

1/28: I) Do the following problem from your text: Chapter 4: #22.

**4.22** Using the  $D_{2d}$  character table,

a. Determine the order of the group.

*Answer.*  $h = 8$ ; count the number of symmetry elements.  $\square$

b. Verify that the  $E$  irreducible representation is orthogonal to each of the other irreducible representations.

*Answer.*

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{A_1}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{A_2}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(-1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{B_1}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(-1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{B_2}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(1) = 0$$

$\square$

c. For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

*Answer.*

$$\sum_{R_c} g_c [\chi_{A_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot 1^2 = 8$$

$$\sum_{R_c} g_c [\chi_{A_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot (-1)^2 = 8$$

$$\sum_{R_c} g_c [\chi_{B_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot (-1)^2 = 8$$

$$\sum_{R_c} g_c [\chi_{B_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot 1^2 = 8$$

$$\sum_{R_c} g_c [\chi_E(R_c)]^2 = 1 \cdot 2^2 + 2 \cdot 0^2 + 1 \cdot (-2)^2 + 2 \cdot 0^2 + 2 \cdot 0^2 = 8$$

$\square$

d. Reduce the following representations to their component irreducible representations.

$D_{2d}$	$E$	$2S_4$	$C_2$	$2C'_2$	$2\sigma_d$
$\Gamma_1$	6	0	2	2	2
$\Gamma_2$	6	4	6	2	0

*Answer.* For  $\Gamma_1$ :

$$a_{A_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{A_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(1)] = 2$$

$$a_{A_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{A_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(-1)] = 0$$

$$a_{B_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{B_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(-1)] = 1$$

$$a_{B_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{B_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(1)] = 1$$

$$a_E = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_E(R_c) = \frac{1}{8} [(1)(6)(2) + (2)(0)(0) + (1)(2)(-2) + (2)(2)(0) + (2)(2)(0)] = 1$$

Therefore, we know that

$$\Gamma_1 = 2A_1 + B_1 + B_2 + E$$

For  $\Gamma_2$ :

$$a_{A_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{A_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(1)] = 3$$

$$a_{A_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{A_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(-1)] = 2$$

$$a_{B_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{B_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(-1)] = 1$$

$$a_{B_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{B_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(1)] = 0$$

$$a_E = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_E(R_c) = \frac{1}{8} [(1)(6)(2) + (2)(4)(0) + (1)(6)(-2) + (2)(2)(0) + (2)(0)(0)] = 0$$

Therefore, we know that

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

□

II) Decompose the following reducible representations into their irreducible components. Ordering of the classes is the same as in the character tables in Appendix C of your text.

a)  $D_{3h}$ : 5, 2, 1, 3, 0, 3

*Answer.*

$$a_{A'_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_1}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(1)] = 2$$

$$a_{A'_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_2}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(-1)] = 0$$

$$a_{E'} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E'}(R_c) = \frac{1}{12} [(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(3)(0)] = 1$$

$$a_{A''_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_1}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(-1)] = 0$$

$$a_{A''_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_2}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(1)] = 1$$

$$a_{E''} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E''}(R_c) = \frac{1}{12} [(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(-2) + (2)(0)(1) + (3)(3)(0)] = 0$$

Therefore, we know that

$$\Gamma = 2A'_1 + E' + A''_2$$

□

b)  $D_{3h}$ : 3, 0, -1, -3, 0, 1

*Answer.*

$$a_{A'_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_1}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(1)] = 0$$

$$a_{A'_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_2}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(-1)] = 0$$

$$a_{E'} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E'}(R_c) = \frac{1}{12} [(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(2) + (2)(0)(-1) + (3)(1)(0)] = 0$$

$$a_{A''_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_1}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(-1)] = 0$$

$$a_{A''_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_2}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(1)] = 1$$

$$a_{E''} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E''}(R_c) = \frac{1}{12} [(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(-2) + (2)(0)(1) + (3)(1)(0)] = 1$$

Therefore, we know that

$$\Gamma = A''_2 + E''$$

□

c)  $C_{2v}$ : 4, 0, 0, 0

*Answer.* We know the following by inspection.

$$\Gamma = A_1 + A_2 + B_1 + B_2$$

□

d)  $C_{2h}$ : 5, 1, 1, 1

*Answer.* We know the following by inspection.

