

CHAPTER 4: SYMMETRY AND GROUP THEORY

- 4.1 a. Ethane in the staggered conformation has 2 C_3 axes (the C–C line), 3 perpendicular C_2 axes bisecting the C–C line, in the plane of the two C's and the H's on opposite sides of the two C's. No σ_h , $3\sigma_d$, i , S_6 . D_{3d} .
- b. Ethane in eclipsed conformation has two C_3 axes (the C–C line), three perpendicular C_2 axes bisecting the C–C line, in the plane of the two C's and the H's on the same side of the two C's. Mirror planes include σ_h and $3\sigma_d$. D_{3h} .
- c. Chloroethane in the staggered conformation has only one mirror plane, through both C's, the Cl, and the opposite H on the other C. C_s .
- d. 1,2-dichloroethane in the *trans* conformation has a C_2 axis perpendicular to the C–C bond and perpendicular to the plane of both Cl's and both C's, a σ_h plane through both Cl's and both C's, and an inversion center. C_{2h} .
- 4.2 a. Ethylene is a planar molecule, with C_2 axes through the C's and perpendicular to the C–C bond both in the plane of the molecule and perpendicular to it. It also has a σ_h plane and two σ_d planes (arbitrarily assigned). D_{2h} .
- b. Chloroethylene is also a planar molecule, with the only symmetry element the mirror plane of the molecule. C_s .
- c. 1,1-dichloroethylene has a C_2 axis coincident with the C–C bond, and two mirror planes, one the plane of the molecule and one perpendicular to the plane of the molecule through both C's. C_{2v} .
- cis*-1,2-dichloroethylene has a C_2 axis perpendicular to the C–C bond, and in the plane of the molecule, two mirror planes (one the plane of the molecule and one perpendicular to the plane of the molecule and perpendicular to the C–C bond). C_{2v} .
- trans*-1,2-dichloroethylene has a C_2 axis perpendicular to the C–C bond and perpendicular to the plane of the molecule, a mirror plane in the plane of the molecule, and an inversion center. C_{2h} .
- 4.3 a. Acetylene has a C_∞ axis through all four atoms, an infinite number of perpendicular C_2 axes, a σ_h plane, and an infinite number of σ_d planes through all four atoms. $D_{\infty h}$.
- b. Fluoroacetylene has only the C_∞ axis through all four atoms and an infinite number of mirror planes, also through all four atoms. $C_{\infty v}$.
- c. Methylacetylene has a C_3 axis through the carbons and three σ_v planes, each including one hydrogen and all three C's. C_{3v} .
- d. 3-Chloropropene (assuming a rigid molecule, no rotation around the C–C bond) has no rotation axes and only one mirror plane through Cl and all three C atoms. C_s .
- e. Phenylacetylene (again assuming no internal rotation) has a C_2 axis down the long axis of the molecule and two mirror planes, one the plane of the benzene ring and the other perpendicular to it. C_{2v} .

- 4.4 a. Naphthalene has three perpendicular C_2 axes, and a horizontal mirror plane (regardless of which C_2 is taken as the principal axis), making it a D_{2h} molecule.
- b. 1,8-dichloronaphthalene has only one C_2 axis, the C–C bond joining the two rings, and two mirror planes, making it a C_{2v} molecule.
- c. 1,5-dichloronaphthalene has one C_2 axis perpendicular to the plane of the molecule, a horizontal mirror plane, and an inversion center; overall, C_{2h} .
- d. 1,2-dichloronaphthalene has only the mirror plane of the molecule, and is a C_s molecule.
- 4.5 a. 1,1'-dichloroferrocene has a C_2 axis parallel to the rings, perpendicular to the Cl–Fe–Cl σ_h mirror plane. It also has an inversion center. C_{2h} .
- b. Dibenzenechromium has collinear C_6 , C_3 , and C_2 axes perpendicular to the rings, six perpendicular C_2 axes and a σ_h plane, making it a D_{6h} molecule. It also has three σ_v and three σ_d planes, S_3 and S_6 axes, and an inversion center.
- c. Benzenebiphenylchromium has a mirror plane through the Cr and the biphenyl bridge bond and no other symmetry elements, so it is a C_s molecule.
- d. H_3O^+ has the same symmetry as NH_3 : a C_3 axis, and three σ_v planes for a C_{3v} molecule.
- e. O_2F_2 has a C_2 axis perpendicular to the O–O bond and perpendicular to a line connecting the fluorines. With no other symmetry elements, it is a C_2 molecule.
- f. Formaldehyde has a C_2 axis collinear with the C=O bond, a mirror plane including all the atoms, and another perpendicular to the first and including the C and O atoms. C_{2v} .
- g. S_8 has C_4 and C_2 axes perpendicular to the average plane of the ring, four C_2 axes through opposite bonds, and four mirror planes perpendicular to the ring, each including two S atoms. D_{4d} .
- h. Borazine has a C_3 axis perpendicular to the plane of the ring, three perpendicular C_2 axes, and a horizontal mirror plane. D_{3h} .
- i. Tris(oxalato)chromate(III) has a C_3 axis and three perpendicular C_2 axes, each splitting a C–C bond and passing through the Cr. D_3 .
- j. A tennis ball has three perpendicular C_2 axes (one through the narrow portions of each segment, the others through the seams) and two mirror planes including the first rotation axis. D_{2d} .
- 4.6 a. Cyclohexane in the chair conformation has a C_3 axis perpendicular to the average plane of the ring, three perpendicular C_2 axes between the carbons, and three σ_v planes, each including the C_3 axis and one of the C_2 axes. D_{3d} .
- b. Tetrachloroallene has three perpendicular C_2 axes, one collinear with the double bonds and the other two at 45° to the Cl–C–Cl planes. It also has two σ_v planes, one defined by each of the Cl–C–Cl groups. Overall, D_{2d} . (Note that the ends of tetrachloroallene are staggered.)

