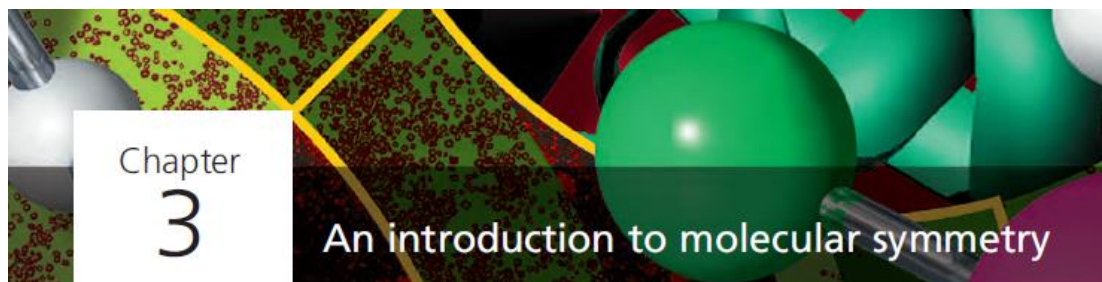


2 GROUP THEORY AND ITS APPLICATIONS



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 BF_3 , 3.1, and BF_2H , 3.2, both of which are planar. A molecule of 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° and the B–F bond distances are all identical (131 pm). It is correct to say that the boron centre in BF_2H , 3.2, is in a *pseudo-trigonal planar* environment but the molecular symmetry properties are not the same as those of BF_3 . The F–B–F bond angle in BF_2H 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° ,

the resulting structure is indistinguishable from the first; another 120° rotation results in a third indistinguishable molecular orientation (Figure 3.1). This is *not* true if we carry out the same rotational operations on BF_2H .

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 XY_2 , XY_3 and 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° rotations to 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 BF_3 molecule through 120° 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° 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 BF_3 molecule in Figure 3.1 gives a value of $n = 3$ (equation 3.1), and therefore we say that the 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, 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 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

example, in square planar 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 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 S_6 (see Box 1.1). Explain why only benzene contains a 6-fold principal rotation axis.
- Among the following, why does only XeF_4 contain a 4-fold principal rotation axis: CF_4 , SF_6 , $[\text{BF}_4]^-$ and 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 B_5H_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 σ). For 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 σ_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 σ_h *only* if the molecule possesses a C_n axis *perpendicular* to the plane. If the plane *contains* the principal axis, it is labelled σ_v . Consider the H_2O molecule. This possesses a C_2 axis (Figure 3.3) but it also contains *two* mirror planes, one containing the H_2O framework, and one perpendicular to it. Each plane contains the principal axis of rotation and so may be denoted as σ_v but in order to distinguish between them, we use the notations σ_v and σ_v' . The σ_v label refers to the plane that bisects the H–O–H bond angle and the σ_v' label refers to the plane in which the molecule lies.

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

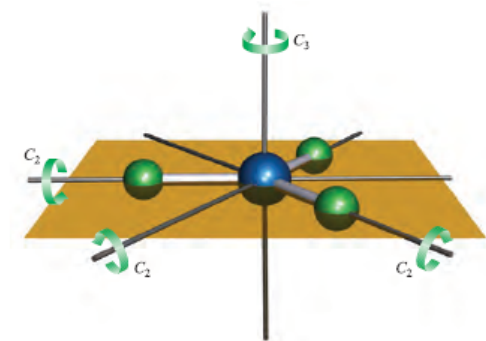


Fig. 3.2 The 3-fold (C_3) and three 2-fold (C_2) axes of symmetry possessed by the trigonal planar BF_3 molecule.

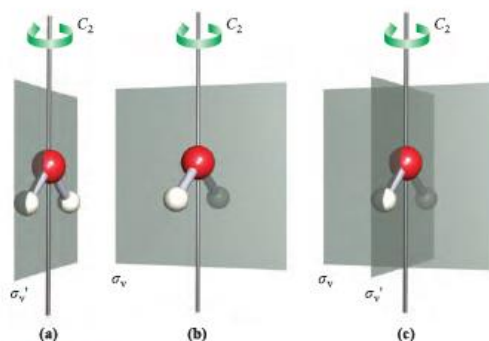


Fig. 3.3 The H_2O molecule possesses one C_2 axis and two mirror planes. (a) The C_2 axis and the plane of symmetry that contains the H_2O molecule. (b) The C_2 axis and the plane of symmetry that is perpendicular to the plane of the H_2O molecule. (c) Planes of symmetry in a molecule are often shown together on one diagram; this representation for H_2O combines diagrams (a) and (b).

adjacent 2-fold axes, is labelled σ_d . A square planar molecule such as XeF_4 provides an example. Figure 3.4a shows that XeF_4 contains a C_4 axis (the principal axis) and perpendicular to this is the σ_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° angle (Figure 3.4). We can now define two sets of mirror planes: one type (σ_v) contains the principal axis and a C_2' axis (Figure 3.4b), while the second type (σ_d) contains the principal axis and a C_2'' axis (Figure 3.4c). Each σ_d plane bisects the angle between two C_2' axes.

