape is

$$(\Omega + R) - (\Omega - R) = 2R \, \text{rad s}^{-1}$$

Since we have

$$\omega = 2\pi\upsilon$$

the width at half height of the absorption shape is R/π = 1/(πT_2), in units of Hz. One could do similar calculation on the dispersion mode also, but is rarely practiced.
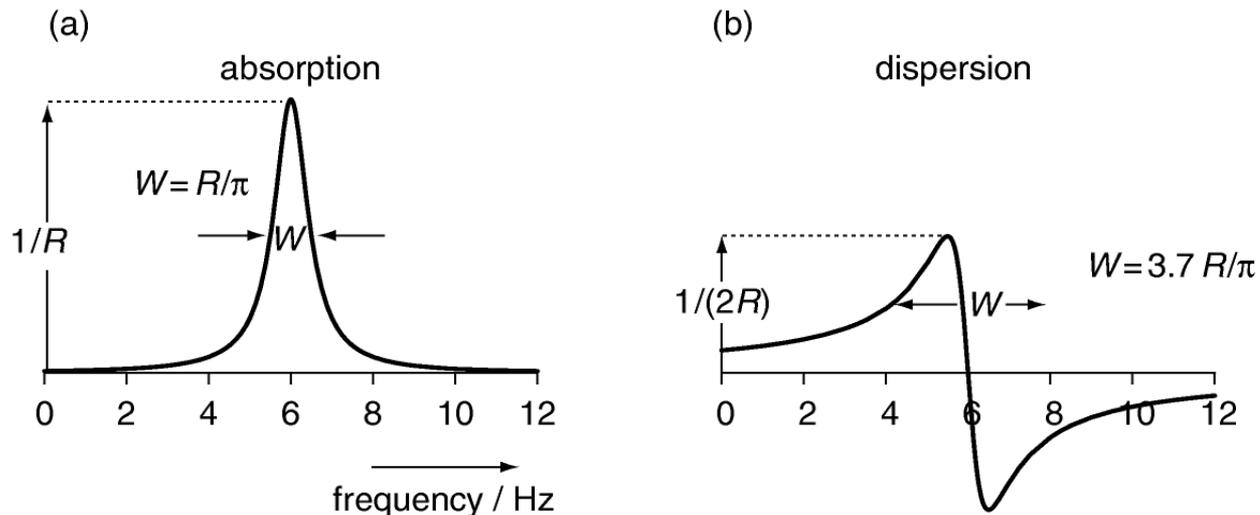
Phase of NMR Spectrum

Whenever we collect a NMR signal and Fourier transform it to look at the spectrum the peak shape may not be exactly either absorption or dispersion. This is a result of the arbitrary initial phase (ϕ) of the signal as detected by the spectrometer. Thus a general signal may be

$$S(t) = S_0 \exp(i\Omega t)\exp(-Rt)\exp(i\phi)$$

and the FT of this signal would be then

$$S(\omega) = S_0[A(\omega) + iD(\omega)]\exp(i\phi)$$

$$S(\omega) = S_0[A(\omega) + iD(\omega)](\cos\phi + i\sin\phi)$$

$$S(\omega) = S_0[\cos\phi A(\omega) - \sin\phi D(\omega)] + iS_0[\cos\phi D(\omega) - \sin\phi A(\omega)]$$

Both real part and imaginary part have absorption and dispersion line shape characteristics.

Phase of NMR Spectrum

The time domain signal and the real and imaginary part are shown in figure for various initial phase. In (a) the initial phase is zero and the spectrum shape is normal. In (b) the phase is $\pi/4$ and the lineshapes are twisted. In (c) the phase is $\pi/2$ and the real and imaginary shapes are exchange with respect to (a) and in (d) the phase is π and the linshapes are just inversion of that in (a).

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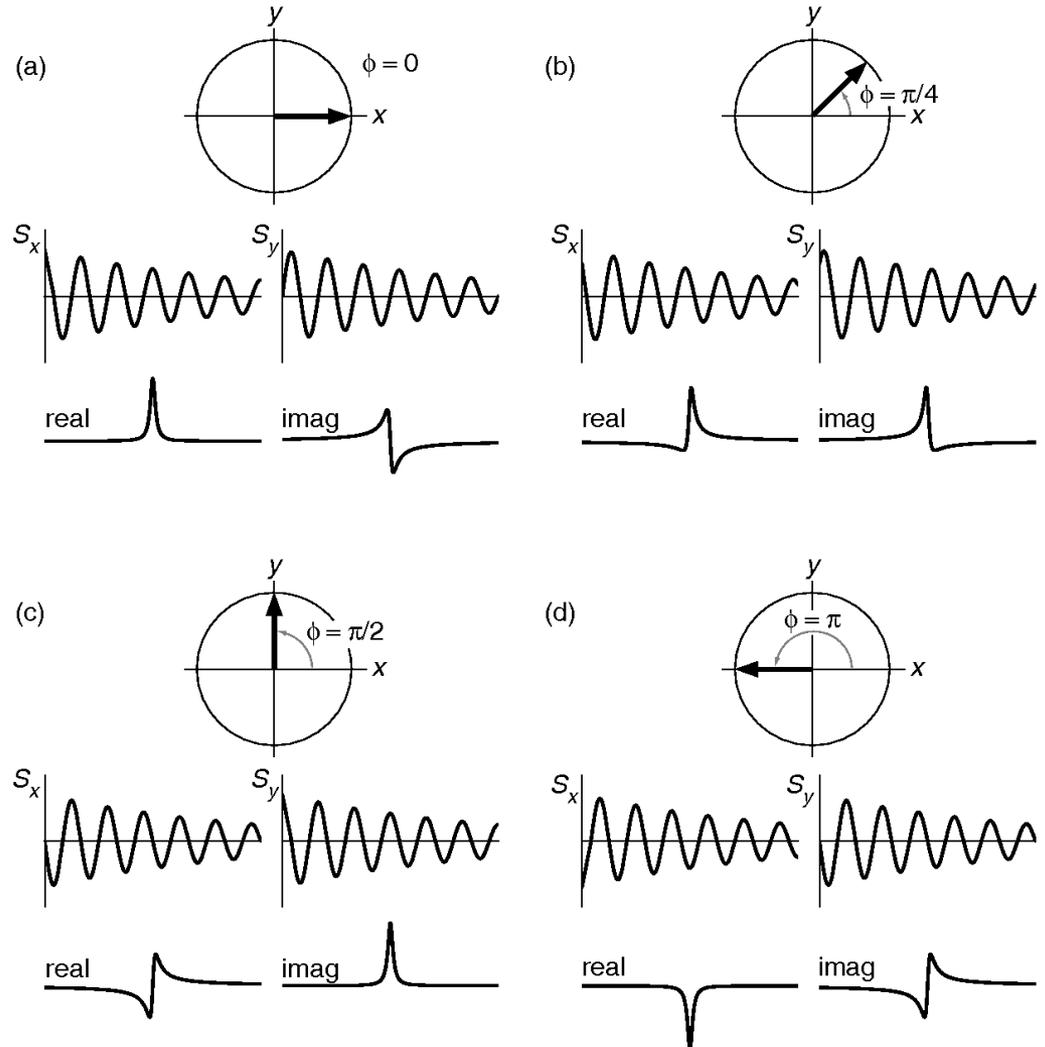
Phasing NMR Spectrum