- c. The sulfate ion is tetrahedral. T_d .
- d. Most snowflakes have hexagonal symmetry (Figure 4.2), and have collinear C_6 , C_3 , and C_2 axes, six perpendicular C_2 axes, and a horizontal mirror plane. Overall, D_{6h} . (For high quality images of snowflakes, including some that have different shapes, see K. G. Libbrecht, *Snowflakes*, Voyageur Press, Minneapolis, MN, 2008.)
- e. Diborane has three perpendicular C_2 axes and three perpendicular mirror planes. D_{2h} .
- f. 1,3,5-tribromobenzene has a C_3 axis perpendicular to the plane of the ring, three perpendicular C_2 axes, and a horizontal mirror plane. D_{3h} .
- 1,2,3-tribromobenzene has a C_2 axis through the middle Br and two perpendicular mirror planes that include this axis. C_{2v} .
- 1,2,4-tribromobenzene has only the plane of the ring as a mirror plane. C_s .
- g. A tetrahedron inscribed in a cube has T_d symmetry (see Figure 4.6).
- h. The left and right ends of B_3H_8 are staggered with respect to each other. There is a C_2 axis through the borons. In addition, there are two planes of symmetry, each containing four H atoms, and two C_2 axes between these planes and perpendicular to the original C_2 . The point group is D_{2d} .
- i. A mountain swallowtail butterfly has only a mirror that cuts through the head, thorax, and abdomen. C_s .
- j. The Golden Gate Bridge has a C_2 axis and two perpendicular mirror planes that include this axis. C_{2v} .
- 4.7 a. A sheet of typing paper has three perpendicular C_2 axes and three perpendicular mirror planes. D_{2h} .
- b. An Erlenmeyer flask has an infinite-fold rotation axis and an infinite number of σ_v planes, $C_{\infty v}$.
- c. A screw has no symmetry operations other than the identity, for a C_1 classification.
- d. The number 96 (with the correct type font) has a C_2 axis perpendicular to the plane of the paper, making it C_{2h} .
- e. Your choice—the list is too long to attempt to answer it here.
- f. A pair of eyeglasses has only a vertical mirror plane. C_s .
- g. A five-pointed star has a C_5 axis, five perpendicular C_2 axes, one horizontal and five vertical mirror planes. D_{5h} .
- h. A fork has only a mirror plane. C_s .
- i. Wilkins Micawber has no symmetry operation other than the identity. C_1 .

- j. A metal washer has a C_∞ axis, an infinite number of perpendicular C_2 axes, an infinite number of σ_v mirror planes, and a horizontal mirror plane. $D_{\infty h}$.
- 4.8
- | | | | |
|----|--------------------------------|----|----------------|
| a. | D_{2h} | f. | C_3 |
| b. | D_{4h} (note the four knobs) | g. | C_{2h} |
| c. | C_s | h. | C_{8v} |
| d. | C_{2v} | i. | $D_{\infty h}$ |
| e. | C_{6v} | j. | C_{3v} |
- 4.9
- | | | | |
|----|----------|----|--------------------|
| a. | D_{3h} | f. | C_s (note holes) |
| b. | D_{4h} | g. | C_1 |
| c. | C_s | h. | C_{3v} |
| d. | C_3 | i. | $D_{\infty h}$ |
| e. | C_{2v} | j. | C_1 |

- 4.10 Hands (of identical twins): C_2 Baseball: D_{2d} Atomium: C_{3v}
 Eiffel Tower: C_{4v} Dominoes: $6 \times 6: C_{2v}$ $3 \times 3: C_2$ $5 \times 4: C_s$

Bicycle wheel: The wheel shown has 32 spokes. The point group assignment depends on how the pairs of spokes (attached to both the front and back of the hub) connect with the rim. If the pairs alternate with respect to their side of attachment, the point group is D_{8d} . Other arrangements are possible, and different ways in which the spokes cross can affect the point group assignment; observing an actual bicycle wheel is recommended. (If the crooked valve is included, there is no symmetry, and the point group is a much less interesting C_1 .)

- 4.11
- | | | | | | | | |
|----|----------------|----|-----------------------------|----|----------------------------------|----|----------------------------------|
| a. | Problem 3.41*: | a. | $\text{VOCl}_3: C_{3v}$ | b. | $\text{PCl}_3: C_{3v}$ | c. | $\text{SOF}_4: C_{2v}$ |
| | | d. | $\text{SO}_3: D_{3h}$ | e. | $\text{ICl}_3: C_{2v}$ | f. | $\text{SF}_6: O_h$ |
| | | g. | $\text{IF}_7: D_{5h}$ | h. | $\text{XeO}_2\text{F}_4: D_{4h}$ | i. | $\text{CF}_2\text{Cl}_2: C_{2v}$ |
| | | j. | $\text{P}_4\text{O}_6: T_d$ | | | | |

* Incorrectly cited as problem 4.30 in first printing of text.

- b.** Problem 3.42*:
- | | | |
|---|--|---|
| a. PH_3 : C_{3v} | b. H_2Se : C_{2v} | c. SeF_4 : C_{2v} |
| d. PF_5 : D_{3h} | e. IF_5 : C_{4v} | f. XeO_3 : C_{3v} |
| g. BF_2Cl : C_{2v} | h. SnCl_2 : C_{2v} | i. KrF_2 : $D_{\infty h}$ |
| j. $\text{IO}_2\text{F}_5^{2-}$: D_{5h} | | |
- 4.12 a.** Figure 3.8:
- | | | |
|--|------------------------------------|------------------------------------|
| a. CO_2 : $D_{\infty h}$ | b. SO_3 : D_{3h} | c. CH_4 : T_d |
| d. PCl_5 : D_{3h} | e. SF_6 : O_h | f. IF_7 : D_{5h} |
| g. TaF_8^{3-} : D_{4d} | | |
- b.** Figure 3.15:
- | | | |
|---|---|---|
| a. CO_2 : $D_{\infty h}$ | b. COF_2 : C_{2v} | c. NO_2^- : C_{2v} |
| d. SO_3 : D_{3h} | e. SNF_3 : C_{3v} | f. SO_2Cl_2 : C_{2v} |
| g. XeO_3 : C_{3v} | h. SO_4^{2-} : T_d | i. SOF_4 : C_{2v} |
| j. ClO_2F_3 : C_{2v} | k. XeO_3F_2 : D_{3h} | l. IOF_5 : C_{4v} |
- 4.13 a.** p_x has $C_{\infty v}$ symmetry. (Ignoring the difference in sign between the two lobes, the point group would be $D_{\infty h}$.)
- b.** d_{xy} has D_{2h} symmetry. (Ignoring the signs, the point group would be D_{4h} .)
- c.** $d_{x^2-y^2}$ has D_{2h} symmetry. (Ignoring the signs, the point group would be D_{4h} .)
- d.** d_{z^2} has $D_{\infty h}$ symmetry.
- e.** f_{xyz} has T_d symmetry.

