

# Infra-Red Absorption Spectroscopy

## Instrumentation

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### Introduction

In this look at instrumentation for IR spectroscopy, we will be limiting our attention to instrumentation concerned with spectroscopy in the middle region ( $4000 - 200\text{cm}^{-1}$ ). It is absorption in this region which gives structural information about a compound.

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### Instrumental components

#### Sources

An inert solid is electrically heated to a temperature in the range 1500-2000 K. The heated material will then emit infra red radiation.

*The Nernst glower* is a cylinder (1-2 mm diameter, approximately 20 mm long) of rare earth oxides. Platinum wires are sealed to the ends, and a current passed through the cylinder. The Nernst glower can reach temperatures of 2200 K.

*The Globar source* is a silicon carbide rod (5mm diameter, 50mm long) which is electrically heated to about 1500 K. Water cooling of the electrical contacts is needed to prevent arcing. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than  $5\text{ }\mu\text{m}$ ) where its output becomes larger.

*The incandescent wire source* is a tightly wound coil of nichrome wire, electrically heated to 1100 K. It produces a lower intensity of radiation than the Nernst or Globar sources, but has a longer working life.

#### Detectors

There are three categories of detector;

- Thermal
- Pyroelectric
- Photoconducting

*Thermocouples* consist of a pair of junctions of different metals; for example, two pieces of bismuth fused to either end of a piece of antimony. The potential difference (voltage) between the junctions changes according to the difference in temperature between the junctions

*Pyroelectric detectors* are made from a single crystalline wafer of a pyroelectric material, such as triglycerine sulphate. The properties of a pyroelectric material are such that when an electric field is applied across it, electric polarisation occurs (this happens in any dielectric material). In a pyroelectric material, when the field is removed, the polarisation persists. The degree of polarisation is temperature dependant. So, by sandwiching the pyroelectric material between two electrodes, a temperature dependant capacitor is made. The heating effect of incident IR radiation causes a change in the capacitance of the material. Pyroelectric detectors have a fast response time. They are used in most Fourier transform IR instruments.

*Photoelectric detectors* such as the mercury cadmium telluride detector comprise a film of semiconducting material deposited on a glass surface, sealed in an evacuated envelope. Absorption of IR promotes nonconducting valence electrons to a higher, conducting, state. The electrical resistance of the semiconductor decreases. These detectors have better response characteristics than pyroelectric detectors and are used in FT-IR instruments - particularly in GC - FT-IR.

## Types of instrument

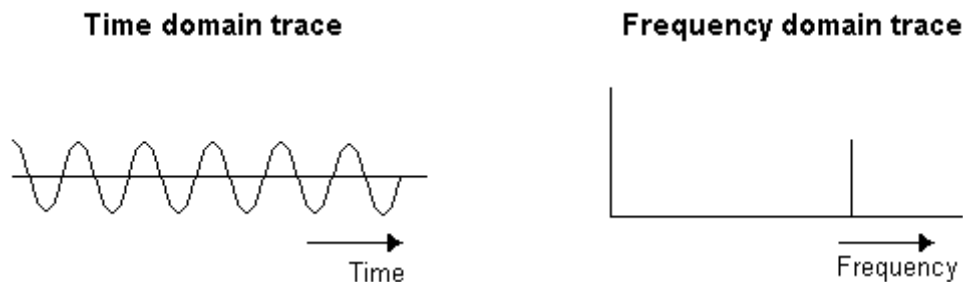
### Dispersive infra red spectrophotometers

These are often double-beam recording instruments, employing diffraction gratings for dispersion of radiation.

Radiation from the source is flicked between the reference and sample paths. Often, an *optical null* system is used. This is when the detector only responds if the intensity of the two beams is unequal. If the intensities are unequal, a light attenuator restores equality by moving in or out of the reference beam. The recording pen is attached to this attenuator.

