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 \( \omega \) is angular frequency \((2\pi \times \text{frequency})\), \( t \) 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 function 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 $[\cos(\omega t) + i \sin(\omega t)]$. We do this at all times between $\infty$ and $-\infty$.

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.

At \( t=0 \), zero path difference between 2 beams for monochromatic radiation; constructive interference; maximum signal at detector. At a later time, path difference \( = \frac{\lambda}{2} \); destructive interference; minimum signal. Later on, .... \( \lambda \).....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

Determines datapoint sampling interval
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
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\(^{\circ}\)C and a black oxide film forms.
Simple, robust, reliable, long lifetime.
b) **Nernst glower**

- Has - temp coefficient. of resistance.

[Diagram of a Nernst glower showing the ceramic holder, aux. heater, ZrO₂, ThO₂, Y₂O₃, Pt leads, and cement.]
# Sources, Beamsplitters and Detectors

<table>
<thead>
<tr>
<th>Sources</th>
<th>Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten-Halogen</td>
<td></td>
</tr>
<tr>
<td>Globar™ Mid-Far IR</td>
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</table>

<table>
<thead>
<tr>
<th>Beamsplitters</th>
<th>Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (15,000 - 3,800 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>CaF(_2) (10,000 - 1,200 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Ge on KBr (5,800 - 400 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Ge on CsI (4,800 - 250 cm(^{-1}))</td>
<td></td>
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<tr>
<td>Solid Substrate™ Far IR (650 - 50 cm(^{-1}))</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Detectors</th>
<th>Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon (15,000 - 8,600 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>PbSe (11,000 - 2,000 cm(^{-1}))</td>
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</tr>
<tr>
<td>InSb (10,000 - 2,000 cm(^{-1}))</td>
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</tr>
<tr>
<td>HgCdTe (A) (6,000 - 700 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>HgCdTe (B) (6,000 - 400 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>DTGS, KBr window (4,800 - 400 cm(^{-1}))</td>
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</tr>
<tr>
<td>DTGS, CsI window (4,800 - 250 cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>DTGS, polyethylene window (650 - 50 cm(^{-1}))</td>
<td></td>
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</tbody>
</table>
c) **Globar**

![Diagram of a Globar source with a SiC rod heated to 1300°C, water-cooled brass tube with a slot, and dimensions of 5 cm height and 6-8 mm diameter.]

<table>
<thead>
<tr>
<th>G</th>
<th>15 µm</th>
<th>NG</th>
<th>10 µm</th>
<th>NG</th>
<th>1 µm</th>
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</thead>
<tbody>
<tr>
<td>650 cm⁻¹</td>
<td>G</td>
<td>1000 cm⁻¹</td>
<td></td>
<td>10000 cm⁻¹</td>
<td></td>
</tr>
</tbody>
</table>
**Infrared radiation detectors**

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

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

\[
\text{CB} \quad \overset{\text{cut-off near}}{\downarrow} \quad h\nu \quad \text{low-energy far-ir} \\
\text{VB}
\]
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.

![Schematic of semiconductor detector](http://www.chem.vt.edu/chem-ed/scidex.html)
Thermal detector: pyroelectric

Noncentrosymmetric crystal – $E$ along polar axis below $T_c$

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

Fast response time: $1\mu s$-1ms

Ignore steady background

TGS, DTGS
$T_c \approx 50^\circ C$
LiTaO3
$T_c \approx 610^\circ C$
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
More concerning interferograms

Each frequency $\nu$ 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:

\[ \Delta v = \frac{1}{(\text{path difference})} \]
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 $t = -\infty$ to $+\infty$, 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.
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, $S/N \propto (\text{measurement time})^{0.5}$

$S/N \propto (\text{no. of scans})^{0.5}$

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

Often 1 scan of sample is ratioed 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