Introductory Fourier Transform Spectroscopy

ROBERT JOHN BELL

Introductory Fourier Transform Spectroscopy

ROBERT JOHN BELL

Department of Physics, University of Missouri-Rolla
Rolla, Missouri

ACADEMIC PRESS
New York San Francisco London 1972
A Subsidiary of Harcourt Brace Jovanovich, Publishers

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 70-182606

PRINTED IN THE UNITED STATES OF AMERICA

Preface

THIS BOOK introduces the subject of Fourier transform spectroscopy from a level that requires a knowledge of *only* introductory optics and mathematics and proceeds to the development of optical theory and equations to the extent required by the advanced student or researcher. Material is included for the physicist, chemist, astronomer, and others who are interested in spectroscopy.

The subject is approached through optical principles, not abstract mathematics. Information theory, Fourier analysis, and mathematical theorems, a very cursory knowledge of which is sufficient, are presented only to complete derivations or to give alternate views of an individual subject.

In some chapters the subject matter is approached in two ways. The first approach is through simple optics and physical intuition. The second, through a knowledge of Fourier analysis and the concepts of convolution and autocorrelation. This dual treatment bridges the gap between the introductory material in the book and the advanced material in the journals.

There is no longer any question about the wide applicability of Fourier transform spectroscopy. For the visible wavenumber range, the requirements of Fourier transform spectroscopy have been met by several laboratories, and at this writing, at least one company markets equipment which spans the spectral region from the visible to the millimeter wavelengths. This span has applications in many fields of study, and because of this, the readers' interests most certainly will be diverse. Thus, a genuine understanding of the techniques can be obtained only through the most basic assumptions.

To aid in the reader's quest for reference material, almost every chapter has a set of pivotal references appended. Bibliographies and indexes, one indexed by author and the other by subject, appear at the end of the book.

If the reader wishes an in-depth treatment of Fourier analysis, Bracewell's book, "The Fourier Transform and Its Application," is recommended. For studies of interferometers, Steel's book, "Interferometry," should be consulted. For Fourier analysis in optics, Mertz's book, "Transformations in

Optics," is an excellent reference. To obtain information about the Cooley-Tukey algorithm, the *IEEE Transactions on Audio and Electroacoustics*, **15** (2), 76, 1967) should be consulted. For the latest developments, the papers that were presented at the Aspen International Conference on Fourier Spectroscopy, 1970 (G. A. Vanasse, A. T. Stair, Jr., and D. J. Baker, eds., AFCRL-71-0019, 5 Jan. 1971, Spec. Rep. No. 114, L. G. Hanscom Field, Bedford, Massachusetts, 1971) should be read. For the physics and chemistry of the far infrared, the book "Far-Infrared Spectroscopy" by K. D. Möller and W. G. Rothschild is recommended.

The author hopes that this book will help students reach a level at which they can undertake advanced research programs in spectroscopy. He has tried to cover most of the major subjects that are needed for such development. However, such subjects as internal modulation, chirping, and other specialized problems not normally encountered have been excluded. The references given at the end of the book should help the reader with such subjects.

Acknowledgments

I AM indebted to Dr. Ralph W. Alexander for his many contributions to and proof reading of the manuscript. Dr. Harold V. Romero has also given aid. There are many who have helped me in the preparation of the manuscript: Dr. Robert McFarland, Dr. Harold Q. Fuller, Dr. John D. Strong, Dr. Ely E. Bell, Dr. Ludwig Genzel, Dr. Ernest V. Loewenstein, Dr. R. Sanderson, Mr. Ken Mustain, Dr. W. Anderson, Mr. G. Kovenor, Mr. A. Purdes, Mr. J. Blea, Dr. T. J. McMahon, Dr. William F. Parks, Mr. John Koenig, Dr. John Bastin, Mr. C. E. Bryson III, Mr. C. Irslinger, Dr. Doran Baker, and many others. I wish also to thank Mrs. Carol Roman, Mrs. Lois Vastano, Miss Mary Meachum, and Miss Lois Watson for typing the manuscript. The staff of Academic Press has made writing this book somewhat tolerable through patience and professional expertise. The University of Missouri-Rolla and the Max-Planck-Institut für Festkörperforschung provided the proper, invigorating environments. Sarah and Rob bore well their father-imposed, involuntary sacrifices. My wife, Carolyn, did the most for me in this effort, and the results are on the following pages.

