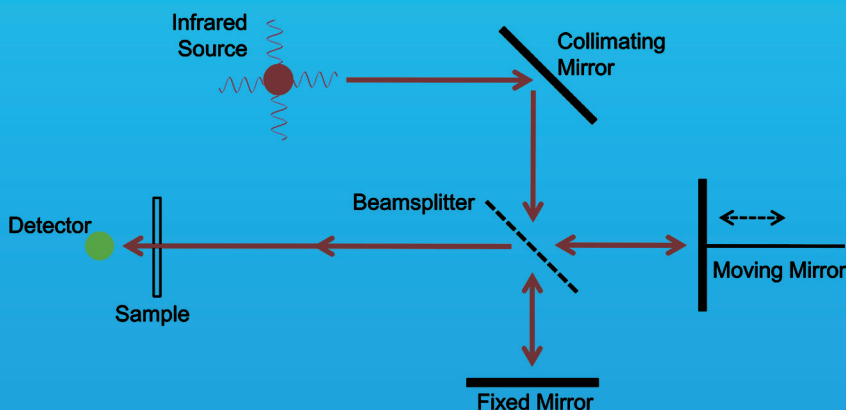


Second Edition

Fundamentals of FOURIER TRANSFORM INFRARED SPECTROSCOPY



Brian C. Smith

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CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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CRC Press is an imprint of Taylor & Francis Group, an Informa business

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-1-4200-6930-3 (Ebook-PDF)

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To my loving and lovely wife, Marian.

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Preface

Why write a second edition of *Fundamentals of FTIR*? Two reasons. First, much has changed since the first edition was published in 1996, particularly the development of diamond ATRs. Second, I have taught FTIR to thousands of people since 1992, and I now do a better job of explaining the important concepts of FTIR than I did then, which is reflected in this book. Those familiar with the first edition of *Fundamentals of FTIR* will recognize very little here; the book has been entirely rewritten and there are dozens of new figures. Topics have been added, expanded, and dropped as appropriate.

So, who do I think you are? This book is aimed at those new to FTIR, particularly non-chemists who need to use FTIR equipment and who seem to be the majority of new users these days. However, journeyman and expert spectroscopists should find this volume a useful reference for its concise and comprehensible explanation of FTIR topics. A nodding familiarity with freshman chemistry and physics will help while reading this volume, but is by no means a necessity. Chemists and non-chemists have told me they benefited from reading the first edition, and I expect the same will be true of this edition.

This book contains six chapters. Chapter 1 is an introduction to the field of infrared spectroscopy, including the strengths and weaknesses of FTIR as a chemical analysis tool. The second chapter, “How an FTIR Works,” is all about the instrument. Topics include how an interferometer generates a spectrum, optimizing spectral quality, and tests to monitor instrument health. Chapter 3 is a discussion of how to properly use spectral processing to increase the information content of a spectrum without damaging the data. My approach to this topic is as unique now as it was in the first edition. Chapter 4 is dedicated to sample preparation. Preparing samples is half the battle in getting a good spectrum—Chapter 4 will teach you to win that battle. The chapter is significantly expanded compared to the first edition, including a lengthening of the ATR section. Chapter 5 is dedicated to single analyte quantitative analyses. Entire books have been written on this topic (including one by me), but the goal here is to introduce you to enough of the theory and practice of this field to allow you to generate your own quality calibrations. Chapter 6 is an overview of infrared microscopy. I estimate that one third of the FTIRs in use have infrared microscope attachments, hence the need to cover this topic in an introductory book.

I hope you find this book a readable and enjoyable introduction to an important field of chemical analysis. I take full responsibility for the contents of the book including all errors, and greatly appreciate your comments whether positive or negative. You can find me by doing an Internet search on “Spectros Associates.”

Happy reading.

Brian C. Smith, Ph.D.

