TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OE CHEMISTRY

Edited by
ARNOLD WEISSBERGER
AND
BRYANT W. ROSSITER

PART III
Optical, Spectroscopic, and Radioactivity Methods

PART IIIB
*Spectroscopy and Spectrometry in the Infrared,
Visible, and Ultraviolet*

TECHNIQUES OF CHEMISTRY

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OF CHEMISTRY

INCORPORATING FOURTH COMPLETELY REVISED AND AUGMENTED
EDITION OF TECHNIQUE OF ORGANIC CHEMISTRY,
VOLUME I, PHYSICAL METHODS OF ORGANIC CHEMISTRY

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Research Laboratories
Eastman Kodak Company
Rochester, New York

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Visible, and Ultraviolet*

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PLAN FOR

PHYSICAL METHODS OF CHEMISTRY

PART I

Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research

PART II

Electrochemical Methods

PART III

Optical, Spectroscopic, and Radioactivity Methods

PART IV

Determination of Mass, Transport, and Electrical-Magnetic Properties

PART V

Determination of Thermodynamic and Surface Properties

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NEW BOOKS AND NEW EDITIONS OF BOOKS OF THE TECHNIQUE OF ORGANIC CHEMISTRY WILL NOW APPEAR IN TECHNIQUES OF CHEMISTRY. A LIST OF PRESENTLY PUBLISHED VOLUMES IS GIVEN BELOW.

TECHNIQUE OF ORGANIC CHEMISTRY
ARNOLD WEISSBERGER, *Editor*

Volume I: Physical Methods of Organic Chemistry
              Third Edition—in Four Parts

Volume II: Catalytic, Photochemical, and Electrolytic
              Reactions
              Second Edition

Volume III: Part I. Separation and Purification
              Part II. Laboratory Engineering
              Second Edition

Volume IV: Distillation
              Second Edition

Volume V: Adsorption and Chromatography

Volume VI: Micro and Semimicro Methods

Volume VII: Organic Solvents
              Second Edition

Volume VIII: Investigation of Rates and Mechanisms
              of Reactions
              Second Edition—in Two Parts

Volume IX: Chemical Applications of Spectroscopy
              Second Edition—in Two Parts

Volume X: Fundamentals of Chromatography

Volume XI: Elucidation of Structures by Physical and
              Chemical Methods
              In Two Parts

Volume XII: Thin-Layer Chromatography

Volume XIII: Gas Chromatography

Volume XIV: Energy Transfer and Organic Photochemistry

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can be easily recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

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Eastman Kodak Company
Rochester, New York

PREFACE

Physical Methods of Chemistry succeeds, and incorporates the material of, three editions of *Physical Methods of Organic Chemistry* (1945, 1949, and 1959). It has been broadened in scope to include physical methods important in the study of all varieties of chemical compounds. Accordingly, it is published as Volume I of the new Techniques of Chemistry series.

Some of the methods described in *Physical Methods of Chemistry* are relatively simple laboratory procedures, such as weighing, and the measurement of temperature or refractive index, and determination of melting and boiling points. Other techniques require very sophisticated apparatus and specialists to make the measurements and to interpret the data; x-ray diffraction, mass spectrometry, and nuclear magnetic resonance are examples of this class. Authors of chapters describing the first class of methods aim to provide all information that is necessary for the successful handling of the respective techniques. Alternatively, the aim of authors treating the more sophisticated methods is to provide the reader with a clear understanding of the basic theory and apparatus involved, together with an appreciation for the value, potential, and limitations of the respective techniques. Representative applications are included to illustrate these points, and liberal references to monographs and other scientific literature providing greater detail are given for readers who want to apply the techniques. Still other methods that are successfully used to solve chemical problems range between these examples in complexity and sophistication and are treated accordingly. All chapters are written by specialists. In many cases authors have acquired a profound knowledge of the respective methods by their own pioneering work in the use of these techniques.

In the earlier editions of *Physical Methods* an attempt was made to arrange the chapters in a logical sequence. In order to make the organization of the treatise lucid and helpful to the reader, a further step has been taken in the new edition—the treatise has been subdivided into technical families and parts:

Part I   Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research
Part II   Electrochemical Methods

This organization into technical families provides more consistent volumes and should make it easier for the reader to obtain from a library or purchase at minimum cost those parts of the treatise in which he is most interested.

