

Fourier Transform Infrared Spectrometry

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PREFACE

The past decade has witnessed a virtual revolution in the way that chemists perceive infrared spectrometry. In the early 1970s, infrared spectrometry was commonly believed to be a dying instrumental technique, being superseded by NMR and mass spectrometry for structural determinations and by gas and liquid chromatography for quantitative analysis. Now, in the mid-1980s, the situation has changed dramatically; indeed, several surveys have found infrared spectrometry to be either the first or second most rapidly growing instrumental technique. This change is largely a result of the rapid commercial development of Fourier transform-infrared (FT-IR) spectrometry.

The development of FT-IR spectrometers began with the invention of the two-beam interferometer by Michelson almost a century ago. Shortly after the conception of the Michelson interferometer, both Michelson and Lord Rayleigh recognized that it was theoretically possible to obtain spectra from the interference pattern generated by the interferometer (now called the *interferogram*) through the computation of its Fourier transform. Michelson even built an ingenious analog computer by which an interferogram could be constructed from a given input spectrum. By comparing calculated and measured interferograms, the spectra of line sources could be deduced. At the turn of the century, however, the only reason for measuring spectra using a Michelson interferometer was its capability to resolve the fine structure of atomic lines. Interferometers were not used for the measurement of infrared spectra for another 50 years.

Around 1950, two key discoveries were made. The first was the recognition by Fellgett that information from all spectral elements is measured simultaneously with an interferometer. This *multiplex* (or Fellgett's) advantage is the fundamental theoretical advantage, not only of FT-IR spectrometers, but also of Fourier transform nuclear magnetic resonance and mass spectrometers. A short time after Fellgett's discovery, Jacquinot derived the fact that the maximum allowed solid angle of the "collimated" beam passing through an interferometer is greater than the solid angle of a beam of the same cross-sectional area at the prism or grating of a monochromator measuring at the same resolution. The Fellgett and Jacquinot advantages combine to form the fundamental basis for the improved performance of FT-IR spectrometers over monochromators.

The next step in the slow acceptance of Fourier spectrometry by the chemical community was the discovery (or more accurately rediscovery) of the fast Fourier transform (FFT) algorithm by Cooley and Tukey in 1964. Instead of requiring minutes or even hours to compute a spectrum from an interferogram using the conventional Fourier transform, the FFT permitted low-resolution spectra to be computed in a matter of seconds. Even then, the need to record interferograms on paper tapes or punched cards, transport them to the computer center, and wait until they were processed (often a matter of days rather than hours) still rendered FT-IR spectrometry unattractive to most analytical chemists.

By the late 1960s, however, two technological developments were made that, when applied to the field of FT-IR spectrometry, finally allowed the skepticism of the chemical community to be overcome. These breakthroughs were the fabrication of minicomputers and small gas lasers. The minicomputer allowed spectra to be computed in the laboratory directly after measurement of the interferogram. Helium-neon lasers are used to monitor the travel of the moving mirror of the interferometer, permitting interferograms to be digitized at precisely equal intervals and giving, in effect, an internal wavenumber standard for all measurements.

By 1975, FT-IR spectrometry had become the accepted technique for measuring high-quality infrared spectra. Nevertheless, the cost of the instruments was still sufficiently high that many more grating spectrophotometers were being sold than FT-IR spectrometers. The development of the microcomputer, together with relatively inexpensive peripheral mass memory devices, terminals, and displays, rapidly altered this picture. Several vendors are now able to sell high-quality FT-IR spectrometers for less than \$50,000. Indeed, it is possible to purchase certain low-resolution instruments for less than \$25,000. At the time of this writing, there are 10 companies in North America (Analect, Beckman, Bomen, Digilab, IBM Instruments, Janos Technology, Mattson, Midac, Nicolet, and Perkin-Elmer) that make FT-IR spectrometers suitable for use by chemists. Other companies in Japan and Europe also manufacture similar instruments. By contrast, only one company in North America (Perkin-Elmer) still makes a grating spectrophotometer. These data are certainly indicative of the revolution that has taken place over the past decade.

In 1974, right at the start of this revolution, one of us (P. R. G.) wrote a book entitled *Chemical Infrared Fourier Transform Spectroscopy*. The present book started its existence 8 years later as the second edition of the earlier volume. By the time we had added 11 chapters and extensively revised most of the other 8, it was obvious that the manuscript represented a new text. A few parts of the original book remain; in particular, much of the theory of the two-beam interferometer described in Chapter 1 is

unchanged. In this respect, we crave the reader's indulgence when encountering any reiterated material.

In this book, we attempt to introduce the theory, instrumentation, and applications of FT-IR spectrometry in a way that can be understood and appreciated by chemists at the bachelor's or doctoral level. In introducing the theory of FT-IR spectrometry, we have steered clear of detailed mathematics whenever it seemed appropriate. Occasionally, we have opted for a simple derivation to yield an approximate answer when a more rigorous, but perhaps less comprehensible, approach is needed to give the exact solution. Our goal has been to lay a sufficient foundation to allow actual and potential users of FT-IR spectrometers to plan their experimental procedure correctly.

