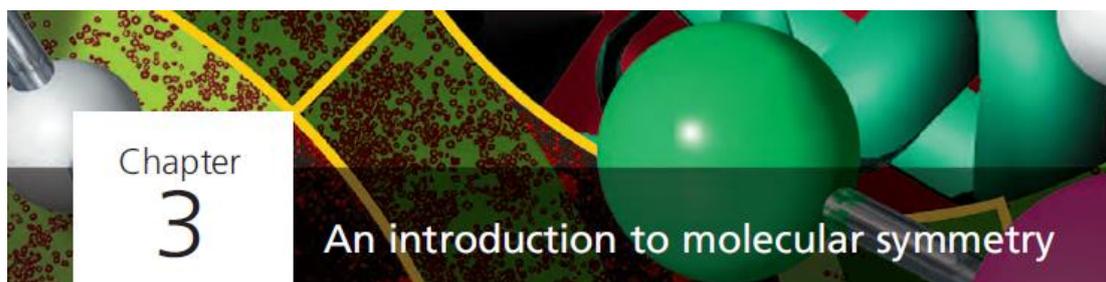


## 2 GROUP THEORY AND ITS APPLICATIONS



### TOPICS

- Symmetry operators and symmetry elements
- Point groups
- An introduction to character tables
- Infrared spectroscopy
- Chiral molecules

### 3.1 Introduction

Within chemistry, symmetry is important both at a molecular level and within crystalline systems, and an understanding of symmetry is essential in discussions of molecular spectroscopy and calculations of molecular properties. A discussion of *crystal symmetry* is not appropriate in this book, and we introduce only *molecular symmetry*. For qualitative purposes, it is sufficient to refer to the shape of a molecule using terms such as tetrahedral, octahedral or square planar. However, the common use of these descriptors is not always precise, e.g. consider the structures of  $\text{BF}_3$ , 3.1, and  $\text{BF}_2\text{H}$ , 3.2, both of which are planar. A molecule of  $\text{BF}_3$  is correctly described as being trigonal planar, since its symmetry properties are fully consistent with this description; all the F–B–F bond angles are  $120^\circ$  and the B–F bond distances are all identical (131 pm). It is correct to say that the boron centre in  $\text{BF}_2\text{H}$ , 3.2, is in a *pseudo-trigonal planar* environment but the molecular symmetry properties are not the same as those of  $\text{BF}_3$ . The F–B–F bond angle in  $\text{BF}_2\text{H}$  is smaller than the two H–B–F angles, and the B–H bond is shorter (119 pm) than the B–F bonds (131 pm).



The descriptor *symmetrical* implies that a species possesses a number of indistinguishable configurations. When structure 3.1 is rotated in the plane of the paper through  $120^\circ$ ,

the resulting structure is indistinguishable from the first; another  $120^\circ$  rotation results in a third indistinguishable molecular orientation (Figure 3.1). This is *not* true if we carry out the same rotational operations on  $\text{BF}_2\text{H}$ .

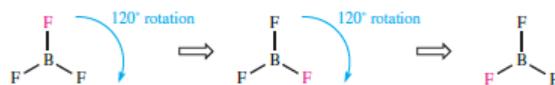
*Group theory* is the mathematical treatment of symmetry. In this chapter, we introduce the fundamental language of group theory (*symmetry operator*, *symmetry element*, *point group* and *character table*). The chapter does not set out to give a comprehensive survey of molecular symmetry, but rather to introduce some common terminology and its meaning. We include in this chapter an introduction to the vibrational spectra of simple inorganic molecules, with an emphasis on using this technique to distinguish between possible structures for  $\text{XY}_2$ ,  $\text{XY}_3$  and  $\text{XY}_4$  molecules. Complete normal coordinate analysis of such species is beyond the remit of this book.

### 3.2 Symmetry operations and symmetry elements

In Figure 3.1, we applied  $120^\circ$  rotations to  $\text{BF}_3$  and saw that each rotation generated a representation of the molecule that was indistinguishable from the first. Each rotation is an example of a *symmetry operation*.

A *symmetry operation* is an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on, the original configuration.

The rotations described in Figure 3.1 were performed about an axis perpendicular to the plane of the paper and



**Fig. 3.1** Rotation of the trigonal planar  $\text{BF}_3$  molecule through  $120^\circ$  generates a representation of the structure that is indistinguishable from the first; one F atom is marked in red simply as a label. A second  $120^\circ$  rotation gives another indistinguishable structural representation.

passing through the boron atom; the axis is an example of a *symmetry element*.

A symmetry operation is carried out with respect to points, lines or planes, the latter being the *symmetry elements*.

### Rotation about an $n$ -fold axis of symmetry

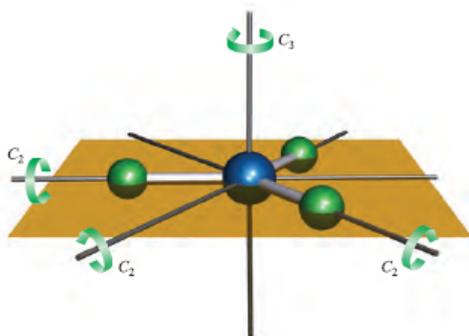
The symmetry operation of rotation about an  $n$ -fold axis (the symmetry element) is denoted by the symbol  $C_n$ , in which the angle of rotation is  $\frac{360^\circ}{n}$ ;  $n$  is an integer, e.g. 2, 3 or 4. Applying this notation to the  $\text{BF}_3$  molecule in Figure 3.1 gives a value of  $n = 3$  (equation 3.1), and therefore we say that the  $\text{BF}_3$  molecule contains a  $C_3$  *rotation axis*; in this case, the axis lies perpendicular to the plane containing the molecule.

$$\text{Angle of rotation} = 120^\circ = \frac{360^\circ}{n} \quad (3.1)$$

In addition,  $\text{BF}_3$  also contains three 2-fold ( $C_2$ ) rotation axes, each coincident with a B–F bond as shown in Figure 3.2.

If a molecule possesses more than one type of  $n$ -axis, the axis of highest value of  $n$  is called the *principal axis*; it is the axis of *highest molecular symmetry*. For example, in  $\text{BF}_3$ , the  $C_3$  axis is the principal axis.

In some molecules, rotation axes of lower orders than the principal axis may be coincident with the principal axis. For



**Fig. 3.2** The 3-fold ( $C_3$ ) and three 2-fold ( $C_2$ ) axes of symmetry possessed by the trigonal planar  $\text{BF}_3$  molecule.

example, in square planar  $\text{XeF}_4$ , the principal axis is a  $C_4$  axis but this also coincides with a  $C_2$  axis (see Figure 3.4).

Where a molecule contains more than one type of  $C_n$  axis, they are distinguished by using prime marks, e.g.  $C_2$ ,  $C_2'$  and  $C_2''$ . We return to this in the discussion of  $\text{XeF}_4$  (see Figure 3.4).

### Self-study exercises

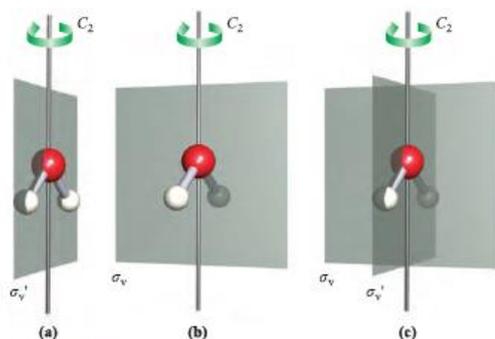
- Each of the following contains a 6-membered ring: benzene, borazine (see Figure 12.19), pyridine and  $\text{S}_6$  (see Box 1.1). Explain why only benzene contains a 6-fold principal rotation axis.
- Among the following, why does only  $\text{XeF}_4$  contain a 4-fold principal rotation axis:  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $[\text{BF}_4]^-$  and  $\text{XeF}_4$ ?
- Draw the structure of  $[\text{XeF}_5]^-$ . On the diagram, mark the  $C_5$  axis. The molecule contains five  $C_2$  axes. Where are these axes? [Ans. for structure, see worked example 1.14]
- Look at the structure of  $\text{B}_5\text{H}_9$  in Figure 12.23b. Where is the  $C_4$  axis in this molecule?

### Reflection through a plane of symmetry (mirror plane)

If reflection of all parts of a molecule through a plane produces an indistinguishable configuration, the plane is a *plane of symmetry*; the symmetry operation is one of reflection and the symmetry element is the mirror plane (denoted by  $\sigma$ ). For  $\text{BF}_3$ , the plane containing the molecular framework (the yellow plane shown in Figure 3.2) is a *mirror plane*. In this case, the plane lies perpendicular to the vertical principal axis and is denoted by the symbol  $\sigma_h$ .

The framework of atoms in a linear, bent or planar molecule can always be drawn in a plane, but this plane can be labelled  $\sigma_h$  *only* if the molecule possesses a  $C_n$  axis *perpendicular* to the plane. If the plane *contains* the principal axis, it is labelled  $\sigma_v$ . Consider the  $\text{H}_2\text{O}$  molecule. This possesses a  $C_2$  axis (Figure 3.3) but it also contains *two* mirror planes, one containing the  $\text{H}_2\text{O}$  framework, and one perpendicular to it. Each plane contains the principal axis of rotation and so may be denoted as  $\sigma_v$  but in order to distinguish between them, we use the notations  $\sigma_v$  and  $\sigma_v'$ . The  $\sigma_v$  label refers to the plane that bisects the H–O–H bond angle and the  $\sigma_v'$  label refers to the plane in which the molecule lies.

