Principles of Fourier-transform infrared spectroscopy

The principle of absorption spectroscopy, whether in the ultraviolet (UV), visible or infrared (IR) is to measure how much light a sample absorbs as a function of wavelength. In the visible and UV the method used is "dispersive spectroscopy". The light source may be a monochromatic scanned beam or a broadband source, but in both cases the light passes through the sample and then is dispersed using a grating to resolve the wavelengths to be measured. In a scanning spectrophotometer individual wavelengths are measured and in a broad band spectrometer the light is dispersed onto a photodiode array. It is possible to use dispersive methods in the infrared region as well. There are certain advantages, particularly when one is interested only in a very narrow range of wavelengths.

Fourier-transform infrared (FTIR) spectroscopy provides an alternative approach to dispersive methods. Rather than directly detecting the dispersed light as a function of wavelength, a broadband source passes through an interferometer. The interferometer consists of a beam splitter and two arms, one of fixed length and second of variable length determined by a moving mirror on track as shown in Figure 1.

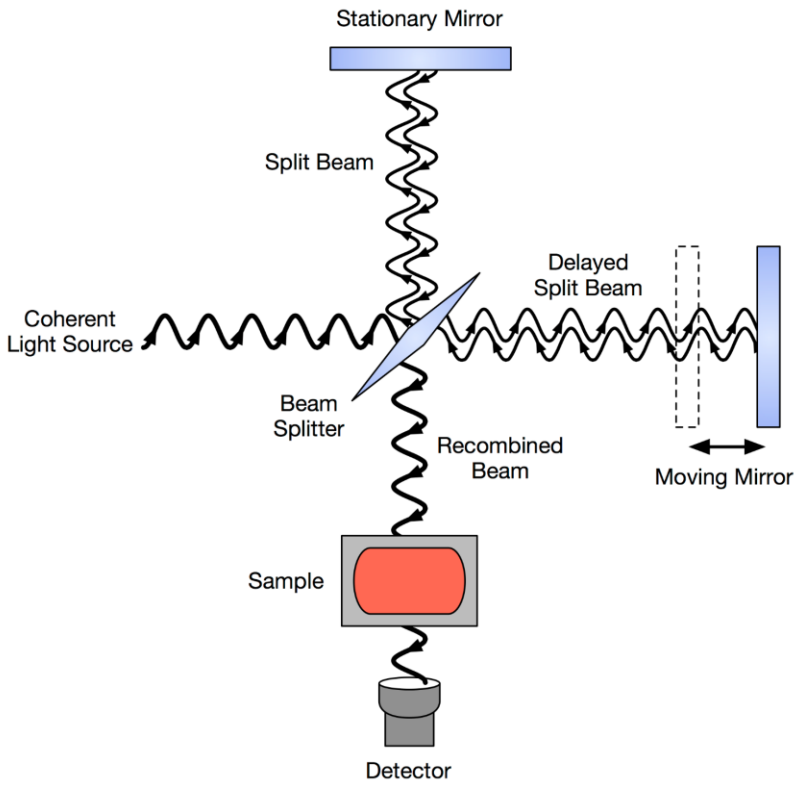

Figure 1. Schematic of a Michelson interferometer used in a FTIR spectrometer.

This method permits high throughput of the light. For infrared measurements the source called a “glow bar” and it is a heated graphite cylinder that emits a thermal or blackbody spectrum. By scanning the moving mirror over a range of distance both shorter and longer than the fixed arm the detected intensities are used to build up an interferogram shown in Figure 2.

