CHEMICAL APPLICATIONS OF INFRARED SPECTROSCOPY

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Preface

This volume aims to present the basic concepts, measurements, and techniques of infrared spectroscopy and to survey, as completely as possible, its chemical applications.

I have tried to present all the available spectra–structure correlations in the near, medium, and far infrared regions, with due attention to the environmental factors affecting the infrared spectra of complex molecules. In addition to discussing group frequencies, this book reviews the applications of infrared spectroscopy in certain specialized branches of study such as transition metal complexes, charge transfer complexes, polymers and proteins, adsorbed molecules, and the matrix isolation technique. Two chapters are devoted to specific applications in organic chemistry and biochemistry.

Infrared spectroscopy is undoubtedly the most powerful physical technique available to chemists for the elucidation of molecular structure and for qualitative and quantitative analyses. This volume has been designed for students, technicians, and research workers as a text or a reference work and as an aid to enable more effective use of infrared spectroscopy in chemistry.

I am indebted to my colleagues Dr. T. R. Kasturi and Dr. L. K. Ramachandran for their kind collaboration as authors of the chapters on specific applications in organic chemistry and biochemistry. For the section on adsorbed molecules I express my thanks to Dr. K. S. Narayan.

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Acknowledgments

In the course of writing this book I have had the advantage of referring to the books and reviews on the subject by other authors— particularly the excellent book by Dr. L. J. Bellamy and the article by Dr. R. N. Jones and Dr. C. Sandorfy.

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My sincere thanks are expressed to the authors of articles and the editors of journals who have kindly granted me permission to reproduce several of the figures that appear in this book. My thanks are due to all the authors who have been kind enough to send me reprints of their papers. But for them, the task of collecting the data would have been formidable.

I am specially indebted to the publishers, Academic Press Inc., and to their editors and staff, for their unfailing cooperation and efforts in bringing out this volume.

I wish to record my gratitude to the authorities of the Indian Institute of Science for the facilities and encouragement for writing this book.

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Introduction

. Modern methods of spectroscopy in the different regions of the electromagnetic spectrum have provided the chemist with indispensable tools for the investigation of molecular structure. The choice of a particular spectroscopic method for a specific problem mostly depends on the kind of information sought. Thus, the detailed structural information on certain types of molecules may be obtained from microwave spectroscopy (1). Electronic (ultraviolet and visible) spectroscopy, on the other hand, does not give much information on the structural details of molecules, but only throws light on their "group" character (2). Infrared spectroscopy is eminently suited for different types of structural investigations because of the ideal wavelength region it covers in the electromagnetic spectrum. One may qualitatively express the suitability and potentialities of microwave, infrared, and electronic spectroscopy for structural studies of molecules, as in Fig. 1. Infrared spectroscopy not only gives considerable information on the structural features, but also provides "fingerprints" of molecules.
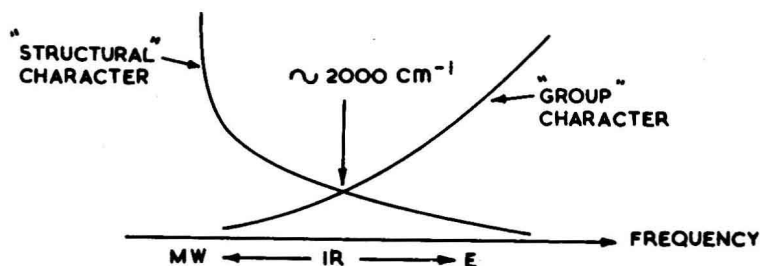
FIG. 1.   The nature of the information obtained in the different spectral regions: MW, microwave; IR, infrared; and E, electronic.

Vibration-rotation spectroscopy of small molecules provide a powerful method for the study of molecular structure and intramolecular forces. This has been due mainly to the use of theoretical methods of analysis (3–6). The analysis of the infrared spectra of complex molecules by theoretical methods would be very difficult and exact solutions of such problems cannot be obtained at present. In the early stages of the study of infrared spectroscopy it appeared as though any kind of knowledge of the vibrational spectra of complex molecules would be impossible to gain. But in spite of the theoretical difficulties, comparative

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studies on the infrared spectra of a large number of different types of complex molecules have made it possible to correlate the spectra with structure and for the past decade the infrared spectrometer has become an essential part of the chemist's laboratory.

