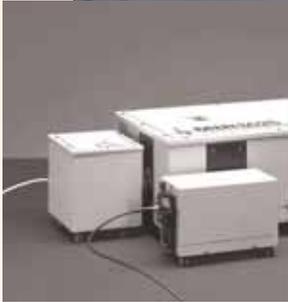


# ORIEL PRODUCT TRAINING



## FT-IR Spectroscopy

### SECTION FOUR FEATURES

- Glossary of Terms
- Introduction to FT-IR Spectroscopy

Before we start the technical discussion on FT-IR Spectrometers, we devote a couple of pages to a Glossary, to facilitate the discussion that follows.

**100% Line:** Calculated by ratioing two background spectra taken under identical conditions. Ideally, the result is a flat line at 100% transmittance.

**Absorbance:** Units used to measure the amount of IR radiation absorbed by a sample. Absorbance is commonly used as the Y axis units in IR spectra. Absorbance is defined by Beer's Law, and is linearly proportional to concentration.

**Aliasing:** If frequencies above the Nyquist Frequency are not filtered out, energy in these will appear as spectral artefacts below the Nyquist Frequency. Optical and electronic anti aliasing can be used to prevent this. Sometimes the higher frequencies are said to be "folded" back so the term "folding" is used.

**Angular Divergence:** The spreading out of an infrared beam as it travels through the FT-IR. Angular divergence contributes to noise in high resolution spectra, and can be a limit to achievable resolution.

**Apodization Functions:** Functions used to multiply an interferogram to reduce the amount of sidelobes in a spectrum. Different types of apodization functions include boxcar, triangle, Beer-Norton, Hanning, and Bessel. The use of apodization functions unavoidably reduces the resolution of a spectrum.

**ATR:** Abbreviation which stands for Attenuated Total Reflectance, a reflectance sampling technique. In ATR, infrared radiation impinges on a prism of infrared transparent material of high refractive index. The total internal reflectance based design assures that the light reflects off the surface of the crystal at least once before leaving it. The infrared radiation sets up an evanescent wave which penetrates a small distance above and below the crystal surface. Samples brought into contact with the surface will absorb the evanescent wave giving rise to an infrared spectrum. This sampling technique is useful for liquids, polymer films, and semisolids.

**Background Spectrum:** A single beam spectrum acquired with no sample in the infrared beam. The purpose of a background spectrum is to measure the contribution of the instrument and environment to the spectrum. These effects are removed from a sample spectrum by ratioing the sample single beam spectrum to the background spectrum.

**Baseline Correction:** A spectral manipulation technique used to correct spectra with sloped or varying baselines. The user must draw a function parallel to the baseline, then this function is subtracted from the spectrum.

**Boxcar Truncation:** With no apodization, all points in an interferogram are given equal weight, up to the edges of the interferogram. If the resolution is less than the smallest linewidth in the spectrum, oscillations appear on the baseline on both sides of the peaks.

**Centerburst:** The sharp, intense part of an interferogram. The size of the centerburst is directly proportional to the amount of infrared radiation striking the detector.

**Coadding:** The process of adding interferograms together to achieve an improvement in signal-to-noise ratio.

**Collimation:** The ideal input beam is a cylinder of light. No beam of finite dimensions can be perfectly collimated; at best there is a diffraction limit. In practice the input beam is a cone that is determined by the source size or aperture used. The degree of collimation can affect the S/N and the resolution.

**Constructive Interference:** A phenomenon that occurs when two waves occupy the same space and are in phase with each other. Since the amplitudes of waves are additive, the two waves will add together to give a resultant wave which is more intense than either of the individual waves.

**Destructive Interference:** A phenomenon that occurs when two waves occupy the same space. Since the amplitudes of waves are additive, if the two waves are out of phase with each other, the resultant wave will be less intense than either of the individual waves.

**Diffuse Reflectance:** The phenomenon that takes place when infrared radiation reflects off a rough surface. The light is transmitted, absorbed, scattered, and reflected by the surface. The light approaches the surface from one direction, but the diffusely reflected light leaves the surface in all directions. A reflectance sampling technique known as DRIFTS is based on this phenomenon.

**Dispersive Instruments:** Infrared spectrometers that use a grating or prism to disperse infrared radiation into its component wavenumbers before detecting the radiation. This type of instrument was dominant before the development of FT-IR.

**DTGS:** Deuterated tri-glycine sulfate pyroelectric detectors are the most common detectors used in FT-IR instruments. They are chosen for their ease of use, good sensitivity, wide spectral responsivity and excellent linearity.

**Duplicate Range:** For an interferogram, it is the ratio of the large centerburst signal at ZOPD to the smallest recorded signal (which must be greater than the noise for any benefit from signal averaging). The A/D used must have sufficient precision to measure the entire range as any clipping or distortion of the largest signal affects the whole spectrum.

**Dynamic Range:** For an interferogram, it is the ratio of the large centerburst signal at ZOPD to the smallest recorded signal (which must be greater than the noise for any benefit from signal averaging). The A/D used must have sufficient precision to measure the entire range as any clipping or distortion of the largest signal affects the whole spectrum.

**Felgett (multiplex) Advantage:** An advantage of FT-IR instrument compared to scanning/single channel dispersive instruments. It is based on the fact that in an FT-IR all the wavenumbers of light are detected at once.

**Fourier Transform:** Calculation performed on an interferogram to turn it into an infrared spectrum.

**Interferogram:** A plot of infrared detector response versus optical path difference. The fundamental measurement obtained by an FT-IR is an interferogram. Interferograms are Fourier transformed to give infrared spectra.

**Jacquinet or J Stop:** An aperture placed in the beam to restrict the divergence to the maximum compatible with the selected resolution. When choosing lower resolution you can improve the S/N by opening the stop. Note that in many instances there is no physically separate stop but there will be some aperture, be it the source size, or the detector active area, that acts as the system J stop.

**Jacquinet Advantage:** This is the throughput advantage of FT-IRs over traditional spectrometers that require a slit aperture. The advantage varies as wavenumber and depends on resolution (because of slit width changes). In practice, any advantage will also depend on source dimensions.

**Mirror Displacement:** The distance that the mirror in an interferometer has moved from zero path difference.

**Normalized:** The process of dividing all the absorbance values in a spectrum by the largest absorbance value. This resets the Y axis scale to 0 to 1.

**Nyquist Frequency:** A term widely used in information theory, but here applies to the highest frequency, shortest wavelength, that can be identified in an interferogram. It is the one for which there are exactly two points per cycle. The contribution of any higher frequency, signal or noise, can be represented by some lower frequency and so will appear aliased or folded into the spectrum.

