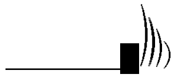
9. Detection

The pulsed NMR experiment consists of the excitation of the spin system with a series of RF pulses and time delays followed by the detection of the observable magnetization. A simple pulse sequence such as,

I 

would be written as:

$$\mathbf{I_z} \;= \pi/2\hat{\mathbf{I}}_\mathbf{x} \Rightarrow -\mathbf{I_y} \;= \omega_I t \hat{\mathbf{I}}_\mathbf{z} \Rightarrow -\mathbf{I_y} \cos \omega_I t + \mathbf{I_x} \sin \omega_I t$$

If the detector is aligned along the -Y axis then the oscillating signal, after removal of the RF carrier frequency (demodulation), can be represented as:

$$F_{-Y}(t) = \cos(\omega_I t) = \cos(2\pi v_I t)$$

Where v is the audio frequency (actually the difference frequency from the carrier frequency) of a spin of interest and t is time. From trigonometry: cos(x) = cos(-x), and therefore the sign (phase) of the NMR signal, v, is ambiguous. It is not known from this signal whether v is greater than or less than the carrier frequency, v_0. If F(t) is subjected to a Fourier transform, the resulting spectrum shows signals at ±v around the carrier frequency (Fig. 9.1a). The absolute frequency is not completely determined.

If the detector is aligned along the X axis, a different signal is detected:

$$F_x(t) = \sin(\omega_I t) = \sin(2\pi v_I t)$$

Since sin is an odd function, i.e. sin(-x) = -sin(x), FT of this signal gives two peaks at ±v, but with amplitudes of opposite signs (Fig. 9.1b). The difference between the behavior of the sine and cosine functions gives a method for detecting the phase of v, i.e. eliminate the ambiguity in whether the frequency is greater or less than the carrier frequency. If two signals are simultaneously detected, one

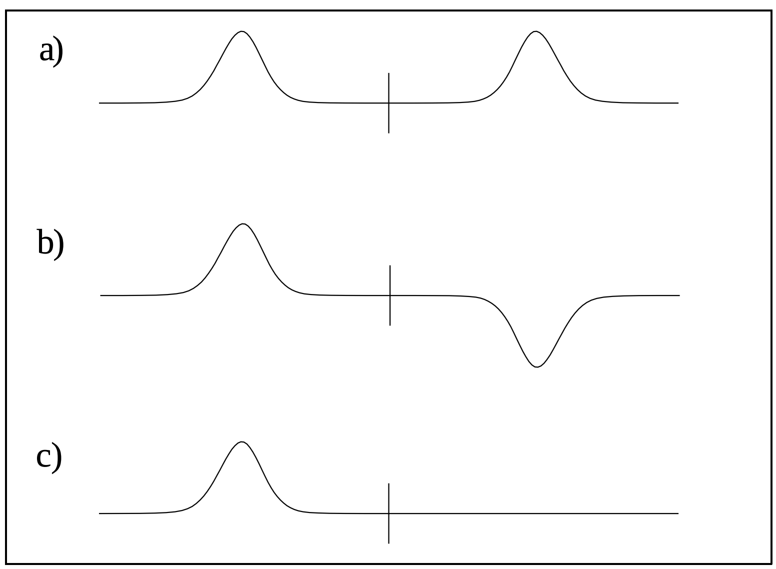


Figure 9.1. Result of a Fourier transform on a) cosine function, b) sine function, and a c) complex function.

along the Y axis and one along the X axis, and the demodulated signals are stored separately as the real and imaginary parts of a complex pair, then by combining the Fourier transforms of the two signals (actually, transforming the complex data), one of the two peaks is canceled (Fig. 9.1c). The absolute frequency with respect to the carrier frequency is then determined.

