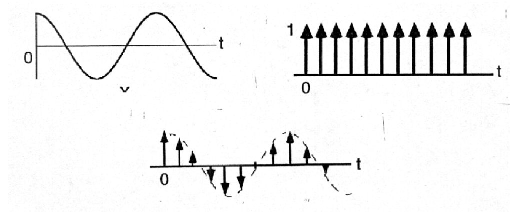
FT Spectroscopy



Fourier relations hold for discrete waveforms via series rather than integrals

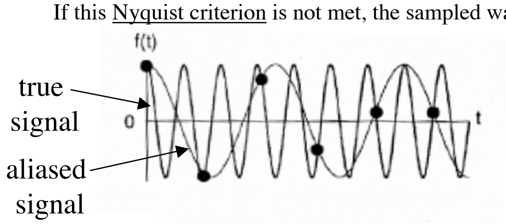
$$\bar{f}(\omega_m) = \sum_{n=0}^{N-1} f(t_n)\exp(-i\,\omega_m t_n)$$

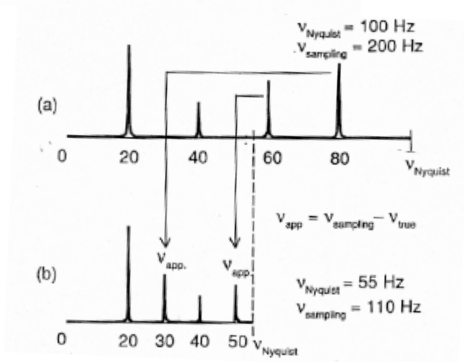
$$f(t_n) = \sum_{m=-(N/2-1)}^{N/2-1} \bar{f}(\omega_m)\exp(i\,\omega_m t_n)$$

$$F = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -i & -1 & i \\ 1 & -1 & 1 & -1 \\ 1 & i & -1 & i \end{bmatrix}$$

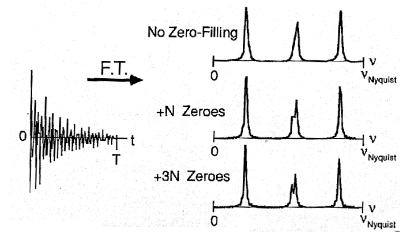
FT Spectroscopy

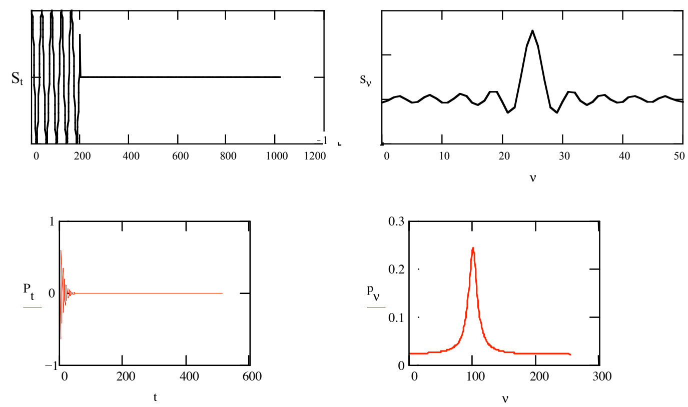
The discrete FT is accurate if highest constituent frequency of our signal f(t), ω_{max}, is sampled twice per cycle. If this Nyquist criterion is not met, the sampled waveform does not reflect ω_{max}:



