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. $\boxed{h = 8}$ — count the number of symmetry elements. □

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

Answer.

$$\sum_{R_c} g_c \chi_E(R_c)\chi_{A_1}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{A_2}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(-1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{B_1}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(-1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{B_2}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(1) = 0$$

□

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

Answer.

$$\sum_{R_c} g_c[\chi_{A_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot 1^2 = 8$$
$$\sum_{R_c} g_c[\chi_{A_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot (-1)^2 = 8$$
$$\sum_{R_c} g_c[\chi_{B_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot (-1)^2 = 8$$
$$\sum_{R_c} g_c[\chi_{B_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot 1^2 = 8$$
$$\sum_{R_c} g_c[\chi_E(R_c)]^2 = 1 \cdot 2^2 + 2 \cdot 0^2 + 1 \cdot (-2)^2 + 2 \cdot 0^2 + 2 \cdot 0^2 = 8$$

□

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

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_2	6	4	6	2	0

Answer. For Γ_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

$$\boxed{\Gamma_1 = 2A_1 + B_1 + B_2 + E}$$

For Γ_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

$$\boxed{\Gamma_2 = 3A_1 + 2A_2 + B_1}$$

□

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

$$\boxed{\Gamma = 2A_1' + E' + A_2''}$$

□

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

$$\boxed{\Gamma = A_2'' + E''}$$

□

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

Answer. We know the following by inspection.

$$\boxed{\Gamma = A_1 + A_2 + B_1 + B_2}$$

□

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

Answer. We know the following by inspection.

$$\boxed{\Gamma = 2A_g + B_g + A_u + B_u}$$

□

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

$$\boxed{\Gamma = 3A_2 + 2E + T_1 + T_2}$$

□

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

Answer. With respect to the two doubly degenerate groups, we must add the two parts together and also double the order that we are dividing out. Note that $\varepsilon = \mathrm{e}^{2\pi i/3} = \cos\left(\frac{2\pi}{3}\right) + i\sin\left(\frac{2\pi}{3}\right) = -0.5 + i\frac{\sqrt{3}}{2}$ and, thus, $\varepsilon^* = -0.5 - i\frac{\sqrt{3}}{2}$. It follows that $\varepsilon + \varepsilon^* = -1$.

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

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

$$2a_{E_g} = \frac{1}{24}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{E_g}(R_c)$$

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

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

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

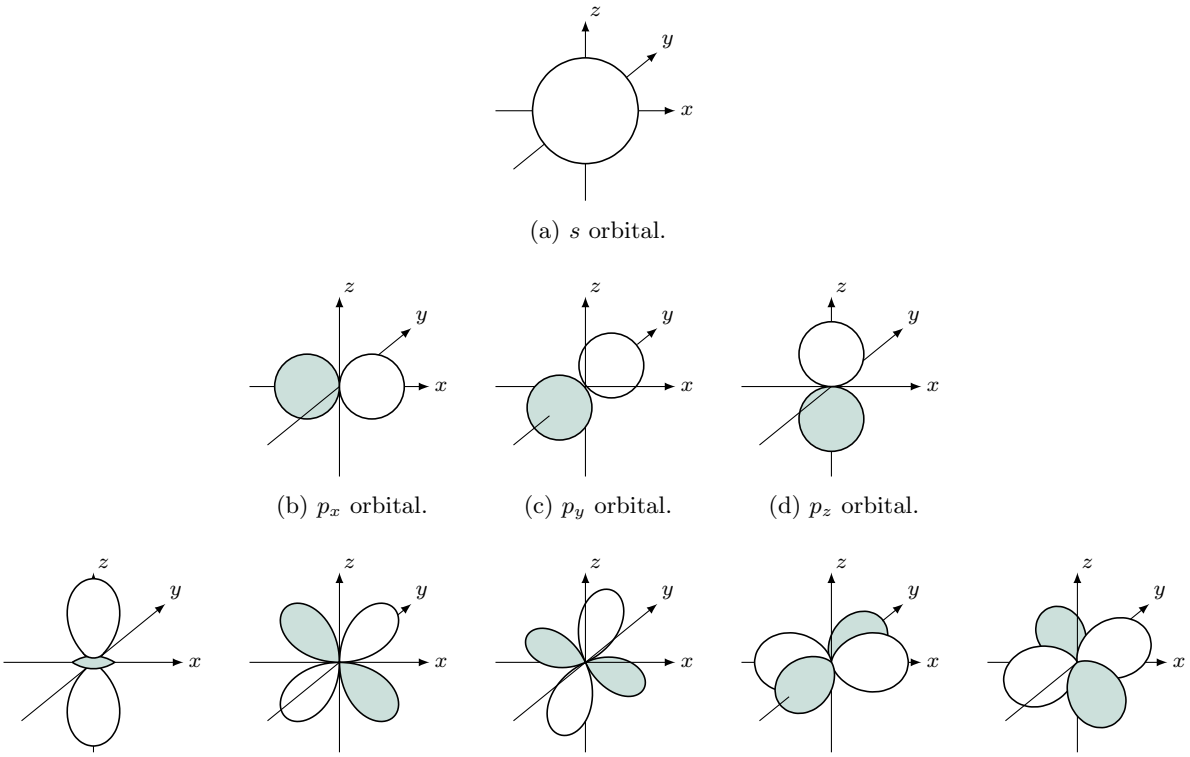
$$a_{T_u} = \frac{1}{24}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{T_u}(R_c)$$
$$= \frac{1}{24}[(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)]$$
$$= 0$$

Therefore, we know that

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

□

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, σ_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.



