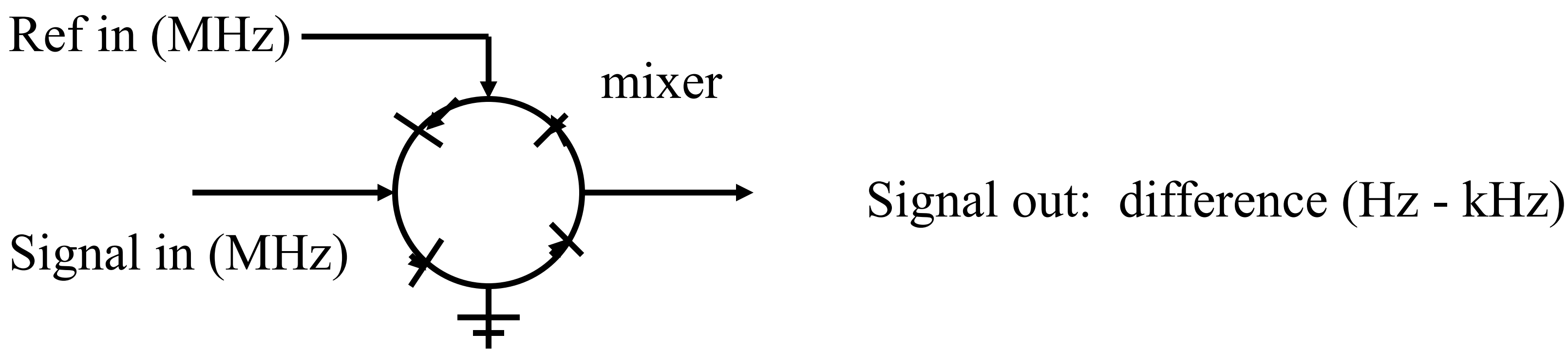
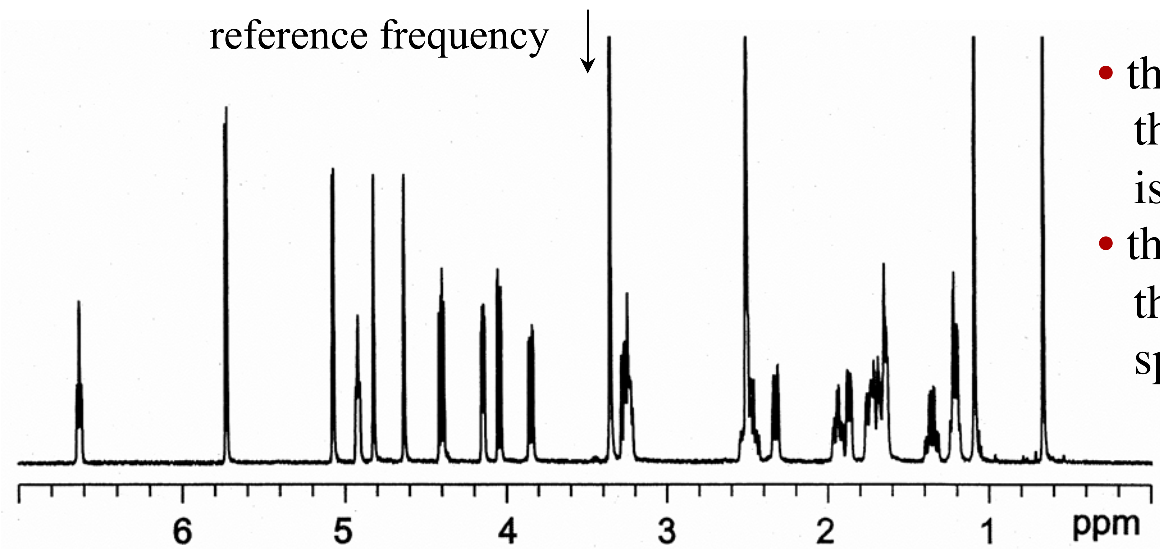
DATA ACQUISITION

Signal Manipulation

- time domain NMR signal in MHz range is converted to kHz (audio) range by mixing with the reference ("**carrier**") frequency



