ABSTRACT

ANALYSIS AND APPLICATIONS OF FTIR SYSTEMS

by
Gunjan Navin Doshi

Fourier Transform Infrared Spectroscopy (FTIR) is a dynamical instrumental technique used in industry for measuring high quality infrared spectra. Over the last 25 years, the increased demand for having an efficient real-time quantitative measurement technique has led to extensive research and development in the field of FTIR Spectroscopy. Through the use of FTIR, sensitivity has increased, size of the smallest sample that can be analyzed has been reduced, and the number of new applications has exploded. In this thesis, an attempt is made to study the principles, theory, instrumentation and applications of FTIR Spectrometry. We survey the working of spectrometer, computation techniques, methodology, spectral manipulations, hardware, trading rules and the applications.

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by
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This work is dedicated to
My Spiritual Master H.D.H. Hariprasad Swami Maharaj
and
His Divine Society

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CHAPTER 1

INTRODUCTION

1.1 History

Sir John F. W. Herschel, son of the discoverer of the infrared, obtained the first infrared spectrum in 1840. Some forty years later Langley published his excellent solar spectra and showed that there were absorption bands superimposed on the solar continuum. When K. J. Angstrom demonstrated that the absorption bands of different gases consisting of the same atoms have different infrared absorption spectra, it became evident that the infrared spectra is related to molecular rather than atomic properties. The characteristic of infrared spectroscopy, which makes it invaluable, is its ability to identify certain molecular groups in compounds.

The development of FTIR spectrometers began with the invention of the two-beam interferometer by Michelson. As technology advanced, the advantages of FTIR spectrometers became clear. Specially, the Fellgett and Jacquinot advantage combine to form the fundamental basis for the improved performance of FTIR spectrometers. The next step in the acceptance of Fourier spectrometry was the discovery of Fast Fourier Transform (FFT) algorithm by Cooley and Tukey. The developments that helped the acceptance of FTIR further were the fabrication of Helium-Neon lasers and minicomputers. Helium-Neon lasers permitted interferograms to be digitized at precisely equal intervals and the minicomputer allowed spectra to be computed in the laboratory directly after the measurement of the interferogram. The technological advancements in the field of Computer hardware design and with the reduction in the price over the years with a concomitant advances in field of Optics has established FTIR spectrometry as a accepted technique for measuring high-quality infrared spectra. The utility of FTIR has increased over the years.

1.2 Objective

The purpose of this thesis is to discuss the theory, instrumentation, and applications of FTIR spectrometry. FTIR is a dynamical instrumental technique, which can be applied to an enormous variety of samples.

Chapter 2 introduces the background required for complete understanding of FTIR working. Also, in this chapter the advantages and the limitations of FTIR are mentioned on a relative basis.

In chapter 3, we deal with the first phase of FTIR spectroscopy, which is using the interferometer to obtain the interferogram. Here, we explicate the construction and working of Michelson's Interferometer, which forms the heart of most FTIRs even today. The different types of interferometer and output obtained from interferometer are also discussed.

How the output of an interferometer i.e. an interferogram, becomes a spectrum, by applying Fourier transform techniques is clarified in chapter 4. It illustrates mathematically, how the Fourier transform technique is utilized to obtain the spectrum.

Chapter 5 deals with several spectral manipulations applied to the spectrum to extract as much information from the spectrum as possible. Spectral subtraction, Baseline Correction, Smoothing, Spectral derivatives, Deconvolution, Curvefitting, Spectral library searching, and quantitative analysis are discussed.

One of the important things that go in the study of FTIR is the instrumentation involved. Chapter 6 mentions the components of FTIR and its working. It specifies right from the interferometer source to the spectrometer electronics that go behind making the FTIR perform successfully.

With different types of FTIR available in the market, important question that arises is what factors should one checkout before selecting an FTIR. Chapter 7 elucidates the different trading rules involved in selecting a FTIR. Various relationships involved are made clear.

With FTIR almost universal in industry for measuring FTIR, chapter 8 shows various applications of FTIR in industry.

CHAPTER 2

FUNDAMENTALS OF FTIR SPECTROSCOPY

2.1 Infrared Region and Spectroscopy

Infrared spectroscopy [1] is the study of the interaction of infrared light with the matter. Light is composed of electric and magnetic waves. These two waves are in planes perpendicular to each other, and the light waves move through space in a plane perpendicular to the plane containing the electric and magnetic fields. It is the electric part of light, called the electric vector, which interacts with molecules.

The wavenumber of a light wave is defined as the reciprocal of the wavelength and is really a measure of the number of waves there are in a centimeter. Wavenumbers are the units typically used in infrared spectroscopy to denote different kinds of light. The wavenumber of a light is directly proportional to the energy as follows:

$$E = hcW \tag{2.1}$$

where

E = Light energy

c = The speed of light (3×10^{8} meters/second)

h = Planck's constant (6.63×10^{-34} Joule- second)

W = Wavenumber

Thus, high wavenumber light has more infrared energy than low wavenumber light. We usually use for our purposes the mid infrared radiation as the light between 4000 and 400 cm-1.

2.2 Infrared Radiation and Matter

2.2.1 Infrared Radiation

Infrared radiation is another name for heat. All objects in the universe above absolute zero, give off infrared radiation. When infrared radiation interacts with the matter, it can be absorbed, causing the chemical bonds in the material to vibrate. The presence of chemical bonds in a material is a necessary condition for the infrared absorbence to occur. Chemical structural fragments within molecules, known as functional groups, tend to absorb infrared radiation in the same wavenumber range, regardless of the structure of the rest of the molecule the functional group is in.

There is a relation between the wavenumbers at which a molecule absorbs infrared radiation and its structure. This correlation allows the structure of unknown molecules to be identified from the infrared spectrum of the molecule.

2.2.2 Infrared Spectrum

A plot of infrared radiation intensity versus wavenumber is known as an infrared spectrum [2]. Traditionally, infrared spectrum is plotted with high wavenumber on the left and low wavenumber on the right. That is as one is looking from left to right in an infrared spectrum one is looking from high energy to low energy.

In addition to the chemical structures, infrared spectra can provide quantitative information as well, such as the concentration of a molecule in a sample. The basis of all quantitative analysis in FTIR is the Beer's law, which relates concentration to absorbance, and has the following form:

$$A = \varepsilon \, l \, c \qquad (2.2)$$

where

A = absorbance

ε = absorptivity

l = Pathlength.

c = concentration

The absorbance is measured as a peak height, peak height ratio, peak area, or peak area ratio from the FTIR spectrum. The absorptivity is the proportionality constant between concentration and absorbance. It changes from molecule to molecule and from wavenumber to wavenumber for a given molecule. For a given molecule and wavenmber, the absorptivity is a fundamental property of the molecule.

2.3 The Advantages and Limitations of the FTIR

An instrument used to measure the infrared spectrum is called an infrared spectrometer. There are several kinds of instrument used to obtain infrared spectra.

The ultimate performance of the infrared spectrometer is determined by measuring its signal-to-noise ratio. For a given sample and set of conditions, an instrument with high SNR will be more sensitive, be applicable to more kinds of samples, and allow absorbance to be measured more accurately than with an instrument with low SNR. To understand the advantages of FTIR and how it became the predominant way of obtaining infrared spectra, the performance of FTIRs must be compared to the type of infrared instruments that were used before it [3]which were called the dispersive instruments. As seen in Figure 2.1, a dispersive instrument has either gratings or prisms

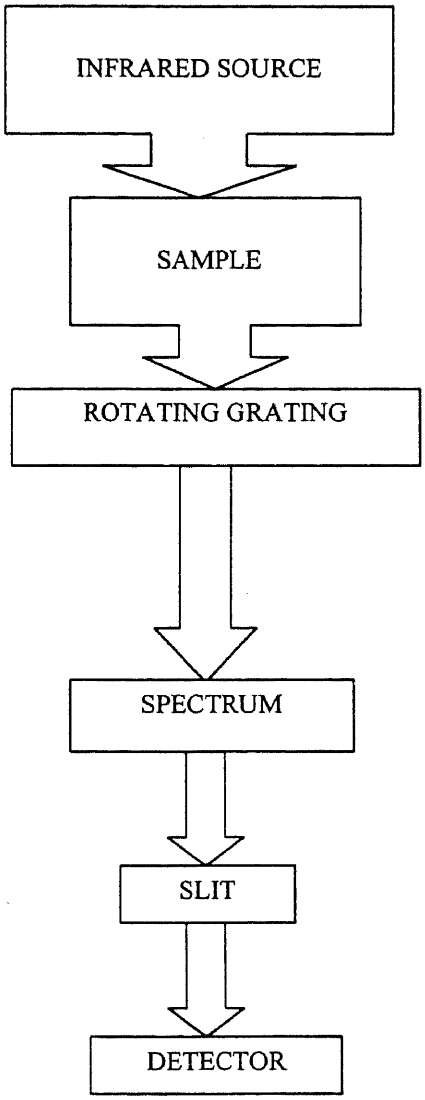

Figure 2.1 Dispersive Spectrometer

as dispersers, which allow the observation of a narrow, predetermined, nearly monochromatic, desired frequency domain. Spectra are resolved by scanning the desired frequency range at successive resolution intervals. The narrow openings of the entrance and exit slits, required to achieve good resolution, limit the energy throughput, so the detector views only a small portion of the energy emitted by the source.

The first advantage is called the throughput or jacquinot advantage of FTIR [17]. As mentioned above there is loss of energy of the input source in a dispersive instrument because of the presence of a grating and slit between the source and the detector. However, in an FTIR instrument, Figure 2.2, all infrared radiation passes through the sample and strikes the detector at once in an FTIR spectrometer. There are no slits to restrict the wavenumber range or reduce the intensity of infrared radiation that strikes the detector. Thus, the detector sees the maximum amount of light at all the points during the scan, resulting in the throughput advantage. FTIR spectrometers use interferometers to obtain the interferogram first, which is then mathematically processed to produce the spectrum. This means that they can be used to great advantage in observing spectra from very weak sources.

The second SNR advantage of FTIR is called the multiplex advantage. It is based on the fact that in an FTIR all the wavenumbers of light are detected at once, where as in the dispersive instruments only a small wavenumber range at a time is measured. In dispersive type, resulting radiation is dispersed by a grating and small segments of the dispersed light fall on a detector after passing through the slit which is set at some width to produce the desired resolution. In FTIR spectrometers, the detector views all of the frequencies, all of the time during the mirror displacement. The principal advantage of

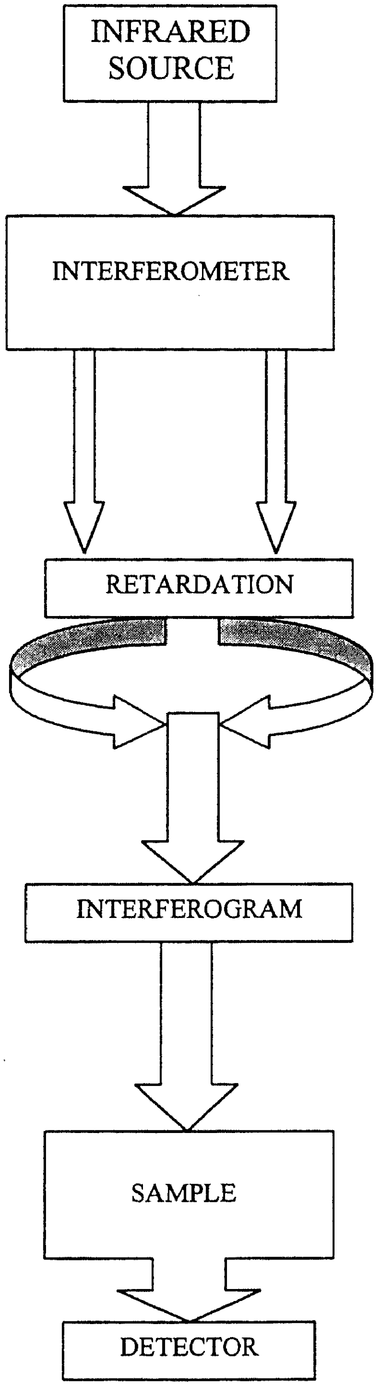

Figure 2.2 Interferometer

multiplexing is that an FTIR can acquire a spectrum much faster than a dispersive instrument.

Despite the advantages of FTIR, there are limitations, on what is achievable with infrared spectroscopy in general, and there is one specific limitation in particular. A general limitation of infrared spectroscopy is that it cannot detect atoms or monatomic ions. Single atomic entities contain no chemical bonds, and do not possess vibrational motion and hence do not absorb infrared radiation. In general, it is impossible for an infrared spectrometer to measure the level of an element in a substance, unless the element is present as a part of a molecule whose spectrum can be detected. In addition, the noble gases such as the helium and argon cannot be detected because they exist as individual molecules. Another class of substances that do not absorb infrared radiation are the homonuclear diatomic molecules. Another limitation of infrared spectroscopy, is its use in analyzing complex mixtures. These samples give rise to complex spectra, whose interpretation is difficult because it is difficult to know which bands are from which molecule in a sample. Infrared spectroscopy is best worked on pure substances, since all bands can be assigned to a specific chemical structure. Before obtaining an infrared spectrum, it is best to separate out the components of complex mixtures using the methods such as recrystallization, distillation and chromatography. Aqueous solutions are also difficult to analyze using infrared spectroscopy. Water is a strong infrared absorber and dissolves many infrared materials used in the cells and as windows. A technique known as liquid ATR enables one to obtain infrared spectra of aqueous solutions.

A specific limitation of FTIR spectrometers is that FTIR is a single beam technique. This means that the background spectrum, which measures the combination of the instrument and the environment to the spectrum, is measured at a different point in time than the spectrum of the sample. If something in the instrument or the environment changes between when the sample and background spectra are obtained, spectral artifacts can appear in the sample spectrum. The artifacts can be misinterpreted and may mask sample absorbances.

Infrared spectroscopy is a wonderful tool for detecting functional groups, but it cannot necessarily be used to elucidate the complete structure of an unknown molecule [4]. Often times an infrared spectrum does not contain enough information, or contains misleading or contradictory information, making the complete determination of an unknown's structure difficult. The best approach is to use FTIR in conjunction with other molecular spectroscopy techniques such as NMR, mass spectrometry, UV/VIS spectroscopy and Raman scattering. All these techniques provide different pieces of information about a molecule's structure, and together provide a powerful means of identifying unknowns.

CHAPTER 3

INTERFEROMETER

3.1 Working of Interferometer

The purpose of an interferometer is to take a beam of light, split into two beams, and make one of the light beams travel a different distance than the other. The difference in the distance traveled by these two light beams is called the optical path difference or optical retardation denoted by the Greek letter δ.