- 4.14 a.** The superimposed octahedron and cube show the matching symmetry elements. The descriptions below are for the elements of a cube; each element also applies to the octahedron.

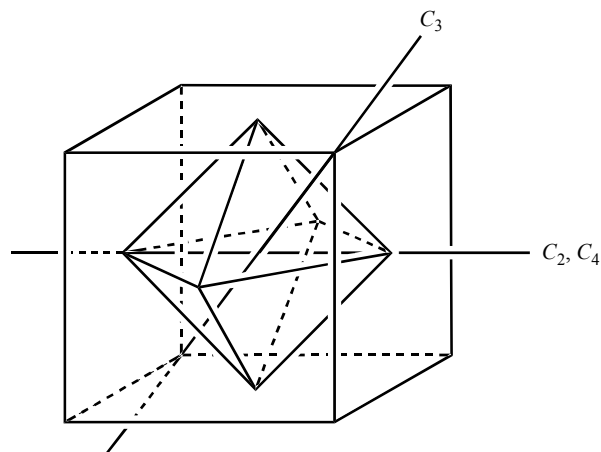
E Every object has an identity operation.

$8C_3$ Diagonals through opposite corners of the cube are C_3 axes.

$6C_2$ Lines bisecting opposite edges are C_2 axes.

$6C_4$ Lines through the centers of opposite faces are C_4 axes. Although there are only three such lines, there are six axes, counting the C_4^3 operations.

$3C_2$ ($=C_4^2$) The lines through the centers of opposite faces are C_4 axes as well as C_2 axes.



* Incorrectly cited as problem 3.41 in first printing of text.

- i The center of the cube is the inversion center.
- $6S_4$ The C_4 axes are also S_4 axes.
- $8S_6$ The C_3 axes are also S_6 axes.
- $3\sigma_h$ These mirror planes are parallel to the faces of the cube.
- $6\sigma_d$ These mirror planes are through two opposite edges.

b. O_h

c. O

- 4.15 a. There are three possible orientations of the two blue faces.

If the blue faces are opposite each other, a C_3 axis connects the centers of the blue faces. This axis has 3 perpendicular C_2 axes, and contains three vertical mirror planes (D_{3d}).

If the blue faces share one vertex of the octahedron, a C_2 axis includes this vertex, and this axis includes two vertical mirror planes (C_{2v}).

The third possibility is for the blue faces to share an edge of the octahedron. In this case, a C_2 axis bisects this shared edge, and includes two vertical mirror planes (C_{2v}).

- b. There are three unique orientations of the three blue faces.

If one blue face is arranged to form edges with each of the two remaining blue faces, the only symmetry operations are identity and a single mirror plane (C_s).


If the three blue faces are arranged such that a single blue face shares an edge with one blue face, but only a vertex with the other blue face, the only symmetry operation is a mirror plane that passes through the center of the blue faces, and the point group is C_s .

If the three blue faces each share an edge with the same yellow face, a C_3 axis emerges from the center of this yellow face, and this axis includes three vertical mirror planes (C_{3v}).

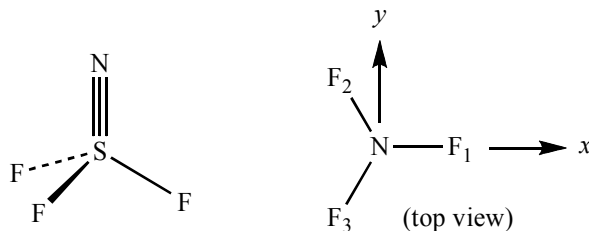
- c. If there are four different colors, and each pair of opposite faces has the identical color, the only symmetry operations are identity and inversion (C_i).

- 4.16 Four point groups are represented by the symbols of the chemical elements. Most symbols have a single mirror in the plane of the symbol (C_s), for example, Cs! Two symbols have D_{2h} symmetry (H, I), and two more (\square , S) have C_{2h} . Seven exhibit C_{2v} symmetry (B, C, K, V, Y, W, U). In some cases, the choice of font may affect the point group. For example, the symbol for nitrogen may have C_{2h} in a sans serif font (\square) but otherwise C_s (N). The symbol of oxygen has $D_{\infty h}$ symmetry if shown as a circle but D_{2h} if oval.

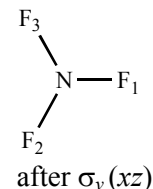
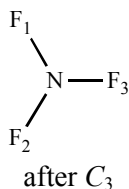
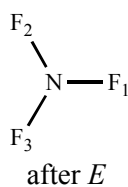
- 4.17 a. on-deck circle $D_{\infty h}$
 b. batter's box D_{2h}
 c. cap C_s
 d. bat $C_{\infty v}$

- e. home plate C_{2v} 
 f. baseball D_{2d} (see Figure 4.1)
 g. pitcher C_1

- 4.18 a. D_{2h} d. D_{4h} g. D_{2h}
 b. C_{2v} e. C_{5h} h. D_{4h}
 c. C_{2v} f. C_{2v} i. C_2

4.19 SNF_3 

Symmetry Operations:



Matrix Representations (reducible):

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3: \begin{bmatrix} \cos \frac{2\pi}{3} & -\sin \frac{2\pi}{3} & 0 \\ \sin \frac{2\pi}{3} & \cos \frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Characters of Matrix Representations:

3

0

1

(continued on next page)

Block Diagonalized Matrices:

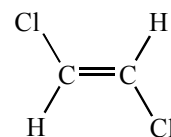
$$\begin{bmatrix} [1 & 0] & 0 \\ [0 & 1] & 0 \\ 0 & 0 & [1] \end{bmatrix} \quad \begin{bmatrix} \left[\begin{array}{cc|c} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \end{array} \right] \\ 0 & 0 & [1] \end{bmatrix} \quad \begin{bmatrix} [1 & 0] & 0 \\ [0 & -1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

Irreducible Representations:

E	$2 C_3$	$3 \sigma_v$	Coordinates Used
2	-1	0	(x, y)
1	1	1	z

Character Table:

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


 4.20 a. C_{2h} molecules have E , C_2 , i , and σ_h operations.

b.

$$\begin{matrix} E: & C_2: & i: & \sigma_h: \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{matrix}$$

 c. These matrices can be block diagonalized into three 1×1 matrices, with the representations shown in the table.