- thus, the frequencies that we observe are relative to a reference (and to one another)



- the reference or carrier frequency is the frequency about which our pulse is applied
- this corresponds (almost always) to the center of our frequency domain spectrum

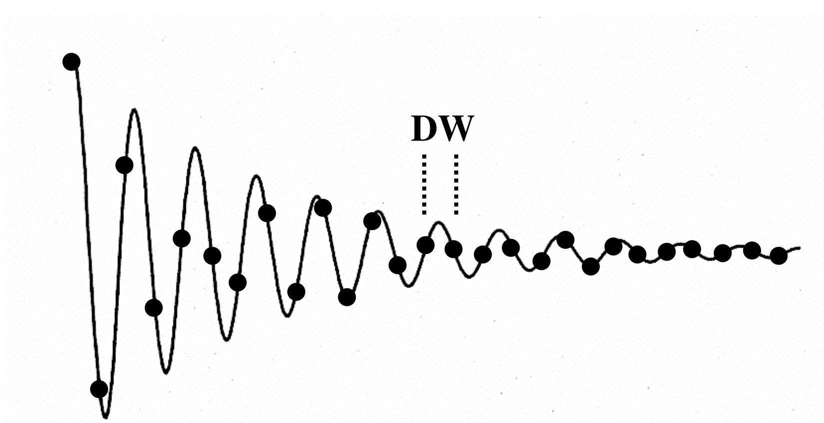
ACQUISITION PARAMETERS (TIME DOMAIN)

- the **spectral width** (in the frequency domain) or **spectral window** (SW) is determined by the rate of digitization of the time domain signal
  - for ^1H, a typical SW might be 10 to 14 ppm (i.e., at 400 MHz, 4000 - 5600 Hz)

12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 (ppm)

- the SW tells us the largest frequency *difference* that we can determine
- the **Nyquist Theorem** states that in order for a frequency difference of SW to be measured, the time domain data (FID) has to be sampled at a frequency not less than 2*SW
  - this frequency is called the **Nyquist frequency**

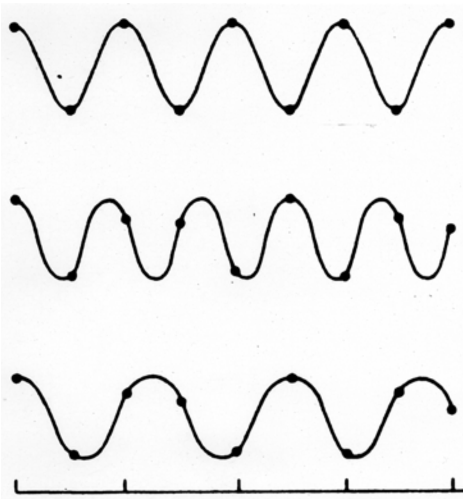
- the **dwell time** (DW) is the time between sampled points and determines SW



$$DW = \frac{1}{2 \times SW}$$

ACQUISITION PARAMETERS (TIME DOMAIN)

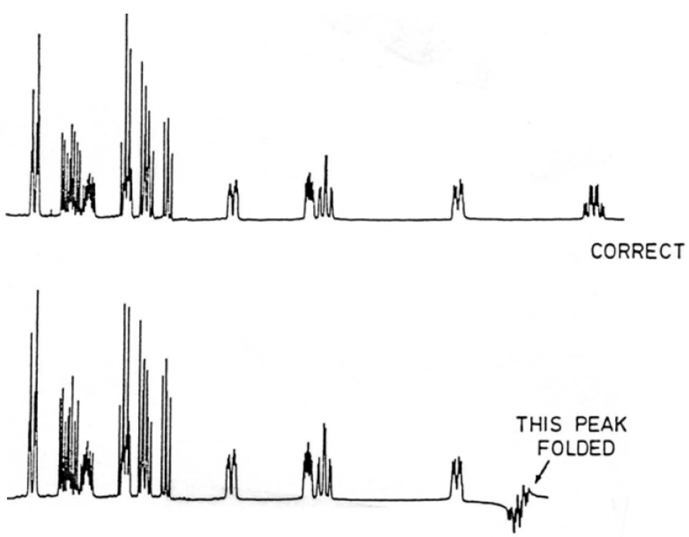
- if the sampling frequency is less than the Nyquist frequency (if DW > 1/(2xSW)), then frequencies greater than or less than the reference frequency cannot be discriminated from one another