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

Self-study exercises

1. N_2O_4 is planar (Figure 14.14). Show that it possesses three planes of symmetry.

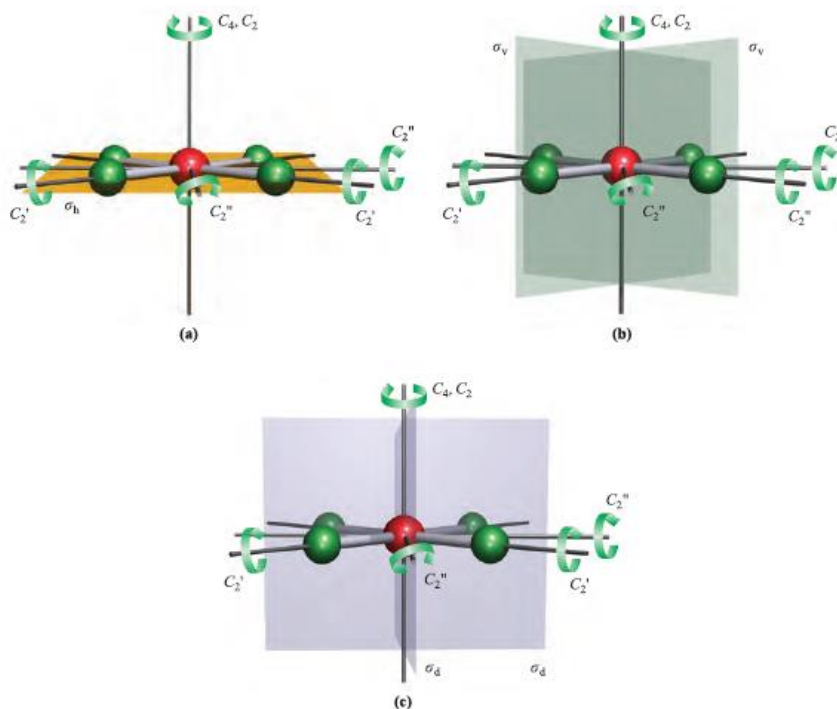
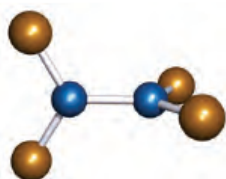


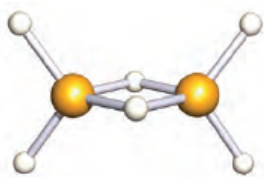
Fig. 3.4 The square planar molecule XeF_4 . (a) One C_2 axis coincides with the principal (C_4) axis; the molecule lies in a σ_h plane which contains two C_2' and two C_2'' axes. (b) Each of the two σ_v planes contains the C_4 axis and one C_2' axis. (c) Each of the two σ_d planes contains the C_4 axis 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:

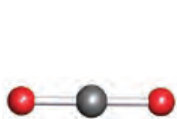


Show that it possesses three planes of symmetry.

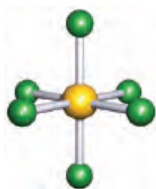
4. Show that the planes of symmetry in benzene are one σ_h , three σ_v and three σ_d .

Reflection through a centre of symmetry (inversion centre)

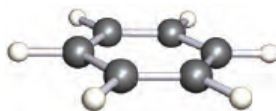
If reflection of *all* parts of a molecule through the centre of the molecule produces an indistinguishable configuration, the centre is a *centre of symmetry*, also called a *centre of inversion* (see also [Box 1.9](#)); it is designated by the symbol i . Each of the molecules CO_2 (3.3), *trans*- N_2F_2 (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.



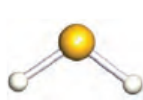
(3.3)



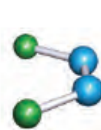
(3.4)



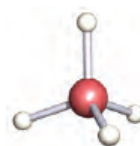
(3.5)



(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 , $[\text{PF}_6]^-$, XeF_4 , I_2 , $[\text{ICl}_2]^-$.
2. $[\text{PtCl}_4]^{2-}$ has a centre of symmetry, but $[\text{CoCl}_4]^{2-}$ 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.

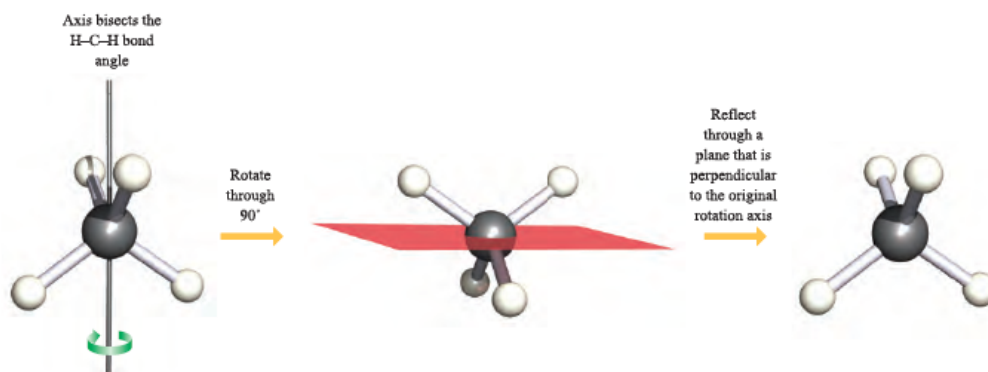
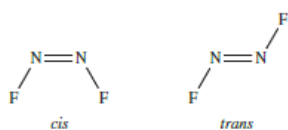