$$\Gamma = 2A_g + B_g + A_u + B_u$$

□

e)  $T_d$ : 13, 1, 5, -3, -3

*Answer.*

$$a_{A_1} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_1}(R_c) = \frac{1}{24} [(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(1) + (6)(-3)(1)] = 0$$

$$a_{A_2} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_2}(R_c) = \frac{1}{24} [(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(-1) + (6)(-3)(-1)] = 3$$

$$a_E = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_E(R_c) = \frac{1}{24} [(1)(13)(2) + (8)(1)(-1) + (3)(5)(2) + (6)(-3)(0) + (6)(-3)(0)] = 2$$

$$a_{T_1} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_1}(R_c) = \frac{1}{24} [(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(1) + (6)(-3)(-1)] = 1$$

$$a_{T_2} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_2}(R_c) = \frac{1}{24} [(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(-1) + (6)(-3)(1)] = 1$$

Therefore, we know that

$$\Gamma = 3A_2 + 2E + T_1 + T_2$$

□

f)  $T_h$ : 8, -1, -1, 4, 8, -1, -1, 4

*Answer.*

$$\begin{aligned} a_{A_g} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_g}(R_c) \\ &= \frac{1}{24} [(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1)] \\ &= 1 \end{aligned}$$

$$\begin{aligned} a_{A_u} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_u}(R_c) \\ &= \frac{1}{24} [(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(-1) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} 2a_{E_g} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E_g}(R_c) \\ a_{E_g} &= \frac{1}{48} [(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2)] \\ &= 2 \end{aligned}$$

$$\begin{aligned} 2a_{E_u} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E_u}(R_c) \\ a_{E_u} &= \frac{1}{48} [(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(-2) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(-2)] \\ &= 0 \end{aligned}$$

$$\begin{aligned}
 a_{T_g} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_g}(R_c) \\
 &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1)] \\
 &= 1
 \end{aligned}$$

$$\begin{aligned}
 a_{T_u} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_u}(R_c) \\
 &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)] \\
 &= 0
 \end{aligned}$$

Therefore, we know that

$$\Gamma = A_g + 2\{E_g\} + T_g$$

□

- III) Draw the set of  $s$ ,  $p$ , and  $d$  orbitals, indicating the Cartesian axes and the proper phases of the orbitals. By noting how each orbital is affected by the symmetry operations in the  $C_{2h}$  point group ( $E$ ,  $C_2$ ,  $i$ ,  $\sigma_h$ ), write an irreducible representation for each orbital. Compare your results with the listing of the orbitals in the character table in Appendix C of the text.

