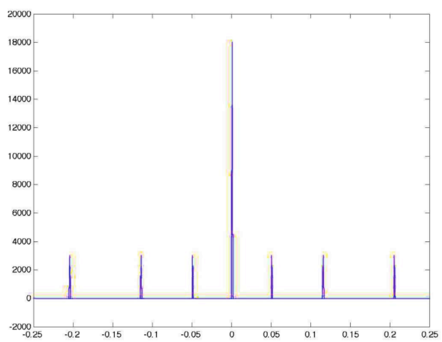
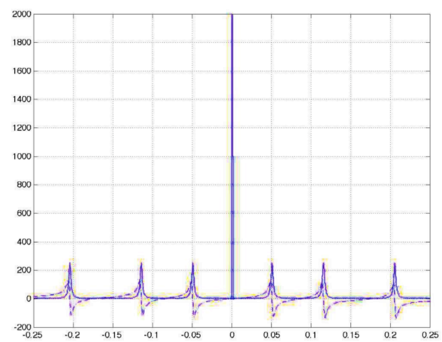
Chemistry 620
Analytical Spectroscopy
PROBLEM SET 6: Due 03/27/08

1. Use graph paper or computer to sketch the spectra of the interferograms depicted in Figure 8.2 of *Chi*. Label and briefly explain your graph.

$$I(\Delta z) = I_0\left(1 + \sum_k f_k \cos(k_i \Delta z)\right) = 3 + 1\cos(\frac{2\pi}{20}\Delta z) + 1\cos(2.3\frac{2\pi}{20}\Delta z) + 1\cos(4.1\frac{2\pi}{20}\Delta z)$$
$$= 3 + 1\cos(\frac{4\pi}{20}\mathrm{v}_{MM}t) + 1\cos(\frac{4\pi}{8.7}\mathrm{v}_{MM}t) + 1\cos(\frac{4\pi}{4.9}\mathrm{v}_{MM}t)$$
$$= 3 + 1\cos(2\pi \cdot 0.1 \cdot \mathrm{v}_{MM}t) + 1\cos(2\pi \cdot 0.230 \cdot \mathrm{v}_{MM}t) + 1\cos(2\pi \cdot 0.41 \cdot \mathrm{v}_{MM}t)$$





The spectra of the interferograms locate the frequencies of the harmonics comprising the the interferograms. The bands locations are the same, the widths of the bands in the spectra of the decaying interferogram are wider.

2. Write the Fourier transform of $\cos(\omega_0 t)\sin(\omega_0 t)$.

$$f(t) = \cos\omega_0 t \sin\omega_0 t = \tfrac{1}{2}\left(\sin 2\omega_0 t\right)$$
$$\hat{F}(\omega) = \int_{-\infty}^{\infty} \frac{1}{2}\left(\sin 2\omega_0 t\right) e^{-i\omega t} dt$$
$$= \frac{1}{2}\int_{-\infty}^{\infty} \left(e^{-i\omega t} \sin 2\omega_0 t\right) dt$$
$$= \frac{1}{2}\left[\frac{i}{2}\left[\delta\left(\omega - 2\omega_0\right) - \delta\left(\omega - 2\omega_0\right)\right]\right]$$

3. Explain why narrow pulses in one domain correspond to broad spectra in the domain of the conjugate variable.

Harmonics at different frequencies are mutually orthogonal (their overlap integrals are zero) so the only way to produce a spike at time t is to use many harmonics of different frequency that have their maximum value at time t. The more oscillations *that are combined, the more **destructive interference** occurs on either side of the point at t and the narrower the resultant band.*

4. Explain the relevance of the sinc function to spectral measurements. In other words, explain how baseline oscillations described by sinc waves occur in experimental spectra.

   The sinc function is the FT of the boxcar function. Whenever a spectroscopic signal is truncated in the time domain, it is the same as multiplying by a rectangle function of width T/2. The FT of the truncated signal is the convolution of the FT of the continuous spectroscopic signal and the sinc function. The shorter the rectangle window, the closer the ripples are to the transformed signal.

5. In the first week of class we saw that the frequency dependence of the refractive index of a dielectric is a complex quantity approximated by

$$n_{real} = D(\omega) = 1 + \frac{Ne^2}{m_e} \cdot \frac{\left(\omega_0^2 - \omega^2\right)}{\left(\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2\right)}$$

$$n_{imag} = A(\omega) = \frac{Ne^2}{m_e} \cdot \frac{2\gamma}{\left(\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2\right)}$$

   Revisit the derivation of these expressions, identify their inverse Fourier transforms and use them to explain what these expressions say about what happens to the electrons when radiation of frequency ω is launched into a dielectric.

