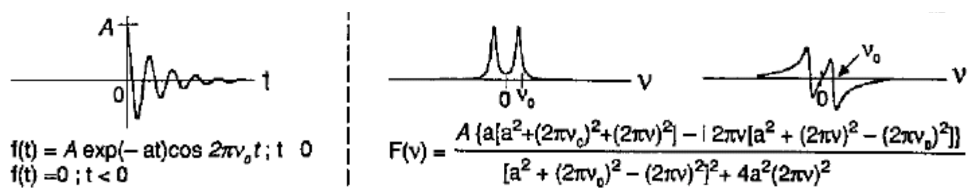
Chemistry 620
Analytical Spectroscopy
PROBLEM SET 7: Due 04/08/08

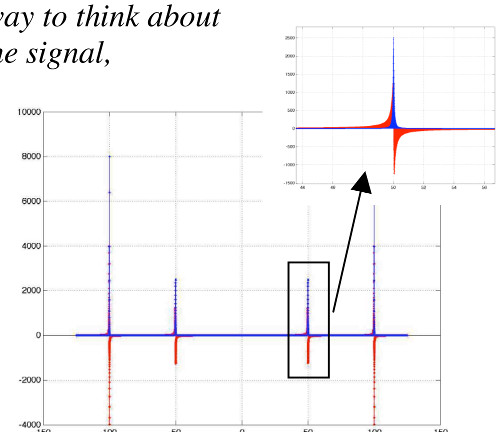
1. Predict the Fourier transform of the following signal if the sampling frequency is 250 Hz and the acquisition period is 200 sec –

   $f(t) = 5\exp(-t/4)\cos(50\pi\ t)+4\exp(-t/16)\cos(100\pi\ t)$

   Since f(t) is the composed of decaying cosines, we know the basic form of the transforms: the real part will be Lorenztian lines (absorption line shape) broadened by the exponential decay shifted to v0 (v_0=50 Hz & v_0=100 Hz) to reflect the contribution of the cosine term; the imaginary part is the dispersion lineshape (broad, zero-crossing function with peaks at v0) shifted to cross the "y-axis" at $\pm v_0$. The basic components of the signal are shown below.

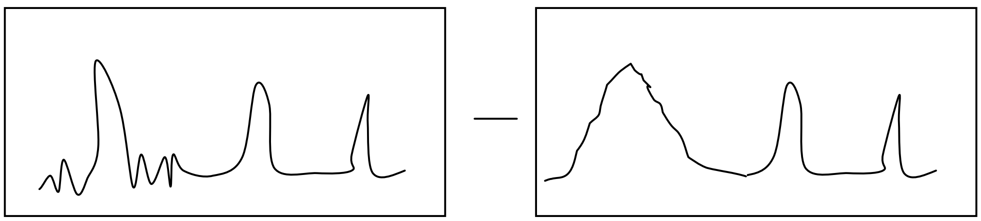


   In this case, there are contributions from signals at two frequencies and the amplitudes of the signals are 5 to 4. The question is 'how do the sampling rate and acquisition time impact the transforms?' The sampling frequency (250 Hz – a point every 4 ms) limits the Nyquist frequency (highest unaliased signal frequency) to 125 Hz. As long as the true frequency is below the Nyquist frequency, as it is in both signal components, the positions of the peaks in the transforms are accurate. The acquisition period (time) truncates the continuous (time-domain) signal and convolutes its transform with the sinc function. The narrower the acquisition time, the broader the transform (sinc) and the larger the impact on the signal transform. Another way to think about it is that a short acquisition time cuts off the signal, introduces sharp edges to the time domain signal and a rippled baseline to the transform. The signal acquisition period is more than 7 times longer than the longer decay time, after the signals have decayed to almost zero, so the acquisition period does not introduce large sharp edges to the time domain signal. The transform of the signal is the sum of the transforms of the two components sampled every 4 ms.



2. Sketch the spectrum you would expect to observe if a signal comprised of three oscillations were being sampled at a rate more than two times the frequency of the fastest component but the acquisition time was so short that the amplitude of the slowest oscillation stayed high. Describe how you would correct this problem and what sketch the corrected spectrum.

   When the FID acquisition time is short enough to truncate a signal before the relaxation (decay) processes are complete, ripples in the baseline (sinc function) occur at frequencies close to band frequency and distort the shape of the spectral bands. This means that the bands in the spectrum will be distorted (the spectrum isn't really crooked, it's just hard to draw free hand in WORD) by sinc waves especially at

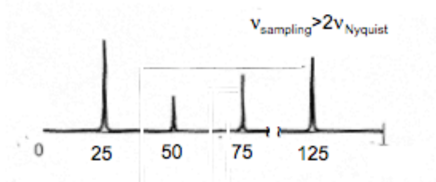
   the low frequency end of the spectrum. This problem can be addressed using apodization functions to reduce the baseline oscillations. The trade-off is in the width of the apodized band.