A special type of  $\sigma$  plane which contains the principal rotation axis, but which bisects the angle between two



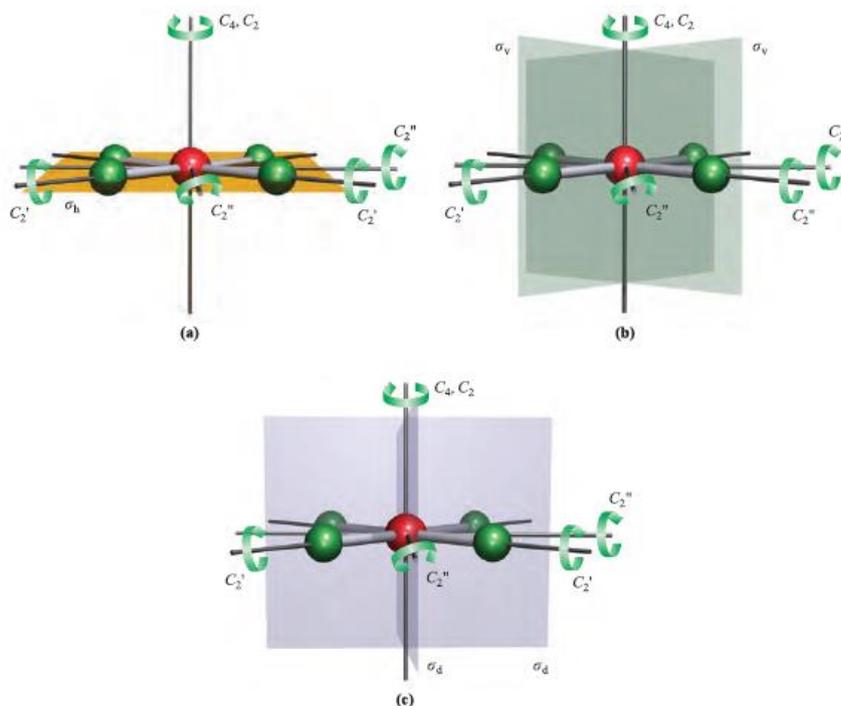
**Fig. 3.3** The  $\text{H}_2\text{O}$  molecule possesses one  $C_2$  axis and two mirror planes. (a) The  $C_2$  axis and the plane of symmetry that contains the  $\text{H}_2\text{O}$  molecule. (b) The  $C_2$  axis and the plane of symmetry that is perpendicular to the plane of the  $\text{H}_2\text{O}$  molecule. (c) Planes of symmetry in a molecule are often shown together on one diagram; this representation for  $\text{H}_2\text{O}$  combines diagrams (a) and (b).

adjacent 2-fold axes, is labelled  $\sigma_d$ . A square planar molecule such as  $\text{XeF}_4$  provides an example. Figure 3.4a shows that  $\text{XeF}_4$  contains a  $C_4$  axis (the principal axis) and perpendicular to this is the  $\sigma_h$  plane in which the molecule lies. Coincident with the  $C_4$  axis is a  $C_2$  axis. Within the plane of the molecule, there are two sets of  $C_2$  axes. One type (the  $C_2'$  axis) coincides with F–Xe–F bonds, while the second type (the  $C_2''$  axis) bisects the F–Xe–F  $90^\circ$  angle (Figure 3.4). We can now define two sets of mirror planes: one type ( $\sigma_v$ ) contains the principal axis and a  $C_2'$  axis (Figure 3.4b), while the second type ( $\sigma_d$ ) contains the principal axis and a  $C_2''$  axis (Figure 3.4c). Each  $\sigma_d$  plane bisects the angle between two  $C_2'$  axes.

In the notation for planes of symmetry,  $\sigma$ , the subscripts h, v and d stand for horizontal, vertical and dihedral respectively.

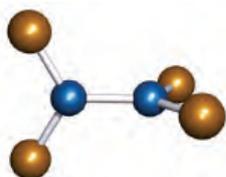
#### Self-study exercises

1.  $\text{N}_2\text{O}_4$  is planar (Figure 14.14). Show that it possesses three planes of symmetry.



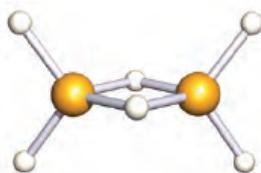
**Fig. 3.4** The square planar molecule  $\text{XeF}_4$ . (a) One  $C_2$  axis coincides with the principal ( $C_4$ ) axis; the molecule lies in a  $\sigma_h$  plane which contains two  $C_2'$  and two  $C_2''$  axes. (b) Each of the two  $\sigma_v$  planes contains the  $C_4$  axis and one  $C_2'$  axis. (c) Each of the two  $\sigma_d$  planes contains the  $C_4$  axis and one  $C_2''$  axis.

2.  $B_2Br_4$  has the following staggered structure:



Show that  $B_2Br_4$  has one less plane of symmetry than  $B_2F_4$  which is planar.

3.  $Ga_2H_6$  has the following structure in the gas phase:

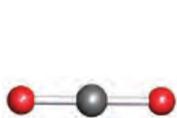


Show that it possesses three planes of symmetry.

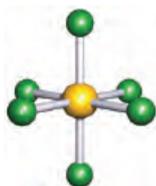
4. Show that the planes of symmetry in benzene are one  $\sigma_h$ , three  $\sigma_v$  and three  $\sigma_d$ .

### Reflection through a centre of symmetry (inversion centre)

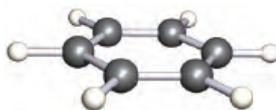
If reflection of *all* parts of a molecule through the centre of the molecule produces an indistinguishable configuration, the centre is a *centre of symmetry*, also called a *centre of inversion* (see also [Box 1.9](#)); it is designated by the symbol *i*. Each of the molecules  $CO_2$  (3.3), *trans*- $N_2F_2$  (see [worked example 3.1](#)),  $SF_6$  (3.4) and benzene (3.5) possesses a centre of symmetry, but  $H_2S$  (3.6), *cis*- $N_2F_2$  (3.7) and  $SiH_4$  (3.8) do not.



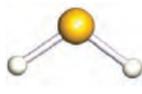
(3.3)



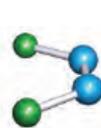
(3.4)



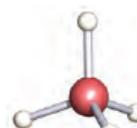
(3.5)



(3.6)



(3.7)



(3.8)

### Self-study exercises

1. Draw the structures of each of the following species and confirm that each possesses a centre of symmetry:  $CS_2$ ,  $[PF_6]^-$ ,  $XeF_4$ ,  $I_2$ ,  $[ICl_2]^-$ .
2.  $[PtCl_4]^{2-}$  has a centre of symmetry, but  $[CoCl_4]^{2-}$  does not. One is square planar and the other is tetrahedral. Which is which?
3. Why does  $CO_2$  possess an inversion centre, but  $NO_2$  does not?
4.  $CS_2$  and  $HCN$  are both linear. Explain why  $CS_2$  possesses a centre of symmetry whereas  $HCN$  does not.

### Rotation about an axis, followed by reflection through a plane perpendicular to this axis

If rotation through  $\frac{360^\circ}{n}$  about an axis, followed by reflection through a plane perpendicular to that axis, yields an indistinguishable configuration, the axis is an *n*-fold rotation–reflection axis, also called an *n*-fold *improper rotation axis*. It is denoted by the symbol  $S_n$ . Tetrahedral species of the type  $XY_4$  (all Y groups must be equivalent) possess three  $S_4$  axes, and the operation of one  $S_4$  rotation–reflection in the  $CH_4$  molecule is illustrated in Figure 3.5.

### Self-study exercises

1. Explain why  $BF_3$  possesses an  $S_3$  axis, but  $NF_3$  does not.
2.  $C_2H_6$  in a staggered conformation possesses an  $S_6$  axis. Show that this axis lies along the C–C bond.
3. Figure 3.5 shows one of the  $S_4$  axes in  $CH_4$ . On going from  $CH_4$  to  $CH_2Cl_2$ , are the  $S_4$  axes retained?

### Identity operator

All objects can be operated upon by the identity operator  $E$ . This is the simplest operator (although it may not be easy to appreciate why we identify such an operator!) and effectively identifies the molecular configuration. The operator  $E$  leaves the molecule unchanged.

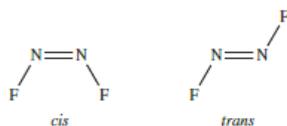


**Fig. 3.5** An improper rotation (or rotation-reflection),  $S_n$ , involves rotation about  $\frac{360^\circ}{n}$  followed by reflection through a plane that is perpendicular to the rotation axis. The diagram illustrates the operation about one of the  $S_4$  axes in  $\text{CH}_4$ ; three  $S_4$  operations are possible for the  $\text{CH}_4$  molecule. [Exercise: where are the three rotation axes for the three  $S_4$  operations in  $\text{CH}_4$ ?]

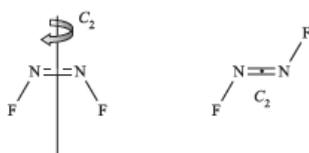
### Worked example 3.1 Symmetry properties of *cis*- and *trans*- $\text{N}_2\text{F}_2$

How do the rotation axes and planes of symmetry in *cis*- and *trans*- $\text{N}_2\text{F}_2$  differ?

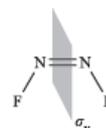
First draw the structures of *cis*- and *trans*- $\text{N}_2\text{F}_2$ ; both are planar molecules.



- The identity operator  $E$  applies to each isomer.
- Each isomer possesses a plane of symmetry which contains the molecular framework. However, their labels differ (see point 5 below).
- The *cis*-isomer contains a  $C_2$  axis which lies in the plane of the molecule, but the *trans*-isomer contains a  $C_2$  axis which bisects the N-N bond and is perpendicular to the plane of the molecule.



- The *cis*- (but not the *trans*-) isomer contains a mirror plane,  $\sigma_v$ , lying perpendicular to the plane of the molecule and bisecting the N-N bond:



- The consequence of the different types of  $C_2$  axes, and the presence of the  $\sigma_v$  plane in the *cis*-isomer, is that the symmetry planes containing the *cis*- and *trans*- $\text{N}_2\text{F}_2$  molecular frameworks are labelled  $\sigma_v'$  and  $\sigma_h$  respectively.

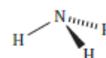
### Self-study exercises

- How do the rotation axes and planes of symmetry in *Z*- and *E*- $\text{CFH}=\text{CFH}$  differ?
- How many planes of symmetry do (a)  $\text{F}_2\text{C}=\text{O}$ , (b)  $\text{ClFC}=\text{O}$  and (c)  $[\text{HCO}_2]^-$  possess? [Ans. (a) 2; (b) 1; (c) 2]

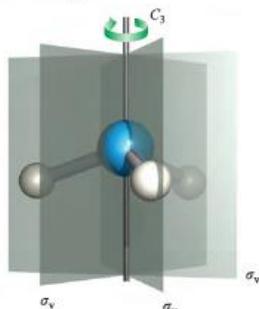
### Worked example 3.2 Symmetry operations in $\text{NH}_3$

The symmetry operators for  $\text{NH}_3$  are  $E$ ,  $C_3$  and  $3\sigma_v$ . (a) Draw the structure of  $\text{NH}_3$ . (b) What is the meaning of the  $E$  operator? (c) Draw a diagram to show the rotation and reflection symmetry operations.

- The molecule is trigonal pyramidal.



- (b) The  $E$  operator is the identity operator and it leaves the molecule unchanged.
- (c) The  $C_3$  axis passes through the N atom, perpendicular to a plane containing the three H atoms. Each  $\sigma_v$  plane contains one N–H bond and bisects the opposite H–N–H bond angle.