Usually the real part of the FT data is presented as spectrum and it is phased in absorption mode lineshape. This process is called phasing the nMR spectrum and involves applying a correction factor. There are two correction factors (1) a constant phase correction for all resonance line and (2) a frequency dependent phase correction that linearly varies with respect to the resonance frequency.

Phasing NMR Spectrum

*Let us look at the constant phase correction factor first. This is also called **zero order** or **frequency independent phase correction**. Suppose the FT data is given as*

$$S(\omega) = S_0[A(\omega) + iD(\omega)]\exp(i\phi)$$

We can then multiply this by a factor exp(iϕ_{corr}) so that

$$S(\omega) = S_0[A(\omega) + iD(\omega)]\exp(i\phi)\exp(i\phi_{corr})$$

$$S(\omega) = S_0[A(\omega) + iD(\omega)]\exp(i\phi + \phi_{corr})$$

If we choose ϕ_{corr}=-ϕ then the phase factor drops out and the real part will give the desired absorption lineshape. The correction phase is obtained by trial and error method.

Zero Order Phase Correction

The phase correction is either done manually or automatically using the NMR software of the spectrometer. In the example shown ϕ_{corr}=-75° is the appropriate phase factor for correction.

un-phased

$\phi_{corr} = -60°$

$\phi_{corr} = -70°$

$\phi_{corr} = -75°$

$\phi_{corr} = -80°$

$\phi_{corr} = -90°$

Frequency Dependent Phase Correction

Sometimes all the magnetization corresponding to different resonances in a spectrum may not experience the same flip angle and then they will end up at different positions in the xy plane after a nominal 90° pulse.

Frequency Dependent Phase Correction

(a)

offset frequency

(b)

slope = k

$\phi_{corr} = k\,\Omega$

offset frequency

(c)
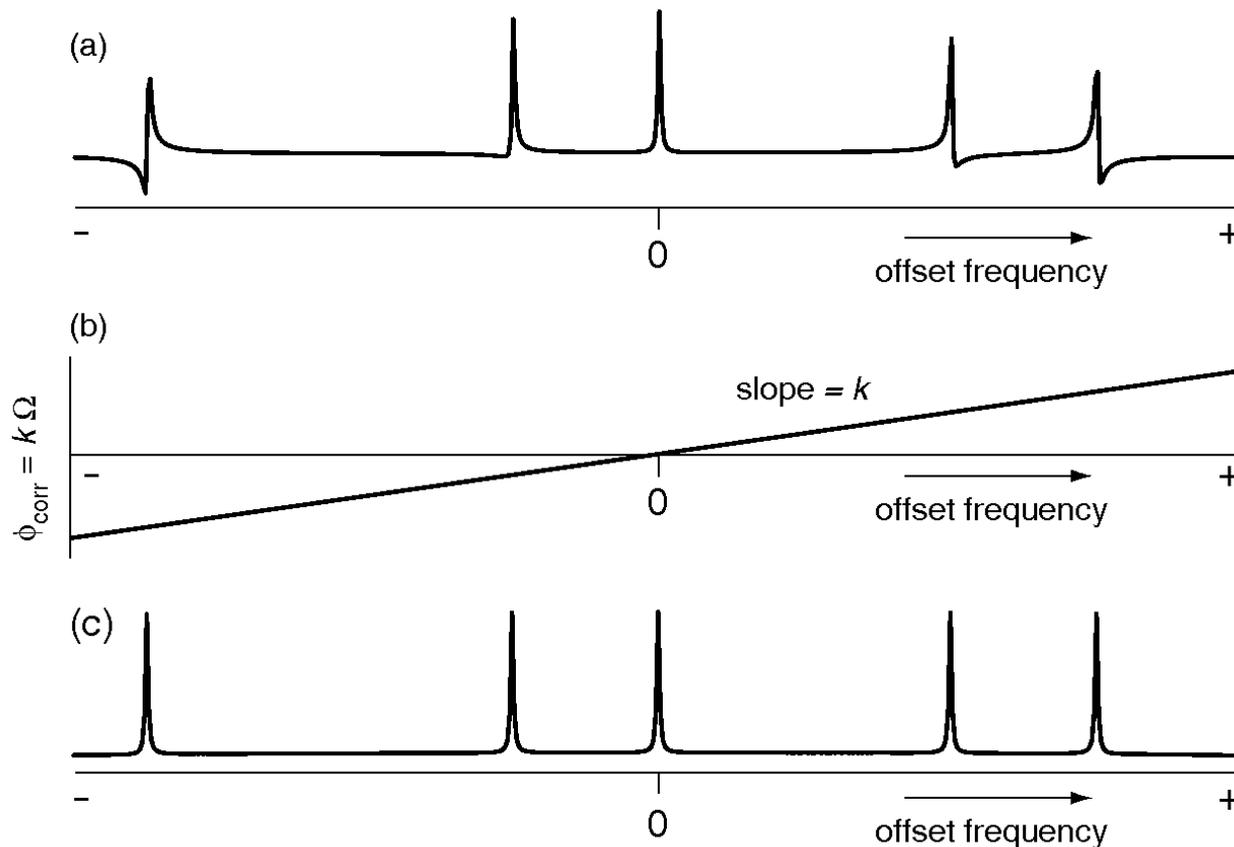
offset frequency

The phase correction is not the same for all resonance lines. The phase correction is proportional to the offset frequency of the resonance. (a) uncorrected spectrum, (b) the phase correction function and (c) the phase corrected spectrum.