**Optical Distance:** Physical distance multiplied by the index of refraction of the medium.

**Optical Path Difference:** The difference in optical distance that two light beams travel in an interferometer.

**Phase Correction:** A software procedure to compensate for not taking a data point exactly at ZOPD, and for frequency dependent variations caused by the beam splitter and signal amplification. The Mertz and Forman corrections are both used with the Mertz applied to double sided interferograms; this is considered in the most accurate approach.

**Resolution:** A measure of how well an IR spectrometer can distinguish spectral features that are close together. For instance, if two features are  $4\text{ cm}^{-1}$  apart and can be discerned easily, the spectrum is said to be at least  $4\text{ cm}^{-1}$  resolution. Resolution in an FT-IR is mainly determined by the optical path difference.

**Sidelobes:** Spectral features that appear to the sides of an absorbance band as undulations in the baseline. Sidelobes are caused by having to truncate an interferogram, as a result of finite scan distance, and can be removed from a spectrum by multiplying the spectrum's interferogram by an apodization function.

**Single Beam Spectrum:** The spectrum that is obtained after Fourier transforming an interferogram. Single beam spectra contain features due to the instrument, the environment, and the sample.

**Smoothing:** A spectral manipulation technique used to reduce the amount of noise in a spectrum. It works by calculating the average absorbance (or transmittance) of a group of data points called the "smoothing window," and plotting the average absorbance (or transmittance) versus wavenumber. The size of the smoothing window determines the number of data points to use in the average, and hence the amount of smoothing.

**Spectral Subtraction:** A spectral manipulation technique where the absorbances of a reference spectrum are subtracted from the absorbances of a sample spectrum. The idea is to remove the bands due to the reference material from the sample spectrum. This is done by simply calculating the difference in absorbance between the two spectra, then plotting this difference versus wavenumber. The reference spectrum is often multiplied by a subtraction factor so that the reference material bands subtract out properly.

**Transmission Sampling:** A sampling method where the infrared beam passes through the sample before it is detected. Samples are typically diluted or flattened to adjust the absorbance values to a measurable range.

**Wavelength:** Distance between adjacent crests or troughs of a light wave.

**Wavenumber:**  $1/\text{wavelength}$ , the units of wavenumbers are  $\text{cm}^{-1}$ , and are most commonly used as the X axis unit in infrared spectra.

$$\begin{aligned}1\ \mu\text{m} &= 1,000\ \text{nm} = 10,000\ \text{cm}^{-1} \\5\ \mu\text{m} &= 5,000\ \text{nm} = 2,000\ \text{cm}^{-1}\end{aligned}$$

**Zero Path Difference, or Zero Optical Path Difference:** The mirror displacement at which the optical path difference for the two beams in an interferometer is zero. At ZPD, ZOPD, the detector signal is often very large, the centerburst.

## WHAT IS AN FT-IR AND AN FT-IR SPECTROMETER?

An FT-IR Spectrometer is an instrument which acquires broadband NIR to FIR spectra. Unlike a dispersive instrument, i.e. grating monochromator or spectrograph, an FT-IR Spectrometer collects all wavelengths simultaneously. This feature, called the Multiplex or Fellgett Advantage, is discussed in detail on page 6.

FT-IR Spectrometers are often simply called FT-IRs. But for the purists, an FT-IR (Fourier Transform InfraRed) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum.

## WHY AN FT-IR SPECTROMETER?

Choose an FT-IR over a dispersive instrument if:

- You work in the infrared
- You need high spectral resolution
- You work with weak signals
- You need to acquire your spectra quickly and with high S/N ratio
- You need high spectral accuracy

FT-IRs possess strong theoretical reasons that enable them to excel in these categories. How much of this potential advantage is realized in your application depends strongly on the instrument's design and the particulars of your measurement.

## HOW DOES AN FT-IR SPECTROMETER WORK?

### The Michelson Interferometer

An FT-IR is typically based on a Michelson Interferometer; an example is shown in Fig. 1. The interferometer consists of a beam splitter, a fixed mirror, and a mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beamsplitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source.

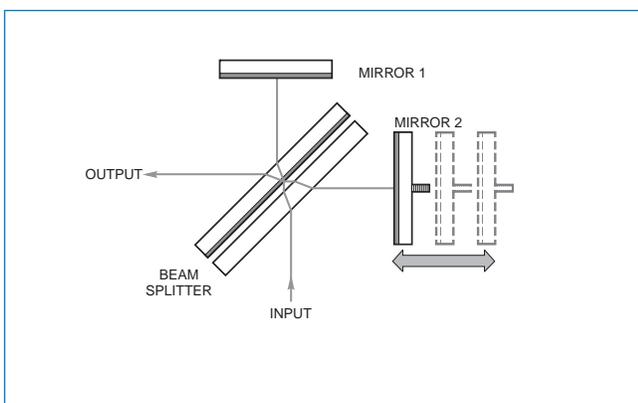


Fig. 1 A Schematic of a generic Michelson interferometer.

## What are OPD and ZPD?

Optical Path Difference (OPD) is the optical path difference between the beams travelling through the two arms of an interferometer. OPD is equal to the product of the physical distance travelled by the moving mirror (multiplied by 2, 4, or other multiplier which is a function of the number of reflecting elements used) and  $n$ , the index of refraction of the medium filling the interferometer arms (air, Nitrogen for purged systems, etc.). The raw FT-IR data consists of a number of (signal, OPD) pairs of values.

FT-IR has a natural reference point when the moving and fixed mirrors are the same distance from the beam splitter. This condition is called zero path difference or ZPD. The moving mirror displacement,  $\Delta$ , is measured from the ZPD. In Fig. 2 the beam reflected from the moving mirror travels  $2\Delta$  further than the beam reflected from the fixed mirror. The relationship between optical path difference, and mirror displacement,  $\Delta$ , is:

$$OPD = 2\Delta n$$

## The Interferogram

Interferogram is the name of the signal format acquired by an FT-IR spectrometer. It is usually significantly more complex looking than a single sinusoid, which would be expected if only a single wavelength of light was present. Fig. 3 shows the beam path of a two wavelength source; Fig. 4 is the interferogram of a broadband light source. The centerburst, the big spike in the center of Fig. 4 is a telltale signature of a broadband source. Its origin lies in the fact that all wavelengths are in-phase at the ZPD. Therefore, their contributions are all at maximum and a very strong signal is produced by the system's detector.

