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Preface

The physical and chemical applications of group theory are usually based on the geometric symmetries of atoms, molecules and crystals, as well as on the symmetries of the equations describing the properties and behaviour of the physical system under consideration. For a contemporary chemist, group theory is not only a key element of the quantum mechanical methods of investigating the electronic structure of matter—knowledge of symmetry and its group theoretical implications is also widely applied in analysing the results of practically all spectroscopic techniques currently employed in organic and inorganic chemistry. In fact, group theory has become a working tool of all present-day chemists concerned not only with the synthesis of new substances but also with their electronic structure and properties.

The present work is intended as a handbook on group theory for chemists and experimental physicists who use spectroscopy and require knowledge of the electronic structures of materials under investigation. The book will be readily understood by students with the background in physics and mathematics provided by an up-to-date degree course in chemistry. Many of the key concepts are introduced in a simple way as the material is presented. Indeed, the first three chapters, covering concepts of geometric symmetry and point groups, might well be assimilated at a pre-university level.

This book's salient features are as follows:

(1) The deductive approach characteristic of many books on mathematics and theoretical physics has been avoided, since it would have been a barrier to approaching the physical and chemical applications that are the main topic of this book. All the fundamental concepts are introduced by way of simple examples, relating to particular chemical and physical problems;

(2) Since neither chemists nor spectroscopists require proofs of the theorems used, very few are supplied. Most attention is paid to explanation of the

principal conclusions, their meaning and the ways in which they are to be used. Proofs are given only when they are necessary for a proper understanding of the principles involved.

(3) In view of the practical bias of the book, the main results of group theory are presented in all sections as procedures, making possible their systematic and step-by-step application. The same approach is adopted in providing a detailed description of the main tables [1–9], whose correct use constitutes a considerable part of the practical application of the theory.

(4) The book is constructed around examples that are analysed in detail. Each chapter contains problems whose solution develops practical skill and provides a valuable supplement to the material presented in the rest of the text.

The structure of this book is as follows. Chapters 1 and 2 give a detailed description of symmetry operations, enumeration of point groups and rules for the determination of molecular symmetry. In Chapter 3, using simple examples, the fundamental concepts of reducible and irreducible representations are introduced, and character tables are described. It is shown in Chapter 4 how the splitting of the central-ion energy levels in a coordination compound leads to the notion of the reduction of a representation. The description of many-electron ions (Chapter 5) is associated with the notions of the reduction of spherical group representations, the direct product of irreducible representations, and Wigner and Clebsch–Gordan coefficients. The projection operator technique, the use of spherical tensors in point groups, and the generation of basis functions are described in Chapter 6, which deals with the semi-empirical theory of the crystal field. The subsequent development of the projection operator technique and the notion of site symmetry are used in the directed valence theory (Chapter 7) and the molecular orbital method (Chapter 8). Chapter 9 is concerned with optical spectra. Here the notion of a selection rule is introduced, and the Wigner–Eckart theorem and the method of the effective dipole moment are described. Because of the wide application of laser spectroscopy in present-day chemistry, a detailed treatment of the selection rules and polarization dependence of two-photon spectra is given. The theory of double groups is considered in connection with the study of spin–orbit interaction (Chapters 10 and 11). The widely used method of invariants is described in Chapter 12 in connection with electron paramagnetic resonance. Through consideration of examples with a gradually increasing degree of sophistication, the analysis of electric field effects in paramagnetic resonance is presented in an easily understandable form. Problems involving polynuclear coordination compounds (Chapter 13) are solved using irreducible tensor methods and through group-theoretical classification of exchange multiplets. Finally, although Chapter 14 does not contain any new group-