Hard Pulse vs Soft Pulse

We com back to this figure where non uniform rotation is taking place with reference to offsets. This happens because the applied pulse does not have the same effect on the spins at different offsets.
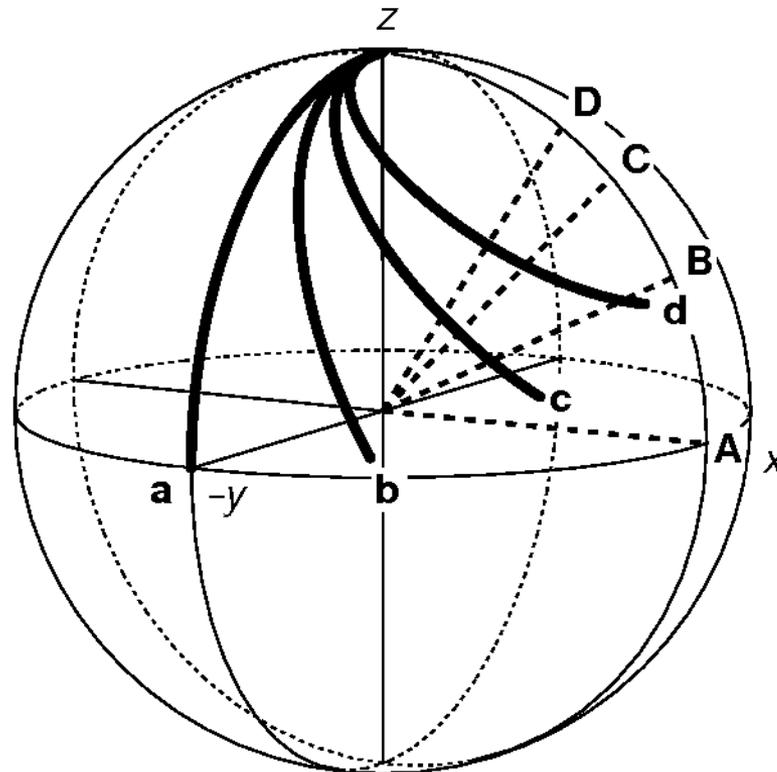
Hard Pulse vs Soft Pulse

We can simply represent a RF pulse as a sinusoidal signal that is gated off except for a time t_p.
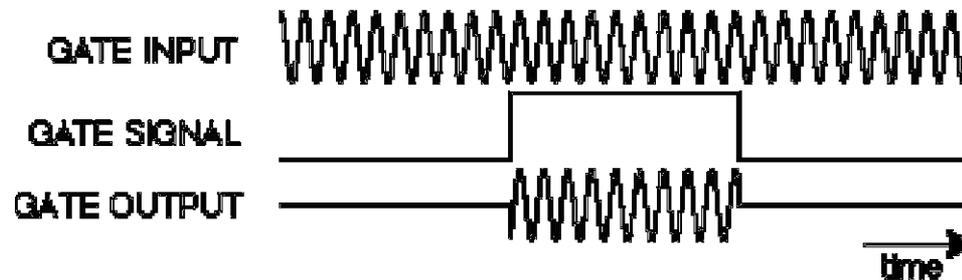
Without loss of generality we can say the pulse is a cosine oscillation at a frequency ω_0. Then the pulse is

$$f(t) = \cos(\omega_o t_p)$$

And to understand the frequency content of this pulse we can Fourier transform this function.

Hard Pulse vs Soft Pulse

The FT of the pulse is

$$F(\omega) = \int_{-t_p/2}^{t_p/2} \cos(\omega_o t) e^{i\omega t}\, dt \qquad\qquad F(\omega) = \frac{1}{2} \int_{-t_p/2}^{t_p/2} \left(e^{i\omega_0 t} + e^{-i\omega_0 t} \right) e^{i\omega t}\, dt$$

$$F(\omega) = \frac{1}{2} \frac{\left(e^{i(\omega_0-\omega)t} \right)}{i(\omega_0-\omega)t} \Bigg|_{-t_p/2}^{t_p/2} + \frac{1}{2} \frac{\left(e^{-i(\omega_0+\omega)t} \right)}{-i(\omega_0+\omega)t} \Bigg|_{-t_p/2}^{t_p/2}$$

$$F(\omega) = \frac{\sin\left((\omega_0-\omega)\frac{t_p}{2} \right)}{(\omega_0-\omega)} + \frac{\sin\left((\omega_0+\omega)\frac{t_p}{2} \right)}{(\omega_0+\omega)}$$

Hard Pulse vs Soft Pulse

Let's just focus on one part of F(ω).

$$F(\omega) = \frac{\sin\left((\omega_0 - \omega)\frac{t_p}{2}\right)}{(\omega_0 - \omega)} = \frac{t_p}{2} \frac{\sin\left((\omega_0 - \omega)\frac{t_p}{2}\right)}{(\omega_0 - \omega)\frac{t_p}{2}}$$

*This function is known **sinc** function.*
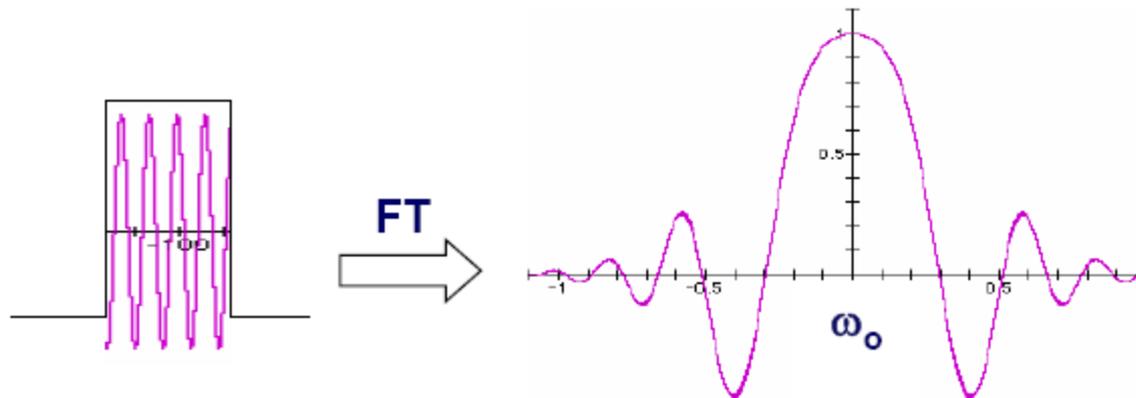
Hard Pulse vs Soft Pulse
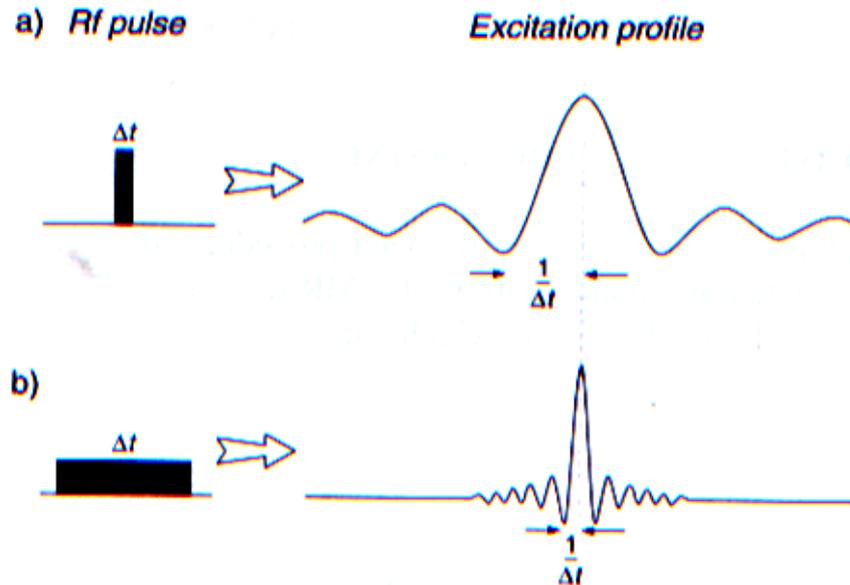
(a) A strong short duration RF pulse has a wide band frequency profile (hard pulse), whereas (b) a weak long duration pulse has a narrow band frequency profile (soft pulse).

