Chapter 1
Spectroscopy Instrumentation

1.1 Introduction

Fourier-transform spectrometers (FTS or FT spectrometers) have been replacing the dispersive instruments in many infrared and near-infrared applications over the last couple of decades. Their inherent advantages compared with the dispersive instruments are proven and well accepted by scientists and engineers working in the field of spectroscopy. This chapter provides a general overview of the types of spectrometers commonly used today, focusing on the differences in their operating principles. An analysis of an FT spectrometer’s advantages over its dispersive counterpart is then presented.

1.2 Types of Spectrometers

Spectrometers can be categorized into three main types based on their principles of operation: dispersive, filter-based, and Fourier-transform instruments.

1.2.1 Dispersive spectrometers

As the name suggests, dispersive spectrometers generate spectra by optically dispersing the incoming radiation into its frequency or spectral components, as illustrated in Fig. 1.1. Common dispersive elements include prisms and gratings. Dispersive spectrometers can be further classified into two types: monochromators and spectrographs. A monochromator uses a single detector, narrow slit(s) (usually two, one at the entrance and another at the exit port), and a rotating dispersive element allowing the user to observe a selected range of wavelength. Figure 1.1 shows the simplified schematic of a monochromator.

A spectrograph, on the other hand, uses an array of detector elements and a stationary dispersive element. In this case, the slit shown in the figure is removed, and spectral elements over a wide range of wavelengths are obtained at the same time, therefore providing faster measurements with a more expensive detection system.
Figure 1.1 Schematics of a monochromator; a dispersive spectrometer. Narrow slits (an input and an output slit) are used to select a particular spectral element whose wavelength depends on the beam’s incident angle on the grating. (Only the output slit is shown in this figure.)

1.2.2 Filter-based spectrometers

Filter-based spectrometers, or often simply called filter spectrometers, use one or more absorption or interference filters to transmit the selected range of wavelength, as illustrated in Fig. 1.2. As the beam passes through the filter, some of its spectral components are blocked through an absorption or interference process, while the desired spectral elements are transmitted. Various interference filters, from the ultraviolet through the far-infrared region, in various dimensions, are available as commercial-off-the-shelf items (e.g., Spectrogon AB, Taby, Sweden, and CVI Laser Corp., Albuquerque, NM, USA).

A commonly used spectroscopic configuration is that of a filter-wheel system, also available commercially. This system consists of a number of filters (with different wavelength responses) placed near the circumference of a rotating wheel. A spectral band is selected by positioning the wheel so that the beam falls on a particular filter. With this configuration, however, only a few discrete bands can be selected, rather than a continuous spectrum as with a monochromator. Another variation of the filter-based systems is the tilting-filter instrument.¹ In this instrument a spectral band is selected by changing the incident angle of the beam on the filter. However, the wavelength tuning range is rather limited at about ±3% of the center wavelength.

Because of the limited number of discrete wavelengths in filter-wheel instruments and the limited range of wavelength in tilting-filter instruments, filter-based spectrometers are dedicated to the specific analyses for which they are designed.
Chapter 2
Signal-to-Noise Ratio

To quantify the instrument’s performance, the spectral signal-to-noise ratio (SNR) is used as the main measure throughout this book. The term has been used somewhat inconsistently; in some cases, it is used to quantify spectral repeatability, and in others, it is used to quantify spectral accuracy. Thus, it is appropriate to start with a clear definition of the term as it applies throughout this book.

2.1 Signal-to-Noise Ratio Defined

In this book, the SNR measures the instrument’s ability to reproduce the spectrum from the same sample, the same conditions, and the same instrumental configurations over a certain amount of time. This, in fact, is a measure of spectral repeatability, which measures the ability of the instrument to detect certain changes in the spectrum such as those caused by changes in the sample’s spectral characteristics. Therefore, noise is the measure of the spectral deviations between measurements, regardless of the output spectrum’s proximity to the “true” value.

Accuracy, on the other hand, is a measure of the discrepancy between the actual measured value and the “true” standard or calibrated value. Wavelength accuracy of a spectrometer is crucial. It is important for the instrument to be able to conform to the “calibrated standard” in producing wavelength information within the instrument’s intended resolution. For example, if the true absorption peak of molecule x is 4000.2 nm, the instrument should be able to give the correct peak wavelength information within its designed resolution. Thus, following the example, if the instrument has a designed resolution of 1 nm, then it should register the peak of molecule x at 4000 nm. This is required for proper information transfer between instruments.

The spectral magnitude accuracy of FT spectrometers, however, is meaningless because it depends on various factors that are difficult to “standardize,” such as the optics’ transmission properties, the detector’s characteristics, the speed of the moving mirror, the electronics’ bandwidth, among various other factors. However, this does not generally cause a problem...
because the instrument’s transfer function is usually zeroed-out by first taking the measurement of a reference spectrum. The reference spectrum may simply be that of the ambient air, or a certain reference sample.

