Physical Methods in Inorganic Chemistry

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Consulting Editors' Statement

Physical methods have become so much a part of modern inorganic chemical research, that it is not surprising to find that numerous authors have written books concerning the theoretical bases for such methods. There are, however, few books which within a single volume, treat the more important physical methods in a manner which makes it convenient for the student or the practicing chemist to learn how to use each method and the kind of information which can be obtained from each. Professor Drago, from his own research, is highly qualified to fill this important gap in the chemical literature. His experience as a teacher and a writer assures the reader that this volume will not only be a trustworthy guide but that its use will be both pleasant and inspiring. We are proud to add this book to the REINHOLD CHEMISTRY TEXTBOOK SERIES.

HARRY H. SISLER
CALVIN A. VANDERWERF

Preface

THE CONTENTS of current research and modern textbooks in the area of inorganic chemistry indicate beyond a doubt that modern inorganic chemists must have a working knowledge of various physical methods. Anyone challenging this statement need only read a current issue of a good inorganic journal, a recent volume in the several series devoted to inorganic chemistry, or a modern inorganic textbook to find many examples in which inorganic problems have been solved by employing physical methods. The modern well-trained inorganic or organic chemist applies any physical method which may possibly produce the results needed to solve his problems. It is necessary to understand the basic principles and limitations of these methods in order to do good research and to read the literature critically. Considering the many incorrect interpretations of results from spectroscopic methods that have appeared in the literature, the latter consideration is most important. It is impossible to be an active, modern, inorganic or organic chemist without a knowledge of the principles, limitations, and different kinds of applications of spectroscopic methods.

This brings up an interesting point concerning current course offerings in inorganic chemistry in many universities. One finds in most inorganic textbooks and in most inorganic course offerings detailed discussions of quantum mechanical calculations (at least for H_2^+ and H_2), procedures for determining electronegativities, and means of evaluating the covalent and ionic radii of atoms. Often very little mention is made of the application and intelligent use of physical methods in inorganic chemistry. The author invites you to investigate the last six issues of *Inorganic Chemistry* and count the number of inorganic research problems solved by physical methods and compare these with the number of times inorganic problem

have been solved by making quantum mechanical calculations, using ionic radii, and evaluating electronegativities. This comparison is made not to de-emphasize the importance of these latter subjects, but to emphasize the importance of giving graduate students instruction in physical methods.

At Illinois, this problem has been in part resolved by offering a course devoted to the application of physical methods in inorganic chemistry. This text has evolved from this course, and it is hoped that it will be influential in initiating instruction of this material to all inorganic chemists. The author feels that the material in this text should be presented either in the senior year or in the first year of graduate school after the student has had an introductory course in inorganic chemistry. The course on physical methods can be followed by special topics courses in transition metal ion chemistry, group theory and molecular orbital theory, nonaqueous solvents, chemistry of the familiar and less familiar elements, etc. These special topics can be treated at an advanced level and the results from studies employing physical methods integrated into these courses with meaning.

If the student has had an introductory inorganic course, the material in the first three chapters of this text is review. This material has been treated in many places, in varying degrees of thoroughness. The main reason for including it in this text is to indicate the level of proficiency needed in these areas to be able to read the ensuing chapters on physical methods. In the course described above, this material is assigned reading and only three lecture periods are spent on various aspects of the material. Special help sessions are held for those having difficulty with the material in the first three chapters.

Two references are used in the course described above to supplement the material in this text: *Chemical Applications of Group Theory* by F. A. Cotton (see Chapter 4 for the complete reference) and *Molecular Structure* by P. J. Wheatley. The former is employed as a reference for lectures on the use of symmetry considerations in ligand field and molecular orbital calculations and the latter as a reference for lectures on dipole moments, x-ray, electron, and neutron diffraction. In view of the length of this text and since the two above mentioned texts should be in the library of most inorganic chemists, this material has not been covered here. In the event that an inorganic chemist may not be concerned with molecular orbital calculations and group theory, Chapter 4 is presented as a brief treatment of symmetry and group theory. It contains the minimum amount of information on this subject necessary for an understanding of physical methods at the level presented in this text.

