



# Chemical Applications of Group Theory

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Second Edition

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# Chemical Applications of Group Theory

BOOKS BY F. ALBERT COTTON:

COTTON AND WILKINSON—ADVANCED INORGANIC  
CHEMISTRY, 2nd edition

To Diane

## Preface

In the seven years since the first edition of *Chemical Applications of Group Theory* was written, I have continued to teach a course along the lines of this book every other year. Steady, evolutionary change in the course finally led to a situation where the book and the course itself were no longer as closely related as they should be. I have, therefore, revised and augmented the book.

The new book has not lost the character or flavor of the old one—at least, I hope not. It aims to teach the use of symmetry arguments to the typical experimental chemist in a way that he will find meaningful and useful. At the same time I have tried to avoid that excessive and unnecessary superficiality (an unfortunate consequence of a misguided desire, evident in many books and articles on “theory for the chemist,” to shelter the poor chemist from the rigors of mathematics) which only leads, in the end, to incompetence and its attendant frustrations. Too brief or too superficial a tuition in the use of symmetry arguments is a waste of whatever time is devoted to it. I think that the subject needs and merits a student’s attention for the equivalent of a one-semester course. The student who masters this book will know *what* he is doing, *why* he is doing it, and *how* to do it. The range of subject matter is that which, in my judgment, the great majority of organic, inorganic, and physical chemists are likely to encounter in their daily research activity.

This book differs from its ancestor in three ways. First, the amount of illustrative and exercise material has been enormously increased. Since the demand for a *teaching textbook* in this field far exceeds what I had previously anticipated, I have tried now to equip the new edition with the pedagogic paraphernalia appropriate to meet this need.

Second, the treatment of certain subjects has been changed—improved, I hope—as a result of my continuing classroom experience. These improvements in presentation are neither extensions in coverage nor rigorizations; they are simply better ways of covering the ground. Such improvements will be found especially in Chapters 2 and 3, where the ideas of abstract group theory and the groups of highest symmetry are discussed.

Finally, new material and more rigorous methods have been introduced in

several places. The major examples are (1) the explicit presentation of projection operators, and (2) an outline of the  $F$  and  $G$  matrix treatment of molecular vibrations. Although projection operators may seem a *trifle* forbidding at the outset, their potency and convenience and the nearly universal relevance of the symmetry-adapted linear combinations (SALC's) of basis functions which they generate justify the effort of learning about them. The student who does so frees himself forever from the tyranny and uncertainty of "intuitive" and "seat-of-the-pants" approaches. A new chapter which develops and illustrates projection operators has therefore been added, and many changes in the subsequent exposition have necessarily been made.

Because chemists seem to have become increasingly interested in employing vibration spectra quantitatively—or at least semiquantitatively—to obtain information on bond strengths, it seemed mandatory to augment the previous treatment of molecular vibrations with a description of the efficient  $F$  and  $G$  matrix method for conducting vibrational analyses. The fact that the convenient projection operator method for setting up symmetry coordinates has also been introduced makes inclusion of this material particularly feasible and desirable.

In view of the enormous impact which symmetry-based rules concerning the stereochemistry of concerted addition and cyclization reactions (Woodward-Hoffman rules) have had in recent years a detailed introduction to this subject has been added.

In conclusion, it is my pleasant duty to thank a new generation of students for their assistance. Many have been those whose questions and criticisms have stimulated me to seek better ways to present the subject. I am especially grateful to Professor David L. Weaver, Drs. Marie D. LaPrade, Barry G. DeBoer and James Smith and to Messrs. J. G. Bullitt, J. R. Pipal, C. M. Lukehart and J. G. Norman, Jr. for their generous assistance in correcting proof. Finally, Miss Marilyn Milan, by the speed and excellence of her typing, did much to lighten the task of preparing a new manuscript.

F. ALBERT COTTON

*Cambridge, Massachusetts*  
*May 1970*

## Preface to the First Edition

This book is the outgrowth of a one-semester course which has been taught for several years at the Massachusetts Institute of Technology to seniors and graduate students in chemistry. The treatment of the subject matter is unpretentious in that I have not hesitated to be mathematically unsophisticated, occasionally unrigorous, or somewhat prolix, where I felt that this really helps to make the subject more meaningful and comprehensible for the average student. By the average student, I mean one who does not aspire to be a theoretician but who wants to have a feel for the strategy used by theoreticians in treating problems in which symmetry properties are important and to have a working knowledge of the more common and well-established techniques. I feel that the great power and beauty of symmetry methods, not to mention the prime importance in all fields of chemistry of the results they give, make it very worthwhile for all chemists to be acquainted with the basic principles and main applications of group theoretical methods.