3.2 Michelson Interferometer

3.2.1 Construction

We will restrict our discussion to the Michelson Interferometer, since it was the first interferometer to be used in commercial FTIR instruments, and is still at the heart of most FTIRs in use. A diagram of a Michelson interferometer is shown in Figure 3.1. Michelson interferometer [5] [6] consists of four arms. The first arm contains a source of infrared light, and the second arm contains a stationary mirror, the third arm contains a moving mirror, and the fourth arm is open. At the intersection of the four arms is the beam splitter, which is designed to transmit half of the radiation that impinges on it and reflect half of it. Consequently, the light transmitted by the beam splitter strikes the fixed mirror and the light reflected by the beam splitter strikes the moving mirror. After recombining off their respective mirrors, the two beams recombine at the beam splitter, then leave the interferometer to interact with the sample and strike the detector.

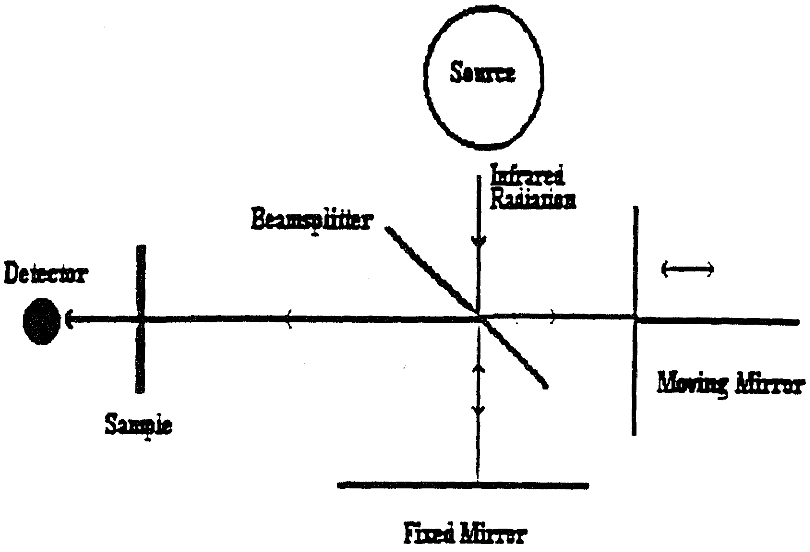

Figure 3.1 Michelson Interferometer

3.2.2 Optics

If the moving mirror and fixed mirror are at the same distance from the beam splitter, the distance traveled by the light beams that reflect off these mirrors is the same. This condition is known as zero path difference (ZPD). In a Michelson interferometer, an optical path difference is introduced between the two light beams by translating the moving mirror away from the beam splitter. The light that reflects off the moving mirror will travel further than the light that reflects off the fixed mirror. The distance that the mirror moves from ZPD is the mirror displacement that is denoted by the symbol Δ. The light that reflects off the moving mirror travels a distance Δ on the way to the mirror and a distance Δ on its return trip to the beam splitter. The extra distance this light beam travels compared to the fixed mirror light beam is equal to the 2Δ. Thus, the relationship between mirror displacement and optical path difference is

$$\delta = 2\Delta \tag{3.1}$$

where δ is the optical path difference and Δ is the mirror displacement.

3.2.3 Working Mechanism

Imagine using a monochromatic light source, such as laser (although lasers are not the light sources in FTIR) of wavelength λ. Also, assume the interferometer is at ZPD as shown in Figure 3.1 [8]. When the beams that have reflected off the fixed and the moving mirrors recombine at the beam splitter they will be in phase. Their crests and trough will overlap as shown in Figure 3.2. The beams leave the beam splitter in phase and since they travel the same distance at the same speed, they are in phase when they recombine at the

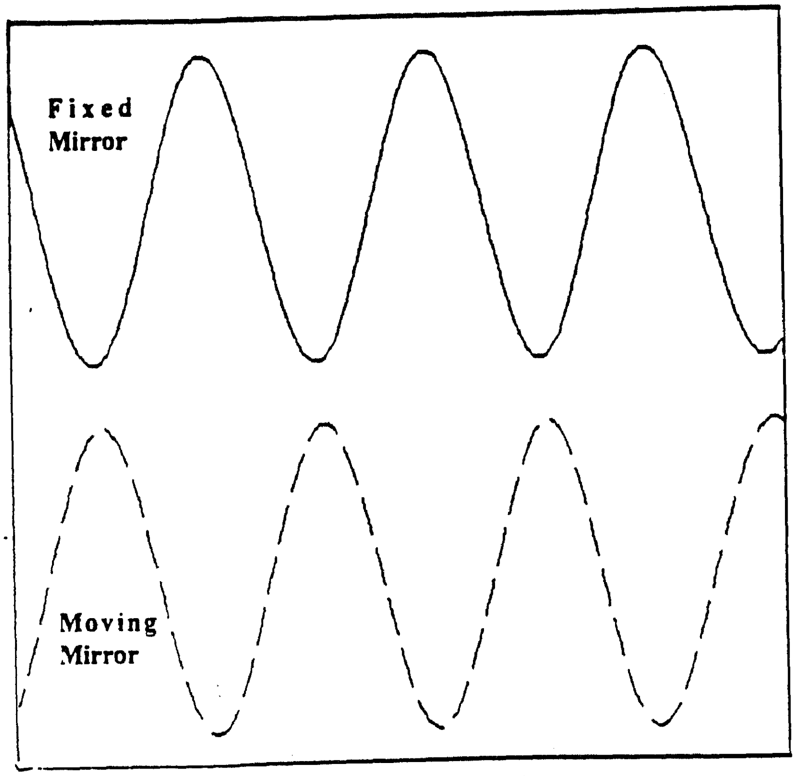

Figure 3.2 Constructive Interference

beam splitter. Now, it is the general property of the waves that their amplitudes are additive. Because of constructive interference, an intense light beam leaves the interferometer. All the wavelengths of light constructively interfere at ZPD. Constructive interference also takes place when the optical path difference is equal to the multiples of λ. In this case, the light beams have traveled different distances, but are out of phase the right amount to lead to a perfect overlap of crests with crests and troughs with troughs. Constructive interference will take place for any value of δ where the two light beams are in phase.

This is summarized as follows:

$$\delta = n\lambda \tag{3.2}$$

where n is any integer. ZPD corresponds to when $n = 0$, and totally constructive interference will take place whenever δ is some multiple of the optical path difference.

Imagine changing the mirror displacement of a Michelson interferometer so that the moving mirror is $1/4\lambda$ away from the ZPD. Since $\delta = 2\Delta$, the optical path difference is $1/2\lambda$. When the fixed and the moving mirror light beams are recombined at the beam splitter they are completely out of phase as seen in Figure 3.3. The crests and troughs of the light waves overlap, and their amplitudes add together and cancel each other, giving a light beam of low intensity. This is known as destructive interference. Total destructive interference takes place, when the optical path difference is $1/2\lambda$ or some multiple of it. The optical path differences at which totally destructive interference takes place is given by

$$\delta = (n+1/2)\lambda \tag{3.3}$$

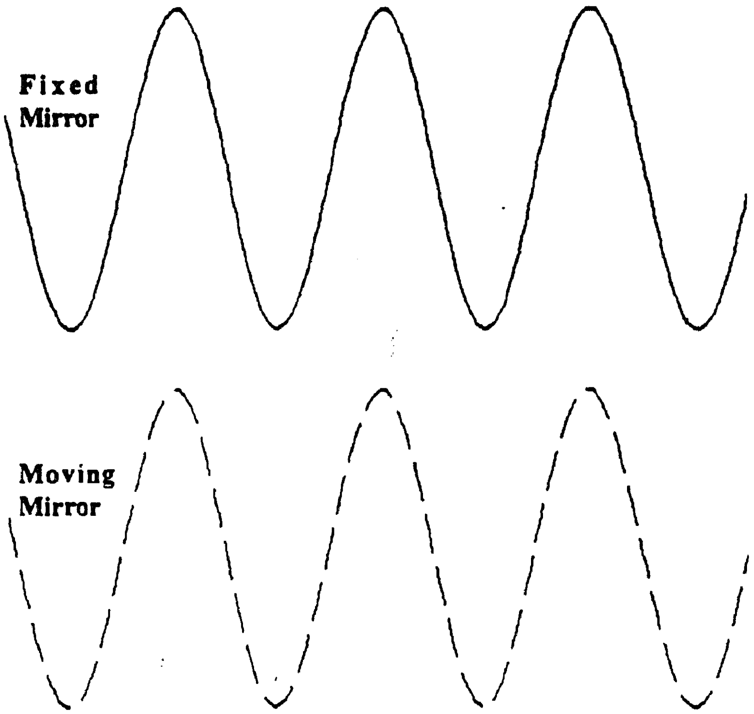

Figure 3.3 Destructive Interference

At optical path differences other than those given in equations 3.2 and 3.3, a combination of constructive and destructive interference takes place, and the light beam intensity is somewhere between very bright and very weak.

3.3 Interferogram

A plot of the light intensity versus the optical path difference is called an interferogram. The optical path difference is measured in the terms of wavelengths. If the mirror is moved at constant velocity, the intensity of infrared radiation increases and decreases smoothly. The variation of light intensity with optical path difference is measured by the detector as a sinusoidal wave (more specifically a cosine wave). The wavelength of the source is fixed but the variations are done in the optical path difference by changing the position of the moving mirror. The fundamental measurement obtained by an FTIR is an interferogram as shown in Figure 3.4, which is then Fourier transformed to give a spectrum. This is where the term Fourier transform infrared spectroscopy comes from. To generate a complete interferogram the moving mirror is translated back and forth once and is known as a scan.

The constructive and destructive interference that takes place in the interferometer affects the light intensity at a given wavelength as if a shutter were opening and closing in the light beam, alternatively blocking the beam and letting the light through. Therefore, a light beam that passes through an interferometer is said to be modulated. Modulated light beams are denoted by the number of times per second they switch between light and dark, known as their frequency.

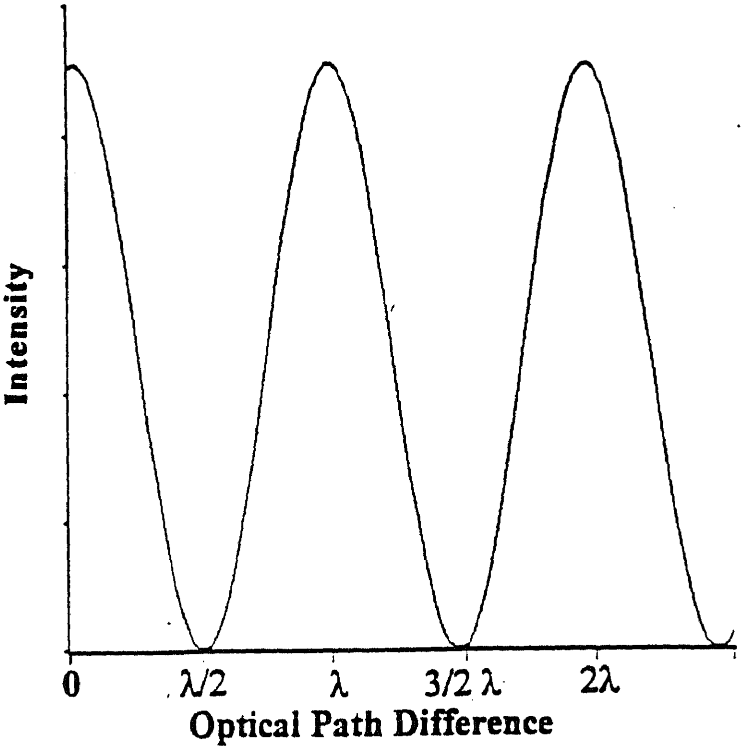

Figure 3.4 Interferogram from a Monochromatic Light Source

The frequency at which the light passing through an interferometer is modulated is given by the following equation:

$$F_v = 2VW \tag{3.4}$$

where

F_v is the modulation frequency,

V is the moving mirror velocity in cm/sec

W is the wavenumber of the light in the interferometer measured in cm^{-1}.

Equation 3.4 gives the frequency of the cosine wave interferogram that is measured by the detector of light of wavenumber W passing through the interferometer. For repeated measurements on the same sample to be reproducible, the interferogram, and hence F_v must be reproducible. This is why it critical that the velocities of the moving mirror in an FTIR is closely controlled.

Interferograms of the two wavelengths will be different. Most of the time the interferogram is a cosine wave, but their frequencies are different. This is how the signal of two different wavenumbers are distinguished by the spectrometer. Each different wavenumber of light gives rise to a sinusoidal wave signal of unique frequency measured by the detector.

Once the light leaves the interferometer it passes through the sample compartment and is focussed upon the detector. The detector is simply an electric signal transducer, and produces an electric signal, be it a voltage, resistance, or current, that is proportional to the amount of infrared radiation striking it. Thus, an interferogram is truly a plot of detector response versus optical path difference [7].

3.4 Coadding

Imagine replacing the monochromatic light source in the interferometer with a broadband infrared source (as is the case in the FTIR). These sources give off light at a continuum of wavelength. The total interferogram measured by the detector is the summation of all the interferograms from all the different infrared wavelengths. In fact, the measured intensity of light at a given λ is determined by the amplitude of that wavelength's interferogram. The intensity information for all the different wavelengths of light are contained in one measured interferogram. Therefore, there is no need to physically separate the light beam into component wavelengths and measure intensities one at a time as in dispersive IR spectroscopy. A simplistic way to think about the process is that the interferometer "encodes" the intensity and wavelength information so all the data can be measured at once, and the Fourier transform decodes the information to obtain the spectrum. [8]

By adding interferograms together in an FTIR, random noise is reduced and the signal-to-noise ratio is improved. This process is known as Coadding. Here is how coadding improves SNR. From scan to scan, the presence of the signal in an interferogram due to an absorbance band is constant, but the magnitude and the sign of the noise is random. The positive and the negative fluctuations in the random noise level cancel themselves as more scans are added together. This is how the multiplex advantage of FTIR works.

The relationship between signal-to-noise ratio and the number of scans obtained at a given resolution is

$$\mathrm{SNR}\ \alpha\ (\mathrm{N})^{1/2} \qquad (3.5)$$

where N is the number of scans added together as a given resolution. Thus, a spectrum consisting of 100 coadded spectra would have an SNR 10 times better than a spectrum comprised of just one scan ($(100)^{½} = 10$). This effect is well illustrated in Figure 3.5.

Table 3.1 Improvement in SNR with Number of Scans

Number of Scans	SNR Improvement over 1 scan
1	-
4	2
16	4
64	8
100	10
256	16
1000	31.6

However, there is a limit to the number of scans beyond which, no improvement in the SNR is obtained. Most of the times coadding 100 scans or less are sufficient to obtain a reasonable SNR. Occasionally, difficult to analyze samples, or samples analyzed outside the sample compartment using techniques of infrared microscopy, may require coadding upwards of 1000 scans to achieve a usable SNR. Coadding more than 1000 scans to obtain an FTIR spectrum is not recommended since it takes a long time, and as mentioned above, may not result in an improvement in SNR.