In an attempt to guard against obsolescence, we have not discussed all commercial spectrometers available in 1985 in detail. Rather we have described selected designs using several of the contemporary instruments as examples. If the number of spectrometers introduced in the past two years is representative, we can expect one or two novel designs to be incorporated in new instruments by the end of 1986. These designs are not, of course, described in this book. Nevertheless, we believe that readers will be able to gain an adequate background to understand the benefits and drawbacks of both the present and future spectrometer designs.

In our coverage of applications of FT-IR spectrometry, we have deliberately not included a detailed bibliography of all papers published on each topic. Several thousand papers and reports have been published over the past 20 years for which FT-IR spectrometry has played a significant role. To describe all this work would, we believe, confuse and overwhelm the reader. Instead, we have selected a few reports of measurements where Fourier spectrometry has been applied in a particularly novel or beneficial manner and have described this work in some detail. Because of this philosophy, it should therefore be recognized that many superb papers have not been referenced in this book. Readers are strongly advised to perform a literature search for each topic of particular interest to them.

Fourier transform infrared spectrometry is a dynamic instrumental technique that can be applied to an enormous variety of samples. We hope that readers of this book will have as much pleasure in working with FT-IR spectrometry as we have.

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CHAPTER

I

THE MICHELSON INTERFEROMETER

I. INTRODUCTION

The design of most interferometers used for infrared spectrometry today is based on that of the two-beam interferometer originally designed by Michelson in 1891 [1,2]. Many other two-beam interferometers have subsequently been designed that may be more useful for certain specific applications than the Michelson interferometer. Nevertheless, the theory behind all scanning two-beam interferometers is similar, and the general theory of interferometry is most readily understood by first acquiring an understanding of the way in which a simple Michelson interferometer can be used for the measurement of infrared spectra.

The Michelson interferometer is a device that can divide a beam of radiation into two paths and then recombine the two beams after a path difference has been introduced. A condition is thereby created under which *interference* between the beams can occur. The intensity variations of the beam emerging from the interferometer can be measured as a function of path difference by a detector. The simplest form of the Michelson interferometer is shown in Fig. 1.1. It consists of two mutually perpendicular plane mirrors, one of which can move along an axis that is perpendicular to its plane. The movable mirror is either moved at a constant velocity or is held at equally spaced points for fixed short time periods and rapidly stepped between these points. Between the fixed mirror and the movable mirror is a *beamsplitter*, where a beam of radiation from an external source can be partially reflected to the fixed mirror (at point *F*) and partially transmitted to the movable mirror (at point *M*). After the beams return to the beamsplitter, they interfere and are again partially reflected and partially transmitted. Because of the effect of interference, the intensity of each beam passing to the detector and returning to the source depends on the difference in path of the beams in the two arms of the interferometer. The variation in the intensity of the beams passing to the detector and returning to the source as a function of the path difference ultimately yields the spectral information in a Fourier transform spectrometer.

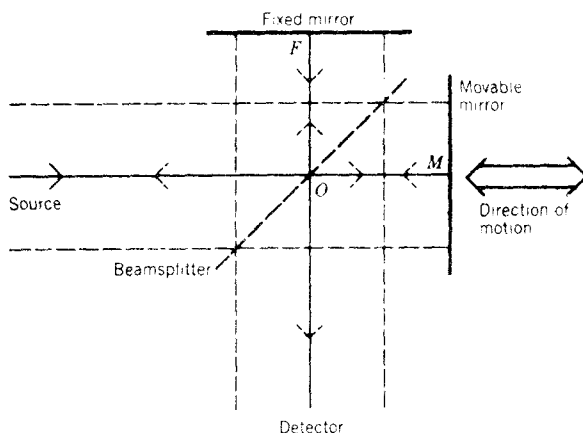


Fig. 1.1. Schematic representation of a Michelson interferometer. The median ray is shown by the solid line, and the extremes of the collimated beam are shown by the broken lines.

The beam that returns to the source is rarely of interest for spectrometry, and usually only the output beam traveling in the direction perpendicular to that of the input beam is measured. Nevertheless, it is important to remember that both of the output beams contain equivalent information. The main reason for measuring only one of the output beams is the difficulty of separating the output beam returning to the source from the input beam. In some measurements, both output beams are measured using two detectors or by focusing both beams onto the same detector. In other measurements, separate input beams can be passed into each arm of the interferometer and the resultant signal measured using one or two detectors. These measurements are generally classified under the heading of dual-beam interferometry and are described in Chapter 8.

II. MONOCHROMATIC LIGHT SOURCES

To understand the processes occurring in a Michelson interferometer better, let us first consider an idealized situation where a source of monochromatic radiation produces an infinitely narrow, perfectly collimated beam. Let the wavelength of the radiation be λ (in centimeters) and its wavenumber be $\bar{\nu}$ (reciprocal centimeters)

$$\bar{\nu} = \frac{1}{\lambda} \quad (1.1)$$

For this example, we will assume that the beamsplitter is a nonabsorbing film whose reflectance and transmittance are both exactly 50%. We first determine the intensity of the beam at the detector when the movable mirror is held stationary at different positions.