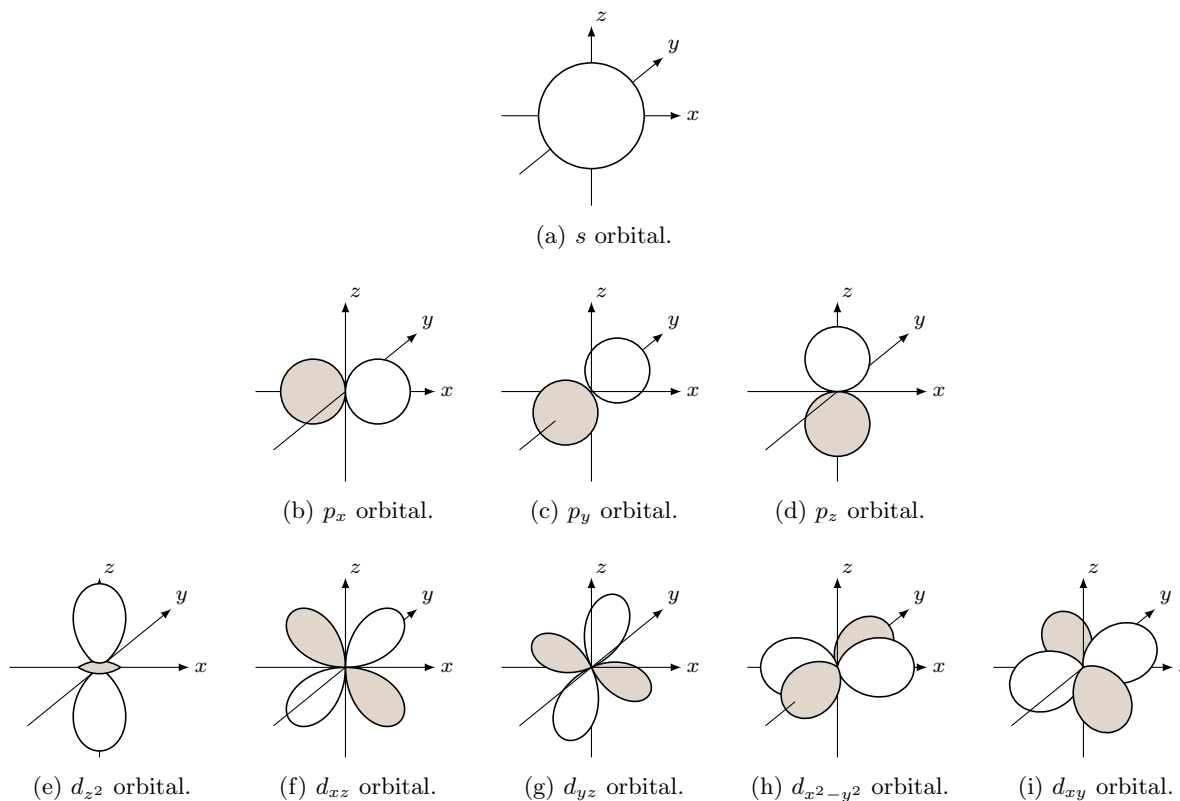


Figure 1:  $s$ ,  $p$ , and  $d$  orbitals.

*Answer.* In Figure 1, white shading means positive phase and orange means negative phase.

Here are irreducible representations for each orbital:

$$\begin{aligned}\Gamma_s &= (1, 1, 1, 1) = A_g \\ \Gamma_{p_x} &= (1, -1, -1, 1) = B_u \\ \Gamma_{p_y} &= (1, -1, -1, 1) = B_u \\ \Gamma_{p_z} &= (1, 1, -1, -1) = A_u \\ \Gamma_{d_{z^2}} &= (1, 1, 1, 1) = A_g \\ \Gamma_{d_{xz}} &= (1, -1, 1, -1) = B_g \\ \Gamma_{d_{yz}} &= (1, -1, 1, -1) = B_g \\ \Gamma_{d_{x^2-y^2}} &= (1, 1, 1, 1) = A_g \\ \Gamma_{d_{xy}} &= (1, 1, 1, 1) = A_g\end{aligned}$$

□

- IV) The molecule  $\text{Co}(\text{CO})_4(\text{SiMe}_3)$  has a structure based on a trigonal bipyramid. The infrared spectrum of  $\text{Co}(\text{CO})_4(\text{SiMe}_3)$  exhibits three  $\nu(\text{CO})$  stretching vibrations at 2100, 2041, and 2009  $\text{cm}^{-1}$ . Draw the two possible structures based on the TBP geometry, assign their proper point groups, and use the infrared data to determine which is the correct structure.

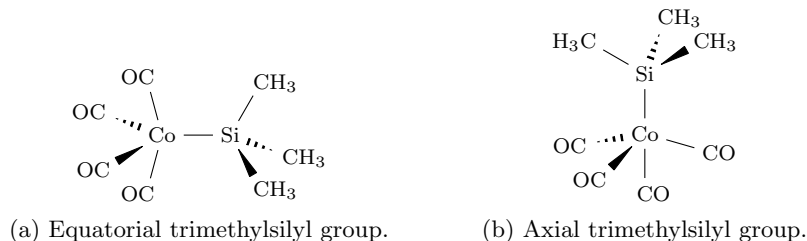


Figure 2: Structures of  $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ .

*Answer.* Note that for the sake of point group assignments, the CO ligands will be treated as identical spheres. Additionally, the  $\text{SiMe}_3$  ligand will be treated as a sphere distinguishable from the CO “spheres.”

The structure in Figure 2a: Not high or low symmetry. Has a  $C_2$  axis. No perpendicular  $C_2$  axes. No  $\sigma_h$ . Has two perpendicular  $\sigma_v$  planes. Therefore, it is of the  $C_{2v}$  point group.

We can determine that  $\Gamma_\nu = (4, 0, 2, 2) = 2A_1 + B_1 + B_2$  by counting how many  $\overrightarrow{\text{Co}-\text{C}\ddot{\text{O}}}$  vectors stay the same under each symmetry operation and decomposing by inspection. With four stretching modes that are all IR active, we can expect there to be four peaks in the infrared spectrum of  $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ . Therefore, this is not the correct structure.