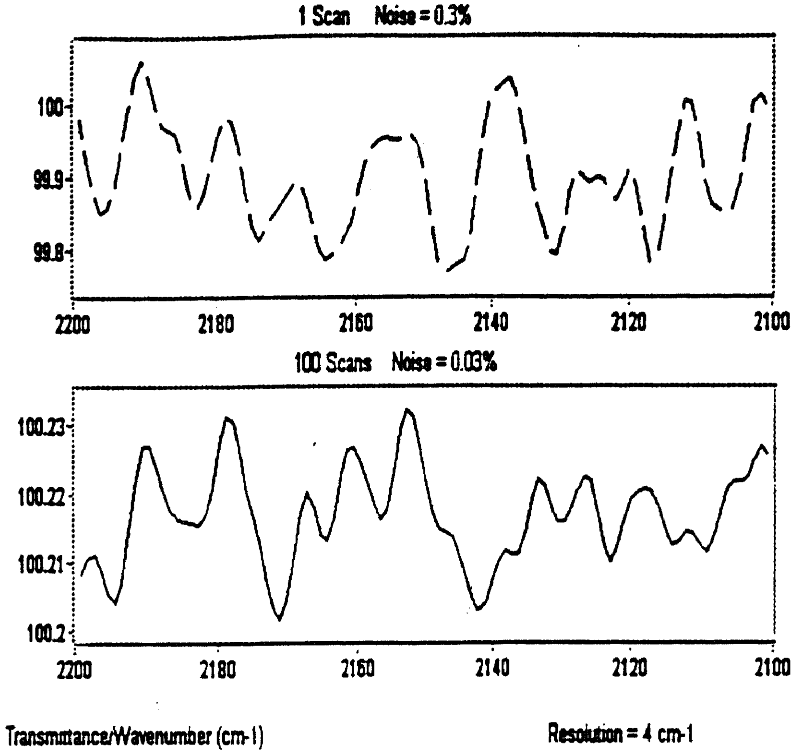

Figure 3.5 Improvement in Noise with Increase in Number of Scans

3.5 Slow-Scan and Rapid-Scan Interferometers

Here we deal with the classification of the interferometers based on the modulation frequency and hence the scan speed of the moving mirror [7].

3.5.1 Slow-Scanning Interferometers

Equation 3.4 states that

$$F_V = 2VW$$

where

F_V is the modulation frequency,

V is the moving mirror velocity in cm/sec,

W is the wavenumber of the light in the interferometer measured in cm^{-1}.

For slow-scanning interferometers, the velocity of the moving mirror, V, is sufficiently slow that the modulation frequency F_V of each of the spectral wavenumber W is generally less than 1 Hz.

Let us consider a typical use of slow-scanning interferometers. This type of system was typically used in 1960's for far-infrared spectrometry, where the highest wavenumber is generally about 600 cm^{-1}. A typical scan speed is on the order of 4μm/sec, so the modulation frequency corresponding to highest wavenumber in the spectrum is

$$F_V = 2 \times 4 \times 10^{-4} \times 600$$

$$= 0.5 \text{ Hz.}$$

Far-infrared wavenumbers fall between about 6 and 600 cm^{-1}, so that if the mirror velocity used in the above example were used for all the measurements, the range of modulation frequencies would be between 5×10^{-3} and 5×10^{-1} Hz.

3.5.2 Stepped-Scan Interferometers

Stepped-Scan Interferometers use a stepping-motor drive. In stepped-scan interferometers, the movable mirror is held stationary at each sampling and then moved rapidly to the next sampling position. The interferogram signal is produced by integrating the detector output signal during the time interval that the mirror is held stationary. The time interval during which the mirror is stepped from one sampling position to the next is lost time that does not contribute to the observation and therefore should be kept short relative to the integration periods. Detail experiments related to step-scan FTIR can be found in [9] [10]. Step-scan FTIR spectrometry has been accepted as a useful tool for obtaining vibrational spectra of a variety of time dependent systems. The success of the technique depends on the capability of the stepping motor to achieve a uniform increase in retardation for every step. Unfortunately, a significant SNR disadvantage has been associated with the step-scan mode of data collection relative to the same data collection time with conventional rapid-scan FTIR spectrometry [17] [18]. Figure 3.6 shows the variation of retardation with time for the three types.

3.5.3 Rapid-Scanning Interferometers

The difference between rapid-scanning interferometers and slow-scanning and stepped-scan interferometers is that the mirror velocity of the interferometer is sufficiently high

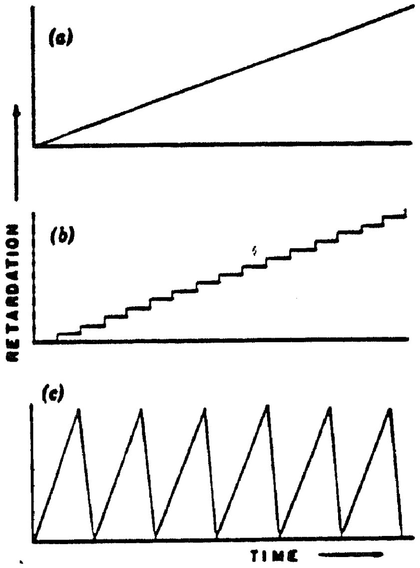

Figure 3.6 Variation in Retardation with Time

that each wavenumber is modulated in the audio-frequency range. Rapid scanning is mandatory for the successful measurement for low or medium–resolution mid-infrared absorption spectra, where the interferogram has an extremely high signal-to-noise ratio (SNR). A typical mirror velocity used for the measurement of spectra between 4000 and 400 cm-1 is 0.158 cm/sec.

The modulation frequencies for the upper and lower limit of this range are, therefore

$$F4000 = 2 \times 0.158 \times 4000$$

$$= 1260 \text{ Hz}$$

$$F400 = 126 \text{ Hz}$$

As seen these modulation frequencies are in the audio range and hence can be easily measured.

3.6 Infrared Sampling Techniques

There are several infrared techniques available and the type to be used depends on the type of the sample [7].

3.6.1 Transmission Methods

Here the infrared beam is passed directly through the sample and hence is called the transmission technique of sampling. The advantages of this type of infrared sampling are that transmission spectra have high signal to noise ratios, and comparatively inexpensive tools are used to prepare the samples for this type of analysis. The major advantage of this technique is that it can be applied universally to solids, liquids, gases, and polymers.

The disadvantage of this method is that the spectra depend on the thickness of the sample. Samples which are thick absorb too much and make it difficult to obtain a spectrum, while samples which are thin have absorbances which are too weak to be detected. Therefore, the challenge in preparing transmission samples is to adjust the thickness or concentration of samples so that the appropriate amount of light passes through the sample. In addition, another disadvantage of this method is that it is time consuming. It takes time to melt, squish, or dilute a sample enough so that it transmits the appropriate amount of light.

3.6.2 Reflectance Techniques

Reflectance sampling techniques differ from transmission techniques in that the infrared beam is bounced off the sample instead of passing through the sample. We define surface normal, as a line drawn perpendicular to the surface of the sample. When discussing reflectance, it is convenient to define a line called surface normal, which is drawn perpendicular to the surface of the sample. The angle of incidence of a light beam is defined as the angle the incoming light ray makes with the surface normal. The angle of reflectance is defined as the angle the outgoing beam makes with the surface normal.

There are two different types of reflection. Specular reflectance occurs when the angle of incidence equals the angle of reflectance. This is the type of reflection that takes place of smooth surfaces, such as that of mirrors. Diffuse reflectance occurs when the angle of incidence is fixed, but the angles of reflection vary from 0 to 360 degrees. Diffuse reflectance occurs on rough surfaces, which are the most common surfaces found.

There are several disadvantages as compared to the transmission technique of infrared sampling. The spectrum obtained depends on the surface of the sample. This is because, in a typical reflection experiment, typical depths of penetration are 1 to 10 microns. This is in contrast to the transmission techniques, where the bulk of a sample rather than the surface contribute to the spectrum. The fact that reflectance techniques obtain the spectrum of the surface is good if the surface is of interest. It is difficult to capture all the light reflected off a sample's surface, so reflection spectra may be noisier than the transmission spectra for a given number of scans and resolution. In addition, reflectance techniques are not universal in that these techniques cannot be applied to gases. Finally, they require special accessories to be placed into the spectrometer's sample compartment.

CHAPTER 4

APPLICATION OF FOURIER TRANSFORM TECHNIQUES

4.1 Fourier Transform Techniques

We have covered how an interferogram is obtained. Now we focus on the techniques for computing the spectrum from the digitized interferogram. Although few people use classical discrete fourier transform to obtain spectrum, an understanding of the conventional fourier transform leads to a better comprehension of more advanced techniques like the fast fourier transform. Let us first consider the basic fourier transform pair. Mathematically, a function F(x) can be written as

$$\mathrm{F(x)} = \int_{-\infty}^{\infty} A(\xi) e^{-i2\pi\xi x} d\xi \equiv \zeta^{-1}\{A(\xi)\} \tag{4.1}$$

$$A(\xi) = \int_{-\infty}^{\infty} F(x) e^{+i2\pi\xi x} dx \equiv \zeta\{F(x)\} \tag{4.2}$$

Equation 4.1 and 4.2 refer to the inverse fourier transform and the fourier transform of function F(x) respectively. The conditions for the existence of the Fourier transform are called Dirichlet conditions [11], which may be summarized as follows:

1. The signal F(x) has finite number of finite discontinuities.
2. The signal has finite number of maxima and minima.
3. The signal is absolutely integrable.

Consider a plane, monochromatic wave at a point z and at time zero. The wave may be represented by

$$y(z,\sigma) = a(\sigma)\cos(kz) = a(\sigma)\cos(2\pi\sigma z) \tag{4.3}$$

Where k is the propagation constant and σ is the wavenumber. If, at a point, one has many waves each of a different frequency and amplitude a(σ), then in a wave train, the resultant amplitude is

$$y(z) = \left(1/\overline{\sigma}\right)\int_0^\infty a(\sigma)\cos(2\pi\sigma z)d\sigma \tag{4.4}$$

Where $\overline{\sigma}$ is some average wave number. One observation we make here is that every function is real and we consider $a(\sigma)/\overline{\sigma}$ as the amplitude density.

Let us introduce another function b(σ) for convenience, which is an Hermitian function, that is the real part of b(σ) is a even function of σ, and the imaginary part is an odd function of σ. It can be easily proved that for the real function b(σ):

$$\int_0^\infty b(\sigma)\cos(2\pi\sigma z)d\sigma = \tfrac{1}{2}\int_{-\infty}^\infty b(\sigma)e^{i2\pi\sigma z}d\sigma \tag{4.5}$$

Let $b(\sigma) = a(\sigma)/\overline{\sigma}$. The resultant amplitude may be expressed as an integral from -∞ to ∞ with the cosine function replaced by $e^{i2\pi\sigma z}$

$$y(z) = \tfrac{1}{2}\int_{-\infty}^\infty b(\sigma)e^{i2\pi\sigma z}d\sigma \tag{4.6}$$

Note that y(z) can be used to represent a wave composed of many frequencies of different amplitudes. Define ½b(σ) ≡ A(σ); electric field amplitude of the wave number σ. Thus, the electric field as a function of position is the fourier transform of the electric field given as a function of frequency.

$$y(z) = \int_{-\infty}^\infty A(\sigma)e^{i2\pi\sigma z}d\sigma \equiv \zeta\{A(\sigma)\} \tag{4.7}$$

The Fourier transform can be used to yield the following equation

$$A(\sigma) = \int_{-\infty}^{\infty} y(z) e^{-i2\pi\sigma z} dz \tag{4.8}$$

4.2 Application of Fourier Analysis to Interferometers

The amplitudes of the two coherent waves[12] [13] which at time zero have the same amplitude A(σ) at wave number σ, but separated by a phase difference kδ = 2πσδ, can be written as

$$y_1(z) = \int_{-\infty}^{\infty} A(\sigma) e^{-i2\pi\sigma z} d\sigma \tag{4.9}$$

$$y_2(z) = \int_{-\infty}^{\infty} A(\sigma) e^{-i2\pi\sigma(z-\delta)} d\sigma \tag{4.10}$$

The equations (4.9) and (4.10) represent the waves from each arm of the interferometer after they are recombined and δ is the optical path difference between the two waves. Using the law of superposition, one has

$$y(z) = y_1(z) + y_2(z) = \int_{-\infty}^{\infty} \left[A(\sigma)\left(1 + e^{-i2\pi\sigma\delta}\right) e^{i2\pi\sigma z} \right] d\sigma \tag{4.11}$$

Let us define the resultant field $A_R(\delta,\sigma)$ as

$$y(z) \equiv \int_{-\infty}^{\infty} A_R(\delta, \sigma) e^{i2\pi\sigma z} d\sigma \tag{4.12}$$

On comparing, the later two equations, we see that

$$A_R(\delta, \sigma) = A(\sigma)\left(1 + e^{-i2\pi\sigma\delta}\right) \tag{4.13}$$

But the intensity B(σ,δ) (irradiance or flux density) is

$$B_R(\sigma, \delta) \equiv \tfrac{1}{2} c K_0 A_R^*(\delta, \sigma) A_R(\delta, \sigma) \tag{4.14}$$

where K_0 is the electric permittivity of free space in MKS units and c is the velocity of light in vacuum.

Doing mathematical manipulations on the equations (4.13) and (4.14) we get an expression for intensity $B(\sigma,\delta)$ as

$$B(\sigma,\delta) = cK_0 A^2(\sigma)[1+\cos(2\pi\sigma\delta)] \tag{4.15}$$

There is no phase relation between the fluxes of different wave numbers at a given path difference δ from a white light source. So, we add the fluxes of different frequencies and define $I_R(\delta)$ as

$$I_R(\delta) \equiv (1/\bar{\sigma})\int_0^\infty B(\sigma,\delta)d\sigma \tag{4.16}$$

Substituting equations (4.15) into (4.16) we get

$$I_R(\delta) \equiv (cK_0/\bar{\sigma})\left\{\int_0^\infty A^2(\sigma)d\sigma + \int_0^\infty A^2(\sigma)\cos(2\pi\sigma\delta)d\sigma\right\} \tag{4.17}$$

From equation (4.17), we get the value of $I_R(\delta)$ for $\delta = 0$ as

$$I_R(0)/2 = (cK_0/\bar{\sigma})\int_0^\infty A^2(\sigma)d\sigma \tag{4.18}$$

Manipulating the equation (4.17) and (4.18) to get

$$\left[I_R(\delta) - \tfrac{1}{2}I_R(0)\right] = (2/\pi)^{1/2}\int_0^\infty \left[(cK_0/\bar{\sigma})A^2(\sigma)(\pi/2)^{1/2}\right]\cos(2\pi\sigma\delta)d\sigma \tag{4.19}$$

$$\left[(cK_0/\bar{\sigma})A^2(\sigma)(\pi/2)^{1/2}\right] = (2/\pi)^{1/2}\int_0^\infty \left[I_R(\delta) - \tfrac{1}{2}I_R(0)\right]\cos(2\pi\sigma\delta)d\delta \tag{4.20}$$

The final result can be expressed as

$$B(\sigma) = (c)\int_0^\infty \left\{\left[I_R(\delta) - \tfrac{1}{2}I_R(0)\right]\cos(2\pi\sigma\delta)\right\}d\delta \tag{4.21}$$

Equation (4.21) is the basic equation of Fourier transform spectroscopy. This equation states that, at a given wavenumber σ, the flux versus the optical path difference δ, the fourier cosine transform of [$I_R(\delta)$ −1/2$I_R(0)$] yields B(σ), the flux density at the wavenumber σ.

