Peter A. Tanner: bhtan@cityu.edu.hk

IR instrumentation

1. Fourier transform
2. Interferometer
3. FTIR spectrometer
4. Principle of operation
5. Components
6. More concerning interferograms
7. Scanning parameters
8. Advantages of FTIR

Fourier Transformation

Fourier theorem: Any waveform can be duplicated by superposing series of cosine waves.

We can describe the waves or physical system in terms of

-frequency (or wavenumber, which is directly proportional)

this is the familiar spectrum

-time

this is an interferogram

The Fourier Transform uses the above concept to convert between two different descriptions of a physical system.

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega)\, e^{-i\omega t} d\omega$$

$$F(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t} dt$$

In these equations ω is angular frequency (2π x frequency), **t** is time, and:

$$e^{i\omega t} = \cos(\omega t) + i \sin(\omega t)$$

where $i = \sqrt{-1}$

http://www.chem.vt.edu/chem-ed/scidex.html

The $F(\omega)$ function gives the frequencies at which the signal is non-zero and the f(t) function gives the times at which the signal is non-zero. Both of these functions are suitable descriptions of a waveform or physical system.

Given a function in time, f(t), we can transform it to an equivalent fuction in frequency, $F(\omega)$. We can look at the second expression in detail to understand what is happening.

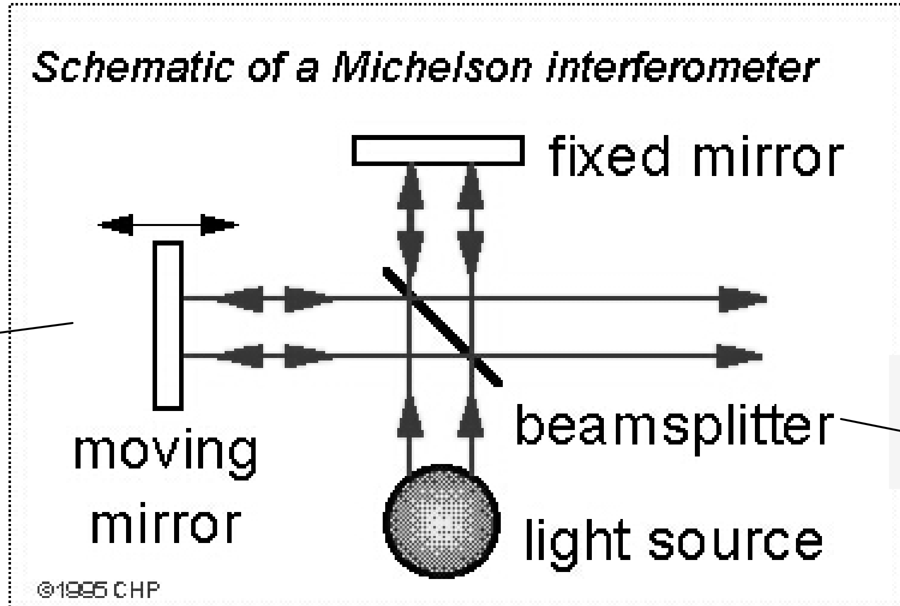
$$F(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t} dt$$

To do the transform we multiply f(t) times [cos(ωt)+i sin(ωt)]. We do this at all times between ∞ and -∞.

http://www.chem.vt.edu/chem-ed/scidex.html

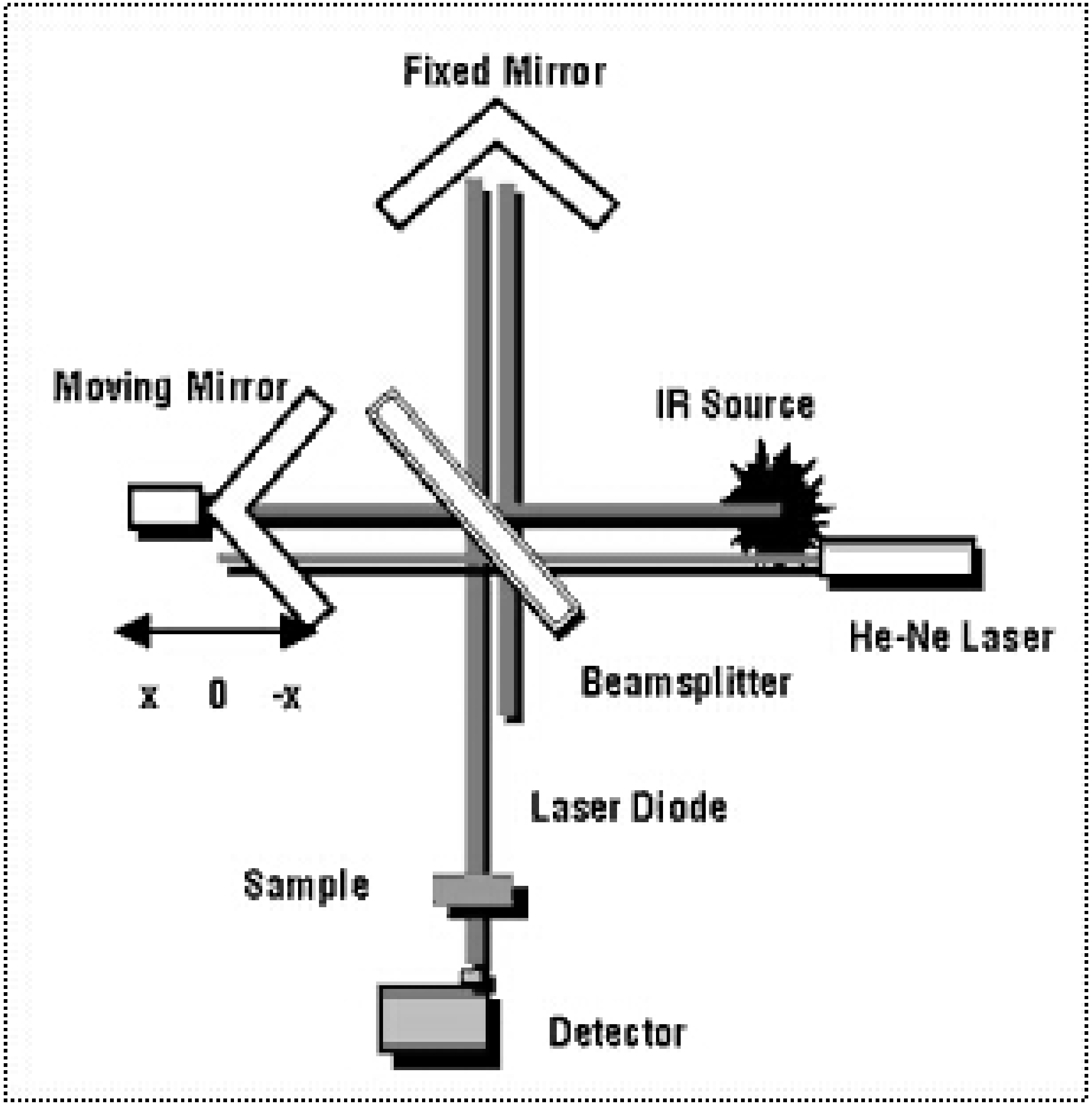
Interferometer produces plot of intensity vs time during 1 scan (interferogram).Interference of beams occurs from fixed and moving mirrors.

Mirror moves to create path difference between 2 beams



Transmits 50%, reflects 50%

At t=0, zero path difference between 2 beams for monochromatic radiation; constructive interference; maximum signal at detector.At a later time, path difference = $\lambda/2$; destructive interference; minimum signal. Later on, …. λ…maximum signal. So interferogram is a cosine wave.



