

**PHYSICAL
METHODS**

**OF
CHEMISTRY**

**Second
Edition**

Volume IIIA

**DETERMINATION OF
CHEMICAL COMPOSITION
AND MOLECULAR
STRUCTURE—PART A**

Editors:

**BRYANT W. ROSSITER
JOHN F. HAMILTON**

PHYSICAL METHODS OF CHEMISTRY

Second Edition

Edited by

BRYANT W. ROSSITER

*ICN Pharmaceuticals, Inc.
Costa Mesa, California*

and

JOHN F. HAMILTON

*Research Laboratories
Eastman Kodak Company
Rochester, New York*

Volume IIIA

DETERMINATION OF CHEMICAL
COMPOSITION AND
MOLECULAR STRUCTURE—PART A

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**Editors: Bryant W. Rossiter
John F. Hamilton**

**Volume I COMPONENTS OF SCIENTIFIC INSTRUMENTS AND
APPLICATIONS OF COMPUTERS TO CHEMICAL
RESEARCH**

Volume II ELECTROCHEMICAL METHODS

**Volume IIIA DETERMINATION OF CHEMICAL COMPOSITION AND
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Volume IV MICROSCOPY

**Volume V DETERMINATION OF STRUCTURAL FEATURES OF
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Volume VI DETERMINATION OF THERMODYNAMIC PROPERTIES

**Volume VII DETERMINATION OF ELASTIC AND MECHANICAL
PROPERTIES**

**Volume VIII DETERMINATION OF ELECTRONIC AND OPTICAL
PROPERTIES**

**Volume IXA INVESTIGATIONS OF SURFACES AND INTERFACES—
PART A**

**Volume IXB INVESTIGATIONS OF SURFACES AND INTERFACES—
PART B**

CONTRIBUTORS

L. S. BIRKS, Bethesda, Maryland

GREGORY R. CHOPPIN, Department of Chemistry, Florida State University, Tallahassee, Florida

JAMES R. DURIG, College of Science and Mathematics, University of South Carolina, Columbia, South Carolina

MICHAEL S. EPSTEIN, National Bureau of Standards, Washington, DC

JOHN V. GILFRICH, Bethesda, Maryland

VINCENT P. GUINN, Department of Chemistry, University of California, Irvine, California

MARLIN D. HARMONY, Department of Chemistry, The University of Kansas, Lawrence, Kansas

ALICE M. MURRAY, Department of Chemistry, University of Texas at Dallas, Richardson, Texas

JOHN ROBOZ, Department of Neoplastic Diseases, Mount Sinai School of Medicine, New York, New York

JAN RYDBERG, Nuclear Chemistry Department, Chalmers Tekniska Hogskola Fack, Gothenburg, Sweden

JOANN F. SULLIVAN, College of Science and Mathematics, University of South Carolina, Columbia, South Carolina

JAMES D. WINEFORDNER, Analytical Division, Department of Chemistry, University of Florida, Gainesville, Florida

PREFACE TO PHYSICAL METHODS OF CHEMISTRY

This is a continuation of a series of books started by Dr. Arnold Weissberger in 1945 entitled *Physical Methods of Organic Chemistry*. These books were part of a broader series, *Techniques of Organic Chemistry*, and were designated Volume I of that series. In 1970, *Techniques of Chemistry* became the successor to and the continuation of the *Techniques of Organic Chemistry* series and its companion, *Techniques of Inorganic Chemistry*, reflecting the fact that many of the methods are employed in all branches of chemical sciences and the division into organic and inorganic chemistry had become increasingly artificial. Accordingly, the fourth edition of the series, entitled *Physical Methods of Organic Chemistry*, became *Physical Methods of Chemistry*, Volume I in the new *Techniques* series. The last edition of *Physical Methods of Chemistry* has had wide acceptance, and it is found in most major technical libraries throughout the world. This new edition of *Physical Methods of Chemistry* will consist of eight or more volumes and is being published as a self-standing series to reflect its growing importance to chemists worldwide. This series will be designated as the second edition (the first edition, Weissberger and Rossiter, 1970) and will no longer be subsumed within *Techniques of Chemistry*.