#### Self-study exercises

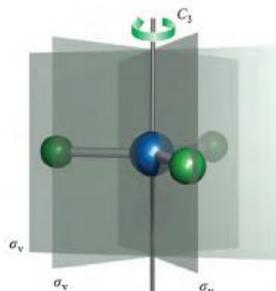
1. What symmetry operators are lost in going from  $\text{NH}_3$  to  $\text{NH}_2\text{Cl}$ ? [Ans.  $C_3$ ; two  $\sigma_v$ ]
2. Compare the symmetry operators possessed by  $\text{NH}_3$ ,  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$  and  $\text{NCl}_3$ .
3. Draw a diagram to show the symmetry operators of  $\text{NClF}_2$ . [Ans. Show one  $\sigma_v$ ; only other operator is  $E$ ]

#### Worked example 3.3 Trigonal planar $\text{BCl}_3$ versus trigonal pyramidal $\text{PCl}_3$

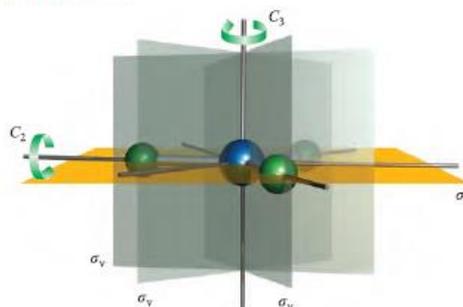
What symmetry elements do  $\text{BCl}_3$  and  $\text{PCl}_3$  (a) have in common and (b) not have in common?

$\text{PCl}_3$  is trigonal pyramidal (use VSEPR theory) and so possesses the same symmetry elements as  $\text{NH}_3$  in worked example 3.2. These are  $E$ ,  $C_3$  and  $3\sigma_v$ .

$\text{BCl}_3$  is trigonal planar (use VSEPR) and possesses all the above symmetry elements:



In addition,  $\text{BCl}_3$  contains a  $\sigma_h$  plane and three  $C_2$  axes (see Figure 3.2).



Rotation through  $120^\circ$  about the  $C_3$  axis, followed by reflection through the plane perpendicular to this axis (the  $\sigma_h$  plane), generates a molecular configuration indistinguishable from the first – this is an improper rotation  $S_3$ .

#### Conclusion:

The symmetry elements that  $\text{BCl}_3$  and  $\text{PCl}_3$  have in common are  $E$ ,  $C_3$  and  $3\sigma_v$ .

The symmetry elements possessed by  $\text{BCl}_3$  but not by  $\text{PCl}_3$  are  $\sigma_h$ ,  $3C_2$  and  $S_3$ .

#### Self-study exercises

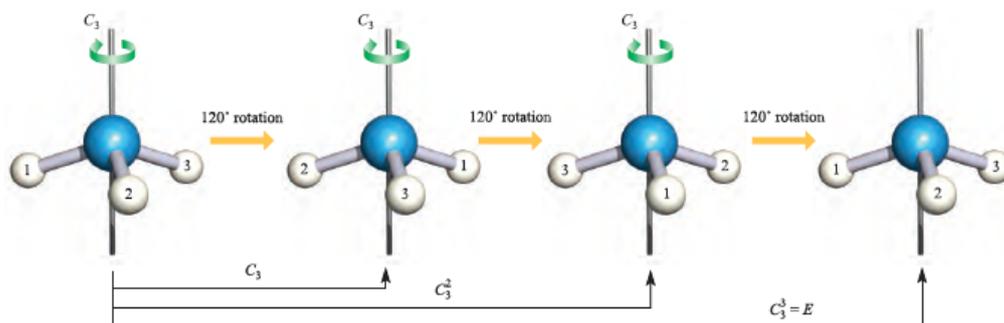
1. Show that  $\text{BF}_3$  and  $\text{F}_2\text{C}=\text{O}$  have the following symmetry elements in common:  $E$ , two mirror planes, one  $C_2$ .
2. How do the symmetry elements of  $\text{ClF}_3$  and  $\text{BF}_3$  differ? [Ans:  $\text{BF}_3$ , as for  $\text{BCl}_3$  above;  $\text{ClF}_3$ ,  $E$ ,  $\sigma_v'$ ,  $\sigma_v$ ,  $C_2$ ]

### 3.3 Successive operations

As we have seen in Section 3.2, a particular symbol is used to denote a specific symmetry operation. To say that  $\text{NH}_3$  possesses a  $C_3$  axis tells us that we can rotate the molecule through  $120^\circ$  and end up with a molecular configuration that is indistinguishable from the first. However, it takes three such operations to give a configuration of the  $\text{NH}_3$  molecule that *exactly* coincides with the first. The three separate  $120^\circ$  rotations are identified by using the notation in Figure 3.6. We cannot *actually* distinguish between the three H atoms, but for clarity they are labelled H(1), H(2) and H(3) in the figure. Since the third rotation,  $C_3^3$ , returns the  $\text{NH}_3$  molecule to its initial configuration, we can write equation 3.2, or, in general, equation 3.3.

$$C_3^3 = E \quad (3.2)$$

$$C_n^n = E \quad (3.3)$$



**Fig. 3.6** Successive  $C_3$  rotations in  $\text{NH}_3$  are distinguished using the notation  $C_3$ ,  $C_3^2$  and  $C_3^3$ . The effect of the last operation is the same as that of the identity operator acting on  $\text{NH}_3$  in the initial configuration.

Similar statements can be written to show the combined effects of successive operations. For example, in planar  $\text{BCl}_3$ , the  $S_3$  improper axis of rotation corresponds to rotation about the  $C_3$  axis followed by reflection through the  $\sigma_h$  plane. This can be written in the form of equation 3.4.

$$S_3 = C_3 \times \sigma_h \quad (3.4)$$

#### Self-study exercises

1.  $[\text{PtCl}_4]^{2-}$  is square planar; to what rotational operation is  $C_4^2$  equivalent?
2. Draw a diagram to illustrate what the notation  $C_6^4$  means with respect to rotational operations in benzene.

### 3.4 Point groups

The number and nature of the symmetry elements of a given molecule are conveniently denoted by its *point group*, and give rise to labels such as  $C_2$ ,  $C_{3v}$ ,  $D_{3h}$ ,  $D_{2d}$ ,  $T_d$ ,  $O_h$  or  $I_h$ . These point groups belong to the classes of  $C$  groups,  $D$  groups and special groups, the latter containing groups that possess special symmetries, i.e. tetrahedral, octahedral and icosahedral.

To describe the symmetry of a molecule in terms of one symmetry element (e.g. a rotation axis) provides information only about this property. Each of  $\text{BF}_3$  and  $\text{NH}_3$  possesses a 3-fold axis of symmetry, but their structures and overall symmetries are different;  $\text{BF}_3$  is trigonal planar and  $\text{NH}_3$  is trigonal pyramidal. On the other hand, if we describe the symmetries of these molecules in terms of their respective point groups ( $D_{3h}$  and  $C_{3v}$ ), we are providing information about *all* their symmetry elements.

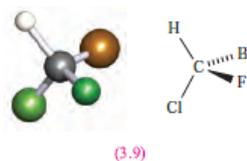
Before we look at some representative point groups, we emphasize that it is not essential to memorize the symmetry elements of a particular point group. These are listed in

*character tables* (see [Sections 3.5](#) and [4.4](#)) which are widely available.

Table 3.1 summarizes the most important classes of point group and gives their characteristic types of symmetry elements;  $E$  is, of course, common to every group. Some particular features of significance are given below.

#### $C_1$ point group

Molecules that appear to have no symmetry at all, e.g. **3.9**, must possess the symmetry element  $E$  and effectively possess at least one  $C_1$  axis of rotation. They therefore belong to the  $C_1$  point group, although since  $C_1 = E$ , the rotational symmetry operation is ignored when we list the symmetry elements of this point group.



#### $C_{\infty v}$ point group

$C_{\infty}$  signifies the presence of an  $\infty$ -fold axis of rotation, i.e. that possessed by a linear molecule (Figure 3.7); for the molecular species to belong to the  $C_{\infty v}$  point group, it must also possess an infinite number of  $\sigma_v$  planes but *no*  $\sigma_h$  plane or inversion centre. These criteria are met by asymmetrical diatomics such as HF, CO and  $[\text{CN}]^-$  (Figure 3.7a), and linear polyatomics (throughout this book, polyatomic is used to mean a species containing three or more atoms) that do not possess a centre of symmetry, e.g. OCS and HCN.

#### $D_{\infty h}$ point group

Symmetrical diatomics (e.g.  $\text{H}_2$ ,  $[\text{O}_2]^{2-}$ ) and linear polyatomics that contain a centre of symmetry (e.g.  $[\text{N}_3]^-$ ,

**Table 3.1** Characteristic symmetry elements of some important classes of point groups. The characteristic symmetry elements of the  $T_d$ ,  $O_h$  and  $I_h$  are omitted because the point groups are readily identified (see Figure 3.8). No distinction is made in this table between  $\sigma_v$  and  $\sigma_d$  planes of symmetry. For complete lists of symmetry elements, character tables should be consulted.

Point group	Characteristic symmetry elements	Comments
$C_s$	$E$ , one $\sigma$ plane	
$C_i$	$E$ , inversion centre	
$C_n$	$E$ , one (principal) $n$ -fold axis	
$C_{nv}$	$E$ , one (principal) $n$ -fold axis, $n$ $\sigma_v$ planes	
$C_{nh}$	$E$ , one (principal) $n$ -fold axis, one $\sigma_h$ plane, one $S_n$ -fold axis which is coincident with the $C_n$ axis	The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$ , there is also an inversion centre.
$D_{nh}$	$E$ , one (principal) $n$ -fold axis, $n$ $C_2$ axes, one $\sigma_h$ plane, $n$ $\sigma_v$ planes, one $S_n$ -fold axis	The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$ , there is also an inversion centre.
$D_{nd}$	$E$ , one (principal) $n$ -fold axis, $n$ $C_2$ axes, $n$ $\sigma_v$ planes, one $S_{2n}$ -fold axis	For $n = 3$ or $5$ , there is also an inversion centre.
$T_d$		Tetrahedral
$O_h$		Octahedral
$I_h$		Icosahedral

$\text{CO}_2$ ,  $\text{HC}\equiv\text{CH}$ ) possess a  $\sigma_h$  plane in addition to a  $C_\infty$  axis and an infinite number of  $\sigma_v$  planes (Figure 3.7). These species belong to the  $D_{\infty h}$  point group.