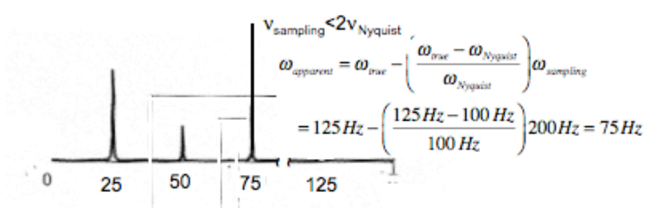
3. A spectrum has resonances at 25, 50, 75 and 125 Hz. The relative amplitudes of the resonances are 1:2:1:5. How many points do you estimate the time domain sequence should have in order to measure all the components accurately? How long is the interval between acquisitions. Predict the spectrum that would be observed if the interferogram were sampled at 200 Hz. What is the Nyquist frequency at this rate?

$$\#\,slowest\ cycle = 25\tfrac{cyeles}{s} / 250\tfrac{pts}{s} = 0.1\tfrac{cycles}{s}$$

$$T_{acq} = 1 cycle / 0.1\tfrac{cycles}{s} = 10s$$

$$N_{pts} = 250\tfrac{pts}{s} \times 10s = 2500\,pts$$





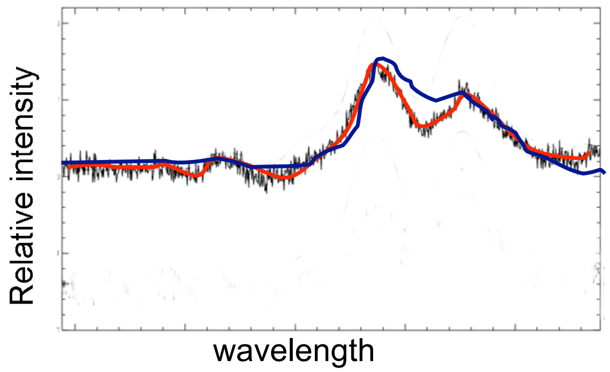
4. Use a computer to calculate the entire discrete convolution of the following pair of sequences, but list which sums contribute to each term of the convolution in a table. f(t) = [0 0.05 0.10 0.15 0.20 0.15 0.10 0.05 0]; h(t) = [0 0 0 1 1 1 0 0 0];

h(k-i) = [0 0 0 1 1 1 0 0 0]; f(5:13) = [0 0.05 0.10 0.15 0.20 0.15 0.10 0.05 0];

i	$g(i)=\sum_{k=1}^{19} h(k-i)f(k)=\left[\sum_{k-i=-1}^{1} h(k-i)f(k)\right]_{i=4}^{i=14}$	g(i)
4	h(3 - 4) f (3) + h(4 - 4) f (4) + h(5 - 4) f (5) 0•1 + 0•1 + 0•1	0
5	h(4 - 5) f (4) + h(5 - 5) f (5) + h(6 - 5) f (6) 0•1 + 0•1 +0.05•1	0.05
6	h(5 - 6) f (5) + h(6 - 6) f (6) + h(7 - 6) f (7) 0•1 + 0.05•1 +0.10•1	0.15
7	h(6 - 7) f (6) + h(7 - 7) f (7) + h(8 - 7) f (8) 0.05•1 +0.10•1 + 0.15•1	0.30
8	h(7 - 8) f (7) + h(8 - 8) f (8) + h(9 - 8) f (9) 0.10•1 + 0.15•1 + 0.20•1	0.45
9	h(8 - 9) f (8) + h(9 - 9) f (9) + h(10 - 9) f (10) 0.15•1 + 0.20•1 + 0.15•1	0.50
10	h(9 - 10) f (9) + h(10 - 10) f (10) + h(11 - 10) f (11) 0.20•1 + 0.15•0 + 0.10•1	0.45
11	h(10 - 11) f (10) + h(11 - 11) f (11) + h(12 - 11) f (12) 0.15•1 + 0.10•1 + 0.05•1	0.30
12	h(11 - 12) f (11) + h(12 - 12) f (12) + h(13 - 12) f (13) 0.10•1 + 0.05•1 + 0•1	0.15
13	h(12 - 13) f (12) + h(13 - 13) f (13) + h(14 - 13) f (14) 0.05•1 + 0•1+ 0•1	0.05
14	h(13 - 14) f (13) + h(14 - 14) f (14) + h(15 - 14) f (15) 0•1+ 0•1+0•1	0

5. Chi describes what happens when a signal is improperly filtered. Use similar concepts to predict and compare the results of using rectangular and Gaussian frequency domain filters of similar widths to filter a noisy spectrum, such as the one shown below. It is important that you draw the noisy spectrum and realize that a spectrum can have a forward transform in which the frequency content of the spectrum is measured.

