

An Introduction to NMR Concepts

By

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Introduction

Nuclear Magnetic Resonance, NMR, is an extremely powerful and complex instrumental technique. This worksheet introduces several important concepts for NMR data acquisition and data processing. Understanding these concepts will help you obtain and process high quality spectra in the shortest amount of time. Acquisition parameters of the instrument, the basis of quadrature detection, apodization and zero filling are all discussed.

Goal

To provide the user with an understanding of how pulsed NMR spectroscopy is performed and the important parameters involved in acquisition and data processing.

Prerequisites

Familiarity with Mathcad functions, graphs and arrays. This document is written with the assumption that students know how to use these Mathcad features.

Performance Objectives

1. Graph the free induction decay (FID), Fourier transform the FID, and graph the real and imaginary spectra. Be able to explain how these are related.
2. Explain the relationship between the number of data points, the dwell time, the acquisition time, the spectral window, and the resolution.
3. Observe aliasing and explain how the data acquisition parameters may be changed to eliminate this effect.
4. Set the acquisition parameters to optimize the resolution and S/N for the spectrum.
5. Explain how quadrature detection is accomplished, the effect on the spectrum, and the significance of this technique.
6. Zero fill an FID and observe the effect on the spectrum.
7. Use various apodization functions, observe their effect on the spectrum, and learn how to optimize the resolution and S/N.

Acquiring an NMR Signal

The Signal. In NMR spectroscopy the signal is produced by the spinning of the charged nuclei. This spinning produces an oscillating magnetic field that is detected by the instrument as a radio frequency signal. Since different nuclei in a molecule spin at different frequencies, each nuclei produces a different signal. NMR data acquisition and signal processing are all about optimizing this signal. Let's begin by generating an NMR signal for a sample with two different protons; one at 20 Hz and the other at 30 Hz.

The two signal frequencies, ν_a and ν_b

$$\nu_a := 20 \cdot \text{Hz}$$

$$\nu_b := 30 \cdot \text{Hz}$$

Since Mathcad calculates sine and cosine functions using radians, angular frequencies must be used for this document. The angular frequency (ω) is defined below for each signal.

Angular Frequency (ω_a and ω_b)

$$\omega_a := 2 \cdot \pi \cdot \nu_a$$

$$\omega_b := 2 \cdot \pi \cdot \nu_b$$

$$\omega_a = 125.664 \text{ rad} \cdot \text{sec}^{-1}$$

$$\omega_b = 188.496 \text{ rad} \cdot \text{sec}^{-1}$$

In the NMR experiment, a radio frequency pulse excites the nuclei. Much like a tuning fork causes a crystal wine glass to vibrate. After the radio frequency pulse ends, the excited nuclei relax back to equilibrium, like the ringing of the wine glass fading after the tuning fork stops. The NMR signal is observed at the frequency of this vibration and it decays with a time constant T. Lets start by setting the relaxation time constant (T) equal to 1 second.

Relaxation time constants, T

$$T := 1 \cdot \text{sec}$$

When acquiring an NMR signal it is not possible to begin acquisition while exciting the nuclei. As a result, the nuclei begin to rotate prior to the first data point. This causes a phase shift in the signal. Latter in this document we will change the phase and observe how it effects the signal. This is important for understanding how to correct the phase during data processing. Let's begin with the phase set to 0 radians.

Signal phase, ϕ

$$\phi := 0 \cdot \text{rad}$$

Acquiring the Signal. The information above defines the behavior of the nuclei. The spectrometer must acquire this signal. Since the spectrometer is a digital instrument there are several important acquisition parameters that must be set. Unlike a chart recorder or an oscilloscope the spectrometer measures the signal at discrete intervals. The frequency that the instrument samples the signal is the sampling rate. The time between each sample is the dwell time. These two are inversely related. We will set the dwell time (DW) to 0.01 seconds.

Dwell Time (DW)

$$DW := 0.010 \cdot \text{sec}$$

Sampling Rate

$$\frac{1}{DW} = 100 \text{ Hz}$$

To use the fast Fourier transform algorithm for processing the data, the number of data points must be a binary number. Set the number of data points to 2^9

Number of Data Points Sampled (N).

$$N := 2^9$$

$$N = 512$$

Calculated Parameters: Based upon the two acquisition parameters defined above, we can calculate a number of additional acquisition parameters that are related to the appearance of the spectrum. These include:

The acquisition time (AT) is the total amount of time that the data is sampled. After this time the acquisition is complete and another experiment may begin. Define the acquisition time using the variables above and determine what the value is for the current settings.

Acquisition Time

$$AT := DW \cdot N$$

$$AT = 5.12 \text{ sec}$$

The spectral window (SW) is another important variable that must be appropriately set to obtain good spectra. The spectral window is the range of frequencies that are measured. This is related to the sampling rate by Nyquist sampling theorem. This theorem states that the highest frequency signal that may be observed is at 1/2 the sampling rate. The spectral window goes from 0 Hz, to 1/2 the sampling rate.

Spectral Window

$$SW := \frac{1}{2 \cdot DW}$$

$$SW = 50 \text{ Hz}$$

Since the data consists of a set number of discrete points, N, and a fixed spectral window, SW, the spacing between the points in the spectrum is fixed. This spacing sets the resolution of the experiment. Resolution in NMR is typically given as 1/AT. This can also be calculated using the spacing between points in the spectrum. To be resolved, two peaks must be separated by a data point.

Digital Resolution

$$\text{Resolution} := \frac{1}{AT}$$

$$\text{Resolution} = 0.195 \text{ Hz}$$

$$\text{Resolution} := 2 \cdot \frac{SW}{N}$$

$$\text{Resolution} = 0.195 \text{ Hz}$$

Index: These indexes are used for various axis and calculations in the document.

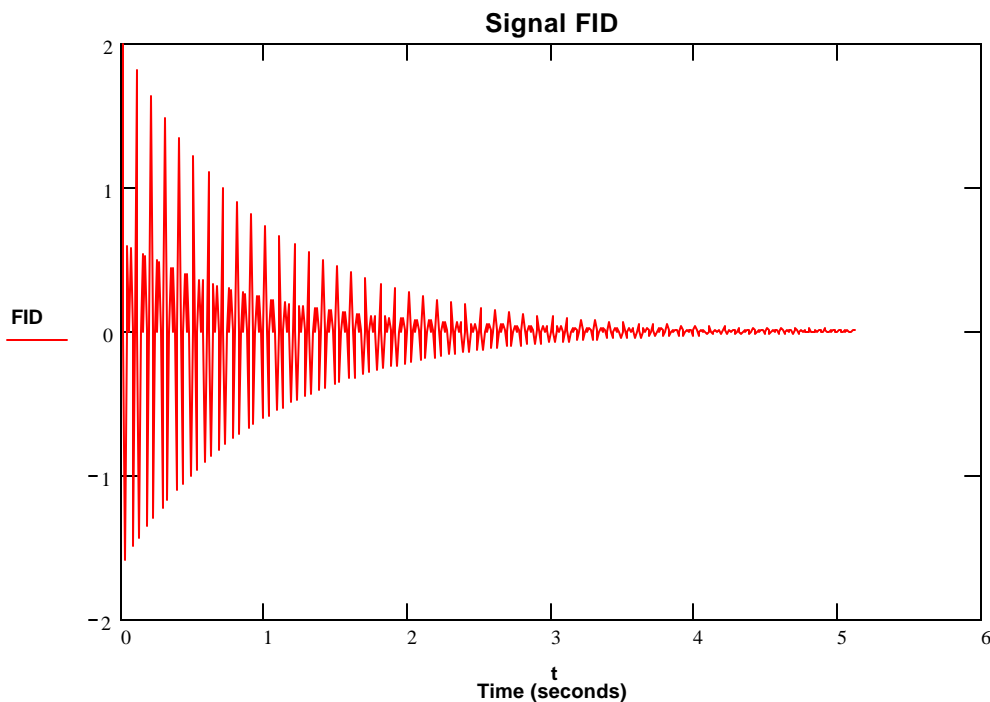
$$i := 0, 1 \dots (N - 1) \quad t_i := i \cdot DW \quad \text{Time index}$$
$$j := 0, 1 \dots \left(\frac{N}{2} - 1 \right) \quad \text{frequency } f_j := \frac{j}{N \cdot DW} \quad \text{Frequency index}$$

Calculate Waveforms: Calculate the FID from the above information.

This equation calculates a cosine wave with a frequency ω , a phase shift ϕ , and an exponential decay with a time constant T . The calculation is done for wave a and wave b. These two are combined to create an FID signal with two frequency components.

$$FID_i := \cos(t_i \cdot \omega_a + \phi) \cdot e^{-\frac{t_i}{T}} + \cos(t_i \cdot \omega_b + \phi) \cdot e^{-\frac{t_i}{T}}$$

Now graph the FID vs. time to observe the NMR signal as it is acquired.