To consider the general case, we can write the above equation as

$$B(\sigma) = \int_{\infty}^{\infty} \left[I_R(\delta) - \tfrac{1}{2} I_R(0) \right] e^{-i2\pi\sigma\delta} d\delta \tag{4.22}$$

4.3 Fast Fourier Transform Techniques

The computation of inverse fourier transform of the interferogram to obtain the spectrum used to be one of the greatest hindrances to Fourier transform spectroscopy. The fast Fourier transform (FFT) [14] is an algorithm that was described by Cooley and Tukey. FFT provides tremendous timesaving for the chemical spectroscopist [19]. Most commercial FTIR systems that have an dedicated minicomputer can perform an 8192 point FFT in under 2 min, and some systems can perform it under 5 sec. An 8192 data point transform using a DFT takes approximately 15 min on most mainframe computer [7]. An excellent description of different types of FFT algorithms is found in the book by Blahut [15].

4.4 Interferogram to Spectrum

4.4.1 Typical Interferogram

Figure 4.1 shows interferogram [8] usually obtained. The interferogram shows a sharp intensity spike, called the centerburst and low intensity at higher optical path

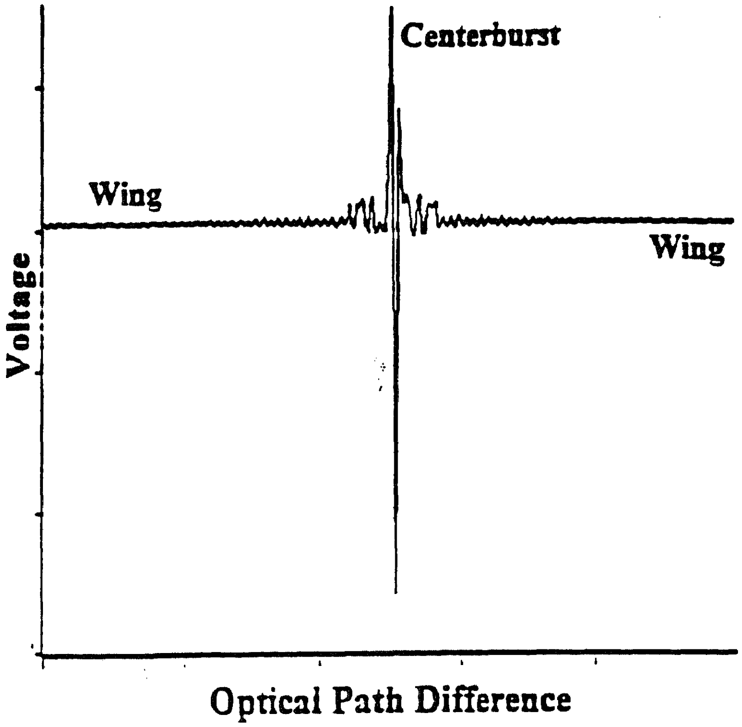

Figure 4.1 Interferogram from a Broadband Infrared Source

differences in the wings of the interferogram. The high intensity of the centerburst is caused by all wavelengths constructively interfering at zero path difference. All the component sinusoidal waves that comprise the interferogram have ZPD as a common point. As optical path difference is increased, sinusoidal waves of different frequency get out of phase with each other and destructively interfere. As a result, the interferogram's intensity drops off rapidly as the mirror moves away from ZPD and into the wings.

4.4.2 Applying Fourier Transform

As stated in the previous chapter, an interferogram is simply a large number of sinusoidal signals added together. According to the theorem developed by Fourier, any mathematical function can be expressed as a sum of sinusoidal waves. Let us consider the infrared spectrum as a mathematical function. An interferogram is a sum of sinusoidal waves, each of which contains information about the wavenumber of a given infrared peak and amplitude information about the peak intensity at that wavenumber. The Fourier transform simply calculates the infrared spectrum from the summed sinusoidal waves in the interferogram.

There is another way to think about the Fourier transform that, although it is not rigorously correct, but is useful in illustrating how the Fourier transform works [8]. The interferogram is a plot of infrared intensity versus optical path difference, which can be measured in cm. By its very nature, when a function is Fourier transformed its X axis units are inverted. The Fourier transform of an interferogram produces a plot of infrared intensity versus inverse centimeters. Inverse centimeters are also known as wavenumbers. A plot of infrared intensity versus wavenumber is an infrared spectrum. In a sense, the

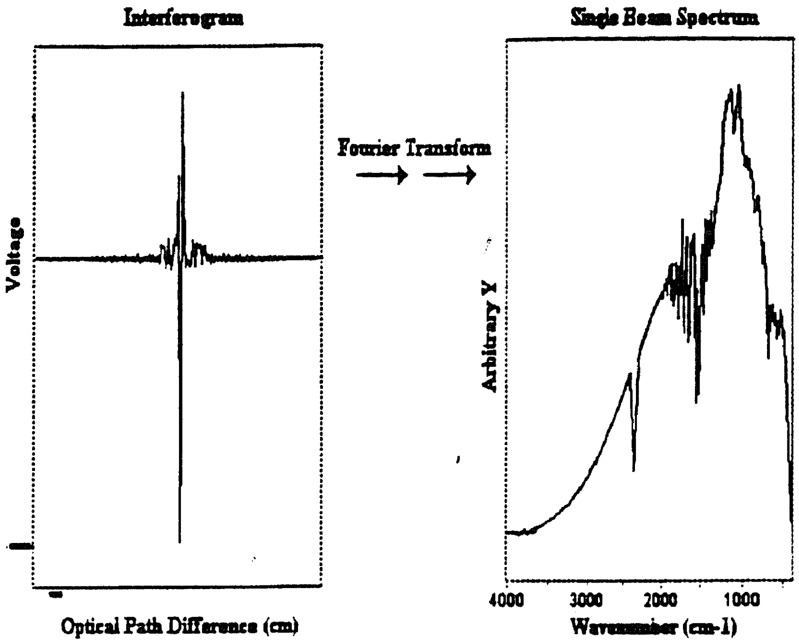

Figure 4.2 Interferogram to Spectrum

Fourier transform inverts the interferogram to produce the infrared spectrum. This process is shown in Figure 4.2.

4.4.3 Apodization

Calculating a Fourier transform involves performing a mathematical integral on the interferogram. Ideally, the limits of this integral should be plus and minus infinity. This means one must use an optical path length of infinity and collect an infinite number of data points to obtain an interferogram that will Fourier transform properly. This is impossible, so the interferogram and the integral must be truncated at some finite point, and the limits of integration are ZPD and maximum optical path difference measured. An unfortunate outcome of the truncating is that line shapes of the peaks in the infrared spectrum are affected. Rather than obtaining true peak shape, the absorbance bands are surrounded by sidelobes, which are sinusoidal undulations in the base line.

Sidelobes are suppressed by multiplying the interferogram by an apodization function. The interferogram is Fourier transformed after this multiplication. A side effect of using apodization function is that spectral resolution is reduced. The apodization function that provides the highest resolution and does the worst job of suppressing sidelobes, is the boxcar apodization function. This apodization function should only be used when high resolution is of utmost importance, and the user can live with the existence of the sidelobes. Apodization functions can vary in how well they suppress sidelobes, and how much they degrade resolution. The apodization function is a user selectable software parameter in most manufacturer's FTIR's systems, and the types of functions available differ from instrument to instrument. For quantitative analysis, the " medium Beer – Norton " function gives the best results. Practically it is upto the user to experiment with apodization functions, and determine which one works best for a given application. Effects of different types of apodization functions on transformed spectrum have been discussed in detail by Codding and Horlick [20]. Different types of apodization functions are explained in [21].

4.4.4 Eliminating the Instrument Response Function

When an interferogram is Fourier transformed, a single beam spectrum is obtained as shown in Figure 4.3. A single beam spectrum is a plot of raw detector versus wavenumber. A single beam spectrum obtained with out a sample in the infrared beam is called a background spectrum. The background spectrum contains the instrument's and the environment's contribution to the infrared spectrum. The contribution of the instrument by itself to the background spectrum is known as the instrument response function. The spectrum seen in Figure 4.3 is a background spectrum. A background spectrum must always be run when analyzing the samples by FTIR.

When an interferogram is measured with a sample in the infrared beam and Fourier transformed, a sample single beam spectrum is produced as shown in Figure 4.4. It looks similar to the background spectrum except the sample peaks are superimposed upon the instrumental and atmospheric contributions to the spectrum. To eliminate these contributions, the sample single beam spectrum must be ratioed against the background spectrum. This produces a transmittance spectrum as shown by the following spectrum as shown by the following equation:

$$\%T = I/I_0 \tag{4.23}$$

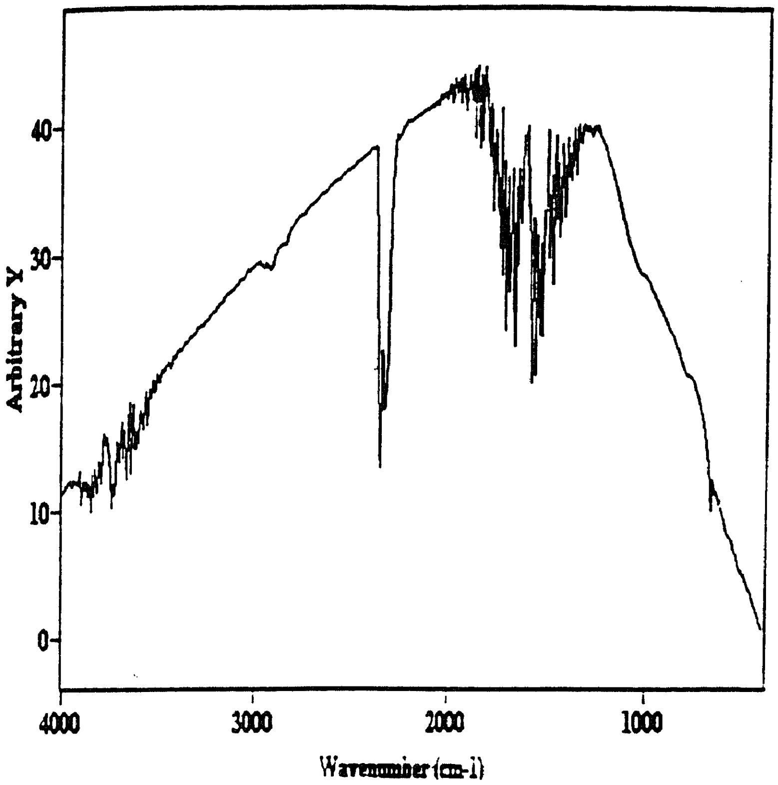

Figure 4.3 Background Spectrum

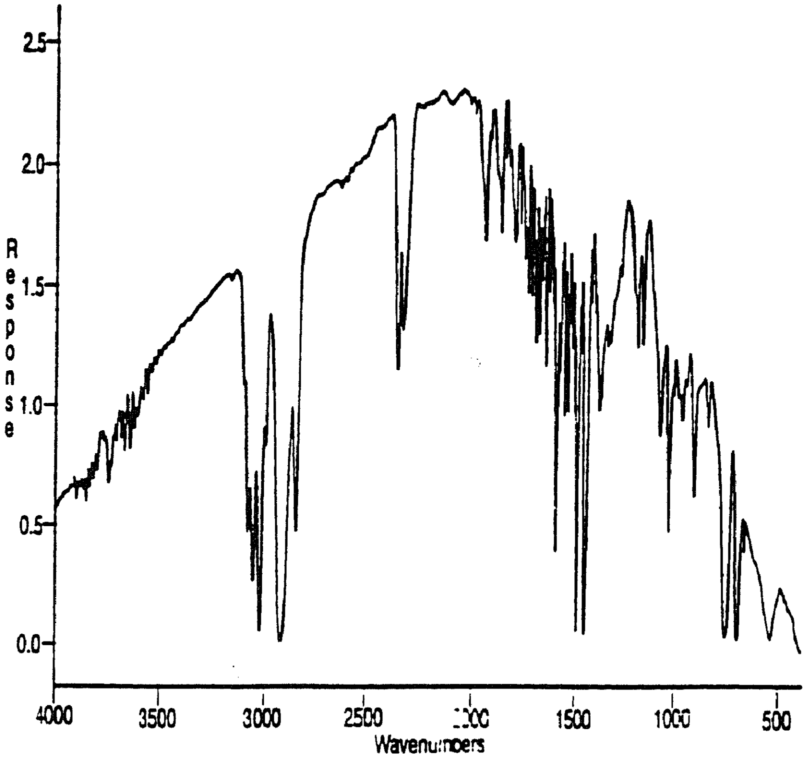

Figure 4.4 Single Beam Spectrum

where

%T = Transmittance

I = Intensity measured with a sample in the beam (from the sample single beam spectrum)

I_0 = Intensity measured with no sample in the beam (from the background spectrum)

The absorbance spectrum can be calculated from the transmittance spectrum using the following equation

$$A = -\log_{10}T \tag{4.24}$$

where

T = transmittance

A = absorbance

Ideally, the final spectrum should be devoid of all the instrumental and environmental contributions, and only contain features due to the sample. For qualitative analysis, the choice of whether to use spectra in absorbance or in transmittance is upto the user. However, absorbance units must be used for quantitative analysis.

CHAPTER 5

SPECTRAL MANIPULATIONS

The purpose of manipulating the spectrum is to extract more information from the spectrum and to enhance the appearance of the spectrum. Usually all the commercial FTIR spectrometers are provided with the software to perform the manipulation of the spectrum. It is very important that the spectral manipulations are performed properly, otherwise it can add artifacts to a spectrum or completely destroy the data. Now we mention the different manipulations that can be performed on the spectrum [8].

5.1 Spectral Subtraction

Many FTIR applications involve obtaining the spectrum of the mixture. If the specific application requires to obtain the spectrum of a component of a mixture, then the technique of spectral subtraction can be very useful. However, to apply the technique it is required that spectra must be in the units that are linearly proportional to concentration, such as absorbance. Transmission and single beam spectra should never be subtracted since their peak heights and areas are not linearly proportional to concentration.