Sensitivity Enhancement Signal Averaging

The acquired NMR spectrum always has noise in addition to the signal. To reduce the noise we repeat the experiment several times and add the signal. The noise builds up only as $N^{1/2}$, whereas the signal increase as N. The net signal to noise gain by doing N signal average is then $N^{1/2}$.
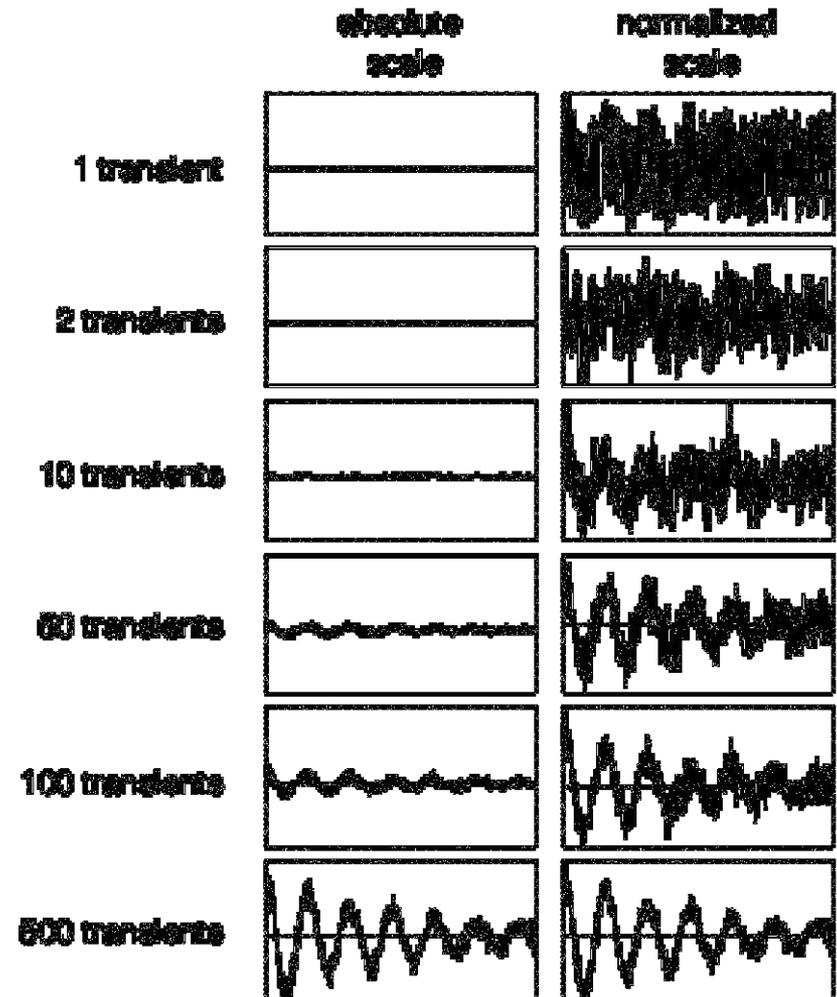
Sensitivity Enhancement

Even the signal averaged FID (an so the spectrum) contain noise albeit reduced. The FID decays over time but noise goes on forever. As we collect data for long time (long acquisition time) the signal has died down but not the noise. Thus limiting acquisition time can improve the quality of the NMR spectrum in terms of signal to noise.
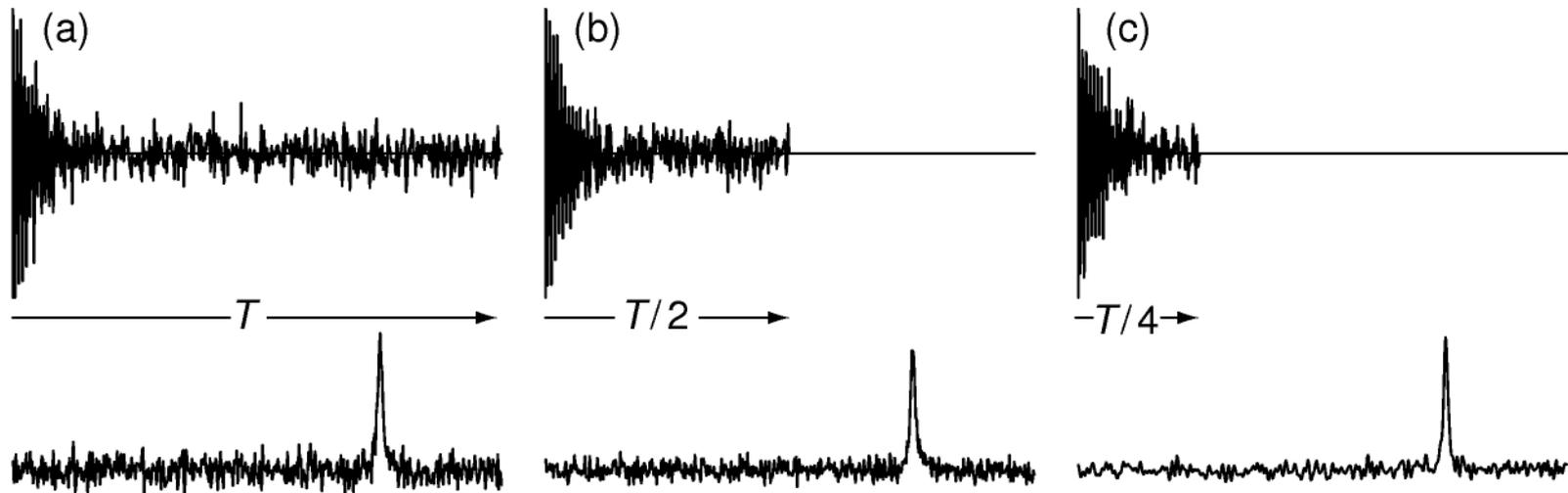
In (a) acquisition time is T, (b) T/2, and in (C) T/4 and the S/N improves as the acquisition time is shortened.