As the optical path difference, OPD, grows, different wavelengths produce peak readings at different positions and, for a broadband signal, they never again reach their peaks at the same time. Thus, as you move away from centerburst, the interferogram becomes a complex looking oscillatory signal with decreasing amplitude.

The X-axis of the interferogram represents the optical path difference. Each individual spectral component contributes to this signal a single sinusoid with a frequency inversely proportional to its wavelength. This leads us to the definition of the unit of spectral measurement. The wavenumber ( $\text{cm}^{-1}$ ), denoted as  $\nu$ . A wavenumber represents the number of full waves of a particular wavelength per cm of length (typically in vacuum; index of refraction  $n=1$ ). The advantage of defining the spectrum in wavenumbers is that they are directly related to energy levels. A spectral feature at  $4,000 \text{ cm}^{-1}$  spectral location represents a transition between two molecular levels separated by twice the energy of a transition with spectral signature at  $2,000 \text{ cm}^{-1}$ .

Table 1 lists a sampling of corresponding wavelength, wavenumber, frequency and energy values.

Table 1 Corresponding Values for Different Units of Measure

$\nu$ ( $\text{cm}^{-1}$ )	$\lambda$ ( $\mu\text{m}$ )	$f$ ( $10^{12}$ Hz)	$E$ (eV)
200	50	5.996	0.02479
500	20	14.99	0.06199
1000	10	29.98	0.12398
2000	5	59.96	0.24797
5000	2	149.9	0.61922
10,000	1	299.8	1.23984

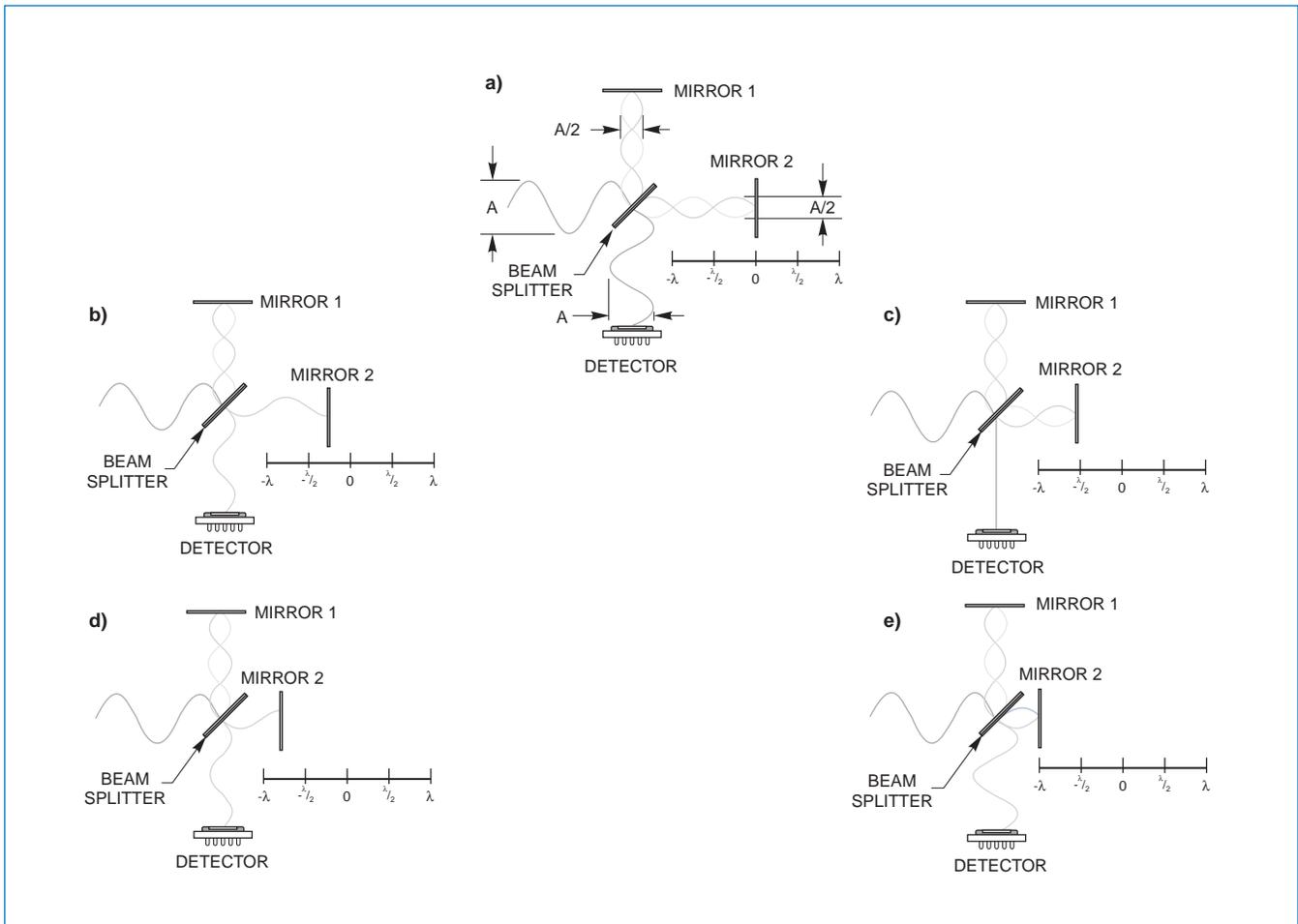


Fig. 2 Schematic representation of waves and their phases, input, output, and the two arms of the interferometer as the scan goes from zero path difference condition to  $OPD=\lambda$ . (a)  $OPD=0$  case. (b)  $\lambda/4$  OPD case. (c)  $\lambda/2$  OPD case. (d)  $3\lambda/4$  OPD case. (e)  $1\lambda$  OPD case.

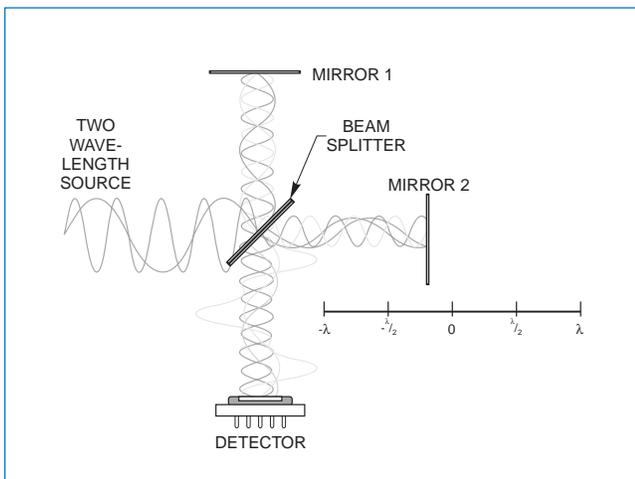


Fig. 3 Two wavelength source case.