   The FT of a decaying cosine is

$$F(e^{-\lambda t}\cos\omega_0 t) = \int_{t=0}^{T} \left(e^{-\lambda t}\cos\omega_0 t\right) e^{-i\omega t}dt = \int_{t=0}^{T} e^{-\lambda t}e^{-i\omega t} \cdot \cos\omega_0 t e^{-i\omega t}dt$$

$$= \int_{k}^{K} \frac{1}{-\lambda - i(\omega - k)} \cdot \frac{1}{2}\left[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)\right]dk$$

$$= \frac{1}{2}\left[\frac{1}{-\lambda - i(\omega-\omega_0)} + \frac{1}{-\lambda - i(\omega+\omega_0)}\right] = \frac{1}{2}\left[\frac{-\lambda + i(\omega-\omega_0)}{\lambda^2 + (\omega-\omega_0)^2} + \frac{-\lambda + i(\omega+\omega_0)}{\lambda^2 + (\omega+\omega_0)^2}\right]$$

$$= \frac{1}{2}\left[\frac{-\lambda + i(\omega-\omega_0)}{\lambda^2 + (\omega-\omega_0)^2} + \frac{-\lambda + i(\omega+\omega_0)}{\lambda^2 + (\omega+\omega_0)^2}\right] = A(\omega_0) + iD(\omega_0)$$

   *The frequency dependence of the real and imaginary refractive index is given by the complex components of the exponentially decaying cosine that describes the **displacement** of polarized electrons in the dielectric.*

6. In *Chi*, it says "All measurements don't end up being improved by Fourier transformation ..." List and discuss the reasons that more than 90% of the infrared absorption spectrometers sold in the world are Fourier transform instruments, but 90% of the UV/VIS absorbance spectrometers are dispersive.

UV/VIS measurements are often ***flicker (source or transmission) noise limited****, so signal averaging results in* ***a multiplex disadvantage*** *rather than the multiplex advantage observed when shot (detector in IR) noise limited data are signal averaged. This disadvantage is exacerbated when spectra are* ***broad or crowded*** *(as UV spectra often are) so there is no advantage and often a disadvantage to using FT methods to collect UV/VIS spectra. Secondly, the resolution of FT spectra is inversely proportional to the distance traveled by the mirror.* ***Longer travel distances*** *(smoother mirror bearings, better vibration isolation, larger instrument footprint) are required in the UV.*

7. Derive expressions that show that the Fourier transform of a unit impulse pulse train (period T) is also a unit impulse pulse train. Compute the pulse spacing in the frequency domain.

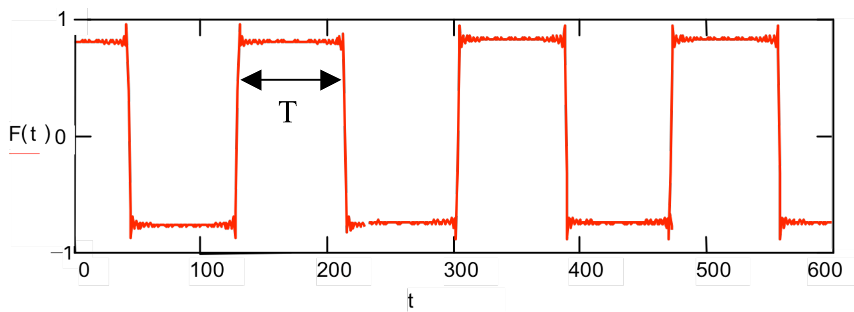
$$f(t) = \sum_n \delta(t - nT)$$

$$F(\omega) = \int_t \sum_n \delta(t - nT) e^{-i\omega t} dt = \int_t \frac{1}{T} \sum_n e^{in\frac{2\pi}{T}t} e^{-i\omega t} dt \text{ because } \frac{2\pi}{T} \text{ is train repetition rate}$$

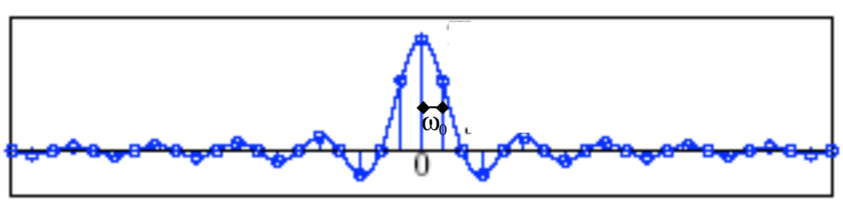
$$= \int_t \frac{1}{T} \sum_n e^{i(n\Omega - \omega)t} dt \, \frac{2\pi}{T} \sum_n \delta(\omega - n\Omega)$$

See: http://en.wikipedia.org/wiki/Dirac_comb

8. Use library functions and convolution ideas to predict the transform of a rectangular pulse train with the period and amplitude of the square wave in Figure 8.6.



Another way to describe the square wave is as the convolution of a rectangle function and pulse train (comb function). This means that the FT is the product of the sinc function and an inverse (frequency domain) pulse train. The frequency spacing of the pulse train is $w_0=\pi/T$.



http://courses.ece.ubc.ca/359/chapter4.pdf