The adoption of infrared spectroscopy by chemists was not a simple process. Chemists took nearly fifty years to realize the importance of spectra-structure correlations. Coblentz (7) had published his excellent collection of the infrared spectra of 135 organic compounds, as early as 1905. In spite of the tedious method employed, Coblentz was able to show that correlations of molecular structure with infrared spectra were possible. In Fig. 2, Coblentz's spectra for the three xylene isomers in
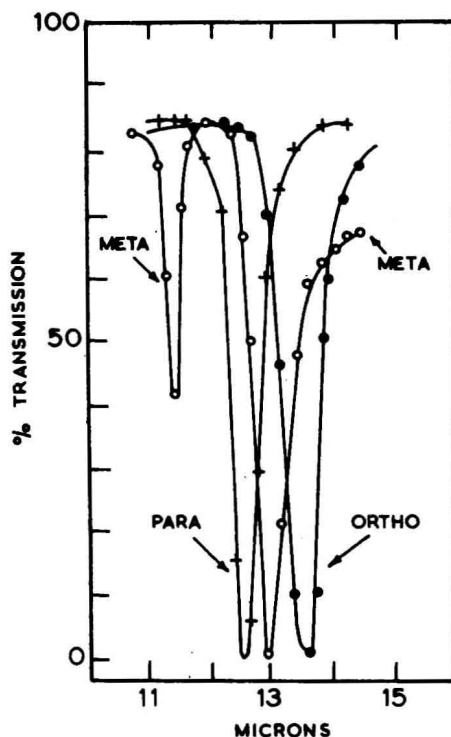
FIG. 2. Coblentz's spectra for the three xylene isomers in the 11–15 μ region.

the 11–15 μ region have been reproduced. The spectra clearly distinguish the three isomers. Even today, quantitative analysis of the xylene isomers is based on these differences in their absorption bands. The classical monograph of Coblentz had escaped the attention of organic chemists, until Lecomte reactivated research in the field of spectra-structure correlations about thirty years ago. It is really unfortunate that chemists

took such a long time to appreciate the significance of this great contribution of physicists, but when they eventually realized the importance of infrared spectroscopy in solving chemical problems, they completely took over the field. Had infrared spectroscopy been discovered today, chemists would have owned the technique in no time. Obviously, there has been a change in the philosophy of the chemist. Now the chemist is completely aware of the need for close collaboration with the physicist.

There is considerable difference in the language used by the physicist and the chemist. The physicist would be horrified by a large complex molecule, were he to attempt the analysis of its spectrum through vibrational analysis by group theory. The chemist thinks of a large molecule as an assembly of small structural units, each of which retains some of its individuality even when present in different types of compounds. According to the physicist's concept of the vibrating molecule, any variation in molecular structure should change the symmetry and mass distribution in the molecule and should modify the entire infrared spectrum. However, with the concept of the molecule as an assembly of nearly independent structural units, the chemist would consider the infrared spectrum of a molecule as a combination of sets of bands associated with the different groups. In reality, the situation is somewhat closer to the chemist's concept.

It would not be an exaggeration to say that infrared spectroscopy is the most powerful physical method employed by chemists. Other physical techniques, like x-ray diffraction and electron diffraction, give structural information on molecules only after subjecting the data to intricate analysis, and the methods are very time-consuming. But the chemist prefers techniques which tell him something about the structure of molecules in a fairly short time. The physical method should be more or less another qualitative test in the laboratory. Infrared spectroscopy is the only answer to his needs. Infrared spectrometers which satisfy the different types of needs of chemists are commercially available.

Chemists have studied the infrared spectra of a variety of compounds and have found systematic correlations with structure. They have employed infrared spectroscopy not only as a tool for the study of structures of molecules but also as a method for the quantitative analysis of substances. The number of publications dealing with the chemical applications of infrared spectroscopy is so great that it is impossible to credit properly all the workers who have made important contributions in this field.