For a (old) NMR instrument equipped with only a single detector, the signal obtained is diagrammed in Figure 9.2. Signals with the same frequency that precess in opposite

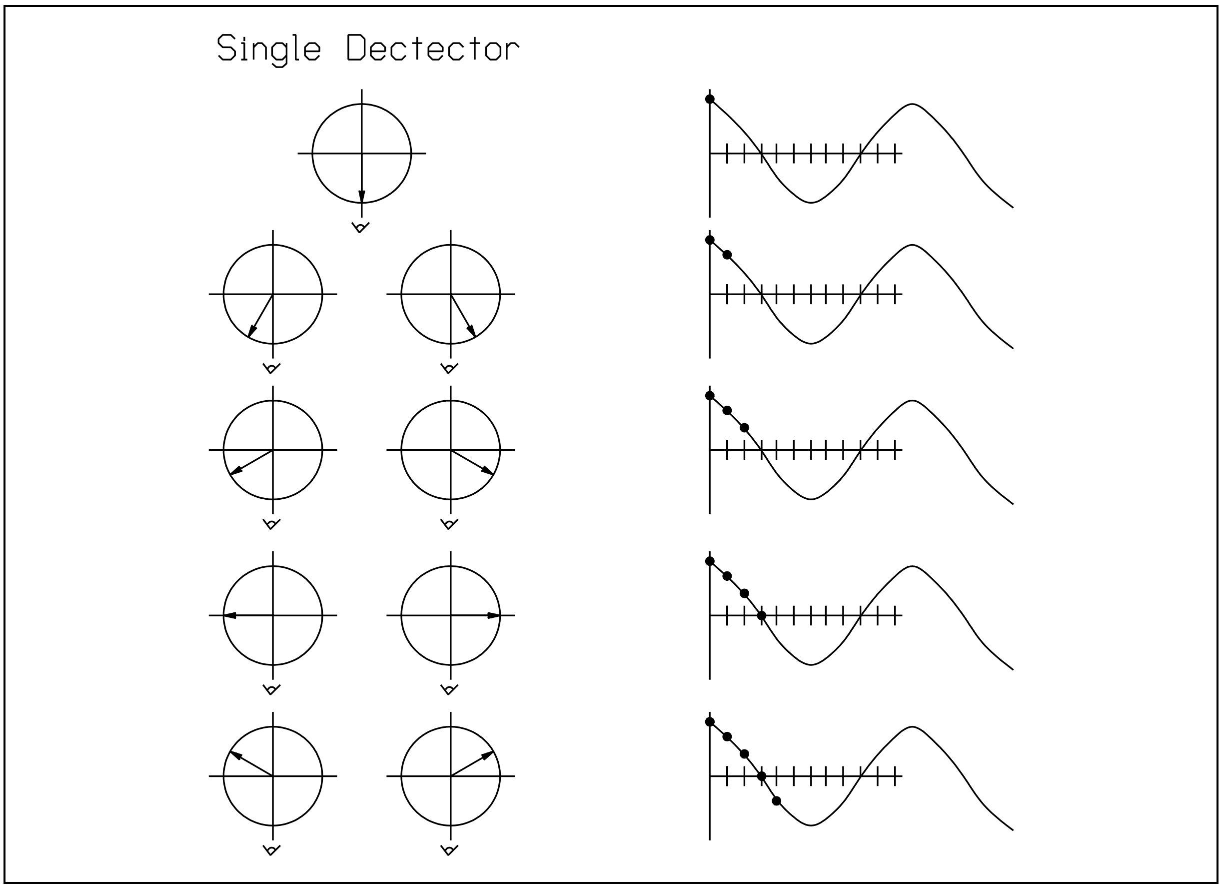


Figure 9.2. Representation of the digitized signal obtained from a single detector.

directions in the rotating frame give rise to the identical signals. The resulting spectrum from either of the signals will consist of two mirror image signals at ±ν. For this detection scheme, the carrier frequency would by necessity be placed at one end of the spectrum so there is no interference between the signals. This places greater demands on the power amplifiers to deliver short pulses in order to avoid large off-resonance effects. As well, a larger sweep width requires more data points for the same resolution. Another disadvantage to this method is that on the "other" side of the carrier frequency is noise; the noise "folds" into the spectrum causing a $\sqrt{2}$ reduction in the signal-to-noise of the spectrum. This can be addressed by single sided filters but overall the single channel detection is not as good as the following methods.

