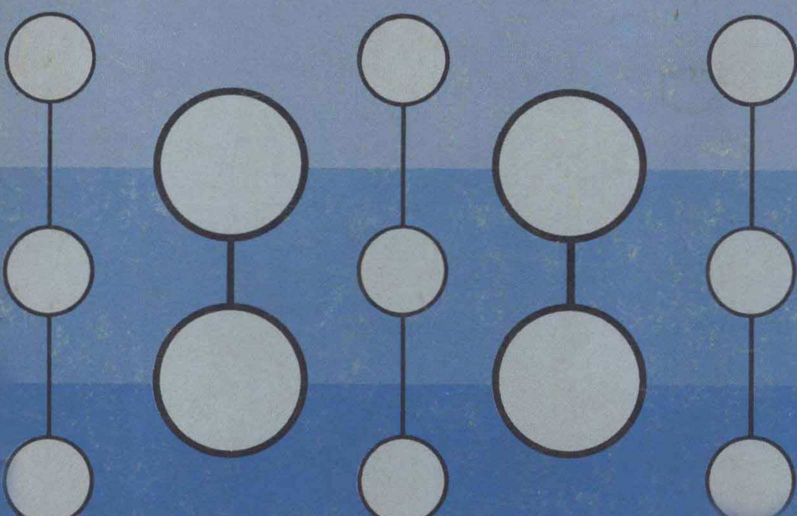
Gordon M. Barrow

THE STRUCTURE OF MOLECULES



The Structure of Molecules

An Introduction to Molecular Spectroscopy

Gordon M. Barrow
Case Institute of Technology

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An Introduction to Molecular Spectroscopy

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The Structure of Molecules

THE GENERAL CHEMISTRY MONOGRAPH SERIES

Russell Johnsen, Editor
Florida State University

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Editor's Foreword

The teaching of general chemistry to beginning students becomes each day a more challenging and rewarding task as subject matter becomes more diverse and more complex and as the high school preparation of the student improves. These challenges have evoked a number of responses; this series of monographs for general chemistry is one such response. It is an experiment in the teaching of chemistry which recognizes a number of the problems that plague those who select textbooks and teach chemistry. First, it recognizes that no single book can physically encompass all the various aspects of chemistry that all instructors collectively deem important. Second, it recognizes that no single author is capable of writing authoritatively on *all* the topics that are included in everybody's list of what constitutes general chemistry. Finally, it recognizes the instructor's right to choose those topics that he considers to be important without having to apologize for having omitted large parts of an extensive textbook.

This volume, then, is one of approximately fifteen in the General Chemistry Monograph Series, each written by one or more highly qualified persons very familiar with the current status of the subject by virtue of research in it and also conversant with the problems associated with teaching the subject matter to beginning students. Each volume deals broadly with one of the subdivisions of general chemistry and constitutes a complete entity, far more comprehensive in its coverage than is permitted by the limitation of the standard one-volume text. Taken together, these volumes provide a range of topics from which the individual instructor can easily select those that will provide for his class an appropriate coverage of the material he considers most important.

Furthermore, inclusion of a number of topics that have only recently been considered for general chemistry courses, such as thermodynamics, molecular spectroscopy, and biochemistry, is planned, and these volumes will soon be available. In every instance a modern structural point of view has been adopted with the emphasis on general principles and unifying theory.

These volumes will have other uses also: selected monographs can be used to enrich the more conventional course of study by providing readily available, inexpensive supplements to standard texts. They should also prove valuable to students in other areas of the physical and biological sciences needing supplementary information in any field of chemistry pertinent to their own special interests. Thus, students of biology will find the monographs on biochemistry, organic chemistry, and reaction kinetics particularly useful. Beginning students in physics and meteorology will find the monograph on thermodynamics rewarding. Teachers of elementary science will also find these volumes invaluable aids to bringing them up to date in the various branches of chemistry.

Each monograph has several features which make it especially useful as an aid to teaching. These include a large number of solved examples and problems for the student, a glossary of technical terms, and copious illustrations.

The authors of the several monographs deserve much credit for their enthusiasm which made this experiment possible. Professor Rolfe Herber of Rutgers University has been of invaluable assistance in the preparation of this series, having supplied editorial comment and numerous valuable suggestions on each volume. Thanks are also due to Professor M. Kasha of the Florida State University for many suggestions during the planning stages and for reading several of the manuscripts.

RUSSELL JOHNSEN

Tallahassee, Florida
October 1962

Preface

It is increasingly important for the student of general chemistry to be able to interpret chemical and physical phenomena in terms of molecular behavior. It follows that he must learn as much as he can about the nature and behavior of individual molecules.

One basic way of determining the "physical" properties of molecules is the measurement of the radiation they emit or absorb. This is spectroscopy, and I have attempted here to provide an introduction to the subject.

The methods by which information is deduced from spectroscopy are described and applied to some relatively simple cases. Although the spectroscopic analysis of more complicated systems demands a mathematical approach, an understanding of the principles and scope of the technique does not. This book shows how the properties of molecules can be gained from spectra, and in so doing provides an extension to the introductory study of chemistry.

