MOLECULAR SPECTROSCOPY

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PREFACE

The primary objective of *Molecular Spectroscopy* is to present to the student a thorough introduction to the relationships among quantum mechanical formulations, experimentally determinable quantities obtained via spectroscopic methods, and physical parameters related to the structure of molecular systems. A second objective is to provide a detailed discussion of the use of matrix mechanics as it applies to spectroscopy, since this method is much less familiar to the chemist than wave mechanical methods.

In order to achieve the stated objectives the following methods will be employed: (1) The main scope of the text has been limited to the development of relationships for elementary systems so that the treatment can be in-depth and of sufficient detail that it can be followed by a student with a background of two years of college mathematics, a year of college physics, and one and one-half years of physical chemistry, including an appreciable introduction to quantum mechanics (wave mechanics) and group theory. (2) The treatment is not intended to be a survey of all areas of spectroscopy, or to discuss the forefront of research in spectroscopy but is designed to provide the student with the necessary foundation for proceeding on to advanced monographs and papers. (3) Quantum mechanics is used as a tool and is not developed fully. (4) The mathematical and quantum mechanical methods employed are either those which are normally covered in those courses listed under Part I or else they are summarized in appendices. (5) The relationship between theory and experimentally determined parameters is constantly emphasized by the inclusion of examples in the text. (6) The presentation is so ordered that the student can proceed through it with a minimum of referral to earlier material or to outside sources. (7) Problem sets are provided at the ends of the chapters so the student can reinforce the discussion. (8) Subjects are introduced at the elementary level, followed through to an advanced stage and frequently referred to in a later treatment at an even higher level, thus gradually building necessary relationships. (9) An effort has been made to eliminate the "it is obvious" statements that so often are not as obvious to the student. (10) A less detailed review of the spectroscopy of more complex

systems is included following the introductory material to provide a more balanced view of the subject.

There are several important aspects which are characteristic of this treatment. The more predominant of these include the extensive use of matrix methods, the inclusion of discussions of nuclear quadrupole resonance, and detailed examples. Following a brief introduction to the subjects of spectroscopy, wave mechanics is reviewed by discussing the harmonic oscillator and rigid rotor. Perturbation theory is also reviewed in order to provide a background for matrix formulation of this method. In Chapter 3 the matrix method is reviewed in detail and the angular momentum and direction cosine matrix elements, which are used extensively in the book, are developed. Chapter 4 reviews point group symmetry and group theory. Chapter 5 provides a brief discussion of the electric and magnetic properties of matter. With the enhanced resolution of electronic spectra due to the use of lasers, the study of electronic spectra of diatomic molecules is becoming a more commonly used method for the determination of molecular parameters so discussion of electronic structure of diatomic molecules has been included in Chapter 6.

Following the preliminary material in the first six chapters the subject of absorption spectroscopy is introduced with the general development of the interaction of radiation and matter and the formulation of absorption coefficients.

The next three chapters provide an introduction to resonance spectroscopy methods and the formulation of relationships using matrix methods. Several concepts necessary to the discussions of spectroscopy in later chapters are introduced here. The subject of magnetic resonance is approached by dividing the subject into the areas of nuclear and electron resonance. Nuclear quadrupole resonance of solids is discussed since this subject is generally omitted from texts of this type.

The next five chapters explore the rotational, vibrational, and electronic spectra of real diatomic molecules. In these chapters dual use of wave mechanics and matrix mechanics is employed in order to ensure that the student understands their interrelationships. Following an introduction to the elementary aspects of vibrotor spectra in Chapters 11 and 12, the discussion returns in Chapters 13 and 14 to cover some of the more detailed concepts relative to the vibration and rotation of diatomic molecules. These will include perturbations due to both external and internal fields, and the Raman effect. The analysis of electronic vibronic and rovibronic spectra in Chapter 15 completes the discussion of diatomic molecules.

Once the basic treatment of rotational, vibrational, and electronic spectroscopy of diatomic molecules has been developed, Chapter 16 directs its attention to the subject of vibration of polyatomic molecules, first by considering the classical problem of normal modes followed by introduction of quantum descriptions and finally a look at the FG matrix treatment. Chapter 17 discusses the rotation of polyatomic molecules. The final chapter is devoted to a discussion of electronic spectra of polyatomic molecules, an important area relative to laser spectroscopy. It is not the intent of these latter chapters to provide either an

in-depth or complete coverage of all aspects of the subjects. Instead, a few elementary topics are selected to illustrate the application of the principles developed earlier. The presentations in the latter three chapters will provide the background from which the student can proceed to the study of more complex problems involving the electronic, vibrational, and rotational spectroscopy of polyatomic systems.

The chapters contain references to two types of articles, ones of specific interest which are referenced in the chapters and ones which are sources of data and general references. At the end of the text is a set of appendices which give concise reviews of mathematical methods, classical physics, and other tangential subjects. While it is impossible to cover these subjects in great detail the presentation will give the students sufficient background to appreciate the methods, its problems, and its potential.

The material in this book is presented at a first or second year graduate level. Both the text and the problems have been used in classroom situations. At Virginia Polytechnic Institute the material from this book has been used in two sequential one-quarter courses, Chemistry 5630, Introduction to Spectroscopy, a first-year graduate course taught in the spring quarter, and Chemistry 6640, Molecular Spectroscopy, a second-year graduate course taught in the fall quarter.