Fig. 3.5 An improper rotation (or rotation-reflection), S_n , involves rotation about $\frac{360^\circ}{n}$ followed by reflection through a plane that is perpendicular to the rotation axis. The diagram illustrates the operation about one of the S_4 axes in CH_4 ; three S_4 operations are possible for the CH_4 molecule. [Exercise: where are the three rotation axes for the three S_4 operations in CH_4 ?]

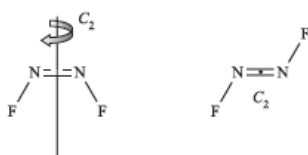
Worked example 3.1 Symmetry properties of *cis*- and *trans*- N_2F_2

How do the rotation axes and planes of symmetry in *cis*- and *trans*- N_2F_2 differ?

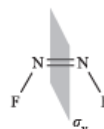
First draw the structures of *cis*- and *trans*- N_2F_2 ; both are planar molecules.



1. The identity operator E applies to each isomer.
2. Each isomer possesses a plane of symmetry which contains the molecular framework. However, their labels differ (see point 5 below).
3. 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.



4. The *cis*- (but not the *trans*-) isomer contains a mirror plane, σ_v , lying perpendicular to the plane of the molecule and bisecting the N–N bond:



5. The consequence of the different types of C_2 axes, and the presence of the σ_v plane in the *cis*-isomer, is that the symmetry planes containing the *cis*- and *trans*- N_2F_2 molecular frameworks are labelled σ_v' and σ_h respectively.

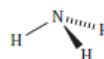
Self-study exercises

1. How do the rotation axes and planes of symmetry in *Z*- and *E*- $\text{CFH}=\text{CFH}$ differ?
2. 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]

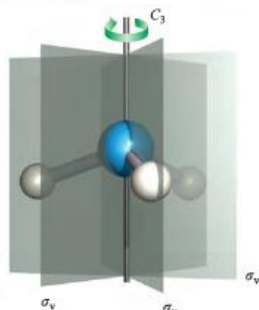
Worked example 3.2 Symmetry operations in NH_3

The symmetry operators for NH_3 are E , C_3 and $3\sigma_v$. (a) Draw the structure of NH_3 . (b) What is the meaning of the E operator? (c) Draw a diagram to show the rotation and reflection symmetry operations.

- (a) 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 σ_v plane contains one N–H bond and bisects the opposite H–N–H bond angle.



Self-study exercises

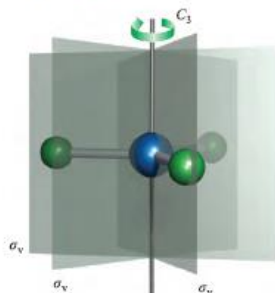
- What symmetry operators are lost in going from NH_3 to NH_2Cl ?
[Ans. C_3 ; two σ_v]
- Compare the symmetry operators possessed by NH_3 , NH_2Cl , NHCl_2 and NCl_3 .
- Draw a diagram to show the symmetry operators of NClF_2 .
[Ans. Show one σ_v ; only other operator is E]

Worked example 3.3 Trigonal planar BCl_3 versus trigonal pyramidal PCl_3

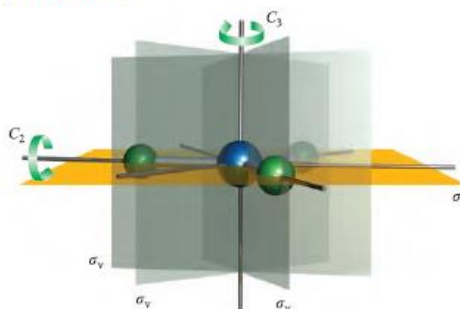
What symmetry elements do BCl_3 and PCl_3 (a) have in common and (b) not have in common?

PCl_3 is trigonal pyramidal (use VSEPR theory) and so possesses the same symmetry elements as NH_3 in worked example 3.2. These are E , C_3 and $3\sigma_v$.

BCl_3 is trigonal planar (use VSEPR) and possesses all the above symmetry elements:



In addition, BCl_3 contains a σ_h plane and three C_2 axes (see Figure 3.2).



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

Conclusion:

The symmetry elements that BCl_3 and PCl_3 have in common are E , C_3 and $3\sigma_v$.

The symmetry elements possessed by BCl_3 but not by PCl_3 are σ_h , $3C_2$ and S_3 .

Self-study exercises

- Show that BF_3 and $\text{F}_2\text{C}=\text{O}$ have the following symmetry elements in common: E , two mirror planes, one C_2 .
- How do the symmetry elements of ClF_3 and BF_3 differ?
[Ans: BF_3 , as for BCl_3 above; ClF_3 , E , σ_v , σ_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 NH_3 possesses a C_3 axis tells us that we can rotate the molecule through 120° 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 NH_3 molecule that *exactly* coincides with the first. The three separate 120° 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 NH_3 molecule to its initial configuration, we can write equation 3.2, or, in general, equation 3.3.