Interferometer

http://www.mattsonir.com/chemist_corner/theory.html

Fourier-Transform IR spectrometer

-**Record interferogram with and without sample**

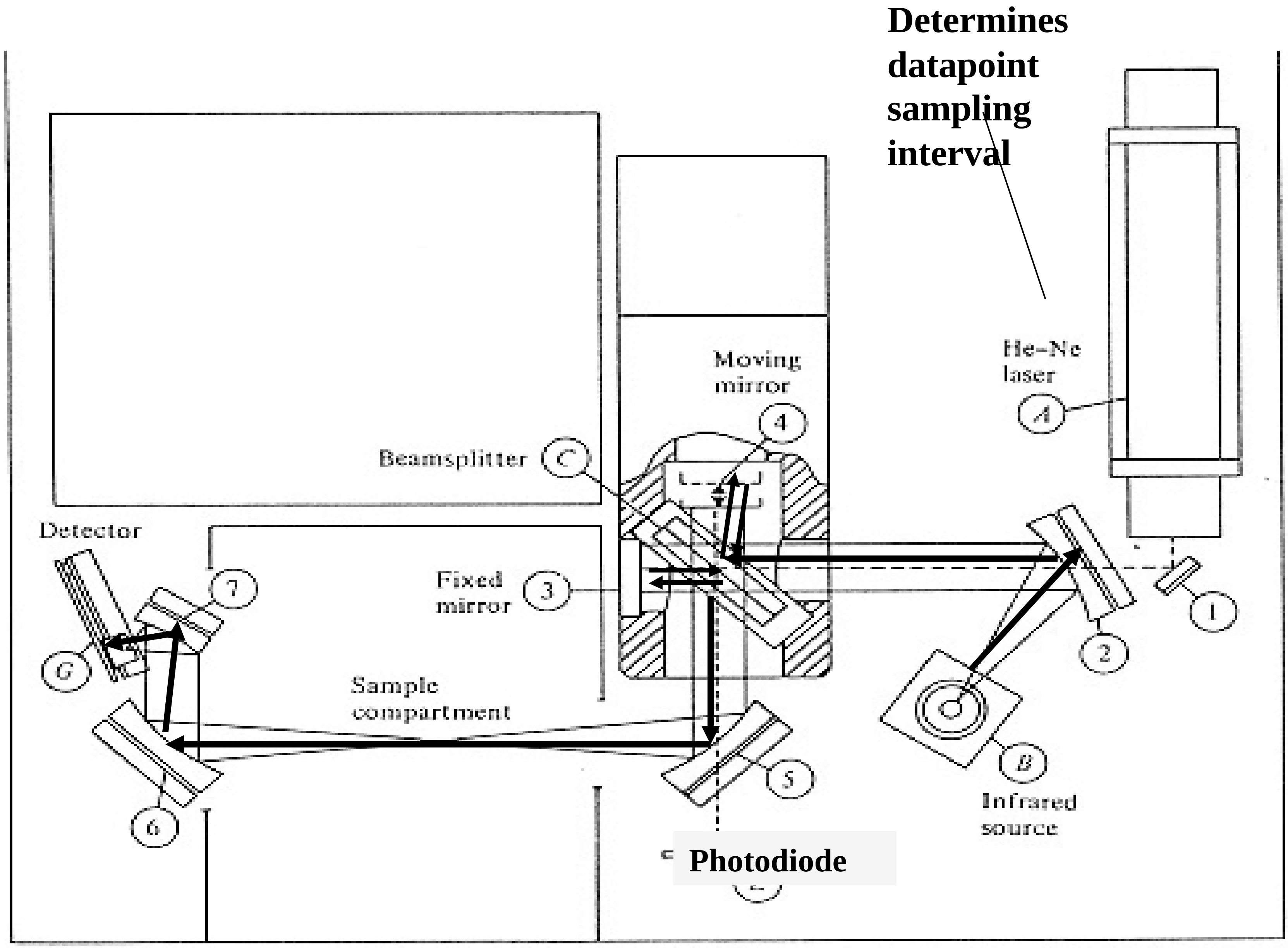
- Interferogram is digitized on collection as a certain number of datapoints.

- Consists of a plot of detector response *vs* time/path distance difference between the 2 mirrors¶

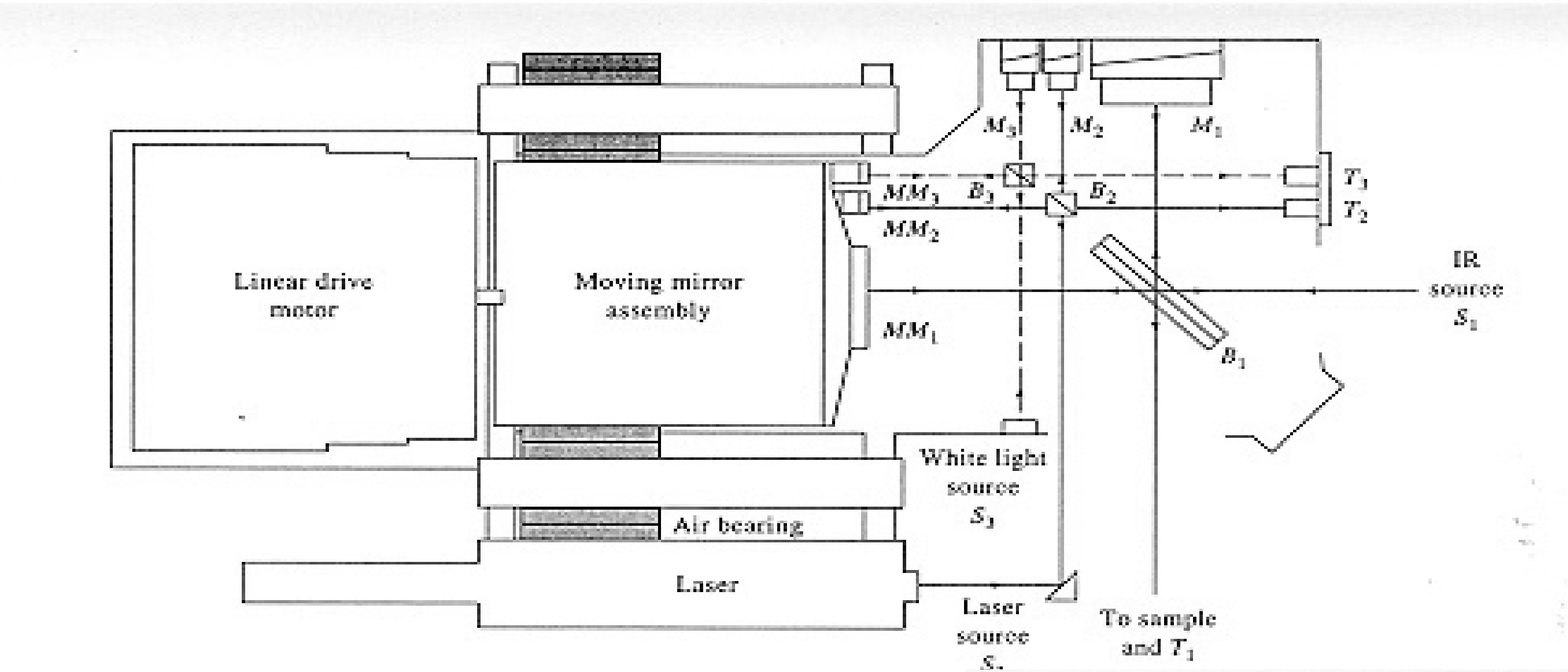
- Fourier transform the interferogram to give response *vs* frequency/wavenumber.

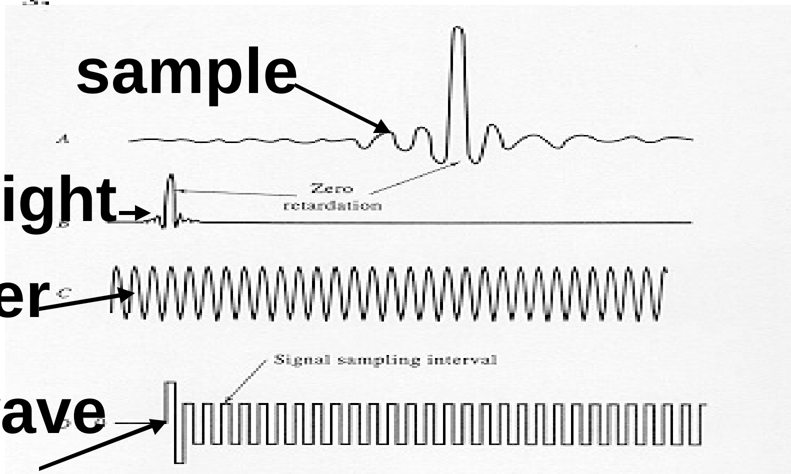
¶ also called retardation = 2xdistance moved by moving mirror.

