



# MOLECULAR SPECTRA *and* MOLECULAR STRUCTURE

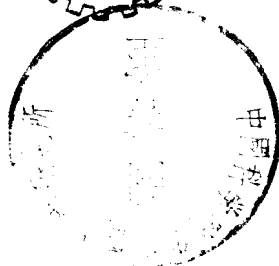
## II. INFRARED AND RAMAN SPECTRA OF POLYATOMIC MOLECULES

BY

GERHARD HERZBERG, F.R.S.C.

*National Research Council of Canada*

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## TO MY WIFE

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## PREFACE

The present volume represents the continuation of a series on Molecular Spectra and Molecular Structure which I started a number of years ago with a volume on Diatomic Molecules. It was originally intended to cover in the present book Infrared and Raman as well as visible and ultraviolet spectra of polyatomic molecules. However, when a first draft had been completed, it appeared that a division into two volumes was necessary. The first of these on Infrared and Raman Spectra is presented herewith. A final volume of the series on Electronic Spectra and Electronic Structure of Polyatomic Molecules is in preparation.

In writing this book I have constantly kept in mind the needs of both the beginner in the field and the more advanced student and research worker. For the benefit of the former I have spared no pains to make the explanations elementary and clear. Although a limited knowledge of elementary wave mechanics is assumed, difficult mathematical developments have been avoided wherever possible. When they were unavoidable they have been given in as straightforward and elementary a manner as possible and without too much regard for mathematical elegance. In particular no knowledge of group theory has been assumed. But, even though a knowledge of group theory is not assumed, many terms such as characters, representations, and so on, which occur frequently in the literature are explained and used wherever necessary.

Throughout it has been one of my main concerns to make the reader visualize clearly the significance and meaning of results of the theory. To assist in this purpose a large number of illustrations has been included, some of which have not before appeared in the literature.

In order to make the book comprehensive and useful for the more advanced student and the research worker, discussions of many special points have been added in small type. This material is not necessary for an understanding of the subsequent text in so far as it is printed in ordinary type. In addition, for the benefit of those carrying out research work in the field of Infrared and Raman spectra or related fields, a large number of tables has been included in which theoretical results are summarized or observed data are collected. These tables are as nearly up to date as possible under present conditions. All assignments and analyses have been critically reviewed and if necessary changed. All data are based on a uniform system of fundamental constants (see the Appendix) and wherever necessary have been recalculated to fit this uniform system. In numerous footnotes to these tables inconsistencies in the

literature have been pointed out or differing data and interpretations have been indicated.

Unfortunately no internationally accepted nomenclature exists for the spectra of polyatomic molecules, as it does for diatomic molecules. I have used a nomenclature as closely similar to that for diatomic molecules as possible.

The very detailed subject index at the end of the book includes also all symbols and quantum numbers, as well as all chemical compounds discussed in the book.

G. HERZBERG

SASKATOON, SASK.

November, 1944

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It gives me great pleasure to acknowledge the help and cooperation I have received from many persons during the preparation of this book. My sincere thanks are due to Professor R. N. H. Haslam who read the entire manuscript and proof and made innumerable suggestions for improving the presentation both with regard to the subject matter and to the style. I am very grateful to Professor K. J. MacCallum who read the entire galley proof with greatest care, made a number of valuable suggestions and spotted many errors. I am particularly indebted to my wife who prepared all the figures, calculated many of the tables and contributed many improvements of the text. Without her help many a figure and table that, I believe, has greatly increased the usefulness of the book would not have been included. Grateful thanks are also due to Professors J. Rud Nielsen, George Glockler and H. V. Houston for having assisted me by supplying valuable spectrograms for the illustrations (see the footnotes below the particular figures). Finally, I wish to express my appreciation to the administration of the University of Saskatchewan for providing assistance in the typing of the manuscript, the tracing of the figures and the checking of the proofs.