As discussed above, detection of the sign of the signal requires observation along two channels. Figure 9.3 diagrams the signals detected from a spectrometer equipped with

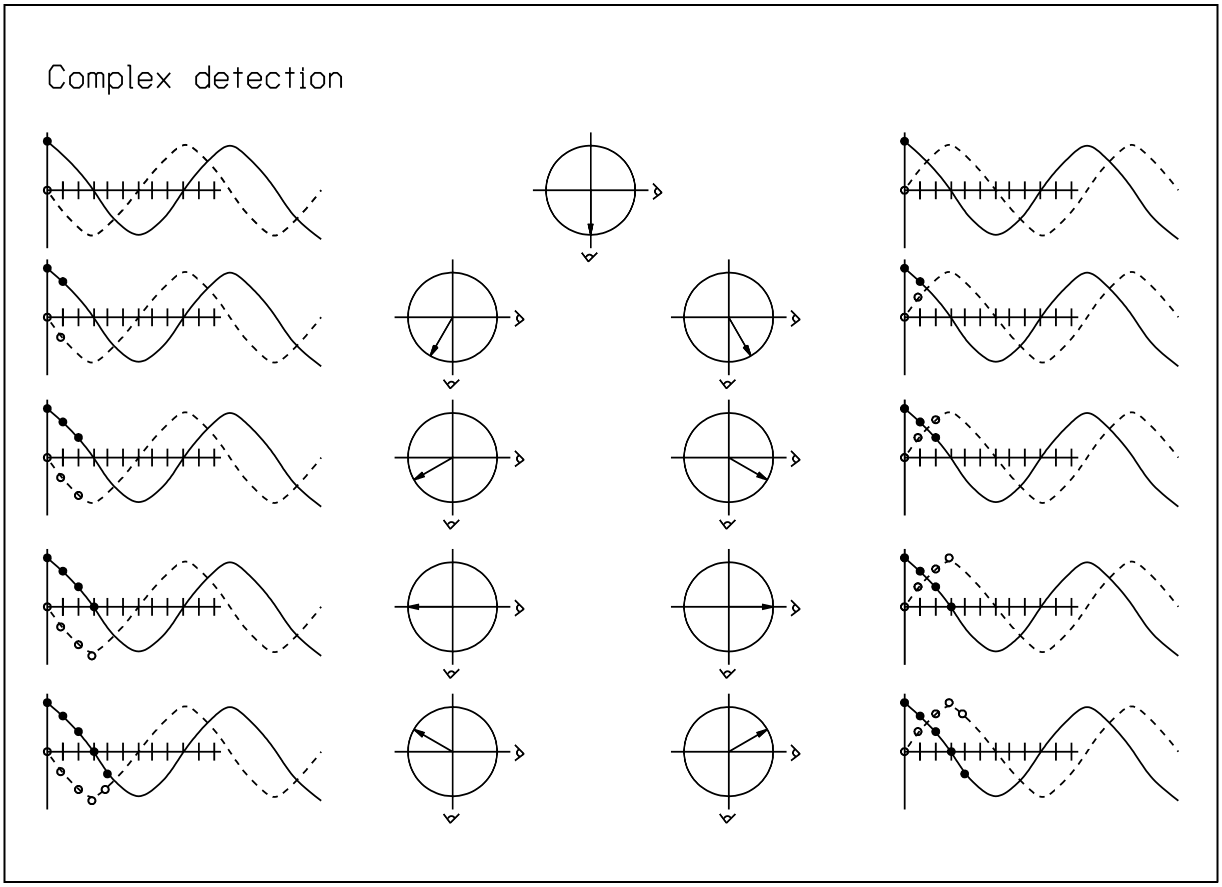


Figure 9.3. Digitization of signals using simultaneous detection on two orthogonal channels.

a two channel detector. The two counter-rotating vectors that represent signals at ±v about the carrier, give rise to different "patterns" in the two channel detection system. The signals are the real and imaginary components of the complex FID, exp(i2πvt). A spectrum obtained from the Fourier transform of these signals would distinguish ±v signals. This implies that the carrier can be placed in the center of the spectrum without interference between signals above and below the carrier frequency.