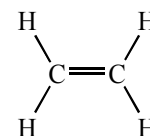
	$\chi(E)$	$\chi(C_2)$	$\chi(i)$	$\chi(\sigma_h)$	
B_u	1	-1	-1	1	from the x and y coefficients
A_u	1	1	-1	-1	from the z coefficients

 The total is $\Gamma = 2B_u + A_u$.

 d. Multiplying B_u and A_u :

$$1 \times 1 + (-1) \times 1 + (-1) \times (-1) + 1 \times (-1) = 0, \text{ proving they are orthogonal.}$$

- 4.21 a. D_{2h} molecules have E , $C_2(z)$, $C_2(y)$, $C_2(x)$, i , $\sigma(xy)$, $\sigma(xz)$, and $\sigma(yz)$ operations.



b.

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2(z): \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2(y): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$C_2(x): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad i: \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \sigma(xy): \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\sigma(xz): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \sigma(yz): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

c.

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
χ	3	-1	-1	-1	-3	1	1	1	
d. Γ_1	1	-1	-1	1	-1	1	1	-1	matching B_{3u}
Γ_2	1	-1	1	-1	-1	1	-1	1	matching B_{2u}
Γ_3	1	1	-1	-1	-1	-1	1	1	matching B_{1u}

e. $\Gamma_1 \times \Gamma_2 = 1 \times 1 + (-1) \times (-1) + (-1) \times 1 + 1 \times (-1) + (-1) \times (-1) + 1 \times 1 + 1 \times (-1) + (-1) \times 1 = 0$

$$\Gamma_1 \times \Gamma_3 = 1 \times 1 + (-1) \times 1 + (-1) \times (-1) + 1 \times (-1) + (-1) \times (-1) + 1 \times (-1) + 1 \times 1 + (-1) \times 1 = 0$$

$$\Gamma_2 \times \Gamma_3 = 1 \times 1 + (-1) \times 1 + 1 \times (-1) + (-1) \times (-1) + (-1) \times (-1) + 1 \times (-1) + (-1) \times 1 + 1 \times 1 = 0$$

- 4.22 a. $h = 8$ (the total number of symmetry operations)

b.

$$A_1 \times E = 1 \times 2 + 2 \times 1 \times 0 + 1 \times (-2) + 2 \times 1 \times 0 + 2 \times 1 \times 0 = 0$$

$$A_2 \times E = 1 \times 2 + 2 \times 1 \times 0 + 1 \times (-2) + 2 \times (-1) \times 0 + 2 \times (-1) \times 0 = 0$$

$$B_1 \times E = 1 \times 2 + 2 \times (-1) \times 0 + 1 \times (-2) + 2 \times 1 \times 0 + 2 \times (-1) \times 0 = 0$$

$$B_2 \times E = 1 \times 2 + 2 \times (-1) \times 0 + 1 \times (-2) + 2 \times (-1) \times 0 + 2 \times 1 \times 0 = 0$$

c.

$$E: 4 + 2 \times 0 + 4 + 2 \times 0 + 2 \times 0 = 8$$

$$A_1: 1 + 2 \times 1 + 1 + 2 \times 1 + 2 \times 1 = 8$$

$$A_2: 1 + 2 \times 1 + 1 + 2 \times 1 + 2 \times 1 = 8$$

$$B_1: 1 + 2 \times 1 + 1 + 2 \times 1 + 2 \times 1 = 8$$

$$B_2: 1 + 2 \times 1 + 1 + 2 \times 1 + 2 \times 1 = 8$$

d. $\Gamma_1 = 2A_1 + B_1 + B_2 + E:$

$$A_1: 1/8[1 \times 6 + 2 \times 1 \times 0 + 1 \times 2 + 2 \times 1 \times 2 + 2 \times 1 \times 2] = 2$$

$$A_2: 1/8[1 \times 6 + 2 \times 1 \times 0 + 1 \times 2 + 2 \times (-1) \times 2 + 2 \times (-1) \times 2] = 0$$

$$B_1: 1/8[1 \times 6 + 2 \times (-1) \times 0 + 1 \times 2 + 2 \times 1 \times 2 + 2 \times (-1) \times 2] = 1$$

$$B_2: 1/8[1 \times 6 + 2 \times (-1) \times 0 + 1 \times 2 + 2 \times (-1) \times 2 + 2 \times 1 \times 2] = 1$$

$$E: 1/8[2 \times 6 + 2 \times 0 \times 0 + (-2) \times 2 + 2 \times 0 \times 2 + 2 \times 0 \times 2] = 1$$

$$\Gamma_2 = 3A_1 + 2A_2 + B_1:$$

$$A_1: 1/8[1 \times 6 + 2 \times 1 \times 4 + 1 \times 6 + 2 \times 1 \times 2 + 2 \times 1 \times 0] = 3$$

$$A_2: 1/8[1 \times 6 + 2 \times 1 \times 4 + 1 \times 6 + 2 \times (-1) \times 2 + 2 \times (-1) \times 0] = 2$$

$$B_1: 1/8[1 \times 6 + 2 \times (-1) \times 4 + 1 \times 6 + 2 \times 1 \times 2 + 2 \times (-1) \times 0] = 1$$

$$B_2: 1/8[1 \times 6 + 2 \times (-1) \times 4 + 1 \times 6 + 2 \times (-1) \times 2 + 2 \times 1 \times 0] = 0$$

$$E: 1/8[2 \times 6 + 2 \times 0 \times 4 + (-2) \times 6 + 2 \times 0 \times 2 + 2 \times 0 \times 0] = 0$$