ν

$\nu + \Delta\nu$

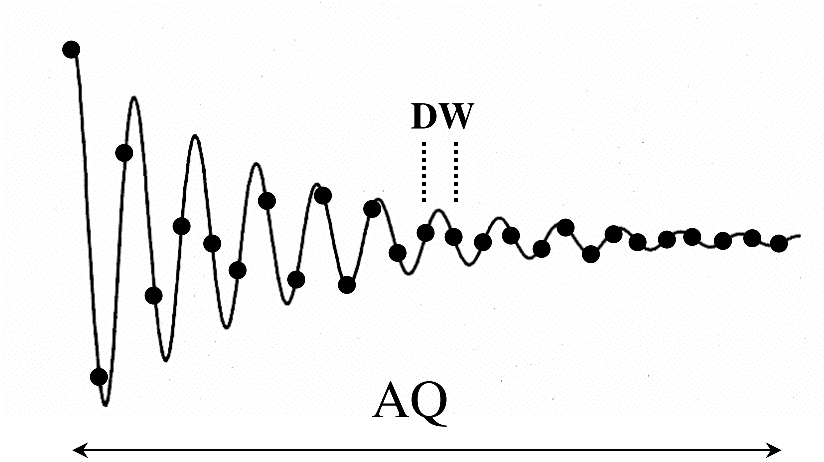
$\nu - \Delta\nu$



- at a frequency ν, sampling occurs at 1/(2xSW)
- if the same sampling frequency is used to digitize two additional signals, one at $\nu + \Delta\nu$ and one at $\nu - \Delta\nu$, we cannot discriminate between the faster and the slower signal
  - note that for the signals at $\nu + \Delta\nu$ and at $\nu - \Delta\nu$, at each point sampled, the signal amplitudes are identical
- for signals outside of SW (for signals digitized at a frequency less than the Nyquist frequency), the peaks corresponding to the signals will be folded in the spectrum
  - folded peaks are often characterized by aberrant amplitude and phase characteristics

ACQUISITION PARAMETERS (TIME DOMAIN)

- the total **number of points digitized** (NP) multiplied by the dwell time (DW) represents the total time that the FID is sampled and is called the **acquisition time** (AQ)