G. HERZBERG

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## INTRODUCTION

**General remarks.** The study of the spectra of diatomic molecules leads to precise information about their rotational, vibrational, and electronic energy levels, and from these energy levels the internuclear distances, the vibrational frequencies and force constants, the energies of dissociation, and other data concerning the structure of diatomic molecules may be determined accurately. (See the writer's *Molecular Spectra and Molecular Structure I. Diatomic Molecules*.<sup>1</sup>) Similar information about the structure of polyatomic molecules may be obtained from their spectra. The present volume deals with the information obtainable from the infrared and Raman spectra. A further volume is planned to deal with the information obtainable from visible and ultraviolet (electronic) band spectra. In the case of *polyatomic molecules* the situation is often greatly complicated by the fact that there are *several* internuclear distances, several force constants, several dissociation energies, and so on, which usually have to be determined simultaneously. To this complication of the structure corresponds in general a much greater complexity of the spectra of polyatomic as compared to diatomic molecules. Therefore it will not be practical to start, as can be done in the case of diatomic molecules, from the empirical regularities; instead we have first to develop the theory and then use it as a guide in interpreting the observed spectra. As in *Molecular Spectra I* we shall restrict our considerations mainly to the spectra of gases and vapors.

While one of the ultimate aims is to determine accurately all internuclear distances in polyatomic molecules, an important step forward in a specific case is made if it is possible to determine qualitatively the *shape of the molecule*, that is, the arrangement of the atoms (whether or not the molecule is linear, and so on). Frequently, qualitative features of the spectrum are sufficient to allow one to draw such conclusions, particularly if the molecule has some symmetry. Quite generally, molecules of different symmetry have qualitatively different spectra. This is of much greater importance for polyatomic molecules than for diatomic molecules since for the former many more different types of symmetry (point groups) are possible than for the latter, which display only the homonuclear and heteronuclear varieties. It is therefore imperative, before we begin our discussion of the spectra, to study the *symmetry properties* of polyatomic molecules.

**Symmetry elements and symmetry operations.** By symmetry of a molecule we mean the symmetry of the configuration of its nuclei or, in other words, of the nuclear frame. The position and the type of the nuclei determine this symmetry.

A molecule, just as any other geometrical figure or object, may have one or several *symmetry elements*, such as a plane of symmetry, a center of symmetry, an axis of symmetry. To each symmetry element corresponds a *symmetry operation*—that is, a coordinate transformation (reflection or rotation) that will produce a configuration of the nuclei indistinguishable from the original one. Let us consider the various possible symmetry elements in more detail.

<sup>1</sup> In the future this book [see reference (9) of the bibliography] will be referred to as *Molecular Spectra I*.

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(1) A *plane of symmetry*, usually designated by  $\sigma$ . By carrying out the corresponding symmetry operation (also called  $\sigma$ ), *reflection at the plane*, the molecule, if it has a plane of symmetry, is transformed into one that is indistinguishable from the original one since only equal atoms are exchanged. In brief: by the reflection the molecule is transformed into itself (or goes over into itself). In such a molecule having a plane of symmetry all atoms except those on the plane occur in pairs—to every atom on one side of the plane there is an equal atom at the other side in a corresponding position. As an example consider the (non-linear) molecule  $XY_2$  in which the two X—Y distances are equal (Fig. 1a). The plane perpendicular to the plane of the molecule and bisecting the angle  $YXY$  is a plane of symmetry; but also the plane  $YXY$  is a plane of symmetry. The molecule  $H_2O$  is an example (see p. 280). A molecule  $XY_3$  may have three planes of symmetry perpendicular to the plane formed by  $Y_3$  (see Fig. 1b) and if it is a plane molecule the plane of the molecule is also a plane of symmetry. The  $BF_3$  molecule is such a case (see p. 298).