Truncation

*The previous example was unique such that reducing the acquisition time did not distort the signal but improved S/N. If the signal is strong then reducing acquisition time will truncate the signal and cause wiggles (**sinc wiggles**) in the spectrum (Figure below).*
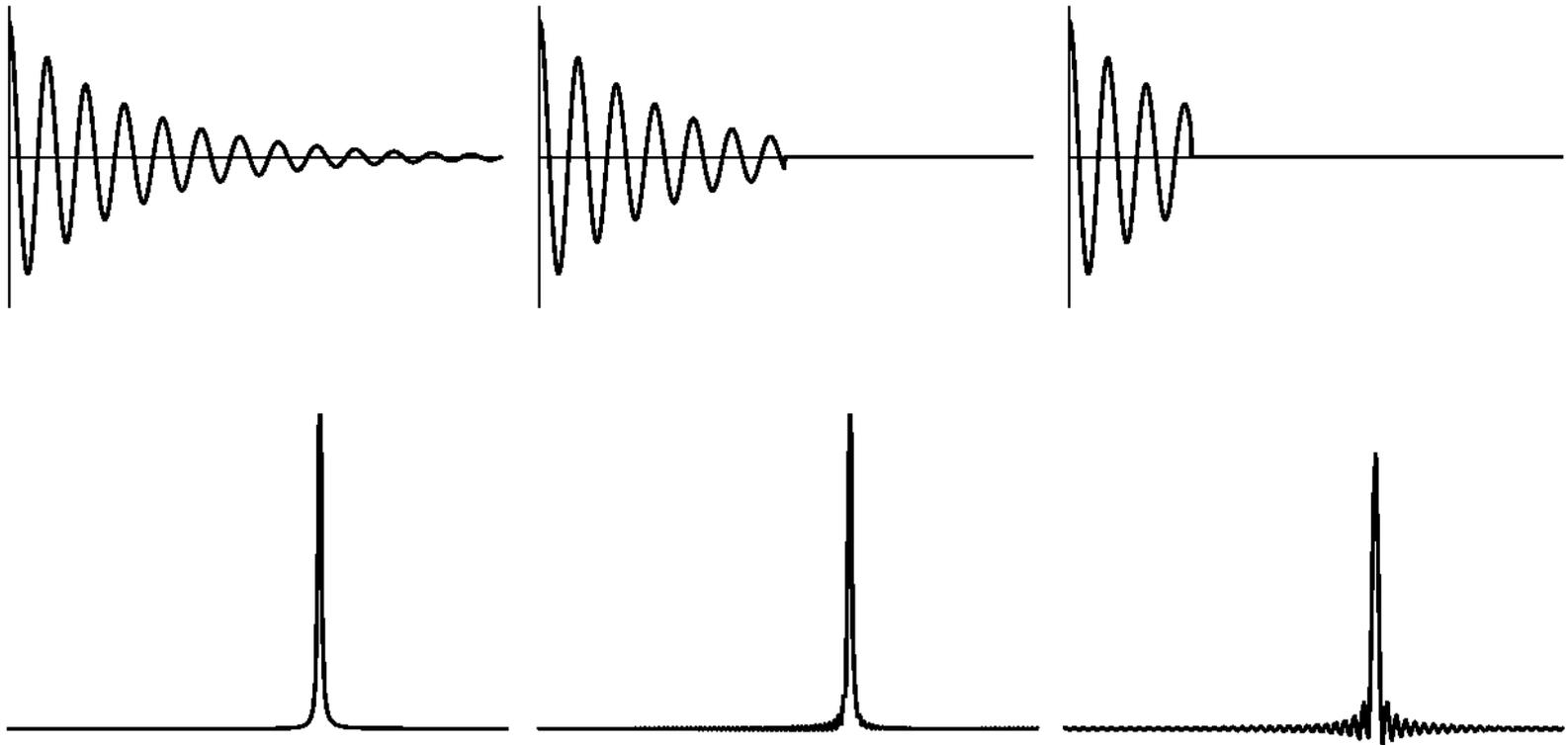
Sensitivity Enhancement By Weighting

*In general, a spectrum may contain strong signal as well as very weak signal. Thus limiting acquisition time is not the best way to enhance sensitivity. Instead one can multiply the time domain signal by an exponentially decaying function. This process is called applying a **window function** or **apodization**.*

$$W_{LB}(t) = \exp(-R_{LB}t)$$
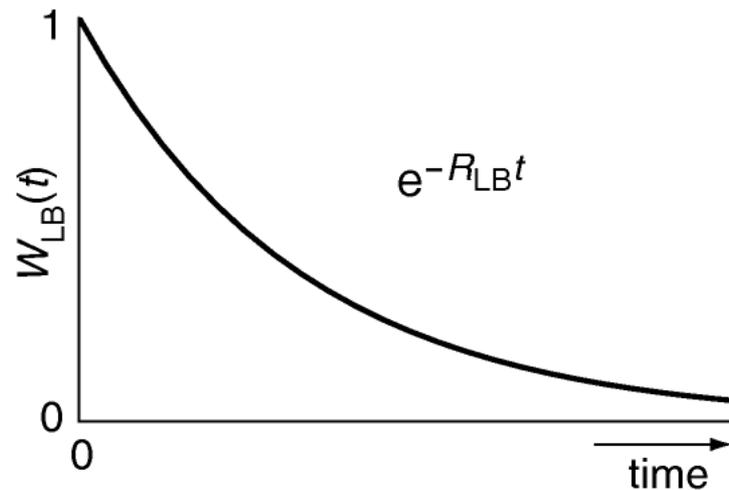
Sensitivity Enhancement By Weighting

The application of the window function will broaden the lines while improving S/N.

