Symmetry and Group Theory

3.1
Fig. 3.2 (a) \( C_i \) (b) \( C_{2v} \) (c) \( C_{3v} \) (d) \( C_1 \)
Fig. 3.4 (a) \( T_d \) (b) \( D_{5h} \) (c) \( O_h \)
Fig. 3.7 (a) \( C_3 \) (b) \( D_{3h} \) (c) \( O_h \)

3.2
Fig. 3.5 \( C_{3v} \)  Fig. 3.6 \( C_{2v} \)  Fig. 3.8 (a) \( D_{5h} \) (b) \( D_{3d} \)

3.3
a. cyclopropane, \( D_{3h} \)  b. \( \text{SO}_2 \), \( C_{2v} \)  c. \( \text{CO}_2 \), \( D_{2h} \)
d. \( \text{B}_2\text{H}_6 \), \( D_{3h} \)  e. \( \text{P}_4 \), \( T_d \)  f. \( \text{Cl}_2\text{C} = \text{C} = \text{CCl}_3 \), \( D_{3d} \)
g. \( \text{BF}_3 \), \( D_{3h} \)  h. \( \text{PH}_3 \), \( C_{3v} \)  i. \( \text{OSCl}_2 \), \( \times C_{2v} \)
j. \( \text{O}_2\text{SCL}_2 \), \( C_{2v} \)  k. \( \text{B(OH)}_3 \), \( C_{3v} \)  l. \( \text{P}_2\text{I}_4 \), \( C_{2v} \)

3.4
a. \( \text{tris(oxalato)chromium(III)} \), \( D_3 \)
b. \( \text{tris(carbonato)cobalt(III)} \), \( D_3 \)
c. Two diastereoisomers are possible for \( \text{tris(glycinato)cobalt(III)} \). The cis form has \( C_3 \) symmetry and the trans form has \( C_1 \) symmetry.

3.5  [Flow chart practice. Answers are in text.]
3.6  Cubane, \( O_h \); pentagonal dodecahedron, \( I_h \). Other common dodecahedra are the trigonal dodecahedron, \( D_{3d} \), and the rhomboidal dodecahedron, \( O_h \). The pentagonal dodecahedron is one of the five Platonic solids (tetrahedron, cube, octahedron, pentagonal dodecahedron, and icosahedron) with all faces, edges, and vertices equivalent.
3.7  a. The face of the Black-eyed Susan will have an approximate \( C_n \) axis. The value of \( n \) will be the number of petals.

\(^1\)This was incorrectly listed as \( \text{OSCl}_2 \) in the first printing.
b. The entire Black-eyed Susan will have no symmetry elements overall but one can see localized symmetry. Each leaf on the stem will have an approximate plane of symmetry that bisects it. The two upper leaves are arranged to give an approximate $C_2$ axis. The flower face has already been described in part (a).

c. If we stretch out the red feet, it will have a plane of symmetry that bisects its length (just as does Homo sapiens). Most vertebrates are, to a first approximation, externally achiral (having a mirror plane) with the exception of flatfish like sole and flounder.²

d. The diamond will have a proper axis of order 8.

e. No elements of symmetry are found in the paisley tie.

f. The snail shell has no overall symmetry. However, if viewed from the top, the line of sight approximates a $C_\infty$ axis, which would be a true axis rotation if the shell were a true cone and the banded pattern consisted of concentric circles. Because it has $C_1$ symmetry, the shell is chiral, and shells are left-handed and right-handed.

g. The Monarch butterfly has a plane of symmetry that bisects it (left wing reflected into right).

3.8

If the distance between corresponding points on successive ducks (one unit cell length) is taken as $a$, the strobe is blinking $n$ times per second, and the ducks are moving with a linear velocity of $a$ sec⁻¹, then the ducks will move one unit cell/flash and appear motionless.

b. The distance $a$ will represent $a/2\pi r$ of a revolution ($r$ = radius of wheel) and if that distance is covered in one flash, then the angular velocity of the wheel must be $na/2\pi r$ sec⁻¹ if the strobe is flashing $n$ sec⁻¹.