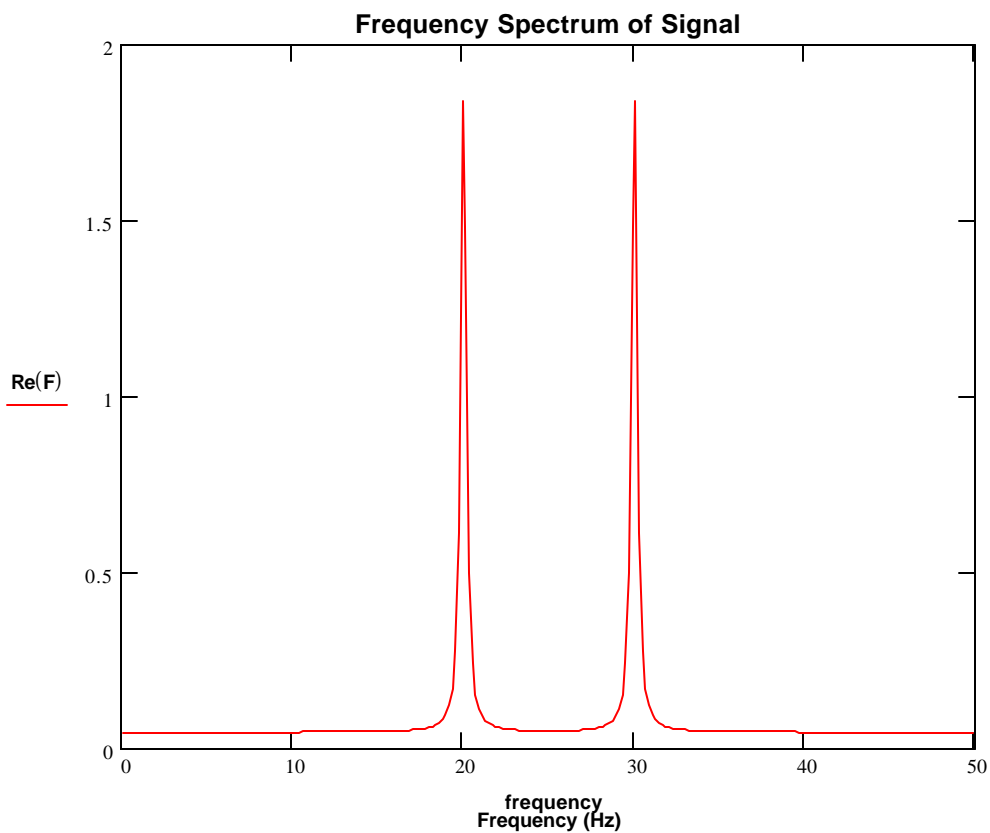


Fourier Transforms: The FID is Fourier transformed to produce the spectrum. For additional details on how the Fourier Transform works see "An Introduction to the Fourier Transform" by S.E. Van Bramer. *J. Chem. Educ.*, **1999**, *76*, 286 and "Exploring Fourier Transform Techniques with Mathcad " Iannone, M. *J. Chem. Educ.*, **1999**, *76*, 286.

Fast Fourier Transform of the FID to produce the frequency domain spectrum (F)

$$F := \text{fft}(\text{FID})$$

Graph of the frequency spectrum (F) vs. the frequency. Note: The FFT produces a real and an imaginary spectrum, we are currently interested in the real spectrum. The Re function extracts the real part of this complex number.



Questions about data acquisition.

1. Change the signal frequency (Edit; Go to Page; 2) and observe how this changes the FID and the spectrum. Change the frequency so that it is greater than the spectral window. What happens? Enter a negative frequency. What happens?

2. Change the phase of the signal and observe how this changes the FID and the spectrum (Edit: Go to Page 2). Keep in mind that the phase is in radians, so 2π is a complete cycle. The phase of $\frac{1}{2}\pi$, π , and $\frac{3}{2}\pi$ are of particular interest.

3. Change the relaxation time constant and observe how this effects the FID and the spectrum (Edit; Go to Page; 2). What happens if the relaxation rate is very long? What happens if it is very short?

4. Change the number of data points acquired, try 2^{10} , 2^9 , 2^8 , 2^7 , 2^6 , and 2^4 (Edit; Go to Page; 3). Notice what happens to the acquisition time and the spectral window. What changes in the FID? What changes in the spectrum? What is the advantage of increasing N? Is there a point where no additional change is observed? What are the advantages and disadvantages of longer acquisition and shorter acquisition? Change the relaxation rate to 0.1 seconds and then to 10 seconds and repeat the changes in the number of data points. You may want to print out the graph for several different settings to help make comparisons. Based upon your observations, what should determine the number of data points (or the acquisition time)?

5. Now reset the relaxation rate to 1.0 seconds and the number of data points to 2^9 . Change the dwell time to 0.02 seconds and see how this effects the spectrum. Notice what happens to the acquisition time, the spectral window and the axis on the FID and the spectrum. Try 0.03 and 0.1 seconds. What happens? How do you determine the settings to use for the dwell time?

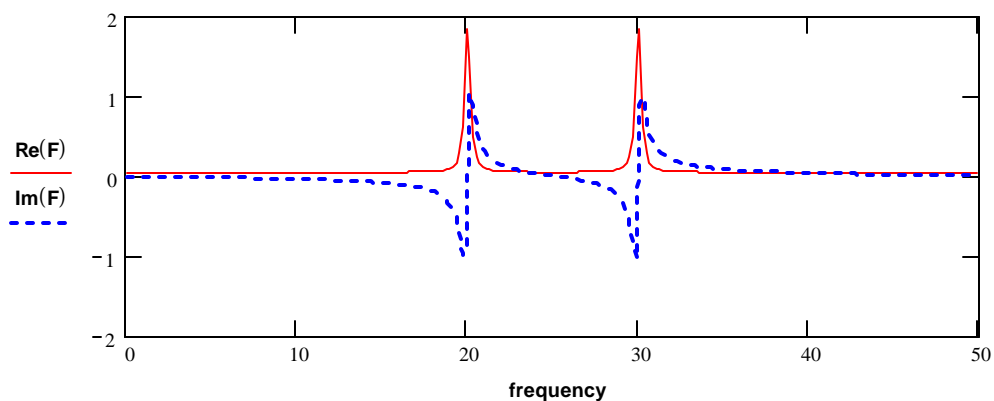
Quadrature Detection

One of the problems that should be apparent after observing the spectrum and the FID is that it is not possible to determine if the frequency is positive or negative. Under normal conditions this would not be a problem. After all, what is a negative frequency? The problem arises in NMR because the signals are at very high frequencies. In a typical magnet with a 7 Tesla field, protons are observed at approximately 300 MHz. At such a high frequency it is very difficult and expensive to detect, transmit, amplify and sample the signal. These acquisition problems are simplified by looking at frequency differences. The instrument uses a spectrometer frequency and all signal frequencies are measured relative to the spectrometer frequency. If a molecule produces two signals, one at 300,000,001 Hz and another at 299,999,999 Hz, and the spectrometer frequency is 300,000,000 Hz, the first signal is at +1 Hz and the second is at -1 Hz. Electronically the lower frequency signals are very easy frequency to detect, transmit, amplify and sample.

The complication with this rotating frame of reference is that a single detector can not distinguish positive and negative frequencies. Double check this by changing the sign of the signal above and observing the spectrum. Where is the signal observed in the spectrum?

This problem is why quadrature detection is important. Quadrature detection uses two detector channels separated by 90 degrees. These are referred to as the real channel and the imaginary channel. Using these two channels, it is possible to distinguish positive and negative frequencies. This section shows how the quadrature signal is processed to obtain an NMR spectrum.

The Fourier transform produces a complex number with a real and an imaginary component. The Re function extracts the real spectrum and the Im function extracts the imaginary spectrum from the complex number.



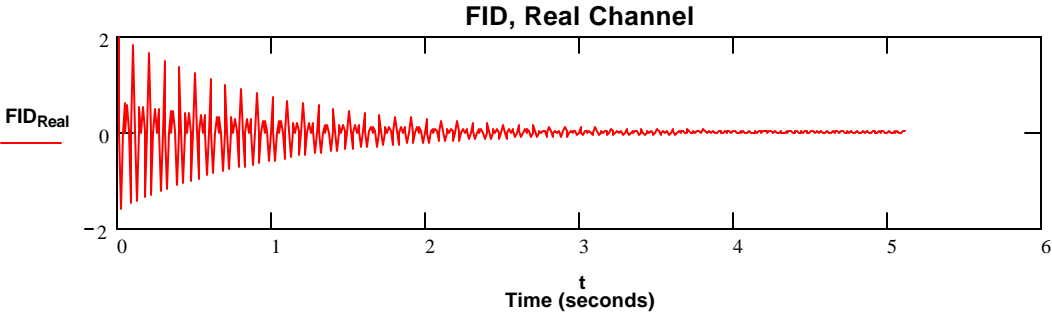
It is important to keep track of the real and imaginary components for quadrature phase detection. First, there is the real and the imaginary channel. A FID is produced by each of these channels. When these FID are transformed, each of them produces a real and an imaginary spectra. For the real channel, these are labeled the real spectrum of the real channel (real of the real) and the imaginary spectrum of the real channel (imaginary of the real). For the imaginary channel these are called the real spectrum of the imaginary channel (real of the imaginary) and the imaginary spectrum of the imaginary channel (imaginary of the imaginary). Are you confused yet? Hang on, this is just a labeling convention.

Now to see how this works, change the 20 Hz signal for ν_a to -20 Hz (Edit; Go to Page; 2). Remember, that the frequencies are for the rotating frame. A negative frequency just means that the signal is rotating in the opposite direction. If we are using the right hand rule, positive frequencies are rotating counterclockwise around the z axis, and negative frequencies are rotating clockwise around the z axis. The following graphs will show how the quadrature signal is processed.

Real Channel: For quadrature detection, two signal channels are used. One is called the real channel. The real channel corresponds to a cosine wave. This is the same as the signal used previously.

