Molecular Symmetry

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Preface

Symmetry is central to spectroscopy, chemical bonding theory and many other aspects of the molecular sciences. The idea of this book is to introduce the topic in a graduated way, from molecular structure, through point groups, leading into the powerful tools that group theory provides. Example models and applications are used at all stages to show how the sometimes abstract ideas are relevant to practical problems. It is designed to be a useful companion at all levels of undergraduate study and beyond.

Chapters 1 and 2 introduce the ideas of symmetry elements and operations for the description of molecular geometry; this sets up the required symbols through examples of particular molecules. Chapter 3 looks from a slightly different perspective, laying out all the sets of operations that are contained in the common point groups and discussing why only certain sets are possible. For all three chapters Appendices 1, 2 and 4 give some paper models that can be used for visualization of the shapes that are not easily built using a molecular modeling kit. These paper models will also be available from the website. The reader interested in the applications of symmetry, without too much detail of the background, may wish to skip over Chapter 3 on the first reading.

Chapters 4 and 5 introduce the concepts of group theory, which makes symmetry indispensible for understanding many areas of chemistry. This book concentrates on applications in vibrational spectroscopy and molecular orbital theory and so illustrative examples are drawn from these areas.

Chapter 6 covers applications in vibrational spectroscopy, specifically dealing with infra-red and Raman. The chapter explains how symmetry is used to rationalise experimental data to help determine the shape and structure of molecules. To do this some background on the physical origin of spectral bands and the role of symmetry in determining selection rules is given.

Finally, Chapter 7 deals with molecular orbital theory. Molecular orbital pictures are quite straightforward to produce with modern software and the results of such calculations are used as illustrations throughout. The aim of this chapter is to demystify how molecular orbitals are obtained from sets of atomic orbitals. Some fundamental concepts, such as the idea of electronegativity and the factors that influence the strength of bonding are reviewed.

Further appendices are linked to each chapter to provide a more detailed coverage of material such as spectroscopic selection rules, the mathematics of matrices and background quantum mechanics. The flow of the text will work without these, but curiosity should hopefully draw the reader to them.

Many people have helped me in the production of this book, most notably those that have reviewed various parts of the manuscript; Mike Hewlins, Peter Knowles, Massimo Mella, Jamie Platts and Edward Jeffery. They have been thorough in their reading of the text and frank in their comments on it, for which I am very grateful. Dai Hibbs, Bernard Richardson and Mike Coogan also provided some images from their own research, which has notably enlivened the presentation of the practical implications of symmetry. I have also taught the topic for a number of years with Simon Aldridge and Chris Morley, and have benefited greatly from their ideas.

David J. Willock
Cardiff, November 2008.

Powerpoint slides of all figures from this book, along with other supplementary material can be found on this book's webpage at www.wileyeurope.com/college/willock

1

Symmetry Elements and Operations

1.1 Introduction

Symmetry and group theory provide us with a formal method for the description of the geometry of objects by describing the patterns in their structure. In chemistry, it is a powerful method that underlies many apparently disparate phenomena. Symmetry allows us to describe accurately the types of bonding that can occur between atoms or groups of atoms in molecules. It also governs the transitions that may occur between energy levels in molecular systems, which in turn allows us to predict the absorption properties of molecules and, hence, their spectra.

This book will lay out the formal language used in the area, using illustrative examples of particular molecules throughout. We will then apply the ideas of symmetry to describe molecular structure and bonding in molecules and to consider the implications in spectroscopy.

Even in our surroundings we often look for symmetry, Figure 1.1 shows a picture of a wood engraving entitled *Fish, Vignette* made in 1955 by the artist M.C. Escher. In this work, the intertwined fish are shown set inside a hexagonal border. All of the fish illustrated have the same shape and they are designed to fit together perfectly. Six of the fish touch fins in the centre of the image and each of these has a partner with a fin on a corner of the hexagon. If we imagine rotating the picture by 60° about the central point, each fish would move to a new position and exactly replace a fish of opposite colour. This property gives the picture an attractive quality, but it also tells us that we could reconstruct the whole image by knowing the shape of the fish and the initial position of any pair, simply using six equivalent sections placed according to the rotation. At each step all we need do is remember to change the colours of the fish. The image is said to have rotational symmetry, and the techniques of this book provide a concise method of stating the rules for the construction of the picture.

Molecular Symmetry David J. Willock

Figure 1.1 *M.C. Escher's 'Fish, Vignette' Copyright 2008 The M.C. Escher Company-Holland. All rights reserved. www.mcescher.com.*

Figure 1.2 shows the ceiling of the Arab Room of Cardiff Castle. It is clear that the decorators have gone to a lot of trouble to use symmetry. In this case, a rotation of the image through 90° would interchange the positions of the windows; but, since they are identical, the pattern would appear unchanged. Four such rotations are possible, with the last returning each part of the ceiling to exactly its initial location. This image also has additional symmetry properties not possessed by Escher's fish. Imagine a line drawn horizontally across the image so that it passes through the centre of the left- and right-hand windows. The two sections of the image are now reflections of each other, with each feature in the upper part of the picture repeated in the lower half, as if reflected in a mirror standing