One further way that the advantages of quadrature detection can be realized is by a sequential sampling method, in which the phase of the single channel detector is shifted by 90° with each data point that is digitized. Figure 9.4 diagrams this type of quadrature detection, which is referred to as Time Proportional Phase Incrementation

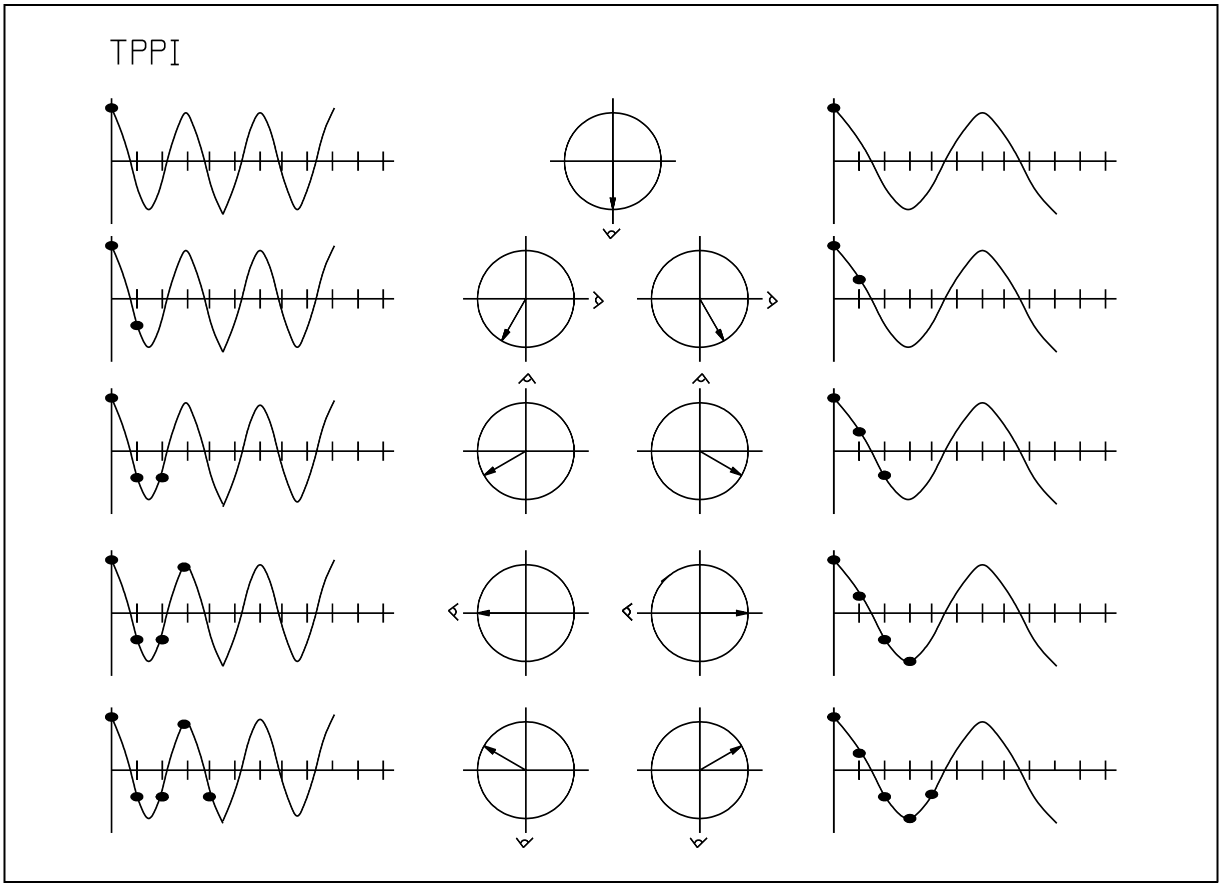


Figure 9.4. Digitization of a signal by phase shifting the receiver channel by 90° at each subsequent data point.

(TPPI) in the context of two dimensional NMR. The effect of the phase rotation of the receiver is to artificially move the carrier frequency to one end of the spectrum. One-half of the spectral width is subtracted from frequencies that are positive with respect to the true carrier frequency and one-half of the spectral width is added to frequencies that are negative. The resulting data is "real" but the disadvantages of the single sided detector are alleviated.