The more systematic organization has caused additional labor for the editors and the publisher. We hope that it is worth the effort. We thank the many authors who made it possible by adhering closely to the agreed dates of delivery of their manuscripts and who promptly returned their proofs. To those authors who were meticulous in meeting deadlines we offer our apologies for delays caused by late arrival of other manuscripts, in some cases necessitating rewriting and additions.

The changes in subject matter from the Third Edition are too numerous to list in detail. We thank previous authors for their continuing cooperation and welcome new authors to the Series. New authors of Part IIIB are Dr. Robert T. Ambrose, Dr. Hermann Bücher, Dr. James R. Durig, Mr. Franc Grum, Mr. William C. Harris, Dr. William G. Herkstroeter, Dr. Hans Kuhn, Dr. Dietmar Möbius, and Dr. Gisela K. Oster.

We are grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of the manuscripts. These are, for Part IIIB, Dr. Gary L. Bottger, Dr. Albert V. Buettner, Dr. Karl Drexhage, Mrs. Ardelle Kocher, Mrs. Donna S. Roets, and Dr. William West.

The senior editor expresses his gratitude to Bryant W. Rossiter for joining him in the book and taking on the very heavy burden with exceptional devotion and ability.

September 1971
Research Laboratories   ARNOLD WEISSBERGER
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Rochester, New York

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INFRARED SPECTROSCOPY

Don H. Anderson and Norman B. Woodall

I ORIGIN OF INFRARED SPECTRA

Infrared spectra in the 2 to 50-μm region originate essentially in the vibrational motion of the atoms within molecules. Like all spectral processes, they are due to a transition from one energy state to another; one or more vibrational quanta may be absorbed from radiation, superimposed on which, in gases, there is often a change in the rotational state of the molecule.

A nonlinear molecule of n atoms has in all $3n$ degrees of freedom, 3 for each atom, of which 3 are associated with translational motion of the molecule as a whole and 3 with rotations of the molecule about the three principal axes. The remaining $3n - 6$ degrees of freedom are associated with vibrations of the atomic nuclei within the molecule. It behaves as if it could carry out $3n - 6$ independent modes of vibration, the *normal vibrations*, in each of which all of the atoms move in phase. Each of these modes is quantized and, if the change from one vibrational level to another in any mode causes a change in the position of the electrical center of the molecule, it can be excited by radiation of a frequency $\bar{\nu}$ given by the universal law $h\nu = E_2 - E_1$. The theory shows that if one quantum of vibrational energy of any normal mode is added to the molecule, the frequency of the radiation absorbed is nearly equal to the mechanical frequency of the vibration. This frequency is the greater, the smaller the mass of the vibrating particles and the greater the force restoring the nuclei to the equilibrium position about which they oscillate. The expression for the frequency of vibration of masses m_1 and m_2 vibrating about an equilibrium point with simple harmonic motion is

$$\bar{\nu} = \tfrac{1}{2}\pi\sqrt{\frac{k}{\mu}} \tag{1.1}$$

where k is the restoring force per unit displacement from the equilibrium point and μ the reduced mass, $m_1 m_2 / m_1 + m_2$.