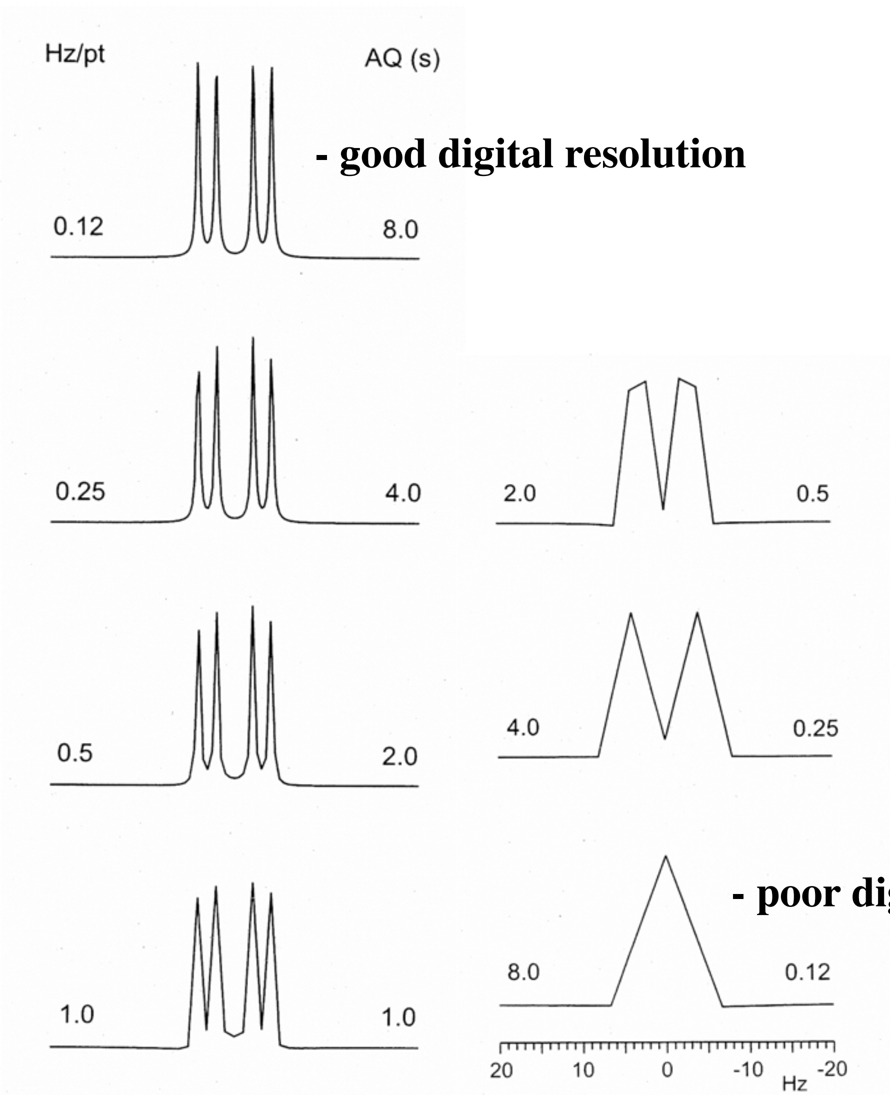
$$AQ = DW \times NP$$

- thus, SW, DW, AQ and NP are all interrelated:

$$DW = \frac{1}{2 \times SW} \qquad AQ = DW \times NP = \frac{NP}{2 \times SW}$$

Acquisition Parameters (Time Domain)

- the **digital resolution** (DR) is defined as twice the spectral width (in Hz) divided by the number of digitized points (NP) (thus, units are Hz/point)