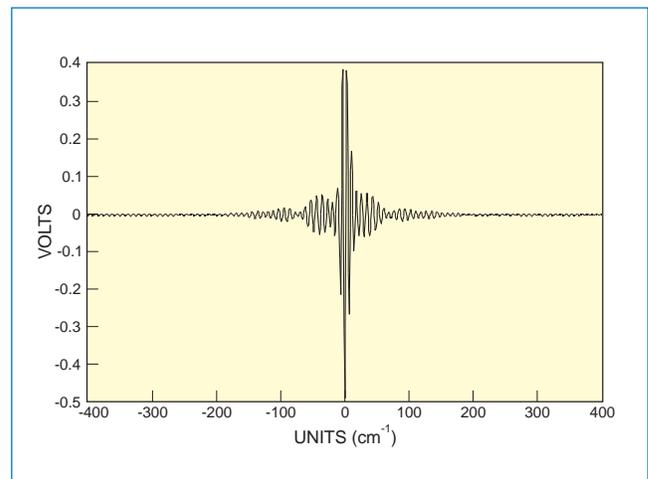


Fig. 4 Broadband source interferogram.

### The Fourier Transform Algorithm

Once an interferogram is collected, it needs to be translated into a spectrum (emission, absorption, transmission, etc.). The process of conversion is through the Fast Fourier Transform algorithm. The discovery of this method by J.W. Cooley and J.W. Tukey in 1965, followed by an explosive growth of computational power at affordable prices, has been the driving force behind the market penetration of FT-IR instruments.

A number of steps are involved in calculating the spectrum. Instrumental imperfections and basic scan limitations need to be accommodated by performing phase correction and apodization steps. These electronic and optical imperfections can cause erroneous readings due to different time or phase delays of various spectral components. Apodization is used to correct for spectral leakage, artificial creation of spectral features due to the truncation of the scan at its limits (a Fourier transform of sudden transition will have a very broad spectral content).

FT-IRs are capable of high resolution because the resolution limit is simply an inverse of the achievable optical path difference, OPD. Therefore, a 2 cm OPD capable instrument, such as our MIR 8000™, can reach 0.5 cm<sup>-1</sup> resolution. Table 2 shows the relationship between resolution expressed in wavenumbers and the one expressed in nanometers, as is customary in dispersive spectroscopy.

**Table 2 Resolution Values in Wavenumbers and Nanometers**

Wavelength (μm)	Resolution (cm <sup>-1</sup> )	Resolution (nm)
0.2	1	0.004
0.5	1	0.025
1	1	0.1
2	1	0.4
5	1	1.0
10	1	10
20	1	40

### ADVANTAGES OF FT-IR INSTRUMENTS OVER DISPERSIVE INSTRUMENTS

Following, we talk about three significant advantages that FT-IR instruments hold over dispersive spectrometers, but first we compare the two instruments.

**Table 3 FT-IR and Dispersive Spectrometer Comparison**

	MIR 8000™ FT-IR	Cornerstone™ 260 1/4 m Grating Monochromator
Wavelength Range	700 nm - 28 μm	180 nm - 24 μm
Max. Resolution	0.024 nm @ 700 nm	0.15 nm
Étendue@1 μm, 0.15 nm resolution	0.38	0.001

### Multiplex ( Fellgett) Advantage

In a dispersive spectrometer, wavenumbers are observed sequentially, as the grating is scanned. In an FT-IR spectrometer, all the wavenumbers of light are observed at once. When spectra are collected under identical conditions (spectra collected in the same measurement time, at the same resolution, and with the same source, detector, optical throughput, and optical efficiency) on dispersive and FT-IR spectrometers, the signal-to-noise ratio of the FT-IR spectrum will be greater than that of the dispersive IR spectrum by a factor of  $\sqrt{M}$ , where  $\sqrt{M}$  is the number of resolution elements. This means that a 2 cm<sup>-1</sup> resolution 800 - 8000 cm<sup>-1</sup> spectrum measured in 30 minutes on a dispersive spectrometer would be collected at equal S/N on an FT-IR spectrometer in 1 second, provided all other parameters are equal.

The multiplex advantage is also shared by array detectors (PDAs and CCDs) attached to spectrographs. However, the optimum spectral ranges for these kinds of systems tend to be much shorter than FT-IRs and therefore the two techniques are mostly complementary to each other.

### The Throughput Advantage

FT-IR instruments do not require slits (in the traditional sense) to achieve resolution. Therefore, you get much higher throughput with an FT-IR than you do with a dispersive instrument. This is called the Jacquinot Advantage. In reality there are some slit-like limits in the system, due to the fact that one needs to achieve a minimum level of collimation of the beams in the two arms of the interferometer for any particular level of resolution. This translates into a maximum useable detector diameter and, through the laws of imaging optics, it defines a useful input aperture.

### High Resolution

Spectral resolution is a measure of how well a spectrometer can distinguish closely spaced spectral features. In a 2 cm<sup>-1</sup> resolution spectrum, spectral features only 2 cm<sup>-1</sup> apart can be distinguished. In FT-IR, the maximum achievable value of OPD, determines spectral resolution. The interferograms of light at 2000 cm<sup>-1</sup> and 2002 cm<sup>-1</sup> can be distinguished from each other at values of 0.5 cm or longer.

**FT-IR INSTRUMENTS HAVE A SHORT WAVELENGTH LIMIT**

A collimated, monochromatic light source will produce an interferogram in the form of a sinusoid, at the detector. When the light intensity goes from one maximum of the interferogram to the next maximum, the optical path difference between the two legs of the interferometer changes by exactly 1 wavelength of the incoming radiation.

To determine the wavelength of the incoming radiation, we can measure the frequency  $f_i$  or period  $t_i = 1/f_i$  of the interferogram with, say, an oscilloscope. Then we can find the wavelength through the formula:

$$\lambda_i = V_0 * t_i = V_0 / f_i \dots\dots\dots (1)$$

Where:

$V_0$  = the speed of change of the optical path difference ( $V_0$  is directly related to the speed of the scanning mirror. For MIR 8000™,  $V_0$  is 4 times the optical speed of the scanning mirror:  $V_0 = 4nV_m$ )

There is, however, an important practical difficulty. We need to maintain the velocity  $V_m$  constant at all times, and we need to know what this velocity is, with a high degree of accuracy. An error in the velocity value will shift the wavelength scale according to (1). Fluctuations in  $V_m$  have a different effect; they manifest themselves as deviations of the interferogram from a pure sine wave that in turn will be considered as a mix of sinusoids. In other words, we will think that there is more than one wavelength in the incoming radiation. This behavior produces what are called "spectral artefacts".

