Lecture Notes in Chemistry

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Symmetry Properties of Molecules

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Introduction

The aim of the present article is to give a critical exposition of the theory of the symmetry properties of rigid and nonrigid molecules. Despite the fact that several accounts of the subject, both technical and didactic, are now available, and despite the extensive discussion of nonrigid molecule symmetry that has been going on since the classic papers of Hougen and Longuet-Higgins, there remains a need for a unifying survey of the problem. Previous treatments have tended to emphasize one or the other particular viewpoint at the expense of a broader view.

Renewed interest in the details of the symmetry classification of rotation-vibration states of highly symmetric (octahedral) molecules has led to a reexamination of the relation between conventional point group operations and permutations of identical nuclei in rigid molecules, together with a clarification of the fundamental role of the Eckart constraints and associated Eckart frame. As is shown below, analogous insights can also be obtained in the case of nonrigid molecule symmetry, where the Eckart-Sayvetz conditions provide a natural generalization of the Eckart constraints.

The importance of particular definitions of the 'molecule-fixed' frame in the theory of molecular symmetry can be better appreciated by examining their dynamical origin. Chapter 1 is therefore devoted to a description of the derivation of the usual Wilson-Howard-Watson form of the molecular Hamiltonian, together with its generalization to nonrigid molecules. Particular attention is given to the introduction of molecular models and use of the Eckart and Eckart-Sayvetz constraints. Some other approaches to nonrigid molecule dynamics are also examined.

After a brief review of the fundamental symmetries of the complete molecular Hamiltonian, Chapter 2 gives a treatment of the symmetry properties of rigid molecules based upon the static molecular model, following closely that of Louck and Galbraith. Both the interpretation of feasible nuclear permutations and the invariance group of the Eckart frame are discussed in detail. The important problem of a correct definition of the parity of rotational wavefunctions, and hence of molecular systems, is also considered. The formal theory is illustrated by application to the symmetry classification of states of diatomic molecules.

Chapter 3 then develops a unified approach to the symmetry properties of nonrigid molecules. The formalism is based explicitly upon the properties of the semi-rigid molecular model, and is a straightforward generalization of the theory given for rigid molecules in Chapter 2. A symmetry group of the semi-rigid model is defined, and identified as the nonrigid molecule group. Induced transformations of Born-Oppenheimer variables result in feasible permutations of nuclei. It is shown that previous approaches can thereby be encompassed within a unified scheme.

Having dealt with fundamental matters concerning the nature of symmetry operations in nonrigid molecules, attention is turned to the related technical problem of handling the large symmetry groups involved. An investigation of the structure of nonrigid molecule symmetry groups is clearly important for the practical implementation of the theory. The formalism developed in Chapter 3 is well suited to the recognition and exploitation of nontrivial structure in nonrigid molecule groups. As recognized early on by McIntosh and by Altmann, these groups can often be written as semi-direct products. The systematic theory of semi-direct products is briefly reviewed in an appendix, while Chapter 4 applies the theory to derive character tables for various nonrigid molecule groups. Recognition of semi-direct product structure allows a straightforward correlation to be made between the irreducible representations of rigid and nonrigid molecule symmetry groups. Such correlations can be exploited in the general theory of vibrations in nonrigid molecules, but the details of this application have yet to be worked out.

The appendices develop in detail several important topics touched upon in the text. A glossary of mathematical symbols and abbreviations has been included for the convenience of the reader.