In the following chapters, an attempt has been made to present the basic concepts and techniques of infrared spectroscopy and to survey the applications in elucidation of molecular structure and in qualitative

and quantitative analyses in the different branches of chemistry. Two separate chapters have been devoted to the discussion of specific applications in organic chemistry and biochemistry, wherein several examples taken from the recent literature have been cited. The factors influencing the infrared spectra of complex molecules, such as substituent effects, solvent eqects and hydrogen bonding, have been given considerable importance all through the chapters on group frequencies and particularly in Chapters I, III, and XII. Importance of infrared intensity data in structural work has been pointed out with suitable illustrations. Available data on the near and far infrared spectra of molecules have been presented. Several aspects of interest such as transition metal complexes, charge-transfer complexes, dichroism studies of polymers, adsorbed molecules, matrix-isolation studies, and solid-state anomalies have also been discussed. Quantitative analysis forms the subject matter of Chapter XI. In an attempt to make each chapter or section complete in itself, it has been necessary in some places to repeat some of the information already discussed earlier. It is the hope of the author that the readers will overlook such minor defects which are unavoidable in writing a book of this kind.

The wave number units (cm^{-1}) have been employed in this book. A wave number–micron conversion table has been included at the end of the book. In the tables and charts, band intensities have been roughly indicated by the symbols: S, strong; M, medium; W, weak, and V, variable. Several figures have been included with a view to improving the presentation of the subject matter. Detailed tables and charts of spectra-structure correlations are given in the chapters on group frequencies and the general spectra-structure correlation charts for group frequencies in organic compounds are given at the end of the book. In the case of the carbonyl group, the stretching frequencies in representative compounds of each type of carbonyl function have been tabulated in Section III.4. An appendix on the teaching of infrared spectroscopy has been added.

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Basic Concepts,
Instrumentation, and Techniques

When a molecule absorbs radiation, its energy increases in proportion to the energy of the photon as expressed by the relation,

$$\Delta E = h\nu' = hc/\lambda, \tag{I.1}$$

where h is the Planck's constant, ν' and λ the frequency and the wavelength of the radiation, and c the velocity of light. The increase in energy may be in the electronic, vibrational, or rotational energy of the molecule. Changes in the electronic energy involve relatively large quanta. Changes in the vibrational energy involve smaller quanta and the changes in the rotational energy involve quanta even smaller than those of vibrational energy. If a molecule absorbs radiation in the microwave or the far infrared region, only its rotational energy will change, no matter which vibrational or electronic state it is in. If the radiation is in the medium infrared region, both the vibrational and rotational energies of the molecule will change. If the energy of the radiation is much greater, as in the case of ultraviolet light, there will be changes in the electronic, vibrational, and rotational energies of the molecule. Thus, the infrared absorption spectra of molecules result from transitions between vibrational and rotational energy levels.

The infrared region of the electromagnetic spectrum covers a wide range of wavelengths, from about 8000 Å (end of the visible region) to about 0.2 mm (beginning of the microwave region). The units of wavelength commonly employed in the infrared region are the micron, μ ($1\,\mu = 10^4\,\text{A} = 10^{-4}$ cm) and the wave number, $\nu = 1/\lambda$, in reciprocal centimeters (cm^{-1}). The reciprocal centimeter unit has also been referred to as the "Rydberg" and the "Kayser." The infrared region may be further subdivided into three regions: the near infrared region between 12,500 and 4000 cm^{-1}, the medium infrared region from 4000 to 650 cm^{-1}, and the far infrared region extending from 650 to about 100 cm^{-1}.

1. ORIGIN OF VIBRATIONAL SPECTRA

The basic problem of vibrational spectroscopy is to correlate the experimentally observed energy levels with the structure and force function of the molecule. The energy states of infrared transitions may be obtained from solutions of the Schrödinger wave equation in coordinates of the nuclei. The potential energy function corresponds to a fixed electron configuration of lowest energy. Infrared frequencies are determined mainly by the mechanical motions in the molecule while the intensities are related to the electrical properties. Vibrational transitions without rotation may be discussed in terms of the harmonic oscillator model and pure rotational transitions may be understood in terms of the rigid rotator model.