Since the manufacture of an interferometrically accurate drive is extremely expensive, FT-IR designers added an internal reference source into the interferometer to solve the drive performance problem. A HeNe laser emits light with a wavelength which is known with a very high degree of accuracy and which does not significantly change under any circumstance. The laser beam parallels the signal path through the interferometer and produces its own internal interferogram at a separate detector. This signal is used as an extremely accurate measure of the interferometer displacement (optical path difference).

We can, therefore, write the following equation for a HeNe based FT-IR:

$$\lambda_i = \lambda_r * (f_r / f_i) \dots\dots\dots (2)$$

Where subscript r denotes HeNe reference.

We can now calculate the spectrum without extremely tight tolerances on the velocity.

This was just a theoretical example. Now let us see how the reference interferogram is actually used in the MIR 8000™. The signal from the interfering beams of the HeNe are monitored by a detector. What is observed is a sinusoidal signal. The average value is the same as you would see if the beam was not divided and interference produced. The sinusoid goes positive and negative about this value. The average signal level is called zero level. A high precision electronic circuit produces a voltage pulse when the HeNe reference sinusoid crosses zero level. By use of only positive zero crossings, the circuitry can develop one pulse per cycle of the reference interferogram, or use all zero crossings for two pulses per cycle of this interferogram. The latter case is often called oversampling. These pulses trigger the A/D converter which immediately samples the main interferogram.

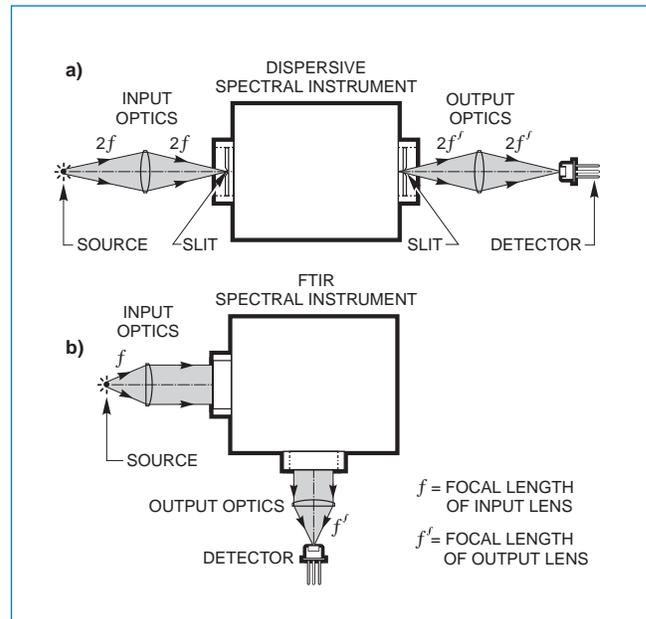


Fig. 5 Diagram of a dispersive spectral instrument and an FT-IR spectral instrument.

There is a fundamental rule called the Nyquist Theorem which can be paraphrased to state that a sinusoid can be restored exactly from its discrete representation if it has been sampled at a frequency at least twice as high as its own frequency. If we apply this rule to the above formula we find immediately that since the minimum value of  $(f_r/f_i)$  is 2, so the minimum value of  $\lambda_i$  is twice the wavelength of the reference laser:

$$\lambda_{min} = 633 \text{ nm} * 2 = 1.266 \mu\text{m}$$

With oversampling, the reference laser wavelength is effectively halved. So in this case:

$$\lambda_{min} = (633 \text{ nm} / 2) * 2 = 633 \text{ nm}$$

In practice, the FFT math runs into difficulties close to the theoretical limit. That is why we say 1.4  $\mu\text{m}$  is the limiting wavelength without oversampling, and 700 nm is the limiting wavelength with oversampling.

**THE RELATIONSHIP BETWEEN RESOLUTION AND DIVERGENCE**

The FT-IR principle of operation is very different from that of dispersive instruments. Many aspects of this relatively new approach are counter intuitive to those of us weaned on dispersive techniques, starting of course with the funny wavenumber units that go the wrong way!

Fig. 5a shows a typical optical layout of external optics relative to a dispersive monochromator. Fig. 5b shows the same for an FT-IR spectrometer. The main optical feature of the FT-IR is that there are no focusing elements inside the instrument; it works with parallel beams. Dispersive instruments from the input slit to an output slit are self contained in the sense that major spectral characteristics do not depend very much on how you illuminate the input slit and how you collect the light after the output slit. Manipulating the light with external optics just gains or loses you sensitivity and adds or reduces stray light and aberrations.

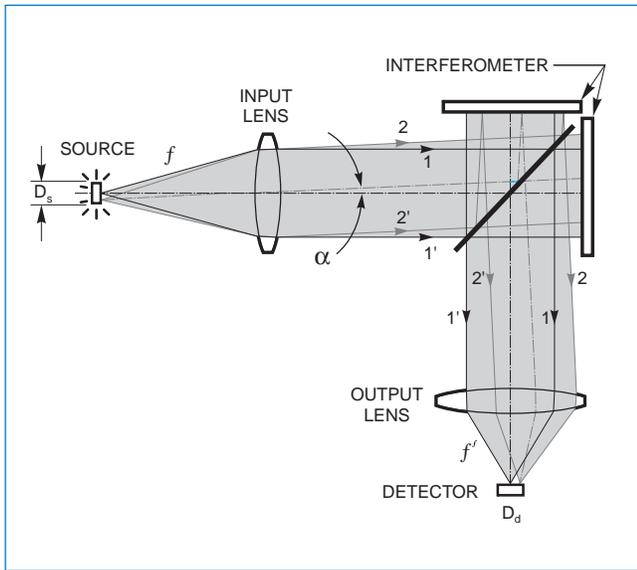


Fig. 6 Scanning Michelson Interferometer.

This is not the case with FT-IRs. External optics are important for proper functioning of the instrument as its internal parts. Fig. 6 shows in a bigger scale a simplified scanning Michelson interferometer together with a source and a detector. Suppose first that the source is a (monochromatic) point source and therefore the beam entering the interferometer (rays 1 - 1') is perfectly parallel. Exiting the interferometer it will be focused into a point on the detector surface. With motion of the scanning mirror the detector will register an interferogram - a sequence of constructive and destructive interactions between two portions of the beam in the interferometer. The further the scanning mirror is traveling, the longer the interferogram and the higher the spectral resolution that can be achieved.