3.9

If SF₄ had a square pyramidal geometry it would have $C_4v$ symmetry, but it does not. The four fluorine atoms are not equidistant from sulfur; two are nearly axial and two are equatorial based on trigonal bipyramidal electronic geometry. VSEPR Theory predicted such distorted TBP geometry. See Chapter 6, Fig. 6.4.

3.10

The symmetry elements in an octahedron are: four $C_3$ axes (there are eight faces—the $C_3$ axes pass through opposite faces); three $C_4$ axes (there are six vertices—the $C_4$ axes pass through opposite vertices); six $C_2$ axes (there are twelve edges—the $C_2$ axes pass through opposite edges); three additional $C_1$ axes that are colinear with the three $C_4$ axes; a center of symmetry, $i$; three $S_4$ axes that are colinear with the three $C_1$ axes; four $S_6$ axes that are colinear with the four $C_1$ axes; three planes of symmetry that are perpendicular to the three $C_4$ axes; six planes of symmetry that bisect the twelve edges.

These symmetry elements, along with the identity element ($E$), generate a total of 48 symmetry operations: $E = 1$; $4C_3$, $4C_3^2 = 8$; $3C_4$, $3C_4^2 = 6$; $6C_2 = 6$; $3C_2 = 3$; $i = 1$; $3S_4$, $3S_4^3 = 6$; $4S_6$, $4S_6^3 = 8$; $9\sigma = 9$.

3.11

The energy barrier that exists between the ring conformers is very small. As a result the average conformation will be neither delta nor lambda (see page 500 of the text) at room

²For an interesting discussion of "handedness" in animals other than human, see Babcock, Loren E. Natural History 1993, 102(7), 32-39.
temperature. If, however, one considered static structures, it would be necessary to distinguish between the $M\delta\delta\delta$, $M\delta\delta\lambda$, $M\delta\lambda\lambda$, and $M\lambda\lambda\lambda$ isomers. The first and the last would have rigorous $C_3$ symmetry. The $C_3$ axis would not be present for the two mixed structures and the symmetry would be reduced to $C_1$.

**Sketch 3.1 XeF$_4$.**

3.12 cis, $C_{3v}$; trans, $C_{2v}$.

3.13 See, for example, XeF$_4$, Sketch 3.1.

3.14 The eclipsed conformer has $C_s$ symmetry. The conformer with like groups trans to one another has $C_1$ symmetry. Other conformers are chiral ($C_1$). The barrier to rotation about the carbon-carbon bond is very small. Thus there are an infinite number of conformations. Chiral molecules that rotate the plane of polarized light to the left are matched by an equal number of chiral molecules that rotate the plane of polarized light to the right. The overall effect is a zero net rotation of polarized light. If all molecules were frozen in the same chiral conformation, the compound would be optically active.

3.15 ClF ($C_1$) and OF$_2$ ($C_{3v}$) will have dipole moments. BF$_3$ ($D_{3h}$) and CS$_2$ ($D_{3h}$) will not have dipole moments.

3.16 Nitrogen trifluoride, a nonlinear molecule, will have six vibrational degrees of freedom (3 N - 6). It has $C_{3v}$ symmetry. The character table for this point group shows three classes of symmetry operations: $E$, $2C_3$, and $3\sigma_v$. The number of atoms that are unshifted when these operations are carried out are counted and multiplied by the contribution per atom to give a reducible representation:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshifted atoms</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Next we find the irreducible components:

\[ N(A_1) = \frac{1}{6}[12(1)(1) + 0(1)(2) + 2(1)(3)] = 3 \]

\[ N(A_2) = \frac{1}{6}[12(1)(1) + 0(1)(2) + 2(-1)(3)] = 1 \]

\[ N(E) = \frac{1}{6}[12(1)(2) + 0(-1)(2) + 2(0)(3)] = 4 \]