This edition heralds profound changes in both the perception and practice of chemistry. The discernible distinctions between chemistry and other related disciplines have continued to shift and blur. Thus, for example, we see changes in response to the needs for chemical understanding in the life sciences. On the other hand, there are areas in which a decade or so ago only a handful of physicists struggled to gain a modicum of understanding but which now are standard tools of chemical research. The advice of many respected colleagues has been invaluable in adjusting the contents of the series to accommodate such changes.

Another significant change is attributable to the explosive rise of computers, integrated electronics, and other "smart" instrumentation. The result is the widespread commercial automation of many chemical methods previously learned with care and practiced laboriously. Faced with this situation, the task of a scientist writing about an experimental method is not straightforward.

Those contributing to *Physical Methods of Chemistry* were urged to adopt as their principal audience intelligent scientists, technically trained but perhaps inexperienced in the topic to be discussed. Such readers would like an introduction to the field together with sufficient information to give a clear

understanding of the basic theory and apparatus involved and the appreciation for the value, potential, and limitations of the respective technique.

Frequently, this information is best conveyed by examples of application, and many appear in the series. Except for illustration, however, no attempt is made to offer comprehensive results. Authors have been encouraged to provide ample bibliographies for those who need a more extensive catalog of *applications*, as well as for those whose goal is to become more expert in a *method*. This philosophy has also governed the balance of subjects treated with emphasis on the *method*, not on the results.

Given the space limitations of a series such as this, these guidelines have inevitably resulted in some variance of the detail with which the individual techniques are treated. Indeed, it should be so, depending on the maturity of a technique, its possible variants, the degree to which it has been automated, the complexity of the interpretation, and other such considerations. The contributors, themselves expert in their fields, have exercised their judgment in this regard.

Certain basic principles and techniques have obvious commonality to many specialties. To avoid undue repetition, these have been collected in Volume I. They are useful on their own and will serve as reference material for other chapters.

We are deeply sorrowed by the death of our friend and associate, Dr. Arnold Weissberger, whose enduring support and rich inspiration motivated this worthy endeavor through four decades and several editions of publication.

BRYANT W. ROSSITER
JOHN F. HAMILTON

*Research Laboratories
Eastman Kodak Company
Rochester, New York
March 1986*

PREFACE

This is the first of two volumes entitled *Determination of Chemical Composition and Molecular Structure*. Admittedly, this grouping of techniques is somewhat arbitrary and overlaps with a later volume entitled *Determination of Structural Features of Crystalline and Amorphous Solids*. Nonetheless, the ordering offers more consistent volumes for those interested in certain types of chemical determinations as opposed to the grouping of similar techniques used for a variety of measurements. This should make it easier for the reader to obtain from the library, or purchase at minimum cost, those parts of the treatise of greatest personal value.

Chapters have been written by world-class authors who are widely recognized in their fields. Authors have directed their writings to the competent, professional scientist who is interested in obtaining information provided by the technique, but who is perhaps not an expert in the use of the method. In each case, authors of chapters have supplied, either in the text or through liberal reference to monographs and other scientific literature, sufficient information for the investigator to apply the techniques successfully in the laboratory.

We acknowledge our deep gratitude to the contributors who have spent long hours over manuscripts. We greet previous contributors: Professor James R. Durig, Professor Vincent P. Guinn, and Professor John Roboz, and welcome several new contributors to Volume IIIA: Dr. Laverne S. Birks, Professor Gregory R. Choppin, Dr. Michael S. Epstein, Dr. John V. Gilfrich, Dr. Marlin D. Harmony, Dr. Alice M. Murray, Dr. Jan Rydberg, Dr. Joann F. Sullivan, and Dr. James D. Winefordner.

We are also extremely grateful to the many colleagues from whom we have sought counsel on the choice of subject matter and contributors. We express our gratitude to Mrs. Ann Nasella for her enthusiastic and skillful editorial assistance. In addition, we heartily thank the specialists whose critical readings of the manuscripts have frequently resulted in the improvements accrued from collective wisdom. For Volume IIIA they are Dr. D. Ekimoff, Dr. N. S. Ferris, Mr. R. S. Gohlke, Mrs. A. Kocher, Dr. P. D. LaFleur, Professor J. S. Muentert, and Dr. D. L. Smith.