Consider, for example, methyl chloride, for which various lines of evidence indicate a tetrahedral structure as shown in Fig. 1.1. It has $3 \times 5 - 6 = 9$ normal vibrations, approximately represented in the diagrams of Fig. 1.1. In the mode ν_1 the greatest amplitude of motion is in the hydrogen atoms which oscillate about their mean positions along the direction of the valence bonds. The frequency can conveniently be termed a C–H *bond frequency* or, since one phase of the motion involves the stretching of the bond against the valence forces, it may be called a *stretching frequency*. Mode ν_2 is also a C–H bond frequency, in which the phase of one H atom differs by 180° from that of the others. The C and Cl nuclei are represented as vibrating in the plane of the paper, but the same frequency would be
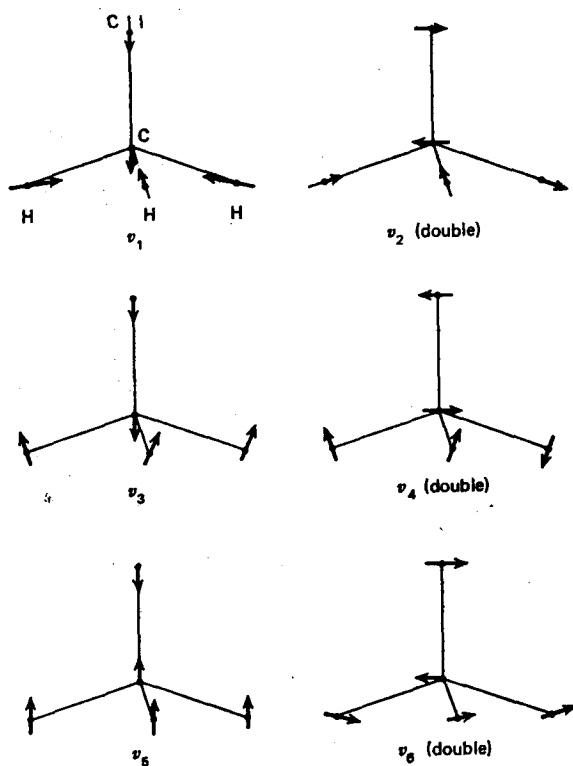
Fig. 1.1   Normal vibrations of CH_3Cl.

attached to a motion in which these atoms move at right angles to the plane of the paper. The actual motion of the nuclei is therefore the resultant of these equal frequencies and the frequency ν_2 is said to be *doubly degenerate*. It is to be counted twice in the enumeration of the normal frequencies. In ν_3 the greatest amplitude of motion is still in the hydrogen atoms, which move—all in the same phase—perpendicularly to the bond; this frequency may be termed a *bending frequency*. Mode ν_4 is the corresponding degenerate frequency. In ν_5 and ν_6 the motion is essentially a vibration of the methyl group with respect to the Cl nucleus; in ν_5 the direction of motion is along the C–Cl bond, while in the double frequency, ν_6, the motion is a rocking of the methyl group with respect to the Cl nucleus. The sum of the vibration forms is 9, of which 3, in this highly symmetrical molecule, are doubly degenerate,

so that only 6 separate bands corresponding to the fundamental normal vibrations will be observed.

In the nondegenerate vibrations the electrical center vibrates along the C–Cl axis, and in the degenerate ones, perpendicularly to this axis. The bands associated with these motions are called *parallel* and *perpendicular*, respectively, and have spectral features which usually allow ready discrimination between the two types of motion. Two types of structure are present in the bands of a molecule like methyl chloride (Fig. 1.2): (*1*) in which the
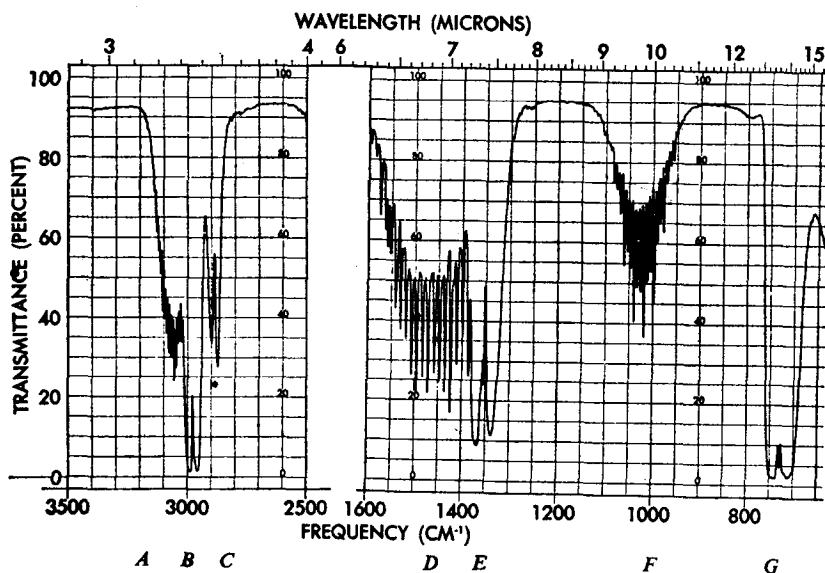

Fig. 1.2   Spectrum of CH₃Cl.