Acknowledgments

No book is an island; authors need the assistance of numerous people to turn a book idea into reality, all of whom deserve credit. I would first like to thank the folks at CRC Press. I have been one of their authors for 17 (!) years, and I still enjoy my relationship with them. I would particularly like to thank my publisher, Fiona Macdonald, and my editor, Barbara Glunn. Barb has been particularly patient and gracious with me through many delays and frustrations. I am grateful that my Ph.D. advisor from Dartmouth College, Prof. John Winn, is still part of my life, and I would like to thank him for reviewing parts of this book. Much of the spectral data in this book was processed and plotted using the GRAMS/AI™ software package from ThermoFisher Scientific. I would like to thank them for supplying me with the software. Some of the spectra were measured using an ALPHA FTIR from Bruker Optics. I would like to thank Haydar Kustu from Bruker Optics for making the ALPHA available to me. Ken Kempfert of PIKE Technologies supplied many of the pictures of sampling accessories. Thanks Ken! I also thank my “partner in crime” here at Spectros Associates, Peg Veal, for her many years of dedicated service.

I have made my living as an FTIR trainer and consultant since 1992. In that time thousands of people have patronized my business, and I would like to thank each and every one of them, including you, for allowing me to have such a fun and interesting career.

1 Introduction to Infrared Spectroscopy

The purpose of this book is to introduce the reader to the fundamental concepts of Fourier Transform Infrared (FTIR) spectroscopy. The discussion assumes no previous background in FTIR, but a familiarity with the basic concepts of chemistry and physics will be helpful in understanding this text. This book teaches the basics of FTIR to those new to the field, and will serve as an excellent reference guide for experienced users. All terms shown in *italics* will be defined in the glossary at the end of the book.

I. TERMS AND DEFINITIONS

Half the battle in learning any new field is understanding the jargon. To aid you in learning about FTIR, a number of the terms used in the field of infrared spectroscopy are defined below.

Spectroscopy – the study of the interaction of light with matter.

Infrared Spectroscopy – the study of the interaction of infrared light with matter.

Mid-Infrared – light from 4000 to 400 *wavenumbers* (cm^{-1}).

Spectrum – a plot of measured light intensity versus some property of light such as *wavelength* or *wavenumber*.

Spectrometer – an instrument that measures a spectrum.

Infrared Spectrometer – an instrument that measures an infrared spectrum.

FTIR – Fourier Transform Infrared, a specific type of infrared spectrometer.

Analysis of infrared spectra can tell you what molecules are present in a sample and at what concentrations; this is why infrared spectroscopy is useful. There are several types of infrared spectrometers in the world, but the most widely used ones are FTIRs, which is the focus here. This book will teach you how FTIRs work, how to use them to obtain the best spectra, how to use FTIR software to assist in data analysis, how to properly prepare samples for FTIR analysis, how to quantify concentrations in samples using FTIR spectra, and infrared microscopy. In essence, we will be studying everything involved in obtaining a good infrared spectrum. For information on how to interpret an infrared spectrum to determine the structures of molecules present in a sample please consult my book on infrared spectral interpretation [1].

II. THE PROPERTIES OF LIGHT

The proper term used to describe light is *electromagnetic radiation*. Light is composed of electric and magnetic waves called the *electric vector* and the magnetic vector. These two waves undulate in planes mutually perpendicular to each other, and move through space in a third direction perpendicular to the planes of undulation. It is the interaction of the electric vector with matter that leads to the absorbance of light. The amplitude of the electric vector changes over time and has the form of a sine wave as shown in Figure 1.1. The + and – signs in the figure indicate that the polarity of the electric vector alternates over time.

Since the motion of waves is repetitive, they go through *cycles*. For a wave a *cycle* begins at zero amplitude and ends when the wave has crossed zero amplitude a third time as illustrated in Figure 1.1. The distance forward traveled by a wave during a cycle is called its *wavelength*. The units of the wavelength are distance per cycle, although typically just the distance units are noted. Different types of light waves have different wavelengths. For example, the mid-infrared radiation typically used to measure infrared spectra has wavelengths of about 10 microns, which is a little smaller than the diameter of a human hair. Scientists use the Greek letter lambda (λ) to denote wavelength. The arrows in Figure 1.1 show the wavelength of the light wave. In the older scientific literature you will sometimes see infrared spectra plotted with wavelength on the x-axis.

Another important property of a light wave is its *wavenumber*, which is denoted by the letter W. The wavenumber measures the number of cycles a wave undergoes per unit length. Wavenumbers are measured in units of cycles per centimeter, which are frequently abbreviated as cm^{-1} and can be pronounced as “inverse centimeters,” “reciprocal centimeters,” or “wavenumber.” If a spectrum has a peak at 3000 cm^{-1} it means the sample absorbed infrared light that underwent 3000 cycles per centimeter. Most infrared spectra are plotted from 4000 to 400 cm^{-1} on the x-axis, as seen in Figure 1.2.

