Fourier Transform Infrared Spectroscopy

Part II. Advantages of FT-IR

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Part I of this paper addressed the subject of FT-IR instrumentation. We saw that a Fourier Transform Infrared Spectrometer was essentially a single-beam instrument in which the transmission spectrum was obtained by ratioing a single beam spectrum of the sample against a single-beam spectrum of the background. These two single-beam spectra were generated mathematically by computing the Fourier transform of their corresponding interferograms. It seems like a rather complex process, and one may ask why this procedure would be preferable to using the traditional double-beam dispersive spectrophotometer in which the spectrum is generated by scanning the wavenumber range of the instrument in real time.

Energy Advantages of FT-IR Spectroscopy

There are several advantages that an FT-IR spectrometer has when compared to a dispersive instrument. Perhaps the most significant of these is the much higher signal-to-noise ratio of the FT-IR system. Peter Fellgett pointed out that in a dispersive instrument the spectrum is examined one resolution element at a time as the dispersed spectrum is swept past the exit slits of the monochromator. In contrast, the interferometer sees all of the wavelengths present all of the time during the scan. Expressed quantitatively the magnitude of the signal-to-noise advantage is equal to the square root of the number of resolution elements in the wavenumber range that is being scanned:

\[ \text{Fellgett's advantage} = \sqrt{ \frac{r_1 - r_2}{\Delta r} } \]  

where \( r_1 \) and \( r_2 \) are the limits of the region scanned and \( \Delta r \) is the resolution. For example, if we scan from 4000 to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) (a typical survey scan on either type of instrument), the advantage would be a factor of 30. From eq 1 it is readily apparent that the factor of improvement, known as the Fellgett advantage (also referred to as the multiplex advantage) will become greater with increasing resolution and/or with wider scanning ranges.

While the full magnitude of Fellgett's advantage is not realized because of other factors such as beam-splitter efficiency, detector frequency response, and source characteristics, to name a few, it is nevertheless substantial and is the most significant single factor favoring the FT-IR technique. The Fellgett advantage is realized only when the system is detector-noise-limited, that is, detector noise remains constant as the signal increases. This is the case for thermal detectors such as the deuterated triglycine sulfate (DTGS) detectors commonly used in most FT-IR spectrometers.

Another advantage claimed for the interferometer is that a greater throughput of energy can be achieved than for a dispersive instrument using a monochromator. This benefit was pointed out by Pierre Jacquinot and is usually referred to as the Jacquinot advantage (sometimes also called the throughput advantage). Unfortunately, the argument has frequently been misstated in the literature, leading to erroneous calculations of the magnitude of the benefit.

An optical system is characterized by its limiting apertures, and the energy throughput, or étendue, is calculated as the product of the area of a limiting aperture times the solid angle of the beam subtended at that aperture. In the case of a monochromator we may calculate étendue as the product of slit area times the solid angle of the beam at the slits. For the Michelson interferometer the calculation involves an aperture known as the Jacquinot stop (used to define the collection of the beam going to the beam-splitter and hence a factor that limits interferometer resolution) and the solid angle at the J-stop. When these computations are made on comparable-sized instruments (grating area comparable to beam-splitter area), the Jacquinot advantage turns out to be generally less than the Fellgett advantage and may even favor the dispersive instrument at longer wavelengths where slit widths can become quite large. In chemical spectroscopy the sample size may further limit throughput. The error that has crept into the literature has been to compare monochromator slit area with interferometer beam-splitter area and totally to neglect the solid angle term. Obviously this would grossly inflate the magnitude of the advantage assigned to the interferometer, but the computation is of course totally invalid.

The energy advantages can be stated in more practical terms that reflect the real benefit to the interferometer user. If a specified amount of time is spent collecting spectral data, the interferometer will generate a spectrum with a much higher signal-to-noise ratio (SNR) than the dispersive instrument. Alternatively, if a given SNR must be reached, the interferometer will produce it in a much shorter time than the dispersive instrument.

It may also be convenient to make the comparison in terms of applications. Sometimes our sample is available for observation for only a short period of time. Examples are kinetic studies and the observation of gas chromatography fractions on the fly (i.e., as they elute from the column). Typical gas chromatography (GC) peaks have widths of several seconds. Dispersive spectrophotometers usually require 3-5 minutes to scan a full range spectrum, and even the fastest commercially available systems require at least a minute, thus limiting their use for examining GC fractions to the somewhat tedious "trap and transfer" process or to stopped-flow experiments. On the other hand, a spectrum can be generated from a single interferogram, and in most FT-IR spectrometers this is done in a second or less using the normal DTGS detector, and as many as 20 to 30 scans per second are possible when using a mercury-cadmium-telluride cooled detector. Clearly, when observation times are limited, the interferometer can generate data, and the dispersive instrument cannot.