- good digital resolution

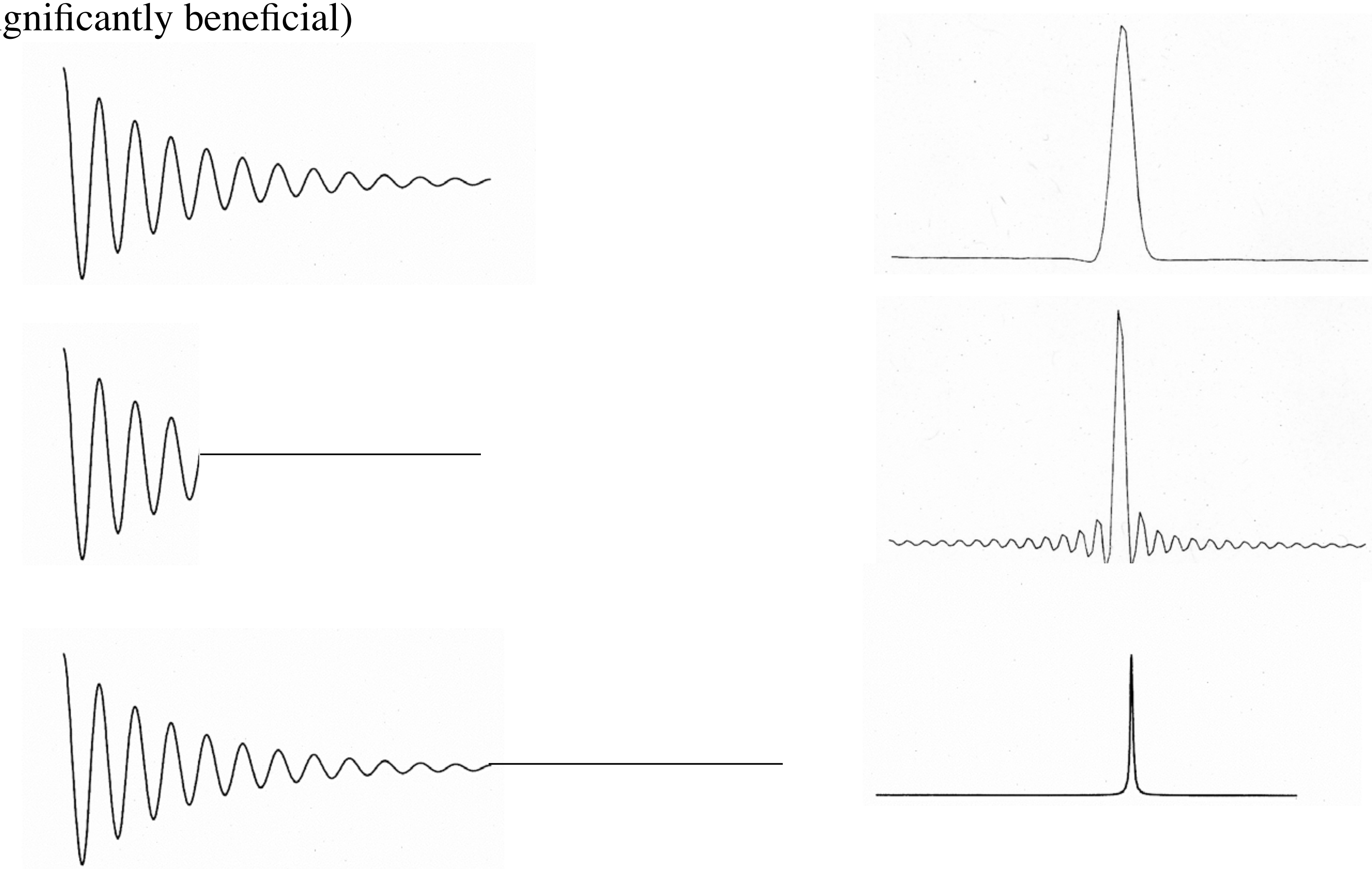
- poor digital resolution

$$DR = \frac{2 \times SW}{NP} = \frac{1}{AQ}$$

- the digital resolution is also, thus, the reciprocal of the acquisition time
- better (*improved*) digital resolution means DR is smaller
- the digital resolution can therefore be *improved* by decreasing SW or increasing NP (i.e. increasing the acquisition time)