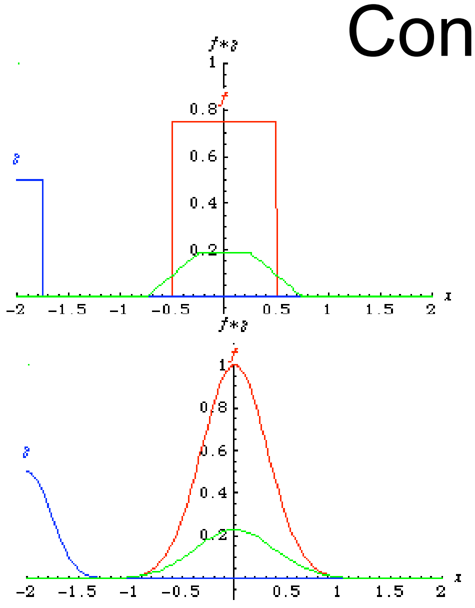


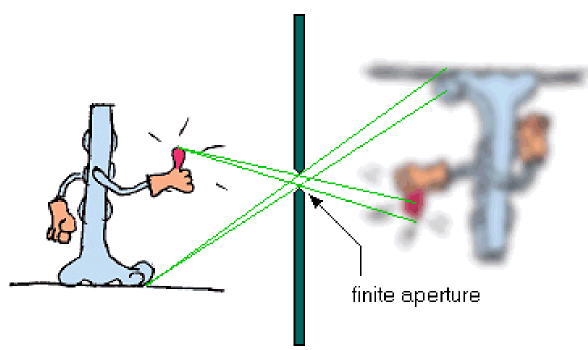
FT Spectroscopy





Convolution





http://mathworld.wolfram.com/Convolution.html

http://www.vias.org/tmdatanaleng/cc_convolution.html

$$g(i)=\sum_{k=1}^{k=11} h(k-i)f(k)=\sum_{k-i=-1}^{k-1=1} h(k-i)f(k)$$

k =		1	2	3	4	5	6	7	
Spectrum, f(k):				1	2	1			
Slit, h(i-7):							1	1	1
k-i							6-7	7-7	8-7
k-i							-1	0	1
Spectrum, f(k):				1	2	1			
Slit, h(i-6):						1	1	1	
k-i						5-6	6-6	7-6	
k-i						-1	0	1	
Spectrum, f(k):				1	2	1			
Slit, h(i-5):					1	1	1		
k-i					4-5	5-5	6-5		
k-i					-1	0	1		
Spectrum, f(k):				1	2	1			
Slit, h(i-4):				1	1	1			
k-i				3-4	4-4	5-4			
k-i				-1	0	1			
Spectrum, f(k):				1	2	1			
Slit, h(i-3):			1	1	1				
k-i			2-3	3-3	4-3				
k-i			-1	0	1				
Spectrum, f(k):				1	2	1			
Slit, h(i-2):		1	1	1					
k-i		1-2	2-2	3-2					
k-i		-1	0	1					
Spectrum, f(k):				1	2	1			
h(i-1):	1	1	1						
k-i	0-1	1-1	2-1						
k-i	-1	0	1						
Detector, g(i):		0	1	3	4	3	1	0	
i =		1	2	3	4	5	6	7	

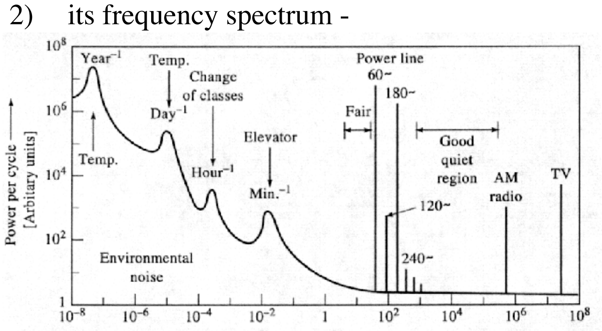
Noise

Noise are random fluctuations superimposed on the analytical signal. Noise is characterized by

1) its magnitude -

In the simplest settings (no background signal)

2) its frequency spectrum -



Skoog, Nieman, Holler, Principles of Instrumental Analysis, 1998, 5th Ed.

Noise

Noise are random fluctuations superimposed on the analytical signal. Noise also is characterized by

3) Its source -

Rem: variances are additive. So each noise source can be further analyzed.