In most laboratories, however, the need to obtain spectra quickly is not the governing criterion. There is usually an ample amount of sample and adequate time to make the scan using either technique. In these cases the advantages of the interferometer are often not fully utilized. The dispersive instrument can produce a good-quality survey scan in 3-5 minutes, and at the end of that period one also has a hard-copy spectrum drawn on the instrument's own recorder. An FT system, using a previously stored background, can average several scans and display a comparable-quality spectrum on the CRT screen in no more than 15-30 seconds, but, if hard copy is required, plotting may take 1 to 2 additional minutes depending on equipment. If one needs only to view the spectrum—for example, to determine whether a cell has the proper thickness or...
Wavenumber Accuracy

Another advantage of Fourier Transform spectroscopy is that of greater wavenumber accuracy. Most commercial FT instruments specify an accuracy of \( \pm 0.01 \) cm\(^{-1} \). While it is questionable that this value can be attained when measuring real absorption bands with finite half-widths, accuracies of the order of a few tenths of a wavenumber are realistically achieved. In contrast the wavenumber accuracy of most dispersive instruments falls in the range of \( \pm 0.2 \) cm\(^{-1} \) to as much as \( \pm 4 \) cm\(^{-1} \) depending on the quality of the spectrophotometer. How does the interferometer achieve this higher level of performance? Certainly a number of design and construction factors contribute, but since the spectrum is calculated from the interferogram, an accurate spectrum implies an accurately sampled interferogram. The interferogram is a continuous function of intensity vs. optical retardation, but when it is transformed it must be handled mathematically by a computer as a discrete function, that is, a table of individual ordinate data points taken at equal retardation intervals. If the transformation is to yield an accurate (including wavenumber accuracy) spectrum, it is imperative that these data points be taken at very precisely equal intervals of retardation (or mirror travel).

In modern interferometers this is accomplished by using the zero crossings of the interferogram from a helium-neon laser to trigger the sampling of the infrared interferogram. Figure 1 helps to explain how this process can be carried out. The left-hand portion of the figure depicts the infrared interferometer exactly as described in part I of this paper. FM1 is the fixed mirror; BS1 is the beamsplitter; MM is the moving mirror; and D1 is the infrared detector producing the interferogram that is then transformed into the spectrum. Consider, however, a system in which MM, the moving mirror, is aluminized on both sides and in which it also serves as the moving mirror for a second, separate interferometer shown on the right-hand part of the figure. This second interferometer utilizes a helium-neon laser as its source and a photodiode (D2) as its detector. The interferogram corresponding to a single frequency source is a cosine function, and the zero crossings of this reference interferogram can now be used to trigger the collection of the data points sampled from the infrared interferogram. Thus the uniformity of the data sampling interval is constant as the frequency of the helium-neon laser. It is this precise method of collecting data from the interferogram that makes possible the high wavenumber accuracy of FT-IR spectrometers. The first use of a helium-neon laser to trigger data collection is attributable to Mertz, but the benefit was soon recognized by Connes and is sometimes referred to in the literature as the Connes’s advantage.

The system shown in Figure 1 is a simplification used to illustrate the principle. Some very early designs did utilize a two-sided moving mirror common to both the infrared and the laser reference interferometers, but most instruments today direct the relatively small helium-neon laser beam into the main interferometer cavity where it takes up only a small fraction of the overall beam area.

Other Advantages

The energy advantages and the increased wavenumber accuracy are probably the major reasons for the rapidly growing popularity of the FT-IR spectrometer. There are, however, a few other aspects in which the interferometer has an advantage over dispersive instruments, and these deserve at least brief mention.

Constant Resolution

Dispersive spectrophotometers, in order to maintain approximately constant energy throughput over the scanning range, are operated with programmed slits whose width increases with increasing wavelength to compensate for the long wavelength fall-off of source energy. Since spectral bandpass varies directly with slit width, resolution degrades as we scan to lower frequencies. In a typical survey scan on a grating spectrophotometer, the time advantage may still be significant, and one saves the cost of chart paper. But, if a hard-copy spectrum is required, the interferometer’s advantage shrinks, and the time for sample preparation rather than scan time may limit the laboratory’s throughput.

Consider, finally, the hard-to-do samples. Typically these include microsamples, samples with very low overall transmission, samples producing very weak spectra, and samples that require the use of low-efficiency accessories. This is where the interferometer enjoys its greatest practical advantage. In order to be readable, these spectra usually require significant ordinate expansion, and the signal-to-noise ratio becomes limiting. The traditional methods to enhance signal-to-noise ratio are moving-point polynomial smoothing (Golay–Savitzky smoothing) and spectral averaging. Both have been used extensively, but spectral averaging has the advantage that it does not risk the distortion of data. Averaging (or smoothing) can be done on either dispersive or FT instruments. One must take care at this point to distinguish the benefits of computerized data processing from the benefits of the FT technique itself. Once a spectrum has been obtained, on either instrument, its information content can often be enhanced by computer manipulation, and these benefits are independent of how the spectrum was generated. The FT instrument, of course, already includes a computer (to transform the interferogram); the dispersive instrument is usually interfaced to an external laboratory computer, although the more recently introduced dispersive spectrophotometers now tend to have built-in computer capability that includes averaging, smoothing, spectral subtraction, and some reformatting capabilities, as well as the computing of difference spectra.