(a) Original FID. (b) and (c) are two weighting function. (d) and (e) are the product of the original FID with the weighting functions in (b) and (c) respectively. The spectrum in (f), (g), and (h) are Ft of (a), (d), and (e) respectively. In these the linewidth increases as the weighting function becomes rapidly decaying. In (i), (j), and (k) the peak height is plotted at the same level to show the sensitivity enhancement.
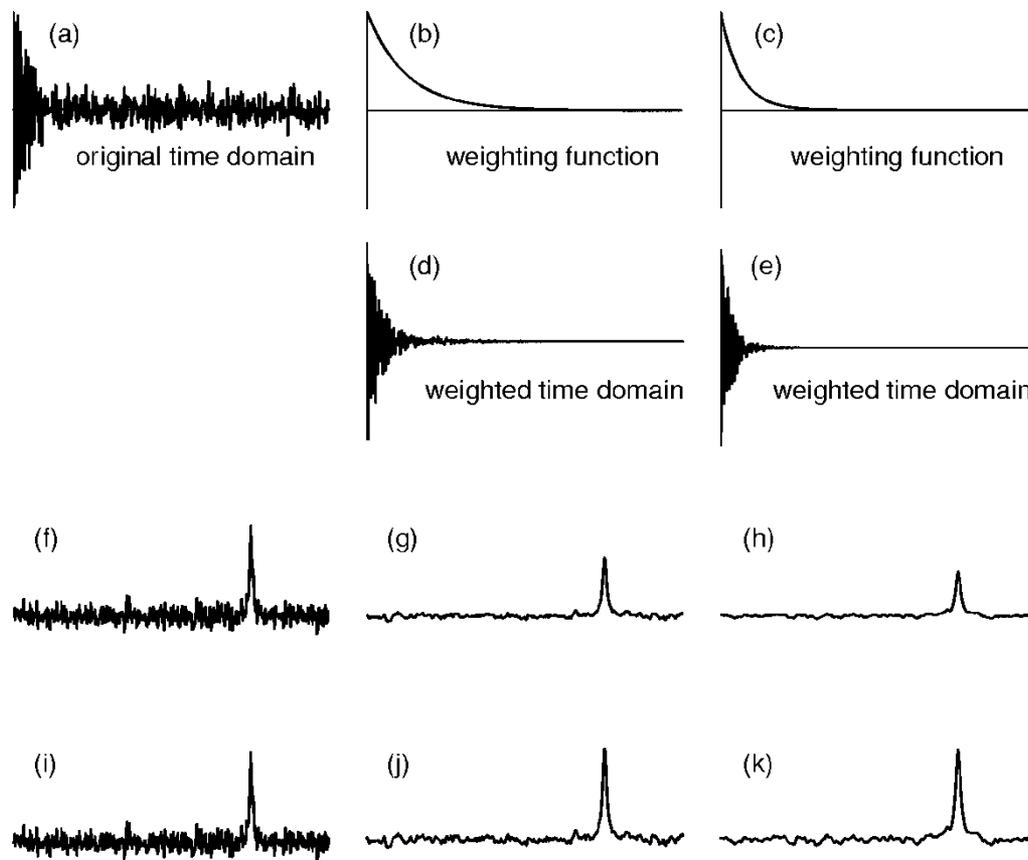
Matched Filter

The window function that gives the greatest increase in S/N is known as **matched filer**. *Suppose a exponentially decaying weighting function is applied, then the signal is*

$$S(t) = \exp(-R_{LB}t)S_0 \exp(i\Omega t)\exp(-Rt)$$

$$S(t) = S_0 \exp(i\Omega t)\exp(-(R + R_{LB})t)$$

The effect of weighting is to increase the decay constant to $R+R_{LB}$. If we apply a filter such that the extra line broadening equal to the natural linewidth ($R=R_{LB}$) then the S/N gain is optimum and we can say a matched filter has been applied. In any spectrum, however, one decay constant may not characterize the linewidths of every resonance lines and also the optimum value may not be suitable for required resolution to observe fine splitings. So a compromise value is to be chosen.

Other Weighting Functions

Exponentially decaying weighting function is the one most of ten used. But there are other useful functions that are also valuable in NMR applications.

(1) Resolution Enhancement Function: Instead of applying a decaying function one can apply a exponentially growing function that will reduce the linewidth at the expense of increased noise.

$$W_{RE}(t) = \exp(R_{RE}t) \quad R_{RE} > 0$$
$$S(t) = S_0 \exp(i\Omega t)\exp(-R + R_{RE})t)$$
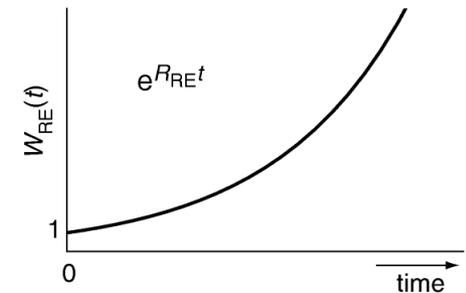
(2) Gaussian Function: To reduce the increase in noise from above apodization another function is applied that is decaying, namely a Gaussian function.

$$W_G(t) = \exp(-\alpha t^2)$$
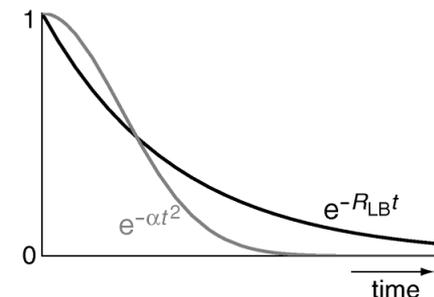
Lorentz-Gauss Transformation

