CHEM 20100 (Inorganic Chemistry I) Problem Sets

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Contents

0 Course Prep Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A\sin rx + B\cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

Solution.

$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2\Psi(x)}{\partial x^2} = E\Psi(x)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2}{\partial x^2}(A\sin rx + B\cos sx) = E(A\sin rx + B\cos sx)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial}{\partial x}(Ar\cos rx - Bs\sin sx) = E(A\sin rx + B\cos sx)$$
$$\frac{-h^2}{8\pi^2 m}\cdot\left(-Ar^2\sin rx - Bs^2\cos sx\right) = E(A\sin rx + B\cos sx)$$
$$\frac{Ar^2h^2}{8\pi^2 m}\sin rx + \frac{Bs^2h^2}{8\pi^2 m}\cos sx = AE\sin rx + BE\cos sx$$
$$0 = \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx$$

Choose $x = 0$.

$$= \frac{Bs^2h^2}{8\pi^2 m} - BE$$
$$E = \frac{s^2h^2}{8\pi^2 m}$$
$$\frac{8\pi^2 mE}{h^2} = s^2$$
$$s = \sqrt{\frac{8\pi^2 mE}{h^2}}$$
$$\boxed{s = \sqrt{2mE}\frac{2\pi}{h}}$$

With this result ...

$$0 = \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(B\left(\frac{s^2h^2}{8\pi^2 m}\right) - BE\right)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + (BE - BE)\cos sx$$
$$= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2h^2}{8\pi^2 m} - AE$$

$$\boxed{r = \sqrt{2mE}\frac{2\pi}{h}}$$

□

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned}
1 &= \int_{\text{all space}} \Psi\Psi^* \, \mathrm{d}\tau \\
&= \int_0^a \left(A \sin \frac{n\pi x}{a}\right)\left(A \sin \frac{n\pi x}{a}\right) \mathrm{d}x \\
&= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x
\end{aligned}$$

Use $\sin^2 u = \frac{1-\cos 2u}{2}$.

$$\begin{aligned}
&= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, \mathrm{d}x \\
&= \frac{A^2}{2}\left(\int_0^a \mathrm{d}x - \int_0^a \cos \frac{2n\pi x}{a} \, \mathrm{d}x\right) \\
&= \frac{A^2}{2}\left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a}\right]_0^a\right) \\
&= \frac{A^2}{2}\left((a-0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0\right)\right) \\
&= \frac{A^2}{2}\left(a - \left(\frac{a}{2n\pi} \sin 2n\pi\right)\right)
\end{aligned}$$

Since n is an integer, $\sin 2n\pi = 0$.

$$\begin{aligned}
&= \frac{aA^2}{2} \\
\frac{2}{a} &= A^2 \\
\boxed{A &= \sqrt{\frac{2}{a}}}
\end{aligned}$$

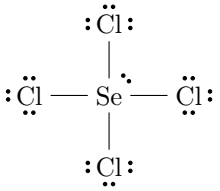
□

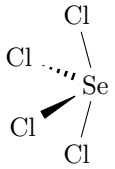
1 VSEPR and Point Groups

1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

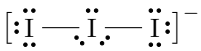
3.8 Give Lewis dot structures and sketch the shapes of the following:

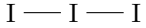
a. $SeCl_4$



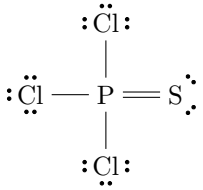


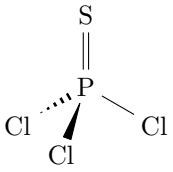
b. I_3^-



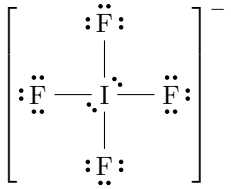


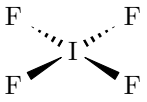
c. $PSCl_3$



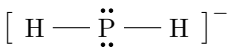


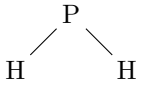
d. IF_4^-



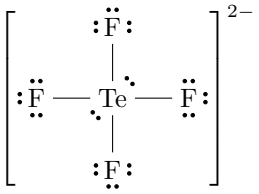


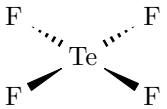
e. PH_2^-



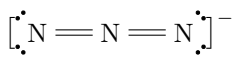


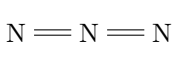
f. TeF_4^{2-}





g. N_3^-





h. $SeOCl_4$

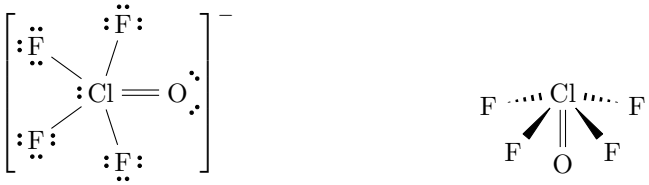
i. PH_4^+

3.9 Give Lewis dot structures and sketch the shapes of the following.

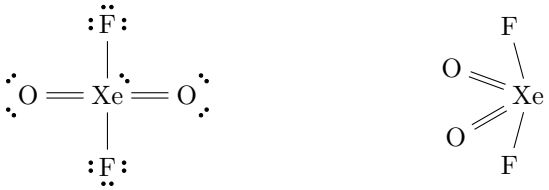
f. $IO(OH)_5$

g. $SOCl_2$

h. $ClOF_4^-$ [1]