envelope is like that in bands *A*, *D*, and *F*, which, theory shows, is characteristic of perpendicular bands; and (*2*) as in *B*, *C*, *E*, and *G*, in which three more or less well-defined branches occur. The latter type of structure is characteristic of parallel bands. The central branch, weak in *B*, *C*, and *E*, and strong in *G*, is the so-called *Q* or *zero branch*. This branch is composed of rotational lines exceedingly close to one another which correspond to zero change in the rotational quantum number as the molecule is excited vibrationally. The branch on the short-wave side of the *Q* branch is the *R* or *positive branch*, in which the vibrational excitation is accompanied by an increase of rotational quantum number, and the branch on the long wave side is the *P* or *negative branch*, corresponding to vibrational excitation

accompanied by a decrease in the rotational quantum number. In most diatomic molecules the Q branch is absent.

It is not difficult to make a reasonable assignment of the theoretical vibrational pattern to observed bands. The two bands of longest wavelength must be associated with the relatively slow vibrations of the methyl group with respect to the Cl atom: in other words, G is $\nu_5 = 732$ cm^{-1} and F is $\nu_6 = 1020$ cm^{-1}. The group about 7 μ will be associated with the bending vibrations of the H atoms, which are slower than the stretching vibrations, since the restoring force for bending is less than that for stretching. E must be $\nu_3 = 1355$ cm^{-1} and D, $\nu_4 = 1460$ cm^{-1}. The group of bands between 3.2 and 3.5 μ, in so far as they may be fundamentals, must be associated with stretching frequencies of the C–H bonds; A is the double frequncy $\nu_2 = 3047$ cm^{-1}. It will be observed that there is one more band in the spectrum than corresponds to the 9 fundamentals (3 are double); one of the pair B and C cannot be a fundamental. The high intensity of B might suggest it as a fundamental; C would then be either the *second harmonic* of a longer band at about double its wavelength, or a *combination frequency*. In the former case the absorption corresponds to the excitation of two quanta in a mode of vibration, in the latter to the simultaneous excitation of two of the normal modes, for example, ν_3 and ν_4. It should perhaps be mentioned that the bands B and C may suffer a kind of degeneracy due to their rather close approximation to the frequencies associated with the excitation of two quanta of ν_3 and ν_4 and that ν_1, ν_3, and ν_4 probably participate to different degrees in both bands B and C.

In *liquids* rotational structure almost invariably disappears even when it can be readily resolved in the gas. The absorption bands of liquids are often remarkably sharp; they sometimes show structure, but it is not related to the P,Q,R structure of gas bands, and apparently arises from circumstances characteristic of the condensed state. Liquid bands are usually displaced with respect to the corresponding gas bands, stretching vibrations are displayed to lower frequencies, and bending vibrations sometimes to higher frequencies.