According to the terminology used in the FTIR industry, the spectrum of the mixture is called the sample, and the spectrum of a component to be subtracted from the sample spectrum is called the reference. The principle behind spectral subtraction is simple: the absorbance values of the reference are subtracted from the absorbance values of the sample.

Performing subtractions in such a direct manner ignores the fact that the concentration of the reference material may have been different in the sample and reference spectra. To get around this problem the reference spectrum is multiplied times a subtraction factor. The general equation used to perform subtractions is as follows:

$$\text{(sample)} - \text{(Subtraction factor)} * \text{(Reference)} = \text{Result} \qquad (5.1)$$

The absorbance units of the reference spectrum are multiplied by the subtraction factor(also called the scale factor), then subtracted point by point from the absorbance values of the sample spectrum. Ideally to obtain desired results the absorbances of the sample and the reference must be the same and the subtraction factor is close to one. The subtraction factor is the only user adjustable parameter in the subtraction process.

5.2 Baseline Correction

Due to several factors like sample scattering, inappropriate choice of background, and instrument drift, baseline of the spectrum may not be flat but sloping or curved baselines. To correct such spectra to those with a flat baseline, baseline correction is applied. The technique is very simple in that first generate a function e.g. a straight line or a curve, that parallels the shape of the baseline in the sample spectrum. The function is then subtracted from the sample spectrum, yielding a result that should be devoid of the curved or sloped baseline.

An example of successful baseline correction is shown in Figure 5.1. The top spectrum is of a polystyrene film with a sloping baseline and the bottom spectrum is the one after baseline correction. The function to be generated is very much dependent on the software that comes with the FTIR spectrometer. It is vital that the function subtracted

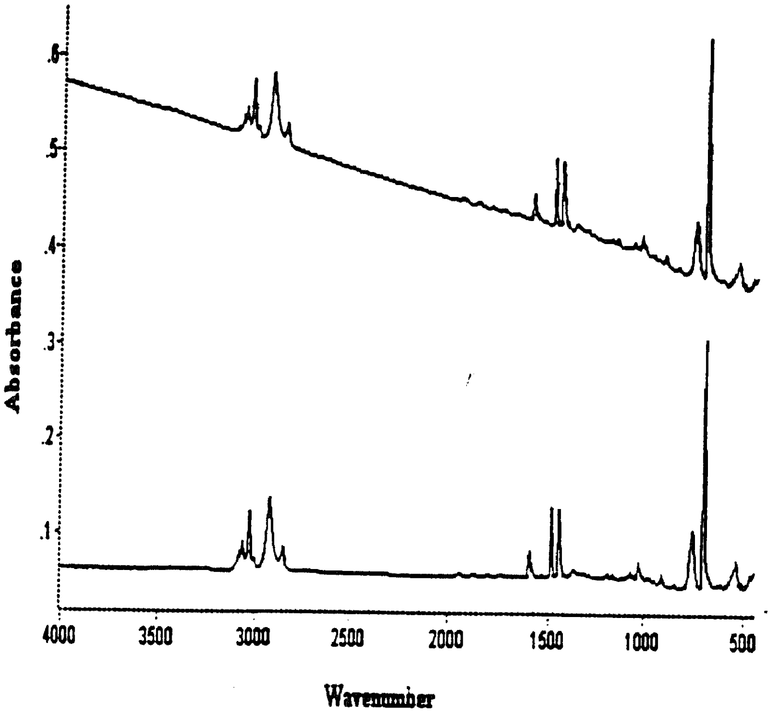

Figure 5.1 Baseline Correction

from the sample spectrum be parallel to the baseline; or artifacts will be introduced into the corrected spectrum.

5.3 Smoothing

If the final spectra obtained is found to be noisy, smoothing must be applied on the spectrum. Smoothing is used on noisy spectra to reduce the noisy level, so features that may have been hidden under the noise can be seen more readily. In addition, it helps improving the overall appearance of the spectra.

The simplest method of applying smoothing, called the boxcar smooth, works as follows. Imagine taking several data points in a spectrum in a spectrum and drawing a box around them. This box is known as the smoothing window. Assume the smoothing window contains 9 data points. Now, take the Y axis values (either absorbance or transmittance) of these 9 data points, add them together, then divide by 9 to calculate the average of the values. Assign the average Y-axis value to the middle of the 9 X-axis data points. Next, move the box over one data point, calculate the average for this set of 9 data points, assign a new average to the middle X axis data point and so on. Eventually the smoothing window is passed over the entire spectrum to obtain the a running average of the Y-axis values. The total number of data points in the spectrum is affected slightly depending on the smoothing algorithm used. The noise in the smoothed spectrum is reduced because fluctuations in the sign of random noise cancel out when the Y-axis values are averaged. The amount of smoothing is proportional to the number of points in the smoothing window. The more points in the window, greater the extent of the smoothing.

The effect of smoothing on noisy data is shown in Figure 5.2. The bottom spectrum in the figure contains a large amount of noise. The top spectrum is spectrum is result of performing a 9 point smoothing. Note that the overall noise level has gone down, and that absorbance peaks that were previously difficult to see can now be seen easily.

5.4 Spectral Derivatives

An infrared spectrum being a mathematical function, its derivative can be calculated. The derivatives of the spectrum can be taken many times, producing spectra of different orders.

First derivatives help pinpoint the peak position of a band. There is one upward and one downward pointing feature in the derivative for each absorbance peak in the original spectrum. The wavenumber at zero absorbance in a first derivative corresponds to the wavenumber at the top of the absorbance band in the original spectrum. An example of the first derivative is shown in Figure 5.3.

5.5 Deconvolution

It may so happen that several narrow bands may overlap to give a broad spectrum. Deconvolution can help determine the number and positions of the overlapped bands and hence enhance resolution. The process of deconvolution retains peak information, but peak areas and peak shapes are altered in the process. The power of deconvolution is that it enables new features that may contain important information about a sample's composition.

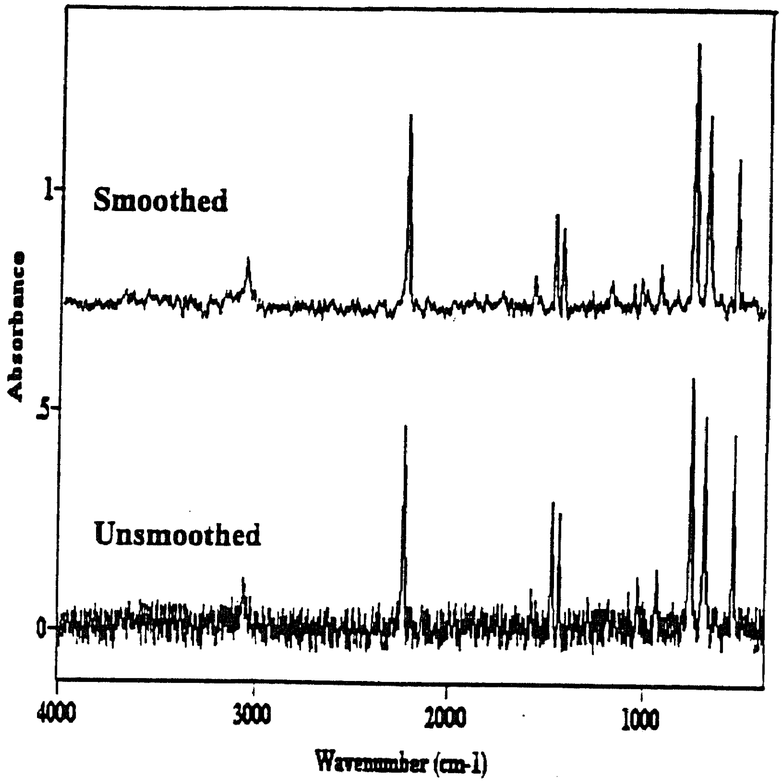

Figure 5.2 Smoothing of a Noisy spectrum

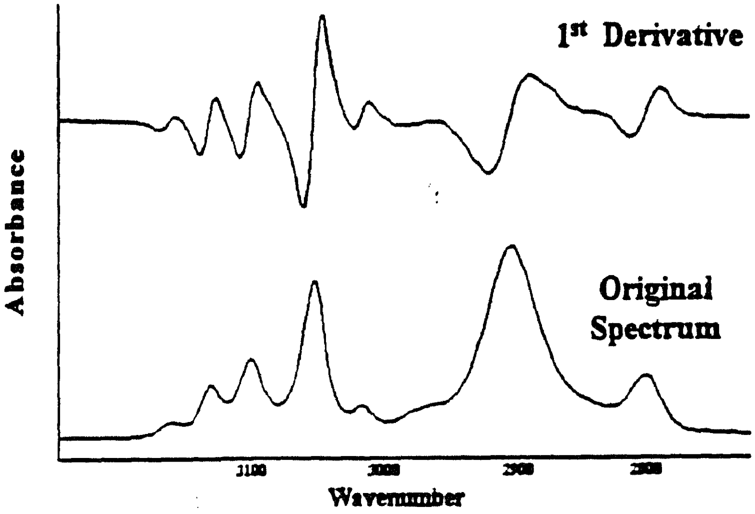

Figure 5.3 First Derivative of a Spectrum

Deconvolution is used on bands whose widths are inherently broader than the instrument resolution used [22]. The entire deconvolution is illustrated in Figure 5.4. The first step in the process is to choose a section of the spectrum containing bands that need to be resolved. A reverse Fourier transform is performed on this part of the spectrum to produce a result called cepstrum. A cepstrum is very similar to the interferogram, except that it corresponds to piece of a spectrum rather than to the whole spectrum. Cepstrums have some unique properties as shown in Figure 5.5. Narrow infrared bands give cepstrums with significant amplitude in the wings, while wide infrared bands give cepstrums with low amplitude in the wings. The idea behind deconvolution is to make the cepstrum of a wide band look like the cepstrum of a narrow band. This is done by increasing the wing intensity of the cepstrum obtained from a wide band by multiplying it by an exponential function. The altered cepstrum is Fourier transformed to obtain the resolution-enhanced spectrum. The altered spectrum has more and/or narrow bands than the original spectrum.

5.6 Curvefitting

Curvefitting addresses the same problem as deconvolution, trying to determine the position and intensity of a several peaks that overlap to give a broad spectral feature. However, the problem is handled in totally different way than deconvolution. The broad overlapped feature of interest is examined, and an estimate of the number, width, height, location, and shape of the underlying peaks is needed. To assist in this process, the second derivative of the spectrum can be examined, or the spectrum can be deconvolved before curvefitting. Based on this assessment of the spectrum, an initial estimate as to

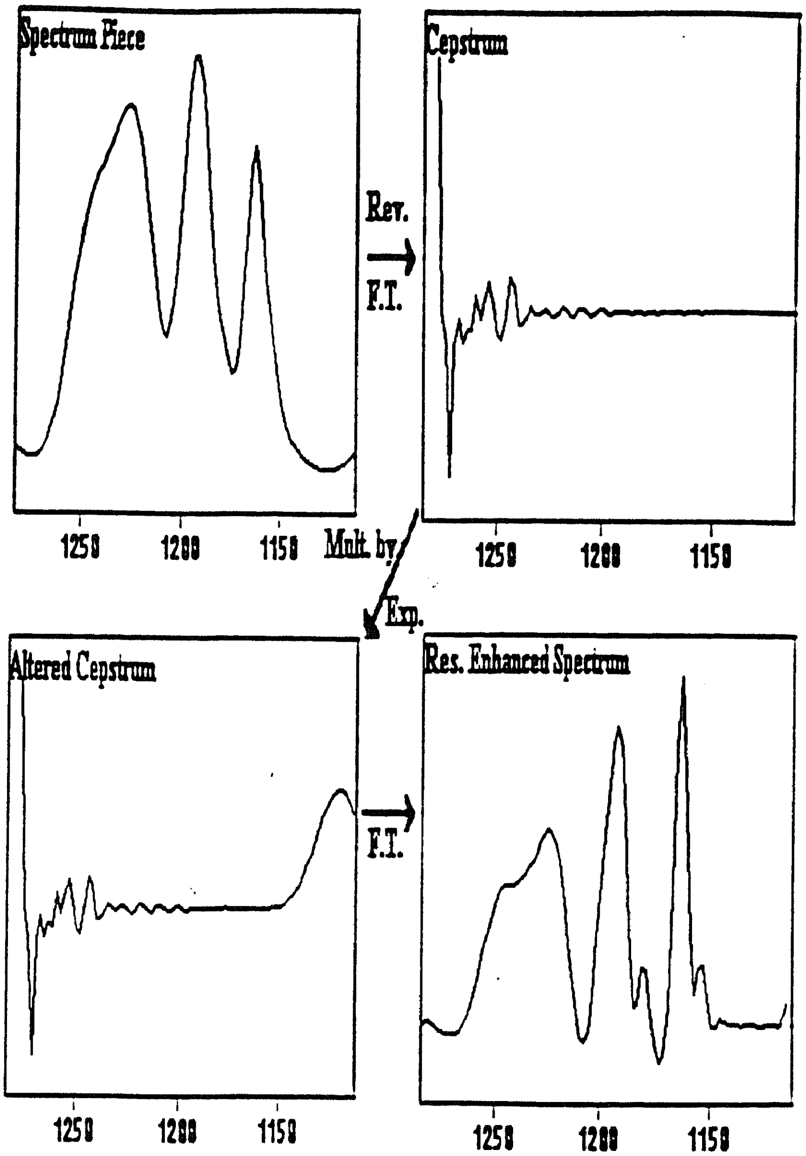

Figure 5.4 Deconvolution Process

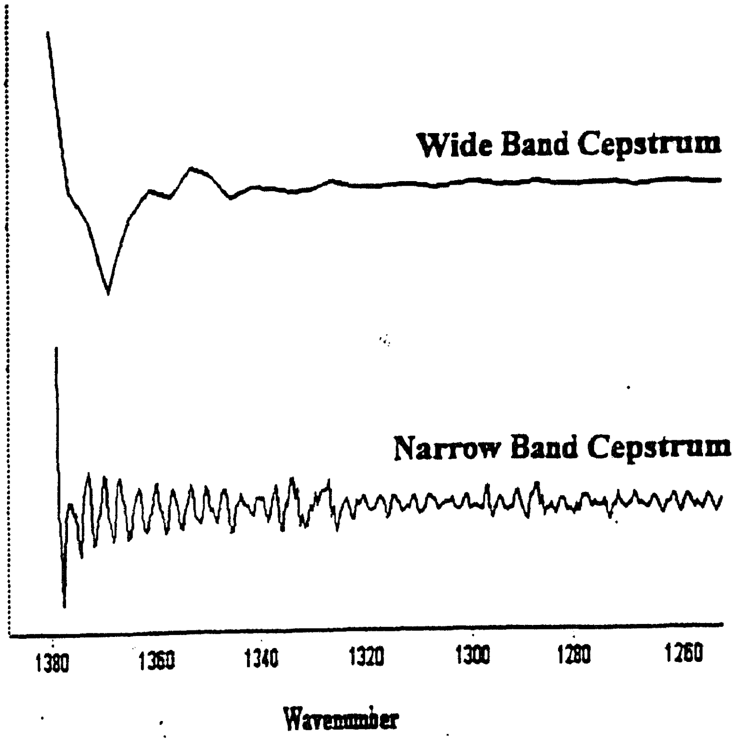

Figure 5.5 Cepstrums of Wide and Broad Infrared Band

the nature of the underlying peaks is entered into the computer. Once the initial estimate has been entered into the computer, the software uses a least squares fitting algorithm to vary and optimize all the parameters. Curvefitting is an iterative process, and the program may need to be run many times to achieve good results. The results of the curvefitting process are a set of bands with specific widths, heights, positions, and shapes. When combined, these bands should generate a spectrum that closely matches the sample spectrum.