### Fourier-transform spectrometers

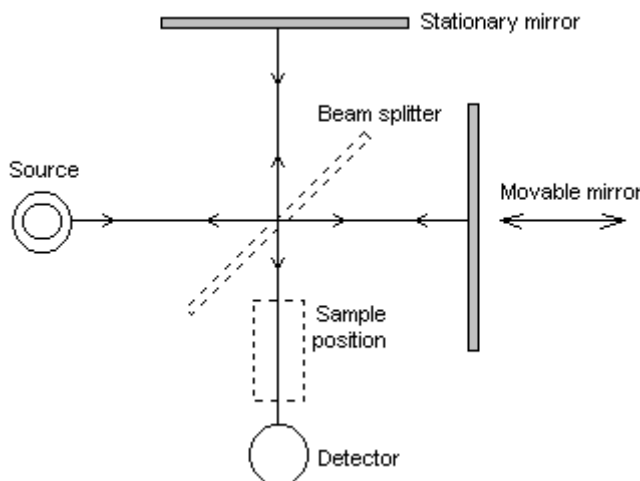
Any waveform can be shown in one of two ways; either in *frequency domain* or *time domain*.



Dispersive IR instruments operate in the frequency domain. There are, however, advantages to be gained from measurement in the time domain followed by computer transformation into the frequency domain.

If we wished to record a trace in the time domain, it could be possible to do so by allowing radiation to fall on a detector and recording its response over time. In practice, no detector can respond quickly enough (the radiation has a frequency greater than  $10^{14}$  Hz). This problem can be solved by using interference to modulate the i.r. signal at a detectable frequency. The *Michelson interferometer* is used to produce a new signal of a much lower frequency which contains the same information as the original IR signal. The output from the interferometer is an *interferogram*.

### The Michelson interferometer



Radiation leaves the source and is split. Half is reflected to a stationary mirror and then back to the splitter. This radiation has travelled a fixed distance. The other half of the radiation from the source passes through the splitter and is reflected back by a **movable** mirror. Therefore, the path length of this beam is variable. The two reflected beams recombine at the splitter, and they interfere (e.g. for any one wavelength, interference will be constructive if the difference in path lengths is an exact multiple of the wavelength. If the difference in path lengths is half the wavelength then destructive interference will result). If the movable mirror moves away from the beam splitter at a constant speed, radiation reaching the detector goes through a steady sequence of maxima and minima as the interference alternates between constructive and destructive phases.

If monochromatic IR radiation of frequency,  $f(ir)$  enters the interferometer, then the output frequency,  $f_m$  can be found by;

$$f_m = \frac{v}{1.5 \times 10^{11}} \times f(ir)$$

where  $v$  is the speed of mirror travel in mm/s

Because **all** wavelengths emitted by the source are present, the interferogram is extremely complicated.

The moving mirror must travel smoothly; a frictionless bearing is used with electromagnetic drive. The position of the mirror is measured by a laser shining on a corner of the mirror. A simple sine wave interference pattern is produced. Each peak indicates mirror travel of one half the wavelength of the laser. The accuracy of this measurement system means that the IR frequency scale is accurate and precise.

In the FT-IR instrument, the sample is placed between the output of the interferometer and the detector. The sample absorbs radiation of particular wavelengths. Therefore, **the interferogram contains the spectrum of the source minus the spectrum of the sample**. An interferogram of a reference (sample cell and solvent) is needed to obtain the spectrum of the sample.

After an interferogram has been collected, a computer performs a *Fast Fourier Transform*, which results in a frequency domain trace (i.e intensity vs. wavenumber) that we all know and love.

The detector used in an FT-IR instrument must respond quickly because intensity changes are rapid (the moving mirror moves quickly). Pyroelectric detectors or liquid nitrogen cooled photon detectors must be used. Thermal detectors are too slow.

To achieve a good signal to noise ratio, many interferograms are obtained and then averaged. This can be done in less time than it would take a dispersive instrument to record one scan.

### Advantages of Fourier transform IR over dispersive IR;

- Improved frequency resolution
- Improved frequency reproducibility (older dispersive instruments must be recalibrated for each session of use)
- Higher energy throughput
- Faster operation
- Computer based (allowing storage of spectra and facilities for processing spectra)
- Easily adapted for remote use (such as diverting the beam to pass through an external cell and detector, as in GC - FT-IR)

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## Review your learning

You should be aware of the various sources and detectors used in IR spectroscopy. You should also have an understanding of how a Fourier transform instrument operates (including the interferometer), and the advantages that this kind of instrument gives over the dispersive type.

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◀ [Infra red Absorption Spectroscopy - Theoretical Principles Quiz](#)

● **Infra red Absorption Spectroscopy - Instrumentation**

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