Principle of operation of FTIR spectrometer



Principle of operation of FTIR spectrometer



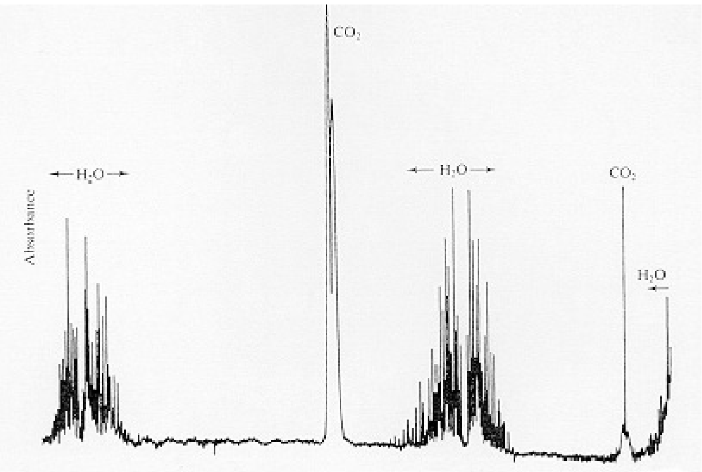


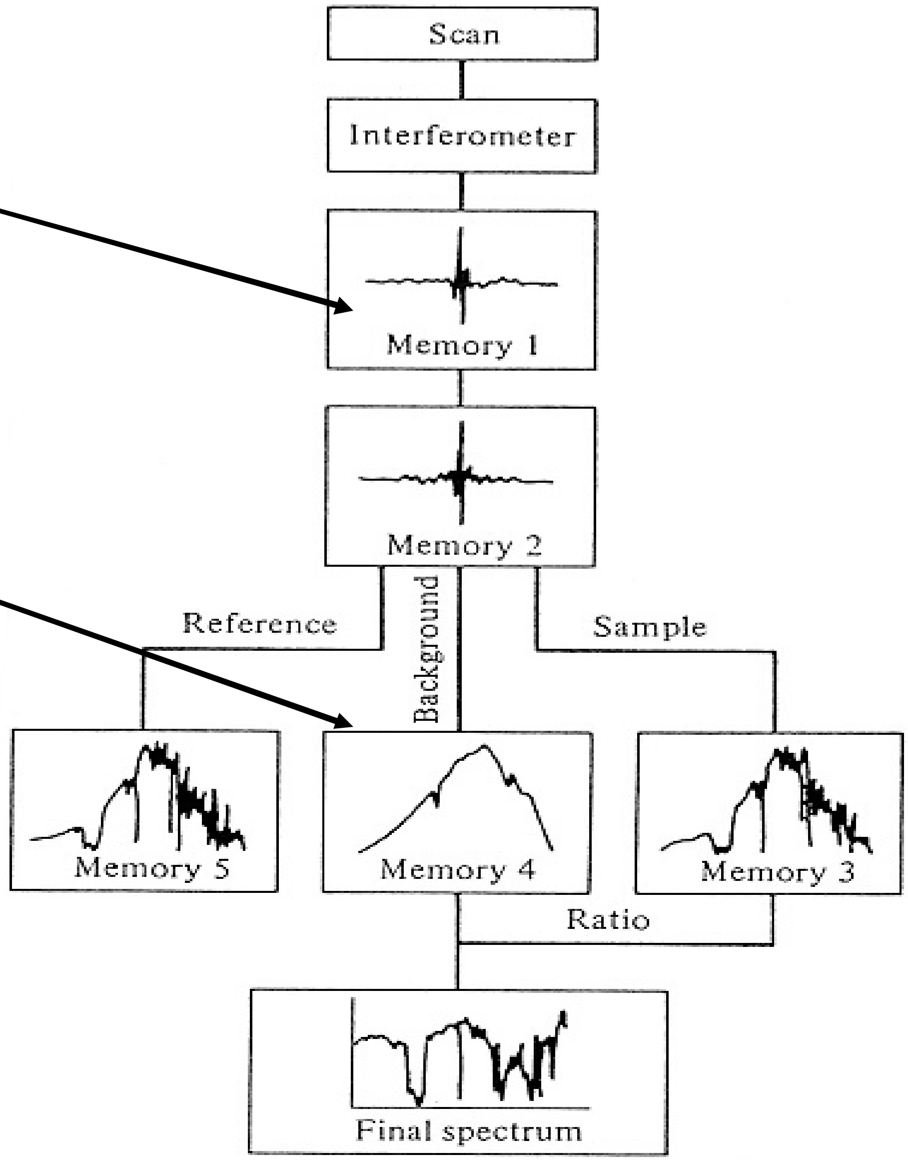
Skoog: Instrumental Analysis, p. 394

Schematic of steps in spectrum collection

End of scan from (i) white light source or (ii) centreburst

Background spectrum





Components of spectrometer

Sources of continuous radiation

A hot material emits a continuum of radiation.

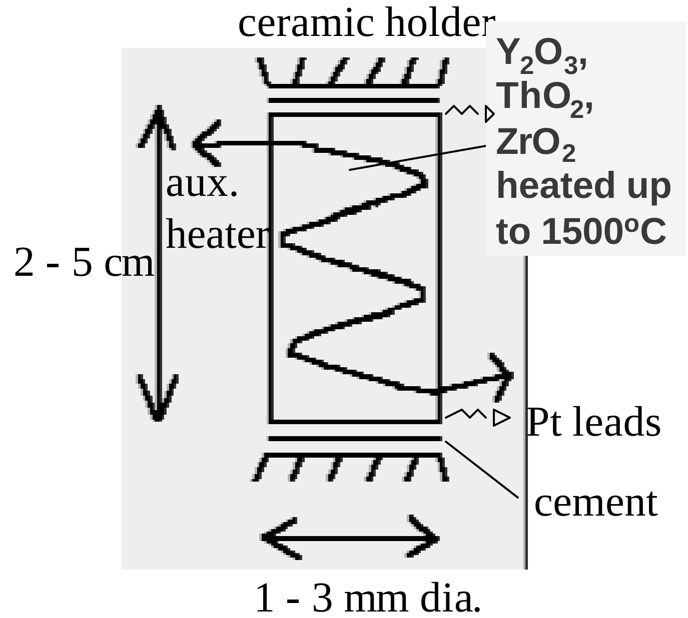
Blackbody (no envelope): intensity highest near 5000 cm^{-1};

about 100 times lower near 500 cm^{-1}.

a) **Nichrome coil** heated electrically to 1100^{o}C and a black oxide film forms.

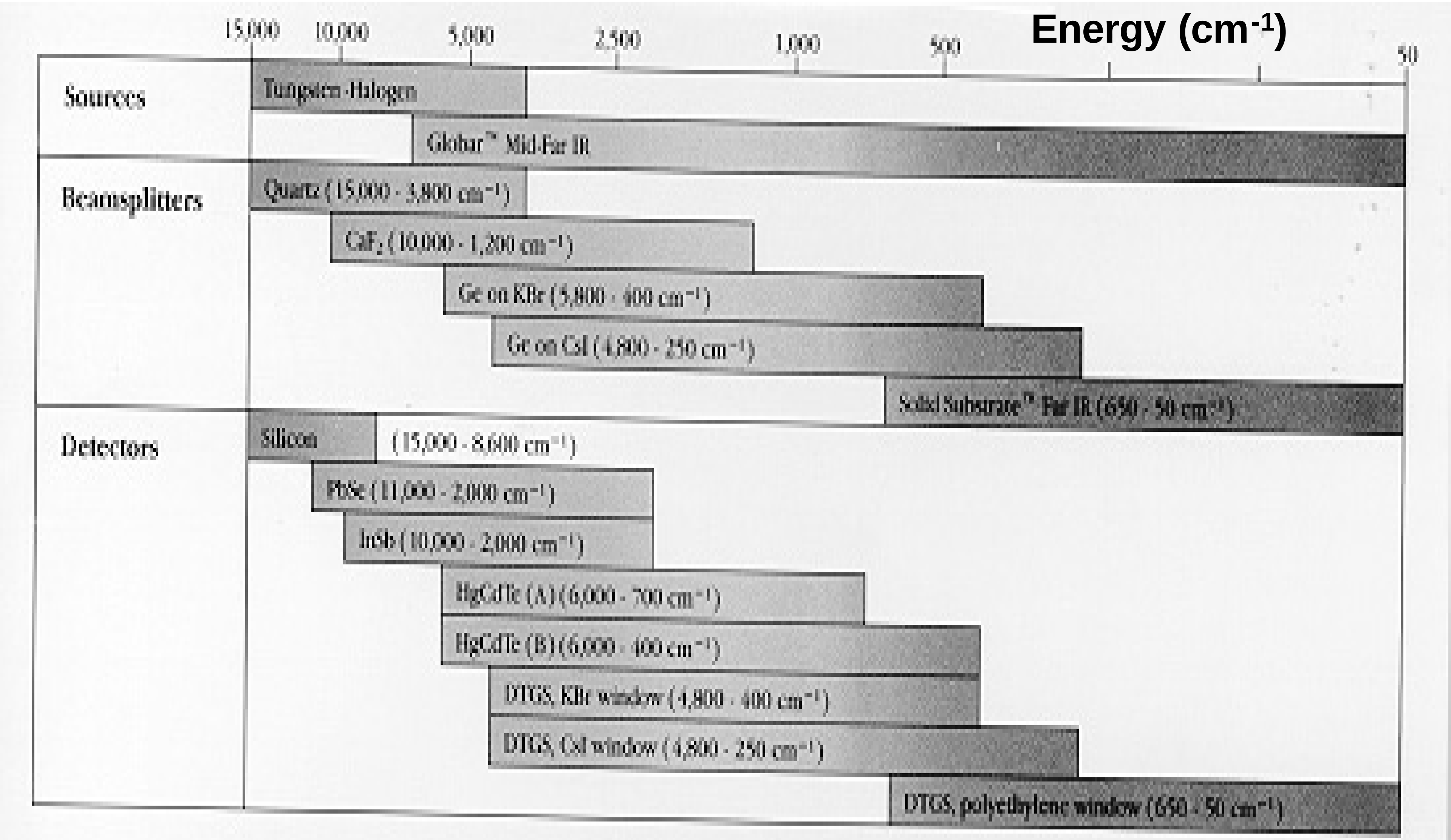
Simple, robust, reliable, long lifetime.