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

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

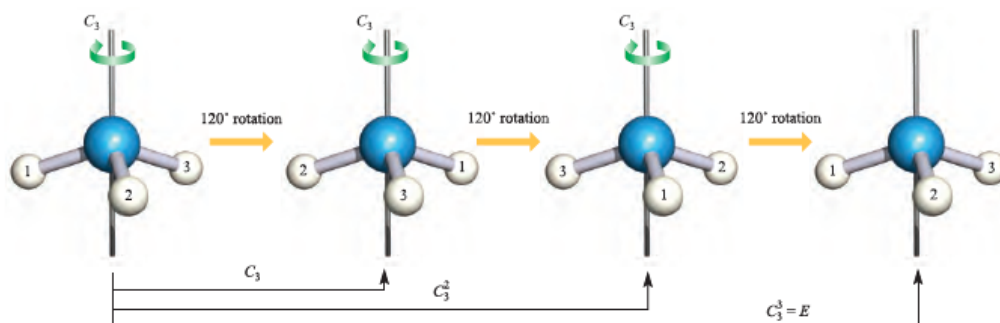


Fig. 3.6 Successive C_3 rotations in NH_3 are distinguished using the notation C_3 , C_3^2 and C_3^3 . The effect of the last operation is the same as that of the identity operator acting on NH_3 in the initial configuration.

Similar statements can be written to show the combined effects of successive operations. For example, in planar BCl_3 , the S_3 improper axis of rotation corresponds to rotation about the C_3 axis followed by reflection through the σ_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 BF_3 and NH_3 possesses a 3-fold axis of symmetry, but their structures and overall symmetries are different; BF_3 is trigonal planar and 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.

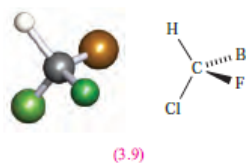
Before we look at some representative point groups, we emphasize that it is not essential to memorize the symmetry elements of a particular point group. These are listed in

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_{∞} signifies the presence of an ∞ -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 σ_v planes but *no* σ_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. 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 σ_v and σ_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 σ plane	
C_i	E , inversion centre	
C_n	E , one (principal) n -fold axis	
C_{nv}	E , one (principal) n -fold axis, n σ_v planes	
C_{nh}	E , one (principal) n -fold axis, one σ_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 σ_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 σ_h plane, n σ_v planes, one S_n -fold axis	The S_n axis necessarily follows from the C_n axis and σ_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 σ_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

CO_2 , $\text{HC}\equiv\text{CH}$) possess a σ_h plane in addition to a C_∞ axis and an infinite number of σ_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 SiF_4 , $[\text{ClO}_4]^-$, $[\text{CoCl}_4]^{2-}$, $[\text{NH}_4]^+$, P_4 (Figure 3.9a) and B_4Cl_4 (Figure 3.9b). Those with octahedral symmetry include 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.

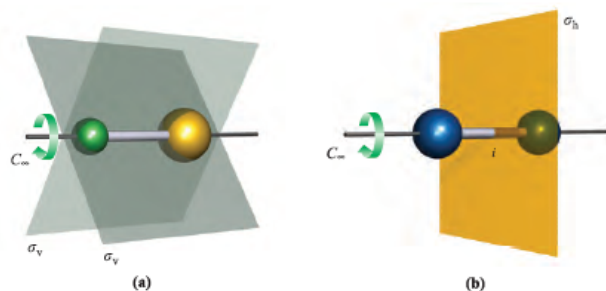


Fig. 3.7 Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not. All linear species possess a C_∞ axis of rotation and an infinite number of σ_v planes; in (a), two such planes are shown and these planes are omitted from (b) for clarity. 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 $D_{\infty h}$.



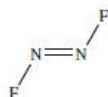
Fig. 3.8 The tetrahedron (T_d symmetry), octahedron (O_h symmetry) and icosahedron (I_h symmetry) possess four, six and twelve vertices respectively, and four, eight and twenty equilateral-triangular faces respectively.

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 <i>trans</i> - 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 σ_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} .

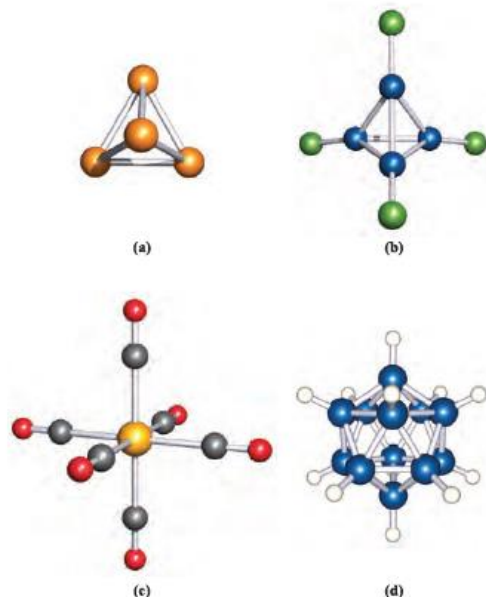
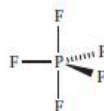


Fig. 3.9 The molecular structures of (a) P_4 , (b) B_4Cl_4 (the B atoms are shown in blue), (c) $[W(CO)_6]$ (the W atom is shown in yellow and the C atoms in grey) and (d) $[B_{12}H_{12}]^{2-}$ (the B atoms are shown in blue).