Applying the two window functions together minimizes the noise increase and decreases the line width and the effect is often termed as Lorentz-Gauss transformation as the resulting line shape is Gaussian than Lorentzian.
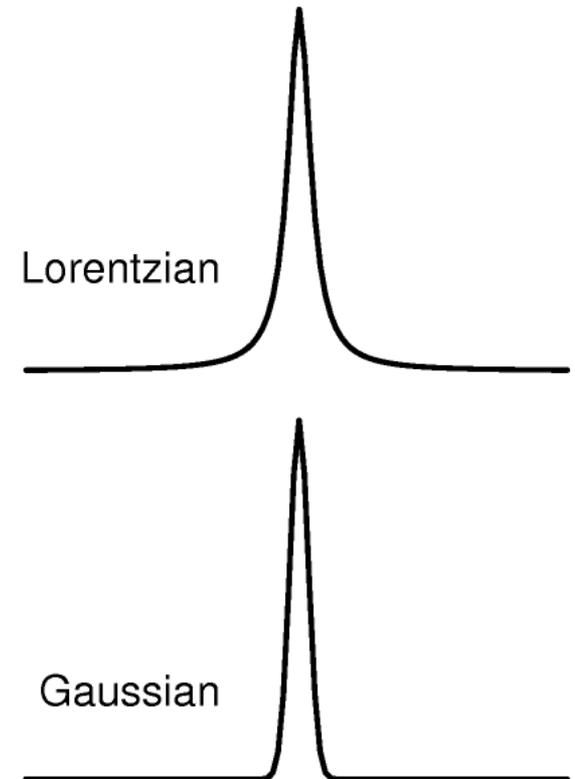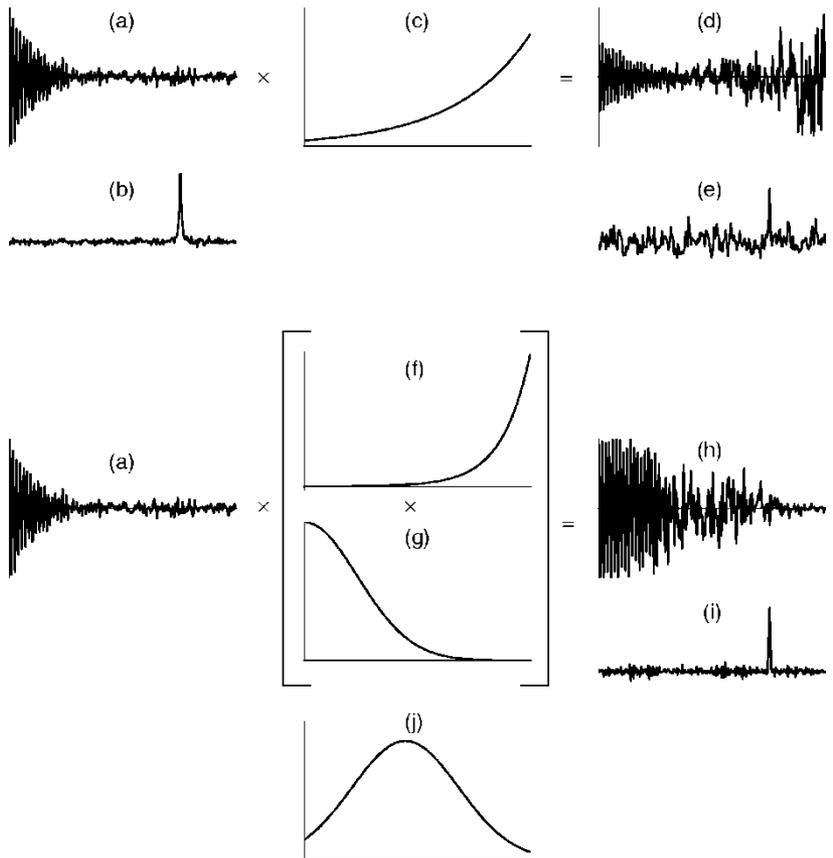
Sine Bell Function

*There are two other useful window functions known as **sine bell and sine bell squared** functions. When the phase φ=0 these resemble the Lorentz-Gauss transform function.*

$$W_{SB}(t) = \sin\left(\frac{(\pi - \phi)t}{t_{acq}} + \phi\right) \qquad W_{SBS}(t) = \sin^2\left(\frac{(\pi - \phi)t}{t_{acq}} + \phi\right)$$
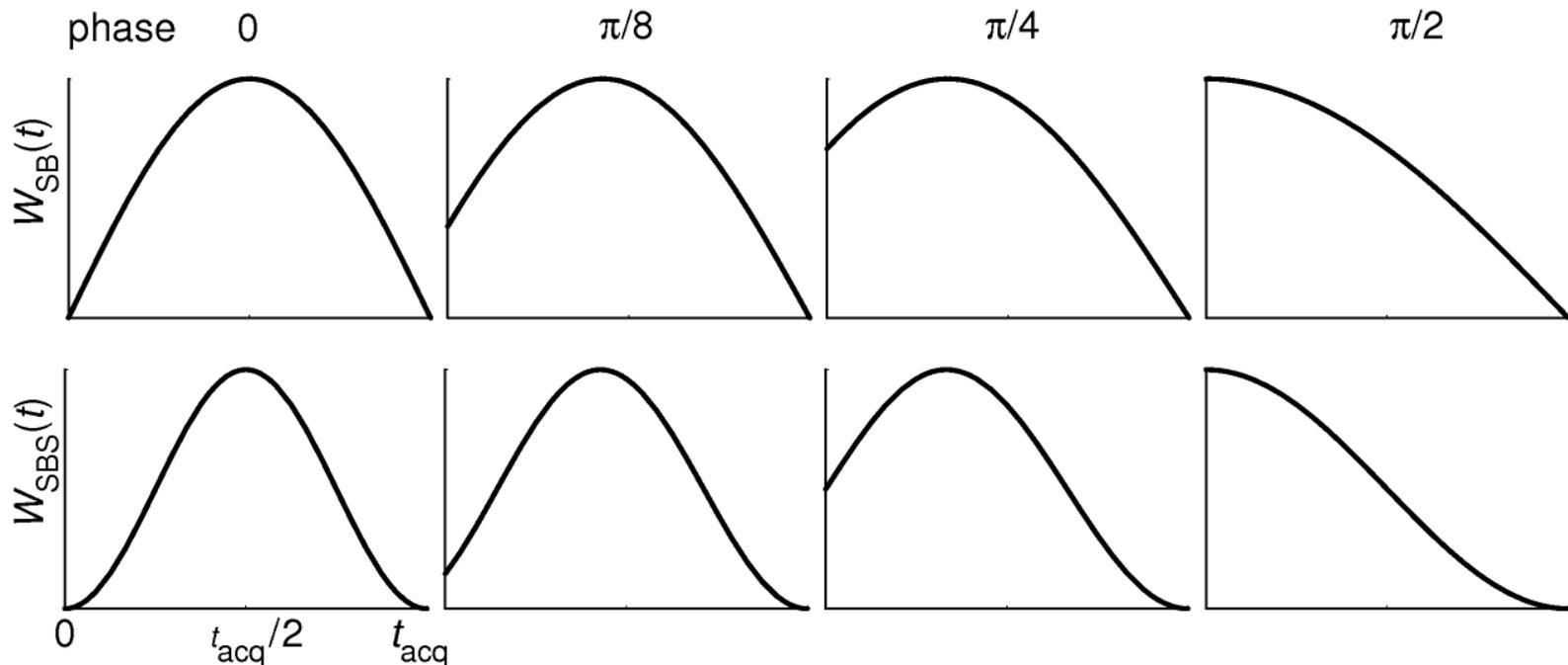
Zero Filling