Thus $\Gamma_{total} = 3A_1 + A_2 + 4E$. Subtracting the translational modes ($A_1 + E$) leaves $2A_1 + A_2 + 3E$. Subtracting the rotational modes ($A_2 + E$) gives $2A_1 + 2E$. The symmetric stretching mode and the symmetric bending mode are both nondegenerate and belong to the totally symmetric representation, $A_1$. The asymmetric stretch and the asymmetric bend are both doubly degenerate and belong to the irreducible representation $E$.

OF$_2$ has the same number of atoms and the same symmetry as H$_2$O. The latter was used as a textbook example, page 67. As shown in Table 3.3 of the text:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_z(xz)$</th>
<th>$\sigma_z(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshifted atoms</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Contribution per atom</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_z(xz)$</th>
<th>$\sigma_z(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>
tive indicates that the osmyl group always adds in the same manner, namely across a C₆-C₆
"double bond", as shown in the crystal structure. The fact that no evidence can be found for
the second possible regioisomer (addition across a C₅-C₆ bond) provides further evidence
that the bonds are more localized in buckyball than in benzene.

By analogy with the ortho, meta, and para isomers of benzene, there are regioisomers of bis(osmyl)fullerene, corresponding to the possible distributions of two adducts on
the surface of the buckyball.

3.36 Since the electrons in M₃C₆₀ are not localized on the K or the Rb atoms, but delocalized
over the entire structure, "protecting" the K and Rb by enclosing them within the buckyballs
is not likely to stabilize the structures very much, although to the extent that the hydration
energies (for example) of K⁺ or Rb⁺ ions were reduced some resistance to reaction with compounds such as water might be achieved.

3.37 a. baseball = D₃h; b. baseball glove = C₁ (chiral);
c. baseball bat = C₃ᵥ; d. volleyball = Tₕ;
d. hockey puck = D₅h; e. soccer ball = Iₕ;
g. seamless rubber ball = Kₜ (perfect sphere; highest possible symmetry, though not applicable to a real, finite molecule.)

3.38 Construction of models.

3.39 The triacontahedron has icosahedral symmetry. The "clue" is the five-fold symmetry
mentioned in the question and shown in Fig. 3.35 where five rhombs come to an apex
creating a five-fold rotational axis. For a line drawing of a triacontahedron as well as
further crystals such as shown in Fig. 3.35, see Dubost, B.; Lang, J-M.; Tanaka, M.;
Sainfort, P.; Audier, M. Nature 1986, 324, 48-50. A stereoview of a triacontahedron is
given in Knowles, K. Nature 1986, 324, 12. For an interesting discussion of the dimensions
and other properties of a triacontahedron, see Andersson, S.; Lidin, S.; Jacob, M.; Tersaki,

3.40 Fig. 3.36 has 1) mirror planes through the lines of head-to-head butterflies (and likewise one
each through the bats, birds, and bees); 2) Cᵥ axes at: butterfly-head/bird-tail contact and the
seven other head-to-tail contacts.

Fig. 3.37 consists of unit cells each of which contains one "molecule" (fish). If the
eyes of the fish are ignored, each has Cᵥᵥ point group symmetry: Cᵥ axis, 2σᵥ, E. The space

group would be Pmm2.

3.41 These are all primitive (P) monoclinic space groups with a two-fold screw axis (C₂ᵥ). In
addition, there may be a mirror plane (/m) or glide plane (/c) perpendicular to that axis. The
latter planes also create a center of symmetry.

3.42 If the H₂F⁺ ion is on a center of symmetry of the crystal, it must have its own center of
symmetry and hence it has the trans structure, b.