5.7 Spectral Library Searching

The main use of library searching is as an interpretation aid [23]. The idea is to compare an unknown (or sample) spectrum against a collection of spectra of known compounds contained in a library. It is assumed that if the two spectra are similar, the molecules in the two samples are similar. A library match is called a "hit". A good hit occurs when the match between two spectra is close, a bad hit occurs when the two spectra are dissimilar.

5.8 Quantitative Analysis

To determine the concentration of molecule or molecules in a sample, infrared quantitative analysis is widely used [24]. Many of the more important data processing algorithms used in FTIR spectrometry, such as spectral subtraction, Fourier self-deconvolution, and factor analysis, rely on the intensities of spectral bands being linearly proportional to the concentration of each component in the sample. For infrared quantitative analysis, it is the absorption spectra that is used for computation of concentration.

Analyte is the term used to specify the molecule whose concentration is to be determined. The height or the area of a peak in an absorbance spectrum is directly proportional to the concentration of the analyte in the infrared beam. First, the infrared absorbance spectrum for the samples with accurately known amount of the analyte are measured. These samples are called standard. Once the standard is obtained, then a calibration phase is carried out, where in a mathematical model between the concentration and absorbance is obtained. Using this model, the concentrations of analytes in unknown samples can be predicted.

5.8.1 Beer's Law

For absorption spectrometry, the law relating band intensity to concentration is the well-known Bouger-Beer-Lambert law, which will be referred to simply as Beer's law [25]. As stated in equation (2.2)

$$A = \varepsilon\, l\, c \tag{5.2}$$

where

A = absorbance,

ε = absorptivity,

l = Pathlength,

c = concentration.

The absorptivity is the proportionality constant between concentration and absorbance. It changes from wavenumber to wavenumber for a given molecule, and is different for different molecules. However, for a given molecule and wavenumber of absorbance, the absorptivity is a fundamental physical property of the molecule. The units of ε are usually given in (concentration x pathlength)$^{-1}$, so the absorptivity cancels the units of the other two variables in Beer's law. This is necessary because absorbance is a unit less quantity.

For quantitative analysis, it is absolutely necessary that the infrared spectra are plotted in absorbance and not transmittance. This is because absorbance is linearly proportional to concentration, but transmittance and the concentration are related through an inverse algorithm.

To perform a calibration using Beer's law, it is important to check for the linear relationship. Let us compare equation (5.2) with a slope intercept form of straight line

$$y = mx + c \tag{5.3}$$

where m is the slope and c is the y intercept. Therefore, absorbance on the y-axis and concentration on the x-axis should be straight line with slope of εl and y intercept of zero. once the standard developed and the absorbance of the analyte measured, the concentration can be determined from equation (5.2) as

$c_{unknown} = A/\varepsilon l = A/slope$

where $c_{unknown}$ is the concentration of analyte in unknown sample.

Thus, predicting the concentration of an analyte in an unknown sample is simply a matter of dividing the measured absorbance of the unknown sample by the slope of the calibration curve.

CHAPTER 6

FTIR HARDWARE

The wide variety of interferometers, detectors, beamsplitters, and sources available for FTIRs today can be bewildering. This chapter discusses how commonly used interferometers, sources, beamsplitters, and detectors work, and the relative advantages and disadvantages of each [8].

6.1 Interferometers

In the FTIR spectrometer, the moving mirror is the only moving part in an FTIR spectrometer. It is vital that the position of the moving mirror be precisely controlled so the optical path difference can be measured accurately. The moving mirror will encounter friction with its housing. Therefore, interferometers contain bearings to reduce or eliminate friction and to insure smooth mirror motion [26].

Examples of two different types of bearings used in Michelson interferometer are shown in Figure 6.1. In an air bearing type, the shaft attached to the moving mirror is surrounded with a cushion of air upon which it floats. The advantage of air bearings is that they are frictionless and rarely wear out. A disadvantage of air bearing interferometers is they require a source of clean dry air, which can be expensive or difficult to obtain. Air bearings are somewhat sensitive to vibrations, which can cause the shaft to bounce around and contact the housing. This leads to errors in the measurement of the interferogram. Air bearings are also expensive because they must be precisely machined.

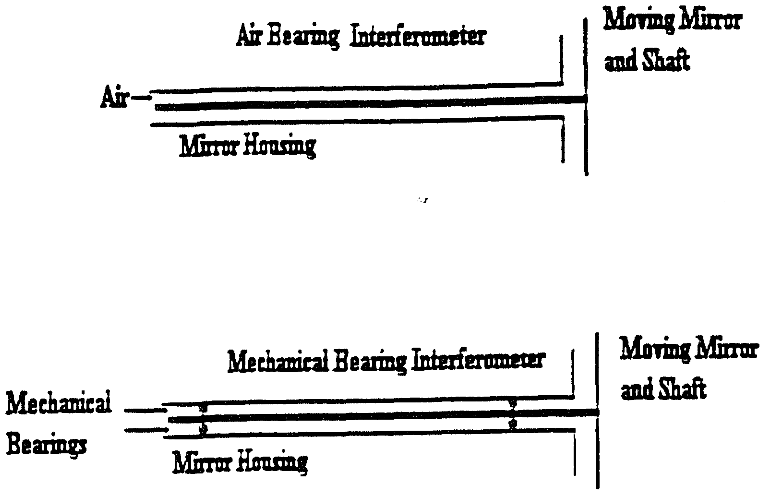

Figure 6.1 Air Bearing and Mechanical Bearing Interferometer

The second way of dealing friction in an inteferometer is to use mechanical means to reduce friction, known as mechanical bearings. Ball bearings, ruby balls, and teflon pads have all been used in mechanical bearing interferometers to reduce friction. The advantage of mechanical bearing systems is they tend to be cheaper than air bearings, are less sensitive to vibrations, and require no source of dry air. The disadvantage of mechanical bearings is that they wear out. This means unpredictable amounts of down time, and the possible expense and hassle of bearing replacement.

6.2 Sources

The purpose of infrared source is to provide radiant energy in the infrared region of the electromagnetic spectrum. Examples of two different types of infrared source are shown in Figure 6.2. The simplest infrared source is the air-cooled source. The temperature of the source is maintained by air currents in the spectrometer, hence its name. It consists of an element that may be made up of a coil of Nichrome wire or a small ceramic piece. Electricity is passed through the element, and the resistance of the element to the electricity causes it to heat up and give off infrared radiation. Often times, these sources are mounted with a mirror behind them to catch the radiation that would have escaped in a direction away from the sample. This helps increase the amount of infrared radiation that gets to the detector. Air cooled sources typically run temperatures from 1100 to 1400 K. The advantage of air cooled sources is that they are inexpensive, and are convenient, since they require no special cooling. However air cooled sources may not provide enough infrared intensity for some applications.

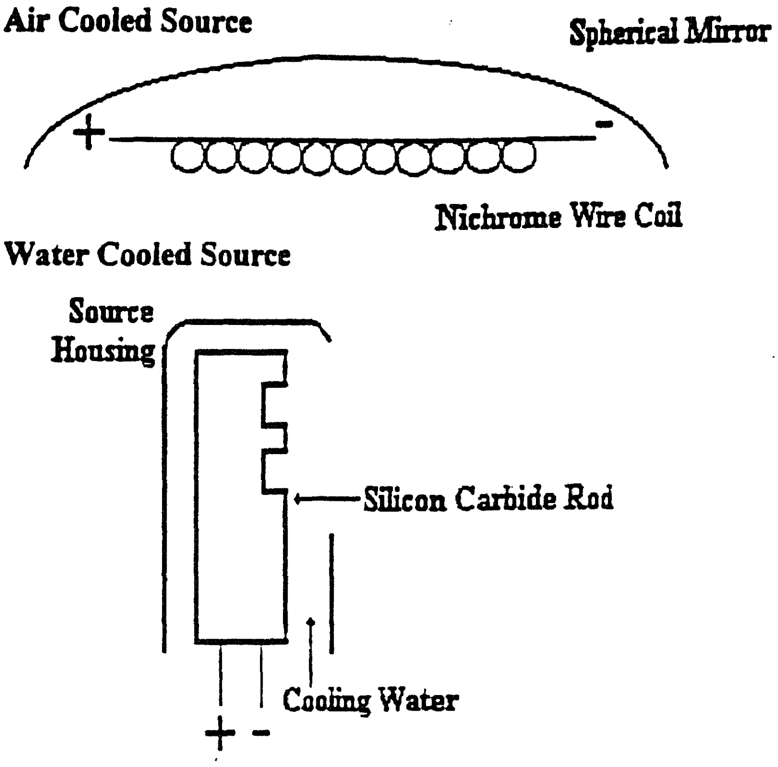

Figure 6.2 Infrared Sources

The other major type of infrared source is the water-cooled source, otherwise known as globar. A diagram of globar is shown in Figure 6.2. It consists of a rod of silicon carbide, and is resistively heated like the air-cooled source. Water-cooled sources are cooled with running water to keep them from overheating, hence their name. Globars operate at temperature above 1400 K, so the advantage of giving off more infrared radiation than air-cooled sources. This means that FTIR will have higher throughput and lower noise will be observed in your spectra. The disadvantage of globars is the need for cooling water, which is an added expense, and may not be available in some locations. Globars also cost more than air cooled sources.

6.3 Beamsplitters

The purpose of beamsplitter is to split the light beam in two. So, some of the light reflects off the moving mirror and some of the light reflects off the fixed mirror. Potassium Bromide (KBr) is almost universally used as a substrate material in FTIR beamsplitters. A thin coating of germanium is sandwiched between two pieces of KBr, and it is this Ge coating that splits the beam. It acts similarly to a partially silvered mirror that reflects light but it is still partially transparent. The KBr acts as a substrate for the beam splitter coating, and protects it from the environment. Therefore, these devices are properly called Ge on KBr beamsplitters. These are usable from 4000 to 400 cm $^{-1}$, covering the mid infrared very well. The only problem with KBr is that it is hygroscopic, meaning that it will absorb water from the atmosphere and fog. This is one reason, why it is essential that all FTIR spectrometer benches be purged with dry nitrogen to maintain a low relative humidity, or be sealed and desiccated to keep water out altogether. The other material typically used in the mid infrared beamsplitters is cesium iodide (CsI). This material transmits from 4000 cm^{-1} to 200 cm^{-1}, a 200 cm^{-1} wider range than KBr. In general, unless the spectral region from 400 to 200 cm^{-1} is very important, use of CsI beamsplitters is not encouraged [28].

6.4 Detectors

The detector element is usually enclosed behind an infrared transparent window to protect it from the environment [28] [29]. The element is connected to the spectrometer's electronics, and its job is to act as a transducer, turning infrared intensity into an electrical signal. The signal is ultimately turned into voltage, which is amplified, processed, and digitized before being Fourier transformed into a spectrum.

There are three major categories of detectors:

- Thermal
- Pyroelectric
- Photoconducting

6.4.1 Thermal Detectors

Thermal detectors have been conceived on the notion of the heating effect of radiation. When the radiation incident upon the receiver is absorbed, its temperature rises. The temperature increment may then be observed by measuring some material property, which depends on temperature. There are three types of thermal detectors currently in use: pneumatic cells, thermocouples, and bolometers. Typical of thermal detectors is their flat spectral response. If they have been properly blackened, their responsivity remains nearly constant over a very wide range of wavelength [1].

Pneumatic detectors make use of the large thermal expansivity of gas as the temperature-sensitive material property. Thermocouples or the thermal detectors 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 between the junction changes according to the difference in temperature between the junctions. The temperature-dependent property utilized in the bolometer is the electrical resistivity of a metal or a semiconductor. Usually, the change of resistance caused by heating of the bolometer element is converted into a voltage by connecting the bolometer in a Wheatstone bridge circuit.

6.4.2 Pyroelectric Detectors

Pyroelectric detectors are made from a 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 polarization persists. The degree of polarization is temperature dependent. So, by sandwiching the pyroelectric material between the two electrodes, a temperature dependent 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.

The most commonly used detector material in the mid-infrared region is deuterated triglycine sulfate (DTGS). The DGTS detector is known as pyroelectric bolometer, and works as follows. Changes in the amount of infrared radiation striking the detector cause the temperature of the DGTS element to change. The dielectric constant of the materials such as DGTS change with temperature. The resultant change in the capacitance with temperature is measured as a voltage across the detector element. DGTS detectors equipped with KBr window cover the mid-infrared range from 4000 to 400 cm^{-1}. The advantages of DGTS detectors are that they are simple, inexpensive, and robust. The major drawback of DGTS detectors is that they are less sensitive than other detectors available. In addition, they are more slow, which means the moving mirror can not translate very fast while an interferogram is being measured. This means fewer scans per minute, and a longer analysis time.

6.4.3 Photoelectric Detectors

Photoelectric detectors such as mercury cadmium telluride detectors comprise a film if semiconductor 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-FTIR.

The major detector used in the mid infrared range is the mercury cadmium telluride (HgCdTe) or "MCT" detector. The MCT element consists of an alloy of these three elements, and it is a semiconductor. The detector element absorbs infrared photons, and as a result, electrons are promoted from the valence band to the conduction band. Once electrons are in the conduction band, they can respond to an applied voltage, giving rise to an electric current. The electric current is a measure of the number of electrons, and so is directly proportional to the number of infrared photons hitting the detector. Thus, the current generated by the detector element is a direct measure of the infrared intensity. The energy difference between the valence band and the conduction band is called the bandgap. Photons with an energy less than the bandgap will not be detected since they do not promote electrons to the conduction band. Photons with an energy greater than the bandgap will promote electrons to the conduction band and will be detected. Thus, the low wavelength cutoff of these detectors is determined by their bandgaps. The bandgap is adjusted by changing the composition of the MCT alloy. "Narrow band" MCT detectors are sensitive down to 700 cm^{-1}, wideband MCT detectors are sensitive down to 400 cm^{-1}. The major advantage of MCT detectors is their sensitivity. They are upto 10 times more sensitive than DGTS detectors, unfortunately there is a tradeoff between bandwidth and sensitivity with MCT detectors. Another advantage of MCT detectors is that they are fast. As a result, one can scan many times faster than with a DGTS detector, and obtain high SNR spectra faster.