b) **Nernst glower**

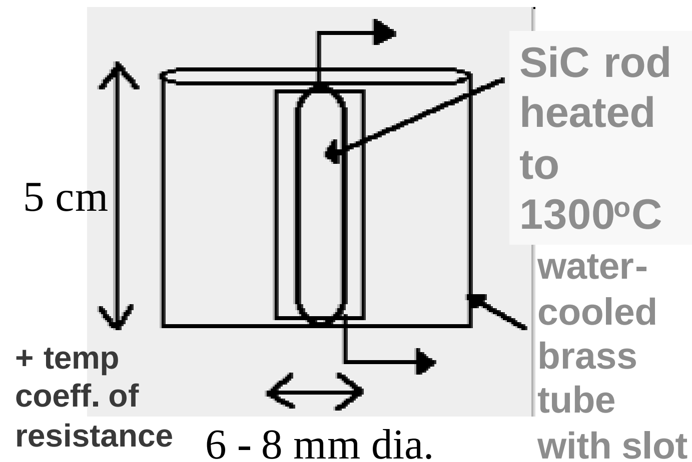


Has - temp coefficient.
of resistance.

Sources, Beamsplitters and Detectors



c) **Globar**

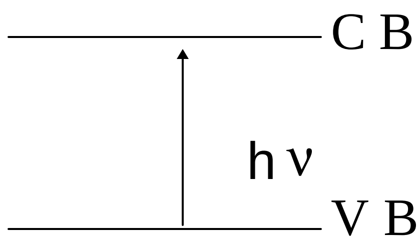


G	15 µm	NG	10 µm	NG	1 µm
	650 cm^{-1}	G	1000 cm^{-1}		10000 cm^{-1}

Infrared radiation detectors

Thermal: heat changes a property.*
Small active element, large ΔT.
Blackened, insulated.
e.g. *expansion of volume; R; V; electric polarization.

Photon: $h\nu$ produces e^- and holes$^+$ in semiconductor.



cut-off near
low-energy far-ir

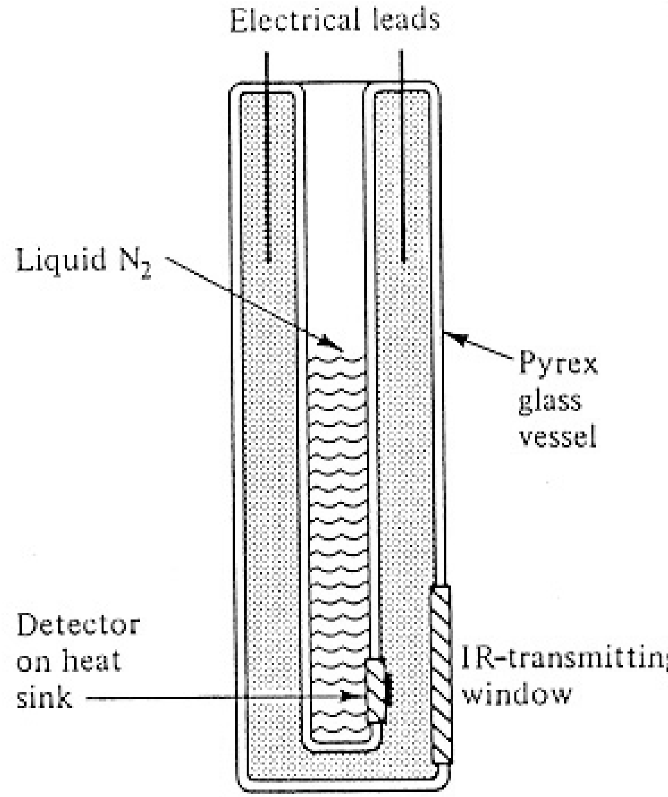
Photon detectors

e- promoted from valence band to unfilled conduction band, causing e- hole pair formation. No. of pairs depends on light intensity.

photovoltaic:
pd caused by separation of e-hole pairs between n, p layer.

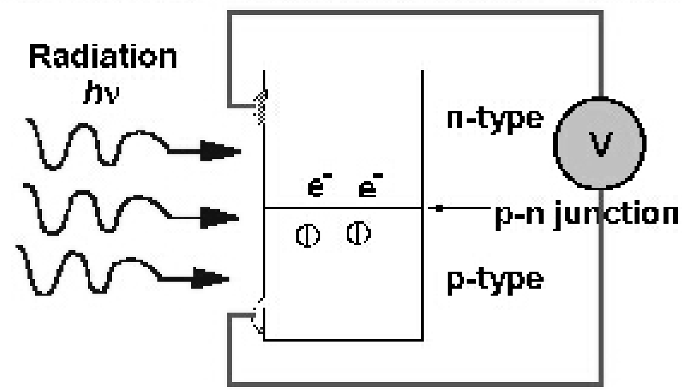
photoconductive:
R changes with radiation power, for semiconductor.

photoelectromagnetic:
utilise Hall Effect in semiconductor.



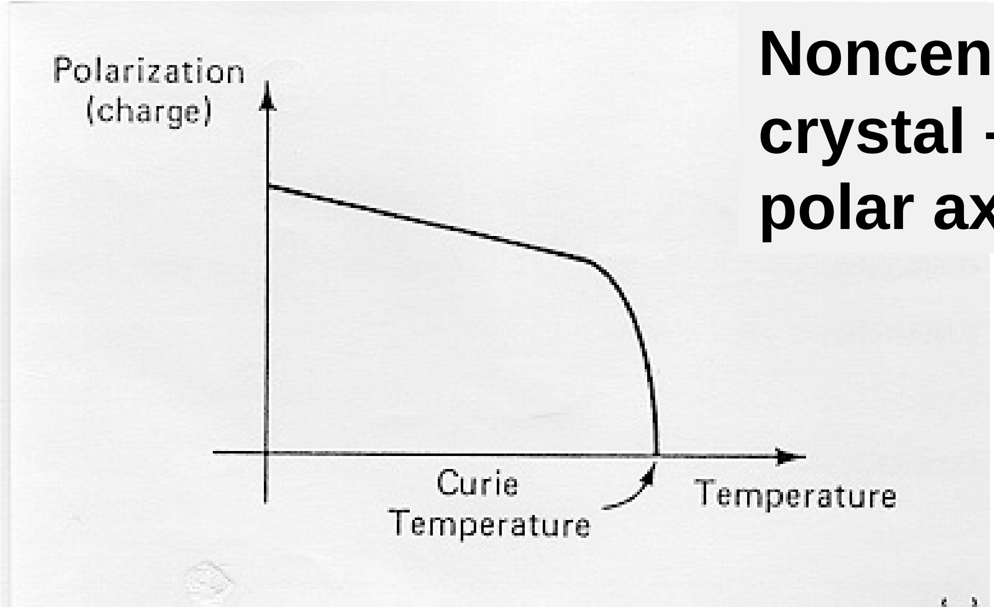
Detector type	λ (μ)
Si	0.2 - 1.1
Ge	0.4 - 1.8
InAs	1.0 - 3.8
InSb	1.0 - 7.0
InSb (77K)	1.0 - 5.6
HgCdTe (77K)	1.0 -25.0