3.43 The properties of both a screw axis and a center of inversion are such that all parts of the
molecule(s) in the unit cell will be symmetrically disposed with respect to them. This is
obvious for the center of inversion—all atoms will be connected with their opposites by tie
The irreducible components (page 63 of the text) are $3A_1 + A_2 + 2B_1 + 3B_2$. Subtracting the translational and rotational modes (page 68) gives the irreducible representations of the vibrational modes, $2A_1 + B_2$. The symmetric stretch and the symmetric bend both transform as the totally symmetric representation, $A_1$, and the asymmetric stretch belongs to the irreducible representation $B_2$.

3.17 Four fundamentals are expected for CO$_2$ ($3N - 5$ rule for a linear molecule). The symmetric stretch will not involve a change in dipole moment and will be infrared inactive. Bending modes (doubly degenerate) at right angles to one another involve a change in dipole moment and are infrared active. In addition, the asymmetric stretch involves a change in dipole moment and will be infrared active. See the following problem.

3.18

\[ \overline{\text{O}} \overline{\text{C=O}} \]

$\nu_1$ Raman active

\[ \overline{\text{O}} \overline{\text{C=O}} \]

$\nu_2$ Infrared active

3.19 The fundamental vibrational absorption frequencies (in cm$^{-1}$) of the hydrogen difluoride anion and the deuterium-substituted anion are as listed below.

<table>
<thead>
<tr>
<th>HF$_2^-$</th>
<th>DF$_2^-$</th>
<th>Activity</th>
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<tbody>
<tr>
<td>1550 cm$^{-1}$</td>
<td>1140 cm$^{-1}$</td>
<td>IR</td>
</tr>
<tr>
<td>1200 cm$^{-1}$</td>
<td>860 cm$^{-1}$</td>
<td>IR</td>
</tr>
<tr>
<td>675 cm$^{-1}$</td>
<td>675 cm$^{-1}$</td>
<td>Raman</td>
</tr>
</tbody>
</table>

These data are consistent with a linear arrangement of atoms with equal bond lengths. Note that this arrangement has the same symmetry as CO$_2$ discussed in problems 3.17 and 3.18. Two absorptions in the infrared spectrum (nondegenerate asymmetric stretch at 1550 cm$^{-1}$, degenerate bend at 1200 cm$^{-1}$) and one absorption in the Raman spectrum (nondegenerate symmetric stretch at 675 cm$^{-1}$) would be expected. The symmetric stretch frequency would not be expected to change upon deuterium because it involves no H or D motion (see the discussion of isotopic substitution for BF$_3$ on page 69 of the text).

3.20 The molecule has $D_{4h}$ symmetry. A reducible representation can be obtained as follows:

<table>
<thead>
<tr>
<th>$E$</th>
<th>$2C_4$</th>
<th>$C_2$</th>
<th>$2C_2'$</th>
<th>$2C_2''$</th>
<th>$i$</th>
<th>$2S_4$</th>
<th>$\sigma_h$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Unshifted atoms

<table>
<thead>
<tr>
<th>Contribution per atom</th>
<th>$\Gamma_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>-1</td>
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<tr>
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<td>-3</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The irreducible representations are found as follows:

$N(A_{1g}) = \frac{1}{16}[(15)(1)(1) + (1)(1)(2) + (-1)(1)(1) + (-3)(1)(2) + (-1)(1)(2) + (-3)(1)(1) + (-1)(1)(2) + (5)(1)(1) + (3)(1)(2) + (1)(1)(2)] = 1$ (3.20a)

$N(A_{2g}) = \frac{1}{16}[(15)(1)(1) + (1)(1)(2) + (-1)(1)(1) + (-3)(1)(2) + (-1)(1)(2) + (-3)(1)(1) + (-1)(1)(2) + (5)(1)(1) + (3)(-1)(2) + (1)(-1)(2)] = 1$ (3.20b)