BRYANT W. ROSSITER
JOHN F. HAMILTON

Costa Mesa, California
Rochester, New York
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Chapter 1

INFRARED AND RAMAN SPECTROSCOPY

James R. Durig and Joann F. Sullivan

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1 INTRODUCTION

Vibrational spectroscopy is one of the most widely used techniques for relatively rapid qualitative analysis and molecular structure determinations in organic chemistry, and it has become increasingly more important to both inorganic and organometallic chemists. This has resulted because molecular functional groups have characteristic *group frequencies* that can be used for identification purposes. The fact that these group frequencies are not really constant but have a slight dependence on the *adjacent* chemical substituents makes them even more valuable. For example, the organic chemist easily distinguishes among aldehydes, ketones, acids, and esters from the relative frequency of the carbonyl group frequency. Of the experimental methods used to determine the frequency of molecular vibrations, infrared absorption and Raman scattering, the infrared technique has been predominant since relative advances in instrumentation after World War II made it possible to manufacture inexpensively small infrared instruments. However, since the 1970s tremendous strides have been made with Raman spectroscopy, mainly because of the routine use of lasers as excitation sources. Indeed, the availability of a range of excitation frequencies from both pulsed and continuous wave lasers has resulted in the development and application of numerous new techniques using both the linear and nonlinear aspects of the Raman effect. Infrared spectroscopy has also emerged as one of the principal techniques for the applied chemist who carries out a variety of sophisticated investigations, primarily because of the advances made with computerized instrumentation and Fourier transform infrared spectrometers. In this light, and because of the complementary nature of infrared and Raman spectroscopy, an in-depth review of the advances in both areas with regard to instrumentation, applications, and techniques is appropriate.

The existence of infrared radiation was first recognized in 1800 by Sir William Herschel [1] who, with a glass prism and blackened thermometers, observed an increase in temperature in the region beyond the red end of the projected solar spectrum. Design of thermopiles by Nobili, construction of the first mid-infrared spectrometer upon the discovery of the transparency of sodium chloride to infrared radiation by Melloni, and progress in emission spectroscopy in the visible occurred from 1830 to 1870. In addition, the invention of the bolometer by Langley in 1878 enabled the design of infrared spectrometers with much higher resolution.

In the late 1800s, Michelson's expertise in optics culminated in the design of an instrument, termed an interferometer, in which the relative path differences of two interfering beams could be easily and precisely varied to produce an interference pattern [2, 3]. However, it was not until 1911 that the first true infrared interferogram was published by Rubens and Wood [4]. Although Ruben's interferometer differed slightly from the Michelson design, they suffered the same major problem, that is, the lack of computational resources with which to transform an interferogram into a spectrum.

In the meantime, dispersive spectroscopy had greatly advanced, as evidenced

by the publication in 1905 [5] of the infrared spectra of hundreds of compounds, both organic and inorganic, by W. W. Coblentz. The establishment of quantum physics and the development of molecular spectroscopy came about in the 1920s and 1930s, and commercial dispersive infrared spectrometers were produced in the early 1940s because of wartime needs. During this period the science of electronics was also advanced.

The first Fourier transform calculation by Fellgett [6] in 1949 marked a new era in the potential uses of interferometry. In the early 1950s J. D. Strong assembled a group of investigators, including H. A. Gebbie, E. V. Loewenstein, and G. Vanasse, who showed that the advantages of multiplexing and throughput claimed for interferometry by Fellgett [7] and Jacquinot and Dufour [8] could be realized. Although it was now possible to calculate the necessary Fourier transforms, the procedure was laborious and time-consuming. At this point, the investigations in multiplex spectroscopy diverged into the development of different interferometers. Gebbie, in conjunction with G. W. Chantry, J. E. Chamberlain, and J. E. Gibbs, turned to Michelson interferometers, while Strong and Vanasse developed the lamellar grating interferometer. At the onset of the 1960s, interest in interferometric spectroscopy was growing, and the decade brought many advances in the theory of interferometric measurements and its application to physical systems, as well as great strides in equipment and technology. Some of the researchers associated with this period who deserve recognition include P. Connes and J. Connes, for their astronomical spectra; E. E. Bell and R. Sanderson, for their work in asymmetric Fourier transform spectroscopy; J. M. Dowling and C. M. Randall, who studied atmospheric gases; and L. Mertz, who contributed greatly to the design of current instrumentation. However, the key developments of this period did not come from spectroscopists. The availability of inexpensive, powerful minicomputers and the publication of the Cooley-Tukey algorithm for fast Fourier transformation, which was a real breakthrough for mid-infrared Fourier transform spectroscopy, removed the last major drawbacks to interferometric spectroscopy. In the early 1970s it became possible to purchase commercial interferometric instruments, and the field has had exceptional growth as the price of interferometers has steadily decreased and the ability to manipulate the spectral data has continued to improve with increased computer capacity and decreasing costs.