(2) A *center of symmetry*, usually designated by  $i$ . By carrying out the corresponding symmetry operation (also called  $i$ ), *reflection at the center (inversion)*, a molecule having such a center is transformed into itself. In other words, if a line is drawn from one atom through the center and continued it will meet an equal atom at the same distance from the center but on the opposite side (if  $x$ ,  $y$ , and  $z$  are the coordinates of the one atom with respect to the center as origin,  $-x$ ,  $-y$ ,  $-z$  are the coordinates of the other equal atom). Examples are the molecules  $X_2Y_4$ ,  $X_2Y_2Z_2$ ,  $XY_2Z_2$  if they have the structures indicated in Fig. 1c, d, and e. A molecule can have only one center of symmetry. There may or may not be an atom at the center of symmetry (see the examples  $XY_2Z_2$  and  $X_2Y_2Z_2$ ). All other atoms occur in pairs.

(3) A *p-fold axis of symmetry*, usually designated by  $C_p$ , where  $p = 1, 2, 3, \dots$  ( $C$  stands for cyclic). By carrying out the corresponding symmetry operation, *rotation by an angle  $360^\circ/p$  about the axis*, a configuration indistinguishable from the original one is obtained. The same applies, of course, if this operation is carried out twice, three times, and so on in succession—that is, if the system is rotated by  $n(360/p)$  degrees where  $n = 1, 2, 3, \dots, p - 1$ . These operations are called  $C_p$ ,  $(C_p)^2$ ,  $(C_p)^3, \dots$ , respectively. If  $n = p$  the original configuration is obtained. Therefore it follows that to every atom not on the axis there are  $p - 1$  other equal atoms at the same distance from the axis, in the same plane and equally spaced about the axis. A *one-fold axis*, of course, means no symmetry at all. If a *two-fold axis*,  $C_2$ , is present, a rotation of  $180^\circ$  about the axis will transform the molecule into itself. In the molecule  $XY_2$  (Fig. 1a) the line bisecting the  $YXY$  angle is a two-fold axis. In the molecule  $X_2Y_4$  (Fig. 1c) there are three mutually perpendicular two-fold axes. In the molecule  $XY_3$ , if it is plane (Fig. 1b), there are three two-fold axes going through each one of the lines  $XY$ . The molecules  $X_2Y_2Z_2$  (Fig. 1d) and  $XY_2Z_2$  (Fig. 1e) each have a two-fold axis perpendicular to the plane of the molecule and  $XY_2Z_2$  has in addition two two-fold axes in the plane. In the case of a *three-fold axis*,  $C_3$ , a rotation by  $120^\circ$  transforms the molecule into itself. There must be at least one set of three equivalent atoms. An example is the molecule  $XY_3$  (Fig. 1b), even if X is not in the plane  $Y_3$ .  $NH_3$  represents such a case (see p. 294). The three-fold axis is of course perpendicular to the plane formed by the three Y atoms and goes through X. A molecule  $X_2Y_6$  is a further example (see Fig. 1f) if the six Y atoms are arranged in two groups that are symmetrical about the X—X axis (ethane,  $C_2H_6$ , see p. 342). Examples of molecules with four-, five-, and six-fold axes of symmetry

are given in Fig. 1g, h, i. The axes are perpendicular to the plane of the paper. A rotation by  $90^\circ$ ,  $72^\circ$ , and  $60^\circ$ , respectively, transforms the configurations shown into themselves. The  $C_6H_6$  molecule (see p. 363) represents an actual case of a