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 _{eq} bond

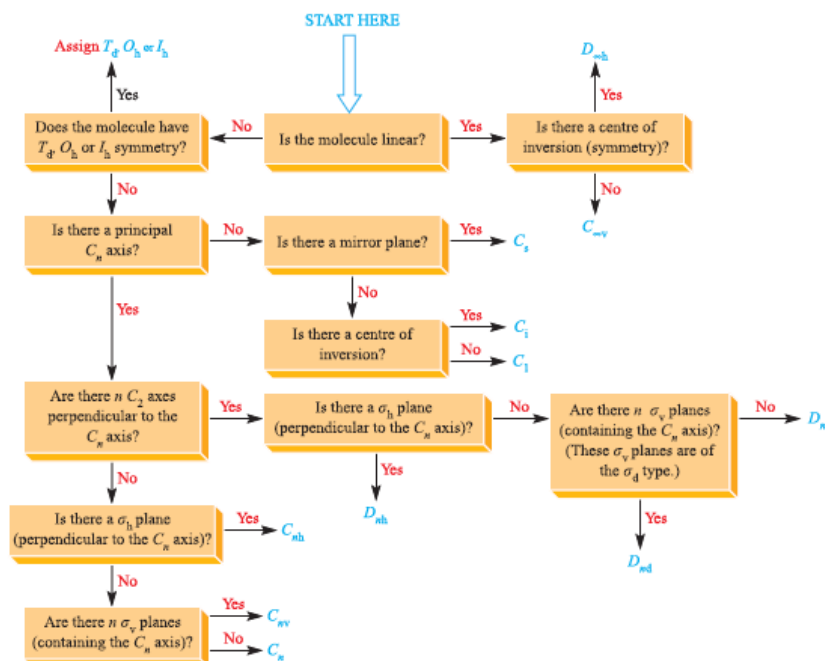


Fig. 3.10 Scheme for assigning point groups of molecules and molecular ions. Apart from the cases of $n = 1$ or ∞ , n most commonly has values of 2, 3, 4, 5 or 6.

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

The point group is D_{3h} .

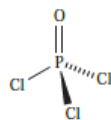
Self-study exercises

1. Show that BF_3 belongs to the D_{3h} point group.
2. Show that OF_2 belongs to the C_{2v} point group.

Worked example 3.6 Point group assignments: 3

To what point group does POCl_3 belong?

The structure of POCl_3 is:



Apply the strategy shown in Figure 3.10:

START \Rightarrow

Is the molecule linear? No
 Does 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 σ_h plane (perpendicular to the principal axis)? No

Are there n σ_v planes (containing the principal axis)? Yes; each contains the one Cl and the O and P atoms

\Rightarrow STOP

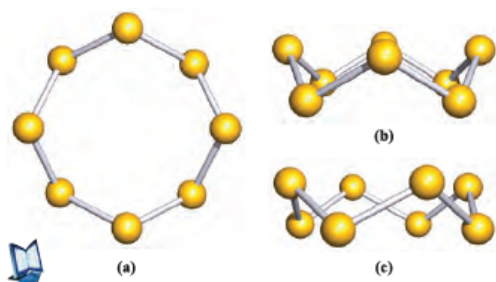
The point group is C_{3v} .

Self-study exercises

1. Show that CHCl_3 possesses C_{3v} symmetry, but that CCl_4 belongs to the T_d point group.
2. Assign point groups to (a) $[\text{NH}_4]^+$ and (b) NH_3 .
[Ans. (a) T_d ; (b) C_{3v}]

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 σ_h plane (perpendicular to the principal axis)? | No |
| Are there n σ_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

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

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

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 H_2O molecule has C_{2v} symmetry and when we looked at the symmetry elements of H_2O 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 σ_v and σ_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 NH_3 molecule possesses C_{3v} symmetry, and worked example 3.2 illustrated the principal axis of rotation and planes of symmetry in NH_3 . In the character table, the presence of three σ_v planes in 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 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	$2S_4$	σ_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 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_4^2 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 σ_h , two σ_v and two σ_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 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).

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

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

For example, from equation 3.6, the linear 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, ν (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, ν_0 , equal to that of the incident radiation, and
- Raman scattering involves radiation of frequencies $\nu_0 \pm \nu$ where ν 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_2 (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^{-1} 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. Cradock (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_4 , XeF_4 and SF_4 . Assign a point group to each molecule. Show that the number of degrees of vibrational freedom is independent of the molecular symmetry. [Ans. T_d ; D_{4h} ; C_{2v}]

2. Why do CO_2 and SO_2 have a different number of degrees of vibrational freedom?

3. How many degrees of vibrational freedom do each of the following possess: SiCl_4 , BrF_3 , POCl_3 ? [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.