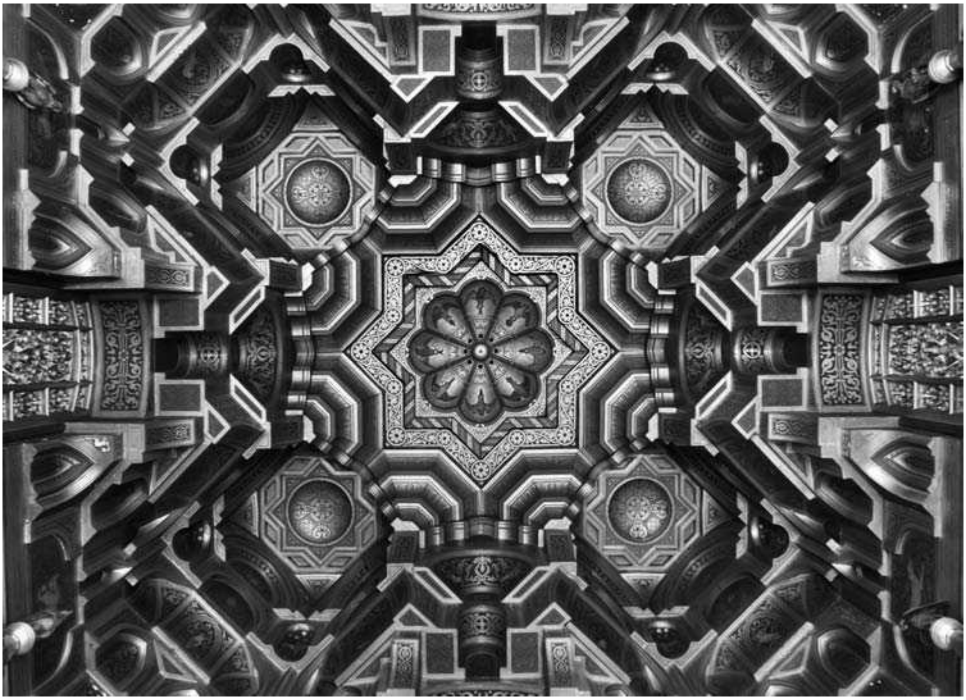

Figure 1.2 Arab Room ceiling, Cardiff Castle. Copyright: Cardiff Council.

perpendicular to the line. The mirror can be thought of as a plane of symmetry, and this image contains four such planes.

We can also look for planes of symmetry in nature. The fern frond shown in Figure 1.3 looks perfectly normal at first glance. However, on close inspection it can be seen that the left side of the leaf is just a reflection of the right-hand side on the surface of a pond. The picture is shown with the water surface vertical, which enhances the illusion. From half the leaf and its reflected image we can easily imagine the complete structure.

In chemistry, symmetry is not simply to do with beauty. It affects the properties of molecules and, in particular, influences the spectra we observe. For instance, most people would say that benzene is a ‘more’ symmetric molecule than fluorobenzene (Figure 1.4), since the fluorinated carbon should be different to the other carbon atoms. Figure 1.5 shows that this simple substitution has a profound affect on the infrared (IR) spectra of the two molecules.

The IR spectrum of benzene is very simple, showing only four main bands. On substitution with a single fluorine atom to give fluorobenzene, the spectrum becomes much more complex, with many more bands appearing between 400 and 1600 cm^{-1}.

We know that IR spectra are the result of radiation exciting vibrational modes in a molecule. The number of possible lines is related to the number of vibrational modes for the molecule in question. Since each atom in a molecule can move in three dimensions (X, Y, Z), both benzene and fluorobenzene will have a total of 36 degrees of freedom. For

Figure 1.3 *The frond of a fern imaged at the surface of a pond. Although we see a complete leaf, the left-hand side is actually a reflection. In fact, the segments (or pinna) on opposite sides of a frond are usually not quite mirror images of one another, as the points at which the pinna attach to the stem are staggered.*

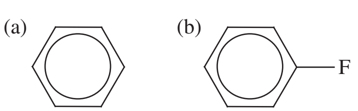

Figure 1.4 *The structures of (a) benzene and (b) fluorobenzene.*

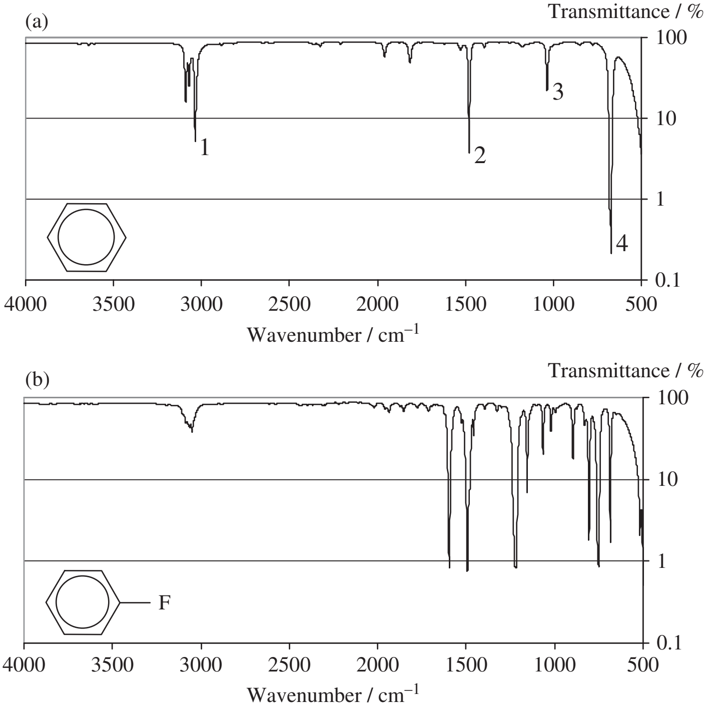

Figure 1.5 *The infra-red spectra of (a) benzene and (b) fluorobenzene. Note that the transmittance scale is logarithmic and the drop in the base line between around 700 and 500 cm^{-1} is a feature of the instrument. Data kindly provided by Dr Mike Coogan, School of Chemistry, Cardiff University.*

a nonlinear molecule there are six degrees of freedom associated with the motion of the molecule as a whole (three translations and three rotations), and these are not vibrations. So, we expect the number of vibrational modes for a molecule containing N atoms to be $3N - 6$. Both benzene and fluorobenzene have 12 atoms, and so have 30 vibrational modes. The fact that this does not result in 30 IR absorptions is a result of the symmetry of the molecules; and because benzene is ‘more’ symmetric than fluorobenzene, fewer modes of vibration are detected in the spectrum of benzene than in that of fluorobenzene.

