Fourier Transformation

\[ S(\omega) = \int_{-\infty}^{\infty} S(t) \exp(-i\omega t) \, dt = \int_{-\infty}^{\infty} S(t) (\cos(\omega t) - i \sin(\omega t)) \, dt \]

\[ S(k/(2dtN)) = \sum_{J=0}^{N-1} S(jdt) \exp(-i2\pi j (k/2dtN)) \]
Visualization of FT

\[ M_y(t) = S(k-1) + S(k) + S(k+1) \]

Frequency (\( \omega \))
Lorenzian Lines

$$S(\omega) = \frac{(M_0 T_2)}{(1 + T_2^2(\omega_0 - \omega)^2)}$$

Signal is maximum at $\omega_0$

At $\frac{1}{2}$ height, $T_2^2(\omega_0 - \omega)^2 = 1$

Implies $\Delta\omega_{1/2} = 2/T_2, \Delta\nu_{1/2} = 1/(\pi T_2)$
Digitizing Data and Setting Sweep Widths (sw)

Data points define frequency well

Nyquist frequency – minimum points

Ambiguities arise at higher frequencies

Note: pattern of points is the same

real spectrum

observed spectrum
Phase Cycling Reduces Artifacts

One artifact is a glitch at zero frequency (middle of spectrum). This can come from imbalance of quadrature channels. Adding scans with $180^\circ$ phase shift of pulse and receiver eliminates

Another artifact is a quadrature image. Cycling x and y channels Along with a $90^\circ$ phase shift of the pulses eliminates this (cyclops)
Zero Order Phase Correction

Phase of reference frequency is arbitrary:
My is not pure cos and Mx is not pure sin

Observe:

In general:
\[ My = Mr(\cos \phi) + Mi(\sin \phi) \]
\[ Mx = Mi(\cos \phi) - Mr(\sin \phi) \]

To recover:
\[ Mr = My(\cos \phi) - Mx(\sin \phi) \]

Done interactively to get:
First Order Phase Correction

Phi ($\phi$) can be frequency dependent: $\phi_0 + \nu \phi_1$

Actual start of collection: phase is not zero and error is greater for higher frequencies
Signal Averaging

NMR is not a high sensitivity technique: signal averaging improves the signal to noise ratio

$\text{S/N defined as: } 2.5 \times \text{S/pp}$

On averaging signal adds as number of scans, noise adds as the root of the number of scans

$\text{S/N } \propto \frac{N}{\sqrt{N}} = N^{1/2}$

$4 \times \text{scans} = 2 \times \text{S/N}$
Best Single Scan Parameters

how rapidly should we recycle?
what pulse $\phi$ should we use?

opposing factors on recycle rate:

1) recovery of magnetization:
   \[ M_z(t) = M_0 (1 - e^{-\frac{T}{T_1}}) \]
   $\Rightarrow$ wait $3 \times T_1$

2) more scans/unit time:
   \[ S/N \propto N^{1/2} \]

Compromise: use $\beta < 90^\circ$

Ernst:
\[ \cos \beta_{opt} = \exp(-\frac{T}{T_1}) \]
Example

Small molecule. $T_2$ limited by shimming: $T_2^* \approx 0.3$ s (1 Hz)

$T_1 = 2.0$ s collect. 0.6 s to optimize resolution

$\cos \beta_{opt} \approx \exp\left(-\frac{0.6}{2}\right) \Rightarrow \beta = 42^\circ$

Cost: may not have unit intensity for all resonances if $T_1$s differ.

Waiting $3 \times T_1$ for recovery, and using 90°

10 scans/min @ unit intensity = $\sqrt{10} \approx 3.1$

vs. 100 scans/min @ .67 intensity = 10 \times .67 = 6.7
How Long Should Acquisition Be?

Opposing factors:

1) long acquisition $\Rightarrow$ high resolution

2) long acquisition $\Rightarrow$ low S/N

Compromise $T \approx (1-2)T_2$
Some Other Processing Details

Matched Filters - Maximize $S/N$

$T_2^*$

$\uparrow$

high $S/N$

$\rightarrow t$

$\rightarrow T_2^*$

$\uparrow$

low $S/N$.

$\uparrow$

high amp

low amp

Often Used:

sinx/hell (resolution enhanced)

Kaiser (no truncation)

$\exp(-\frac{t}{T_2^*})$

$\rightarrow 1 \leftarrow \phi$

No

$\downarrow$

Trunc.
Alternate Methods of Signal Processing

What is Wrong with FT?

1) no assumption about max # lines
2) any shape of line assumed.
3) FFT assumes uniform distribution of points.

Alternatives

1) Maximum Entropy
2) Linear Prediction Z transform
3) Linear Prediction singular value decomp.

Cautions - Noise may be in peak positions too.