The book was developed over a period of several years and my primary thanks go to the many students who, over that span of time, have provided suggestions for improvement of the presentations and have labored through the problems which are included in the chapters. I particularly wish to thank Professor C. D. Cornwell of the University of Wisconsin who was an inspiring teacher and research director and who provided many valuable suggestions during the writing of this book. I also wish to thank Professor J. C. Schug of Virginia Polytechnic Institute and State University for reviewing some of the material. Additional thanks go to the following reviewers whose comments contributed greatly to the final product: Dewitt Coffey, San Diego State University; Lawrence W. Johnson, York College of the City University of New York; Willem R. Leenstra, University of Vermont; Lee Pedersen, University of North Carolina; and Jeffrey Steinfeld, Massachusetts Institute of Technology.

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As with most textbooks this one draws on the original literature and, in some instances, comprehensive monographs for data are used in the examples. For historical background, brief mention of concepts and experimental results, problems and referrals to a more extensive discussion of subjects, appropriate references are given at the ends of the chapters and noted in the text. Where extensive exemplary use has been made of material from a particular source the authors are acknowledged. It is with appreciation that I acknowledge the use of such material in the following chapters. (Tables and figures utilizing cited data are given in parentheses following the acknowledgment.)

Chapter 6

1 Dr. G. Herzberg for permission to use information from Tables 26, 28, 30, 31, 32 and 34 and Figure 169 from *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules.* (Tables 6.4, 6.6, 6.8, 6.9, 6.10 and 6.11 and Figures 6.2, 6.12, 6.13, 6.14, 6.19, 6.23 and 6.24 and Problem 7)

Chapter 8

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Chapter 13

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Chapter 15

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3 The Canadian Journal of Physics for permission to use data on CuH from *Can. J. Phys.*, **46**, 2291 (1918). (Table 15.8)
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CONTENTS

CHAPTER 1

INTRODUCTION

1.1 AN OVERVIEW

During the first half of the twentieth century the methods of thermodynamics and kinetics dominated the ways used to investigate chemical systems. Such methods provided enormous insight into the bulk behavior of matter but could not provide much detailed information regarding the properties of individual molecules. Building on the development of modern quantum mechanics, which has accelerated rapidly since the initial work of Schrödinger and Heisenberg in 1926, and employing sophisticated methods for handling electromagnetic radiation and processing data, the area of spectroscopy has achieved a status equivalent to that of thermodynamics and kinetics. The scope of spectroscopy is very extensive and is closely related in many instances to the nature of the information obtained in complementary areas such as neutron, X-ray and electron diffraction, mass spectrometry, magnetic and electric susceptibility measurements, electron microscopy, optical rotatory dispersion, and circular dichroism, to cite some major ones. These complementary methods, other than diffraction, for the most part give useful information regarding gross structures and nongeometric molecular parameters. The techniques of spectroscopy and diffraction are the primary sources of information regarding detailed molecular geometries.

The primary structural parameters which determine the geometry of a molecule are the bond lengths and interbond angles. If one can accurately measure all such parameters for a given molecule, then the geometry is known. The magnitudes of the structural parameters are frequently found to correlate with chemical properties, particularly for series of related molecules, so that reciprocal

predictions of parameters and properties can be made. For many molecules, especially large ones, a complete determination of all structural parameters is often impossible or impractical. In such cases it is possible to acquire a great deal of useful information regarding the general nature of the symmetry and geometry of the system by the judicious application of selected techniques of spectroscopy. Thus, one of the primary uses for the results of spectroscopic experiments is to determine molecular geometries. In addition to geometric parameters, spectroscopic experiments yield a wide variety of information related to other features of the system being studied. Typical of such information would be parameters which are measures of electron distribution, electrical polarizability, bond strengths, intramolecular magnetic interactions, and energy level arrangements, to mention a few.

The experimental methods of spectroscopy used for the determination of molecular parameters involve the interaction of electromagnetic radiation and matter. These methods may examine radiation emitted, radiation absorbed, or radiation scattered by a system. The techniques and theories of electron, X-ray, and neutron diffraction are very valuable for the determination of molecular geometries, particularly of large molecules in the solid state, but they are sufficiently unrelated to those of spectroscopy that they will not be included in this book.

A complete discussion of the subject of spectroscopy will fill a multivolume treatise so any presentation of a reasonable size requires some judicious choices of subjects for inclusion and the adoption of a particular plan of presentation. These are three topics which contribute heavily to the subject of spectroscopy: (1) the relationships between the experimentally observed spectroscopic parameters and the individual molecular parameters, (2) the relationships between the molecular parameters and the structures of the molecules, and (3) the experimental and instrumental aspects of particular branches of spectroscopy. In this presentation the primary emphasis will be on the development, via the medium of quantum mechanics, of the analytical relationships between experimental spectroscopic data and the properties and parameters of individual molecules. The spectroscopic data will be the frequencies and intensities of radiation which is emitted, absorbed, or scattered from molecules. The development of these relationships will proceed by considering for each area of spectroscopy: (1) the specific features of quantum mechanics which are needed for the development, (2) the nature of the atomic and molecular energy-level schemes and allowed spectroscopic transitions among them, (3) the relationships between the observed transition frequencies and molecular properties and parameters, and (4) reviews of specific examples. The object will be to provide a comprehensive treatment of simple systems in order for the reader to build a fundamental background and to be able to proceed independently to more advanced works. There will be only limited development of the analytical relationships between the structure of molecules and the spectroscopically determined molecular parameters. Details regarding experimental methods will be at a minimum with any such discussions being brief and general in nature.