In real life, point sources as well as purely parallel beams, do not exist. A finite size source produces a fan of parallel beams inside the interferometer.

A marginal beam, 2 - 2', of this fan is shown in Fig. 6. This beam will be focused at some distance from the center of the detector. To be exact it will be focused into a ring if the source has a round shape. Now the simple picture we had before becomes much more complex since interference conditions will be different for the beams 1-1' and 2 - 2'.

At ZPD, both beams 1-1' and 2-2' are at constructive interference conditions and the whole detector will sense a high level of intensity. But while the scanning mirror moves away from ZPD, the next condition of constructive interference will happen sooner for beam 2-2' than for beam 1-1'. As a result of that, different parts of the detector will see different phases of the interference pattern: a maximum in the center will be surrounded by a ring of minimum intensity, then a ring at maximum intensity again, etc.

The farther the scanning mirror moves, the tighter this ring pattern becomes, so the detector will see an average level of intensity, and the distinct interference picture recorded for the collimated input will be smeared. To get it back, we need to have just one fringe across the detector when the ring pattern is the tightest, in other words, when the OPD has its maximum value.

EXTERNAL OPTICS FOR FT-IR INSTRUMENTS

General considerations

The function of external optics for FT-IRs is not only to collect and collimate light, but also to provide a certain acceptance angle in the system according to the resolution formula:

$$\alpha_{max} = \sqrt{\Delta\sigma / \sigma_{max}} \dots\dots\dots (3)$$

Where:

$\alpha_{max}$  = the maximum divergence half angle (in radians)

$\sigma_{max}$  = the maximum wavenumber in the spectrum

$\Delta\sigma$  = spectral resolution

To be able to perform calculations for FT-IR auxiliary optics we will need first to revisit some basic optical ideas.

Consider light collected by a lens onto a focal spot or emitted by a source placed in the focal plane of a lens. The solid angle of the cone of rays collected from the source, or alternately directed onto the focal spot, is given by:

$$\Omega = A_L / f^2 \dots\dots\dots (4)$$

Where:

$A_L$  = the area of the collecting/focusing lens  
 $f$  = lens focal length

Both  $f$  and  $A_L$  are expressed in the same units, e.g. m, m<sup>2</sup>, or mm, mm<sup>2</sup>. We can use F/# instead of focal length,

$$\Omega = \pi / (4(F/\#)^2) \text{ sr} \dots\dots\dots (5)$$

So, an F/4 lens collects a solid 0.05 sr, while an F/1 lens collects 0.79 sr. In the more familiar two dimensional picture we use the divergence angle related to the solid angle by:

$$\alpha^2 = \Omega / \pi \text{ radians}^2 \dots\dots\dots (6)$$

The product of solid angle and area of an image at a plane where the solid angle originates is called by various names, optical extent, geometrical extent or étendue. (Often, the term throughput is used instead of étendue.) Étendue determines the "radiation capacity" of an optical system. The fundamental law of optics states that any optical system can be characterized by an optical extent/étendue/throughput which stays constant through all optical transformations:

$$G = A * \Omega = \text{constant} \dots\dots\dots (7)$$

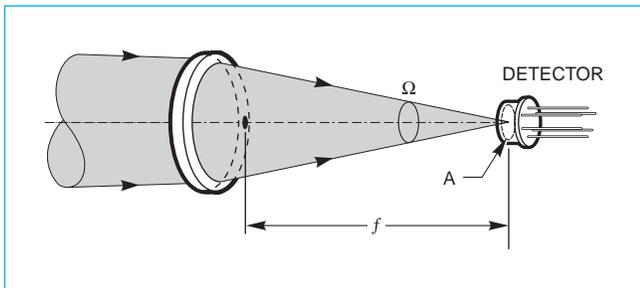


Fig. 7 Detector and optical system.

Note that in Fig. 7, the area A is that of the “detector.” The relevance of this is that every optical system has something that sets or limits the value of G and it is often the detector section. Knowing what part that is and improving it as best as possible is fruitful. Working to increase the G value for another part of the system is a waste of time, but a very common waste of time.

In what follows, we consider the étendue of the MIR 8025™. In general we like to start by calculating what is the largest étendue we can tolerate to get the resolution we need. If the étendue of the instrument, including source and detector, is larger than that value, then we have to limit it.

Let's determine the resolution limit on étendue for the MIR 8000™. We know that it has an aperture of 1.25 inches (31.75 mm). We can also find a maximum allowed divergence angle of a beam propagating through it according to a maximum wavenumber in a spectrum and required resolution. From this we can find the maximum solid angle of the fan of rays by making use of equation (6). Thus, we will find the étendue of the interferometer:

$$G_{\text{infr}} = 2.5 \cdot 10^3 \cdot [\Delta\sigma] / [\sigma_{\text{max}}] \text{mm}^2 \text{sr} \dots \dots \dots (8)$$

When collecting spectra with wavelengths longer than 2 μm,  $\sigma_{\text{max}} = 5,000 \text{ cm}^{-1}$ , and  $\Delta\sigma = 0.5 \text{ cm}^{-1}$ ,

$$G_{\text{infr}} = 0.25 \text{ mm}^2 \text{sr}$$

**Detector Optics**

Now let us consider auxiliary optics; first, on the detector side. Suppose that the allowed acceptance angle is filled fully with light. Continuing the conditions cited in the example above, we want to collect this light and squeeze it onto the smallest possible detector, since smaller detectors have better noise characteristics. To do this we will take a very fast lens with  $F/\# = 1$ . Then according to (5) the solid angle at the focal spot will be:

$$\Omega = 0.79 \text{ sr}$$

and useful detector diameter,

$$D = 2 \times \sqrt{(0.25 / (\pi \cdot 0.79))} \dots \dots \dots (9)$$

or

$$D = 0.6 \text{ mm}$$

Table 4 shows some other detector diameters useful at different resolutions and wavelength ranges. Similar relations apply to the source side. If we optimize the system for high resolution, we miss the opportunity to pump in a lot more radiation at lower resolutions.

What can we do in this situation? We do not have the luxury of using a different detector for each resolution. For general use, we can choose one detector which corresponds to a reasonably high but not necessarily the highest resolution. 4 cm<sup>-1</sup> is a popular choice for this, because 4 cm<sup>-1</sup> resolution is adaptable for condensed phase work. What if subsequently we need a higher resolution? There are a couple of ways to handle this eventuality. One way is to increase the focal length of the detector's fore optics. Longer focus means higher F/#, lower throughput and a higher allowed resolution. It means, of course, a radiation loss also.