In any event, samples in the hard-to-do category usually require some amount of signal averaging in order to improve the signal-to-noise ratio prior to viewing or further data processing. The noise level is reduced in proportion to the square root of the number of scans averaged. To reduce the noise in a single scan by a factor of 2 requires that 4 scans be averaged; a factor of 4 requires 16 scans; and a factor of 10 requires 100 scans. With a scan time of 3–5 minutes for a dispersive instrument, even a 10-scan average requires 30–50 minutes, and that gives only a little more than a threefold improvement in signal-to-noise ratio. Assuming a 1-second scan time for the interferometer, the improvement in signal-to-noise ratio is almost a factor of 8 for a 1 minute average and more than 17-fold for 5 minutes of averaging. (N.B. Do not assume that a single 1-second scan on the interferometer is necessarily equivalent to one scan on the dispersive instrument; this relationship will depend entirely on the specifications of the two instruments.) It is clear to see that when one is severely energy limited, the Fellgett advantage makes it possible to obtain data on the interferometer that one either could not obtain on a dispersive system or perhaps that one would not be willing to spend the time obtaining.
terometer the resolution may vary from 3–4 cm\(^{-1}\) at the shorter wavelengths to as much as 10 cm\(^{-1}\) or more at the end of the scanning range. In the interferometer, resolution is determined largely by the distance that the moving mirror travels and by the choice of apodization function. Hence it is constant across the scanning range. This advantage is somewhat offset by another characteristic. The dispersive instrument has a constant noise level throughout its scan while the interferometer, which ratios two black-body-like curves to produce a transmission spectrum, exhibits higher noise levels at the two extremes of its scan. In summary, the interferometer has constant resolution and variable noise level; the dispersive instrument has constant noise but variable resolution.

**Polarization Effects**

One of the most efficient polarizers for infrared radiation is a diffraction grating. In fact, one technique for making infrared light is passed through a grating like infrared radiation is a diffraction grating. In contrast, a prism acts as a polarizer, which ratios two wavevectors. Vignetting the sample has the transmission shows a strong wavelength dependence, and there are abrupt discontinuities at grating or order changes. Figure 2 shows the comparable data taken at the Grating Changes

Those who have used grating spectrophotometers have probably had occasions when they have observed sharp discontinuities or steps in the spectrum at grating and order changes. Stepping can occur as a result of vignetting the sample beam of a double-beam instrument in a manner different from that of the reference beam. It is related to the abrupt discontinuity of the slit program at grating and order changes. It occurs most often when accessories with focusing optics, such as beam condensers or reflectance accessories, are used in the sample beam and/or when reference beam attenuators are used in the reference beam. It may also be observed when scanning samples with high refractive index or when running badly scattering potassium bromide pellets. The interferometer has no varying slits with discontinuities in their programs and hence is free of the stepping phenomenon.

**Availability of Cooled Detectors**

This benefit is one that results from commercial practice, and it has a practical rather than a theoretical basis. The benefit is nonetheless real. Infrared spectrometers, whether dispersive or interferometric, usually have a room temperature detector as their normal detector (a thermocouple for dispersive systems and a pyroelectric detector for FT systems). Greater detectivity and hence enhanced signal-to-noise ratio can be realized for either type of instrument by replacing the room temperature detector with a cooled detector. A narrow-band, liquid-nitrogen-cooled, mercury–cadmium–telluride (MCT) detector can enhance the signal-to-noise ratio by as much as one to two orders of magnitude. MCT detectors are standard options on almost all commercially available FT-IR spectrometers. There is no reason why they cannot be used with dispersive instruments with a similar benefit. Indeed there have been instances where individuals have modified their dispersive instruments to accept cooled detectors. Yet in more than 30 years of infrared history the author has never known a cooled detector to be offered by the manufacturer as a standard option or accessory for a dispersive instrument. Perhaps the times were just not right, or maybe the cost of a cooled detector was considered to be too large an increase to the cost of the basic spectrometer. In any event, the ready availability of the MCT detector as an option for the interferometer must be considered as a very important practical advantage.

**Summary**

In Part II of this paper we have discussed the advantages that FT-IR spectrometers have when compared to dispersive instruments. The FT instrument can obtain good quality spectra, rapidly, under sampling conditions that are difficult or impossible for the dispersive spectrophotometer. In the third and final part of this paper we will describe a wide variety of practical applications where FT-IR is being used routinely to carry out these previously difficult analyses.