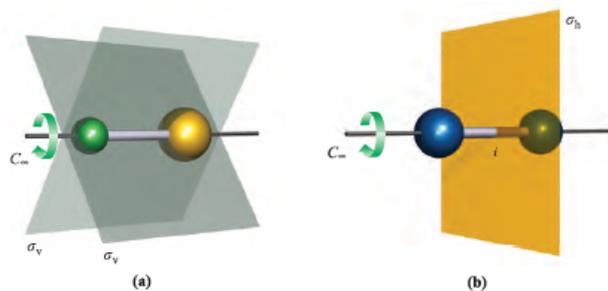
### $T_d$ , $O_h$ or $I_h$ point groups

Molecular species that belong to the  $T_d$ ,  $O_h$  or  $I_h$  point groups (Figure 3.8) possess many symmetry elements, although it is seldom necessary to identify them all before the appropriate point group can be assigned. Species with tetrahedral symmetry include  $\text{SiF}_4$ ,  $[\text{ClO}_4]^-$ ,  $[\text{CoCl}_4]^{2-}$ ,  $[\text{NH}_4]^+$ ,  $\text{P}_4$  (Figure 3.9a) and  $\text{B}_4\text{Cl}_4$  (Figure 3.9b). Those with octahedral symmetry include  $\text{SF}_6$ ,  $[\text{PF}_6]^-$ ,  $\text{W}(\text{CO})_6$  (Figure 3.9c) and  $[\text{Fe}(\text{CN})_6]^{3-}$ . There is no centre of symmetry in a tetrahedron but there is one in an octahedron, and this distinction has consequences with regard to the

observed electronic spectra of tetrahedral and octahedral metal complexes (see Section 20.6). Members of the icosahedral point group are uncommon, e.g.  $[\text{B}_{12}\text{H}_{12}]^{2-}$  (Figure 3.9d).

### Determining the point group of a molecule or molecular ion

The application of a *systematic* approach to the assignment of a point group is essential, otherwise there is the risk that symmetry elements will be missed with the consequence that an incorrect assignment is made. Figure 3.10 shows a procedure that may be adopted; some of the less common point groups (e.g.  $S_n$ ,  $T$ ,  $O$ ) are omitted from the scheme. Notice that it is *not* necessary to find all the symmetry elements (e.g. improper axes) in order to determine the point group.



**Fig. 3.7** Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not. All linear species possess a  $C_\infty$  axis of rotation and an infinite number of  $\sigma_v$  planes; in (a), two such planes are shown and these planes are omitted from (b) for clarity. Diagram (a) shows an asymmetrical diatomic belonging to the point group  $C_{\infty v}$ , and (b) shows a symmetrical diatomic belonging to the point group  $D_{\infty h}$ .



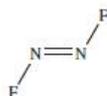
**Fig. 3.8** The tetrahedron ( $T_d$  symmetry), octahedron ( $O_h$  symmetry) and icosahedron ( $I_h$  symmetry) possess four, six and twelve vertices respectively, and four, eight and twenty equilateral-triangular faces respectively.

We illustrate the application of Figure 3.10 with reference to four worked examples, with an additional example in Section 3.8. Before assigning a point group to a molecule, its structure must be determined by, for example, microwave spectroscopy, or X-ray, electron or neutron diffraction methods.

#### Worked example 3.4 Point group assignments: 1

Determine the point group of *trans*- $N_2F_2$ .

First draw the structure.



Apply the strategy shown in Figure 3.10:

**START**  $\Rightarrow$

Is the molecule linear? No  
 Does *trans*- $N_2F_2$  have  $T_d$ ,  $O_h$  or  $I_h$  symmetry? No  
 Is there a  $C_n$  axis? Yes; a  $C_2$  axis perpendicular to the plane of the paper and passing through the midpoint of the N–N bond

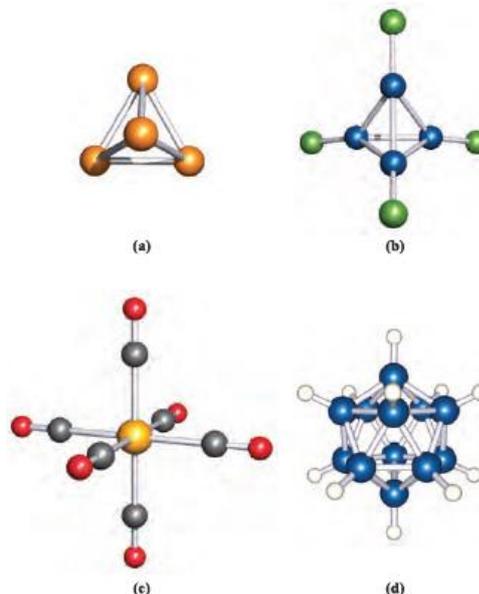
Are there two  $C_2$  axes perpendicular to the principal axis? No  
 Is there a  $\sigma_h$  plane (perpendicular to the principal axis)? Yes

$\Rightarrow$  STOP

The point group is  $C_{2h}$ .

#### Self-study exercises

1. Show that the point group of *cis*- $N_2F_2$  is  $C_{2v}$ .
2. Show that the point group of *E*- $CHCl=CHCl$  is  $C_{2h}$ .

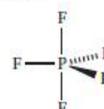


**Fig. 3.9** The molecular structures of (a)  $P_4$ , (b)  $B_4Cl_4$  (the B atoms are shown in blue), (c)  $[W(CO)_6]$  (the W atom is shown in yellow and the C atoms in grey) and (d)  $[B_{12}H_{12}]^{2-}$  (the B atoms are shown in blue).

#### Worked example 3.5 Point group assignments: 2

Determine the point group of  $PF_5$ .

First, draw the structure.



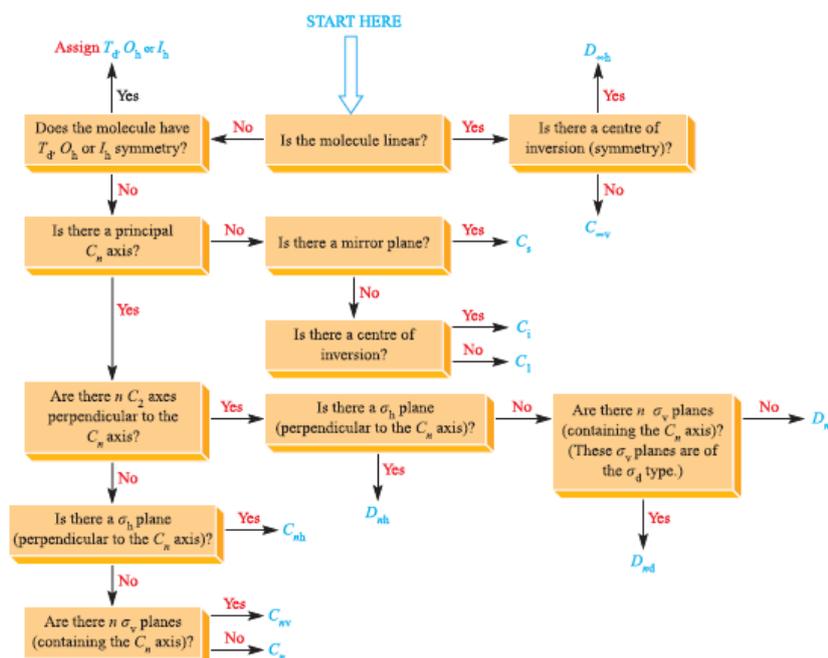
In the trigonal bipyramidal arrangement, the three equatorial F atoms are equivalent, and the two axial F atoms are equivalent.

Apply the strategy shown in Figure 3.10:

**START**  $\Rightarrow$

Is the molecule linear? No  
 Does  $PF_5$  have  $T_d$ ,  $O_h$  or  $I_h$  symmetry? No  
 Is there a  $C_n$  axis? Yes; a  $C_3$  axis containing the P and two axial F atoms

Are there three  $C_2$  axes perpendicular to the principal axis? Yes; each lies along a P–F<sub>eq</sub> bond



**Fig. 3.10** Scheme for assigning point groups of molecules and molecular ions. Apart from the cases of  $n = 1$  or  $\infty$ ,  $n$  most commonly has values of 2, 3, 4, 5 or 6.

Is there a  $\sigma_h$  plane (perpendicular to the principal axis)? Yes; it contains the P and three  $F_{\text{eq}}$  atoms.  $\Rightarrow$  STOP

The point group is  $D_{3h}$ .

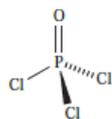
#### Self-study exercises

1. Show that  $\text{BF}_3$  belongs to the  $D_{3h}$  point group.
2. Show that  $\text{OF}_2$  belongs to the  $C_{2v}$  point group.

#### Worked example 3.6 Point group assignments: 3

To what point group does  $\text{POCl}_3$  belong?

The structure of  $\text{POCl}_3$  is:



Apply the strategy shown in Figure 3.10:

START  $\Rightarrow$

Is the molecule linear? No

Does  $\text{POCl}_3$  have  $T_d$ ,  $O_h$  or  $I_h$  symmetry? No (remember that although this molecule is loosely considered as being tetrahedral in shape, it does *not* possess tetrahedral symmetry)

Is there a  $C_n$  axis? Yes; a  $C_3$  axis running along the O–P bond

Are there 3  $C_2$  axes perpendicular to the principal axis? No

Is there a  $\sigma_h$  plane (perpendicular to the principal axis)? No

Are there  $n$   $\sigma_v$  planes (containing the principal axis)? Yes; each contains the one Cl and the O and P atoms  $\Rightarrow$  STOP

The point group is  $C_{3v}$ .

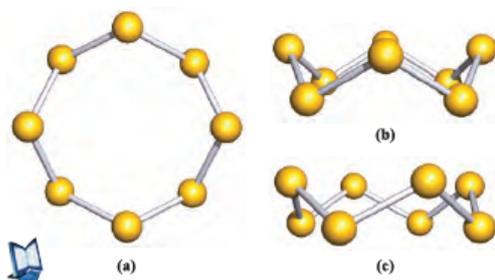
## Self-study exercises

- Show that  $\text{CHCl}_3$  possesses  $C_{3v}$  symmetry, but that  $\text{CCl}_4$  belongs to the  $T_d$  point group.
- Assign point groups to (a)  $[\text{NH}_4]^+$  and (b)  $\text{NH}_3$ .  
[Ans. (a)  $T_d$ ; (b)  $C_{3v}$ ]

- $S_8$  has the chair conformation shown in Box 1.1. Confirm that this molecule contains a centre of inversion.

## Worked example 3.7 Point group assignments: 4

Three projections of the cyclic structure of  $S_8$  are shown below; all S–S bond distances are equivalent, as are all S–S–S bond angles. To what point group does  $S_8$  belong?



Follow the scheme in Figure 3.10:

START  $\Rightarrow$ 

Is the molecule linear?	No
Does $S_8$ have $T_d$ , $O_h$ or $I_h$ symmetry?	No
Is there a $C_n$ axis?	Yes; a $C_4$ axis running through the centre of the ring; perpendicular to the plane of the paper in diagram (a)
Are there 4 $C_2$ axes perpendicular to the principal axis?	Yes; these are most easily seen from diagram (c)
Is there a $\sigma_h$ plane (perpendicular to the principal axis)?	No
Are there $n$ $\sigma_d$ planes (containing the principal axis)?	Yes; these are most easily seen from diagrams (a) and (c)

$\Rightarrow$  STOP

The point group is  $D_{4d}$ .