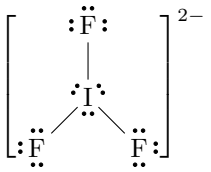


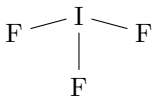
i. XeO_2F_2



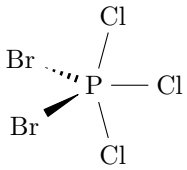
[1]Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

3.20 Predict and sketch the structure of the (as yet) hypothetical ion $IF_3{}^{2-}$.





3.29 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.



Answer. Bromine is more electropositive than chlorine. Thus, by Bent's rule, the bromines will bond to the hybrid orbitals with greater s-character (the equatorial sp^2 ones) first. □

II) Assign the symmetry point group to the 13 ions and molecules in problems #8, 9f-i in Chapter 3 of your text.

3.8

a. $SeCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeCl_4$ is of the C_{2v} point group. □

b. I_3^-

Answer. I_3^- is of the $D_{\infty h}$ point group. □

c. $PSCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $PSCl_3$ is of the C_{3v} point group. □

d. IF_4^-

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, IF_4^- is of the D_{4h} point group. □

e. PH_2^-

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, PH_2^- is of the C_{2v} point group. □

f. TeF_4^{2-}

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, TeF_4^{2-} is of the D_{4h} point group. □

g. N_3^-

Answer. N_3^- is of the $D_{\infty h}$ point group. □

h. $SeOCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeOCl_4$ is of the C_{2v} point group. □

i. PH_4^+

Answer. PH_4^+ is of the T_d point group. □

3.9

f. $IO(OH)_5$

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $IO(OH)_5$ is of the C_{4v} point group. □

g. $SOCl_2$

Answer. $SOCl_2$ is of the C_s point group. □

h. $ClOF_4^-$

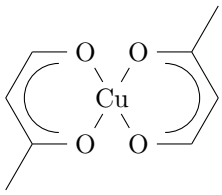
Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $ClOF_4^-$ is of the C_{4v} point group. □

i. XeO_2F_2

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, XeO_2F_2 is of the C_{2v} point group. □

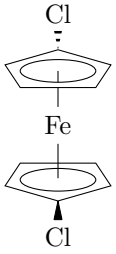
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

a) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h.
Therefore, the above molecule is of the C_{2h} point group. □

b) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h
Therefore, the above molecule is of the C_{2h} point group. □

c) $POCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $POCl_3$ is of the C_{3v} point group. □

d) Tennis ball (including the seam)

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. No σ_h. Has two perpendicular σ_d planes.
Therefore, a tennis ball is of the D_{2d} point group. □

e) *trans*-$[CrCl_2(H_2O)_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$[CrCl_2(H_2O)_4]^+$ is of the D_{4h} point group. □

f) 1,3,5-trichlorobenzene.

Answer. Not low or high symmetry. Has a C_3 axis. Has 3 perpendicular C_2 axes. Has σ_h.
Therefore, 1,3,5-trichlorobenzene is of the D_{3h} point group. □

g) *trans*-$Pt(NH_3)_2Cl_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$Pt(NH_3)_2Cl_2$ is of the D_{2h} point group. □

h) SF_5Cl

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, SF_5Cl is of the C_{4v} point group. □

i) BFClBr

Answer. BFClBr is of the C_s point group. □

j) $PF_2{}^+$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $PF_2{}^+$ is of the C_{2v} point group. □

IV) In the octahedral ion FeF_6^{3-}, what symmetry elements are destroyed if two *trans* F ions are moved away from the Fe^{3+} center in an equidistant fashion?

Answer. If the described change is made, the point group changes from O_h to D_{4h}. In this change, every C_3 and S_6 axis, two of the three C_4 axes, four C_2 axes, and every σ_d that does not contain the axis along which the F ions are stretched are destroyed. □

2 Representations, Character Tables, and Vibrations

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. □

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

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

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

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

□

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.