$N(B_{1g}) = \frac{1}{16}[(15)(1)(1) + (1)(-1)(2) + (-1)(1)(1) + (-3)(1)(2) + (-1)(-1)(2) + (-3)(1)(1)$
\[ + (-1)(-1)(2) + (5)(1)(1) + (3)(1)(2) + (1)(-1)(2) = 1 \]  
(3.20c)

\[ N(B_{2g}) = \frac{1}{16}((15)(1)(1) + (1)(-1)(2) + (-1)(1)(1) + (-3)(-1)(2) + (-1)(1)(2) + (-3)(1)(1) + 
(-1)(-1)(2) + (5)(1)(1) + (3)(-1)(2) + (1)(1)(2)) = 1 \]  
(3.20d)

\[ N(E_g) = \frac{1}{16}((15)(2)(1) + (1)(0)(2) + (-1)(-2)(1) + (-3)(0)(2) + (-1)(0)(2) + (-3)(2)(1) + 
(-1)(0)(2) + (5)(-2)(1) + (3)(0)(2) + (1)(0)(2)) = 1 \]  
(3.20e)

\[ N(A_{1u}) = \frac{1}{16}((15)(1)(1) + (1)(1)(2) + (-1)(1)(1) + (-3)(1)(2) + (-1)(1)(2) + (-3)(-1)(1) + 
(-1)(-1)(2) + (5)(-1)(1) + (3)(-1)(2) + (1)(-1)(2)) = 0 \]  
(3.20f)

\[ N(A_{2u}) = \frac{1}{16}((15)(1)(1) + (1)(1)(2) + (-1)(1)(1) + (-3)(-1)(2) + (-1)(1)(2) + (-3)(-1)(1) + 
(+1)(-1)(2) + (5)(1)(1) + (3)(1)(2) + (1)(1)(2)) = 2 \]  
(3.20g)

\[ N(B_{1u}) = \frac{1}{16}((15)(1)(1) + (1)(-1)(2) + (-1)(1)(1) + (-3)(1)(2) + (-1)(1)(2) + (3)(1)(1) + 
(-1)(1)(2) + (5)(1)(1) + (3)(-1)(2) + (1)(1)(2)) = 0 \]  
(3.20h)

\[ N(B_{2u}) = \frac{1}{16}((15)(1)(1) + (1)(-1)(2) + (-1)(1)(1) + (3)(-1)(2) + (-1)(1)(2) + (3)(-1)(1) + 
(-1)(1)(2) + (5)(-1)(1) + (3)(1)(2) + (1)(-1)(2)) = 1 \]  
(3.20i)

\[ N(E_u) = \frac{1}{16}((15)(2)(1) + (1)(0)(2) + (-1)(-2)(1) + (-3)(0)(2) + (-1)(0)(2) + (-3)(-2)(1) + 
(-1)(0)(2) + (5)(-2)(1) + (3)(0)(2) + (1)(0)(2)) = 3 \]  
(3.20j)

Subtracting rotational modes \(A_{2g}\) and \(E_g\), and translational modes \(A_{2u}\) and \(E_u\), leaves the following vibrational modes: \(A_{1g} + B_{1g} + A_{2g} + B_{2g} + 2E_u\). All of the gerade modes are Raman active but not IR active. The \(B_{2g}\) mode is neither Raman nor IR active. The \(A_{2u}\) and \(E_u\) modes are IR active but not Raman active. Note that none of the fundamental vibrations are simultaneously Raman and IR active, consistent with the rule of mutual exclusion which tells us that a molecule with a center of symmetry cannot have fundamental vibrations that are both Raman and IR active.

First obtain a reducible representation.