Fourier-transform spectroscopic measurements generally involve two steps: first is the recording of the reference spectrum, and second is the recording of the sample spectrum. This should apply to both the absorption and the emission studies. Theoretically, the results are then independent of the instrument’s transfer function, and are transferable between different instruments. For this to be true, however, the recorded intensity at each wavelength has to have high repeatability, and be within the linear range of the detection unit. The importance of the detector’s linearity is discussed in Sec. 8.4.4.

### 2.2 Quantifying Signal-to-Noise Ratio

Most of the measurements using FT spectrometers rely on the single beam technique that involves taking the ratio of the sample’s transmission spectrum to the reference spectrum at two separate times. Consequently, spectral noise $N(\nu)$ can be computed according to the following equation:

$$ N(\nu) = 1 - \frac{T_a(\nu)}{T_b(\nu)}, \quad (2.1) $$

where $T_a$ and $T_b$ are the transmission spectra of the same sample/buffer taken at two different times, as illustrated in Fig. 2.1. This method can also be applied to the double-beam measurements, in which case $T_a$ and $T_b$ are taken simultaneously. In the case of zero noise, $N(\nu)$ will be a flat line at zero across the wavelength range. A 100% line is defined by $100 \times T_a(\nu) / T_b(\nu)$ and is usually specified in the FT spectrometer’s manufacturer’s data sheet.

The root-mean-square (rms) value of the spectral noise $N_{\text{rms}}$ can then be computed as

$$ N_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} [N(\nu_i)]^2}, \quad (2.2) $$

where $n$ is the number of spectral elements being observed. The range of the spectral elements should cover only the spectral range of interest. Note that the rms value is usually three to five times smaller than the peak-to-peak noise value. Finally, spectral SNR can be computed as

$$ \text{SNR} = \frac{1}{N_{\text{rms}}}. \quad (2.3) $$
Chapter 3
Principles of Interferometer Operation

The interferometer is the core of every Fourier-transform spectrometer. Today’s FT spectrometers use a variety of interferometer designs. However, they are all still based on the simple, yet historically most important, Michelson interferometer.

In this chapter, the operating principle of the Michelson interferometer for FT spectroscopy is discussed. It is the objective of this chapter to provide a thorough physical understanding of how a spectrum is generated in an FT spectrometer. Enough mathematics is used to aid comprehension. First, a qualitative overview is provided, which is followed by a more detailed explanation starting with the wave description of light. Then, the factors that limit the output spectral resolution are explored, and finally, the interferogram processing techniques sometimes necessary to obtain accurate spectra are briefly discussed.

3.1 Overview

Figure 3.1 shows a schematic of a Michelson’s interferometer. It consists of a beamsplitter and two plane mirrors that are perpendicular to each other. One of the plane mirrors, $M_2$, moves linearly in the direction shown by the arrow. As light enters the interferometer, it is amplitude divided at the beamsplitter. Approximately one-half of the light is transmitted and the other half is reflected. The transmitted and reflected beams are then reflected at mirrors $M_2$ and $M_1$, respectively. The beams are then recombined at the beamsplitter and detected by a photodetector.

Under first consideration is light from a monochromatic source. When $L_1$ is equal to $L_2$, the two beams travel the same distance from the point they leave the beamsplitter to the point where they recombine at the beamsplitter. Being in-phase, they interfere constructively (Fig. 3.2) and the detector sees a maximum intensity. As $L_2$ moves away from the zero optical path difference (OPD), the
Figure 3.1 Schematic of a two-plane mirror Michelson interferometer.

Figure 3.2 Monochromatic waves at zero OPD.

Intensity starts to decrease as phase difference is introduced. Note that the OPD is equal to twice the mirror retardation distance because the OPD corresponds to the distance traveled by the beam to and from the moving mirror. When the OPD is equal to $\lambda/2$, destructive interference occurs as the two recombined beams become out-of-phase with each other. Thus, as the moving mirror travels at a constant velocity, the detector sees a sinusoidal-varying intensity. This sinusoidal signal is a function of mirror $M2$ displacement with a period of $\lambda/2$. The recombined interfering beams’ intensity fluctuation as a function of mirror displacement is called an interferogram. The interferogram is then Fourier transformed to obtain the spectrum. Figure 3.3 shows an interferogram from a monochromatic source and its spectrum.
When the radiation comes from a broadband source, the interferogram contains a peak at zero mirror retardation, and when all wavelength components interfere constructively, they decay quickly as the mirror moves. Figure 3.4 shows an experimentally obtained interferogram of a broadband near-infrared source and its resulting spectrum.

### 3.2 Quantitative Explanation

#### 3.2.1 Light as a wave

To fully understand light interference and interferogram generation, light as an electromagnetic wave must be considered. A monochromatic light contains a single-frequency wave, though no real waves are truly monochromatic. A source...