4.23 C_{3v}

$$\Gamma_1 = 3A_1 + A_2 + E:$$

$$A_1: 1/6[1 \times 6 + 2 \times 1 \times 3 + 3 \times 1 \times 2] = 3$$

$$A_2: 1/6[1 \times 6 + 2 \times 1 \times 3 + 3 \times (-1) \times 2] = 1$$

$$E: 1/6[2 \times 6 + 2 \times (-1) \times 3 + 3 \times 0 \times 2] = 1$$

$$\Gamma_2 = A_2 + E:$$

$$A_1: 1/6[1 \times 5 + 2 \times 1 \times (-1) + 3 \times 1 \times (-1)] = 0$$

$$A_2: 1/6[1 \times 5 + 2 \times 1 \times (-1) + 3 \times (-1) \times (-1)] = 1$$

$$E: 1/6[2 \times 5 + 2 \times (-1) \times (-1) + 3 \times 0 \times (-1)] = 2$$

 O_h

$$\Gamma_3 = A_{1g} + E_g + T_{1u}:$$

$$A_{1g}: 1/48[6 + 0 + 0 + 12 + 6 + 0 + 0 + 0 + 12 + 12] = 1$$

$$A_{2g}: 1/48[6 + 0 + 0 - 12 + 6 + 0 + 0 + 0 + 12 - 12] = 0$$

$$E_g: 1/48[12 + 0 + 0 + 0 + 12 + 0 + 0 + 0 + 24 + 0] = 1$$

$$T_{1g}: 1/48[18 + 0 + 0 + 12 - 6 + 0 + 0 + 0 - 12 - 12] = 0$$

$$T_{2g}: 1/48[18 + 0 + 0 - 12 - 6 + 0 + 0 + 0 - 12 + 12] = 0$$

$$A_{1u}: 1/48[6 + 0 + 0 + 12 + 6 + 0 + 0 + 0 - 12 - 12] = 0$$

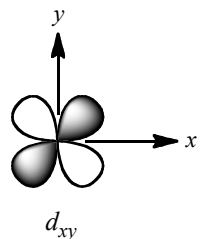










$$A_{2u}: 1/48[6 + 0 + 0 - 12 + 6 + 0 + 0 + 0 - 12 + 12] = 0$$

$$E_u: 1/48[12 + 0 + 0 + 0 + 12 + 0 + 0 + 0 - 24 + 0] = 0$$

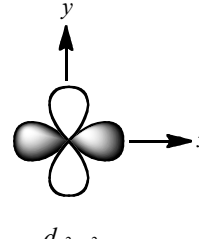










$$T_{1u}: 1/48[18 + 0 + 0 + 12 - 6 + 0 + 0 + 0 + 12 + 12] = 1$$

$$T_{2u}: 1/48[18 + 0 + 0 - 12 - 6 + 0 + 0 + 0 + 12 - 12] = 0$$

4.24 The d_{xy} characters match the characters of the B_{2g} representation:

	d_{xy}	χ
		1
		-1
		1
		-1
		1
		1
		-1
		1
		-1
		1

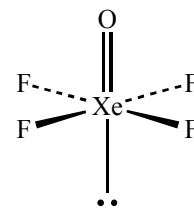
The $d_{x^2-y^2}$ characters match the characters of the B_{1g} representation:

	$d_{x^2-y^2}$	χ
		1
		-1
		1
		1
		-1
		1
		-1
		1
		1
		-1

4.25 Chiral: 4.5: O_2F_2 , $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ 4.6: none 4.7: screw, Wilkins Micawber 4.8: recycle symbol 4.9: set of three wind turbine blades, Flying Mercury sculpture, coiled spring

4.26 a. Point group: C_{4v}

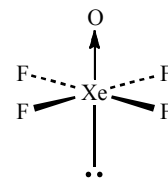
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
Γ	18	2	-2	4	2	
A_1	1	1	1	1	1	z
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$



b. $\Gamma = 4A_1 + A_2 + 2B_1 + B_2 + 5E$

c. Translation: $A_1 + E$ (match x, y , and z)
 Rotation: $A_2 + E$ (match R_x, R_y , and R_z)
 Vibration: all that remain: $3A_1 + 2B_1 + B_2 + 3E$

d. The character for each symmetry operation for the Xe–O stretch is +1. This corresponds to the A_1 irreducible representation, which matches the function z and is therefore IR-active.



- 4.27 For SF₆, the axes of the sulfur should point at three of the fluorines. The fluorine axes can be chosen in any way, as long as one from each atom is directed toward the sulfur atom. There are seven atoms with three axes each, for a total of 21.

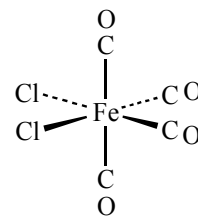
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
Γ	21	0	-1	3	-3	-3	-1	0	5	3		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2u}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)	

Reduction of Γ gives $\Gamma = 3T_{1u} + T_{1g} + A_{1g} + E_g + T_{2g} + T_{2u}$. T_{1u} accounts for translation and also infrared active vibrational modes. T_{1g} is rotation. The remainder are infrared-inactive vibrations.

- 4.28 a. *cis*-Fe(CO)₄Cl₂ has C_{2v} symmetry.

The vectors for CO stretching have the representation Γ :

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ	4	0	2	2	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y



$$n(A_1) = 1/4[4 \times 1 + 0 \times 1 + 2 \times 1 + 2 \times 1] = 2$$

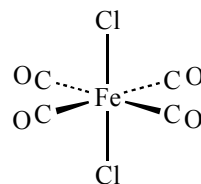
$$n(A_2) = 1/4[4 \times 1 + 0 \times 1 + 2 \times (-1) + 2 \times (-1)] = 0$$

$$n(B_1) = 1/4[4 \times 1 + 0 \times (-1) + 2 \times 1 + 2 \times (-1)] = 1$$

$$n(B_2) = 1/4[4 \times 1 + 0 \times (-1) + 2 \times (-1) + 2 \times 1] = 1$$

$$\Gamma = 2A_1 + B_1 + B_2, \text{ all four IR active.}$$

- b. *trans*-Fe(CO)₄Cl₂ has D_{4h} symmetry.



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ	4	0	0	2	0	0	0	4	2	0	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)

Omitting the operations that have zeroes in Γ :

$$n(A_{2u}) = 1/16[4 \times 1 + 2 \times 2 \times (-1) + 4 \times (-1) + 2 \times 2 \times 1] = 0$$

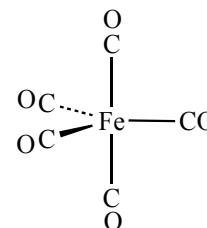
$$n(E_u) = 1/16[4 \times 2 + 2 \times 2 \times 0 + 4 \times 2 + 2 \times 2 \times 0] = 1 \quad (\text{IR active})$$

Note: In checking for IR-active bands, it is only necessary to check the irreducible representations having the same symmetry as x , y , or z , or a combination of them.