<table>
<thead>
<tr>
<th>Unshifted atoms</th>
<th>(E)</th>
<th>(8C_3)</th>
<th>(3C_2)</th>
<th>(6S_4)</th>
<th>(6G_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contribution per atom</td>
<td>15</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Next find the irreducible components of the reducible representation.

\[ N(A_1) = \frac{1}{24}((15)(1)(1) + (0)(1)(8) + (-1)(1)(3) + (-1)(1)(6) + (3)(1)(6)) = 1 \]  
(3.21a)

\[ N(A_2) = \frac{1}{24}((15)(1)(1) + (0)(-1)(8) + (-1)(1)(3) + (-1)(-1)(6) + (3)(-1)(6)) = 0 \]  
(3.21b)

\[ N(E) = \frac{1}{24}((15)(2)(1) + (0)(0)(8) + (-1)(2)(3) + (-1)(0)(6) + (3)(0)(6)) = 1 \]  
(3.21c)

\[ N(T_1) = \frac{1}{24}((15)(3)(1) + (0)(0)(8) + (-1)(-1)(3) + (-1)(1)(6) + (3)(-1)(6)) = 1 \]  
(3.21d)

\[ N(T_2) = \frac{1}{24}((15)(3)(1) + (0)(0)(8) + (-1)(-1)(3) + (-1)(-1)(6) + (3)(-1)(6)) = 3 \]  
(3.21e)

Subtracting the rotational mode, \(T_1\), and the translational mode, \(T_2\), provides the vibrational modes, \(A_1 + E + 2T_2\). The \(A_1\) and \(E\) modes are Raman active while the \(T_2\) modes are both Raman and infrared active. None of the absorptions for \(XeF_4\), as shown by the data on page
70, are both Raman and infrared active. This strongly implies a center of symmetry, which is not present in tetrahedral XeF₄. Furthermore the infrared spectrum for tetrahedral XeF₄ should show only two fundamental absorptions while the actual spectrum shows seven. Thus the number of absorptions and the rule of mutual exclusion are both consistent with square planar XeF₄.

The ion has \( D_{3h} \) symmetry. The reducible representation is obtained as follows:

<table>
<thead>
<tr>
<th>Unshifted atoms</th>
<th>( E )</th>
<th>( C_2^*(z) )</th>
<th>( C_2^*(y) )</th>
<th>( C_2^*(x) )</th>
<th>( i )</th>
<th>( \sigma(xy) )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contributions per atom</td>
<td>5</td>
<td>1</td>
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<td>3</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( \Gamma_{\text{total}} )</td>
<td>15</td>
<td>-1</td>
<td>-3</td>
<td>-3</td>
<td>-3</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

The irreducible components are found as follows:

\[ N(A_{1g}) = \frac{1}{2} [(15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 2 \quad (3.22a) \]

\[ N(B_{1g}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 2 \quad (3.22b) \]

\[ N(B_{2g}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 1 \quad (3.22c) \]

\[ N(B_{3g}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 1 \quad (3.22d) \]

\[ N(A_{2u}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 0 \quad (3.22e) \]

\[ N(B_{1u}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 3 \quad (3.22f) \]

\[ N(B_{2u}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 3 \quad (3.22g) \]

\[ N(B_{3u}) = \frac{1}{2}[ (15)(1)(1) + (-1)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (-3)(1)(1) + (5)(1)(1) + (3)(1)(1) + (3)(1)(1)] = 3 \quad (3.22h) \]

Subtracting the \( B_{1g}, B_{2g}, \) and \( B_{3g} \) rotational modes and the \( \mathcal{B}_1, \mathcal{B}_2, \) and \( \mathcal{B}_3 \) translational modes leaves \( 2A_{1g} + B_{1u} + 2B_{2u} + 2B_{3u} \) vibrational modes. The gerade modes are Raman active and the ungerade modes are infrared active.

3.23 Following footnote 28, the square of any of the nondegenerate representations, will be \( A_{1g} \).

The character table for \( D_{3h} \) shows that \( A_{1g} \) will be Raman active (transforms as a binary product) but not IR active. Thus of the overtones associated with fundamental vibrations of \([\text{PtCl}_2\text{Br}_3]^2-\) none will be IR active.