A drawback to MCT detectors is that they must be cooled, typically with liquid nitrogen. Without this cooling, heat given off by the detector element itself is detected, giving rise to a large noise signal. These detectors are well equipped with dewars to hold liquid nitrogen which are easily filled, and hold enough liquid to keep detector cool for 8 or more hours. Another disadvantage of MCT detector is their cost, which is 5 to 10 times higher than DGTS detector. Finally, MCT detectors saturate easily. That is, if the infrared light hitting the detector element is too intense, all the available electrons will be promoted to the conduction band, and any further increase in infrared signal will give no further change in the measured electrical current.

6.5 Spectrometer Electronics

6.5.1 Laser

Every commercial FTIR contains He-Ne laser. The purpose of the laser is two fold. First, the laser acts as an internal wavenumber standard. He-Ne lasers give off light at precisely 15,798.637 cm^{-1}. All infrared wavenumbers are measured relative to it.

The second purpose of He-Ne laser is to track the position of the moving mirror so the optical path difference can be measured properly. This is done as follows. The laser beam follows a path through the interferometer similar to that of the infrared beam. A small laser detector is mounted somewhere in the spectrometer and measures the interferogram of the laser beam. It is found that the laser interferogram will pass through a maximum whenever the mirror moves 0.632 microns.

6.5.2 Phase Correction

In an ideal spectrometer, the interferograms measured would be symmetrical about the centerburst. This means that the two wings would be identical to each other, and that only the centerburst and one wing of the interferogram need to be measured to enable a spectrum to be computed, which is known as measuring a single sided interferogram. In the real world, the spectrometer introduces asymmetries into the interferogram, which might necessitate measuring double-sided interferograms to obtain an accurate spectrum. Therefore, a technique called phase correction is applied. At the beginning of a scan, a quick, low resolution, two-sided interferogram (measuring both wings) is obtained. A function is calculated describing the interferogram's asymmetries. Each subsequent interferogram measured during an experiment is multiplied by this function to make it symmetric. As a result of phase correction, the advantages of collecting one-sided interferograms can be enjoyed without worrying about interferogram asymmetries.

6.5.3 Digitization of the Interferogram

Once an interferogram is measured, it is digitized using an analog-to-digital converter (ADC). The purpose of the ADC is to turn the signal from volts (the analog signal) to a digital signal (base two number) the language the computer understands. ADCs with high bit count are inherently better at picking up weak signals than ADCs with a low bit count. The difference between the highest and the lowest numbers that an ADC can measure is called the dynamic range. A large dynamic range is good because it gives one greater flexibility in the types of experiments that can be performed [30].

It is the size of the centerburst that determines how many bits of the ADC are used. If the centerburst overfills the ADC, it will be truncated, and hence part of the interferogram will not be measured. This phenomenon is known as clipping and is one of the major source of noise in FTIR spectrometer. To adjust the interferogram intensity to its optimum value and avoid clipping, the entire interferogram is amplified using a gain amplifier (gain setting).

Since the intensity is weak in the wings of an interferogram, only the wings are amplified and not the centerburst. In the process known as gain ranging, an amplifier is turned on after a certain number of interferogram data points are collected, so the interferogram intensity in wing is increased without increasing the intensity of the centerburst. Once the interferogram is measured, the portion that was amplified is divided by the amplification factor to preserve the quantitative efficiency of the data.

As discussed previously, an interferometer modulates the intensity of infrared radiation, producing a cosine wave signal at the detector. In a typical mid-infrared spectrum, the highest wavenumber of interest is 4000 cm^{-1}, which would result in an interferogram signal whose highest frequency is 8000V (where V is the moving mirror velocity). Any signals above 8000V in frequency are not of interest, and hence are noise. These high frequency signals are eliminated from the interferogram by using an electronic low pass filter. This filter only lets signals below a certain frequency to pass. The frequencies that a low pass filter must eliminate must be programmable because the frequencies to be eliminated depend on the moving mirror velocity, and the wavenumber range of interest. In some software systems, the cutoff frequency of the low pass filter is a user adjustable software parameter.

CHAPTER 7

TRADING RULES IN FTIR SPECTROMETRY

The quantitative relationships between Signal-to-Noise Ratio (SNR), resolution, and measurement time are commonly referred to as trading-rules. We attempt to analyze how SNR may vary with parameters such as measurement time, resolution, throughput, and scan speed [13].

7.1 Spectral Resolution

When spectra are displayed or plotted they look like continuous functions, but in reality consist of a number of discreet data points. Spectral resolution is a measure of ability of an instrument to distinguish spectral features that are close together.

The instrument resolution used in measuring a spectrum determines the number of data points in the spectrum. For instance, a 4 cm^{-1} resolution spectrum contains a data point every 4 cm^{-1}, and a 32 cm^{-1} spectrum contains a data point every 32 cm^{-1}. The number of data points can be easily calculated from the resolution and the wave number range of the data. The number of data points in a 4 cm^{-1} resolution spectrum from 4000 to 400 cm^{-1} is calculated as follows:

$$4000\ cm^{-1} - 400\ cm^{-1} = 3600\ cm^{-1}\ \text{range}$$

$$3600\ cm^{-1} / (4\ cm^{-1} / \text{data point}) = 900\ \text{data points}$$

The impact of using different resolutions on the appearance of a spectrum is seen in Figure 7.1,which shows the spectra of water vapor taken at 4 and 32 cm^{-1} resolution respectively [8]. The 32 cm^{-1} spectrum is broad and featureless while the 4 cm^{-1} shows

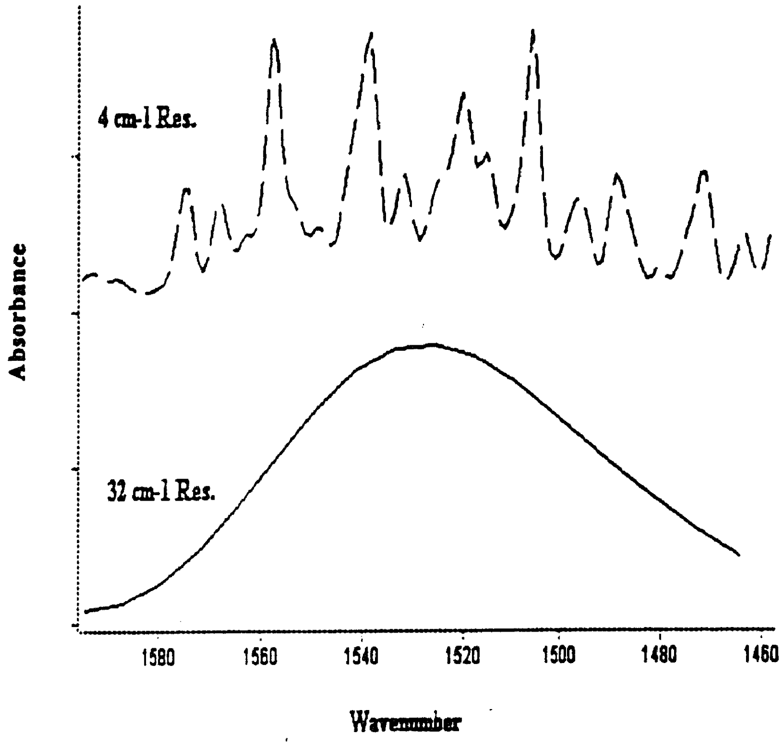

Figure 7.1 Effect of Resolution

many sharp features. The 32 cm^{-1} spectrum is said to be taken at low resolution because it does not distinguish spectral features well, while the 4 cm^{-1} spectrum is said to be taken at high resolution because it resolves many spectral features. So, high resolution is denoted by a small wavenumber value, and large resolution is denoted by a large wavenumber value.

The reason the low resolution spectrum looks broad and featureless in Figure 7.1 is that the features more than 32 cm^{-1} apart can be distinguished, the data point spacing is too wide to see any features close together. In a high resolution spectrum, features that are 4 cm^{-1} or more apart are resolved because the data point is small enough to allow these features to be seen [29].

7.2 Resolution and Optical Path Difference

Assume a spectrum of the sample has two absorbance bands that are close in wavenumber, say at 3000 and 3001 cm^{-1}. These bands give rise to very similar sinusoid interferogram signals as seen in Figure 7.2. If the mirror is moved only a short distance, and only a small portion of the spectrum are sampled, the instrument cannot distinguish between the two interferograms as they look identical at small values of δ. If the interferogram is measured with a large δ, the instrument will distinguish between the sinusoids and spectral features less than 1 cm^{-1} apart can be distinguished. Therefore as the optical path difference increases, the ability of the spectrometer to distinguish nearby features increases.

This can be summarized in equation form as follows:

$$\text{Resolution} \propto 1/\delta \qquad (7.1)$$

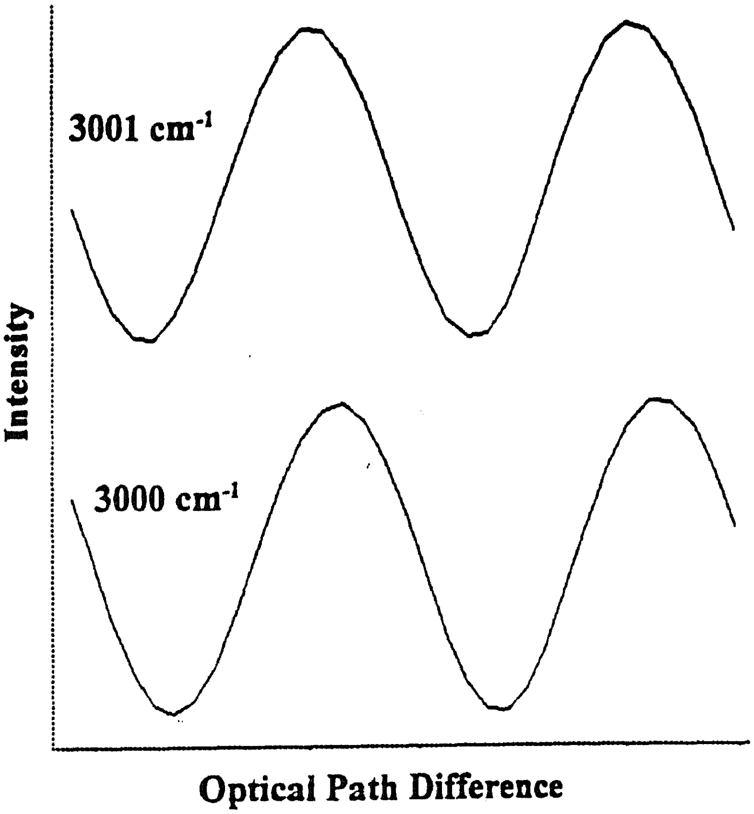

Figure 7.2 Two Closely Spaced Interferograms

where resolution is defined in cm^{-1} and optical path difference is defined in cm. Above equation says that as optical path difference is increased, the value of resolution decreases. The lower the value of resolution, sharper is the spectral resolution.

The number of data points in an interferogram is determined by the maximum optical path difference used to measure the interferogram. Therefore, long interferograms have more data points than short interferograms. This is why high resolution spectra contain more data points, and more data points per cm^{-1} than low resolution spectra.

7.3 Resolution and Noise

The drawback of obtaining high resolution spectra is that they are much noisier than low resolution spectra. The relation can be written as

$$\text{SNR} \; \alpha \; \text{Resolution} \tag{7.2}$$

Thus, we come across a very important trade-off. High resolution spectra are inherently noisier, but may contain a lot of information. The best solution depends on the sample and what information is needed from the spectrum.

There is another phenomenon that contributes to higher resolution spectra being noisier than low resolution spectra. In an ideal interferometer, the light beam is perfectly collimated cylinder, and all light rays are parallel to each other. In reality, the optics in spectrometers is not perfect, and the infrared beam shape is not a cylinder, but a cone. The light rays in an infrared beam are not parallel but form an angle to each other as shown in Figure 7.3 . This phenomenon is known as angular divergence. Because of angular divergence, light on outside of the beam travels a different distance than in the center of the beam. These light beams destructively interfere with one another, reducing

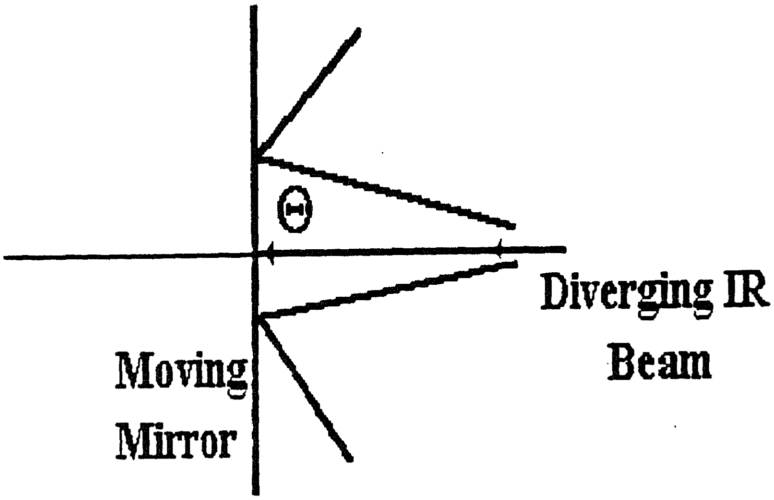

Figure 7.3 Angular Divergence

the amount of infrared light returning to the beamsplitter. Angular divergence increases with the optical path difference because the light beam has more of a chance to spread out the further it travels. As a result, light intensity decreases as optical path difference increases, causing noise to increase with the optical path difference.

An aperture can be placed in the infrared beam to counteract the effects of angular divergence. Most high resolution FTIR systems contain computer controlled apertures that automatically adjust to the right size. The use of apertures is however another reason that high resolution spectra are noisier than low resolution spectra.

7.4 Resolution and the Time to Measure the Spectrum

When interferograms are added together the sign of random noise cancels itself out. However, it turns out that time spent measuring random noise is the real quantity that influences SNR. The more time spent measuring random noise, the more chances it has to cancel itself, leading to a better SNR. This can be summarized as follows:

$$\mathrm{SNR} \ \alpha \ (\mathrm{T})^{1/2} \tag{7.3}$$

where T is the time spent measuring the spectrum. When comparing two spectra taken at the same resolution, more scans give a better SNR than few scans because more time is spent measuring the data when many scans are coadded.