Another way is to use an aperture (Jacquinot Stop) to increase the F/#, by decreasing the effective source size; this reduces the spot size on the detector.

**Source Optics**

The source with its optics will typically present a beam with étendue greater than the required étendue of the interferometer. We have seen that the étendue of the instrument is usually limited by the desired resolution or detector size and optics.

Table 4 Maximum Detector Diameter (mm), at F/1, vs Shortest Wavelength and Resolution

$\lambda$ \ $\Delta\sigma$	0.5	1	2	4	8
0.7	0.4	0.5	0.75	1.1	1.5
2	0.6	0.9	1.3	1.8	2.5
4	0.9	1.3	1.8	2.5	3.6

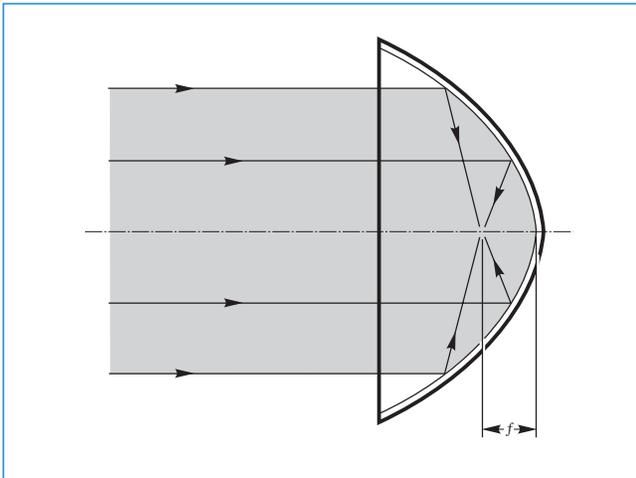


Fig. 8 Light from a point source placed at the focus of a parabola.

**MORE CONSIDERATIONS ON OPTICAL ELEMENTS FOR FT-IR**

**Parabolic Mirrors**

Most FT-IR instruments use off-axis parabolic mirrors for collimating and focusing light external to the interferometer. These gold coated mirrors are very broadband, from 0.7 to 10 microns they reflect more than 98% (see the reflectance curves on page 15-10 in the Book of Photon Tools), and it stays in this range up to 25 microns (bear in mind that for wavelengths shorter than 0.6 micron, gold is a bad reflector; its reflectivity drops abruptly to less than 40%). An important feature of mirrors in general also is that they do not have any dispersion; there is no chromatic aberration so the focal spot stays at the same place for any wavelength. They do have monochromatic aberrations.

Parabola are devices ideally suited for collimating light from small sources and conversely for tightly focusing collimated beams of radiation. They are, however, limited to this purpose. They cannot be used for imaging of larger objects.

Light from a point source placed in a focus of a parabola (Fig. 8) will be transformed after reflection into an ideally parallel beam. Accordingly, a parallel beam will be focused into a tiny focal spot. This is true for any section of the parabola. So, an off-axis section of the paraboloidal mirror can be cut out for convenience (see Fig. 9).

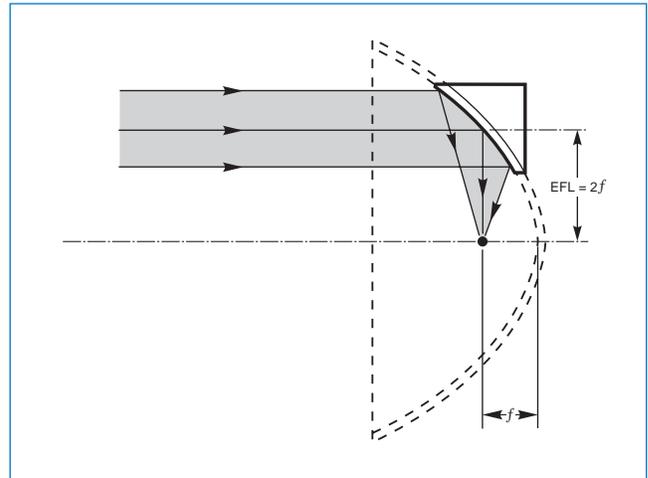


Fig. 9 Section of off-axis parabolic mirror.

The arrangement shown in Fig. 9 is described as a 90° off-axis mirror since the ray striking the center of the aperture and parallel to the main axis turns exactly at 90° and comes into the focal point. The distance from the point on the surface of the parabola at the center of the aperture, to the focal point, is called effective focal length (EFL) and it is exactly two times the focal length of the parabola.

$$EFL = 2f \dots\dots\dots (10)$$

F/numbers of off-axis parabolic mirrors can reach very low values; F/1 or even less is practical. If a finite size source, instead of a point source, is placed in the focal point of the parabola, the reflected beam will not be ideally parallel any more. It will have some angular divergence according to the angular size of the source. On top of that it will suffer significant aberrations. Accordingly, a parallel incoming beam will be focused into, not a spot, but a blurred spot.

It is important to analyze how the angular divergence of a beam turns into a blur spot in a parabola focus. We created, with an optical design software package, the optical schematic of MIR 8025™ with an F/1 parabolic mirror at the output. We traced rays with different divergence through the system and watched for the focal spot size.

Fig. 10 shows a graph of the diameter of the focal spot vs. angular divergence of the beam propagating through the interferometer.

The limit on divergence angle in the interferometer we found from formula (3) (page 8), at the smallest possible  $\Delta\sigma$  which is  $0.5 \text{ cm}^{-1}$  and the highest possible  $\sigma$  which is  $14,000 \text{ cm}^{-1}$ , is  $0.006 \text{ rad}$ . The graph shows that the diameter of the focal spot which corresponds to this value is about  $0.5 \text{ mm}$ . (The rough estimate, of the same value made with the formulae on the preceding pages, gives a value of  $0.4 \text{ mm}$ ). With increasing divergence of the beam, the diameter of the focal spot also increases, as we see, but it has some limit between  $1.5$  and  $2 \text{ mm}$ . The reason for this is that the interferometer itself is blocking high angle rays and they cannot reach the parabola. The maximum value of angle of rays that can get through the interferometer is  $0.06 - 0.07 \text{ rad}$ . This is exactly the region where the curve in Fig. 10 starts to flatten out.