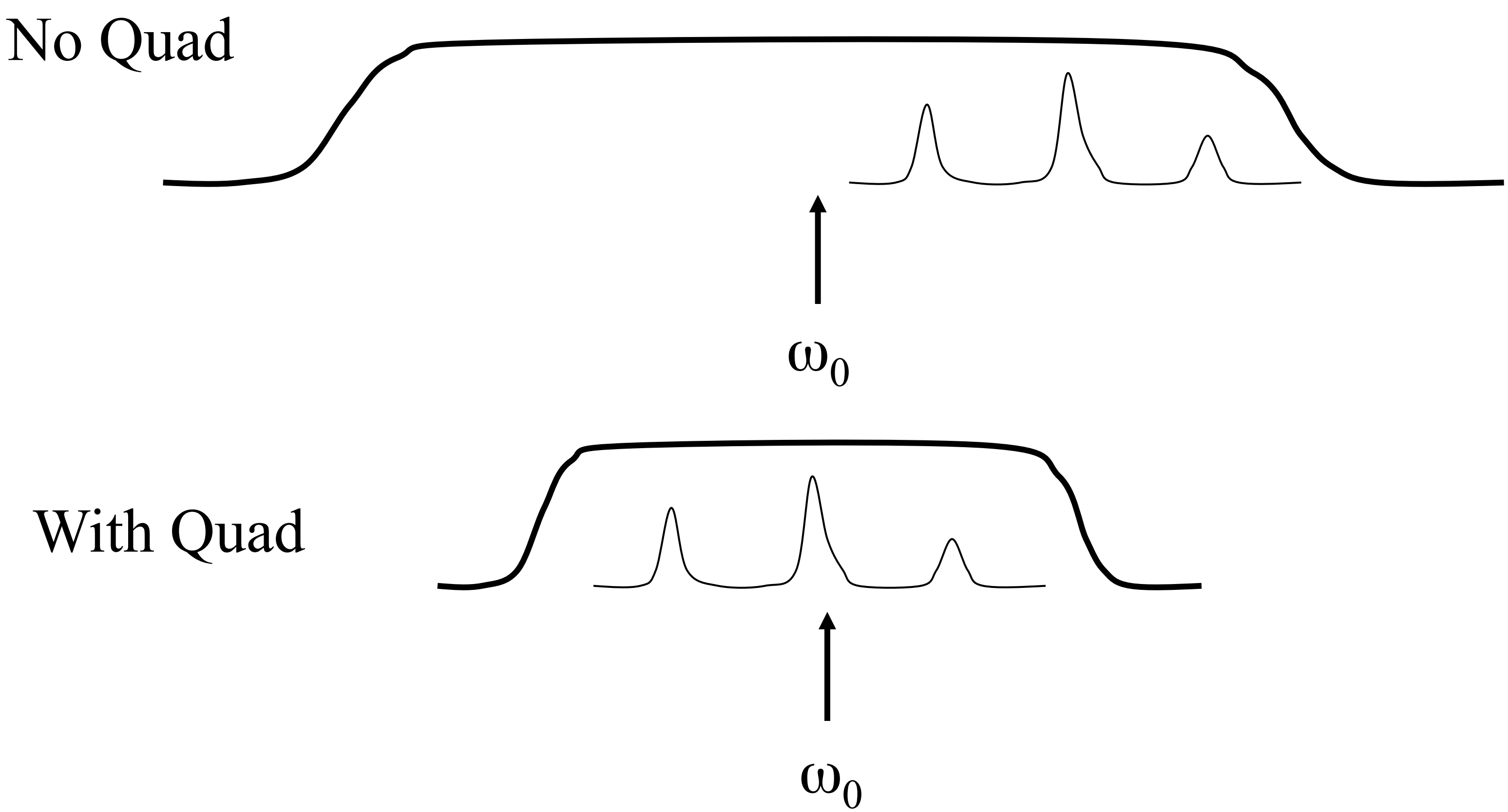
ACQUISITION PARAMETERS (TIME DOMAIN)

- increasing AQ leads to better digital resolution and sharper lines. Truncating the FID (very short AQ) leads to baseline artifacts
- a good rule of thumb is that AQ ≈ T_2 to 2xT_2 (acquisition times longer that 2xT_2 are not significantly beneficial)