Schematic of semiconductor detector



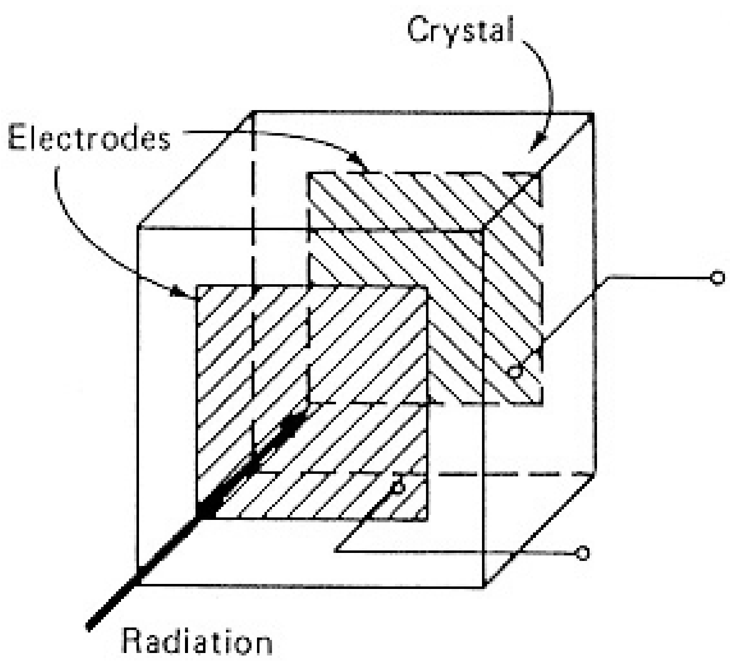
http://www.chem.vt.edu/chem-ed/scidex.html

Thermal detector: pyroelectric



Noncentrosymmetric crystal – E along polar axis below T_c

TGS, DTGS
T_c~50°C;
LiTaO3
T_c~610°C



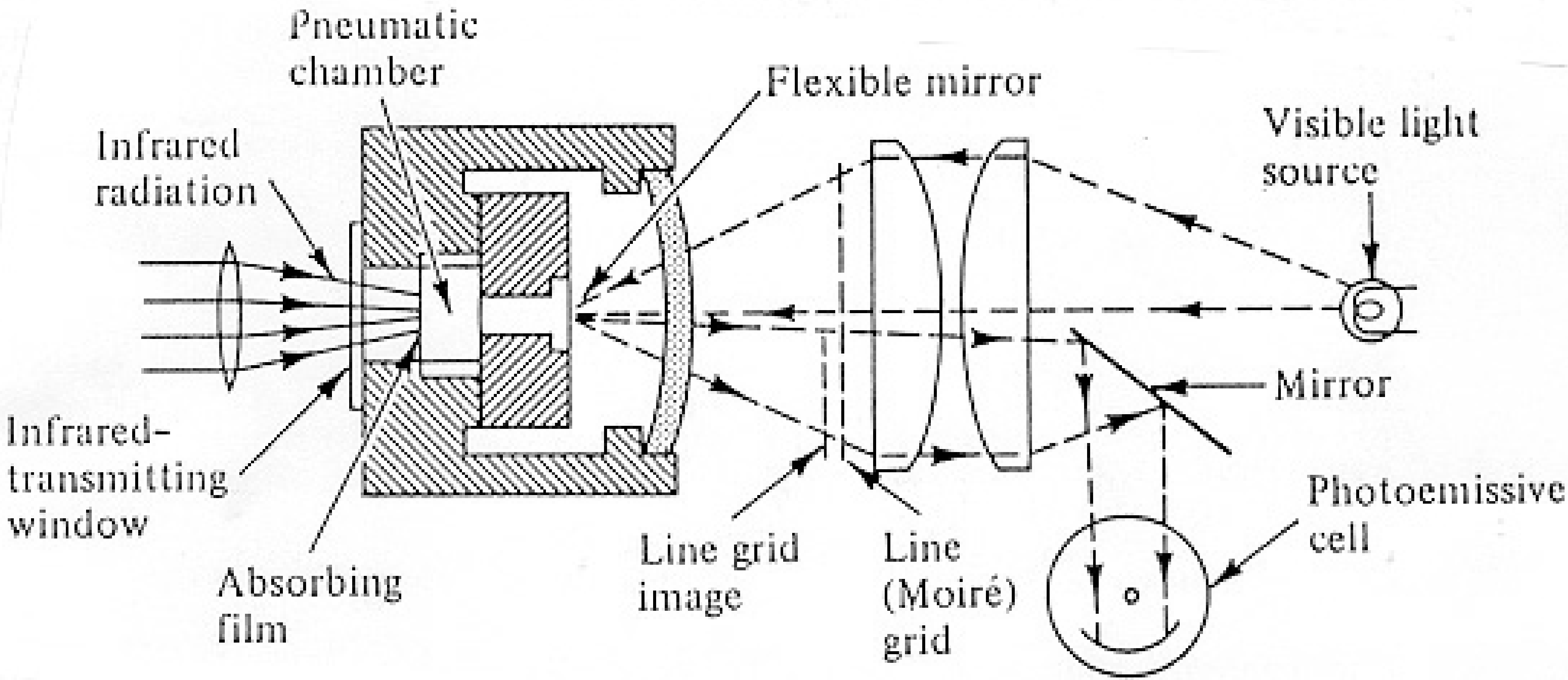
Change in detector temp. by IR absorption changes lattice spacing and polarization – charge moves.

Fast response time: 1μs-1ms

Ignore steady background

Golay detector for far-ir

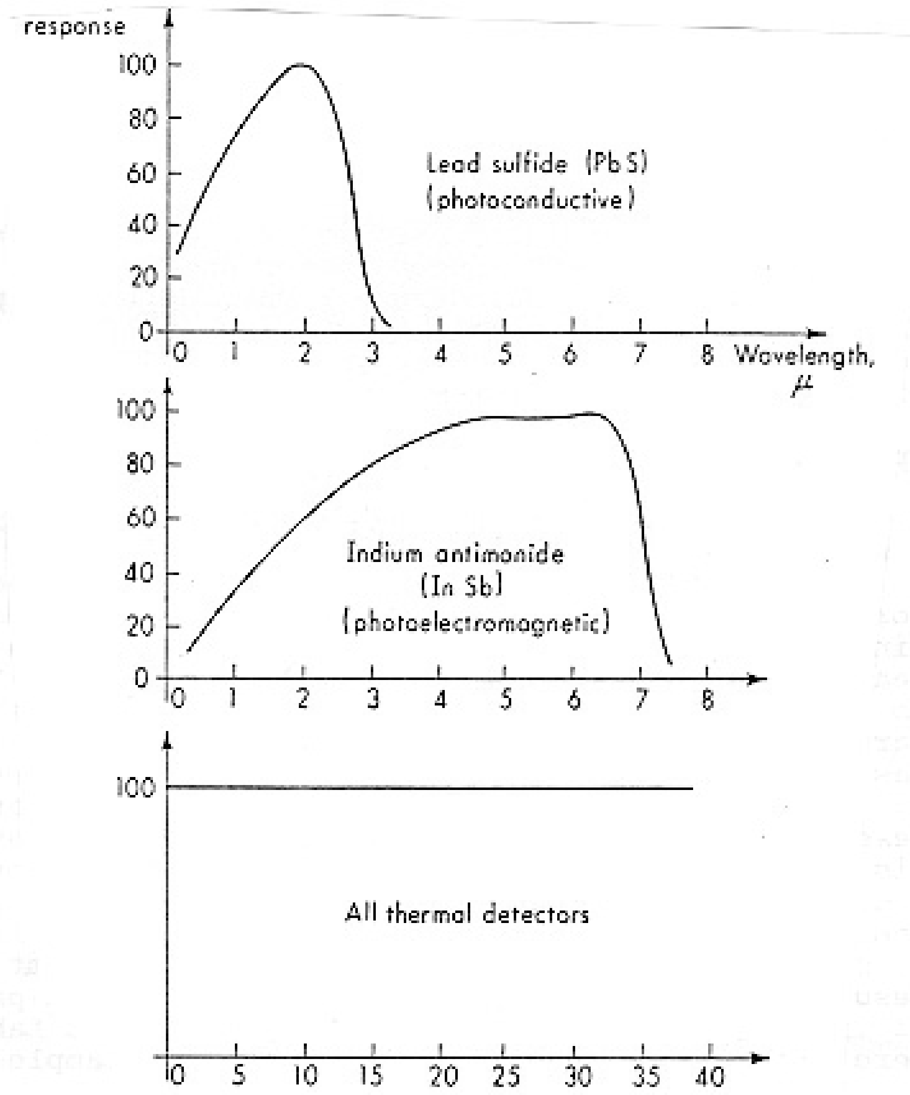
Uses light pointer from gas expansion on heating.