The use of dispersive infrared spectrometers has gradually decreased since the early 1980s as interferometers have replaced them. However, by adding a small microcomputer to a dispersive instrument it is possible to provide the same data-handling capability of the interferometers. Nevertheless, it appears that interferometers will shortly become the instrumentation for both the medium- and low-price range, and it is possible that the commercial infrared dispersive instrumentation will disappear from the market over the next decade. Therefore when we review infrared instrumentation, the major emphasis is on interferometers rather than dispersive spectrophotometers.

The utilization of Raman spectroscopy for obtaining vibrational frequencies occurred relatively late compared to infrared spectroscopy. Whereas infrared

spectroscopy is either absorption or emission of radiation, Raman spectroscopy is a scattering phenomenon that changes the frequency of the incident light falling on a sample from ν_0 to another frequency, say ν_v . The frequency difference $\Delta\nu = \nu_0 - \nu_v$ may be either positive or negative, and its magnitude is called the *Raman frequency*. The name of this phenomenon is derived from the experimental discoverer, Sir C. V. Raman [9, 10], who in 1928 observed this effect during his studies on light scattering. Smekal [11] had also predicted this effect some five years earlier, and Landsberg and Mandelstam [12] reported the effect in quartz at about the same time as Raman's paper. However, Raman's study was more complete, and in 1930 he was awarded the Nobel Prize for his investigations. Reference [13] contains an account of the Raman effect.

In Raman's initial instrument sunlight was used as the source and his eyes as the detector. The instrumentation improved rather rapidly with the early developments centered mainly on better sources. Mercury lamps were used as Raman sources in the 1930s, and the development in 1952 by Welsh and co-workers [14] of the mercury Toronto arc served as the ultimate in this type of excitation. The big breakthrough in the search for more intense Raman sources was realized with the application of the continuous helium-neon gas laser in 1963 by Kogelnik and Porto [15]. The first photoelectronic Raman spectrometers appeared after World War II with the Cary Model 81 spectrometer providing high sensitivity and ease of operation. This particular instrument played a major role in the resurgence of the field of Raman spectroscopy in the late 1950s and early 1960s. The continual development of better phototubes as well as easier operation places Raman spectroscopy on par or, in some cases even ahead of, the infrared technique as an analytical tool for the chemist. Also, since the 1960s there have been tremendous advances in laser technology, and continual progress in this area has enabled researchers to conduct routine Raman experiments on virtually any material. An additional outcome of laser technology has been the development of numerous nonlinear Raman effects, although their present applications are relatively limited.

It is interesting to compare and contrast the relative advantages of current infrared interferometry to Raman spectroscopy for the study of molecular vibrations. Since most chemists are quite familiar with infrared spectroscopy, it is probably more useful to consider the advantages of Raman spectroscopy, in terms of sample handling, applications, and instrumentation, over infrared spectroscopy when it exists and then to point out the limitations (Table 1.1).

In terms of sample handling, Raman spectroscopy has the advantage over infrared except for the study of gases. In today's commercial Raman instruments only 2–25 μL of liquid samples are employed routinely, and they can be held in melting-point capillaries or in specially designed cells for multipassing the laser beam. Powders can also be contained in melting-point tubes or they can be lightly pressed into pellets. Also, the laser beam is relatively small and can be further focused onto a very small sample target, which makes it possible to obtain Raman spectra of microsamples without special devices. In addition, by utilizing special microscope sampling arrangements it is possible to obtain both