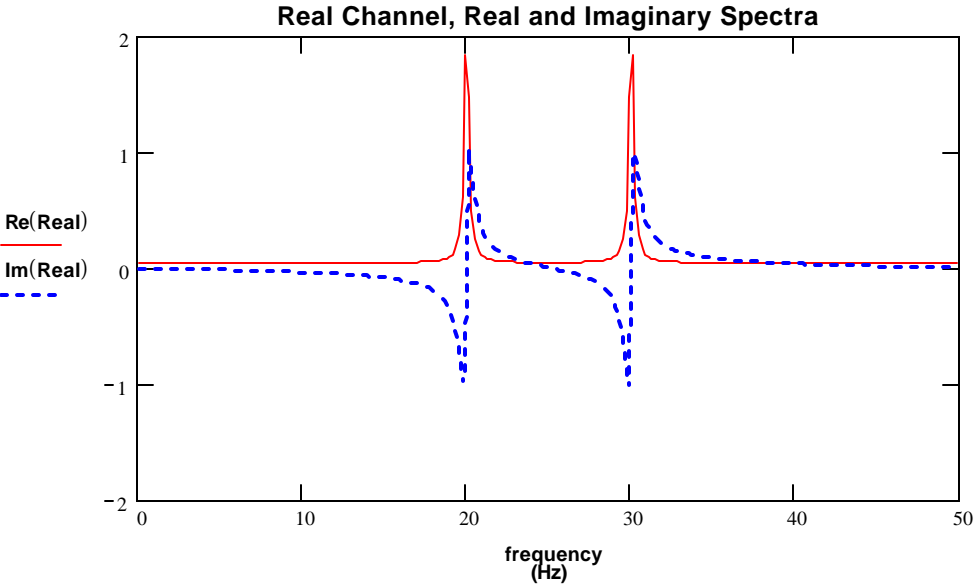
Calculate FID: $FID_{Real} := FID$

Plot the FID of the real channel.



Fourier Transform of Real Channel FID: The FT of the real channel produces a real and imaginary spectrum. These are labeled the real spectrum of the real channel, and the imaginary spectrum of the real channel. Plot the real and imaginary spectra for the real channel using the Re and Im functions for the y-axis. For both the real and the imaginary spectra, note the phase relationships between the two signals (one with positive frequency and one with negative frequency). Would it be possible to distinguish between a positive frequency and a negative frequency in this spectrum?

FFT of Real FID (Sum) $Real := fft(FID_{Real})$



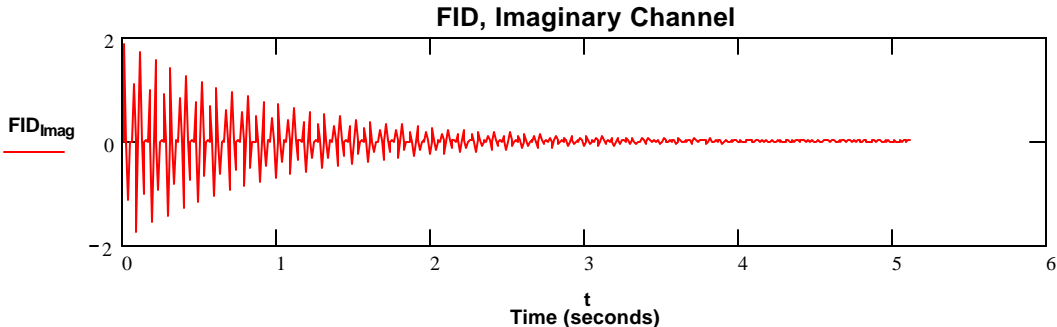
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Imaginary Channel. The second quadrature channel is called the imaginary channel. It is oriented 90 degrees from the real channel. This produces a signal that corresponds to a sine wave.

Generating FID:

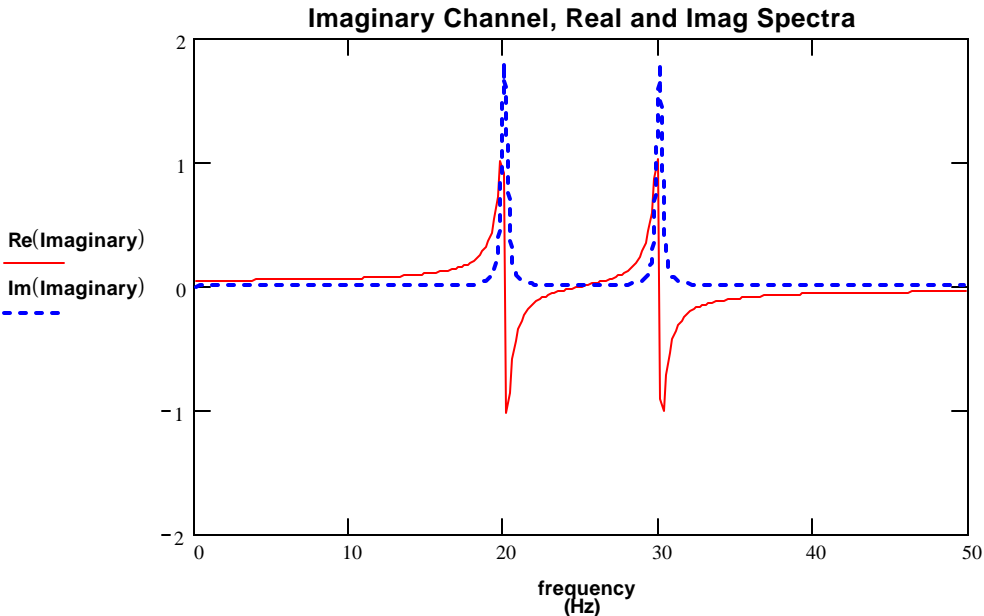
$$FID_{Imag_i} := \left(\sin(t_i \cdot \omega_a + f) \cdot e^{-\frac{t_i}{T}} + \sin(t_i \cdot \omega_b + f) \cdot e^{-\frac{t_i}{T}} \right)$$

Plot the FID for the imaginary channel



Fourier Transform of Imaginary Channel FID: The FT of the imaginary channel also produces a real and imaginary spectrum. These are labeled the real spectrum of the imaginary channel, and the imaginary spectrum of the imaginary channel. Plot the real and imaginary spectra for the imaginary channel using the Re and Im functions for the y-axis. For both the real and the imaginary spectra, note the phase relationships between the two signals (one with positive frequency and one with negative frequency). Would it be possible to distinguish between a positive frequency and a negative frequency in this spectrum?

FFT of Imaginary Channel FID (Sum) **Imaginary := fft(FID_{Imag})**



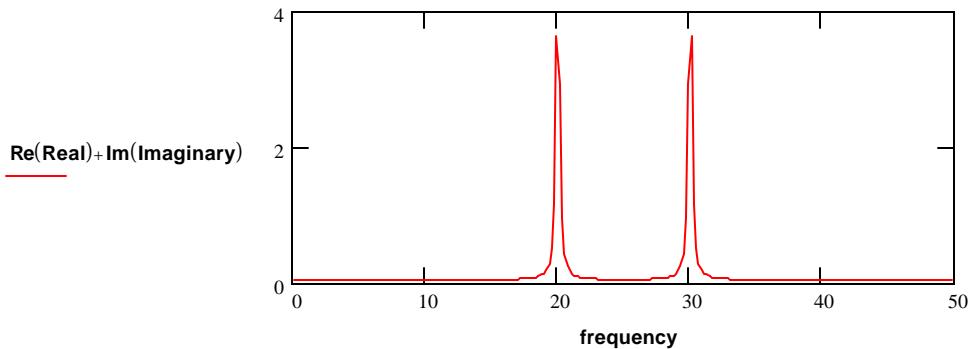
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Quadrature Manipulation. The quadrature spectrum is generated by combining the above spectra. So, take a look at the real and imaginary spectra from the real and the imaginary channels. How can they be combined (added or subtracted) to get one spectrum that only contains positive frequencies and another that only contains negative frequencies?

To help see how this will work, it is useful to distinguish between absorption mode spectra and dispersion mode spectra. An absorption mode spectrum is like a typical spectra, consisting of peaks. A dispersion mode spectrum looks like the first derivative of an absorption spectrum. In the real channel the real spectrum is the absorption spectrum. In the imaginary channel the imaginary spectrum is the absorption spectrum. So if we want to produce an absorption spectrum (which is what you are used to looking at) we will need to use the real of the real and the imaginary of the imaginary.

With that in mind, what happens when the real of the real and the imaginary of the imaginary are added or subtracted.

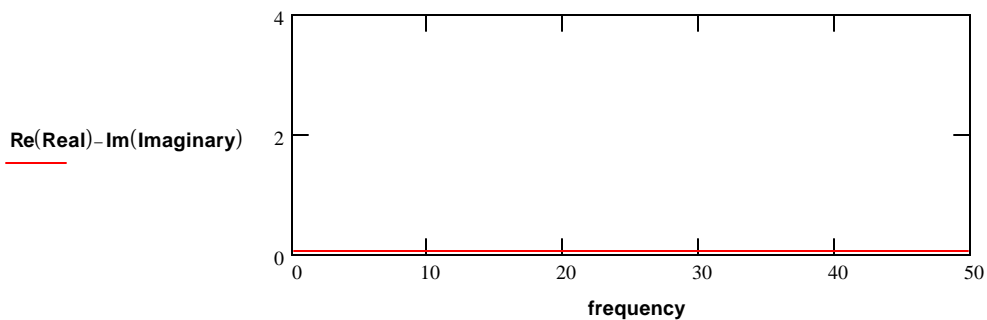
First make a graph where the two are added together.



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Which peaks are observed in this spectrum? Take a look at the individual spectra to figure out why? How is this useful?

Next make a graph where the two are subtracted.



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Which peaks are observed in this spectrum? Take a look at the individual spectra to figure out why? How is this useful?

Generating the Real Spectrum: The quadrature spectrum is displayed with zero frequency in the center of the spectrum. To the right is increasingly positive frequency and to the left is increasingly negative frequencies. Remember the significance of quadrature detection is to distinguish between negative and positive frequencies, or clockwise and counterclockwise rotation with respect to the spectrometer frequency in the rotating frame.