Responses of thermal *vs* photon detectors

Photon - more sensitive but depends on energy; have cut-off

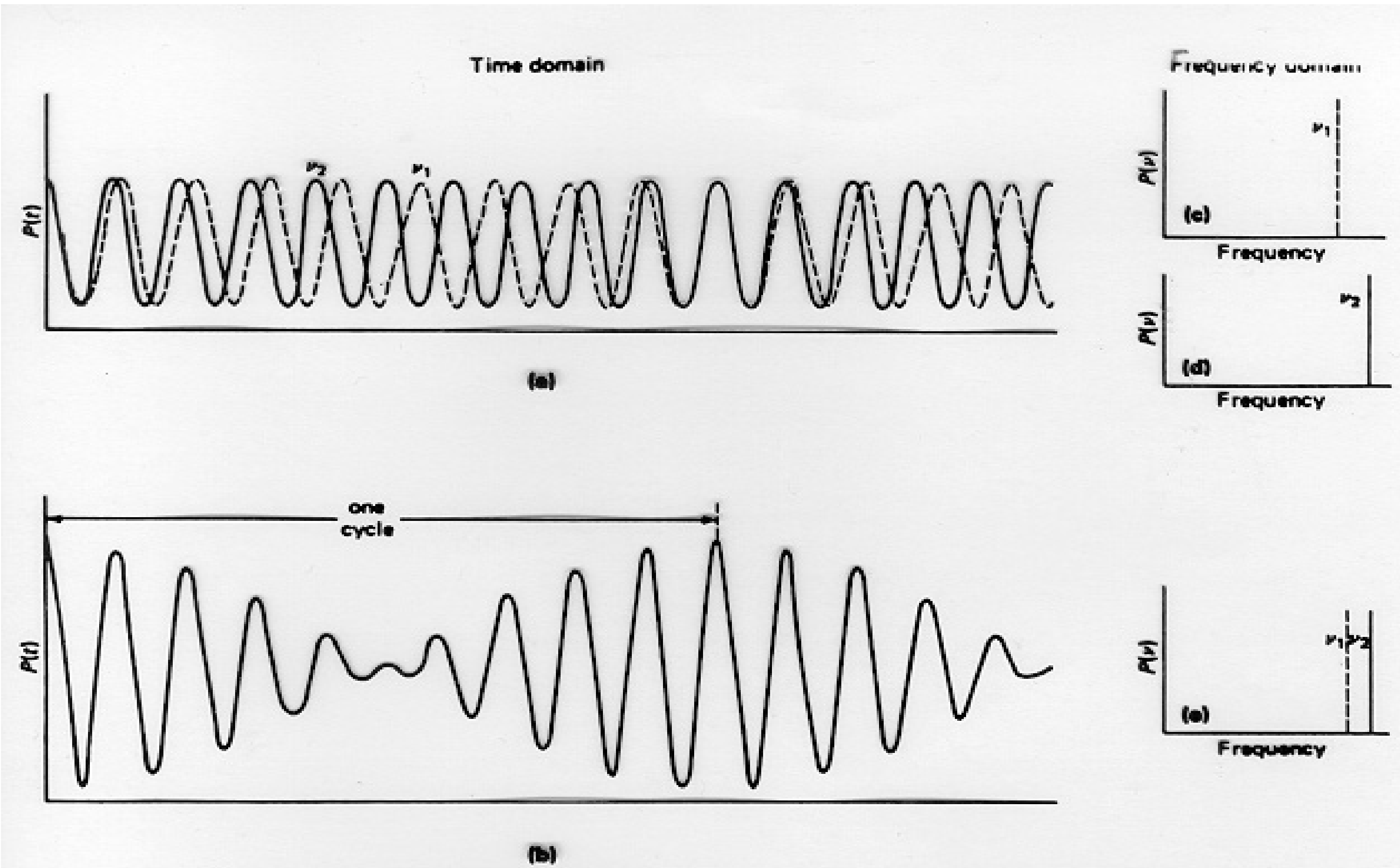
Thermal – less sensitive; flat response



Radiation-detector spectral sensitivity.

More concerning interferograms

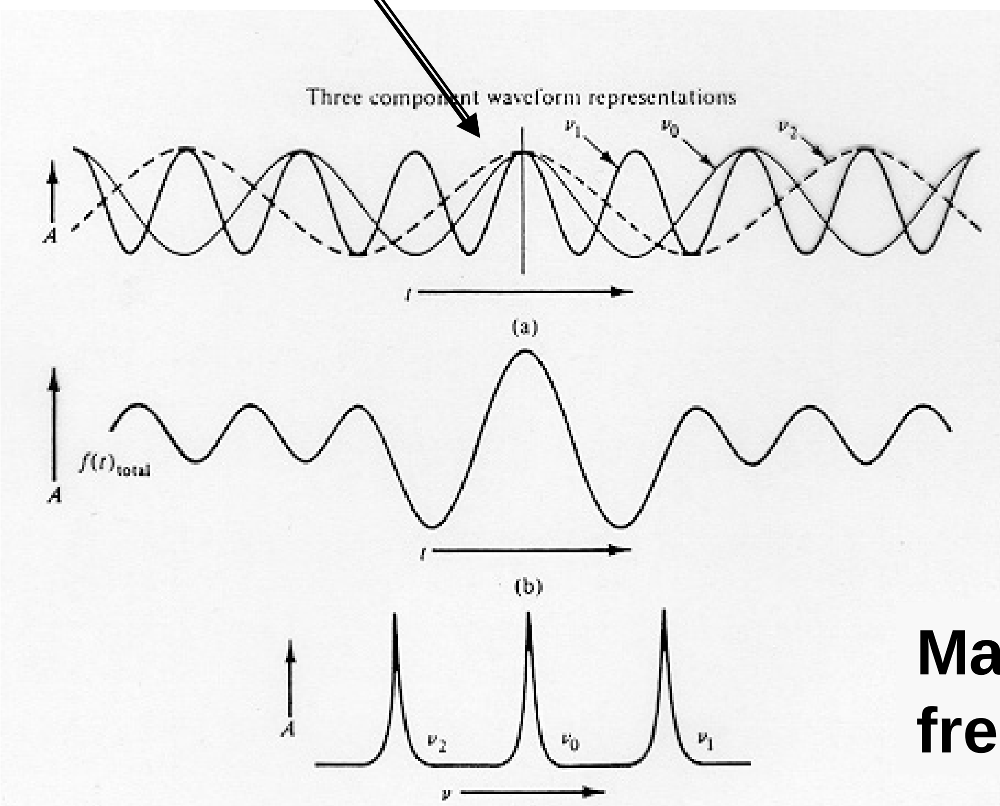
Each frequency ν gives one cosine wave, with max. amplitude at zero retardation.

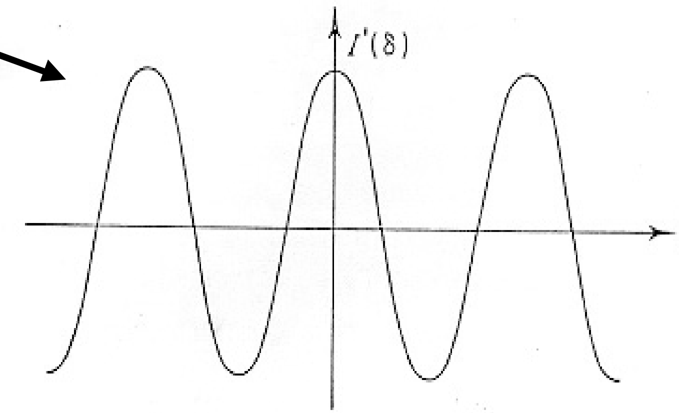


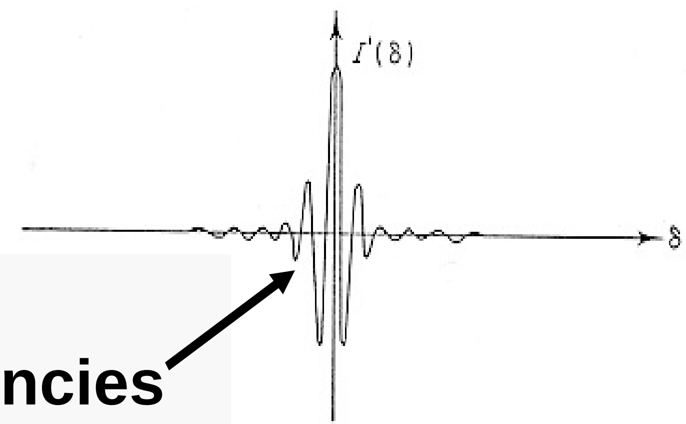
Centreburst grows when more frequencies are present