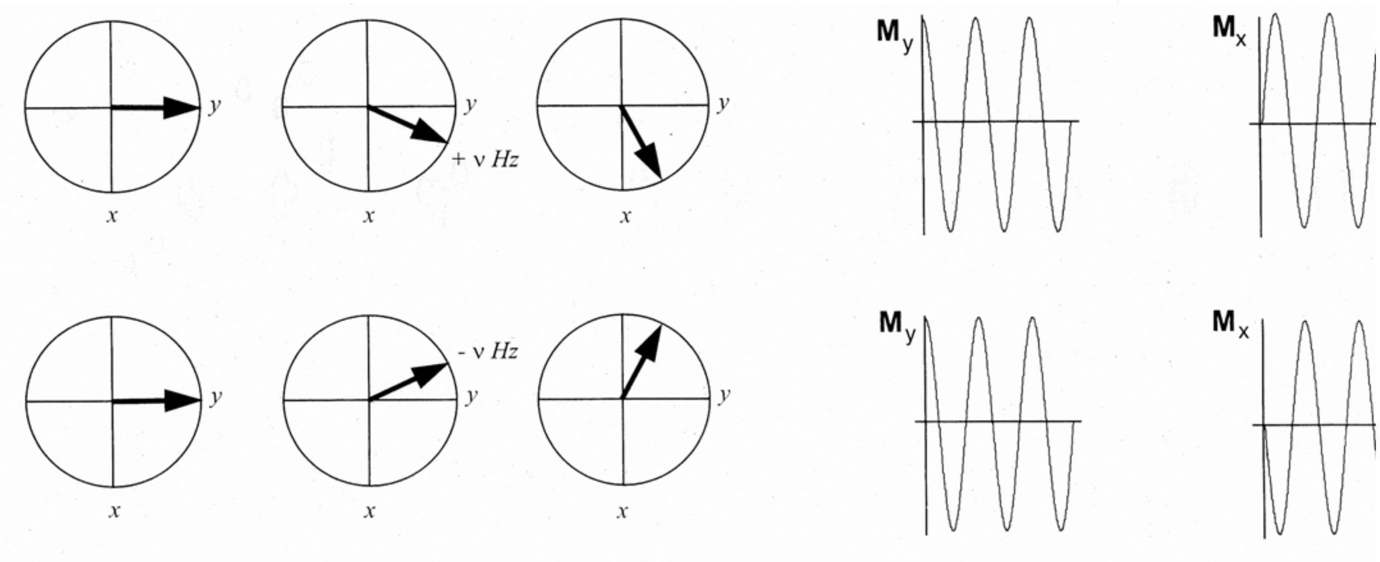
Quadrature Detection

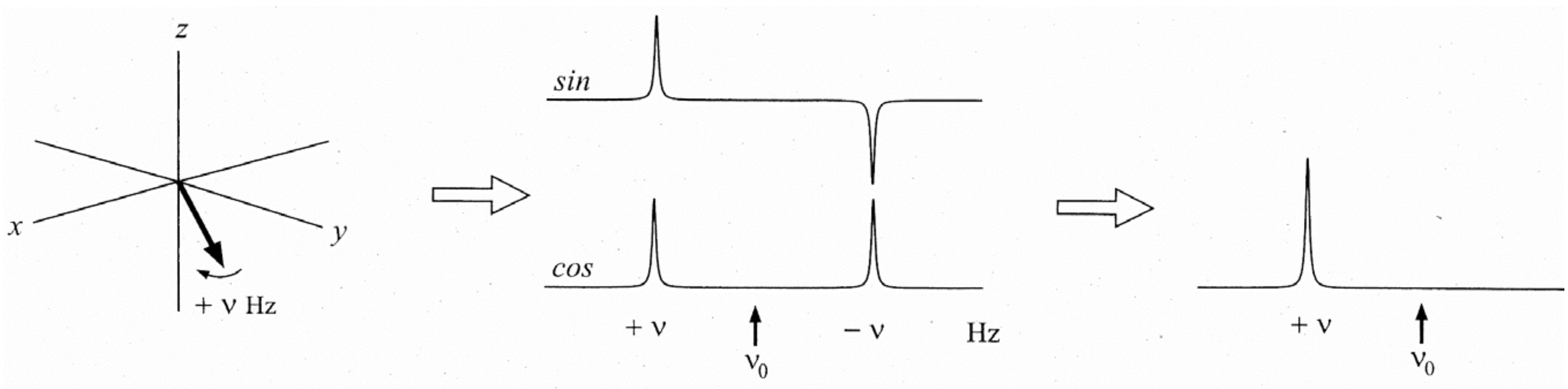
- if NMR signal is detected on a single axis (*x* or *y*), the Fourier Transform cannot distinguish between signals that are larger than or smaller than the reference frequency by the same amount
- using such a single channel detection scheme, the carrier or reference frequency is placed at one edge of the spectrum of expected signals
- quadrature detection alleviates this problem and permits the reference to be placed in the center of the spectrum



Quadrature Detection

- quadrature detection permits discrimination between positive and negative signals (below)
- quadrature detection permits a smaller SW, improved digital resolution and, as it turns out, an increase in S/N of $\approx 2^{1/2}$





OPTIMIZING PULSE WIDTH

What is the optimal pulse width/length/angle to use?