## Self-study exercises

- Copy diagram (a) above. Show on the figure where the  $C_4$  axis and the four  $C_2$  axes lie.

## 3.5 Character tables: an introduction

While Figure 3.10 provides a point group assignment using certain diagnostic symmetry elements, it may be necessary to establish whether any additional symmetry elements are exhibited by a molecule in a given point group.

Each point group has an associated *character table*, and that for the  $C_{2v}$  point group is shown in Table 3.2. The point group is indicated at the top left-hand corner and the symmetry elements possessed by a member of the point group are given across the top row of the character table. The  $\text{H}_2\text{O}$  molecule has  $C_{2v}$  symmetry and when we looked at the symmetry elements of  $\text{H}_2\text{O}$  in Figure 3.3, we labelled the two perpendicular planes. In the character table, taking the  $z$  axis as coincident with the principal axis, the  $\sigma_v$  and  $\sigma_v'$  planes are defined as lying in the  $xz$  and  $yz$  planes, respectively. Placing the molecular framework in a convenient orientation with respect to a Cartesian set of axes has many advantages, one of which is that the atomic orbitals on the central atom point in convenient directions. We return to this in Chapter 4.

Table 3.3 shows the character table for the  $C_{3v}$  point group. The  $\text{NH}_3$  molecule possesses  $C_{3v}$  symmetry, and worked example 3.2 illustrated the principal axis of rotation and planes of symmetry in  $\text{NH}_3$ . In the character table, the presence of three  $\sigma_v$  planes in  $\text{NH}_3$  is represented by the notation ' $3\sigma_v$ ' in the top line of the table. The notation ' $2C_3$ ' summarizes the two operations  $C_3^1$  and  $C_3^2$ . The operation  $C_3^3$  is equivalent to the identity operator,  $E$ , and so is not specified again.

Figure 3.4 showed the proper axes of rotation and planes of symmetry in the square planar molecule  $\text{XeF}_4$ . This has  $D_{4h}$  symmetry. The  $D_{4h}$  character table is given in Appendix 3, and the top row of the character table that summarizes the symmetry operations for this point group is as follows:

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
----------	-----	--------	-------	---------	----------	-----	--------	------------	-------------	-------------

**Table 3.2** The character table for the  $C_{2v}$  point group. For more character tables, see Appendix 3.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$A_1$	1	1	1	1	$z$ $x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$ $xy$
$B_1$	1	-1	1	-1	$x, R_y$ $x, xz$
$B_2$	1	-1	-1	1	$y, R_x$ $y, yz$

**Table 3.3** The character table for the  $C_{3v}$  point group. For more character tables, see [Appendix 3](#).

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$	
$A_1$	1	1	1	$z$ $x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$
$E$	2	-1	0	$(x, y) (R_x, R_y) (x^2 - y^2, xy) (xz, yz)$

In Figure 3.4 we showed that a  $C_2$  axis is coincident with the  $C_4$  axis in  $\text{XeF}_4$ . The  $C_2$  operation is equivalent to  $C_4^2$ . The character table summarizes this information by stating ' $2C_4 C_2$ ', referring to  $C_4^1$  and  $C_4^3$ , and  $C_4^2 = C_2$ . The operation  $C_4^4$  is taken care of in the identity operator  $E$ . The two sets of  $C_2$  axes that we showed in Figure 3.4 and labelled as  $C_2'$  and  $C_2''$  are apparent in the character table, as are the  $\sigma_h$ , two  $\sigma_v$  and two  $\sigma_d$  planes of symmetry. The symmetry operations that we did not show in Figure 3.4 but that are included in the character table are the centre of symmetry,  $i$ , (which is located on the Xe atom in  $\text{XeF}_4$ ), and the  $S_4$  axes. Each  $S_4$  operation can be represented as  $(C_4 \times \sigma_h)$ .

The left-hand column in a character table gives a list of *symmetry labels*. These are used in conjunction with the numbers, or *characters*, from the main part of the table to label the symmetry properties of, for example, molecular orbitals or modes of molecular vibrations. As we shall see in Chapter 4, although the symmetry labels in the character tables are upper case (e.g.  $A_1, E, T_{2g}$ ), the corresponding symmetry labels for orbitals are lower case (e.g.  $a_1, e, t_{2g}$ ). In Chapter 4, we use character tables to label the symmetries of orbitals, and to understand what orbital symmetries are allowed for a molecule possessing a particular symmetry.

Appendix 3 gives character tables for the most commonly encountered point groups, and each table has the same format as those in Tables 3.2 and 3.3.

### 3.6 Why do we need to recognize symmetry elements?

So far in this chapter, we have described the possible symmetry elements that a molecule might possess and, on the basis of these symmetry properties, we have illustrated how a molecular species can be assigned to a particular point group. Now we address some of the reasons why the recognition of symmetry elements in a molecule is important to the inorganic chemist.

Most of the applications of symmetry fall into one of the following categories:

- constructing molecular and hybrid orbitals (see [Chapter 4](#));
- interpreting spectroscopic (e.g. vibrational and electronic) properties;
- determining whether a molecular species is chiral.

The next two sections deal briefly with the consequences of symmetry on observed bands in infrared spectra and with the relationship between molecular symmetry and chirality. In [Chapter 20](#), we consider the electronic spectra of octahedral and tetrahedral  $d$ -block metal complexes and discuss the effects that molecular symmetry has on electronic spectroscopic properties.

## 3.7 Infrared spectroscopy

The discussion that follows is necessarily selective and is pitched at a simplistic level. Although in this section we derive the number of vibrational modes for some simple molecules, for more complicated species it is necessary to use character tables. The reading list at the end of the chapter gives sources of detailed discussions of the relationship between group theory and normal modes of vibration.

Infrared (IR) and Raman (see [Box 3.1](#)) spectroscopies are branches of *vibrational spectroscopy* and the former technique is the more widely available of the two in student teaching laboratories.

### How many vibrational modes are there for a given molecular species?

Vibrational spectroscopy is concerned with the observation of the *degrees of vibrational freedom*, the number of which can be determined as follows. The motion of a molecule containing  $n$  atoms can conveniently be described in terms of the three Cartesian axes; the molecule has  $3n$  *degrees of freedom* which together describe the *translational, vibrational and rotational* motions of the molecule.

The translational motion of a molecule (i.e. movement through space) can be described in terms of three degrees of freedom relating to the three Cartesian axes. If there are  $3n$  degrees of freedom in total and three degrees of freedom for translational motion, it follows that there must be  $(3n - 3)$  degrees of freedom for rotational and vibrational motion. For a *non-linear molecule* there are three degrees of rotational freedom, but for a *linear molecule*, there are two degrees of rotational freedom. This difference arises because there is no rotation about the molecular axis in a linear molecule. Having taken account of translational and rotational motion, the number of degrees of vibrational freedom can be determined (equations 3.5 and 3.6).

$$\text{Number of degrees of vibrational freedom for a non-linear molecule} = 3n - 6 \quad (3.5)$$

$$\text{Number of degrees of vibrational freedom for a linear molecule} = 3n - 5 \quad (3.6)$$

For example, from equation 3.6, the linear  $\text{CO}_2$  molecule has four *normal modes of vibration* and these are shown in Figure 3.11. Two of the modes are *degenerate*; i.e. they possess the

## CHEMICAL AND THEORETICAL BACKGROUND

## Box 3.1 Raman spectroscopy

Infrared and Raman spectroscopies are both concerned with the study of molecular vibrations, and while IR spectroscopy is used routinely in the practical laboratory, Raman spectroscopy is a more specialized technique. When radiation of a particular frequency,  $\nu$  (usually from a laser source), falls on a molecule, some radiation is scattered. The scattered radiation is of two types:

- Rayleigh scattering involves radiation of frequency,  $\nu_0$ , equal to that of the incident radiation, and
- Raman scattering involves radiation of frequencies  $\nu_0 \pm \nu$  where  $\nu$  is a fundamental frequency of a vibrational mode of the molecule.

The selection rules for Raman and IR active vibrations are different. A vibrational mode is Raman active if the polarizability of the molecule changes during the vibration. Changes in polarizability (for Raman spectra) are not as easy to visualize as changes in electric dipole moments (for IR spectra) and in most cases it is necessary to use group theory to determine whether or not a mode will be Raman active.

A combination of IR and Raman spectroscopic data is often of great use. Molecules with a centre of symmetry are

subject to the *rule of mutual exclusion* which states that in such a molecule, a vibrational mode which is IR active is Raman inactive, and vice versa. Thus, for a molecule with an inversion centre, a 'missing' absorption in the IR spectrum may be observed in the Raman spectrum. However, the presence of symmetry elements other than the inversion centre does result in some exceptions to the rule of mutual exclusion and it must be applied with caution. We exemplify the rule with reference to CO<sub>2</sub> (Figure 3.11). The two vibrational modes which are asymmetric with respect to the inversion centre (i.e. the carbon atom) are IR active and Raman inactive, while the symmetric stretch is IR inactive but Raman active. Thus, the value of 1333 cm<sup>-1</sup> for this latter vibration can be confirmed from a Raman spectrum.

For more detailed accounts of the Raman effect, see: E.A.V. Ebsworth, D.W.H. Rankin and S. Craddock (1991) *Structural Methods in Inorganic Chemistry*, 2nd edn, Blackwell Scientific Publications, Oxford, Chapter 5. K. Nakamoto (1997) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th edn, Wiley, New York.

same energy and could be represented in a single diagram with the understanding that one vibration occurs in the plane of the paper and another, identical in energy, takes place in a plane perpendicular to the first.

## Self-study exercises

1. Using VSEPR theory to help you, draw the structures of CF<sub>4</sub>, XeF<sub>4</sub> and SF<sub>4</sub>. Assign a point group to each molecule. Show that the number of degrees of vibrational freedom is independent of the molecular symmetry. [Ans. T<sub>d</sub>; D<sub>4h</sub>; C<sub>2v</sub>]

2. Why do CO<sub>2</sub> and SO<sub>2</sub> have a different number of degrees of vibrational freedom?

3. How many degrees of vibrational freedom do each of the following possess: SiCl<sub>4</sub>, BrF<sub>3</sub>, POCl<sub>3</sub>? [Ans. 9; 6; 9]

## Selection rule for an infrared active mode of vibration

One of the important consequences of precisely denoting molecular symmetry is seen in infrared spectroscopy. An IR spectrum records the frequency of a molecular vibration, but not all modes of vibration of a particular molecule give rise to observable absorption bands in the IR spectrum. This is because the following selection rule must be obeyed: for a vibrational mode to be IR active, it must give rise to a change in the molecular dipole moment (see Section 1.16).