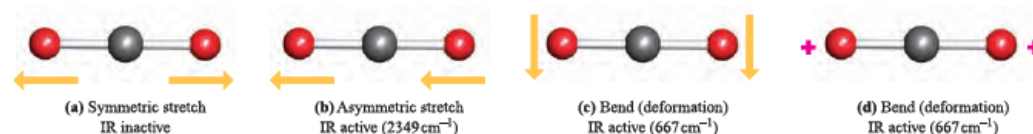


Fig. 3.11 The vibrational modes of CO_2 ($D_{\infty h}$); in each mode of vibration, the carbon atom remains stationary. Vibrations (a) and (b) are stretching modes. Bending mode (c) occurs in the plane of the paper, while bend (d) occurs in a plane perpendicular to that of the paper; the + signs designate motion towards the reader. The two bending modes require the same amount of energy and are therefore *degenerate*.

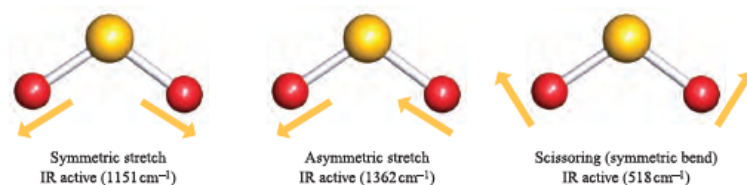


Fig. 3.12 The vibrational modes of SO_2 (C_{2v}).

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 CO_2 . The two C–O bond distances are equal (116 pm) and the molecule is readily identified as being ‘symmetrical’; strictly, CO_2 possesses $D_{\infty h}$ symmetry. As a consequence of its symmetry, 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 CO_2 .

Now consider 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 CO_2 and SO_2 illustrates that vibrational spectroscopy can be used to determine whether an X_3 or XY_2 species is linear or bent.

Linear molecules of the general type XYZ (e.g. OCS or 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 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 cm^{-1} in the IR spectrum of HCN are assigned to the H–C stretch, the $\text{C}\equiv\text{N}$ stretch and the HCN bend, respectively.

A stretching mode is designated by the symbol ν , while a deformation (bending) is denoted by δ .
For example, ν_{CO} stands for the stretch of a C–O bond.

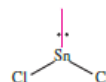
Worked example 3.8 Infrared spectra of triatomic molecules

The IR spectrum of SnCl_2 exhibits absorptions at 352, 334 and 120 cm^{-1} . What shape do these data suggest for the molecule, and is this result consistent with VSEPR theory?

For linear 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 SnCl_2 , C_{2v} , the symmetric stretching, asymmetric stretching and scissoring modes are all IR active.

The data therefore suggest that 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 XeF_2 are at 555, 515 and 213 cm^{-1} but only two are IR active. Explain why this is consistent with XeF_2 having a linear structure.
- How many IR active vibrational modes does CS_2 possess, and why? Hint: CS_2 is isostructural with CO_2 .
- The IR spectrum of SF_2 has absorptions at 838, 813 and 357 cm^{-1} . Explain why these data are consistent with SF_2 belonging to the C_{2v} rather than $D_{\infty h}$ point group.
- To what point group does F_2O belong? Explain why the vibrational modes at 928, 831 and 461 cm^{-1} are all IR active.

[Ans. C_{2v}]

XY_3 molecules with D_{3h} or C_{3v} symmetry

A molecule of the type 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 SO_3 , BF_3 and BCl_3 exhibit three absorptions in

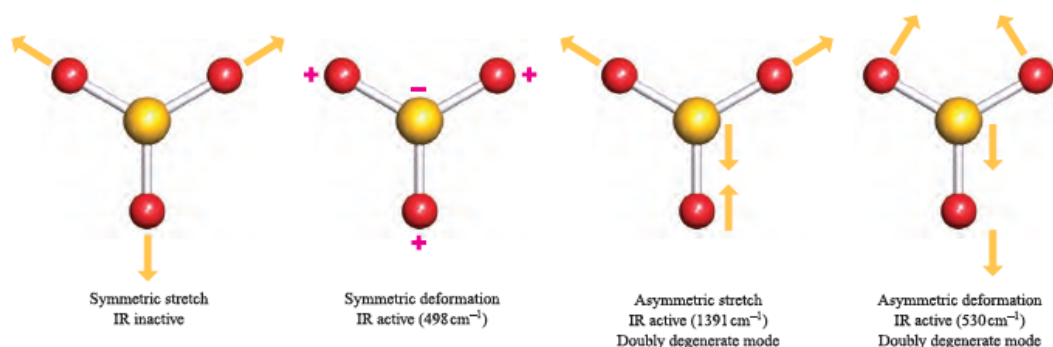
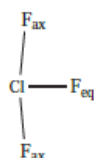


Fig. 3.13 The vibrational modes of SO_3 (D_{3h}); only three are IR active. The + and – notation is used to show the ‘up’ and ‘down’ motion of the atoms during the mode of vibration. [Exercise: Two of the modes are labelled as being degenerate: why is this?]