To understand and quantify these differences in spectra we need more rigorous definitions of symmetry than simply saying benzene is ‘more’ symmetric than fluorobenzene. The geometric constructs of molecular symmetry help us to define a molecule’s symmetry and the use of group theory allows us to predict the number of absorption lines that will be observed.

To achieve this we look for features in the geometry of a molecule that give rise to its symmetry. The most easily recognized of these features, or *symmetry elements*, are rotational axes (lines of symmetry) and mirror planes (planes of symmetry). These will be discussed in the remaining sections of this chapter, along with the inversion centre, which is a point of symmetry. There are other symmetry elements and operations that are possible, and we will meet these in Chapter 2. The symmetry elements imply that there are symmetry operations: actions that can be carried out which appear to leave the molecule unchanged. If a molecule has multiple symmetry elements then there will be at least one point in space which lies within them all. For example, Figure 1.8 shows that all the rotation axes of ferrocene meet at the central point where the Fe atom is located. For this reason, the symmetry of molecules is often referred to as *point group symmetry*. The idea of this book is to introduce the ideas of point group symmetry and its application in vibrational spectroscopy and the molecular orbital (MO) description of chemical bonding.

In periodic systems (such as crystal structures), other symmetries exist to do with translation between equivalent molecules. See the Further Reading section at the end of this chapter for a book on this topic.

1.2 Symmetry Elements and Operations

1.2.1 Proper Rotations: C_n

The geometric properties of shapes that make them symmetric can be classified by their symmetry elements. The validity of a symmetry element can be checked by carrying out the corresponding operation and then comparing the object with the starting point. For example, imagine constructing an axis for a water molecule which runs through the oxygen atom, bisecting the H—O—H angle, with the axis in the plane of the molecule. This construction is shown in Figure 1.6, which also illustrates the result of rotating the molecule by 180° around the axis. After the rotation, we end up with a view of the water molecule identical to the starting point, so much so that if we had not labelled the hydrogen atoms it would be indistinguishable from the original. This result shows that the axis we have drawn is a symmetry element of the molecule and the act of rotating the molecule is the corresponding symmetry operation. The rotation operation also shows that the two hydrogen atoms in the water molecule are equivalent; if a symmetry operation can interchange two atoms, then the atoms must occupy identical chemical environments.

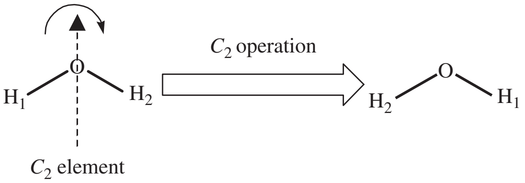

Figure 1.6 *The C_2 symmetry element of water and the result of the C_2 operation.*

Rotational elements and operations are labelled using a capital *C*. For rotations by 180° there are two positions of the molecule which appear identical, the starting point and the molecule after the rotation, so a subscript 2 is added to the label: C_2. This subscript is known as the *order* of the rotation axis.

To emphasize the difference between elements and operations further, consider the structure of ammonia shown in Figure 1.7. A C_3 axis is present: the symmetry element is a line running through the nitrogen atom and the centre of the triangle formed by the three hydrogen atoms.

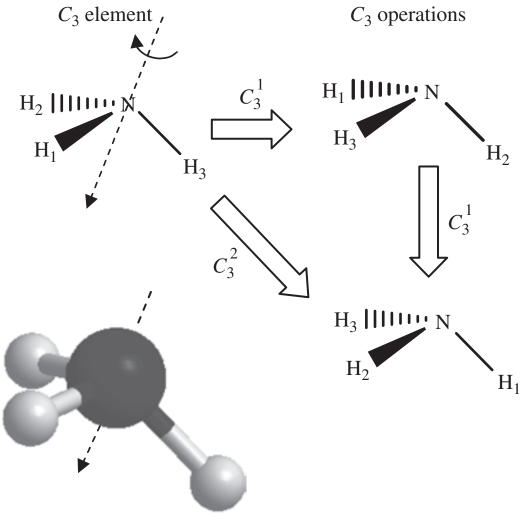

Figure 1.7 *The C_3 axis of ammonia and the corresponding operations. The lower image shows a ball-and-stick model of ammonia in roughly the same orientation as the chemical drawing pictures above. The superscript on the operations gives the number of rotations starting from the initial configuration.*

The C_3 axis actually has two symmetry operations associated with it, as can be seen in Figure 1.7: a rotation by 120° and a rotation by 240°. By convention, a rotation operation moves the atoms clockwise when looking down the axis direction. In the first step of the operation sequence shown in Figure 1.7, a clockwise rotation by 120° takes each hydrogen atom to the position of one of its neighbours. A second application of the operation takes each hydrogen atom to the original position of its other neighbour. To distinguish the two operations we add a superscript to indicate how many times the operation has been applied. So $C_3{}^2$ means that, starting from the original configuration, two successive rotations of 120° are applied, i.e. a total of 240°.