From above we can see that when the real of the real and the imaginary of the imaginary are added together, signals with a negative frequency cancel, while those with a positive frequency add. Since the right part of a quadrature spectrum contains signals with a positive frequency, the right part is produced by adding the two spectra.

When the real of the real and the imaginary of the imaginary are subtracted, signals with positive frequencies cancel and signals with a negative frequency add. Since the left part of the quadrature spectrum contains signals with a negative frequency, the left part may be produced by subtracting. Note that the resulting matrix is inverted to follow convention for the display of spectra.

The final spectrum is displayed by placing the two spectra side by side. 0 Hz is in the center. To the right is increasing frequency, to the left is reduced frequency (relative to the spectrometer frequency). This conforms with standard NMR data presentation.

$$\text{REAL}_{\text{left}} := \text{Re}(\text{Real}) - \text{Im}(\text{Imaginary})$$

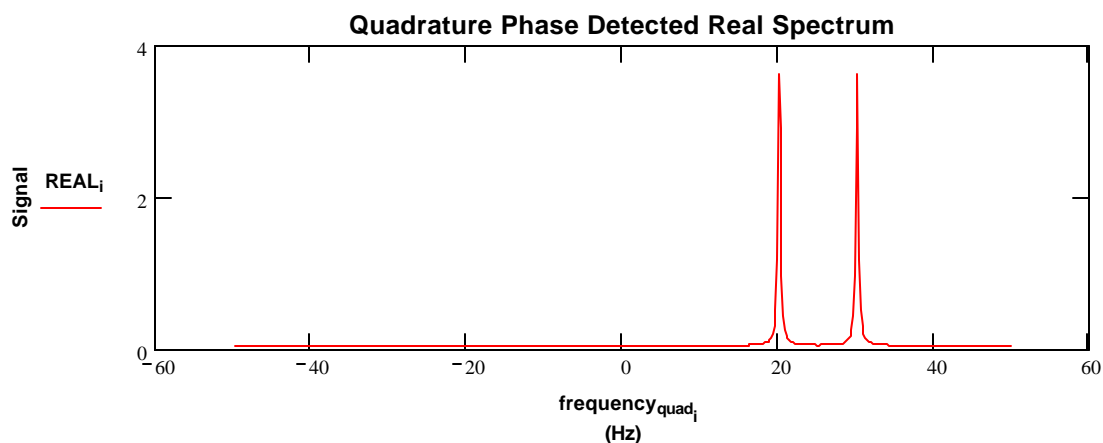
$$\text{REAL}_{\text{right}} := \text{Re}(\text{Real}) + \text{Im}(\text{Imaginary})$$

$$\text{REAL}_j := \text{REAL}_{\text{left}}\left(\frac{N}{2}-1-j\right)$$

$$\text{REAL}\left(\frac{N}{2}+j\right) := \text{REAL}_{\text{right}}_j$$

Index: Since the chemical shift scale is different for a quadrature spectrum, we need to define the frequency index for quadrature spectra.

$$\text{frequency}_{\text{quad}_i} := \left(\frac{i}{N \cdot \text{DW}}\right) - \frac{N-1}{2 \cdot N \cdot \text{DW}}$$



Now that this is all set up. Let's make some changes and observe what happens. The significance of quadrature phase detection is to distinguish positive and negative frequencies. So make some changes in the signal frequencies and observe what happens in the intermediate and the final spectra. What happens if both signals are positive? If both are negative? If they are greater than the spectral window?

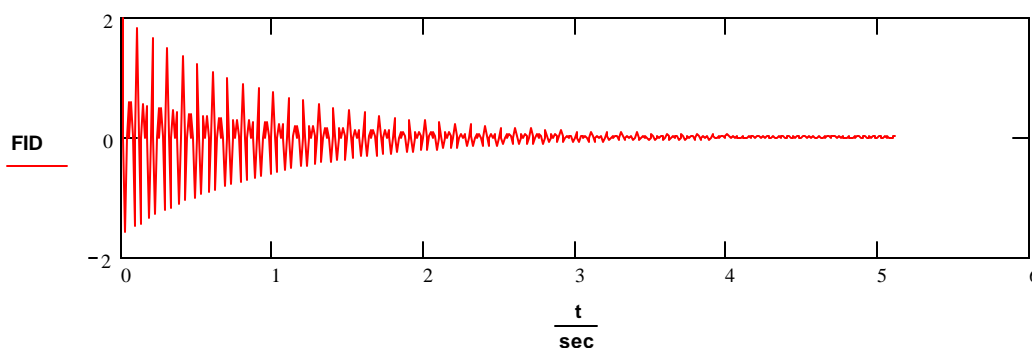
Zero Fill and Apodization.

Zero filling and apodization are two data processing techniques that are used to enhance the resolution and the S/N of the NMR spectrum. The resolution of the spectrum refers to how clearly defined two adjacent peaks are, this is typically expressed in Hz. A smaller number means that the peaks are narrower and that the resolution is higher. The S/N is expressed as a ratio of the peak height over the standard deviation of the background signal. The minimum S/N of 3 is required for detection of a peak.

First let's examine the limitations to resolution in an NMR experiment. As you found above, the resolution is limited by the acquisition time so that:

$$\text{resolution} = \frac{1}{AT}$$

From this equation it is apparent that the resolution of the spectrum could be enhanced by increasing the acquisition time. The problem with this is that the NMR signal is undergoing exponential decay as shown in the FID below.



Because the NMR signal decays during data acquisition while the noise is constant, the signal to noise ratio, S/N, is not constant. This has several important implications in how the data is acquired that limit the S/N and resolution of an experiment. In this section of the document you will learn how zero filling and apodization are used to enhance the resolution and the S/N. Understanding how these signal processing methods work depends upon understanding the properties of the FID.

Let's begin by adding some noise to the FID that we have been using up to this point. This will let us observe how the S/N of the spectrum is effected by the manipulations that we perform. The following equations define a noise level (which you may change), calculate a random noise, and adds this to the FID.

Noise

$$s := 0.2$$

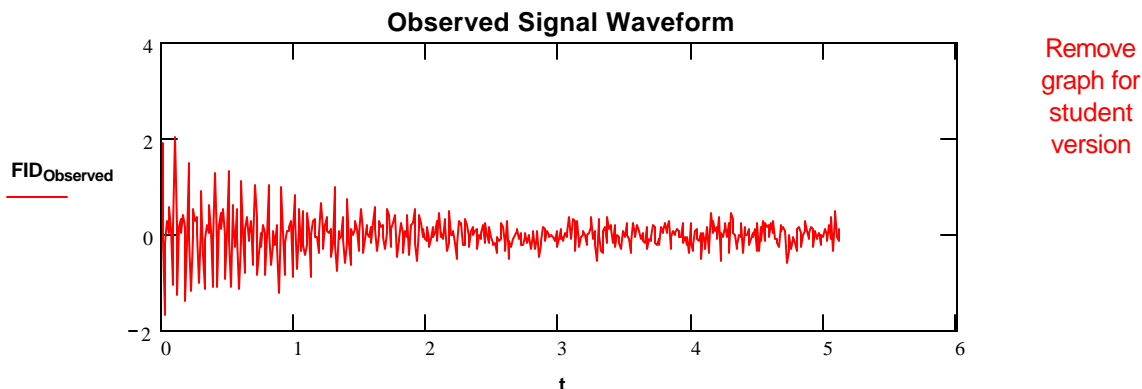
Random Noise

$$\text{Noise} := \text{rnorm}(N, 0, s)$$

Original Signal Waveform

$$\text{FID}_{\text{observed}} := \text{Noise} + \text{FID}$$

Now graph the observed FID:



Compare the observed FID with the added noise and the FID shown previously. Think about the intensity of the signal and the intensity of the noise at various times in the FID. How does the S/N change during the data acquisition? Where is the highest S/N, where is the lowest? And finally think about how the acquisition time and the decay of the signal effect the resolution of the spectrum. If necessary, return to the first part of this document and review some of the discussion there.

Fourier Transforms: Fourier transform the FID to generate a frequency domain signal, the spectrum. The denominator in this expression normalizes the intensity of the spectrum.

$$F_{\text{Observed}} := \frac{\text{fft}(\text{FID}_{\text{Observed}})}{\max(\text{Re}(\text{fft}(\text{FID}_{\text{Observed}})))} \quad F := \frac{\text{fft}(\text{FID})}{\max(\text{Re}(\text{fft}(\text{FID})))}$$

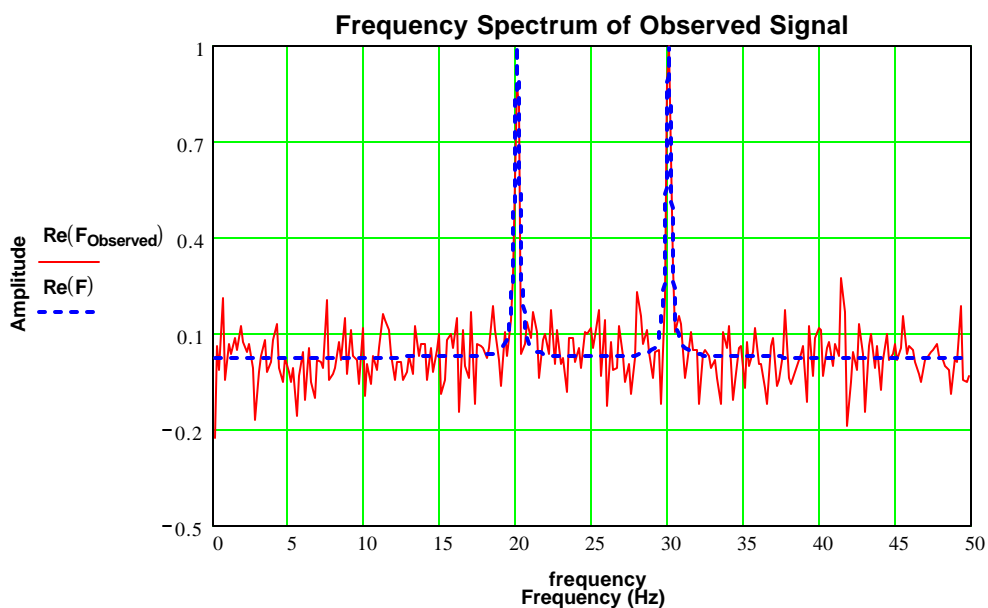
Signal to Noise Ratio: The two effects we are looking for in the spectra are changes in the S/N and changes in the resolution of the experiments. You can observe changes in the resolution by looking at the spectra and zooming in on the peaks. For the S/N it is more meaningful to calculate the S/N. This is simply the maximum signal (which will be 1 for these examples) divided by the standard deviation of the baseline. The following function will perform this calculation for a spectrum X. Set the signal frequencies to 20 Hz and 30 Hz.