The structure in Figure 2b: Not high or low symmetry. Has a  $C_3$  axis. No perpendicular  $C_2$  axes. No  $\sigma_h$ . Has three  $\sigma_v$  planes all offset by  $60^\circ$ . Therefore, it is of the  $C_{3v}$  point group.

We can determine that  $\Gamma_\nu = (4, 1, 2) = 2A_1 + E$  by counting how many  $\overrightarrow{\text{Co}-\text{C}\ddot{\text{O}}}$  vectors stay the same under each symmetry operation and decomposing by inspection. With three  $\nu(\text{CO})$  stretching modes that are all IR active, we can expect there to be three peaks in the infrared spectrum of  $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ . This confirms that this is the correct structure.  $\square$

V) Determine the number and symmetry types of normal vibrations in the following molecules:

- a)  $\text{H}_3\text{PBH}_3$ : with a staggered ethane-like geometry.

*Answer.*  $\text{H}_3\text{PBH}_3$  has  $3(8) - 6 = 18$  normal vibrations.

Not high or low symmetry. Has a  $C_3$  axis. No perpendicular  $C_2$  axes. No  $\sigma_h$ . Has three  $\sigma_v$  planes all offset by  $60^\circ$ . Therefore,  $\text{H}_3\text{PBH}_3$  is of the  $C_{3v}$  point group.

We can determine that  $\Gamma_{x,y,z} = (3, 0, 1)$ . We can also figure out that the number of atoms unmoved after applying each symmetry operation is  $(8, 2, 4)$ . Thus,  $\Gamma_{3N} = (24, 0, 4)$ . We can reduce this by inspection to  $\Gamma_{3N} = 6A_1 + 2A_2 + 8E$ .

Since  $\Gamma_{\text{trans}} = A_1 + E$  and  $\Gamma_{\text{rot}} = A_2 + E$ , we have by subtraction that  $\Gamma_{\text{vibs}} = 5A_1 + A_2 + 6E$ . Thus, of the 18 normal vibrations, 5 have symmetry  $A_1$ , 1 has symmetry  $A_2$ , and 12 have symmetry  $E$  (note that these 12 modes pair up into 6 pairs of vibration modes of the same type).  $\square$

- b)  $\text{Zr}_2\text{F}_{13}^{5-}$ : Each Zr is seven coordinate with monocapped trigonal prismatic geometry. The cap is a bridging F (linear Zr-F-Zr linkage) on the unique square face of the prism. The anionic complex has an eclipsed geometry about the bridging F.

*Answer.*  $\text{Zr}_2\text{F}_{13}^{5-}$  has  $3(15) - 6 = 39$  normal vibrations.

Not high or low symmetry. Has a  $C_2$  axis. Has 2 perpendicular  $C_2$  axes. Has a  $\sigma_h$  plane. Therefore,  $\text{Zr}_2\text{F}_{13}^{5-}$  is of the  $D_{2h}$  point group.

We can determine that  $\Gamma_{x,y,z} = (3, -1, -1, -1, -3, 1, 1, 1)$ . We can also figure out that the number of atoms unmoved after applying each symmetry operation is  $(15, 3, 1, 1, 1, 1, 7, 3)$ . Thus,  $\Gamma_{3N} = (45, -3, -1, -1, -3, 1, 7, 3)$ . We can reduce this as follows.

$$\begin{aligned} a_{A_g} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{A_g}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(1)] \\ &= 6 \end{aligned}$$

$$\begin{aligned} a_{B_{1g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{1g}}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(-1)] \\ &= 4 \end{aligned}$$

$$\begin{aligned} a_{B_{2g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{2g}}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(-1)] \\ &= 6 \end{aligned}$$

$$\begin{aligned} a_{B_{3g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{3g}}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(1)] \\ &= 5 \end{aligned}$$



$$\begin{aligned}
a_{A_u} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{A_u}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(-1)] \\
&= 4
\end{aligned}$$

$$\begin{aligned}
a_{B_{1u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{1u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(1)] \\
&= 7
\end{aligned}$$

$$\begin{aligned}
a_{B_{2u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{2u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(1)] \\
&= 6
\end{aligned}$$

$$\begin{aligned}
a_{B_{3u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{3u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(-1)] \\
&= 7
\end{aligned}$$