Molecules may contain more than one rotation axis, and those axes may have different orders. In this situation, the highest order axis is termed the *principal axis*. As an example, Figure 1.8 shows the structure of ferrocene (di-cyclopentadienyl iron(II)). This complex has a C_5 axis, which is the line joining the centres of the cyclopentadiene rings through the Fe centre (Figure 1.8a). In addition, there are five C_2 axes that run through the Fe atom parallel to the ring systems and perpendicular to the principal axis. These are best seen looking down the principal axis direction, as shown in Figure 1.8b. The C_2 rotation operations cause the exchange of the cyclopentadiene rings, whereas the C_5 operation simply rotates each cyclopentadiene ring around its centre. There is a convention that molecules are orientated so that the principal axis defines the vertical direction and that this is also aligned with the Cartesian Z-axis. This means that the vertical direction in Figure 1.8a runs up the page, whereas 'vertical' in Figure 1.8b is into the page.

The symmetry elements for a molecule are fixed in space: as we move the atoms under a given operation the symmetry elements are not shifted. For ferrocene, the atoms of the complex can be moved between any of five arrangements using the principal axis. In any

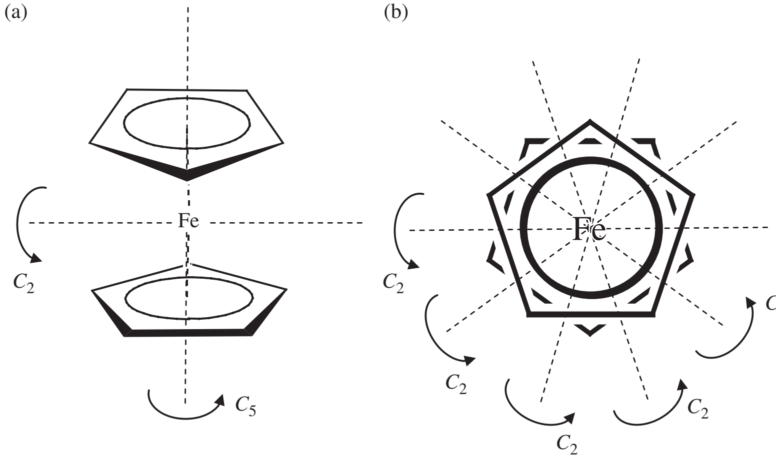

Figure 1.8 *The structure of ferrocene, illustrating (a) the* C_5 *axis and an example* C_2 *axis; (b) a plan view of the molecule showing all five* C_2 *axes.*

of these, each of the C_2 axes remains a symmetry element. The five C_2 axes meet at a point on the principal axis and they have an angular spacing of 72°, i.e. the angle of rotation for the C_5^1 operation. So, after a C_5^1 operation, the arrangement of the atoms around any of the C_2 axes is shifted to one of its neighbours; this implies that all the C_2 axes have an equivalent environment of atoms, and so they are treated as equivalent axes.

It is also possible for a molecule to contain axes of the same order that are not equivalent to one another. Figure 1.9 shows the structure of benzene, a molecule which has a C_6 principal axis perpendicular to the molecular plane. Each of the carbon atoms in benzene can be placed at any of the six positions by successive applications of the C_6 rotation and so all of the carbon atoms are in identical environments. Each C_6 operation rotates the molecule about its centre by 60°. Two C_6 operations, C_6^2, will give a rotation of 120°, which we have already seen corresponds to a C_3^1 rotation. We will usually use the lowest order alternative when listing symmetry operations, so that the C_6 axis has associated with it:

$$C_6^1, \text{ which is unique}$$

$$C_6^2 = C_3^1$$

$$C_6^3 = C_2$$

$$C_6^4 = C_3^2$$

$$C_6^5, \text{ which is unique.}$$

This means that the C_6 axis gives rise to two C_6 operations, two C_3 operations and a C_2 operation, and so there must always be C_3 and C_2 axes collinear with a C_6.

In the plane of the benzene molecule there are also C_2 axes that pass through opposite carbon atoms. The rotations about these axes must not be confused with the C_2 operation from the principal axis, and so the axes are labelled C_2', as shown in Figure 1.9. The C_2'

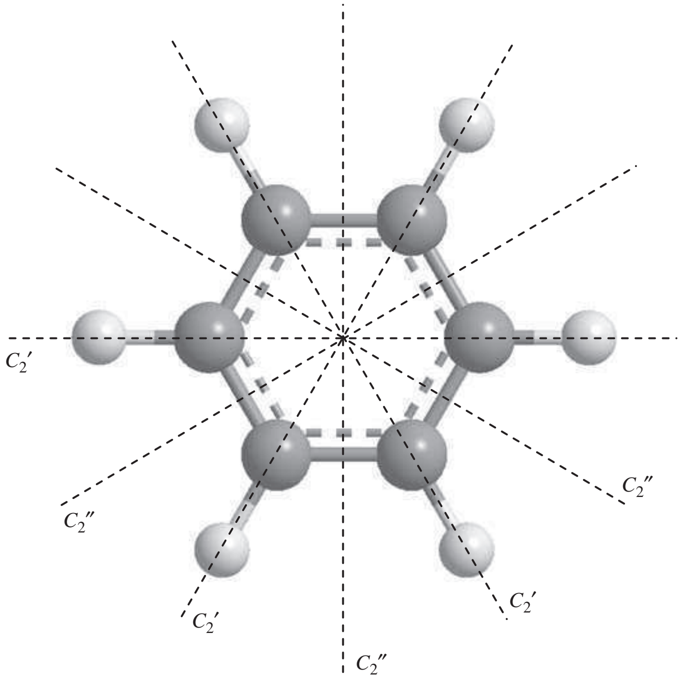

Figure 1.9 *The structure of benzene showing the two sets of three C_2 axes in the molecular plane; the principal C_6 axis is perpendicular to the plane and passes through the centre of the molecule at the crossing point of the C_2' and C_2'' axes.*