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} XY_3 species such as NH_3 , PCl_3 , 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 XY_3 molecules possessing C_{3v} or D_{3h} symmetry is a method of distinguishing between these structures. Further, XY_3 molecules with T-shaped structures (e.g. 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} XY_3 species.



See also Figure 1.30

(3.10)

For the C_{2v} molecules ClF_3 (3.10) or 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

1. The IR spectrum of BF_3 shows absorptions at 480 , 691 and 1449 cm^{-1} . Use these data to decide whether BF_3 has C_{3v} or D_{3h} symmetry. [Ans. D_{3h}]

2. In the IR spectrum of NF_3 , there are four absorptions. Why is this consistent with NF_3 belonging to the C_{3v} , rather than D_{3h} point group?

3. The IR spectrum of BrF_3 in an argon matrix shows six absorptions. Explain why this observation confirms that BrF_3 cannot have C_{3v} symmetry.

XY_4 molecules with T_d or D_{4h} symmetry

An 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 CCl_4 , TiCl_4 , 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}) 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} XY_4 structures are rare; the observation of absorptions at 586 , 291 and 161 cm^{-1} in the IR spectrum of XeF_4 is consistent with the structure predicted by VSEPR theory.

Self-study exercises

1. The IR spectrum of gaseous ZrI_4 shows absorptions at 55 and 254 cm^{-1} . Explain why this observation is consistent with molecules of ZrI_4 having T_d symmetry.
2. The $[\text{PdCl}_4]^{2-}$ ion gives rise to three absorptions in its IR spectrum (150 , 321 and 161 cm^{-1}). Rationalize why this provides evidence for a D_{4h} rather than T_d structure.
3. SiH_2Cl_2 is described as having a tetrahedral structure; SiH_2Cl_2 has eight IR-active vibrations. Comment on these statements.

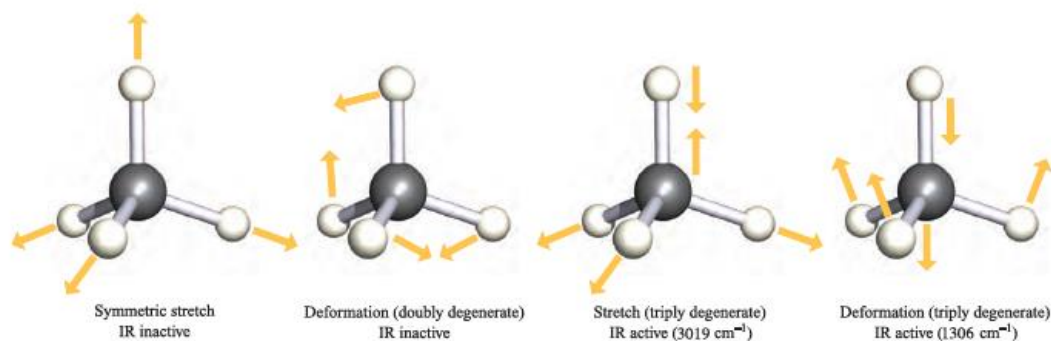


Fig. 3.14 The vibrational modes of CH_4 (T_d), only two of which are IR active.

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 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 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 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 cm^{-1} range; common materials are NaCl and KBr and these materials 'cut off' at 650 and 385 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.

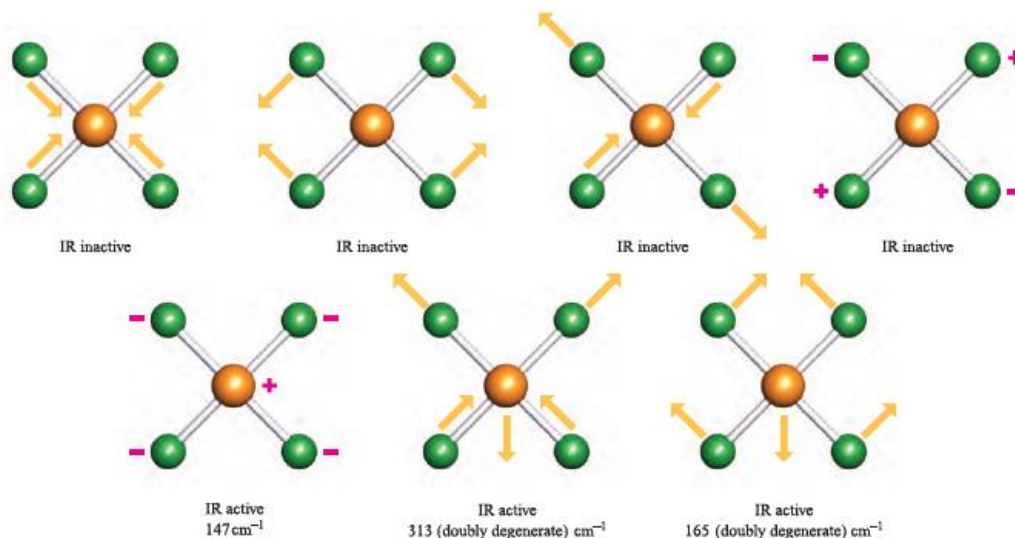


Fig. 3.15 The vibrational modes of $[\text{PtCl}_4]^{2-}$ (D_{4h}); only the three modes (two of which are degenerate) shown in the lower row are IR active. The + and - notation is used to show the 'up' and 'down' motion of the atoms during the mode of vibration.