For a mode of vibration to be infrared (IR) active, it must give rise to a change in the molecular electric dipole moment.

In the discussions of IR spectroscopy that follow, we are concerned only with *fundamental* absorptions, these being the dominant features of IR spectra.

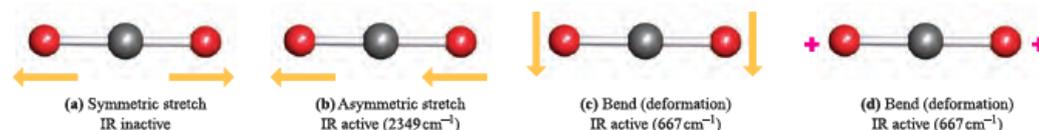


Fig. 3.11 The vibrational modes of CO<sub>2</sub> (*D*<sub>∞h</sub>); in each mode of vibration, the carbon atom remains stationary. Vibrations (a) and (b) are stretching modes. Bending mode (c) occurs in the plane of the paper, while bend (d) occurs in a plane perpendicular to that of the paper; the + signs designate motion towards the reader. The two bending modes require the same amount of energy and are therefore *degenerate*.

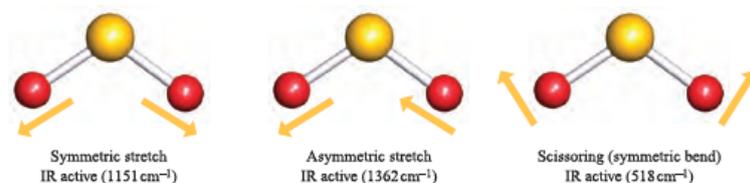


Fig. 3.12 The vibrational modes of  $\text{SO}_2$  ( $C_{2v}$ ).

The transition from the vibrational ground state to the first excited state is the *fundamental* transition.

### Linear ( $D_{\infty h}$ or $C_{\infty v}$ ) and bent ( $C_{2v}$ ) triatomic molecules

We can readily illustrate the effect of molecular symmetry on molecular dipole moments, and thus on infrared active modes of vibration, by considering the linear molecule  $\text{CO}_2$ . The two C–O bond distances are equal (116 pm) and the molecule is readily identified as being 'symmetrical'; strictly,  $\text{CO}_2$  possesses  $D_{\infty h}$  symmetry. As a consequence of its symmetry,  $\text{CO}_2$  is non-polar. Although both the asymmetric stretch and the bend (Figure 3.11) give rise to a change in dipole moment (generated transiently as the vibration occurs), the symmetric stretch does not. Thus, only two fundamental absorptions are observed in the IR spectrum of  $\text{CO}_2$ .

Now consider  $\text{SO}_2$  which is a bent molecule ( $C_{2v}$ ). Figure 3.12 shows the three normal modes of vibration; *all* give rise to a change in molecular dipole moment and are therefore IR active. A comparison of these results for  $\text{CO}_2$  and  $\text{SO}_2$  illustrates that vibrational spectroscopy can be used to determine whether an  $\text{X}_3$  or  $\text{XY}_2$  species is linear or bent.

Linear molecules of the general type  $\text{XYZ}$  (e.g.  $\text{OCS}$  or  $\text{HCN}$ ) possess  $C_{\infty v}$  symmetry and their IR spectra are expected to show three absorptions; the symmetric stretching, asymmetric stretching and bending modes are all IR active. In a linear molecule  $\text{XYZ}$ , provided that the atomic masses of X and Z are significantly different, the absorptions observed in the IR spectrum can be assigned to the X–Y stretch, the Y–Z stretch and the XYZ bend. The reason that the stretching modes can be assigned to individual bond vibrations rather than to a vibration involving the whole molecule is that each of the symmetric and asymmetric stretches is dominated by the stretching of one of the two bonds. For example, absorptions at 3311, 2097 and  $712\text{ cm}^{-1}$  in the IR spectrum of  $\text{HCN}$  are assigned to the H–C stretch, the  $\text{C}\equiv\text{N}$  stretch and the  $\text{HCN}$  bend, respectively.

A stretching mode is designated by the symbol  $\nu$ , while a deformation (bending) is denoted by  $\delta$ . For example,  $\nu_{\text{CO}}$  stands for the stretch of a C–O bond.

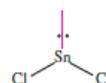
### Worked example 3.8 Infrared spectra of triatomic molecules

The IR spectrum of  $\text{SnCl}_2$  exhibits absorptions at 352, 334 and  $120\text{ cm}^{-1}$ . What shape do these data suggest for the molecule, and is this result consistent with VSEPR theory?

For linear  $\text{SnCl}_2$  ( $D_{\infty h}$ ), the asymmetric stretch and the bend are IR active, but the symmetric stretch is IR inactive (no change in molecular dipole moment).

For bent  $\text{SnCl}_2$ ,  $C_{2v}$ , the symmetric stretching, asymmetric stretching and scissoring modes are all IR active.

The data therefore suggest that  $\text{SnCl}_2$  is bent, and this is consistent with the VSEPR model since there is a lone pair in addition to two bonding pairs of electrons:

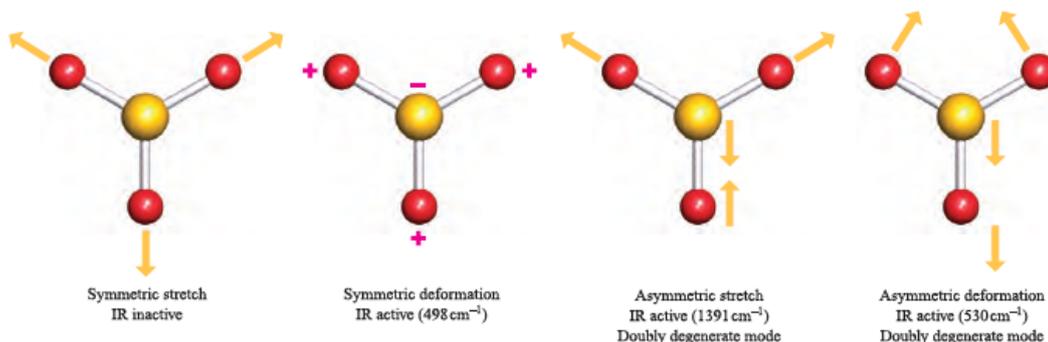


#### Self-study exercises

- The vibrational modes of  $\text{XeF}_2$  are at 555, 515 and  $213\text{ cm}^{-1}$  but only two are IR active. Explain why this is consistent with  $\text{XeF}_2$  having a linear structure.
- How many IR active vibrational modes does  $\text{CS}_2$  possess, and why? Hint:  $\text{CS}_2$  is isostructural with  $\text{CO}_2$ .
- The IR spectrum of  $\text{SF}_2$  has absorptions at 838, 813 and  $357\text{ cm}^{-1}$ . Explain why these data are consistent with  $\text{SF}_2$  belonging to the  $C_{2v}$ , rather than  $D_{\infty h}$  point group.
- To what point group does  $\text{F}_2\text{O}$  belong? Explain why the vibrational modes at 928, 831 and  $461\text{ cm}^{-1}$  are all IR active. [Ans.  $C_{2v}$ ]

### $\text{XY}_3$ molecules with $D_{3h}$ or $C_{3v}$ symmetry

A molecule of the type  $\text{XY}_3$  with  $D_{3h}$  symmetry undergoes the normal modes of vibration shown in Figure 3.13. The symmetric stretch is not accompanied by a change in molecular dipole moment and is *not* IR active. The remaining three normal modes are IR active and so molecules such as  $\text{SO}_3$ ,  $\text{BF}_3$  and  $\text{BCl}_3$  exhibit three absorptions in

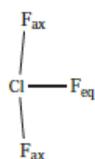


**Fig. 3.13** The vibrational modes of  $\text{SO}_3$  ( $D_{3h}$ ); only three are IR active. The + and – notation is used to show the ‘up’ and ‘down’ motion of the atoms during the mode of vibration. [Exercise: Two of the modes are labelled as being degenerate: why is this?]

their IR spectra. The IR spectra of anions such as  $[\text{NO}_3]^-$  and  $[\text{CO}_3]^{2-}$  may also be recorded, but the counterion may also give rise to IR spectroscopic bands. Therefore, simple salts such as those of the alkali metals are chosen because they give spectra in which the bands can be assigned to the anion.

A set of normal modes of vibration similar to those shown in Figure 3.13 can also be drawn for a  $C_{3v}$   $\text{XY}_3$  species such as  $\text{NH}_3$ ,  $\text{PCl}_3$ ,  $\text{AsF}_3$ ,  $[\text{H}_3\text{O}]^+$  or  $[\text{SO}_3]^{2-}$ . Each mode is IR active and so we expect to observe four absorptions in the IR spectrum of such a species.

Differences in the IR spectra of  $\text{XY}_3$  molecules possessing  $C_{3v}$  or  $D_{3h}$  symmetry is a method of distinguishing between these structures. Further,  $\text{XY}_3$  molecules with T-shaped structures (e.g.  $\text{ClF}_3$ ) belong to the  $C_{2v}$  point group, and vibrational spectroscopy may be used to distinguish their structures from those of  $C_{3v}$  or  $D_{3h}$   $\text{XY}_3$  species.



See also Figure 1.30

(3.10)

For the  $C_{2v}$  molecules  $\text{ClF}_3$  (3.10) or  $\text{BrF}_3$ , there are six normal modes of vibration, approximately described as equatorial stretch, symmetric axial stretch, asymmetric axial stretch and three deformation modes. All six modes are IR active.

#### Self-study exercises

- The IR spectrum of  $\text{BF}_3$  shows absorptions at 480, 691 and  $1449\text{ cm}^{-1}$ . Use these data to decide whether  $\text{BF}_3$  has  $C_{3v}$  or  $D_{3h}$  symmetry. [Ans.  $D_{3h}$ ]

- In the IR spectrum of  $\text{NF}_3$ , there are four absorptions. Why is this consistent with  $\text{NF}_3$  belonging to the  $C_{3v}$  rather than  $D_{3h}$  point group?

- The IR spectrum of  $\text{BrF}_3$  in an argon matrix shows six absorptions. Explain why this observation confirms that  $\text{BrF}_3$  cannot have  $C_{3v}$  symmetry.

#### $\text{XY}_4$ molecules with $T_d$ or $D_{4h}$ symmetry

An  $\text{XY}_4$  molecule with  $T_d$  symmetry has nine normal modes of vibration (Figure 3.14) but only six of them are IR active. The IR spectra of species such as  $\text{CCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{OsO}_4$ ,  $[\text{ClO}_4]^-$  and  $[\text{SO}_4]^{2-}$  exhibit two absorptions because of degeneracies.