axes are 60° apart, and so successive C_6 operations will alter which particular atoms are on which C_2' axes. However, each C_2' axis always contains two C and two H atoms, and so the three axes are equivalent. There is a second set of axes which join opposite bond centres, and these are labelled C_2'' to distinguish them from the C_2' axes. We can tell that the C_2'' and C_2' axes form distinct sets both from their chemical environments (one set join bond centres and one set join atoms) and from the fact that the C_6 operations never interchange a bond centre and an atom position. We have made the choice that the axes joining opposite atoms should be labelled C_2' and that those between the bond centres that do not contain any atoms in the symmetry element are labelled C_2''.

A further possibility for multiple rotation axes is to have more than one candidate for the principal axis. For example, the highest order axis for ethene is a twofold axis, but there are three nonequivalent C_2 axes, as shown in Figure 1.10. The choice of principal axis is now arbitrary, and it is usual to assign each axis a Cartesian label (X,Y or Z) so that they can be referred to explicitly.

1.2.2 The Plane of Symmetry: σ

If a plane exists for which reflection of each atom in a molecule gives an indistinguishable configuration, the molecule is said to have a plane of symmetry, which is given the label σ.

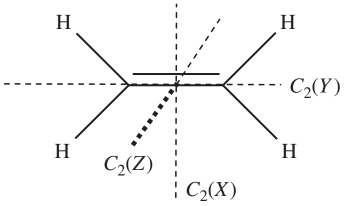

Figure 1.10 The structure of ethene showing three distinct C_2 axes.

The symmetry element is the plane itself, since all points in the plane remain unchanged by the operation of reflection. For the water molecule there are two planes of symmetry, as shown in Figure 1.11. These are distinguished by labelling the plane perpendicular to the molecule σ and the plane of the molecule itself σ'. The C_2 axis of water is the only axis, and so it is also the principal axis defining the vertical direction. This means that the mirror planes are standing vertically, and so a subscript is added to remind us of this, giving σ_v and σ_v'.

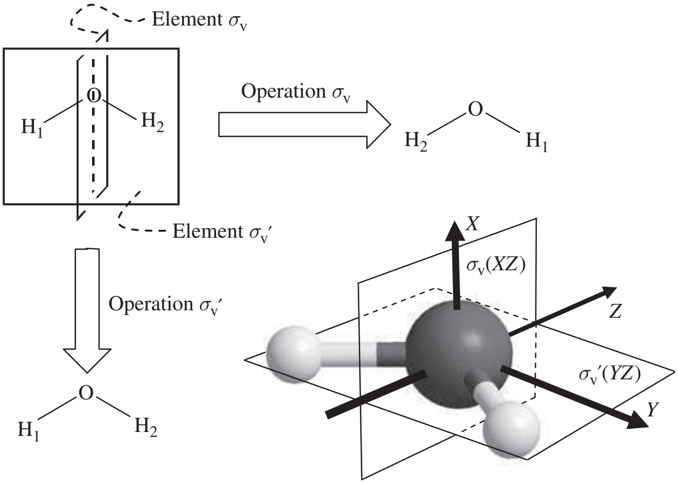

Figure 1.11 The two mirror planes for the H_2O molecule showing the difference between σ_v and σ_v' operations. The inset shows the relationship between the mirror planes and a reference axis system.

Which plane is which is a somewhat arbitrary choice; however, the designation described here is quite widely used and is based on the alignment of the symmetry planes with the Cartesian axis system. Figure 1.11 shows that the two planes intersect in the line of the C_2 axis we identified earlier; the planes of symmetry are said to *contain* the rotational axis. The principal axis gives us the Cartesian Z-direction, which, in this case, is in the molecular plane. We also take Y to be in the molecular plane, and so X must be perpendicular to it. The full labels for the mirror planes of water become $\sigma_v(XZ)$ and $\sigma_v'(YZ)$, but it is common to omit the Cartesian parts of these labels.

Some molecules have multiple axes and mirror planes. For example, boron trifluoride (BF_3) is a planar molecule with a C_3 axis perpendicular to the plane and passing through the boron atom, as shown in Figure 1.12. However, there are also C_2 axes in the plane of the molecule which run along each of the B—F bonds.

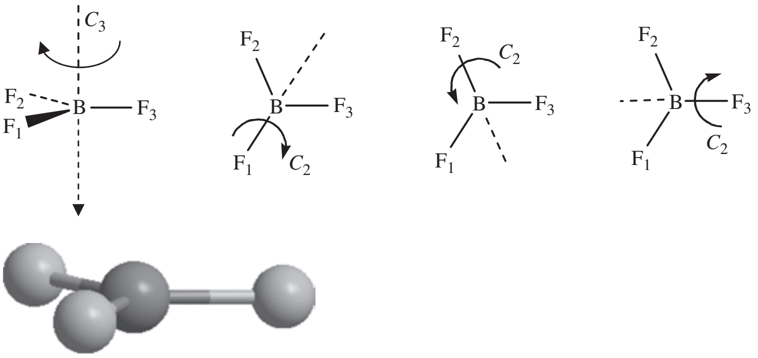

Figure 1.12 *The rotational symmetry elements of BF_3. To the left is a flying wedge drawing looking from the side of the molecule in the same orientation as the perspective ball-and-stick model below it. The C_2 axes are shown with the molecule viewed looking down on the molecular plane.*

The highest order axis present is taken to be the principal axis and gives us the 'vertical' direction. So, BF_3 has three vertical mirror planes, each of which contains a B—F bond; an example of a vertical mirror plane in BF_3 is shown in Figure 1.13a. The C_3 operations will move the fluorine atoms between these planes, but each will always contain one fluorine atom and reflect the other two into one another. So, although there are three vertical planes, they are identical, requiring only the single label σ_v, and there are three σ_v operations. The plane of the molecule for BF_3 is also a plane of symmetry, as illustrated in Figure 1.13b. This contains all three of the B—F bonds, but not the principal axis. In fact, the plane is perpendicular to the C_3 axis, i.e. the plane is horizontal and so is labelled σ_h.