The function is set to use the first 1/4 of the spectrum where no signal is observed. Adjust these values if needed.

$$\text{SN}(X) := \frac{1}{\text{stdev}\left(\text{submatrix}\left(X, 0, \frac{N}{8}, 0, 0\right)\right)} \quad N = 512$$

$$\text{SN}(F_{\text{Observed}}) = 9.095$$

Finally graph the observed spectrum and the signal together.



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$$\text{SN}(F_{\text{Observed}}) = 9.095$$

Now, let's look at how the data acquisition parameters effect the S/N and the resolution of the spectrum. The first effect to investigate is what happens to the S/N as the acquisition time changes. Zoom in on the spectrum above so that you can observe the change in the resolution. Choose a convenient reference point to measure the peak width, typically the width of the peak at half height or 10% of the peak height is used for determining the resolution. You may want to turn on the gridlines in the graph to help with this. Now change the number of data points, try 2^6 , 2^7 , 2^8 , 2^9 , 2^{10} , 2^{11} , 2^{12} (Edit; Go to Page; 3). What acquisition time results in the best resolution? What acquisition time results in the best S/N? Look at the FID and think about what effects the S/N and the resolution. Briefly describe the tradeoff involved here. When you are done, reset the number of data points to 2^9 .

Zero Fill: The above discussion leads to an interesting idea. If we know that at a certain time 95% of the signal has decayed, what would happen if we just add zeros to the end of the FID? How would this effect the resolution and the S/N of the spectrum?

Zero filling is a data processing technique where zero's are simply added to the end of the FID. Since the number of data points in the FID must be kept as a binary number (2^n) the number of points in the FID must be increased by multiples of two. For one zero fill, the number of data points doubles. For two zero fills, the number quadruples. Let's take a look and see what effect this has on the spectrum.

Number of zero fills: **ZF := 1**

This next section creates a new data array, the corresponding time and frequency indexes, and the normalized spectrum..

Create zero array: $k := 0, 1.. (N) \cdot (2^{ZF} - 1) - 1$ $zero_k := 0$

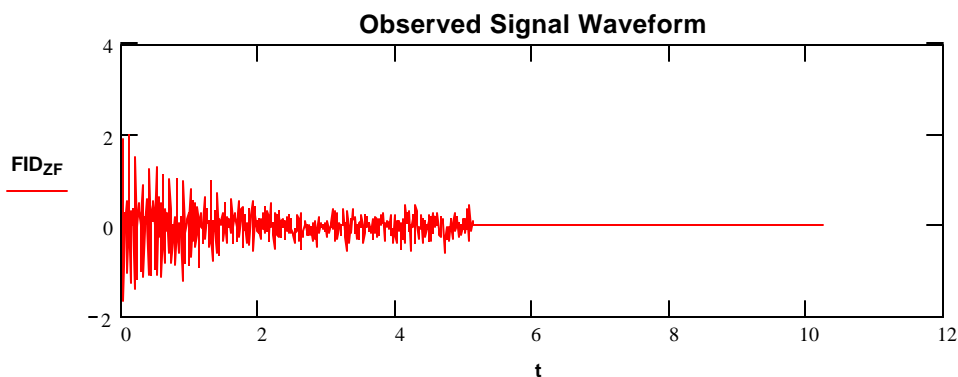
Reset indexes and data array:

$$N := N + (N) \cdot (2^{ZF} - 1) \quad i_{zf} := 0, 1.. (N - 1) \quad j_{zf} := 0, 1.. \left(\frac{N}{2} - 1 \right) \quad t_{i_{zf}} := i_{zf} \cdot DW$$

$$frequency_{j_{zf}} := \frac{j_{zf}}{N \cdot DW}$$

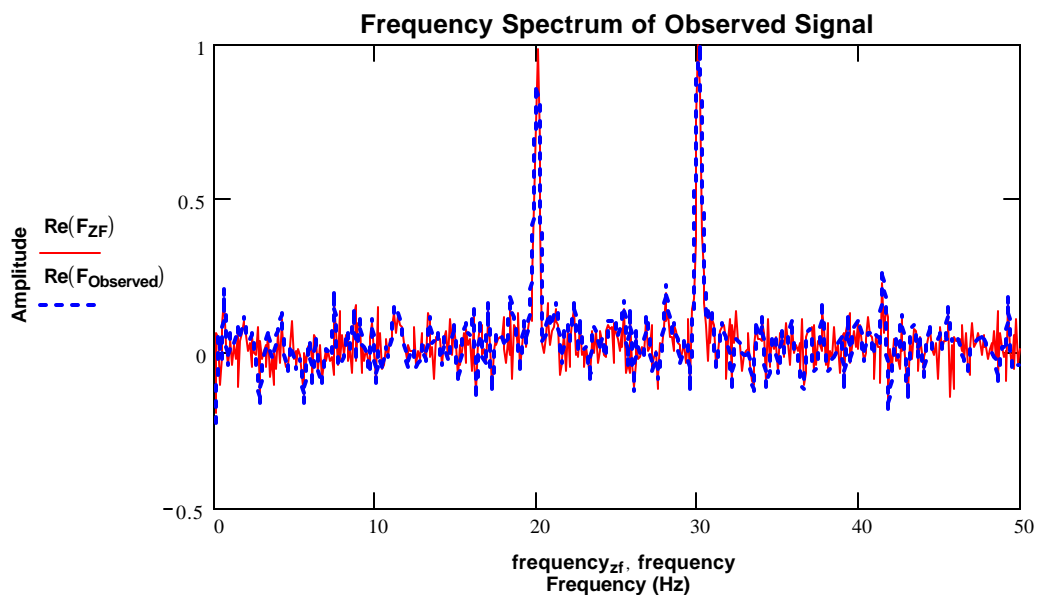
$$FID_{ZF} := stack(FID_{Observed}, zero) \quad F_{ZF} := \frac{fft(FID_{ZF})}{\max(\text{Re}(fft(FID_{ZF})))}$$

Graph the zero filled FID. Notice the changes in the axis and the apperance of the data. Based upon the change in the x-axis, what effect do you expect zero filling to have on the spectrum?



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Graph the real components of the observed spectrum, F_{Observed} , and the zero filled spectrum F_{ZF} . Calculate the S/N (using the SN function defined above).



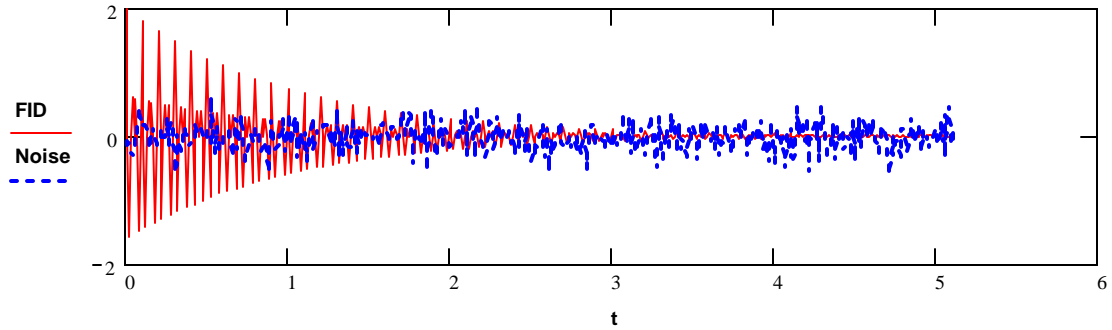
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$$\text{SN}(F_{\text{ZF}}) = 10.7$$

$$\text{SN}(F_{\text{Observed}}) = 9.1$$

Zoom in on the spectrum above so that you can see how wide the peaks are. Choose a convenient reference point to measure the peak width, typically the width of the peak at half height or 10% of the peak height are used for determining the resolution. You may want to turn on the gridlines in the graph to help with this. What effect did the zero fill have on the spectrum? Change the number of zero fills and see what happens. Is there a practical limit to any improvements that you can make? Are there any tradeoffs involved? Use the "Math", "Calculate Worksheet" to regenerate all the random noise. Now change the number of data points, try 2^6 , 2^7 , 2^8 , 2^9 , 2^{10} , 2^{11} , 2^{12} (Edit; Go to Page; 3). How does the zero fill change the acquisition time that results in the best resolution? How does the zero fill change what acquisition time results in the best S/N? Look at the FID and think about what effects the S/N and the resolution. Briefly describe the tradeoff involved here. When you are finished reset the number of data points to 2^9 .