Therefore, we know that  $\Gamma_{3N} = 6A_g + 4B_{1g} + 6B_{2g} + 5B_{3g} + 4A_u + 7B_{1u} + 6B_{2u} + 7B_{3u}$ . Since  $\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u}$  and  $\Gamma_{\text{rot}} = B_{1g} + B_{2g} + B_{3g}$ , we have by subtraction that  $\Gamma_{\text{vibs}} = 6A_g + 3B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 6B_{1u} + 5B_{2u} + 6B_{3u}$ . Thus, of the 39 normal vibrations, 6 have symmetry  $A_g$ , 3 have symmetry  $B_{1g}$ , 5 have symmetry  $B_{2g}$ , 4 have symmetry  $B_{3g}$ , 4 have symmetry  $A_u$ , 6 have symmetry  $B_{1u}$ , 5 have symmetry  $B_{2u}$ , and 6 have symmetry  $B_{3u}$ .  $\square$

VI) Benzene ( $\text{C}_6\text{H}_6$ ) is a planar molecule.

a) Assign the symmetry group.

*Answer.* Not high or low symmetry. Has a  $C_6$  axis. Has 6 perpendicular  $C_2$  axes. Has a  $\sigma_h$  plane. Therefore,  $\text{C}_6\text{H}_6$  is of the  $D_{6h}$  point group.  $\square$

b) Determine the number and symmetries of the C–H stretching modes in benzene.

*Answer.* We can determine that  $\Gamma_\nu = (6, 0, 0, 0, 2, 0, 0, 0, 0, 6, 0, 2)$  by counting how many  $\overrightarrow{\text{C-H}}$  vectors stay the same under each symmetry operation. We can reduce this as follows.

$$\begin{aligned} a_{A_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(1) + (3)(0)(1) \\ &\quad + (1)(0)(1) + (2)(0)(1) + (2)(0)(1) + (1)(6)(1) + (3)(0)(1) + (3)(2)(1)] \\ &= 1 \end{aligned}$$

$$\begin{aligned} a_{A_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{2g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(-1) + (3)(0)(-1) \\ &\quad + (1)(0)(1) + (2)(0)(1) + (2)(0)(1) + (1)(6)(1) + (3)(0)(-1) + (3)(2)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{B_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(1) + (3)(0)(-1) \\ &\quad + (1)(0)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(-1) + (3)(0)(1) + (3)(2)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{B_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{2g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(-1) + (3)(0)(1) \\ &\quad + (1)(0)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(-1) + (3)(0)(-1) + (3)(2)(1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{E_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) + (3)(2)(0) + (3)(0)(0) \\ &\quad + (1)(0)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(-2) + (3)(0)(0) + (3)(2)(0)] \\ &= 0 \end{aligned}$$

$$\begin{aligned}
a_{E_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{2g}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{A_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(-1) + (3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{A_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(-1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(1) + (3)(2)(1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{B_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(-1) + (3)(2)(1)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{B_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(-1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(1) + (3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{E_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{E_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(1) + (2)(0)(1) + (1)(6)(-2) + (3)(0)(0) + (3)(2)(0)] \\
&= 0
\end{aligned}$$

Therefore, we know that  $\Gamma_\nu = A_{1g} + E_{2g} + B_{1u} + E_{1u}$ . Thus, there are 6 C–H stretching modes in benzene: 1 with symmetry  $A_{1g}$ , 2 with symmetry  $E_{2g}$  (note that these 2 modes form a pair vibration modes of the same type), 1 with symmetry  $B_{1u}$ , and 2 with symmetry  $E_{1u}$  (again, these pair up).  $\square$

- c) Determine the Raman and infrared activities for each vibration.

*Answer.* Since the  $A_{1g}$ ,  $E_{1g}$ , and  $E_{2g}$  irreducible representations are Raman active, we know that the  $A_{1g}$  and  $E_{2g}$  C–H stretching modes are Raman active. The others are Raman silent. Additionally, since the  $A_{2u}$  and  $E_{1u}$  irreducible representations are IR active and two of the C–H stretching vibration modes are of the  $E_{1u}$  type, the  $E_{1u}$  vibrations are both IR active. The others are IR silent.  $\square$