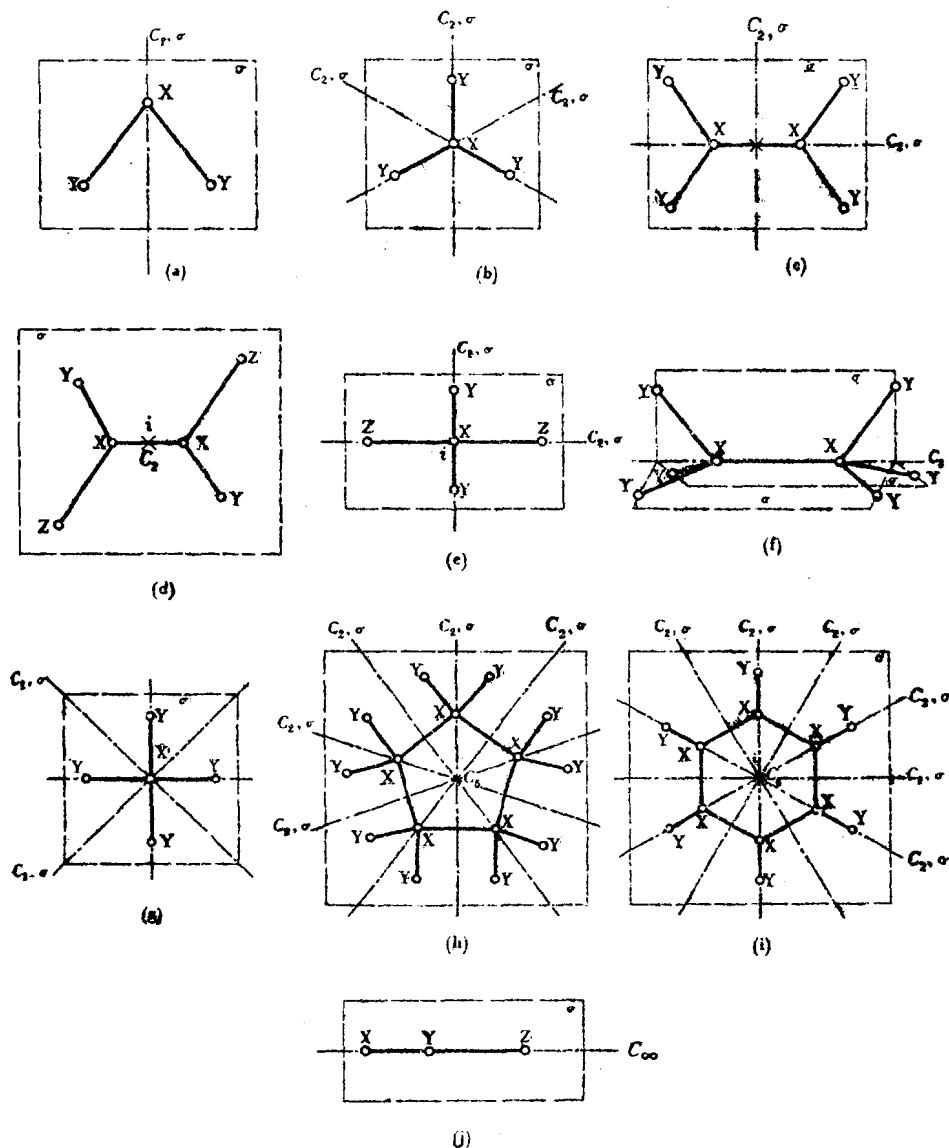


FIG. 1. Illustrations of symmetry elements in polyatomic molecules.—Planes of symmetry are indicated by broken lines (long dashes), axes of symmetry by dot-dash lines.

molecule having the structure shown in Fig. 1i. In principle, any higher-fold axis is possible; but in practice such axes are not of great importance except for the  $\infty$ -fold axes ( $C_\infty$ ), also called infinite axes of symmetry. In a molecule with an  $\infty$ -fold axis



a rotation of  $360^\circ/\infty$ , that is, of an infinitely small angle, and therefore also of any angle, will transform the molecular configuration into an indistinguishable one. Such molecules are the linear molecules in which all atoms lie on one straight line, namely the  $\infty$ -fold axis. Fig. 1k gives an example. HCN is an actual case (see p. 279). All diatomic molecules have such an  $\infty$ -fold axis.