Despite the fact that there seems to be a growing desire among chemists at large to acquire this knowledge, it is still true that only a very few, other than professional theoreticians, have done so. The reason is not hard to discover. There is, so far as I know, no book available which is not likely to strike some terror into the hearts of all but those with an innate love of apparently esoteric theory. It seemed to me that ideas of the sort developed in this book would not soon be assimilated by a wide community of chemists until they were presented in as unpretentious and down-to-earth a manner as possible. That is what I have tried to do here. I have attempted to make this the kind of book which "one can read in bed without a pencil," as my colleague, John Waugh, once aptly described another textbook which has found wide favor because of its down-to-earth character.\*

Perhaps the book may also serve as a first introduction for students intend-

\* This statement is actually (and intentionally) not applicable to parts of Chapter 3 where I have made no concessions to the reader who refuses to inspect steric models in conjunction with study of the text.

ing to do theoretical work, giving them some overall perspective before they aim for depth.

I am most grateful for help I have received from many quarters in writing this book. Over the years students in the course have offered much valuable criticism and advice. In checking the final draft and the proofs I have had very welcome and efficient assistance from Dr. A. B. Blake and Messrs. R. C. Elder, T. E. Haas, and J. T. Mague. I, of course assume sole responsibility for all remaining errors. Finally, I wish to thank Mrs Nancy Blake for expert secretarial assistance.

F. ALBERT COTTON

*Cambridge, Massachusetts*  
*January 1963*

Part I

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# Principles

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## Introduction

The experimental chemist in his daily work and thought is concerned with observing and, to as great an extent as possible, understanding and interpreting his observations on the nature of chemical compounds. Today, chemistry is a vast subject. In order to do thorough and productive experimental work, one must know so much descriptive chemistry and so much about experimental techniques that there is not time to be also a master of chemical theory. Theoretical work of profound and creative nature requires a vast training in mathematics and physics which is now the particular province of specialists. And yet, if one is to do more than merely *perform* experiments, one must have some theoretical framework for thought. In order to formulate experiments imaginatively and interpret them correctly, an understanding of the ideas provided by theory as to the behavior of molecules and other arrays of atoms is essential.

The problem in educating student chemists—and in educating ourselves—is to decide what kind of theory and how much of it is desirable. In other words, to what extent can the experimentalist afford to spend time on theoretical studies and at what point should he say, “Beyond this I have not the time or the inclination to go”? The answer to this question must of course vary with the special field of experimental work and with the individual. In some areas fairly advanced theory is indispensable. In others relatively little is really useful. For the most part, however, it seems fair to say that molecular quantum mechanics, that is, the theory of chemical bonding and molecular dynamics, is of general importance.

As we shall see in Chapter 5, the number and kinds of energy levels which an atom or molecule may have are rigorously and precisely determined by the symmetry of the molecule or of the environment of the atom. Thus, from symmetry considerations alone, we can always tell what the qualitative features of a problem must be. We shall know, without any quantitative calculations whatever, how many energy states there are and what interactions and transitions between them *may* occur. In other words, symmetry considerations *alone* can give us a complete and rigorous answer to the question

“What is possible and what is completely impossible?” Symmetry considerations alone *cannot*, however, tell us how likely it is that the possible things will actually take place. Symmetry can tell us that, *in principle*, two states of the system *must* differ in their energy, but only by computation or measurement can we determine how great the difference will be. Again, symmetry can tell us that only certain absorption bands in the electronic or vibrational spectrum of a molecule may occur. But to learn where they will occur and how great their intensity will be, calculations must be made.

Some illustrations of these statements may be helpful. Let us choose one illustration from each of the four major fields of application which are covered in Part II. In Chapter 7 the symmetry properties of molecular orbitals are discussed, with emphasis on the  $\pi$  molecular orbitals of unsaturated hydrocarbons, although other systems are also treated. It is shown how problems involving large numbers of orbitals and thus, potentially, high-order secular equations can be formulated so that symmetry considerations simplify these equations to the maximum extent possible. It is also shown how symmetry considerations permit the development of rules of great simplicity and generality (the so-called Woodward-Hoffman rules) governing certain concerted reactions. In Chapter 8, the method of constructing hybrid orbitals is explained, the molecular orbital approach to molecules of the  $AB_n$  type is outlined, and the relationship between the two treatments is explored.

In Chapter 9 the symmetry considerations underlying the main parts of the crystal and ligand field treatments of inner orbitals in complexes are developed. Finally, in Chapter 10, it is shown that by using symmetry considerations alone we may predict the number of vibrational fundamentals, their activities in the infrared and Raman, and the way in which the various bonds and interbond angles contribute to them for any molecule possessing some symmetry. The actual magnitudes of the frequencies depend on the interatomic forces in the molecule, and these cannot be predicted from symmetry properties. However, the technique of using symmetry restrictions to set up the equations required in calculations in their most amenable form (the *FG* matrix method) is presented in detail.

The main purpose of this book is to describe the methods by which we can extract the information which symmetry alone will provide. An understanding of this approach requires only a superficial knowledge of quantum mechanics. In several of the applications of symmetry methods, however, it would be artificial and stultifying to exclude religiously *all* quantitative considerations. Thus, in the chapter on molecular orbitals, it is natural to go a few steps beyond the procedure for determining the symmetries of the possible molecular orbitals and explain how the requisite linear combinations of atomic orbitals may be written down and how their energies may be estimated. It has