Table 1.1 Comparison of Infrared and Raman Spectroscopy^a

	<i>Raman</i>	<i>Infrared</i>
<i>Sample Handling</i>		
General applicability	95%	99%
Sample limitations	Color, fluorescence	Single crystals, metals, aqueous solutions
Ease of sample preparation	Very simple	Variable
1. Liquids	Very simple	Very simple
2. Powders	Very simple	More difficult
3. Single crystals	Very simple	More difficult
4. Polymers	Very simple	More difficult
5. Single fibers	Possible	Very difficult
6. Gases and vapors	Now possible	Simple
Cells	Very simple	More complex
Micro work	Good (nanogram range)	Good (~ 1 ng)
Trace work	Good	Good
High and low temperature	Moderately simple	Moderately simple
<i>Applications</i>		
Assignment work	Excellent	Very good
Fingerprinting	Excellent	Excellent
Best vibrations	Symmetric	Antisymmetric
Group frequencies	Excellent	Excellent
Aqueous solutions	Very good	Difficult
Single crystal studies	Excellent	Difficult
Low-frequency modes	Excellent	Difficult
Quantitative analysis	Difficult	Good
<i>Instrumentation</i>		
Relative complexity	Moderate	Simpler
Source	Laser	Blackbody
Detector	Photomultiplier tube, optical multichannel analyzers	Thermal
Resolution	Approx. 0.25 cm^{-1}	Approx. 0.10 cm^{-1}
Principal limitation	Energy	Energy
Wavenumber range	$10\text{--}4000\text{ cm}^{-1}$	$80\text{--}4000\text{ cm}^{-1}$ (two beam splitters)
Purge requirement	No	Yes
Photometry	SB emission	DB absorption

^aAdapted from H. J. Sloan, *Appl. Spectrosc.*, **25**, 430 (1971).

infrared and Raman spectra of nanogram specimens and identify inclusions in solids. The Raman spectra of solids can usually be obtained without special preparations such as Nujol mulls or KBr pellets, and the advantages of not having to use solvents or matrix techniques is, of course, quite obvious.

Because the vibrational frequencies from Raman spectroscopy are obtained in the visible region of the spectrum, it is possible to construct special Raman cells with Pyrex glass windows or light pipes. Simple and inexpensive cells can be constructed to study samples at both high and low temperatures. For example, low-temperature cells can be constructed where a brass block is used to hold the sample, and Pyrex glass windows can be used on the vacuum jacket. Thus spectra of samples held both at liquid nitrogen and liquid helium temperatures can be obtained routinely. Such spectra have proved to be invaluable in the analysis of ferroelectric materials as well as in the study of molecules with perhaps more than one conformer present in the fluid phases.

In summary, sampling to obtain Raman spectra is relatively simple compared to sampling to obtain infrared spectra, but it is not generally easy to obtain Raman spectra of vapors. To obtain Raman spectra of gases routinely one needs a specially constructed multipass accessory and a relatively high-powered laser with 6–8 W for the excitation source. With this power it is necessary to keep the mirrors and cells scrupulously clean to prevent “burning holes” in the multipass accessory mirrors or to prevent sample decomposition caused by local heating. In addition, Raman spectroscopy has some limitations because of sample fluorescence or sample decomposition. Methods have been developed to minimize these problems. For example, defocusing the laser or rotating the sample will decrease sample decomposition. Sample cooling will also help, and changing the excitation wavelength can frequently be beneficial. Fluorescence is often a problem with polymers, glasses, and biological samples. If the sample is a liquid, the fluorescence is usually caused by an impurity that can be removed by added purification; however, for solid samples, additional purification is usually not possible. For solids it is often possible to diminish the fluorescence by leaving the sample in the laser beam for a period of one, two, or more hours. Also, gentle heating in an oven will sometimes alleviate the problem. If these techniques fail, instrumental parameters such as excitation wavelength and spectral slit width may be optimized. Finally, since the Raman effect is essentially instantaneous (less than 10^{-12} s), whereas fluorescence requires a finite rise and decay time (about 10^{-8} s), the principle of time discrimination can be applied theoretically to any sample to eliminate fluorescence. Therefore Raman spectroscopy is applicable to only about 95% of chemical samples, whereas infrared spectroscopy can be utilized to obtain vibrational data for practically all samples.

In terms of applications, each technique has its own set of advantages. To perform vibrational assignments for most molecules, use of both the infrared and Raman spectra is preferred. However the Raman spectra are usually more valuable because they are usually quite simple compared to the corresponding infrared spectra. Raman activity depends on the change of the polarizability with the normal mode motion. Since the electrons can readily follow the molecular vibrations, there is little electrical anharmonicity associated with the normal vibrations, and consequently overtones and combination bands rarely appear in Raman spectra. This should be contrasted to the infrared spectra