Fundamental noise arises from the particle nature of EMR & matter.
Fundamental noise can never be totally eliminated; often independent of signal.
Non-fundamental noise arises from imperfect instrument components and conditions.
Can be eliminated (at least in principle). Usually proportional to signal.

$$\sigma^2_{signal} = \left(\sigma^2_{signal}\right)_{shot} + \left(\sigma^2_{signal}\right)_{flicker}$$

$$\sigma^2_{background} = \left(\sigma^2_{backgr}\right)_{shot} + \left(\sigma^2_{backgr}\right)_{flicker}$$

$$\sigma^2_{dark} = \left(\sigma^2_{dark}\right)_{shot} + \sigma^2_{xs} + \sigma^2_{\substack{amp\\ r/o}}$$

$$\frac{S}{N} = \frac{E_s}{\sqrt{\left(\sigma^2_s\right)_s + \left(\sigma^2_s\right)_f + \left(\sigma^2_b\right)_s + \left(\sigma^2_b\right)_f + \left(\sigma^2_d\right)_s \sigma^2_{xs} + \sigma^2_{\substack{amp\\ r/o}}}}$$

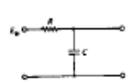
Shot: fundamental noise observed at current interfaces due to random nature of photon emission/arrival

Flicker: signal dependent non-fundamental noise

R/O: fundamental & NF noise in readout circuitry; includes shot, flicker(impurities) & quantization noise due to limited read-out resolution

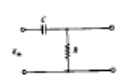
Signal to Noise Enhancement

2. Analog filters



$$v_o = v_i\left(\frac{iX_c}{\sqrt{i^2R^2 + i^2X_c^2}}\right)$$

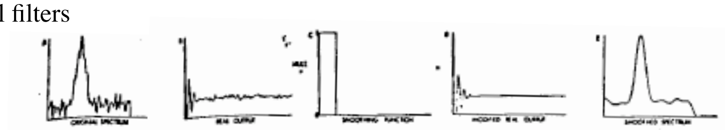
Low pass filter



$$v_o = v_i\left(\frac{iR}{\sqrt{i^2R^2 + i^2X_c^2}}\right)$$

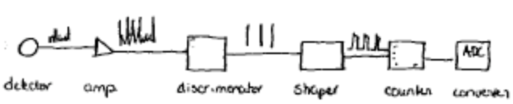
High pass filter

3. Digital filters

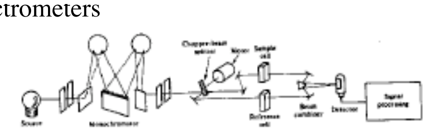


Applied in Time domain by convolution

4. Photon counting

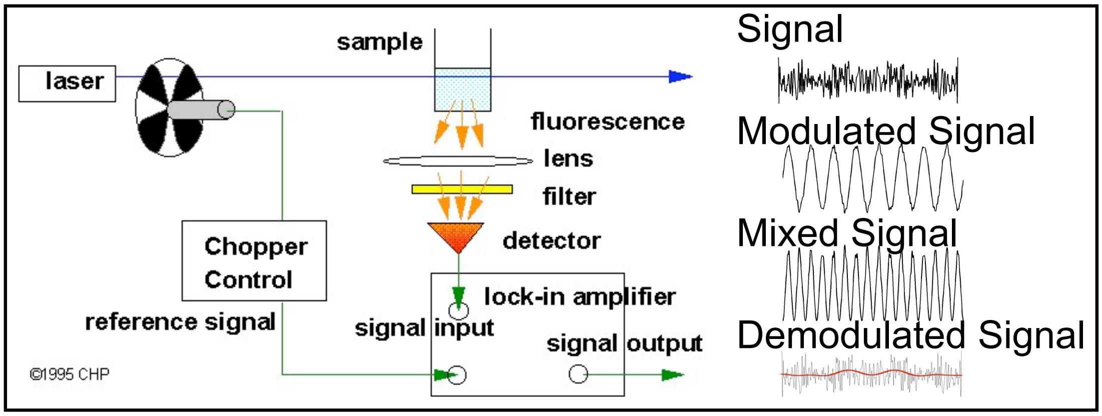


5. Double-beam spectrometers



Signal to Noise Enhancement

Lock-in Amplifiers (LIA)



www.chemistry.adelaide.edu.au/.../ lock-in.png

LIAs use <u>phase-sensitive detection</u> to isolate the signal component at a specific reference frequency AND phase (imposed by the experimenter). This eliminates signals (noise) at frequencies other than the reference frequency so that they do not affect the measurement.