   Rectangular frequency domain filters remove all frequency contributions above a cutoff frequency; baseline oscillations are likely. Gaussian filters reduce the amplitude of high frequency components slowly, producing smoother baselines. The resolution is also lower compared to the spectrum produced by the rectangular filter.



6. Write an expression for the variance of an absorbance measurement. In other words identify which types of noise distort a typical absorbance measurement. How will this expression change for samples that have very small absorbances?

$$\sigma_A^2 = \left(A \frac{-\sigma_T}{T \ln T} \right)^2 = \left(0.43 \frac{\sigma_T}{T} \right)^2 = 0.185 \frac{\sigma_T^2}{T^2}$$

$$= 0.185 \frac{\sigma_{sample}^2 + \cancel{\sigma_{reference}^2} + \sigma_{0\%T}^2}{T^2}$$

$$= 0.185 \frac{\left(\sigma_{signal}^2\right)_{shot} + \left(\sigma_{signal}^2\right)_{flicker} + \sigma_{dark}^2 + \sigma_{ar}^2}{T^2}$$

In an absorbance measurement, the difference in transmittance for the sample and reference are measured. Assuming that the noise produced by the measuring the reference is smaller than that arising from the sample measurement. The variance of the transmittance has fundamental (shot) and non-fundamental (flicker) components and the 0%T measurement is a measurement of the instrument noise that is not source dependent. This expression assumes no contribution from background emission. When the absorbance is small the reference signal and sample signal have similar magnitudes. In this case, this approximation would not be valid; contributions from both sample and reference would be comparable:

$$= 0.185 \frac{\left(\left(\sigma_{signal}^2\right)_{shot} + \left(\sigma_{signal}^2\right)_{flicker}\right)_{sample} + \left(\left(\sigma_{signal}^2\right)_{shot} + \left(\sigma_{signal}^2\right)_{flicker}\right)_{reference} + \sigma_{dark}^2 + \sigma_{ar}^2}{T^2}$$

7. Summarize the basics of using source modulation for signal enhancement and explain what distinguishes it from using a lock-in amplifier to enhance the signal.

   In amplitude modulation techniques, the analytical signal is translated from DC (frequency = 0) which is subject to flicker and shot noise, is ***translated to a "quiet'*** *frequency range at which frequency dependent noise and interferences are low. This is accomplished by imposing a frequency on the signal either by varying the amplitude of the electrical signal stimulating the source or by inserting a chopper into optical path (more common). An important variation of this idea is lock-in-amplification. The noisy modulated carrier signal is detected by* ***a phase sensitive detector****, i.e. a detector to which an oscillation at the same frequency as the carrier signal. A low pass filter demodulates (removes the oscillations) from the product in which the signal is enhanced relative to the noise because the noise includes frequencies other than the reference. Modulation techniques improve S/N when signals are corrupted by low frequency additive (rather than multiplicative) noise that is not picked up by the carrier wave.*

8. Construct a table that shows the size of the signal and noise in spectra that consist of 1, 10 and 100 equal height bands dispersed across 100 detector elements if they were distorted by shot and flicker noise, respectively. Use these expressions to compute the enhancement for each spectrum/noise combination measured using a multichannel detector.

		Single channel detector			Multichannel detector			
Noise	# bands	signal	noise	S/N	signal	noise	S/N	factor
shot	1	s	$\sqrt{s}$	$\sqrt{s}$	100s	$10\ \sqrt{s}$	$10\ \sqrt{s}$	10
	10	s	$\sqrt{s}$	$\sqrt{s}$	100s	$\sqrt{1000s}$	$\sqrt{10s}$	$\sqrt{10}$
	100	s	$\sqrt{s}$	$\sqrt{s}$	100s	$100\sqrt{s}$	$\sqrt{s}$	1
flicker	1	s	χs	$1/\chi$	100s	$100\chi s$	$1/\chi$	1
	10	s	χs	$1/\chi$	100s	$10^3\chi s$	$1/10\chi$	1/10
	100	s	χs	$1/\chi$	100s	$104\chi s$	$1/100\chi$	1/100

factor = enhancement, Notice that some "enhancements" are smaller than 1.