Exponential Multiplication: The next signal processing technique involves the use of apodization, sometimes called a window function. Here the FID is multiplied by a mathematical function which will enhance some part of the signal. The simplest of these functions is an exponential decay. To see why this is useful, look at a graph with both the FID and the noise.



Notice that the FID is decaying and keep in mind that this is the signal. The signal decays exponentially with a rate $1/T$. Look at the function when it is defined at the beginning of the document. Does the noise decay? Compare the S/N is at the beginning of the FID and the S/N at the end of the FID. When is the S/N greatest? When is the S/N the lowest?

In exponential multiplication the FID is multiplied by an exponential decay. The rate for this function is called the line broadening factor. Let's begin with $LB=1$ Hz.

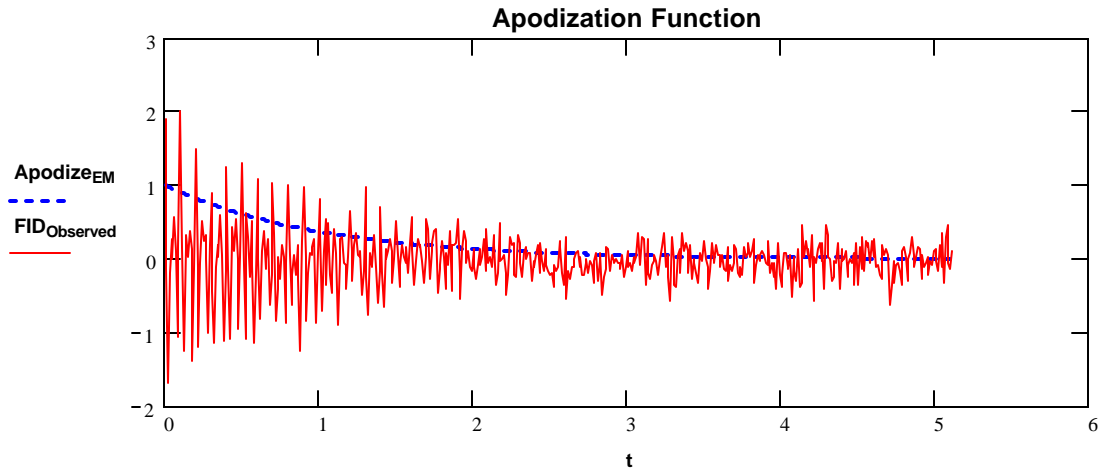
Line Broadening Factor

$$LB := 1 \cdot \text{Hz}$$

Calculate Apodization Function:

$$\text{Apodize}_{EM_i} := e^{-t_i \cdot LB}$$

Graph the apodization function and the observed FID:

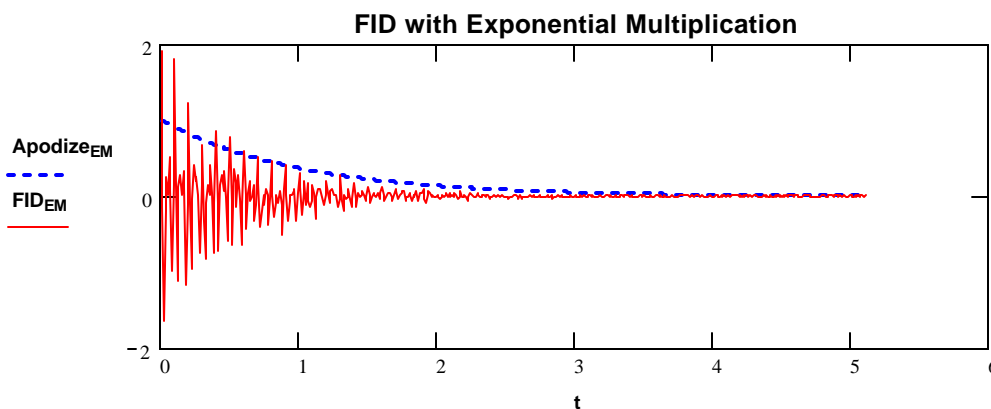


Calculate and Transform Apodized Waveform:

$$FID_{EM_i} := FID_{Observed_i} \cdot Apodize_{EM_i}$$

$$F_{EM} := \frac{fft(FID_{EM})}{\max(\text{Re}(fft(FID_{EM})))}$$

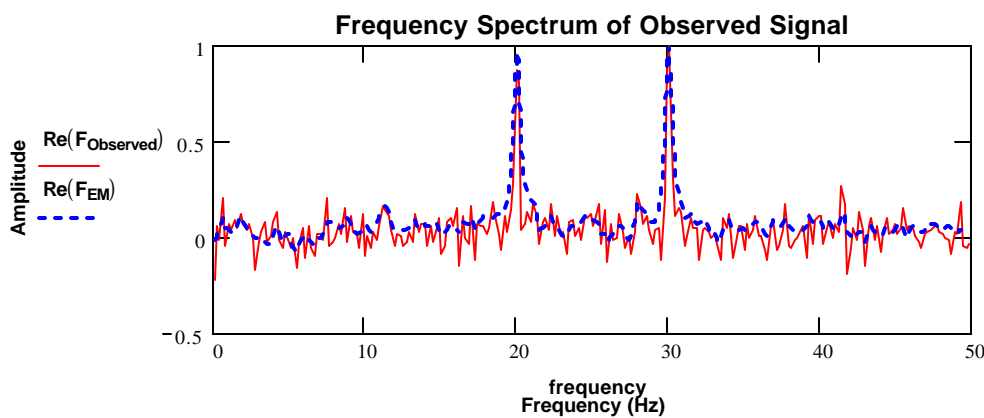
Graph the apodization function and the apodized FID.



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Notice how the exponential multiplication has changed the FID. Go back and change the line broadening, try values of 0.1, 0.5, 1, 2, and 5. How does this effect the FID? Thinking about the S/N of the FID at different times, how do you expect this apodization to effect the S/N of the spectrum? Based upon what determines the resolution of the spectrum, how do you expect this function will effect the resolution of the spectrum?

Next let's see how this apodization effects the spectrum and the S/N



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$$SN(F_{EM}) = 13.822$$

$$SN(F_{Observed}) = 9.095$$

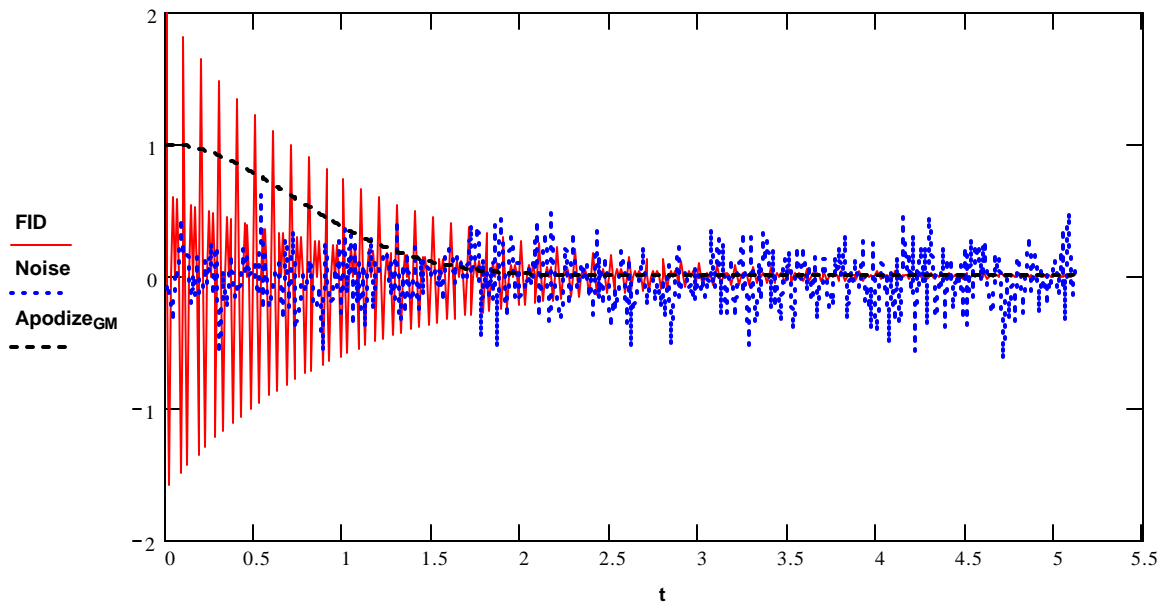
Change the line broadening and see how this effects the S/N and resolution of the spectrum. Zoom in and use the grid to help with your comparisons. Is there an optimum value? What tradeoffs are involved? Try a matched filter where the line broadening is equal to the relaxation rate, $1/T$.

Gaussian Multiplication: There are many other functions that are used to enhance the signal for NMR Spectra. In Gaussian Multiplication, the FID is multiplied by one side of gaussian curve. The line broadening in this case is the standard deviation of a gaussian distribution.

Line Broadening: **LB := 1 · Hz**

Calculate Apodization Function: **Apodize_{GM_i} := e^{-[(t_i · LB)²}**

Look at a graph of the FID, the noise and the gaussian function. Change the line broadening, what effect do you expect this function to have on the spectrum?