One frequency

Three frequencies

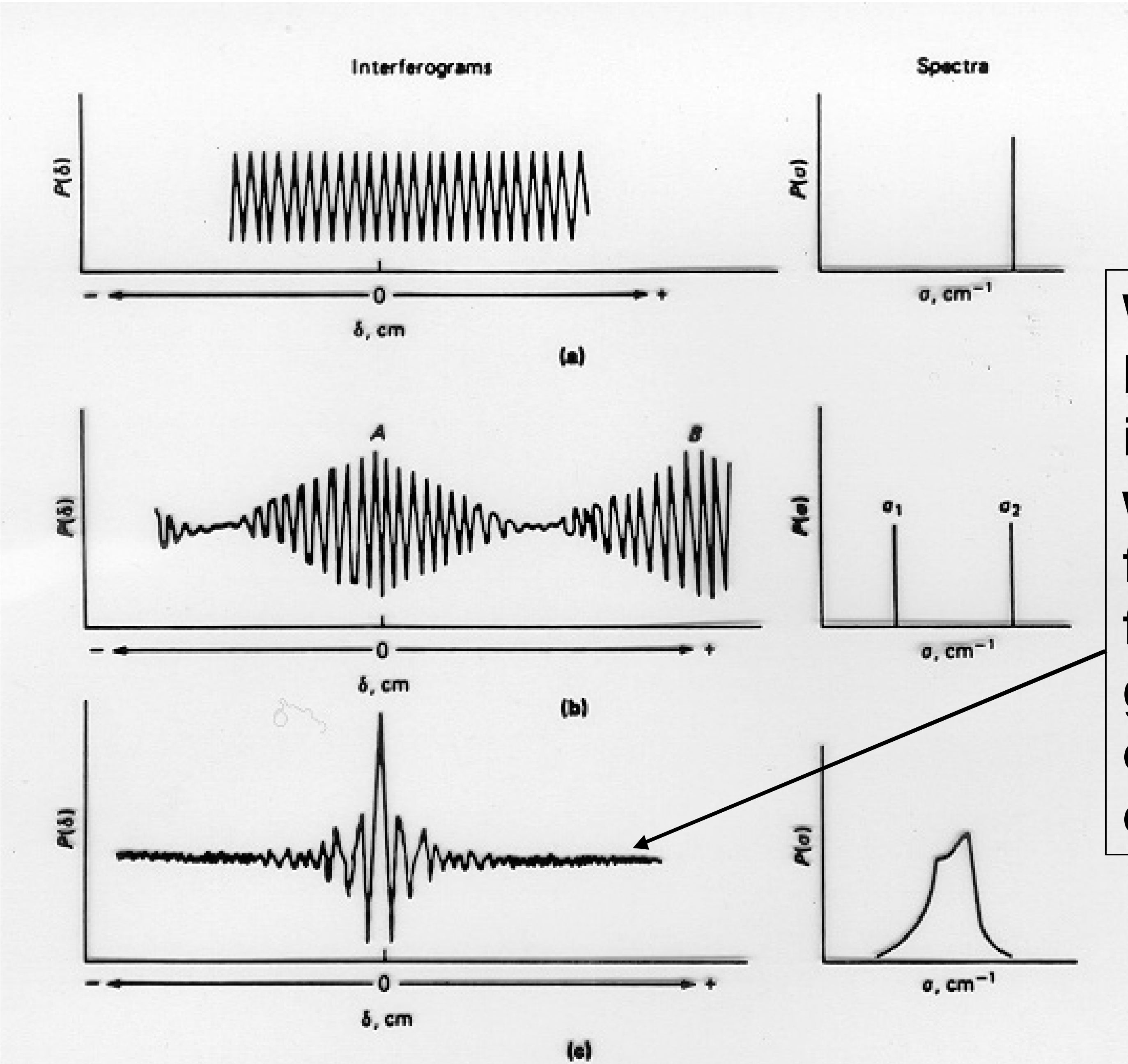






Many frequencies

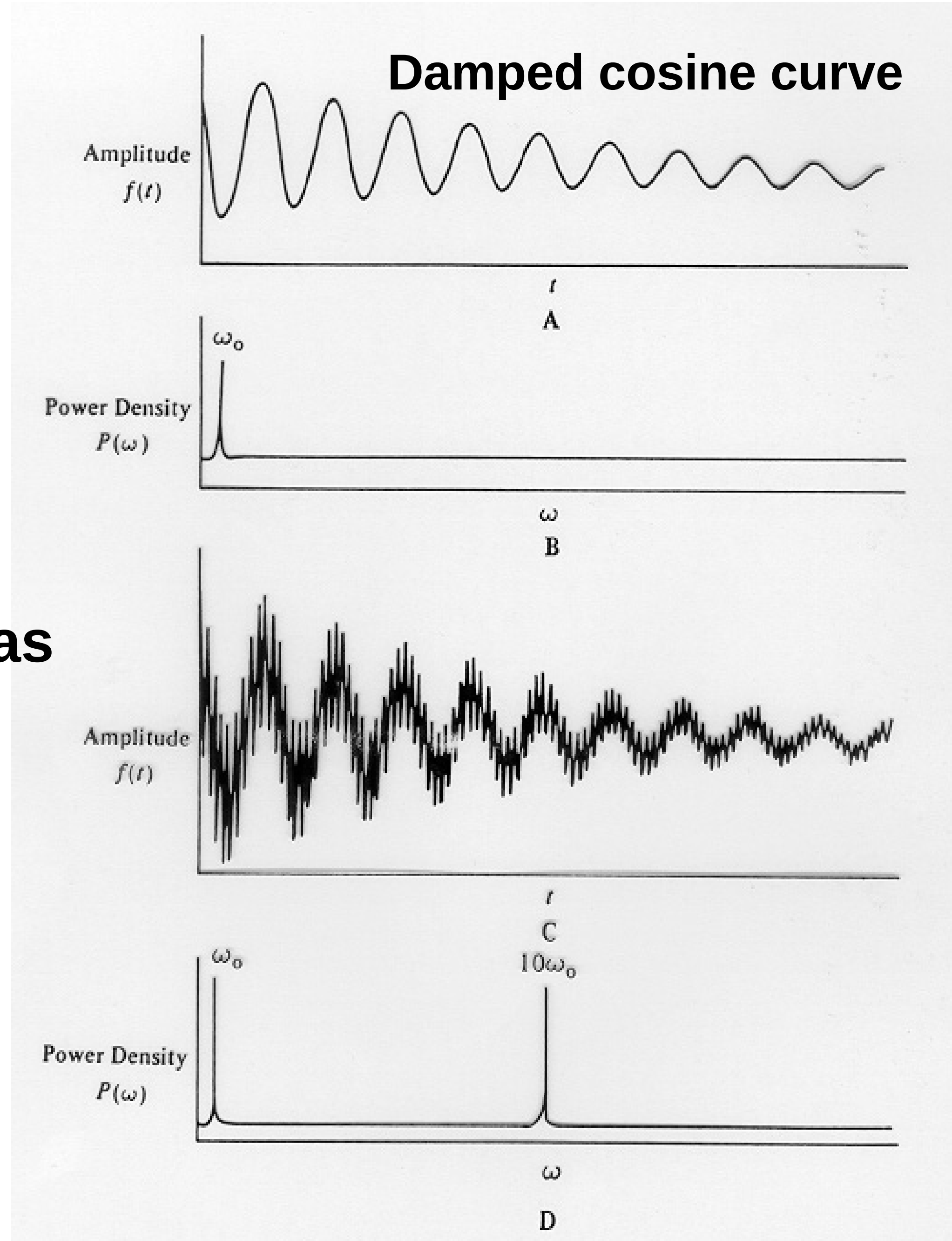
Peak width

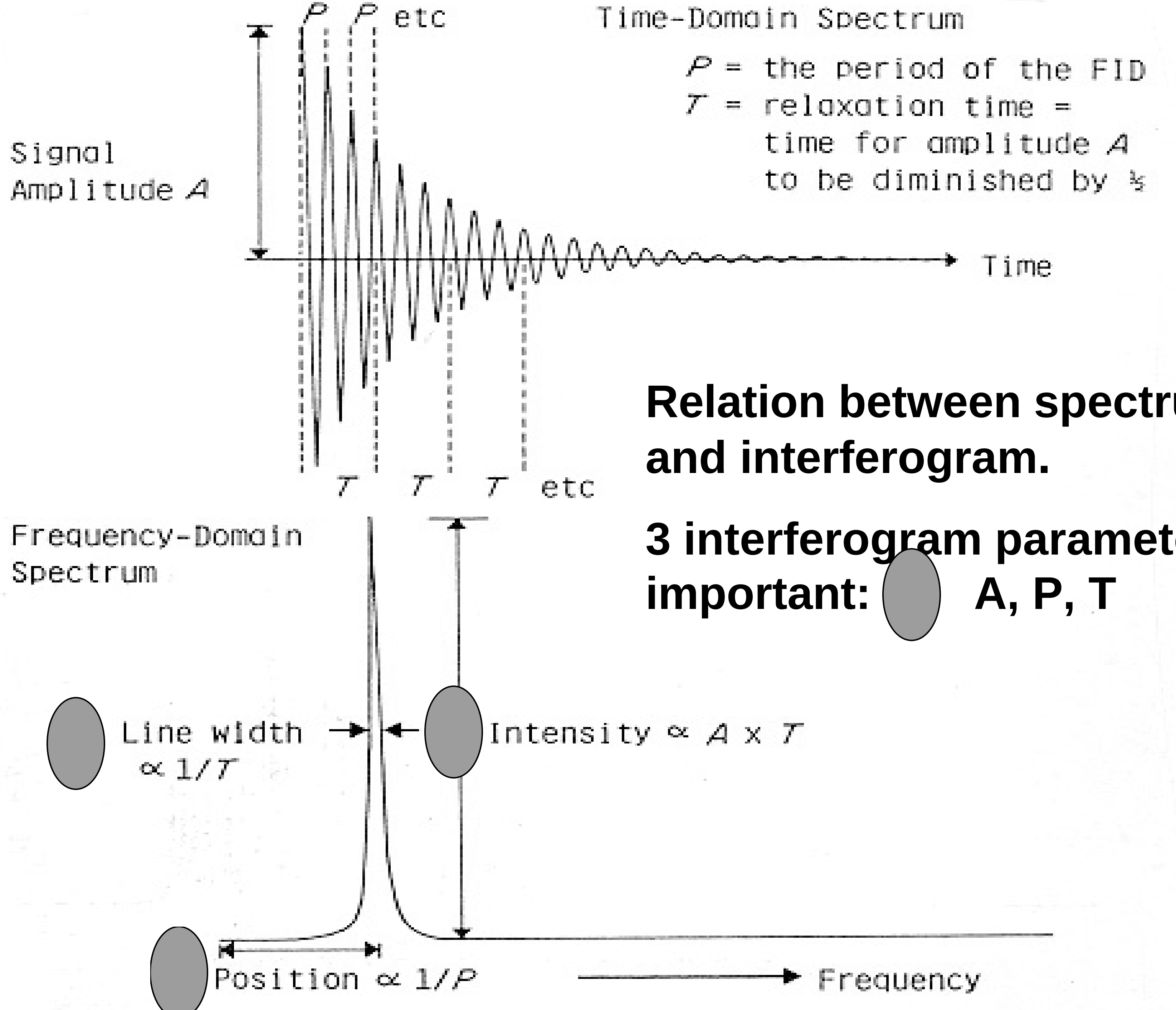


When band is broader, interferogram wings decay faster: more frequencies give more chance of cancellation

Since all peaks have finite widths, all interferograms decay with time.

A broader spectral peak has a faster relaxation time in interferogram.





Relation between spectrum and interferogram.

3 interferogram parameters important: A, P, T

Some FTIR scanning parameters

1. **Resolution**

Two widely-spaced lines in spectrum give an interferogram which repeats over a short distance. Taking data over a short path difference (time) is sufficient to resolve the lines.

Two close lines give an interferogram which repeats over a long distance (because the cosine waves are nearly in phase). The interferogram must be measured over a longer path difference (time) to get a satisfactory spectrum.

Resolution of a F-T spectrometer:

$\Delta\nu = 1 \div$ **(path difference)**

What is optical path difference and mirror movement for a resolution 4 cm^{-1}?

Typical spectral resolution for routine work is 4 cm^{-1}, although most laboratory IR instruments have resolutions down to 0.5-2 cm^{-1}.

Be careful to set same resolution parameter when matching spectra, such as unknown sample and library spectrum.

2. Spectral range depends upon size of data interval chosen when measuring the optical path difference in the interferogram – how many datapoints for every laser fringe? 2 per laser wavelength (632.8 nm; 15803 cm^{-1}) would give a FTIR scan range up to 15800 cm^{-1}. Usually, datapoints are taken on every other zero crossing, covering the range 0-7900 cm^{-1}, giving an undersampling ratio (UDR) of 2.

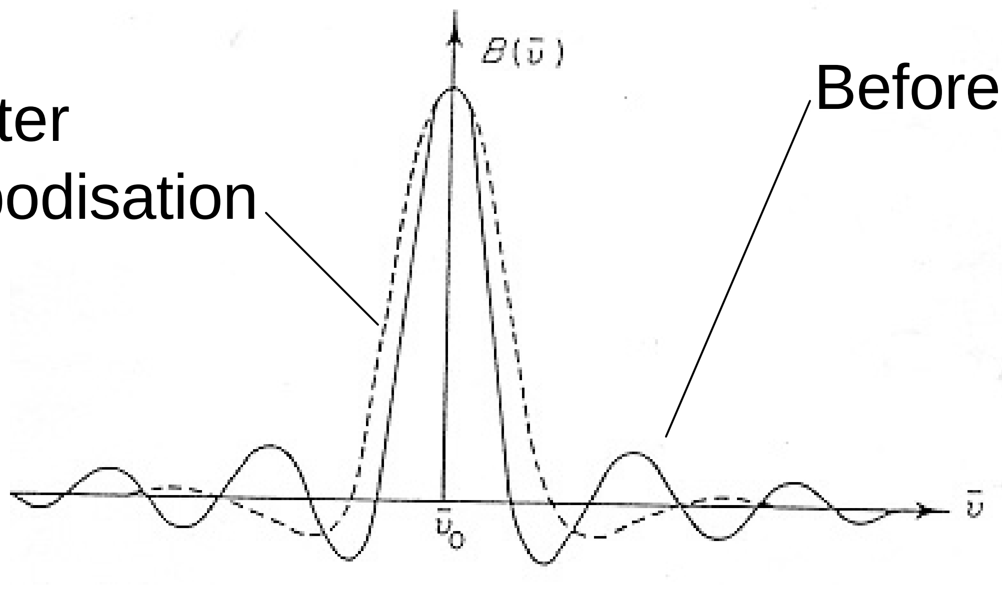