The path difference between the beams traveling to the fixed and movable mirrors is $2(OM - OF)$, see Fig. 1.1. This optical path difference is called the *retardation*, and is usually given the symbol δ . Since δ is the same for all parallel input beams, such as the two broken lines shown in Fig. 1.1, we can relax our criterion for an infinitely narrow input beam, but ideally it should still remain collimated. The effect of having an uncollimated beam is discussed in Section VII of this chapter.

When the fixed and movable mirrors are equidistant from the beamsplitter (zero retardation), the two beams are perfectly in phase on recombination at the beamsplitter (Fig. 1.2a). At this point, the beams interfere *constructively*, and the intensity of the beam passing to the detector is the sum of the intensities of the beams passing to the fixed and movable mirrors. Therefore, all the light from the source reaches the detector at this point and none returns to the source.

If the movable mirror is displaced a distance $\frac{1}{2}\lambda$, the retardation is now $\frac{1}{2}\lambda$. The pathlengths to and from the fixed and movable mirrors are therefore exactly one-half wavelength different. On recombination at the beamsplitter, the beams are out of phase and interfere *destructively* (Fig. 1.2b). At this point, all the light returns to the source and none passes to the detector. A further displacement of the movable mirror by $\frac{1}{2}\lambda$ makes the total retardation λ . The two beams are once more in phase on recombination at the beamsplitter, and a condition of constructive interference again occurs, (Fig. 1.2c). For monochromatic radiation, there is no way to determine whether a particular point at which a signal maximum is measured corresponds to zero retardation or a retardation equal to an integral number of wavelengths.

If the mirror is moved at constant velocity, the signal at the detector will be seen to vary sinusoidally, a maximum being registered each time that the retardation is an integral multiple of λ . The intensity of the beam at the detector measured as a function of retardation is given the symbol $I'(\delta)$. The intensity at any point where $\delta = n\lambda$ (where n is an integer) is equal to the intensity of the source $I(\bar{\nu})$. At other values of δ , the intensity of the beam at the detector, or interference record, is given by

$$I'(\delta) = 0.5I(\bar{\nu}) \left\{ 1 + \cos 2\pi \frac{\delta}{\lambda} \right\} \quad (1.2)$$

$$= 0.5I(\bar{\nu}) \{ 1 + \cos 2\pi \bar{\nu} \delta \} \quad (1.3)$$

THE MICHELSON INTERFEROMETER

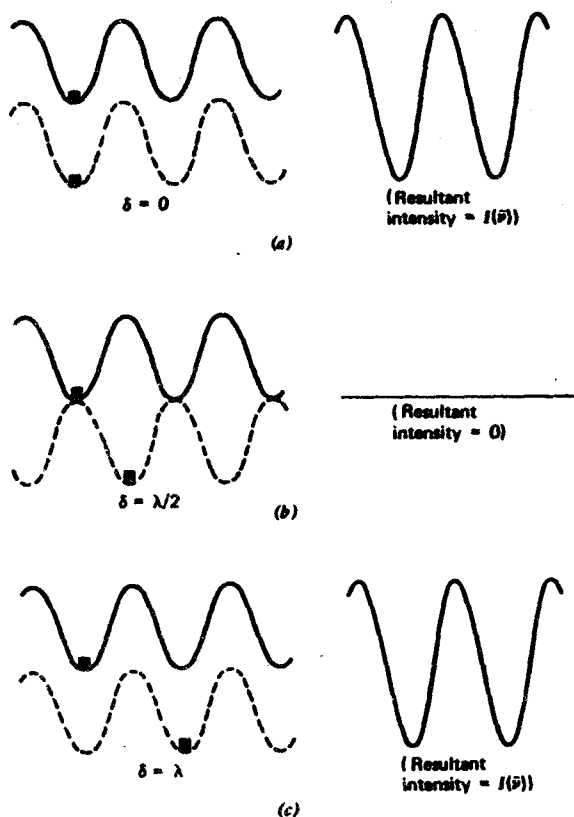


Fig. 1.2. Schematic representation of the phase of the electromagnetic waves from the fixed mirror (solid line) and movable mirror (broken line) at different values of the optical retardation. (a) Zero path difference; (b) path difference of one-half wavelength; (c) path difference of one wavelength. Note that constructive interference occurs for both (a) and (c) and all other retardations of integral numbers of wavelengths.

It can be seen that $I'(\delta)$ is composed of a constant (dc) component equal to $0.5I(\bar{\nu})$, and a modulated (ac) component equal to $0.5I(\bar{\nu}) \cos 2\pi\bar{\nu}\delta$. Only the ac component is important in spectrometric measurements, and it is this modulated component that is generally referred to as the *interferogram*, $I(\delta)$. The interferogram from a monochromatic source measured with an ideal interferometer is given by the equation

$$I(\delta) = 0.5I(\bar{\nu}) \cos 2\pi\bar{\nu}\delta \quad (1.4)$$