(4) A *p*-fold rotation-reflection axis, usually designated by  $S_p$ . In a molecule having such an axis a rotation by  $360^\circ/p$  about the axis followed by a reflection at a plane perpendicular to the axis will transform the molecule into itself. For example, the molecule  $X_2Y_2Z_2$  (Fig. 1d) has a two-fold rotation-reflection axis ( $S_2$ ) in the line X—X and another one perpendicular to this line in the plane of the molecule. While a rotation by  $180^\circ$  about one of these axes does not transform the molecule into itself, a rotation followed by reflection at a plane perpendicular to the axis does. It is seen, however, that a two-fold rotation-reflection axis is always identical with a center of symmetry ( $S_2 = i$ ) since the same pairs of atoms are exchanged in the two operations. Any molecule that has a *p*-fold axis ( $C_p$ ) as well as a plane of symmetry  $\sigma_h$  perpendicular to this axis has of course also a *p*-fold rotation-reflection axis  $S_p$ . But only when *p* is odd does the existence of  $S_p$  necessarily imply the existence of  $C_p$  as well as  $\sigma_h$ . For example, the plane molecule  $XY_3$  in Fig. 1b has the symmetry element  $S_3$  as well as  $C_3$  and  $\sigma_h$ . Similarly the plane molecules  $XY_4$ ,  $X_5Y_{10}$ , and  $X_6Y_6$  in Fig. 1g, h, and i have the symmetry elements  $S_4$ ,  $C_4$ ,  $\sigma_h$ ;  $S_5$ ,  $C_5$ ,  $\sigma_h$ , and  $S_6$ ,  $C_6$ ,  $\sigma_h$ , respectively. But if in  $XY_4$  and  $X_6Y_6$  the Y atoms are alternately above and below the plane of the paper they would still have a four- and six-fold rotation-reflection axis,  $S_4$  and  $S_6$ , respectively, but no longer  $C_4$ ,  $C_6$  and  $\sigma_h$ , since neither rotation by  $360^\circ/4 = 90^\circ$  and  $360^\circ/6 = 60^\circ$  respectively nor reflection in the plane of the paper transforms the molecules into themselves.

(5) *The identity*, here designated by  $I$ .<sup>2</sup> This is a trivial symmetry element which all molecules have no matter how unsymmetrical they are. The corresponding symmetry operation is to leave the molecule unchanged. Naturally, then, the "new" configuration cannot be distinguished from the original one. The reason for the introduction of this symmetry element is a mathematical one. If it is included one can say quite generally that if two symmetry operations are carried out in succession the result is the same as that of one other possible symmetry operation of the molecule. For example, if in the molecule  $XY_3$  of Fig. 1b we label the Y atoms by  $Y_{(a)}$ ,  $Y_{(b)}$ , and  $Y_{(c)}$ , and carry out first a reflection at the plane  $\sigma_{(b)}$  and subsequently a clockwise rotation about  $C_3$  the same result is obtained as if we had carried out only a reflection at  $\sigma_{(c)}$ . If we carry out two reflections at  $\sigma_{(a)}$  in succession we obtain the original configuration: that is, two reflections at the same plane are equivalent to the identity  $I$ . Similarly two successive clockwise rotations about  $C_3$  are equivalent to one counter-clockwise rotation, while three successive rotations are equivalent to the identity. These examples may also be written in the form of equations:

$$\sigma_{(b)} \times C_3 = \sigma_{(c)}, \quad (\sigma_{(a)})^2 = I, \quad (C_3)^2 = (C_3)^{-1}, \quad (C_3)^3 = I.$$

Mathematically a number of elements (of any kind) such that the product of any two is again one of them is called a *group*.

All the above symmetry operations leave at least one point unchanged. In crystals, the operations of translation and screw motion, which leave no point unchanged, have also to be considered.

<sup>2</sup> In the literature it is usually designated by  $E$ . However, since  $E$  is used to indicate a degenerate species (see p. 108) and since both the symbols for identity and for a degenerate species frequently occur in one and the same table (see p. 110f.), we prefer to use  $I$  for identity.