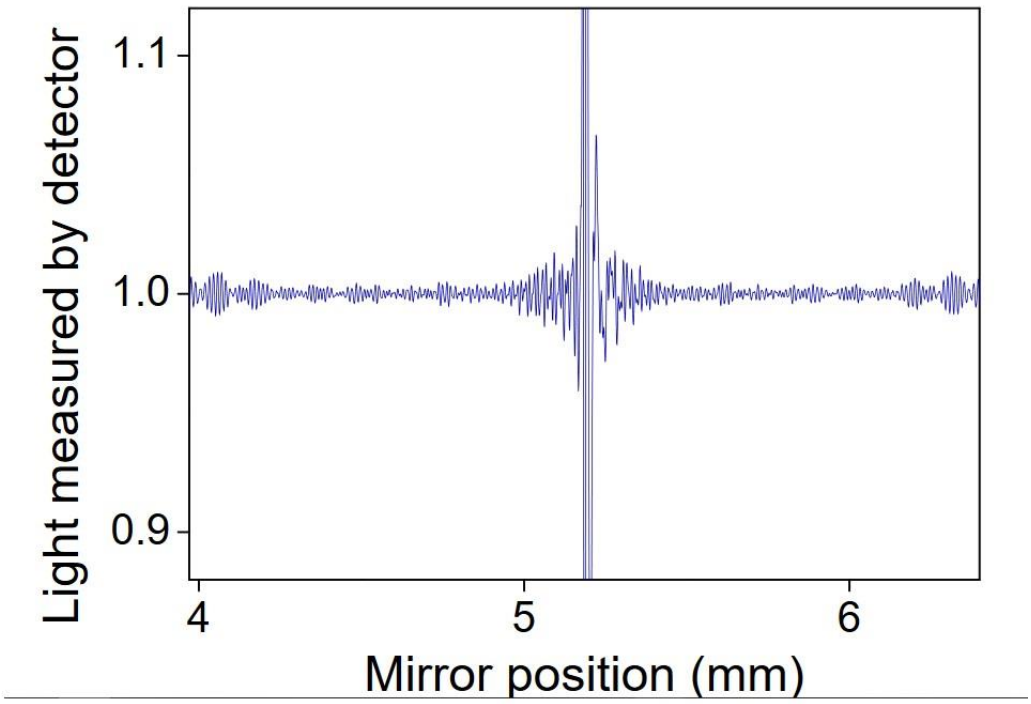

Figure 2. A example interferogram. The fixed arm of the spectrometer has a length of approximately 5.2 mm such that the maximum intensity is obtained when the moving mirror is 5.2 mm from the beam splitter. The pattern is nearly symmetric on either side of this distance.

The Fourier transform of the interferogram gives a spectrum, which consists of the "blackbody" spectrum with any absorption that occurs in the background. Unless the FTIR spectrometer is purged with N_2 gas any H_2O or CO_2 present in the path of the light will absorb light in relevant regions resulting in reductions in intensity in the background spectrum. A spectrum is collected as an average of scans, usually a multiple of 2. Common scan numbers are 16, 32 or 64, but each scan usually requires only 1 second to collect such that scanning for longer times to improve the signal-to-noise ratio is quite feasible. The background thermal (blackbody) spectrum of the glow bar is called a **single beam spectrum** is obtained by taking the Fourier transform (FT) of the light reaching detector when no sample is present. It corresponds to the reference spectrum in a UV-vis experiment. It is the initial intensity, I_0, used to calculate absorbance. Once the single beam has been obtained one places the sample in the path of the beam and scans once again. Following the FT a sample spectrum is obtained. This time the additional reductions in intensity are due to the vibrational modes of the molecules in the sample. The sample spectrum is the intensity, I. One can then calculate the absorption using

$$A = -log_{10}\left(\frac{I}{I_0}\right)$$

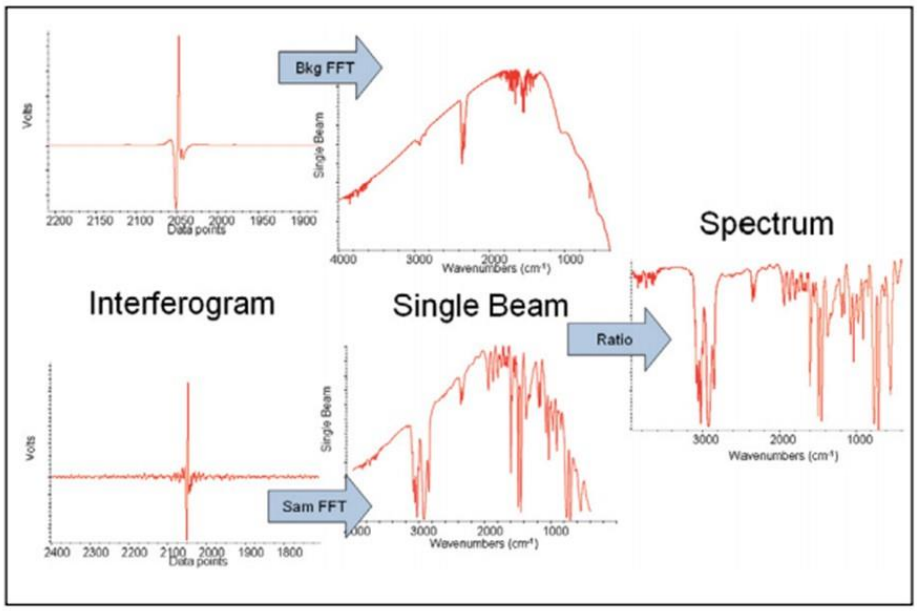

Figure 3: The process of collecting an infrared spectrum in an FT-IR spectrometer

Figure 3 shows the process of collecting two interferograms, one for the background (single beam) and one for the sample. The FT of each gives a different pattern of reductions in intensity Taking the ratio of the two spectra gives the transmission spectrum shown in Figure 3. This spectrum can be reported or further converted into an absorption spectrum by taking the negative logarithm.