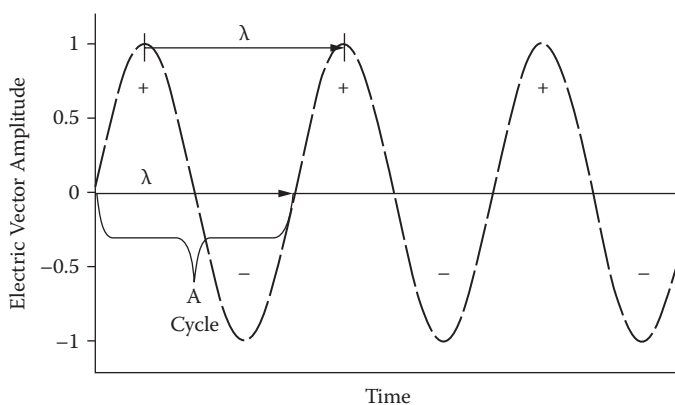


FIGURE 1.1 An example of the electric vector of a light wave. The + and – signs indicate the alternating polarity of the electric vector. The arrows show the wavelength (λ) of the wave. Note where the wave’s cycle begins and ends.

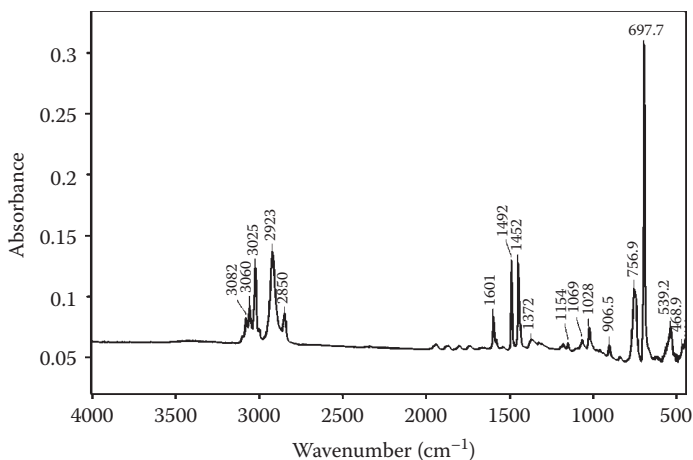


FIGURE 1.2 The infrared spectrum of polystyrene. Note that the x-axis is plotted in wavenumber and that the y-axis is in absorbance.

Since the wavelength has units of distance/cycle and wavenumbers have units of cycles/distance, the two quantities are reciprocals of each other as such:

$$W = 1/\lambda \quad (1.1)$$

Where

W = Wavenumber

λ = Wavelength

If λ is measured in centimeters, then W is calculated in cm^{-1} . One of the interesting properties of W is that it is proportional to the energy of a light wave as follows:

$$E = hcW \quad (1.2)$$

Where

E = Light energy in Joules

c = The Velocity of light ($\sim 3 \times 10^{10}$ cm/second)

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

W = Wavenumber

Since energy is proportional to W , high wavenumber light has more energy than low wavenumber light. Thus, the x-axis of Figure 1.2 is an energy axis with higher energy to the left and lower energy to the right.

Another important property of light waves is their *frequency*, which is a measure of the number of cycles a wave undergoes per unit time. Frequency is typically measured in cycles/second or Hertz (Hz) and the units are frequently written as sec^{-1} . Mid-infrared frequencies are on the order of 10^{14} Hz or ~ 10 terahertz. Scientists represent frequency with the Greek letter nu (ν).