There are nine normal modes of vibration for a square planar ( $D_{4h}$ )  $\text{XY}_4$  molecule but, as can be seen from Figure 3.15, there are only three IR absorptions. Among compounds of the  $p$ -block elements,  $D_{4h}$   $\text{XY}_4$  structures are rare; the observation of absorptions at 586, 291 and  $161\text{ cm}^{-1}$  in the IR spectrum of  $\text{XeF}_4$  is consistent with the structure predicted by VSEPR theory.

#### Self-study exercises

- The IR spectrum of gaseous  $\text{ZrI}_4$  shows absorptions at 55 and  $254\text{ cm}^{-1}$ . Explain why this observation is consistent with molecules of  $\text{ZrI}_4$  having  $T_d$  symmetry.
- The  $[\text{PdCl}_4]^{2-}$  ion gives rise to three absorptions in its IR spectrum (150, 321 and  $161\text{ cm}^{-1}$ ). Rationalize why this provides evidence for a  $D_{4h}$  rather than  $T_d$  structure.
- $\text{SiH}_2\text{Cl}_2$  is described as having a tetrahedral structure;  $\text{SiH}_2\text{Cl}_2$  has eight IR-active vibrations. Comment on these statements.

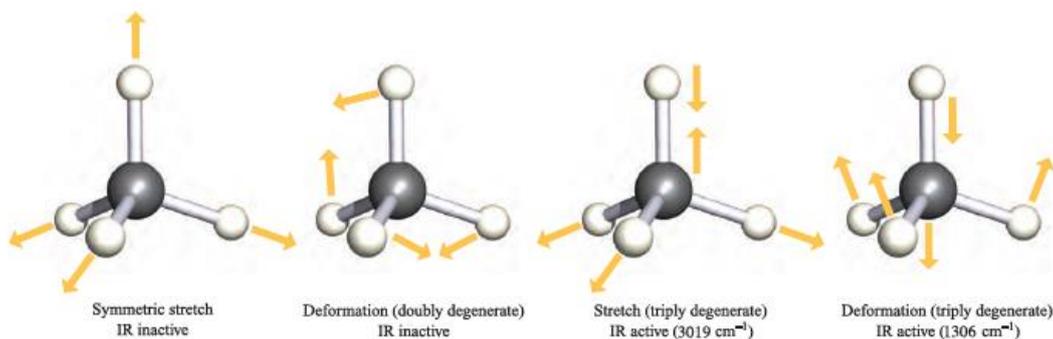


Fig. 3.14 The vibrational modes of  $\text{CH}_4$  ( $T_d$ ), only two of which are IR active.

### Observing IR spectroscopic absorptions: practical problems

We have just described how to establish the number of vibrational degrees of freedom for a simple molecule with  $n$  atoms, how to deduce the total number of normal modes of vibration, and so determine the number of absorptions expected in its IR spectrum. Our premise for using IR spectroscopy to distinguish between, for example, an  $\text{XY}_3$  molecule having  $C_{3v}$  or  $D_{3h}$  symmetry, depends upon being able to observe *all* the expected absorptions. However, a 'normal' laboratory IR spectrometer only spans the range between 4000 and  $200\text{ cm}^{-1}$  and so if the vibration in question absorbs outside this range, the corresponding band will remain unobserved. An example is  $[\text{PtCl}_4]^{2-}$  (Figure

3.15) where two of the three IR active vibrational modes are below  $200\text{ cm}^{-1}$ ; a specialized far-infrared spectrometer may be used to observe such absorptions.

Samples for IR spectroscopy are often prepared in cells with optical windows which themselves absorb within the 4000 and  $200\text{ cm}^{-1}$  range; common materials are NaCl and KBr and these materials 'cut off' at 650 and  $385\text{ cm}^{-1}$  respectively with the effect that absorptions (due to the sample) below these values are masked by the absorption due to the optical window. 'Solution cells' are used, not only for neat liquid samples but for solutions of the sample in a suitable solvent. This adds a further problem, since absorptions due to the solvent may mask those of the sample; in regions of strong solvent absorption, the transmitted radiation is essentially zero and so no absorptions at frequencies due to the sample may be detected.

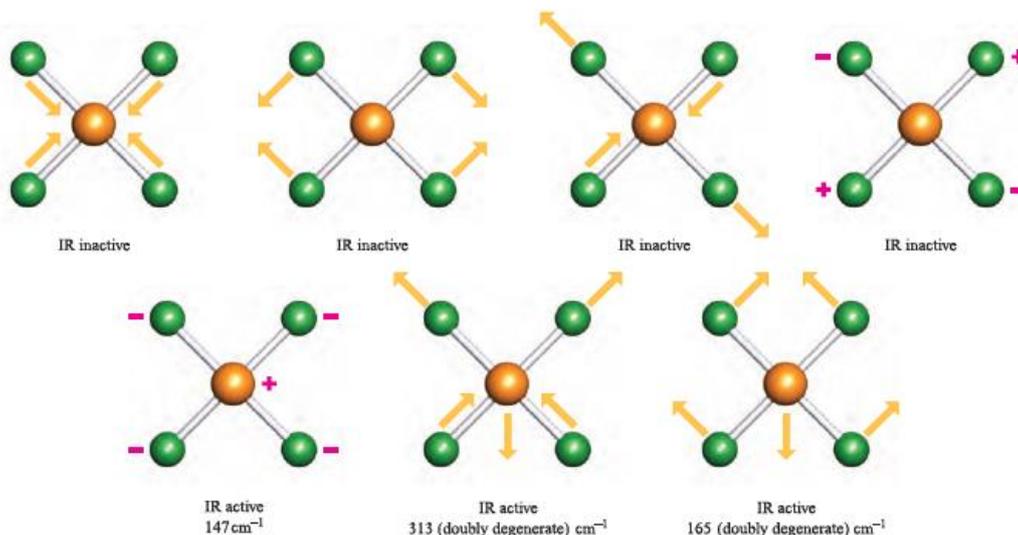
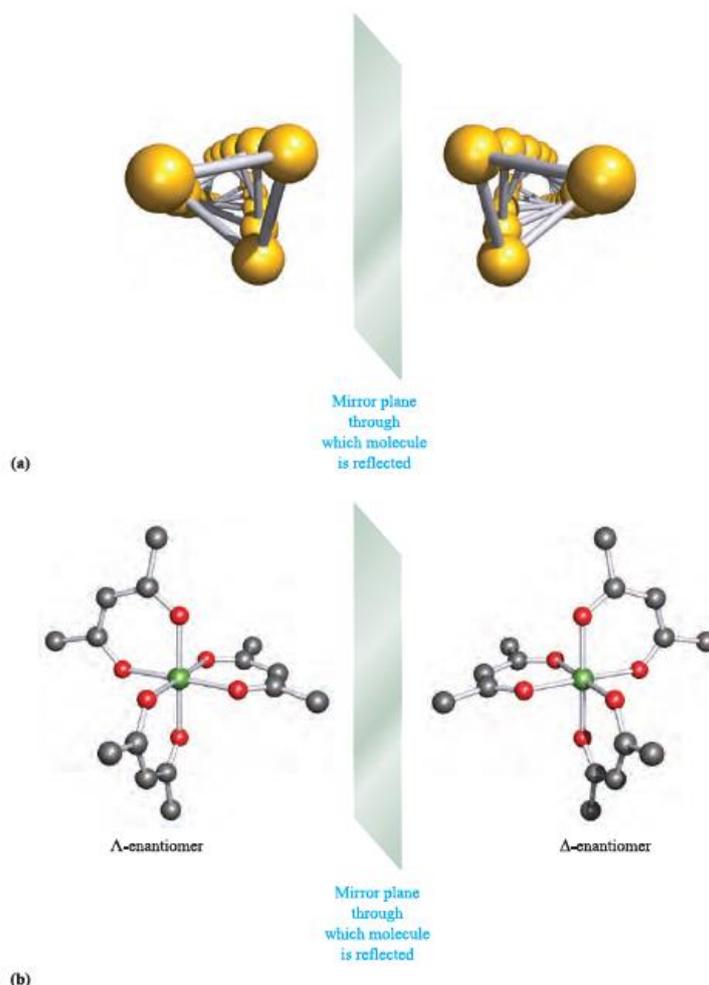


Fig. 3.15 The vibrational modes of  $[\text{PtCl}_4]^{2-}$  ( $D_{4h}$ ); only the three modes (two of which are degenerate) shown in the lower row are IR active. The + and - notation is used to show the 'up' and 'down' motion of the atoms during the mode of vibration.



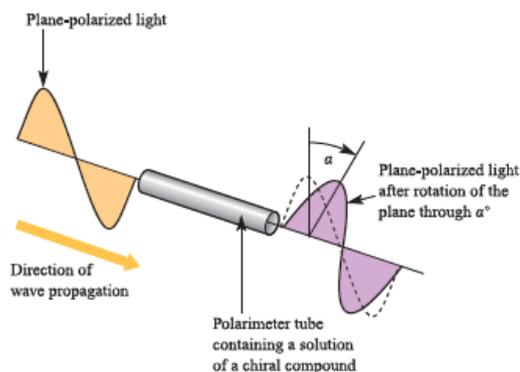
**Fig. 3.16** A pair of enantiomers consists of two molecular species which are mirror images of each other and are non-superposable. (a) Helical  $\text{Se}_\infty$  has either a right- or left-handedness. (b) The six-coordinate complex  $[\text{Cr}(\text{acac})_3]$  contains three identical didentate, chelating ligands; the labels  $\Lambda$  and  $\Delta$  describe the absolute configuration of the molecule (see [Box 3.2](#)).

### 3.8 Chiral molecules

A molecule is chiral if it is non-superposable on its mirror image.<sup>†</sup>

<sup>†</sup> This definition is taken from *Basic Terminology of Stereochemistry: IUPAC Recommendations 1996* (1996) *Pure and Applied Chemistry*, vol. 68, p. 2193.

Helical chains such as  $\text{Se}_\infty$  (Figure 3.16a) may be right- or left-handed and are chiral. Six-coordinate complexes such as  $[\text{Cr}(\text{acac})_3]$  ( $[\text{acac}]^-$ , see [Table 6.7](#)) in which there are three didentate chelating ligands also possess non-superposable mirror images (Figure 3.16b). Chiral molecules can rotate the plane of plane-polarized light (Figure 3.17). This property is known as *optical activity* and the two mirror images are known as *optical isomers* or *enantiomers*. Enantiomers rotate the light to equal extents, but in opposite directions, the dextrorotatory (*d*) enantiomer to the right and the laevorotatory (*l*) to the left (see [Box 3.2](#)). The



**Fig. 3.17** One enantiomer of a chiral compound rotates the plane of polarized light through a characteristic angle,  $\alpha^\circ$ ; the instrument used to measure this rotation is called a polarimeter. The direction indicated (a clockwise rotation as we view the light as it emerges from the polarimeter) is designated as  $+\alpha^\circ$ . The other enantiomer of the same compound would rotate the plane of polarized light through an angle  $-\alpha^\circ$ .

amount of rotation *and* its sign depend upon the wavelength of the incident light. At this point, we note that the observation of optical activity depends upon *chemical* properties of the chiral molecule; if the two enantiomers interconvert rapidly to give an equilibrium mixture containing equal amounts of the two forms, no overall rotation occurs. A mixture of equal amounts of two enantiomers is called a *racemate* or *racemic mixture*. Chiral complexes and the separation of enantiomers are discussed further in [Section 19.8](#).