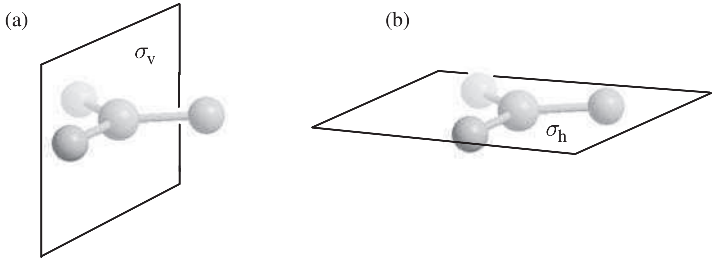

Figure 1.13 *The two types of symmetry plane for BF_3: (a) an example of a vertical plane; (b) the horizontal plane σ_h.*

More complex collections of rotation axes and planes require the definition of an additional type of mirror plane. To illustrate this we can return to the case of benzene. In Figure 1.9 we showed that there are two sets of rotation axes in the molecular plane of benzene and labelled these C_2', for the axes passing through opposite atoms, and C_2'', for the axes passing through opposite bonds. There are also two sets of three mirror planes which each contain the principal axis and either a C_2' or C_2'' axis. Both types of mirror plane are vertical, but we need to distinguish them from one another. Each of the first set contain a C_2' axis and these are labelled σ_v. Planes in the second set are vertical, but are also in between the C_2' axes; this sort of vertical plane is called a dihedral plane and is given the symbol σ_d. The relationship of the σ_v and σ_d planes to the C_2' axes in benzene is shown in Figure 1.14.

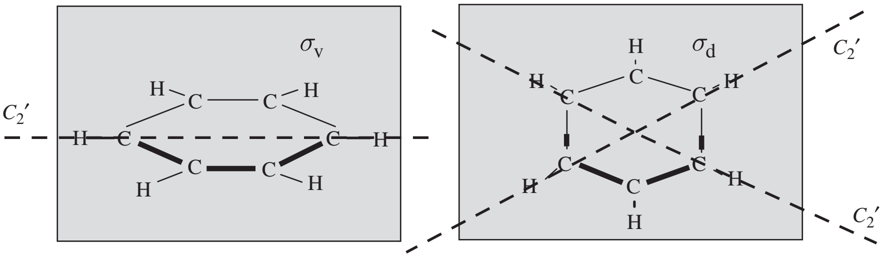

Figure 1.14 *The vertical (σ_v) and dihedral (σ_d) planes of benzene and their relation to the C_2' axes. The bonds in front of the planes have been thickened.*

The dihedral plane has been introduced using an example where there is more than one type of vertical plane. However, σ_d planes are defined by their relationship to the horizontal C_2' axes; this means that molecules do exist in which σ_d is the only type of vertical plane.

An example of a molecule with σ_d but no σ_v planes is ethane in its staggered conformation. The principal axis in this case is a C_3 axis running along the C—C bond, and the molecule is shown orientated vertically in Figure 1.15a. The illustrated dihedral plane of symmetry contains the two carbon atoms, H_1 and H_6. There are horizontal C_2 axes passing through the C—C bond centre, but they are not in the mirror planes, as can be seen from a Newman projection along the principal axis in Figure 1.15b. Figure 1.15a and b shows two of the three C_2 axes: one rotates the molecule so that H_1 and H_4 interchange, while with the other H_1 and H_5 are swapped. The mirror plane in the diagram bisects the angle between these two axes and so is labelled σ_d. The σ_d operation would swap H_5 with H_4 and H_2 with H_3. There are three C_2 axes for ethane and, correspondingly, there are three σ_d planes.

The dihedral plane also occurs when there is more than one type of vertical mirror plane even if there are no horizontal C_2 axes. Figure 1.15c shows a metal complex with four equivalent equatorial ligands. The internal structure of these ligands L will be assumed not to affect the symmetry properties of the complex. The complex has a principal axis of order 4, so there is a vertical C_2 axis ($C_4^2 = C_2$). However, the two axial halogen atoms are different (Cl and Br) and so there are no horizontal C_2 axes. There are two mirror planes that each contain two *trans*-L ligands; these are labelled σ_v. The figure also shows one