The level at which the fundamental principles pertaining to the physical methods are presented is introductory and the reader will be far from expert after digesting the material contained in this text. The approach will be qualitative and, where possible, simplified physical pictures will be presented to aid in understanding the essential principles underlying the application of these methods. The emphasis has been on clarity of presentation for a chemist who is not mathematically inclined. It should be recognized that this procedure often results in incompleteness and oversimplification. However, to do a thorough job would take at least a full semester on any one of these chapters.

The depth at which the topics have been treated is that which the author feels should be background information for a nonspecialist, for example, researchers in nonmetal chemistry should be expected to know at least as much about the electronic spectra of complexes as is presented here. Specialists will have to know considerably more. It is hoped that this treatment will motivate the inorganic chemist to read, and make it easier for him to understand, the more advanced treatments available for each of the spectroscopic methods. At the very least he will know which expert to call upon for help in the solution of his problem.

In addition to the treatment of the fundamental principles, each chapter on physical methods contains examples which describe the application of these methods to the solution of inorganic problems. These examples have been selected to demonstrate the different kinds of information that can be obtained by employing the various physical methods. The coverage is not encyclopedic and, where appropriate, the examples have been selected from the author's research program, for he is most familiar with these problems. Since reasoning by analogy has been used effectively by synthetic chemists for many years, it is hoped that the examples selected will suggest methods for the solution of a broad spectrum of inorganic problems.

In offering any graduate course, it is essential to update the material with recent references from the literature. For a course using this text this should involve mainly presenting new applications and covering different examples.

I would like to take this opportunity to thank several individuals for their assistance and encouragement. I am very grateful to my colleagues, Professors T. L. Brown and T. S. Piper, for several discussions pertaining to material in this text. Many contributions were made by graduate students in my research group who read the chapters and offered many important suggestions. I also consider myself very fortunate to have been associated with some very fine teachers, Professors Harry H. Sisler, John

C. Bailar, and Reynold C. Fuson. I would like to acknowledge my indebtedness to them for giving so freely of their time and helping me in many ways. Finally, I would like to express thanks to my parents, wife, and children for their encouragement and sacrifices.

RUSSELL S. DRAGO

PART I *Atomic and Molecular Structure*

BECAUSE a discussion of physical methods requires a qualitative background in quantum mechanical principles, a brief review of this material is presented in Part I. The background presented in Chapters 1 and 2 will not be rigorous, but will be what the author considers a minimum for a qualitative understanding of the physical methods discussed. The mathematical equations employed in this treatment are presented without proof. The level in these chapters is intended to be about the same as that in the Cotton and Wilkinson text.

This presentation will indicate the assumptions involved and general procedure utilized in arriving at many of the qualitative quantum mechanical concepts currently being used by inorganic chemists concerned with molecular structure, syntheses, and reaction mechanisms.

Contents

1 *Atomic Structure*

WAVE PROPERTIES OF ELECTRONS

As early as the 19th century, it was recognized that light has wave properties, as evidenced by diffraction from a grating. However, subsequent interpretation of the photoelectric effect* required an assignment of corpuscular behavior to light, thereby ascribing to radiation dual properties, those of matter and of waves. The following equations quantitatively describe this duality by relating both the mass and frequency, ν, of radiation to its energy, E:

$$E = \mathbf{h}\nu = mc^2 \tag{1-1}$$

where **h** is Planck's constant, $\mathbf{h}\nu$ is the energy of a photon whose mass equivalent is m, and c is the speed of light. Frequency is related to wavelength, λ, by equation (1-2):

$$\nu = c/\lambda \tag{1-2}$$

Combining (1-1) and (1-2) produces:

$$\lambda = \mathbf{h}/mc \tag{1-3}$$

In 1924, de Broglie proposed that particles, acknowledged to be matter, might also have wave properties. An equation, (1-4), similar to equation (1-3), relates the wavelength of these particles to their mass, m, and velocity, v:

$$v = \mathbf{h}/m\nu \tag{1-4}$$

*For a complete description of this experiment, see: L. Pauling, "General Chemistry," p. 167, W. H. Freeman, San Francisco, 1958; S. Glasstone, "Textbook of Physical Chemistry," pp. 13–34, Van Nostrand, New York, 1946.