The different properties of light waves are related to each other by the following equation:

$$c = v\lambda \quad (1.3)$$

Where

c = The Velocity of light ($\sim 3 \times 10^{10}$ cm/second)

v = Frequency in Hertz (sec^{-1})

λ = Wavelength in cm

A close look at Equation 1.3 shows that the units make sense. When wavelength is measured in centimeters and is multiplied by frequency measured in sec^{-1} , we obtain units of cm/sec, which are the units of velocity. Equation 1.3 shows that the product of frequency times wavelength for a light wave equals a constant, the speed of light. Thus for any light wave you can calculate the frequency if you know the wavelength, and you can calculate the wavelength if you know the frequency. From Equation 1.1 we know that $W = 1/\lambda$, which can be substituted into Equation 1.3 and rearranged to obtain the following:

$$c = v/W \quad (1.4)$$

Where

c = The Velocity of light ($\sim 3 \times 10^{10}$ cm/second)

v = Frequency in Hertz (sec^{-1})

W = Wavenumber in cm^{-1}

Equation 1.4 allows the calculation of the wavenumber of a light wave if frequency is known, or frequency if wavenumber is known.

There are many types of electromagnetic radiation in the universe besides the mid-infrared, the collection of which is called the *electromagnetic spectrum*. A diagram of part of the electromagnetic spectrum is seen in Figure 1.3.

The mid-infrared has been intentionally placed at the center of Figure 1.3. To the right of the mid-infrared between 400 and 4 cm^{-1} is the *far infrared*. When molecules absorb far infrared light they vibrate. Molecules with heavy atoms in them, including many inorganics, absorb in this region. Some FTIRs work in the far infrared. Lower in energy than the far infrared are *microwaves*. When molecules absorb microwaves they rotate faster. Microwave spectra of rotating gas phase molecules have been measured, and this type of spectroscopy can be used to identify and quantify gases in samples. A microwave oven gives off radiation tuned to an absorbance of liquid water. The liquid water molecules in food absorb this energy and rotate rapidly. Collisions with neighboring food molecules transfer energy to them raising their temperature and making your dinner warm.

Higher in energy than the mid-infrared, from 14,000 to 4000 cm^{-1} , is the *near infrared*. Molecules vibrate when they absorb near infrared radiation, but the spectral features are fewer, broader, and more difficult to interpret than in the mid-infrared. Because of certain instrumental advantages, near infrared radiation is frequently

>14,000 cm ⁻¹ Visible & UV	14,000 to 4000 cm ⁻¹ Near IR	4000 to 400 cm ⁻¹ Mid-Infrared	400 to 4 cm ⁻¹ Far Infrared	< 4 cm ⁻¹ Microwaves
Electronic Transitions	Molecular Vibrations	Molecular Vibrations	Molecular Vibrations	Molecular Rotations

Higher Wavenumber	Lower Wavenumber
Higher Frequency	Lower Frequency
Higher Energy	Lower Energy
Shorter Wavelength	Longer Wavelength

FIGURE 1.3 A part of the electromagnetic spectrum.

used to measure sample properties in difficult environments such as in the middle of a chemical reactor or of liquid flowing through a pipe. Some FTIRs work in the near infrared. Higher in energy than the near infrared are visible light and ultraviolet (UV) radiation. These higher energy light waves fall above 14,000 cm⁻¹. When a molecule absorbs visible or ultraviolet light the electrons in the molecule transition from a lower electronic energy level to a higher one. Many molecules have measurable UV and visible spectra, and these spectra can be used to identify and quantitate molecules in samples. FTIRs can be equipped to work in the visible and UV. Figure 1.3 shows that as you move from right to left across the electromagnetic spectrum there is an increase in energy, wavenumber, and frequency, but a decrease in wavelength. Similarly, moving from left to right across Figure 1.3 there is a decrease in energy, frequency, and wavenumber and an increase in wavelength.

III. WHAT IS AN INFRARED SPECTRUM?

A plot of measured infrared light intensity versus a property of light is called an *infrared spectrum*. An example of an infrared spectrum is shown in Figure 1.2. By convention the x-axis of an infrared spectrum is plotted with high wavenumber to the left and low wavenumber to the right. Plots of your FTIR spectra should always follow this convention. Note in Figure 1.2 that 4000 cm⁻¹ is to the left and 500 cm⁻¹ is to the right, and that the spectrum is plotted in Absorbance units, which measure the amount of light absorbed by a sample. As you can see in the figure the peaks point up and their tops denote wavenumbers at which significant amounts of light were absorbed by the sample. The absorbance spectrum of a sample is calculated from the following equation:

$$A = \log(I_0/I) \quad (1.5)$$