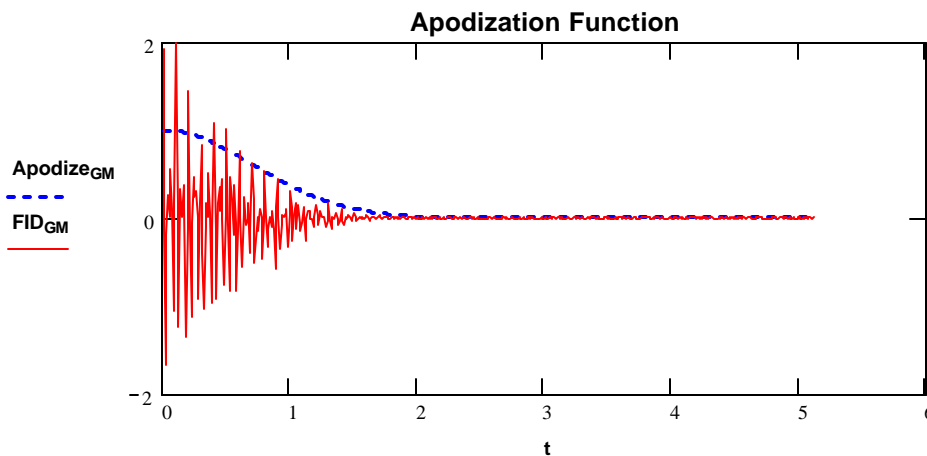


Calculate Apodized Waveform:

$$FID_{GM_i} := FID_{Observed_i} \cdot Apodize_{GM_i}$$

$$F_{GM} := \frac{fft(FID_{GM})}{\max(\text{Re}(fft(FID_{GM})))}$$

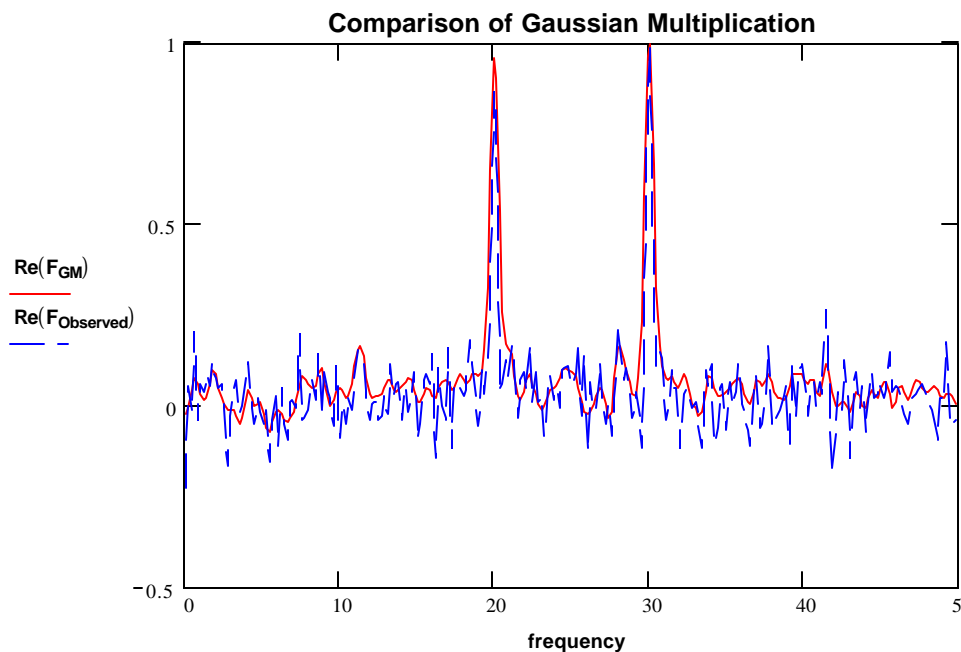
Graph the apodization function and the apodized FID.



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Notice how the gaussian multiplication has changed the FID. Go back and change the line broadening, try values of 0.1, 0.5, 1, 2, and 5. How does this effect the FID? Thinking about the S/N of the FID at different times, how do you expect this apodization to effect the S/N of the spectrum? Based upon what determines the resolution of the spectrum, how do you expect this function will effect the resolution of the spectrum?

Next let's see how this apodization effects the resolution and S/N of the spectrum.



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$$SN(F_{GM}) = 13.892$$

$$SN(F_{Observed}) = 9.095$$

Change the line broadening and see how this effects the S/N and resolution of the spectrum. Zoom in and use the grid to help with your comparisons. Is there an optimum value? What tradeoffs are involved?

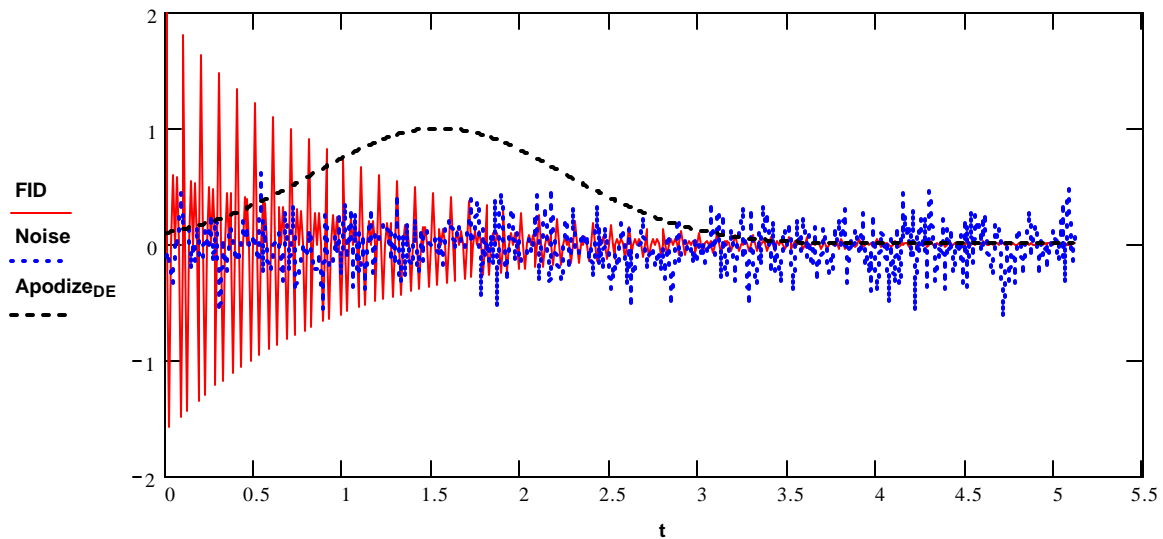
Double Exponential Multiplication: Double exponential multiplication is a variation on the gaussian multiplication discussed above. The difference is that the function does not just use one side of a gaussian distribution. In the double exponential multiplication, the curve is offset so that the maximum is not at time zero in the FID. Two variables are required to define this curve. The line broadening, LB, is the same as above. It is related to the standard deviation of the curve. The other factor is the gaussian multiplication factor, GM, which determines where in the FID the maximum occurs. A value of 0 for GM is equivalent to the Gaussian function used above with the maximum at 0 on the FID. A value equal to 1 sets the maximum at the end of the FID. A value of 0.5 sets the maximum at the center of the FID.

Line Broadening Factor: **LB := 1 · Hz**

Gaussian Multiplication Factor: **GM := .3**

Calculate Apodization Function: **Apodize_{DE_i} := e^{-[[((t_i) · LB)] - GM · LB · AT]²}**

Look at a graph of the FID, the noise and the double exponential function. Change the line broadening and the gaussian multiplication factor, what effect do you expect each of these variables to have on the S/N and resolution of the spectrum?

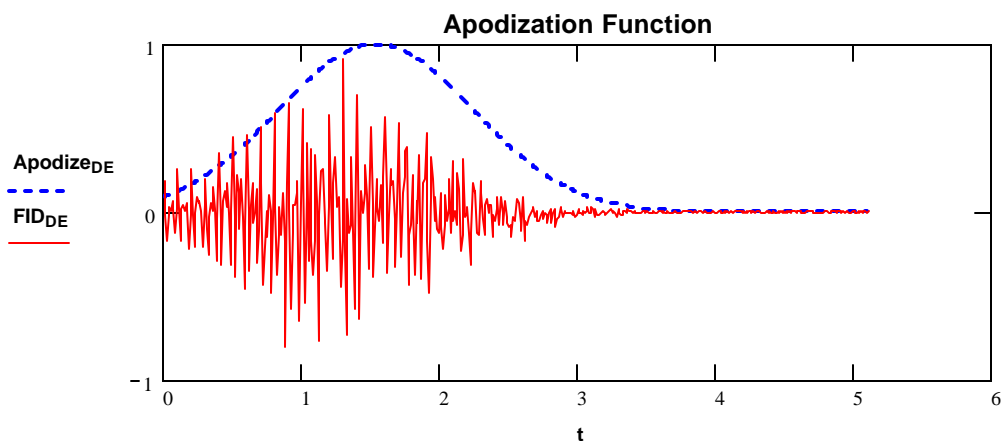


Calculate Apodized Waveform and FT:

$$FID_{DE_i} := FID_{Observed_i} \cdot Apodize_{DE_i}$$

$$F_{DE} := \frac{fft(FID_{DE})}{\max(\text{Re}(fft(FID_{DE})))}$$

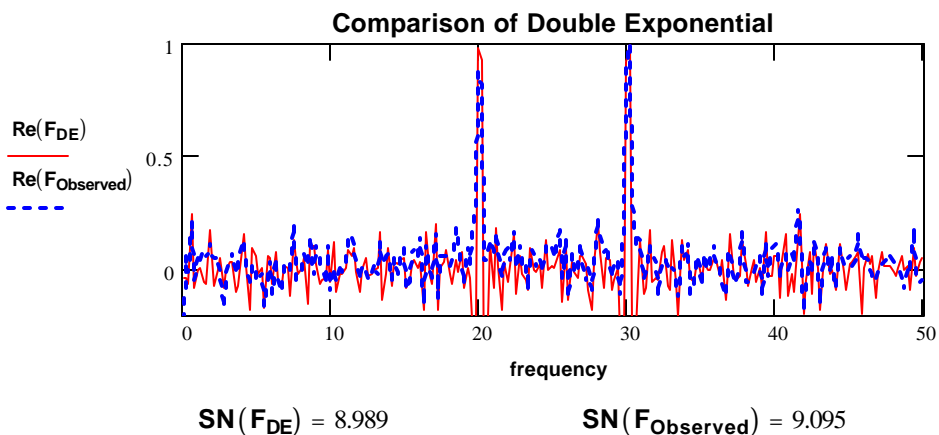
Graph the apodization function and the apodized FID.