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

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

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

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

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

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

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

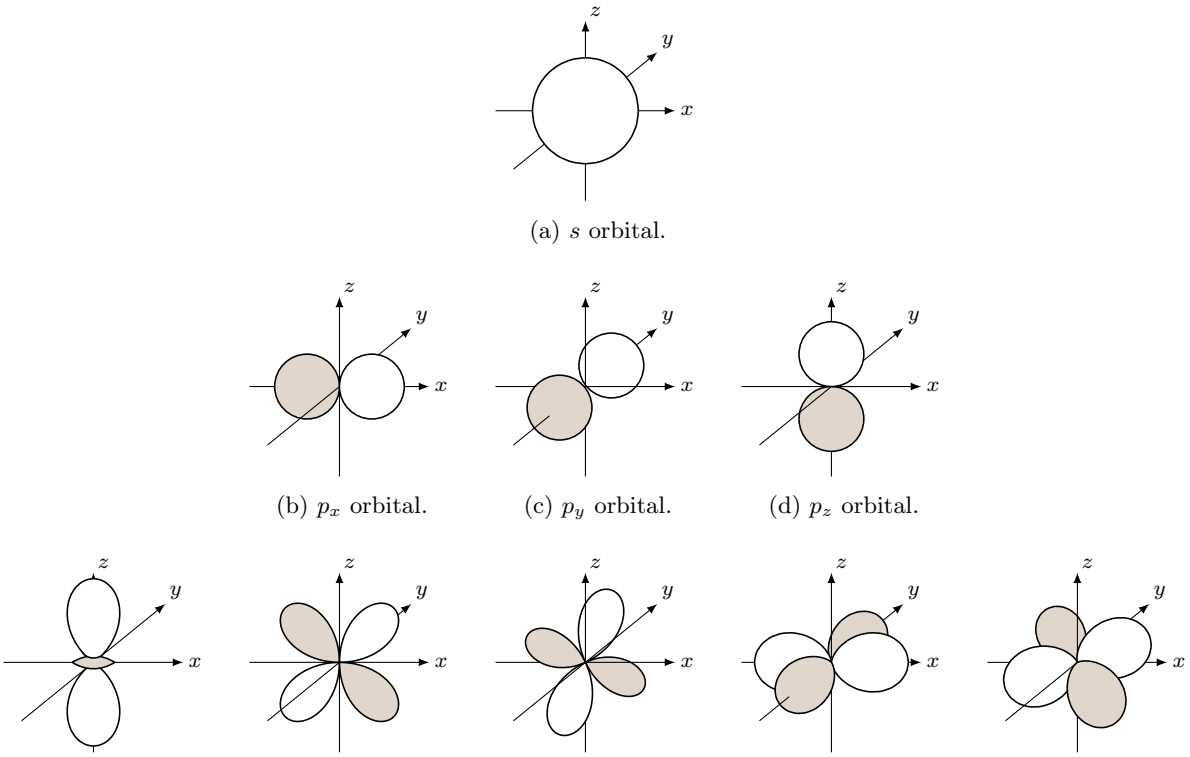
$$
\begin{aligned}
a_{T_u} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{T_u}(R_c) \\
&= \frac{1}{24}[(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)] \\
&= 0
\end{aligned}
$$

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, 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 1: s, p, and d orbitals.

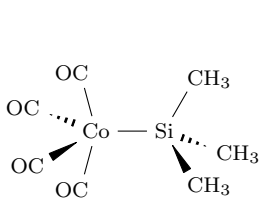
Answer. In Figure 1, white shading means positive phase and orange means negative phase.

Here are irreducible representations for each orbital:

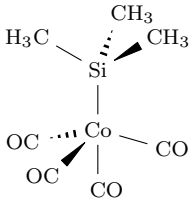
$$\begin{aligned}
\Gamma_s &= (1,1,1,1) = A_g \\
\Gamma_{p_x} &= (1,-1,-1,1) = B_u \\
\Gamma_{p_y} &= (1,-1,-1,1) = B_u \\
\Gamma_{p_z} &= (1,1,-1,-1) = A_u \\
\Gamma_{d_{z^2}} &= (1,1,1,1) = A_g \\
\Gamma_{d_{xz}} &= (1,-1,1,-1) = B_g \\
\Gamma_{d_{yz}} &= (1,-1,1,-1) = B_g \\
\Gamma_{d_{x^2-y^2}} &=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

□

IV) The molecule $Co(CO)_4(SiMe_3)$ 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.



(a) Equatorial trimethylsilyl group.



(b) Axial trimethylsilyl group.

Figure 2: Structures of $Co(CO)_4(SiMe_3)$.

Answer. Note that for the sake of point group assignments, the CO ligands will be treated as identical spheres. Additionally, the $SiMe_3$ 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 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 $\overrightarrow{Co{-}CO}$ 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 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 $\overrightarrow{Co{-}CO}$ vectors stay the same under each symmetry operation and decomposing by inspection. With three $\nu(CO)$ stretching modes that are all IR active, 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.
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). □

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.
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}. □

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