Contents

CHAPTER THREE

Fourier Analysis and Interferometry

CHAPTER FOUR

Sample Calculations of Spectra from Interferograms

CHAPTER FIVE

Apodization—Mathematical Filtering

CHAPTER SIX

Resolution

CHAPTER THIRTEEN

Procedures for Choosing Experimental Parameters

CHAPTER FOURTEEN

Sample Interferograms and Spectra

CHAPTER FIFTEEN

Lamellar Grating Interferometers

CHAPTER SIXTEEN

Computation Techniques

CHAPTER SEVENTEEN

The Cooley–Tukey Algorithm

Ralph W. Alexander and Robert J. Bell

CHAPTER EIGHTEEN

Minicomputers and Real-Time Fourier Analysis

Ralph W. Alexander

CHAPTER NINETEEN

Commercial Instruments

APPENDIX A

Optical Alignment of a Michelson Interferometer

APPENDIX B

Computer Programs

Ralph W. Alexander and Harold V. Romero

APPENDIX C

Mirror Tilt, the Cat's-Eye Retroreflector

CHAPTER ONE

Fourier Transform Spectroscopy

INTRODUCTION

The subject of Fourier transform spectroscopy (FTS) is best introduced by discussing the merits and applications of Fourier transform spectrometers in terms of (1) general advantages over conventional instruments, (2) specific advantages and disadvantages, (3) the resolving power of two-beam interferometers, (4) quality factors, (5) spectral ranges, and (6) utilization in science and industry.

Some mention also needs to be made of the basic similarity of lamellar gratings and Michelson interferometers, the methods of judging interferometers, and the extension of spectral studies into the infrared and far-infrared regions through the the development of interferometry or Fourier transform spectroscopy.

A short article by P. Connes [1] that describes Fourier transform spectroscopy is recommended as supplementary reading. Dr. Pierre Connes and his wife, Dr. Janine Connes, are pioneers in the fields of infrared astronomy and interferometry.

GENERAL ADVANTAGES OF FOURIER TRANSFORM SPECTROMETERS

Basically, the advantages of Fourier transform spectrometers arise from two major concepts known as the Fellgett and Jacquinot advantages. These are discussed in more detail in the following chapter, but they are mentioned here because their physical aspects are easily understood if the reader has a cursory knowledge of spectroscopy

An interferometer receives information from the entire range of a given spectrum during each time element of a scan, whereas a conventional grating spectrometer receives information from only the very narrow region which lies within the exit slit of the instrument. Thus, the interferometer receives information about the entire spectral range during an *entire* scan, while the grating instrument receives information only in a narrow band at a given time. This is a statement of the Fellgett or multiplex advantage.

The interferometer can have a large circular source at the input or entrance aperture of the instrument with no strong limitation on the resolution. Also, it can be operated with small *f*/numbers or with large solid angles at the source and detector. However, the resolution of a conventional grating-type spectrometer depends linearly on the instrument's slit width, and the detected power depends on the square of the area of equal slits. A grating-type spectrometer requires long and narrow slits which never can have the same area for the same resolving power as the interferometer. Also, for high resolution, a spectrometer requires large radii for the collimation mirrors, and this condition in turn necessitates large *f*/numbers or small solid angles. Quantitatively, the ability of interferometers to collect large amounts of energy at high resolution was expressed by Jacquinot as a throughput or *étendue* advantage of interferometers over spectrometers.

SPECIFIC ADVANTAGES AND DISADVANTAGES OF INTERFEROMETERS

Several additional advantages follow from the Fellgett and Jacquinot advantages and can be listed as follows:

1. Very large resolving power.
2. High wavenumber accuracy.
3. Vastly reduced stray or unwanted flux problems.
4. Fast scanning time, which increases the probability of successfully completing an experiment.
5. Large wavenumber range per scan.
6. Possibility of making weak-signal measurements at millimeter wavelengths.
7. Use of small images in sample compartments without requiring special measures.
8. Measurement in amplitude spectroscopy of complex reflection or transmission coefficients.