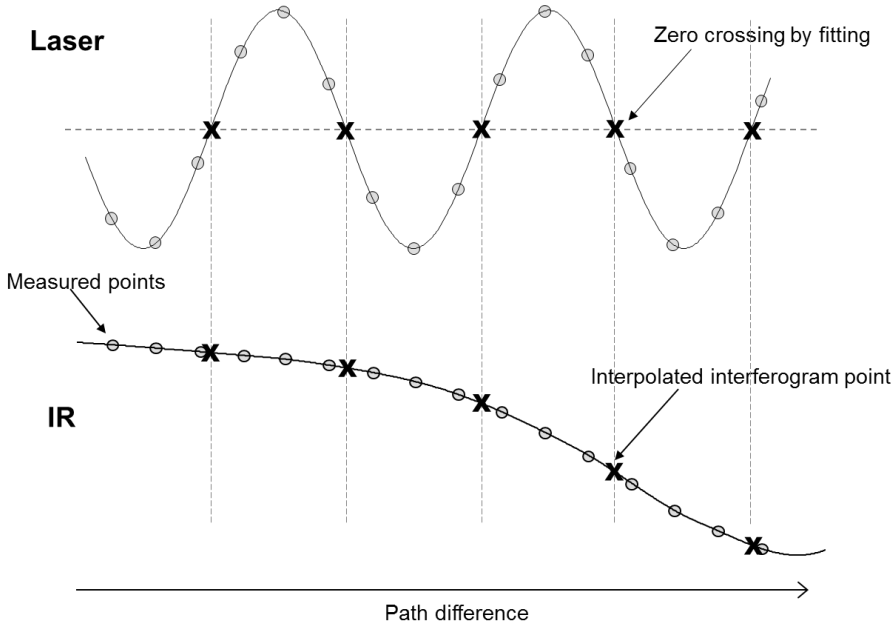

Figure 4. Use of a HeNe laser to determine accurate distances along the moving mirror track.

The interferogram is generated by measuring on either direction from zero path difference to a maximum length that depends on the resolution required. In order to carry out the Fourier transform on the interferogram it must be digitally recorded as a series of values at equal intervals of the path difference between the two beams. A HeNe laser is used to measure the path difference. The laser beam follows the infrared light path through the interferometer. As the moving mirror changes the path length a sinusoidal signal is generated due to the constructive and destructive interference of the HeNe laser light at 632.9 nm. The laser and IR signals are measured synchronously. Subsequently, the IR signal can be interpolated at the laser signal zero crossing points (see Figure 4). This approach permits use of analog-to-digital converters without any need for timing circuits to trigger data collection. Values of the interferogram at times corresponding to zero crossings of the laser signal are found by interpolation (Figure 4). The result is a lower noise than obtained when triggering is used. Since the HeNe laser is red, it can be used to trace the beam path. It is convenient for placing the sample in the sample compartment using home-made sample cells.

FTIR spectroscopy is used for surface spectroscopic measurements, e.g. on Au or Ag surfaces using variable angle reflection absorption spectroscopy. However, the use of attenuated total reflection spectroscopy (ATR) has given rise to the greatest number of applications. The idea behind ATR is that the beam passes through a material where it is totally internally reflected. However, the evanescent wave on the sample side of the material can still absorb IR light and give rise to an absorption spectrum. A multi-pass ATR sample cell is depicted in Figure 5. Fig

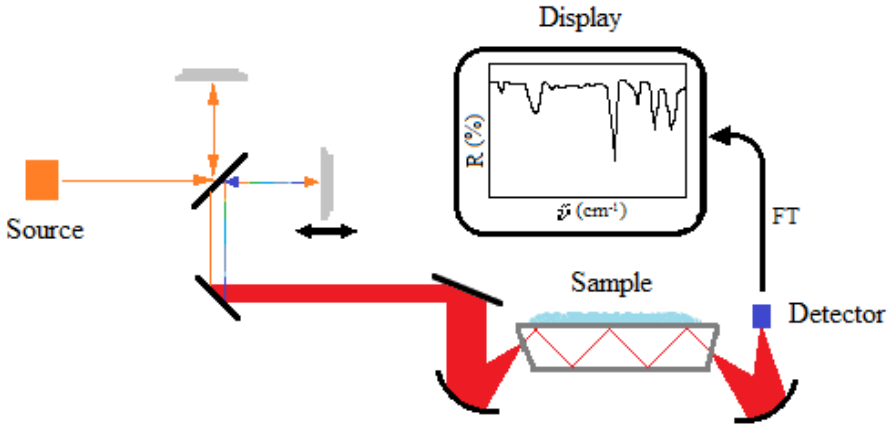

Figure 5. Schematic of a multi-pass ATR-FTIR measurement

For ATR-FTIR one needs a high index of refraction IR transmitting material for a single or multiple bounce beam path. Examples of materials that can be used for ATR detection are Si, Ge, diamond and ZnSe. Diamond has an obvious advantage due to is hardness. One can press solids into contact with the diamond. Diamond is resistant to acids or other potentially corrosive liquids. ATR-FTIR has an effective path length of less than 500 nm because of the decay of the evanescent wave. Thus, concentrated samples are needed. If the sample is sufficiently concentrated the method is extremely convenient since one drop of sample can be sufficient to obtained a spectrum. For this reason ATR-FTIR has become the method of choice for organic chemistry analysis of reaction progress and other applications in chemical synthesis.