The rotation,  $\alpha$ , may be measured in an instrument called a *polarimeter* (Figure 3.17). In practice, the amount of rotation depends upon the wavelength of the light, temperature and the concentration of compound present in solution. The *specific rotation*,  $[\alpha]$ , for a chiral compound in solution is given by equation 3.7. Light of a single frequency is used for specific rotation measurements and a common choice is the *sodium D-line* in the emission spectrum of atomic sodium; the specific rotation at this wavelength is denoted as  $[\alpha]_D$ .

$$[\alpha] = \frac{\alpha}{c \times \ell} \quad (3.7)$$

in which  $\alpha$  = observed rotation,  $\ell$  = path length of solution in the polarimeter (in dm) and  $c$  = concentration (in  $\text{g cm}^{-3}$ ).

## CHEMICAL AND THEORETICAL BACKGROUND

### Box 3.2 Nomenclature of chiral compounds

The nomenclature of chiral compounds is complicated. Historically, compounds were described in terms of the sign of the rotation of plane-polarized light; the rotation was denoted (+) or *d* for dextrorotatory, and (–) or *l* for laevorotatory. The sign and magnitude of rotation are often dependent on the wavelength of light and this was incorporated in the descriptor:  $(-)_D$  or  $(-)_D$  (where D stands for the sodium D-line at a wavelength of 589 nm). Whilst this system is useful provided that the wavelength is specified, it is purely defined in terms of an observable (the rotation); there is *no direct relationship* with the absolute configuration of the molecule.

This problem was first addressed in organic chemistry where a chosen reference compound, glyceraldehyde, was arbitrarily assigned, one absolute configuration to the (+) and the other to the (–) enantiomer. The (+) form was assigned a *D* absolute configuration and the (–) form, an *L* configuration. Chemical transformations between organic molecules then allowed the assignment of *D* or *L* absolute configurations to be related to the arbitrarily assigned glyceraldehyde configuration. A consequence is that, for many organic molecules, the (–) enantiomer may possess a *D* (not an *L*) configuration! Additionally, it is not always easy to relate a *D* or *L* configuration of a highly complicated organic molecule back to the configuration of glyceraldehyde. As a matter of interest, the original arbitrarily assigned configuration to (+)-*D* glyceraldehyde has been shown to be correct by anomalous dispersion X-ray experiments.

In order to describe the absolute configuration of an organic molecule, the Cahn–Ingold–Prelog system was introduced. The descriptors *R* and *S* refer to the *absolute* arrangement of the groups about a centre. A complete description of a molecule will include both the sign of the rotation and the absolute configuration, e.g.  $(+)_D$ -(*R*).

Unfortunately, the Cahn–Ingold–Prelog rules are not directly applicable to most inorganic systems. For example, the three chelating ligands in  $[\text{Cr}(\text{en})_3]^{3+}$  ( $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) are identical and ‘priorities’ (an integral part of the Cahn–Ingold–Prelog rules) cannot be assigned to individual nitrogen-donor atoms. Descriptions based upon the observable rotation are, of course, useful, for example,  $(+)_D$ -( $[\text{Cr}(\text{en})_3]^{3+}$ ) and  $(-)_D$ -( $[\text{Cr}(\text{en})_3]^{3+}$ ). However, these convey no information about the absolute configurations of the complexes.

A number of schemes have been introduced to describe the configurations of such compounds, the most useful of which is the IUPAC recommended  $\Lambda$  and  $\Delta$  system. This is exemplified in Figure 3.16b with the structures of the enantiomers of  $[\text{Cr}(\text{acac})_3]$ .

For further discussion: see [Box 19.2](#) and [Section 19.8](#).

#### Further reading

*Basic Terminology of Stereochemistry: IUPAC Recommendations 1996* (1996) *Pure and Applied Chemistry*, vol. 68, p. 2193.

The importance of chirality is clearly seen in, for example, dramatic differences in the activities of different enantiomers of chiral drugs.<sup>†</sup>

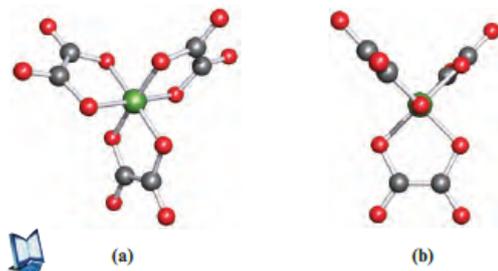
A helical chain such as  $\text{Se}_{\infty}$  is easy to recognize, but it is not always such a facile task to identify a chiral compound by attempting to convince oneself that it is, or is not, non-superposable on its mirror image. Symmetry considerations come to our aid: a chiral molecular species must lack an improper ( $S_n$ ) axis of symmetry.

A chiral molecule lacks an improper ( $S_n$ ) axis of symmetry.

Another commonly used criterion for identifying a chiral species is the lack of an inversion centre,  $i$ , and plane of symmetry,  $\sigma$ . However, both of these properties are compatible with the criterion given above, since we can rewrite the symmetry operations  $i$  and  $\sigma$  in terms of the improper rotations  $S_2$  and  $S_1$  respectively. (See *problem 3.25* at the end of the chapter.) However, a word of caution: there are a few species that are non-chiral (achiral) despite lacking an inversion centre,  $i$ , and plane of symmetry,  $\sigma$ .

### Worked example 3.9 Chiral species

The oxalate ligand,  $[\text{C}_2\text{O}_4]^{2-}$ , is a didentate ligand and the structure of the complex ion  $[\text{Fe}(\text{ox})_3]^{3-}$  is shown below. The view in the right-hand diagram is along one O–Fe–O axis. Confirm that the point group to which the ion belongs is  $D_3$  and that members of this point group are chiral.



Using the scheme in Figure 3.10:

**START**  $\Rightarrow$

Is the molecular ion linear?	No
Does it have $T_d$ , $O_h$ or $I_h$ symmetry?	No
Is there a $C_n$ axis?	Yes; a $C_3$ axis; perpendicular to the plane of the paper in diagram (a)

<sup>†</sup> A relevant article is: E. Thall (1996) *Journal of Chemical Education*, vol. 73, p. 481 – ‘When drug molecules look in the mirror’.

Are there 3 $C_2$ axes perpendicular to the principal axis?	Yes; one runs vertically through the Fe centre in diagram (b)
Is there a $\sigma_h$ plane (perpendicular to the principal axis)?	No
Are there $n$ $\sigma_d$ planes (containing the principal axis)?	No

$\Rightarrow$  STOP

The point group is  $D_3$ .

No centre of symmetry or planes of symmetry have been identified and this alone is sufficient to confirm that molecular species in the  $D_3$  point group are chiral.

### Self-study exercise

By referring to the character table (Appendix 3) for the  $D_3$  point group, confirm that the symmetry elements of the  $D_3$  point group do not include  $i$ ,  $\sigma$  or  $S_n$  axis.

## Glossary

The following terms have been introduced in this chapter.

Do you know what they mean?

- symmetry element
- symmetry operator
- identity operator ( $E$ )
- rotation axis ( $C_n$ )
- plane of reflection ( $\sigma_h$ ,  $\sigma_v$  or  $\sigma_d$ )
- centre of symmetry or inversion centre ( $i$ )
- improper rotation axis ( $S_n$ )
- point group
- translational degrees of freedom
- rotational degrees of freedom
- vibrational degrees of freedom
- normal mode of vibration
- degenerate modes of vibration
- selection rule (for an IR-active mode)
- fundamental absorption
- chiral species
- enantiomer (optical isomer)
- racemic mixture
- specific rotation

## Further reading

### Symmetry and group theory

P.W. Atkins, M.S. Child and C.S.G. Phillips (1970) *Tables for Group Theory*, Oxford University Press, Oxford – A set of

- character tables with useful additional notes and symmetry diagrams.
- R.L. Carter (1998) *Molecular Symmetry and Group Theory*, Wiley, New York – An introduction to molecular symmetry and group theory as applied to chemical problems including vibrational spectroscopy.
- F.A. Cotton (1990) *Chemical Applications of Group Theory*, 3rd edn, Wiley, New York – A more mathematical treatment of symmetry and its importance in chemistry.
- G. Davidson (1991) *Group Theory for Chemists*, Macmillan, London – An excellent introduction to group theory with examples and exercises.
- J.E. Huheey, E.A. Keiter and R.L. Keiter (1993) *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edn, Harper Collins, New York – Chapter 3 provides a useful, and readable, introduction to symmetry and group theory.
- S.F.A. Kettle (1985) *Symmetry and Structure*, Wiley, Chichester – A detailed, but readable, account of symmetry and group theory.
- J.S. Ogden (2001) *Introduction to Molecular Symmetry*, Oxford University Press, Oxford – An Oxford Chemistry Primer that provides a concise introduction to group theory and its applications.
- A. Rodger and P.M. Rodger (1995) *Molecular Geometry*, Butterworth-Heinemann, Oxford – A useful, clear text for student use.
- D.F. Shriver and P.W. Atkins (1999) *Inorganic Chemistry*, 3rd edn, Oxford University Press, Oxford – Contains a clear and concise introduction to symmetry and symmetry-related topics.
- A.F. Wells (1984) *Structural Inorganic Chemistry*, 5th edn, Oxford University Press, Oxford – A definitive work on structural inorganic chemistry; Chapter 2 gives a concise introduction to crystal symmetry.

#### Infrared spectroscopy

- E.A.V. Ebsworth, D.W.H. Rankin and S. Cradock (1991) *Structural Methods in Inorganic Chemistry*, 2nd edn, Blackwell Scientific Publications, Oxford – Chapter 5 deals with vibrational spectroscopy in detail.
- S.F.A. Kettle (1985) *Symmetry and Structure*, Wiley, Chichester – Chapter 9 deals with the relationship between molecular symmetry and molecular vibrations.
- K. Nakamoto (1997) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th edn, Wiley, New York – Part A: Theory and Applications in Inorganic Chemistry – An invaluable reference book for all practising experimental inorganic chemists, and including details of normal coordinate analysis.