9. Low cost of basic optical equipment.
10. Smaller size and lower weight of interferometers than spectrometers.

The few disadvantages of interferometers are that they do require access to computer facilities, and computer costs do have to be considered as factors in their operation. They are also somewhat deficient because absolute magnitudes of flux are sometimes in error by a few per cent, and the interferograms (recorded signals versus interferometer arm displacement) sometimes cannot be visually interpreted, which makes it difficult for an operator to judge quickly whether or not an experiment is satisfactory.

The large resolving power of an interferometer is a result of the Fellgett and Jacquinot advantages and depends linearly on the relative arm displacement of the instrument's movable mirror. Relative mirror displacements of the order of 2 m can be attained with some interferometers. This displacement ability has made it possible to observe weak lines with resolving powers of the order of 10^5 or higher.

The high wavenumber accuracy and the problem of reduced stray light both result from the interference phenomena inherent in the instrument. Accurate movement of an interferometer's movable mirror carriage produces a precise change in the interference pattern which can be capitalized on with excellent wavenumber accuracy in the computed spectrum. Because the unwanted waves which reach the instrument's detector have a definite wavelength, they produce distinct interference patterns which, when transformed into spectra, are identifiable. It is not uncommon to obtain transmittance measurements which are reliable to as low as 0.3%.

Fast scan times (sometimes less than 1 sec), a large wavenumber range (sometimes as large as a decade from the minimum to maximum wave number), and a measurement capability in millimeter wavelengths even when the source is very weak are all gained through the Fellgett and Jacquinot advantages. The ability to use small images at the sample is also derived from the multiplex and *étendue* advantages.

Complex reflection or transmission coefficients can be measured directly in amplitude spectroscopy by placing the sample in one arm of the interferometer. The amplitude and phase angles of the complex reflection or transmission coefficients can be obtained without any special data manipulation, such as is required in a Kramers–Kronig analysis. Thus, complex indices of refraction can be noted experimentally. Also, it is possible to make accurate flux calculations even when the transmitted (reflected) flux is as low as 0.01%. Effects of different boundaries in a sample can also be separated.

Partly because interferometers are relatively simple instruments, their space requirement and weight are small. For example, the U.S. Nimbus III satellite carried a Michelson interferometer which weighed, with its power supply, 14.5 kg and required only 1 or 2 ft^3 of space. This instrument operated for several months in orbit around the earth and took 1% accurate radiometric data between 400 and 2000 cm^{-1}. In the Viking Project, one of the basic instruments in the probe will be an interferometer which will scan the surface of Mars. The optical systems of interferometers are frequently less expensive than those of spectrometers; however, the cost of high-speed data handling systems that are needed for the operation of interferometers can nullify these savings.

The disadvantages of interferometers are few, and these are rapidly being minimized. For instance, when transmittance or reflectance measurements are made, the results can be in error up to 5% of the absolute value. Fluctuations in the interferogram, or recorded signal versus the instrument's arm displacement, can produce this amount or error. If the error is random, repetition of the experiment can reduce the deviation. With some of the commercial instruments, which have scan times of less than 1 sec and computer controls, hundreds of repeated experiments can be performed in minutes and computer-averaged in the laboratory.

Often, a spectrum can be so complicated that the experimenter cannot immediately learn much from the interferogram. This problem can be solved with one of two methods. The low-cost method is through the experimenter's experience and in his knowing a few of the interferogram's signatures or tell-tale features which presage the particular spectral features sought. He can then apply Fourier analysis to a few simple cases, such as a Gaussian spectrum, and can make sliderule estimates of the experimental progress. The more expensive but more satisfying technique is to use real-time analyses or rapid computer calculations. If the experimenter has a minicomputer in his laboratory with a memory of 4000 or more words, he can compute the spectrum over the entire wavenumber range while the data are being recorded. In fact, as the interferometer's mirror carriage moves to larger displacements, he can observe the increase in resolving power, or if the experiment is especially long, he can watch the desired spectral features develop. If it is short, he can obtain the results of the entire scan almost instantly. In addition to the real-time analyses, he can wait until the end of the experiment and make on-line computer calculations of the spectrum in a very short time of seconds or minutes.

Large computers are used by most experimenters to transform the interferograms into spectra if the data points exceed 1024. If on-line computer time-sharing is available with suitable graphic and tabular data return, there is no problem, but if the data have to be recorded on paper tapes and converted to cards, there is usually a delay of one or two days. The computation time can be shortened considerably if the Cooley–Tukey algorithm is used. This