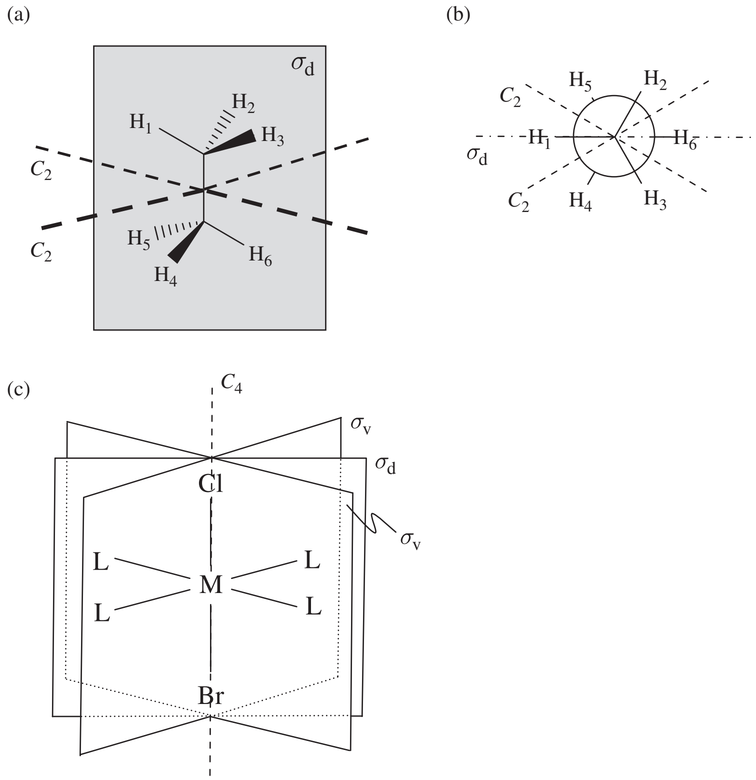

Figure 1.15 *(a) An example dihedral plane σ_d for ethane in the staggered conformation and the two C_2 axes it lies between. (b) A Newman projection view showing the σ_d plane bisects the angle between the C_2 axes. (c) An example metal complex with no horizontal C_2 axes.*

example of another pair of planes that only contain M and the halogen atoms, and reflect *cis*-L ligands into one another. This plane bisects the angle between the two σ_v planes and so is labelled σ_d. The other σ_d plane would be perpendicular to the page.

Problem 1.1: In Section 1.2.3, Figure 1.19 shows the structure of the square planar complex $[PtCl_4]^{2-}$, find and label all the proper rotation axes and planes of symmetry for this structure. Remember to consider the full set of operations for high-order axes.

1.2.3 The Inversion Centre: *i*

So far, we have looked at symmetry operations for which the corresponding elements are the plane (a reflection operation) and a line (the rotation operation). The next symmetry element is the *inversion centre,* labelled *i.* The operation of inversion leaves only a single point unchanged, and so it is often referred to as a centre, or point, of symmetry. The inversion operation is illustrated in Figure 1.16 with two pairs of points, A, A′ and B, B′, which represent atoms in a hypothetical molecule. For each pair, the points are equidistant

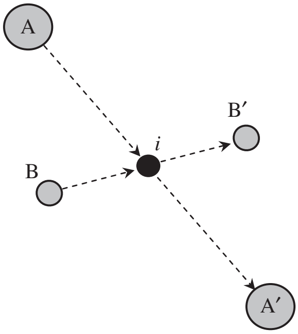

Figure 1.16 *An illustration of the inversion centre operation. Under inversion, each point in a molecule is moved through the inversion centre to a position on the opposite side of the centre and at the same distance from the centre as the original point. In this case, atom pairs A—A′ and B—B′ are linked by the inversion centre i.*

from the inversion centre, and the lines between A and A′ and between B and B′ include *i*. To perform the inversion operation we imagine moving each atom in the molecule along a straight line to the inversion centre and then moving them along the same line beyond the centre to a distance equivalent to their starting point. For the hypothetical example, A and A′ would be interchanged, as would B and B′. If the inversion operation result is indistinguishable from the initial geometry, then the molecule has an inversion centre. The inversion operation can be thought of as similar to the reflection operation, but referred to a point rather than a plane.

In two dimensions, we can illustrate the difference between the inversion centre and a simple reflection using lens optics. In Figure 1.17a, a drinking glass is used as a cylindrical lens behind which a piece of paper carries the word ‘Reflect’ and is backlit in the set-up shown in Figure 1.17a. When viewed through the glass at a distance beyond the focus of the cylindrical lens the word is reversed, as shown in Figure 1.17b. This result is the same as if we had reflected the word through a plane perpendicular to the paper. The optical quality of the drinking glass is low, so distortion of the letters is also apparent. If we use a small pocket lens in a similar set-up (Figure 1.17c), then the result is not only the reversal of the word, but also the top and bottom of the letters are swapped over, as shown in Figure 1.17d. Figure 1.18 shows ray diagrams of the optics for the cylindrical and normal lens. In the cylindrical case (Figure 1.18a) the rays from the object (the word ‘Reflect’ in this case) are bought to a line focus because the lens has no curvature in the vertical direction. When the viewer is placed beyond the focus, rays from the left of the object appear to the right and *vice versa*, leading to the observed reversal. For the hand lens (Figure 1.18b) the focus is a point and so, in addition to left and right reversing, top and bottom are also swapped.

These are two-dimensional examples, because the words are planar; in fact, the third dimension, perpendicular to the paper, is used to carry out the operation using the optics. A square planar species, such as the $[PtCl_4]^{2-}$ ion shown in Figure 1.19a, has a centre of inversion, and the operation seems to act much like our optics example. On inversion, the chlorine atoms *trans* to each other in the original molecule are interchanged.