Inclusion of data at higher frequencies leads to an artifact known as aliasing or folding, so it needs to be filtered optically or electronically.

3. Apodization

Because the interferogram cannot be collected from t = -¥ to +¥, and is truncated, some error arises in the resulting spectrum: the line is broadened with side-lobes. An apodisation function is applied to correct the spectral lineshape, by weighting the points collected in the interferogram. Boxcar truncation gives no apodisation and the narrowest lines.

After apodisation

Before apodisation



4. Phase correction

Ideally, the interferogram is symmetrical about the zero path difference. Various effects (such as the change in beamsplitter RI with wavelength) cause differences between the contributions at different frequencies. These phase errors must be corrected. Usually part of the double-sided interferogram is used for correction.

Instrument scanning

Signal: noise ratio, S/N µ (measurement time)$^{0.5}$

S/N µ (no. of scans)$^{0.5}$

How many scans do I need to reduce the noise in 1 scan by a factor of 4?

Often 1 scan of sample is ratiod against 1 scan of (empty) background. In the ranges 70-35%T and 0-35%T normally the ratio of background:sample scans is increased to 1:2 and 1:4 respectively.

When the energy throughput is reduced by a factor of x for the sample spectrum, x times more scans are required.

Advantages of FT-instrument over dispersive one

1. Fellgett advantage

All frequencies are measured simultaneously. Typical scan times are only a few seconds.

2. Jacquinot advantage

The energy throughput is higher for any resolution, giving a higher signal:noise ratio.

3. Connes advantage

The laser wavelength is used as a reference for the calculation of band positions, and is precise.

4. Stray light

This only comes from aliasing and can be prevented.

5. Resolution

This is constant for the whole spectral range

6. Robustness

FT instruments only have 1 moving part