We can digress a bit here, to show how the multiplex advantage of FTIR works. Imagine taking a 4 cm^{-1} resolution spectrum from 4000 to 400 cm^{-1} on a dispersive infrared spectrometer and on an FTIR. The spectrum consists of 900 data points. Assume that measurement time is 10 minutes on both the instruments. The dispersive instrument measures one data point at a time, so only 1/900th of the measurement is spent observing any given data point, which amounts to about 0.667 second. However in an FTIR, all data points are measured all the time so, each data point in this spectrum is observed for a full 10 minutes (600 seconds). More the scans; more is the time spent to measure spectrum and as seen by the equation 7.3, better is the SNR. The SNR advantage of FTIR compared to dispersive instruments is calculated by taking the square root of the ratio of the time spent observing a data point using each instrument:

$$\text{FTIR SNR advantage} = [\text{ 600 seconds / 0.667 seconds }]^{1/2}$$

$$\text{FTIR SNR advantage} \sim 30$$

When comparing the SNR of spectra taken at a different resolutions and using different number of scans, the total measurement time should be used as a comparison, not the number of scans. The measurement time is easily calculated by multiplying the number of scans times the moving mirror velocity.

7.5 FTIR Trading Rules

When considering how to perform an FTIR analysis, the parameters that need to be optimized are SNR, resolution, and analysis time. Ideally, you want a spectrum with high SNR, obtained with good enough resolution to resolve all the bands in the spectrum, and obtained in as little time as possible. The following trading rules [8] must always be kept in mind when setting the measurement parameters on your FTIR.

1. The SNR is reduced as the square root of the amount of the time spent measuring data:

$$\text{SNR } \alpha \text{ } (T)^{1/2} \qquad (7.3)$$

where SNR is signal to noise ratio, and T is analysis time. When comparing SNRs for spectra taken at the same resolution, the equation simplifies to

$$\text{SNR} \,\alpha\, (\text{N})^{1/2} \tag{7.4}$$

where N is the number of scans.

2. Due to electronic noise, angular divergence, and the need to use apertures, high resolution spectra are inherently noisier than low resolution spectra

$$\text{SNR} \,\alpha\, \text{Resolution} \tag{7.5}$$

where SNR is signal-to-noise ratio, and resolution is measured in cm^{-1}.

3. It takes longer to obtain many scans than to obtain a few scans, so analysis time is related to the number of scans as follows

$$\text{T} \,\alpha\, \text{N} \tag{7.6}$$

It takes longer to obtain a high resolution spectrum than a low resolution spectrum because it takes more time to move the mirror a longer distance. So analysis is related to resolution as such:

$$\text{T} \,\alpha\, 1/\text{Resolution} \tag{7.7}$$

where N is the number of scans, T is the analysis time and resolution is measured in cm^{-1}.

In conclusion, analysis time, resolution and SNR are all related, and one must understand these relationships to optimize scan parameters to obtain high quality FTIR data.

CHAPTER 8

APPLICATIONS OF FTIR SYSTEMS

Infrared Spectroscopy is a widely used industrial tool for the structural and compositional analysis of organic, inorganic, or polymeric samples and for quality control of raw materials and commercial products. It is relatively simple technique, non-destructive, versatile enough to handle solids, liquids and gases with a minimum of sample preparation, and accurate enough for both the qualitative identification of the structure of unknown materials and the quantitative measurement of the components in a complex mixture. Instrumentation has been reliable and low cost.

8.1 FTIR Studies of Polymers

FTIR has found particularly wide application in the field of polymer analysis, not only because of the ability to look at intractable, thick, intensely absorbing materials, but also because of the ability to look at chemical and physical changes in the polymer structure as they are occurring [31]. Vibrational spectrometry has been applied to the identification of polymeric materials for both qualitative and quantitative determination of the chemical composition. Many parameters can be investigated, including polymer end groups, chain branching, configuration and conformation, as well as steric and geometric isomerism. Infrared spectrometry has also been used to identify and determine the concentration of impurities, antioxidants, emulsifiers, additives, plasticizers, fillers, and residual monomers in polymeric materials. The effects of external conditions on polymers have been studied as well. The changes of state with temperature and pressure as well as the effects of irradiation, deformation, fatiguing, and weathering are of interest. The techniques used for the measurement of FTIR spectra of polymers are for the most part are identical to those applied to conventional samples. Polymers may be handled as solutions, solids, powders, and films. The analysis of polymers using FTIR spectrometry relies heavily on the isolation of spectral features. Spectral subtraction is frequently employed to isolate spectral features of a component in a polymer blend, to remove solvent bands, or to isolate spectral features after a chemical reaction or physical change in the sample.

Microanalysis can be applied to the polymer samples and this technique is used to examine relatively large impurities or occlusions in the polymer samples. Transmission utltramicrosampling has been demonstrated for polymer films and fibers. A recent development in the FTIR spectrometry is the interfacing of a transmission or reflection microscope. These microscopes permit the investigation of samples that are as small as 10-15 μm in diameter. The size of the sample is determined by diffraction effects, not by the resolution of the microscope. It is anticipated that infrared microscopes will be very useful in the nondestructive analysis of defects or occlusions in polymers.

Of much interest in polymer analysis, is the change in the chemical composition due to factors such as reaction conditions, oxidation, thermal decomposition, and so on. Often much of the effect of the chemical history of a sample is altered by preparing a sample in the form of a pellet, mull, thin film, or solution for transmission spectrometry. For this reason, more emphasis is being placed on nondestructive analytical methods. One such method for the analysis of powdered polymers is diffuse reflectance spectrometry. Diffusely powdered radiation is collected and directed to the detector. The spectrum is obtained by ratioing the diffuse reflectance spectrum of the spectrum of a nonabsorbing substrate, usually powdered KCl or KBr. Diffuse reflectance spectrometry of non-powdered solid samples, such as pellets, is almost invariably unsuccessful. The entire field of polymer studies is extremely broad and a comprehensive review is beyond the scope.

It is important to recognize that not only the resolution, but also the width of observed infrared bands depend on the truncation i.e. the length of the time the interferogram is sampled and apodization function.

8.2 Biochemical and Biomedical Applications

Infrared spectroscopy has been the late addition to the spectroscopic inventory of the membrane biophysicist. The reason has been the presence of water in Biological membranes. Water, which does not impair spectroscopic measurements using NMR, ESR, UV or Raman techniques is a strong infrared absorber, a fact which has precluded or severely limited the application of conventional infrared spectroscopy to the study of biological systems [32].

Membranes are the most common cellular structures; they are recognized as being involved in almost all aspects of cellular activity ranging from simple functions such as food entrapment in unicellular organisms, to very complex functions such as immunorecognition in higher organisms. This functional diversity rests on a structural diversity, which in turn is reflected in the wide variety of lipids and proteins that compose different membranes.

Physical studies of membranes have concentrated mainly on the organization of the lipid matrix. Perhaps the best studied physical property of membranes is their thermotropic mesomorphism. This change of state induced by temperature is reflected in an order-disorder phase transition of the lipid matrix and is commonly referred to as the gel to liquid crystal phase transition. Infrared spectroscopic experiments directed towards studying the thermotropic phase behavior of membrane lipids involve collecting the spectrum of the same system at various temperatures and monitoring changes in band parameters as a function of temperature. This process can be brought completely under the control of the spectrometer computer, which records a spectrum, increments the temperature, waits for temperature equilibration then records another spectrum. Since the output of modern spectrometers is digitized, the task of data processing is greatly simplified. Frequency and bandwidth values can now be determined routinely with uncertainties of less than $\pm$ 0.05 cm^{-1}. The temperature induced structural changes, which occur in lipid membranes, can be studied by monitoring various infrared absorption bands as a function of temperature. The gel to liquid crystal phase transition involves a large structural rearrangement of the lipid bilayer and produces considerable changes in the infrared spectrum.

8.3 Application to Surface Analysis

FTIR has additional merits such as high sensitivity, high precision, quickness of measurement, and extensive data processing capability besides the intrinsic advantages of infrared spectroscopy such as wide applicability, nondestructiveness, measurement under ambient atmosphere, capability of providing detailed structural information and a huge data base. FTIR has changed infrared spectroscopy from a technique of identification of bulk materials to a comprehensive technique of material characterization and has opened up a new field especially in surface studies and microanalyses of industrial materials. An excellent example of the application of this technique is found in the work done at Toray Research center, Inc., in Japan by Hideyuki Ishida [33]. They carried out the FTIR study of the molecular orientation of Liquid Crystal Display (LCD) alignment films. Homogeneous aligning techniques of liquid crystal molecules are very important in the field of Liquid Crystal Display (LCD). Such homogeneous alignment can be achieved by using directionally controlled alignment layers. At present most of the alignment layers are made by rubbing thin polyimide films on Indium Tin Oxide substrates by nylon or Rayon cloth. It is said that the molecular orientation of thin polyimide films caused by mechanical rubbing plays an important role in the alignment of LC molecules. In order to clarify ambiguous rubbing mechanism, polyimide thin films rubbed at different densities are studied by FTIR from the viewpoint of molecular orientation.

8.4 Application to Ozone Chemistry

The discovery of the "ozone hole" over Antarctica in the eighties has led to considerable research of the chemical composition of the stratosphere and the processes that might be responsible for the depletion of the total amount of ozone. The use of FTIR spectroscopy has become well established as a valuable technique for the study of the constituents of the stratosphere itself, and of laboratory chemical transformations of stratospheric importance. Thus, FTIR-spectroscopy can play an important role in understanding the phenomenon of stratospheric ozone decline in detail. Trace constituents in the stratosphere can be examined either by ground-based or air-borne high resolution IR instruments. Heterogeneous chemical reactions on the surfaces of polar Stratospheric Clouds (PSCs) are considered important for their potential role in ozone depletion processes. FTIR surface studies can be used to probe the growth, transformation and evaporation of PSC films (ice or nitric acid/ice) at stratospheric temperatures.

8.5 Application of FTIR in Environmental Research

FTIR is an efficient method of detecting and quantifying molecules in ambient air and plume mixtures. It provides major advantages compared with in-situ sensors:

- simultaneous and low cost analysis of many components during one scan over the entire IR spectrum,
- surveillance of distant sources,
- no requirement of sample taking and handling,
- no sensor contamination.

An detailed explanation of this can be found in the work done at Fraunhofer Institute of Atmospheric Environmental Research by R. Haus and team [34]. In addition, passive remote detection of atmospheric pollutant using FTIR is discussed in [35].

8.6 Hyphenated Infrared Techniques

As we have seen, all the way that infrared spectroscopy is an excellent tool for determining the identity and quantities of molecules in the sample. However, many other analytical techniques measure the physical properties of a sample and provide little or no information. It would be ideal if both physical and chemical information could be obtained on a sample at the same time using the instrument. By interfacing an FTIR with an instrument that measures a sample's physical properties, both chemical and physical information about a sample could be obtained at the same time. This greatly increases the amount of information acquired about the sample and decreases the amount of analysis time compared to obtaining the information via separate analyses. When FTIRs are interfaced with other pieces of equipment, new techniques are invented and these are called "hyphenated infrared techniques".

8.6.1 Infrared Microscopy

Infrared microscopy involves coupling an FTIR to a visible light microscope, and allows for visual and infrared examination of microscopic samples. Infrared microscopes are often times high quality visible microscopes that have been redesigned for use with infrared radiation. The applications of infrared microscopy are widespread. In fact, many people buy FTIRs for the sole purpose of performing infrared microscopy. One of the most important applications of infrared microscopy is in forensic labs, i.e. police and crime labs. Items left at crime scenes can provide clues as to the perpetrator of a crime. Paint chips are often left behind on victims of hit and run automobile accidents. These chips are recovered from the victim's body, are pressed flat in a diamond anvil cell, and the microscope spectrum obtained in transmission. Automobile manufacturers and law enforcement officials have cooperated to maintain libraries of infrared spectra of paint chips from automobiles. By performing a library search, the make, model, and year of a car can be determined. A search of the Department of Motor Vehicles database can be made to find out who in the area owns the type of car involved in the accident. Clothing fibers are also left behind at crime scenes by criminals. The infrared spectra of clothing fibers are obtained in transmission. By matching fibers from a crime scene with fibers from a suspect's clothing, circumstantial evidence as to the presence of the suspect at the crime scene can be provided. Mary W. Tungol and team have discussed the application of Infrared Microscopy in forensic science [36].

Another application of this technique is detecting microscopic contaminants and defects present in products such as paper, polymer films, and coatings. These defects can consist of foreign particles that create a bump in the sheet, or of areas where the film is too thin. These defects can render the product useless. Infrared microscopy is sometimes used as a tool to analyze these defects. The offending portion of a sheet is cut out, and the reflectance spectrum of the defect is obtained. Once the defect is identified, the source of the contaminant may be found and eliminated.

8.6.2 Gas Chromatography – FTIR (GC – FTIR)

Gas chromatography is a method to analyze mixtures of volatile molecules. The sample is injected into a heated port where it is vaporized. The fundamental measurement taken with a GC is called a chromatogram, which is a plot of detector response vs. time. Gas chromatography is a widely used technique for analyzing the composition of complex mixtures. Its applications include use in environmental analysis, the petroleum industry, and chemical quality control. The applications of GC-FTIR are wide and varied. Analysis of pesticides, herbicides, and polychlorinated biphenyls (PCBs) in environmental samples has been accomplished. The petroleum industry makes use of GC-FTIR to look at the constituents of gasoline, fuel, oil, and other petroleum products. The chemical industry uses GC-FTIR to look at feed streams, intermediates, and final products to ascertain their composition and quality. The flavors and fragrances industry uses GC-FTIR to analyze the components of flavor oils, foods, and beverages that give rise to taste and smell.

At the Armed Forces Institute of Pathology, Washington D.C., Kathryn S. Kalasinsky and group have used FTIR techniques for the analysis of drugs of abuse [37].

CHAPTER 9

CONCLUSION

This thesis surveyed the concepts, methodology, hardware and applications of Fourier Transform Infrared Spectroscopy. The demand for the increasing productivity in analytical techniques that rapidly provide real-time quantitative information about chemical processes has made FTIR as a ideal tool for obtaining high quality infrared spectra. FTIR has additional merits such as high sensitivity, high precision, quickness of measurement, and extensive data processing capability besides the intrinsic advantages of infrared spectroscopy such as wide applicability, non-destructiveness, measurement under ambient atmosphere, capability of providing detailed structural information and a huge data base. Through the use of FTIR spectroscopy, sensitivity has increased, size of the smallest sample that can be analyzed has been reduced and a significant improvement in the resolution has been obtained. Compared to diffraction grating spectrometer of good performance, over most of the spectral region, FTIR enables the attainment of more than an order of magnitude of improvement in SNR for a given time of scan and resolution. With the recent trends towards hyphenated infrared techniques, FTIR is going to be an ideal tool for obtaining infrared spectrum.

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