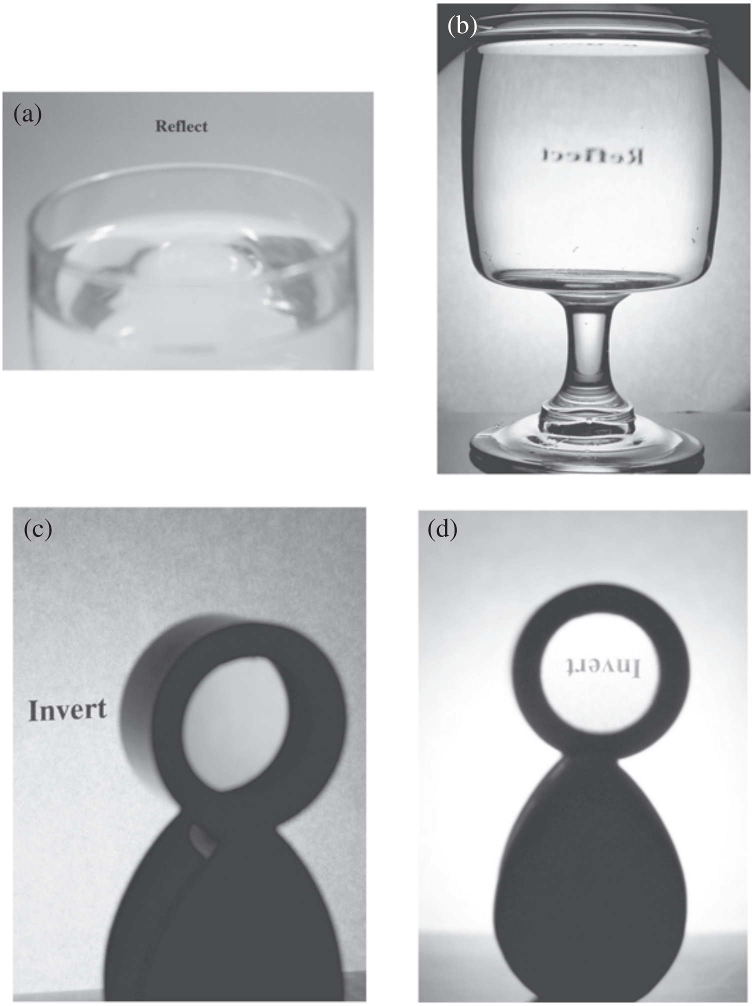

Figure 1.17 *A two-dimensional illustration of the difference between reflection and inversion operations. (a) The set-up used and (b) the result of viewing the word 'Reflect' through a cylindrical lens. (c) The set-up and (d) result of viewing the word 'invert' beyond the focal point of a hand lens.*

However, in three dimensions the inversion operation will swap left with right, top with bottom and back with front simultaneously. For this to be a symmetry operation which leaves the molecule unchanged, the centre of inversion symmetry element will always be at the centre of the structure. So the Pt atom in $[PtCl_4]^{2-}$ remains in the same position after the operation. Figure 1.19b shows the three-dimensional example SF_6; here, the central S atom is on the inversion centre and so remains in the same place after inversion, but, with the F atoms labelled, it can be seen that atoms *trans* to one another are again swapped over. The molecular models of these two structures in Figure 1.19c should help to visualize the process.

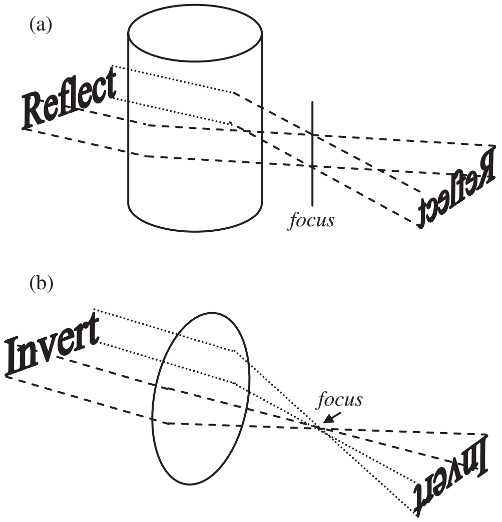

Figure 1.18 Ray tracing diagrams for (a) the reflection and (b) the inversion operations presented in Figure 1.17.

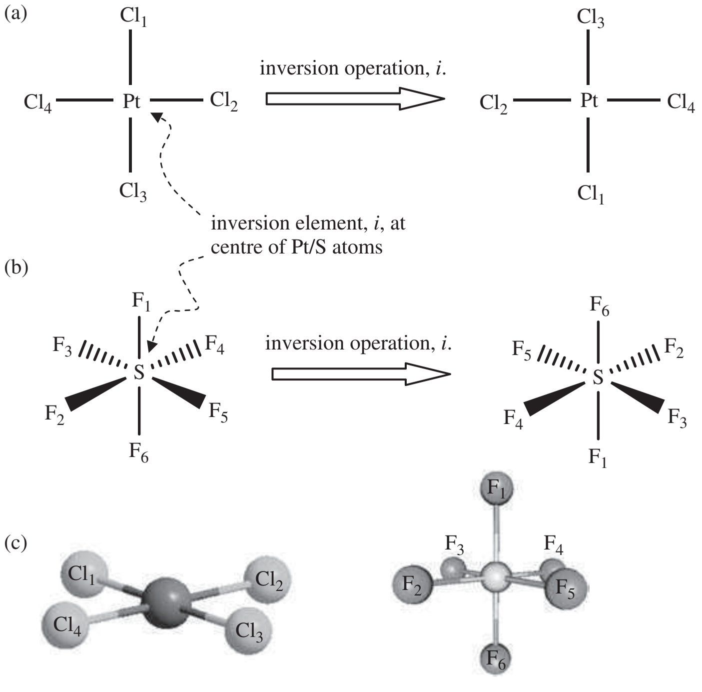

Figure 1.19 The inversion element and operation for (a) a chemical complex $[PtCl_4]^{2-}$ and (b) the molecule SF_6. (c) Ball and stick representations of the two structures used in (a) and (b).