- a 90° pulse angle gives maximum S/N for one pulse, but the delay (d_1) between successive pulses must be long for recovery of equilibrium magnetization
- following a 90° pulse, if (d_1 + AQ) = 5 × T_1, then > 99% of equilibrium magnetization will be recovered before the next pulse
- thus, *for a given number of pulses* (without regards to time), 90° pulses will give maximum sensitivity (as long as (d_1 + AQ) ≥ 5 × T_1)

- other schemes, which permit faster pulsing (shorter d_1) combined with smaller pulse angles are possible
- for optimizing the S/N and total experimental time, the best compromise for the pulse width/angle is the ***Ernst Angle***
- Ernst Angle is in degrees

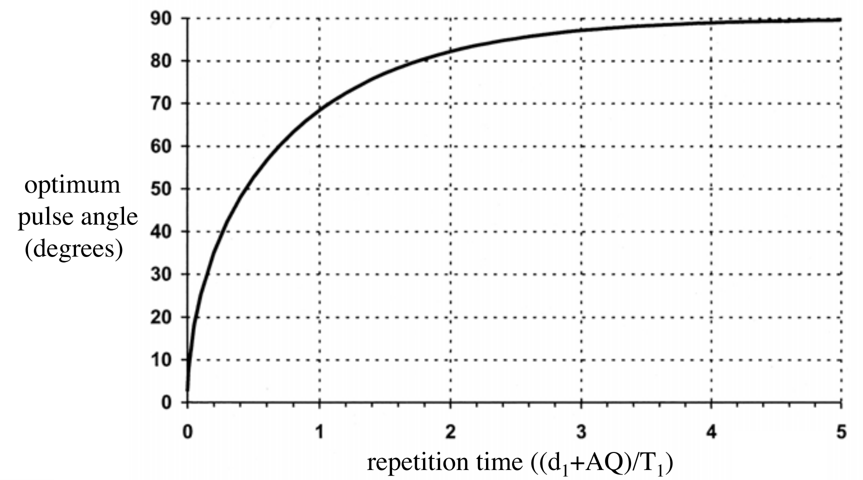
$$\cos\alpha_{\mathrm{Ernst}} = e^{-((\mathrm{d}_1 + \mathrm{AQ})/\mathrm{T}_1)}$$

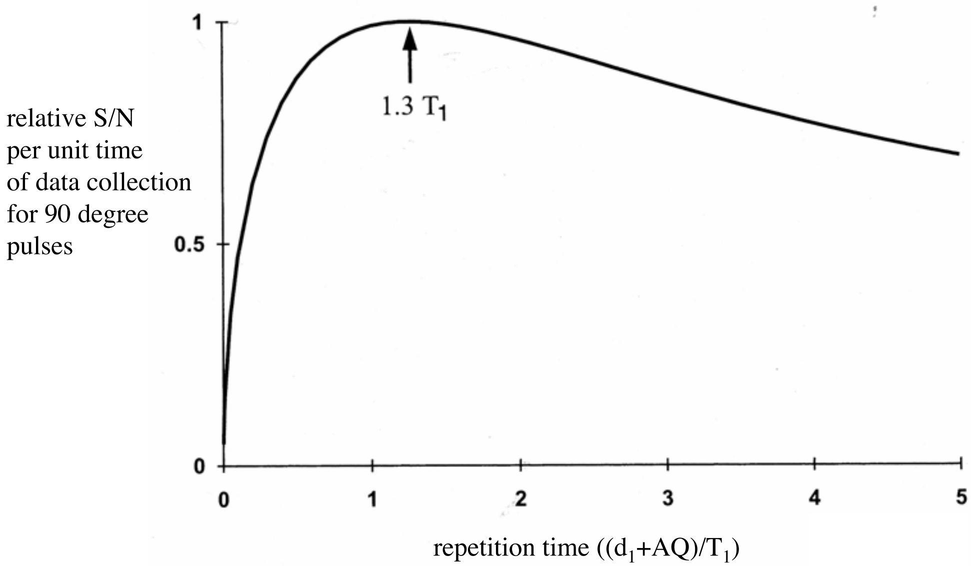
OPTIMIZING PULSE WIDTH

$$\cos\alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)}$$

What is the optimal repetiton time (best S/N) for a given repetiton time?

- the optimal pulse angle is dependent on the repetition time
- as the repetition time shortens, so does the optimal pulse angle





What is the optimal repetiton time (best S/N) for a given experiment time using 90 degree pulses?

- the optimal pulse angle is 1.3 x T_1 for 90 degree pulses for a pre-determined total experiment time