This molecule has \( C_3 \) symmetry. A reducible representation is obtained as follows:

<table>
<thead>
<tr>
<th>Unshifted atoms</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma'(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contributions per atom</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>( \Gamma_{\text{total}} )</td>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
\[ \Gamma_{\text{total}} = 12 -2 2 4 \]

The reduction formula (Eq 3.1 of the text) is used to find the irreducible components:

\[
N(A_1) = \frac{1}{2}[(12)(1)(1) + (-2)(1)(1) + (2)(1)(1) + (4)(1)(1)] = 4 \quad (3.24a)
\]
\[
N(A_2) = \frac{1}{2}[(12)(1)(1) + (-2)(1)(1) + (2)(1)(1) + (4)(-1)(1)] = 1 \quad (3.24b)
\]
\[
N(B_1) = \frac{1}{2}[(12)(1)(1) + (-2)(-1)(1) + (2)(1)(1) + (4)(-1)(1)] = 3 \quad (3.24c)
\]
\[
N(B_2) = \frac{1}{2}[(12)(1)(1) + (-2)(-1)(1) + (2)(1)(1) + (4)(1)(1)] = 4 \quad (3.24d)
\]

Subtracting rotational modes, \( A_3, B_1, \) and \( B_2 \), and translational modes, \( A_1, B_1, \) and \( B_2 \) leaves the vibrational modes, \( 3A_1, B_1, \) and \( 2B_2 \). Fundamentals that transform as these irreducible representations are both Raman and infrared active. We would expect to see six fundamental absorptions in the infrared spectrum, all nondegenerate.

3.25 Inspection of the data reveals that none of the IR absorptions appear in the Raman spectrum and none of the Raman absorptions appear in the IR spectrum. This strongly suggests that the ion has a center of symmetry. A planar \( D_{\text{sh}} \) structure is most plausible.

3.26 The molecule belongs to the \( C_1 \) point group. Its low symmetry leads us to expect a large number of absorptions. The reducible representation is obtained in the usual way:

<table>
<thead>
<tr>
<th>( \Gamma_{\text{total}} )</th>
<th>( E )</th>
<th>( \sigma_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshifted atoms</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Contributions per atom</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \Gamma_{\text{total}} = 15 -5 \]

The irreducible representations are found as follows:

\[
N(A') = \frac{1}{2}[(15)(1)(1) + (5)(1)(1)] = 10 \quad (3.26a)
\]
\[
N(A'') = \frac{1}{2}[(15)(1)(1) + (5)(-1)(1)] = 5 \quad (3.26b)
\]

Subtracting rotational and translational modes gives \( 7A' \) and \( 2A'' \) vibrational modes. All of these are both Raman and infrared active.

3.27 Examination of the character tables for the two point groups in question gives us the irreducible representations to which each orbital or sets of orbitals belong.

<table>
<thead>
<tr>
<th>( A B_3 )</th>
<th>( (D_{3h}) )</th>
<th>( A B_4 )</th>
<th>( (D_{4h}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{2} )</td>
<td>( a' )</td>
<td>( d_{2} )</td>
<td>( a' )</td>
</tr>
<tr>
<td>( d_{2} )</td>
<td>( a' )</td>
<td>( d_{2} )</td>
<td>( a' )</td>
</tr>
</tbody>
</table>
| \( d_{2} \)      | \( e' \) | \( d_{2} \) | \( b_{1g} \)
| \( d_{2} \)      | \( e' \) | \( d_{2} \) | \( b_{1g} \)
| \( d_{2} \)      | \( e' \) | \( d_{2} \) | \( b_{1g} \)
| \( p_{x} \)      | \( e' \) | \( d_{2} \) | \( e_{g} \)
| \( p_{y} \)      | \( e' \) | \( d_{2} \) | \( e_{g} \)
| \( p_{z} \)      | \( a_{1g} \) | \( p_{z} \) | \( a_{1g} \)
| \( s \)          | \( a_{1g} \) | \( s \) | \( a_{1g} \)

3.28 Each of these may be determined by examining the character table for the appropriate point