(a) s orbital.

(b) p_x orbital. (c) p_y orbital. (d) p_z orbital.

(e) d_{z^2} orbital. (f) d_{xz} orbital. (g) d_{yz} orbital. (h) $d_{x^2-y^2}$ orbital. (i) d_{xy} orbital.

Figure 2.1: s, p, and d orbitals.

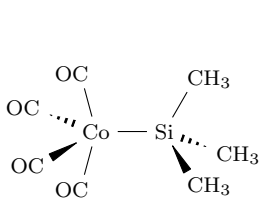
Answer. In Figure 2.1, white shading means positive phase and orange means negative phase.

Here are irreducible representations for each orbital:

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

□

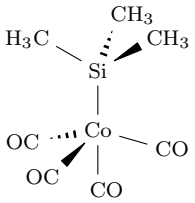
IV) The molecule $Co(CO)_4(SiMe_3)$ has a structure based on a trigonal bipyramid. The infrared spectrum of $Co(CO)_4(SiMe_3)$ exhibits three $\nu(CO)$ stretching vibrations at 2100, 2041, and 2009 cm^{-1}. Draw the two possible structures based on the TBP geometry, assign their proper point groups, and use the infrared data to determine which is the correct structure.



C_{2v}

Incorrect structure.

(a) Equatorial trimethylsilyl group.



C_{3v}

Correct structure.

(b) Axial trimethylsilyl group.

Figure 2.2: Structures of $Co(CO)_4(SiMe_3)$.

Explanation. Note that for the sake of point group assignments, the CO ligands will be treated as identical point particles. Additionally, the $SiMe_3$ ligand will be treated as a point particle distinguishable from the CO point particles.

The structure in Figure 2.2a: Not high or low symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_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 $\overrightarrow{\text{Co}-\text{CO}}$ 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 $Co(CO)_4(SiMe_3)$. Therefore, this is not the correct structure.

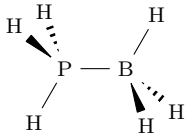
The structure in Figure 2.2b: Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°. Therefore, it is of the C_{3v} point group.

We can determine that $\Gamma_\nu = (4, 1, 2) = 2A_1 + E$ by counting how many $\overrightarrow{\text{Co}-\text{CO}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four $\nu(CO)$ stretching modes that are all IR active (but two of the four being degenerate), we can expect there to be three peaks in the infrared spectrum of $Co(CO)_4(SiMe_3)$. This confirms that this is the correct structure. □

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

a) H_3PBH_3: with a staggered ethane-like geometry.

Answer.



H_3PBH_3 has $3(8) - 6 = 18$ normal vibrations.

Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°. Therefore, H_3PBH_3 is of the C_{3v} point group.

It follows from the C_{3v} character table 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 $\Gamma_{3N} = 6A_1 + 2A_2 + 8E$.

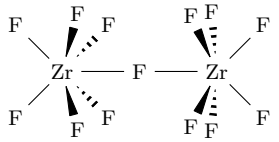
Since $\Gamma_{\text{trans}} = A_1 + E$ and $\Gamma_{\text{rot}} = A_2 + E$ (again from the C_{3v} character table), we have by subtraction that

$$\boxed{\Gamma_{\text{vibs}} = 5A_1 + A_2 + 6E}$$

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). □

b) $Zr_2F_{13}{}^{5-}$: 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.



$Zr_2F_{13}{}^{5-}$ 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 σ_h plane. Therefore, $Zr_2F_{13}{}^{5-}$ is of the D_{2h} point group.

It follows from the D_{2h} character table that $\Gamma_{x,y,z} = (3, -1, -1, -3, 1, 1, 1)$. 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 $\Gamma_{\text{rot}} = B_{1g} + B_{2g} + B_{3g}$ (again from the D_{2h} character table), we have by subtraction that

$$\boxed{\Gamma_{\text{vibs}} = 6A_g + 3B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 6B_{1u} + 5B_{2u} + 6B_{3u}}$$

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}. □

VI) Benzene (C_6H_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 σ_h plane. Therefore, C_6H_6 is of the $\boxed{D_{6h}}$ point group. □

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

$$\boxed{\Gamma_\nu = A_{1g} + E_{2g} + B_{1u} + E_{1u}}$$

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). □

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. □