- c. $\text{Fe}(\text{CO})_5$ has D_{3h} symmetry.

The vectors for C–O stretching have the following representation Γ :

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	5	2	1	3	0	3	
E'	2	-1	0	2	-1	0	(x, y)
A_2''	1	1	-1	-1	-1	1	z



$$n(E') = 1/12 [(5 \times 2) + (2 \times 2 \times -1) + (3 \times 2)] = 1$$

$$n(A_2'') = 1/12 [(5 \times 1) + (2 \times 2 \times 1) + (3 \times 1 \times -1) + (3 \times -1) + (3 \times 3 \times 1)] = 1$$

There are two bands, one matching E' and one matching A_2'' . These are the only irreducible representations that match the coordinates x , y , and z .

- 4.29 In 4.28a, the symmetries of the CO stretching vibrations of *cis*- $\text{Fe}(\text{CO})_4\text{Cl}_2$ (C_{2v} symmetry) are determined as $2A_1 + B_1 + B_2$. Each of these representations matches Raman-active functions: A_1 (x^2, y^2, z^2); A_2 (xy), B_1 (xz); and B_2 (yz), so all are Raman-active.

In 4.28b, the symmetries of the CO stretching vibrations of *trans*- $\text{Fe}(\text{CO})_4\text{Cl}_2$ (D_{4h} symmetry) are $A_{1g} + B_{1g} + E_u$. Only A_{1g} ($x^2 + y^2, z^2$) and B_{1g} ($x^2 - y^2$) match Raman active functions; this complex exhibits two Raman-active CO stretching vibrations.

In 4.28c, the symmetries of the CO stretching vibrations of $\text{Fe}(\text{CO})_5$ (D_{3h} symmetry) are $2A_1' + E' + A_2''$. Only A_1' ($x^2 + y^2, z^2$) and E' ($x^2 - y^2, xy$) match Raman-active functions; this complex exhibits four Raman-active CO stretching vibrations.

- 4.30 a. The point group is C_{2h} .

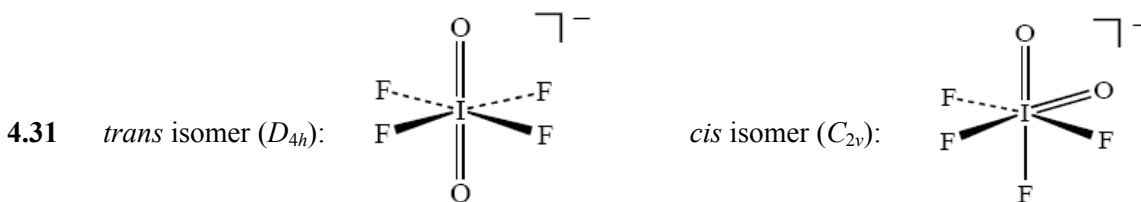
- b. Using the Si–I bond vectors as a basis generates the representation:

C_{2h}	E	C_2	i	σ_h	
Γ	4	0	0	0	
A_g	1	1	1	1	$x^2 + y^2, z^2$
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y

$$\Gamma = A_g + B_g + A_u + B_u$$

The A_u and B_u vibrations are infrared active.

- c. The A_g and B_g vibrations are Raman active.



The simplest approach is to consider if the number of infrared-active I–O stretches is different for these structures. (Alternatively, one could also determine the number of IR-active I–F stretches, a slightly more complicated task.)

trans:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ	2	2	2	0	0	0	0	0	2	2	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z

There is only a single IR-active I–O stretch (the antisymmetric stretch), A_{2u} .

cis:

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
Γ	2	0	2	0	
A_1	1	1	1	1	z
B_1	1	-1	1	-1	x

There are two IR-active I–O stretches, the A_1 and B_1 (symmetric and antisymmetric). Infrared spectra should therefore be able to distinguish between these isomers. (Reversing the x and y axes would give $A_1 + B_2$. Because B_2 matches y , it would also represent an IR-active vibration.)

Because these isomers would give different numbers of IR-active absorptions, infrared spectra should be able to distinguish between them. The reference provides detailed IR data.

- 4.32 a. One way to deduce the number of Raman-active vibrations of AsP_3 is to first determine the symmetries of all the degrees of freedom. This complex exhibits C_3 symmetry, with the C_3 axis emerging from the As atom. The $\chi(E)$ is 12; the x , y , and z axes of the four atoms do not shift when the identity operation is carried out. Only the As atom contributes to the character of the C_3 transformation matrix; the P atoms shift during rotation about the C_3 axis. The general transformation matrix for rotation about the z axis (Section 4.3.3) affords 0 as $\chi(C_3)$ for $\theta = 120^\circ$. The As atom and one P atom do not shift when a σ_v reflection is carried out, and $\chi(\sigma_v) = 2$ (see the $\sigma_{v(xz)}$ transformation matrix in Section 4.3.3 for the nitrogen atom of NH_3 as a model of how the two unshifted atoms of AsP_3 will contribute to the character of the σ_v transformation matrix).



C_{3v}	E	C_3	$3\sigma_v$		
Γ	12	0	2		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_x	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Reduction of the reducible representation affords $3 A_1 + A_2 + 4 E$.

On the basis of the character table, the translational modes of AsP_3 have the symmetries $A_1 + E$, and the rotational modes have the symmetries $A_2 + E$. The six vibrational modes of AsP_3 subsequently have the symmetries $2 A_1 + 2 E$. These vibrational modes are Raman-active, and four absorptions are expected (and observed) since the sets of E modes are degenerate. B. M. Cossairt, M.C. Diawara, C. C. Cummins, *Science* **2009**, 323, 602 assigns the bands as: 313 (a_1), 345 (e), 428 (a_1), 557 (e) cm^{-1} .