We noted that the FID is actually collected as a discrete set of points (N_f) equally spaced in time. The FT of such a digital FID is a spectrum that is also a set of points (N_s) that equally spaced in frequency space. Usually the number of points in the spectrum is equal to the number of points in time domain FID(see (a) in Figure). But we can append an equal number of zeros to the FID and then the spectrum will have twice the number of points (see (b) in Figure) and the line will appear smooth. The smoothness improves when another set of zeros are added (see (c) in Figure). Zero filling is an interpolation and gives smoother line but does not increase resolution.
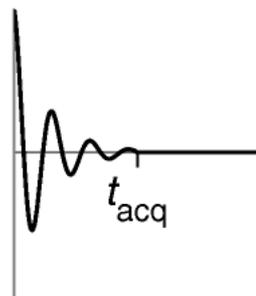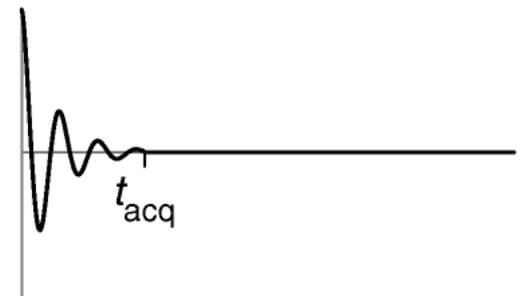
Zero Filling – Digital Resolution

If acquisition time is AQ and the number of points in the FID is N_f, that in spectrum N_s, and the spectral width is sw then

$$AQ = \frac{N_f}{2sw}$$

And the digital resolution (DR) in the spectrum is given by

$$DR = \frac{sw}{N_s} \ \text{Hz/pt}$$

Truncation –Impact on Resolution

To see fine splitting in NMR Spectrum the FID should be acquired at least for a time equal to reciprocal of the splitting in Hz. In the figure on the right, there are two couplings one 6 Hz and another 2Hz. As the acquisition time is increased the lines are resolved.
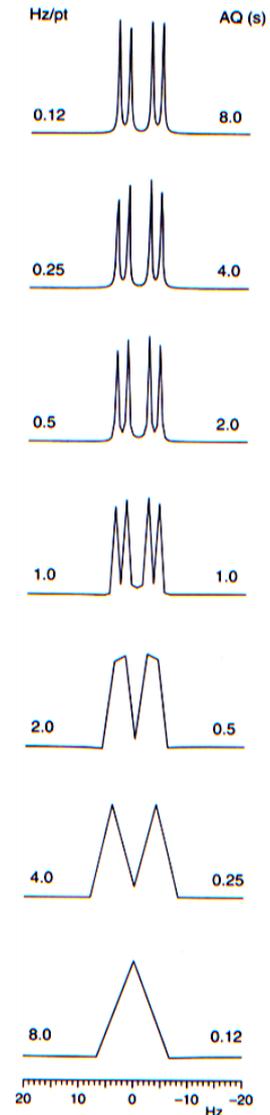
Zero Filling
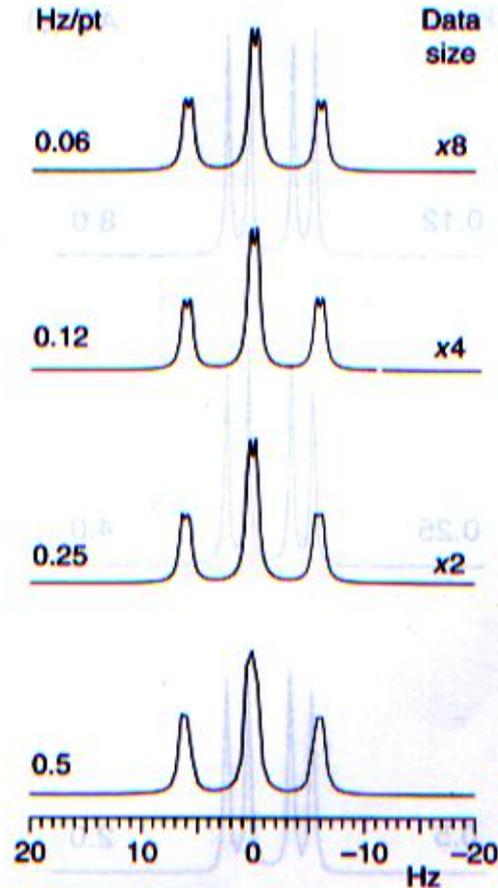
If the acquisition time was long enough, zero filling can increase digital resolution and can be used to enhance fine structure by improving lineshape without adding noise.

Linear Prediction

Zero filling does not add information. It is only an interpolation method. Data extensions or predictions that add points to extend the FID is a procedure often accomplished by linear prediction algorithms. Based on the existing points in the FID additional points are predicted before FT.

$$d_n = a_1 d_{n-1} + a_2 d_{n-2} + a_3 d_{n-3} + \dots$$

(a) Complete FID and its FT, (b) truncated FID and the FID showing sinc wiggles, (C) FID in (b) but multiplied by an exponential window and zero filling and its FT, and (d) FID in (b) has been extended by linear prediction and its spectrum up on FT
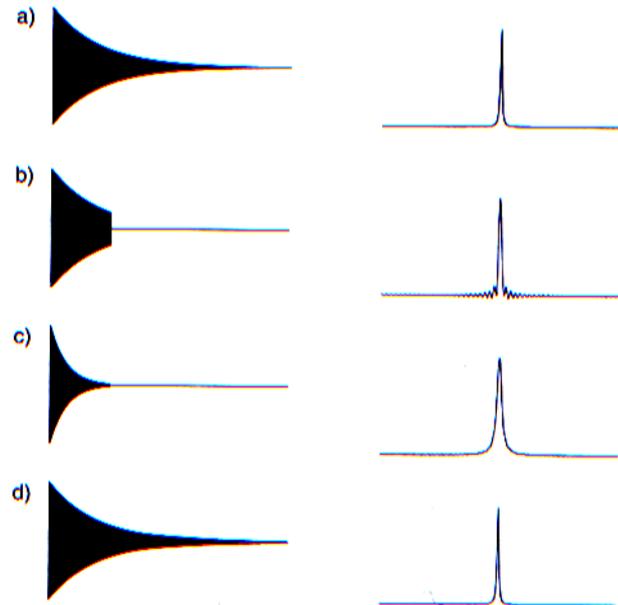
Further Reading

Fourier transform *is an interesting mathematical tool. There are many properties of Fourier transform that are used in NMR and have not been discussed here. We skimmed through the most often used features in routine NMR experiments. One should read a book on Fourier transform to appreciate the power of this method.*
The Fourier Transform and its Applications
R.N. Bracewell (1978), McGraw-Hill