In the harmonic oscillator model, the restoring force is proportional to the first power of the displacement (Hooke's law) and the potential energy function is proportional to the square of the displacement. This model can account for fundamental vibrations occurring between the nonvibrating state and the next vibrationally excited state. In a simple diatomic molecule XY, the only vibration which can occur is the periodic stretching along the X—Y bond. The stretching vibration may be visualized as an oscillation of the two bodies X and Y connected by a spring and Hooke's law is applicable to a first approximation. The vibrational energy of a diatomic molecule is given by

$$E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \, (n + \tfrac{1}{2}), \qquad n = 0, 1, 2, \ldots \qquad (\text{I.2})$$

where h is the Planck's constant, n the vibrational quantum number, k the force constant of the bond, and μ the reduced mass of the molecule defined by

$$\mu = m_X m_Y / m_X + m_Y \qquad (\text{I.3})$$

where m_X and m_Y are the atomic masses of X and Y. The energy change, ΔE_{vib}, for the absorption process, $n = 0 \to 1$ is

$$\Delta E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \qquad (\text{I.4})$$

By applying the Bohr relation one finds

$$h\nu' = hc\nu = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \qquad (\text{I.5})$$

where ν' is the vibrational frequency in sec^{-1}, ν the vibrational frequency in cm^{-1}. It therefore follows that the vibrational frequency in cm^{-1} is

given by

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \tag{I.6}$$

The value of k is of the order of 5×10^5 dynes cm^{-1} for single bonds and is about twice and thrice this value for double and triple bonds. In the case of the HCl molecule, $\mu = 1.6 \times 10^{-24}$ g and by assuming $k = 5 \times 10^5$ dynes cm^{-1} one calculates $\nu = 3000$ cm^{-1}. Thus, the strong infrared absorption band of HCl vapor at 2885 cm^{-1} may be interpreted as due to the H—Cl stretching vibration. Stretching vibrations of individual bonds in more complex molecules may also be treated similarly although the absorption frequencies are influenced by several other factors. Since both the reduced mass and force constant of the bond determine the vibrational frequency, simple correlations based on Eq. (I.6) cannot be precise in the case of complex molecules as effects of neighboring atoms are ignored. Equation (I.6) is useful, however, in predicting frequency changes accompanying small alterations in molecular structure like isotopic substitution. Several empirical relationships relating the force constant, the vibrational frequency, the internuclear distance, and the atomic masses have been proposed. Particular mention should be made of the relationship proposed by Badger (1),

$$k = \frac{1.86 \times 10^5}{(r - d_{ij})^3} \tag{I.7}$$

where r is the internuclear distance and d_{ij} a constant depending on the positions of the atoms i and j in the periodic table.

A nonlinear molecule of n atoms has $3n$ degrees of freedom which are distributed as three rotational, three translational, and $3n$-6 vibrational motions. A nonlinear molecule should then show strong infrared absorp-
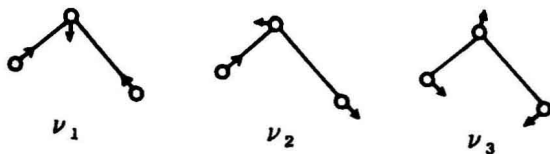

FIG. I.1. Normal modes of vibration of a triatomic nonlinear molecule: ν_1, symmetric stretching; ν_2, asymmetric stretching; and ν_3, symmetric bending.

tion at $3n$-6 different frequencies. The three normal modes of vibration of a nonlinear triatomic molecule such as H_2O are shown in Fig. I.1. A linear triatomic molecule like CO_2 should show $3n$-5 $= 4$ normal vibrational frequencies as pictured in Fig. I.2. Since the normal vibrations 2a and 2b should occur at the same frequency, one would expect three