Alternatively, the set of six bonds may be selected as the basis for a representation focused specifically on stretches of these bonds. This approach generates the following representation:

C_{3v}	E	C_3	$3\sigma_v$		
Γ	6	0	2		

This representation reduces to $2 A_1 + 2 E$, the same result as obtained by first considering all degrees of freedom, then subtracting the translational and rotational modes.

- b. As_2P_2 exhibits C_{2v} symmetry, and (like AsP_3) will have six vibrational modes ($3N - 6$). Inspection of the C_{2v} character table indicates that all vibrational modes will be Raman active. Since each irreducible representation has a dimension of 1, the number of Raman absorptions expected is 6 (that is, there will be no degenerate vibrational modes).



This prediction can be confirmed via deduction of the symmetries of the vibrational modes. As in part a, we will first determine the symmetries of all the degrees of freedom. The $\chi(E)$ of the transformation matrix is 12. In As_2P_2 , the C_2 axis does not pass through any atoms, and all four atoms shift upon rotation; $\chi(C_2) = 0$. Two atoms do not shift upon reflection through each of the σ_v planes. The contribution to the character of the transformation matrix for each of these unshifted atoms is 1, and $\chi(\sigma_v(xz)) = \chi(\sigma_v'(yz)) = 2$.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	12	0	2	2		
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	xz
B_2	1	-1	-1	1	y, R_x	yz

Reduction of the reducible representation affords $4 A_1 + 2 A_2 + 3 B_1 + 3 B_2$.

On the basis of the above character table, the translational modes of As_2P_2 have the symmetries $A_1 + B_1 + B_2$, and the rotational modes have the symmetries $A_2 + B_1 + B_2$. The six anticipated Raman-active vibrational modes of As_2P_2 subsequently have the symmetries $3 A_1 + A_2 + B_1 + B_2$.

(continued on next page)

As in part a, an alternative approach is to select the set of six bonds as the basis for a representation focused specifically on stretching vibrations. This approach generates the following representation:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	6	2	2	2		

This representation reduces to $3 A_1 + A_2 + B_1 + B_2$, the same result as obtained by first considering all degrees of freedom, then subtracting the translational and rotational modes.

- c. The issue here is whether or not P_4 (T_d) exhibits 4 Raman-active vibrations as does AsP_3 . We will first determine the symmetries of all the degrees of freedom. The $\chi(E)$ of the transformation matrix is 12. Only one P_4 atom is fixed upon rotation about each C_3 axis; $\chi(C_3) = 0$. All four atoms are shifted upon application of the C_2 and S_4 axes; $\chi(C_2) = \chi(S_4) = 0$. Two atoms do not shift upon reflection through each of the σ_d planes. The contribution to the character of the transformation matrix for each of these unshifted atoms is 1, and $\chi(\sigma_d) = 2$.



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ	12	0	0	0	2		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

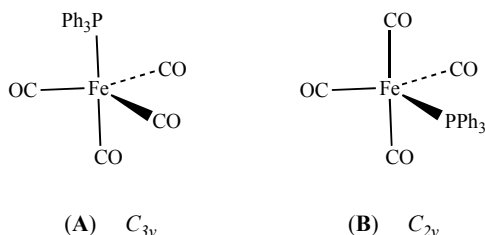
Reduction of the reducible representation affords $A_1 + E + T_1 + 2 T_2$. Since the symmetries of the translational modes and rotational modes are T_2 and T_1 , respectively, the symmetries of the vibrational modes are $A_1 + E + T_2$, all of these modes are Raman-active so three Raman absorptions are expected for P_4 , and P_4 could potentially be distinguished from AsP_3 solely on the basis of the number of Raman absorptions.

The alternative approach, using the set of six P-P bonds as the basis for a representation focused specifically on bond stretches, generates the following representation:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ	6	0	2	0	2		

This representation reduces to $A_1 + E + T_2$, the same result as obtained by first considering all degrees of freedom, then subtracting the translational and rotational modes.

- 4.33 The possible isomers are as follows, with the triphenylphosphine ligand in either the axial (**A**) or equatorial (**B**) sites.



Note that the triphenylphosphine ligand is approximated as a simple L ligand for the sake of the point group determination. Rotation about the Fe–P bond in solution is expected to render the arrangement of the phenyl rings unimportant in approximating the symmetry of these isomers in solution. The impact of the phenyl rings would likely be manifest in the IR $\nu(\text{CO})$ spectra of these isomers in the solid-state.

For **A**, we consider each CO bond as a vector to deduce the expected number of carbonyl stretching modes. The irreducible representation is as follows:

C_{3v}	E	C_3	$3\sigma_v$		
Γ	4	1	2		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_x	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Reduction of the reducible representation affords $2 A_1 + E$. These stretching modes are IR-active and three $\nu(\text{CO})$ absorptions are expected for **A**.

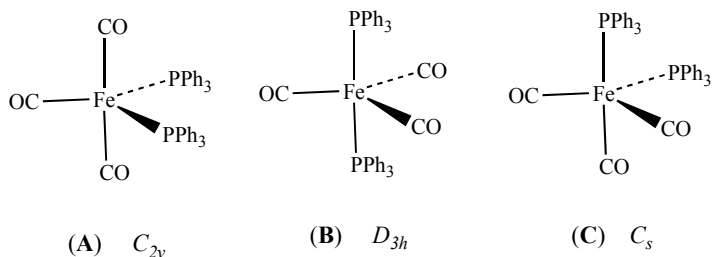
For **B**, a similar analysis affords the following irreducible representation:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	4	0	2	2		
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	xz
B_2	1	-1	-1	1	y, R_x	yz

Reduction of the reducible representation affords $2 A_1 + B_1 + B_2$. These stretching modes are IR-active, and four $\nu(\text{CO})$ absorptions are expected for **A**.

The reported $\nu(\text{CO})$ IR spectrum is consistent with formation of isomer **A**, with the triphenylphosphine ligand in the axial site.

- 4.34 As in 4.33, we consider the triphenylphosphine ligand as a simple L group for point group determination. The point groups for isomers A, B, and C are as follows:



For **A**, the set of irreducible representations for the three CO stretching vibrational modes is $2 A_1 + B_1$. These modes are all IR-active in the C_{2v} character table, and three ν (CO) IR absorptions are expected for isomer **A**.