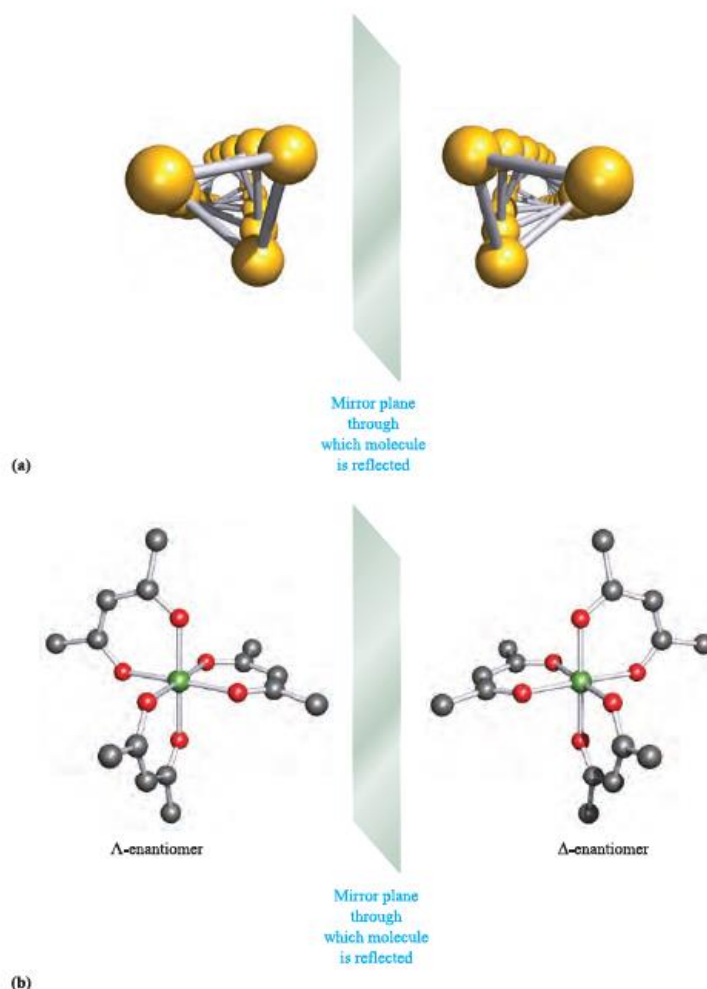


Fig. 3.16 A pair of enantiomers consists of two molecular species which are mirror images of each other and are non-superposable. (a) Helical Se_{∞} has either a right- or left-handedness. (b) The six-coordinate complex $[\text{Cr}(\text{acac})_3]$ contains three identical didentate, chelating ligands; the labels Λ and Δ 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.[†]

[†] 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 Se_{∞} (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

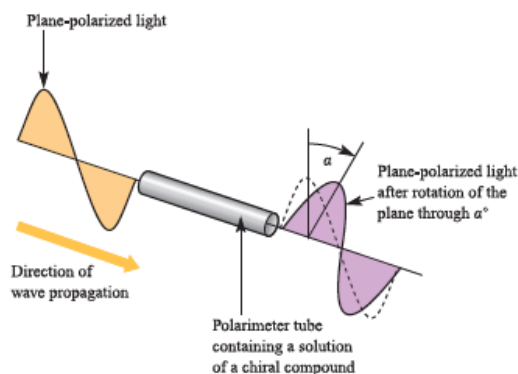


Fig. 3.17 One enantiomer of a chiral compound rotates the plane of polarized light through a characteristic angle, α° ; the instrument used to measure this rotation is called a polarimeter. The direction indicated (a clockwise rotation as we view the light as it emerges from the polarimeter) is designated 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, α , 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 α = observed rotation, ℓ = path length of solution in the polarimeter (in dm) and c = concentration (in 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 Λ and Δ 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.[†]

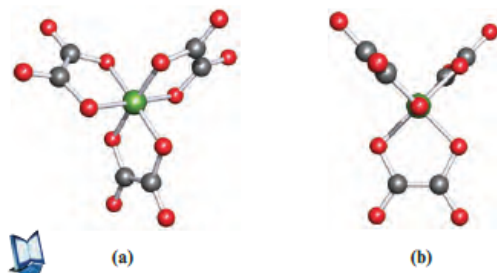
A helical chain such as Se_{∞} is easy to recognize, but it is not always such a facile task to identify a chiral compound by attempting to convince oneself that it is, or is not, non-superposable on its mirror image. Symmetry considerations come to our aid: a chiral molecular species must lack an improper (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, σ . However, both of these properties are compatible with the criterion given above, since we can rewrite the symmetry operations i and σ 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, σ .

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)

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 σ_h plane (perpendicular to the principal axis)?	No
Are there n σ_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 , σ 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 (σ_h , σ_v or σ_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

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

- 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.