The detailed assignment to theoretical normal vibrations of the absorption bands of molecules of some complexity and low symmetry, like most organic molecules, is very difficult; fortunately, it is unnecessary for many purposes of chemical interest. The observed bands may be divided roughly into two classes, those associated with stretching and bending "bond frequencies," and those due to motions in which larger parts of the molecule oscillate as units with respect to one another. It is an experimental fact that characteristic bands can be associated with the presence in the molecule of groups such as C—H, C≡N, C=C, C=O, O—H, N—H, S—H, etc. These bond frequencies, corresponding mostly to absorption
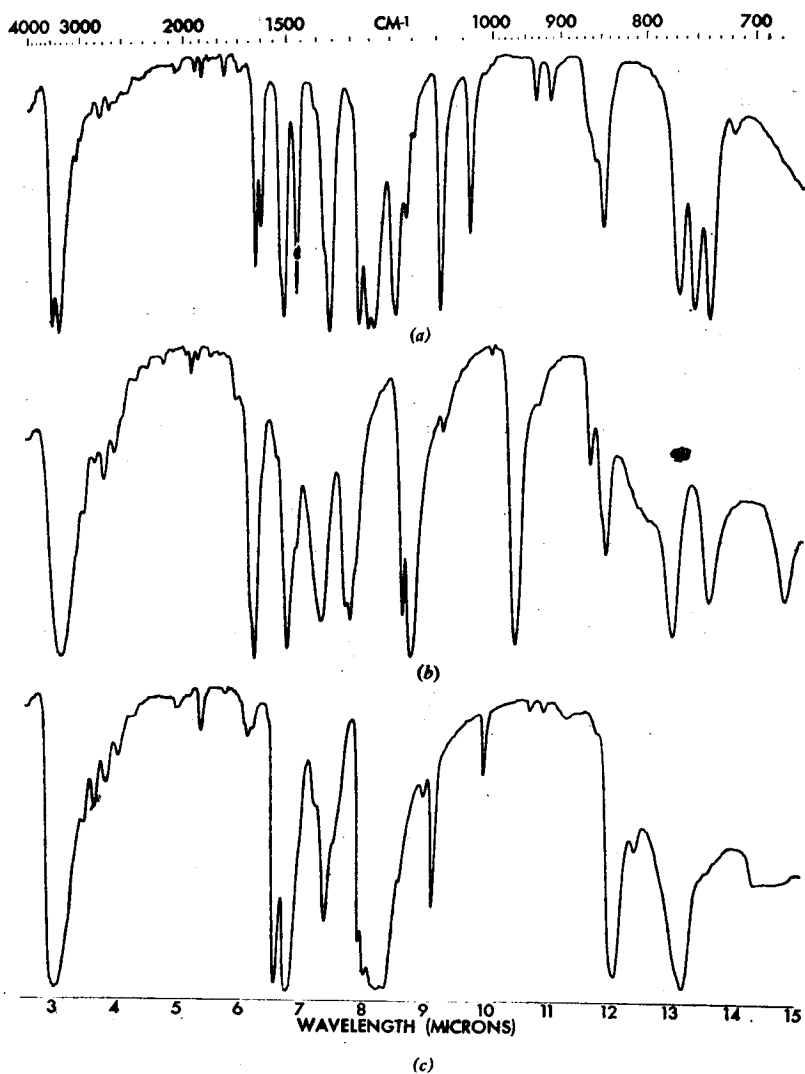
Fig. 1.3 Absorption spectra of dihydroxybenzenes: (*a*) 1,2-(catechol); (*b*) 1,3-(resorcinol); (*c*) 1,4-(hydroquinone).

bands shorter than about 8 μ, although of approximately the same value in different compounds are influenced in definite ways by the structural environment of the bond, for example, certain C—H frequencies assume higher values in ethylenic compounds than in saturated compounds. A knowledge of the bond frequencies of a molecule will therefore enable the organic chemist to characterize the type of molecule in some detail.

The longer wave bands associated with vibrations of the parts of the molecule with respect to one another are useful in the differentiation of compounds with closely similar physical and chemical properties, such as isomeric hydrocarbons or hydrocarbons of closely similar molecular weight. Sometimes the theoretical understanding of these bands is doubtful or wanting, and the method is to make empirical comparisons between the spectra of samples of unknown composition and of pure samples. In this way analyses of such mixtures as the octane fraction of a gasoline sample, the *o*-, *m*-, and *p*-cresols, or the isomeric dimethylbutadienes can be made quickly and accurately. Figure 1.3 illustrates how infrared spectra in the region from 2.5 to 15 μm can be used in the qualitative analysis of isomers such as 1,2-, 1,3-, and 1,4-dihydroxybenzene. Infrared spectroscopy has shown itself particularly well adapted to the study of certain inter- and intramolecular interactions. Inter- and intramolecular hydrogen bonding can be examined in this way.

2 INSTRUMENTAL CONSIDERATIONS

Introduction

Some knowledge of the fundamental parts or components is desirable and if one wishes he can construct spectrometers from a wide variety of standard components. An essential part of the equipment is a source of infrared radiation which is focused on the entrance slit of the spectrometer, within which it is collimated, dispersed, and brought to a focus at an image surface. A narrow band of the dispersed light is selected by an exit slit. The detector could be placed immediately behind the exit slit, but usually greater sensitivity is secured by focusing a reduced image of the exit slit, by means of an elliptical mirror, on a small detecting element. In the spectrometer aluminized mirrors are almost invariably used instead of lenses. Achromatism is thereby secured. These mirrors show strong astigmatism when the direction of the beams does not coincide with that of the optic axis; spherical mirrors show in addition the defects of spherical aberration. In instruments designed for high resolving power, parabolic mirrors are used for collimation, and astigmatism avoided by Pfund's device for working on the axis by means of an auxiliary plane mirror [1], or by so figuring the mirror that its optic axis does not coincide with its geometrical axis (a so-called off-axis mirror, as in