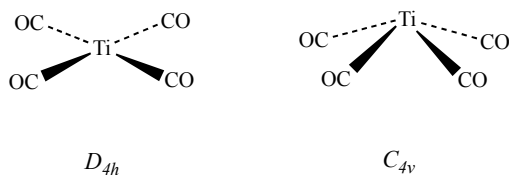
For **B**, the set of irreducible representations for the three CO stretching vibrational modes is $A_1' + E'$. Only the E' mode is IR-active in the D_{3h} point group, and one ν (CO) IR absorption is expected for isomer **B**.

For **C**, the set of irreducible representations for the three CO stretching vibrational modes is $2 A' + A''$. These modes are all IR-active in the C_s point group, and three ν (CO) IR absorptions are expected for isomer **C**.

The single ν (CO) IR absorption reported for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ supports the presence of the D_{3h} isomer **B**.

The *trans* isomer B is reported in R. L. Keiter, E. A. Keiter, K. H. Hecker, C. A. Boecker, *Organometallics*, **1988**, 7, 2466, and the authors observe splitting of the absorption associated with the E' mode in CHCl_3 . The forbidden A_1' stretching mode was observed as a weak absorption.

- 4.35 The IR spectrum exhibits two ν (CO) absorptions. The two proposed metal carbonyl fragments will be considered independently for analysis.



The reducible representation for the four vectors associated with the CO bonds in the C_{4v} fragment is as follows:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0

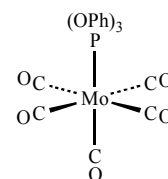
Reduction of this representation affords $A_1 + B_1 + E$. The A_1 and E modes are IR-active, and a titanium complex with a square pyramidal titanium tetracarbonyl fragment is supported by the IR spectral data.

For the D_{4h} fragment, the reducible representation for the set of vectors associated with the CO bonds is:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

Reduction of the reducible representation affords $A_{1g} + B_{1g} + E_u$. Only the E modes are IR-active, and a complex with a square planar titanium tetracarbonyl fragment is expected to exhibit a single IR ν (CO) stretching absorption. This D_{4h} possibility can therefore be ruled out on the basis of the spectrum.

- 4.36** A reasonable product is the C_{4v} molecule $\text{Mo}(\text{CO})_5(\text{P}(\text{OPh})_3)$, with CO replacing a triphenylphosphite ligand.



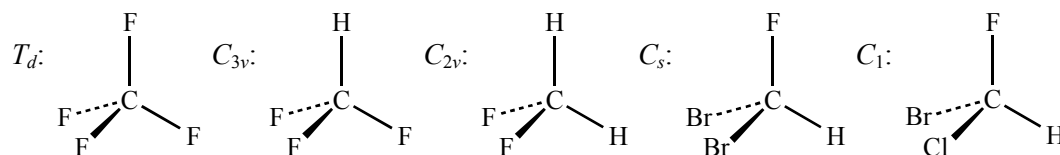
The reducible representation for the five vectors associated with the CO bonds in this molecule is:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ	5	1	1	3	1

Reduction of this representation affords $2A_1 + B_1 + E$. The A_1 and E modes are IR-active, and three IR ν (CO) stretching absorptions are expected. The reported IR spectrum features three strong ν (CO) absorptions, and one “very weak” absorption attributed to the forbidden B_1 mode in D. J. Darensbourg, T. L. Brown, *Inorg. Chem.*, **1968**, 7, 959.

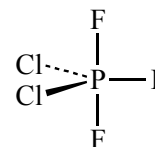
- 4.37** **I** has C_2 symmetry, with a C_2 axis running right to left, perpendicular to the Cl, N, Cl, N and Cl, P, Cl, P faces.
II also has C_2 symmetry, with the same C_2 axis as **I**. (Lower left corner occupied by Cl, not C.)
III has only an inversion center and C_i symmetry.

- 4.38** An example for each of the five possible point groups:



- 4.39**
- The S–C–C portion is linear, so the molecule has a C_3 axis along the line of these three atoms, three σ_v planes through these atoms and an F atom on each end, but no other symmetry elements. C_{3v}
 - The molecule has only an inversion center, so it is C_i . The inversion center is equivalent to an S_2 axis perpendicular to the average plane of the ring.
 - $\text{M}_2\text{Cl}_6\text{Br}_4$ is C_i .
 - This complex has a C_3 axis, splitting the three N atoms and the three P atoms (almost as drawn), but no other symmetry elements. C_3

- e. The most likely isomer has the less electronegative Cl atoms in equatorial positions. Point group: C_{2v}
- 4.40 The structures on the top row are D_{2d} (left) and C_s (right). Those on the bottom row are C_{2h} (left) and C_{4v} (right).
- 4.41 a. C_{3v}
- b. D_{5h}
- c. Square structure: D_{2d} (bottom ligand on lower left Re should be CO instead of L);
Corner structure: C_s
- d. D_{3d}
- 4.42 Web of Science and SciFinder Scholar should be helpful, but simply searching for these symmetries using a general Internet search should provide examples of these point groups. Some examples:



- a. S_6 : $\text{Mo}_2(\text{SC}_6\text{H}_2\text{Me}_3)_6$ (M. H. Chisholm, J. F. Corning, and J. C. Huffman, *J. Am. Chem. Soc.*, **1983**, 105, 5924)
 $\text{Mo}_2(\text{NMe}_2)_6$ (M. H. Chisholm, R. A. Cotton, B. A. Grenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **1976**, 98, 4469)
 $[\text{NaFe}_6(\text{OMe})_{12}(\text{dbm})_6]^+$ (dbm = dibenzoylmethane, $\text{C}_6\text{H}_5\text{COCCOC}_6\text{H}_5$) (F. L. Abbati, A. Cornia, A. C. Fabretti, A. Caneschi, and D. Garreschi, *Inorg. Chem.*, **1998**, 37, 1430)
- b. T $\text{Pt}(\text{CF}_3)_4$, C_{44}
- c. I_h C_{20} , C_{80}
- d. T_h $[\text{Co}(\text{NO}_2)_6]^{3-}$, $\text{Mo}(\text{NMe}_2)_6$

In addition to examples that can be found using Web of Science, SciFinder, and other Internet search tools, numerous examples of these and other point groups can be found in I. Hargittai and M. Hargittai, *Symmetry Through the Eyes of a Chemist*, as listed in the General References section.