Remove graph for student version

Notice how the double exponential multiplication has changed the FID. Go back and change the line broadening and the gaussian multiplication factor, try values of 0.1, 0.5, 1, 2, and 5 for the line broadening. Values of 0, 0.2, 0.5, 0.7 and 1 for GM. How do these effect the FID? Thinking about the S/N of the FID at different times, how do you expect this apodization to effect the S/N of the spectrum? Based upon what determines the resolution of the spectrum, how do you expect this function will effect the resolution of the spectrum?

Next let's see how this apodization effects the S/N and resolution of the spectrum.



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Change the line broadening and GM variables again. How do they each effect the S/N and resolution of the spectrum. Zoom in and use the grid to help with your comparisons. Is there an optimum value for each variable? What tradeoffs are involved?

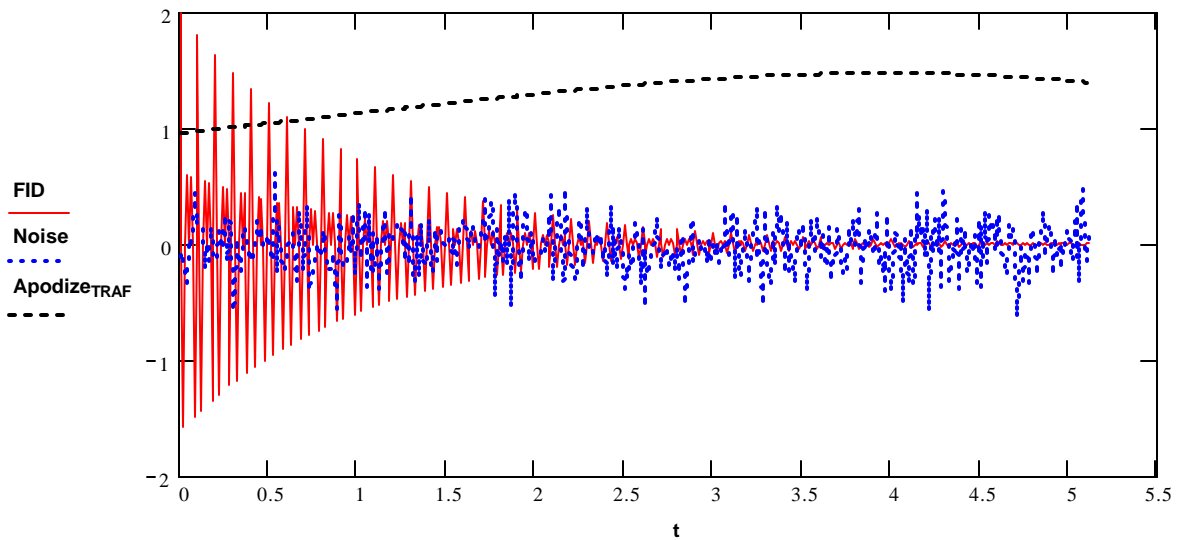
TRAF Function for Resolution Enhancement: In the previous apodization functions you will have noticed that there is a tradeoff between resolution and S/N. Also in the double exponential function there are two variables that must be adjusted to optimize the trade off between S/N and resolution in the spectrum. The TRAF Function for resolution enhancement has a single variable. This function is designed to enhance the resolution without reducing the S/N. In addition to the resolution function given here, there is another version of the TRAF function that is designed to optimize the S/N of the spectrum without reducing the resolution.

Line Broadening Factor:

$$LB := 0.2 \cdot Hz$$

Calculate Apodization Function:

$$Apodize_{TRAF_i} := \frac{[e^{-(t_i) \cdot LB}]^2}{[e^{-(t_i) \cdot LB}]^3 + [e^{-(AT) \cdot LB}]^3}$$

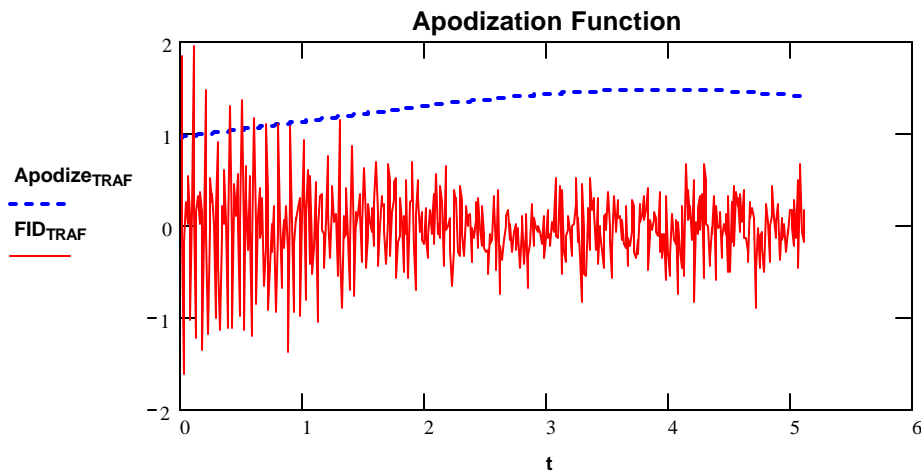


Calculate Apodized Waveform and FT:

$$FID_{TRAF_i} := FID_{Observed_i} \cdot Apodize_{TRAF_i}$$

$$F_{TRAF} := \frac{fft(FID_{TRAF})}{\max(\text{Re}(fft(FID_{TRAF})))}$$

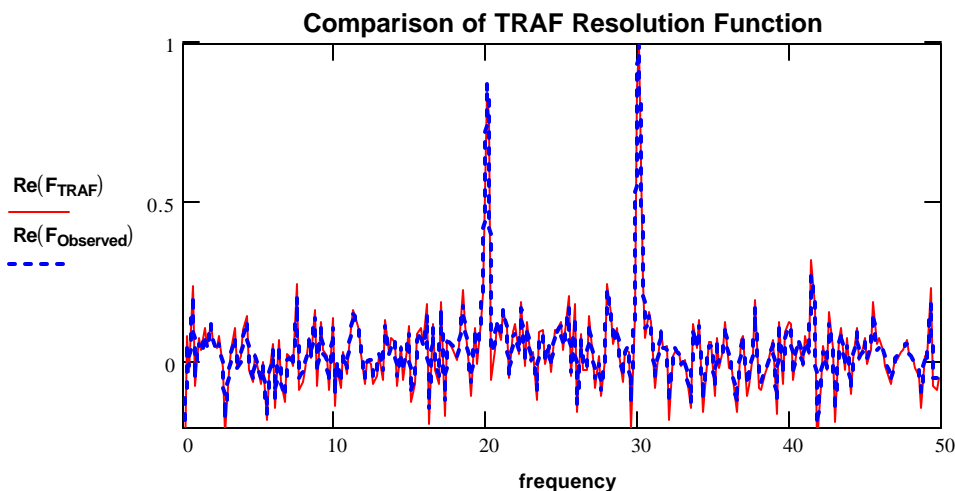
Graph the apodization function and the apodized FID.



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Notice how the TRAF function has changed the FID. Go back and change the line broadening, how does this effect the FID? Thinking about the S/N of the FID at different times, how do you expect this apodization to effect the S/N of the spectrum? Based upon what determines the resolution of the spectrum, how do you expect this function will effect the resolution of the spectrum?

Graph the spectrum and calculate the S/N.



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$$SN(F_{TRAF}) = 7.509$$

$$SN(F_{Observed}) = 9.095$$

Next let's see if this apodization function lives up to the claim of improving the resolution without reducing the S/N. Zoom in on the spectrum and add gridlines. Change the line broadening and see how this effects the spectrum. Is there an optimum value? What tradeoffs are involved? Can you improve the resolution without reducing the S/N?

Mastery Exercise

The tradeoffs between S/N and resolution are different in proton and carbon spectra. In general, resolution is the limiting factor for proton spectra and S/N is the limiting factor for carbon spectra. For a typical NMR experiment protons are observed in a 12 ppm window, while carbons are observed over a range of 220 ppm. The chemical shift scale in nmr δ , is used to account for differences in the magnetic field strength of different instruments. The chemical shift is calculated as:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_{\text{reference}}} \cdot 10^6 \text{ ppm}$$

In a 7 tesla magnet, protons are observed at approximately 300 MHz, so that a 12 ppm window corresponds to a frequency range of:

$$\Delta \nu_{\text{proton}} := \frac{12 \cdot 300 \cdot \text{MHz}}{10^6}$$

$$\Delta \nu_{\text{proton}} = 3600 \text{ Hz}$$

In this same magnet, carbon would be observed at approximately 75 MHz. Calculate the frequency range required for a 220 ppm spectral window.

Based upon this information, outline the data acquisition parameters that need to be adjusted for optimum acquisition of proton and carbon spectra.

What data processing techniques are appropriate to use for proton and carbon spectra?

References and suggested reading

Sanders, Jeremy K.M.; Hunter, Brian K. *Modern NMR Spectroscopy A Guide for Chemists* Oxford: New York, 1993.

Abraham, R.J.; Fisher, J.; Loftus, P *Introduction to NMR Spectroscopy* Wiley: New York, 1988.

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S.E. Van Bramer. *J. Chem. Educ.*, **1999**, *76*, 286

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Acknowledgments

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