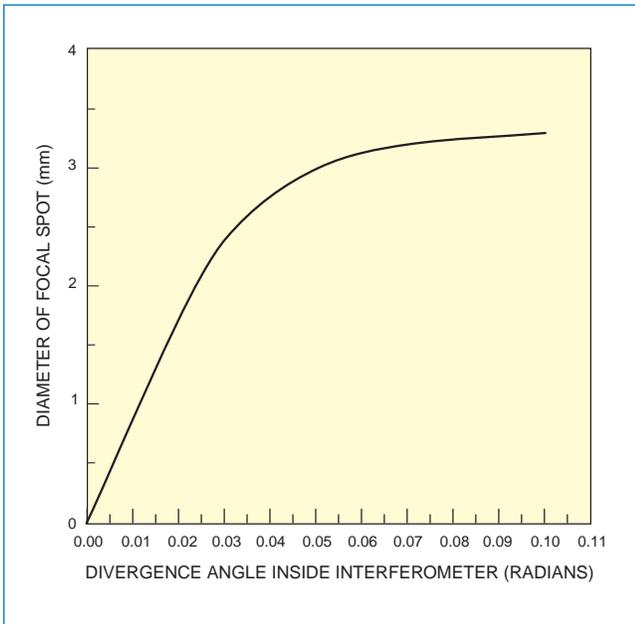


Fig. 10 Diameter of Focal Spot vs Angular Divergence.

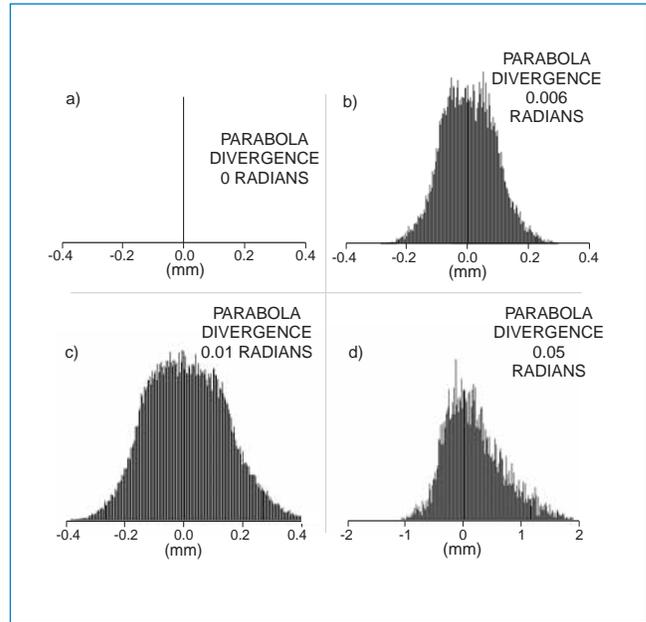


Fig. 11 Energy distribution in the focal plane of an off-axis reflector.

Fig. 11 shows the energy distribution in the focal plane of the off axis reflector for beams of different divergence. This shows the increasing impact of aberrations as the “field of view” of the parabola is increased.

**Lenses**

Despite universality and wide usage of off-axis parabolic mirrors in FT-IR spectroscopy, they have certain disadvantages. They are pretty difficult to align; each reflection turns the beam through  $90^\circ$ , and this may make the system bulky. At low F/#, i.e. large fields of view (high étendue), they suffer from significant aberrations.

In many applications, especially in the Near IR, lenses could be a good choice. Fig. 12 shows the energy distribution in the focal spot of a  $\text{CaF}_2$  lens having about the same focal length and F/# as the parabolic mirror considered earlier.

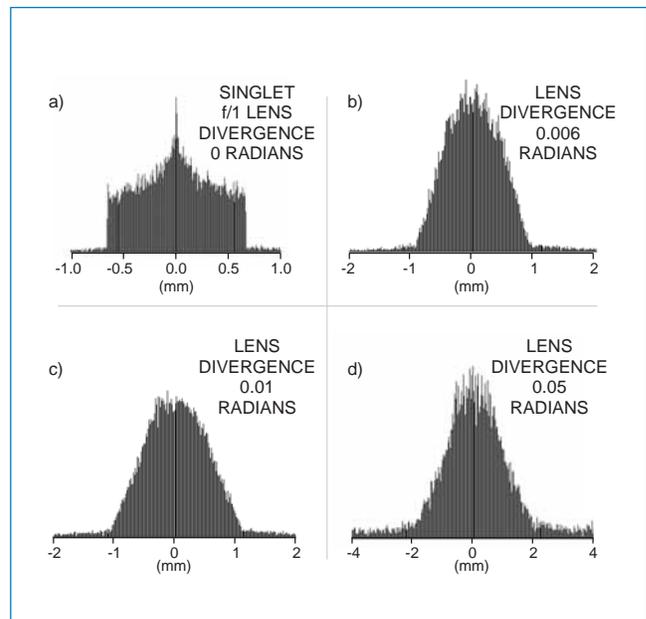


Fig. 12 Energy distribution in the focal plane of a  $\text{CaF}_2$  lens.

When using lenses, you need to consider the lens material. We recommend the use of  $\text{CaF}_2$  lenses in the whole range where the  $\text{CaF}_2$  beam splitter is applicable. In the very Near IR, up to  $3\ \mu\text{m}$ , fused silica lenses are fine, though the water absorption bands can cause some loss with lenses that are not "IR grade". They are somewhat cheaper than  $\text{CaF}_2$  lenses. A wide variety of materials are available for the Mid IR. You usually have a choice among performance, expense, durability, birefringence, etc. The hygroscopic nature of some materials can be a big problem.  $\text{NaCl}$  windows and  $\text{KBr}$  are two such popular materials. Some materials are transparent in the visible and others not; this can be a plus if you are trying to align in the visible, or a negative when you would prefer the material to act as a filter.

A popular rugged and transparent material which is used for manufacturing lenses is  $\text{ZnSe}$ . It has, however, a very high index of refraction that pushes reflectance losses to relatively high levels: up to 30%. Anti-reflection coatings can help, but at further expense, and reduction of the spectral range. We list IR lenses on pages 9-30 to 9-32 in the Book of Photon Tools.

A second issue is dispersion of the lens material. Lenses are definitely good for limited wavelength range applications. For example, the sensitivity range of an  $\text{InGaAs}$  detector is from 800 to 1700 nm. Using a lens should not pose a major problem, though we do see some dispersion in our labs with fused silica lenses over this range; i.e. you can axially move the lens to optimize the long wavelength or short wavelength signal. For a wider wavelength range you should position the detector at the shortest focal length position, in other words, in the position of minimum spot size for the shortest wavelength, since usually system efficiency is the lowest, there.

These examples show us that the auxiliary optics for an interferometer must be carefully chosen and arranged. Poor choices of components will lead to lack of resolution or unnecessary system throughput limitations.