As the student's interest in spectroscopy grows and, when he has acquired an additional background in mathematics and physics, he will want to turn to more advanced works on the subject. A selection of these is given in the following list:

G. M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw-Hill, New York, 1962

R. P. Bauman, *Absorption Spectroscopy*, Wiley, New York, 1962

G. H. Beaven, E. A. Johnson, H. A. Willis, and R. G. T. Miller, *Molecular Spectroscopy: Methods and Applications in Chemistry*, Macmillan, New York, 1961

W. Brügel, *An Introduction to Infrared Spectroscopy*, Wiley, New York, 1962

R. E. Dodd, *Chemical Spectroscopy*, Elsevier, New York, 1962

GORDON M. BARROW

Cleveland, Ohio
January 1963

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Constants

Symbol	*Description*	*Value*
c	Velocity of light	3.00×10^{10} cm/sec
h	Planck's constant	6.62×10^{-27} erg-sec
k	Boltzmann's constant	1.38×10^{-16} erg/deg-molecule
R	Gas constant	1.99 cal/deg-mole

Introduction

The chemist must learn to live in, and to feel at home in, the world of molecules. It is not enough that he knows the chemical constitution and chemical reactions of the materials around him. To be really effective and successful, he must also develop an intimacy with the molecular world. He must fit himself into the molecular scale of things. He must put that first drummed-in chemical fact that molecules are small in the very back of his mind and replace it by a consciousness that molecules are real, intricate, structural arrangements of atoms in space.

No study brings one more quickly to an intimacy with molecules, with their size, shape, flexibility, and so forth, than does spectroscopy. The methods of spectroscopy almost let one "see" individual molecules. The brief account of molecular spectroscopy that follows will, for example, show that we can determine that the bond length of the HF molecule is 0.917×10^{-8} cm (or 0.361×10^{-8} in.) and that that of HCl is 1.275×10^{-8} cm. Furthermore, it will be seen that it is almost exactly twice as difficult to stretch the bond of the HF molecule—by, say, 10 per cent—as it is to do the same to the HCl molecule.

An appreciation that such molecular properties can be measured —and therefore that one can, in a way, see the details of individual molecules—brings one quickly and directly to a "feeling" for the world of molecules. With this philosophy the student can bring to bear on all later studies of chemistry, or biochemistry, the questions that the modern chemist asks: What does this reaction (or rate, or property, etc.) tell me about the behavior of the molecules of the system? How can I understand this reaction, etc., in terms of the known behavior of the molecules of the system?

Although the methods of spectroscopy will be dealt with here primarily in terms of the study of the properties of individual molecules, it must be mentioned that these methods find a wide and ever-increasing use for the identification and analysis of all types of chemical systems. The material to be presented here will provide the background that allows one to understand such practical applications of spectroscopy. The absorption of radiation in the infrared spectral region, for example, turns out to be remarkably characteristic of the molecules of the absorbing material. One can, therefore, use the infrared absorption spectrum of a compound to characterize the compound or to analyze for this compound in a mixture. While such applications can be made without a knowledge of what is happening when the molecules absorb radiation, full use of these techniques in a satisfying way requires the understanding of the molecular basis of spectroscopy that will be reached by a study of this monograph.

I

Radiation and the Energies of Molecules

To begin with, it is perhaps desirable to emphasize that the methods used to find out about molecules by spectroscopy are, to some extent, similar to the procedure of looking at ordinary-sized objects to determine their sizes and shapes. In spectroscopy we "look at" the molecules of a sample by shining light through the sample and measuring, by a suitable instrument, which wavelengths of the light have been absorbed by the molecules of the sample. The material of the following chapters will show that the radiation absorbed by a sample reveals many of the properties of the molecules of the sample. The measurement of the absorption of radiation by a sample, or of the emission of radiation by a hot sample, and the deduction of the properties of the molecules of the sample from these measurements constitutes molecular spectroscopy. The methods of spectroscopy can be adequately illustrated by restricting the treatment to small molecules, and primarily to diatomic molecules. It will be made clear, however, that the principles established here can be extended, with some added complexities, to larger molecules.

Before studying spectra in detail it is necessary to go over some of the general features of the topics which, when combined, will reveal the molecular sizes and shapes in which we are interested. The principal basic topics that will now be introduced are the nature of radiation, the experimental methods available for studying the absorption of radiation, and some of the general features of the energies of individual molecules.

1–1 NATURE OF RADIATION

Here we must talk about the nature of a beam of light so that later we can understand the way in which such a beam interacts with the molecules that are placed in its path. Two rather different descriptions of a light beam are used in spectroscopy. These two views of the nature of a light beam stem from the early, and then opposing, wave and corpuscular theories of the nature of light.

Wave Nature of Radiation

The wave-nature view of radiation is usually adopted, for example, when one considers phenomena such as the spreading out of white, i.e., "ordinary," light into its color components as a result of passage through a prism. The process is indicated in Fig. 1–1.

In this description of radiation the waves consist of electric and

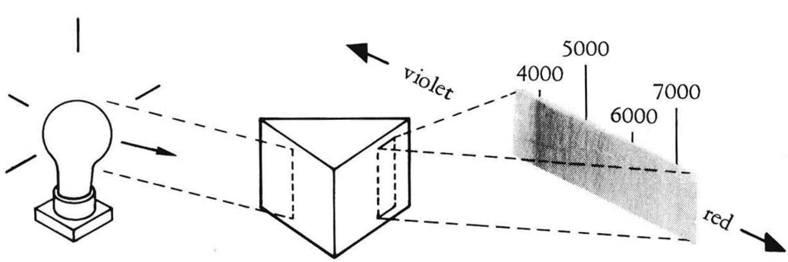

Figure 1–1 The spreading out of a beam of white light by means of a prism.