1. Identify all of the symmetry elements for the following molecules and hence assign the molecule to its point group using the attached flowchart. Identify clearly all the symmetry elements on a diagram.

   (a) O==C==S (4 points)

   \[
   \begin{align*}
   C_{2v} & \rightarrow \sigma_v \text{ reflection planes} \\
   C_{2v} & \rightarrow \text{(since no } i\text{)}
   \end{align*}
   \]

   (b) fluorobenzene (4 points)

   \[\text{C}_2 \text{ axis, } \sigma_v \text{ planes, } C_{2v}.\]

   (c) PCl₃ - trigonal bipyramidal (6 points)

   \[\text{C}_3 \text{ axis, } 5 \sigma_v \text{ (combine the } 3 \text{ C}_2 \text{ axes).}\]

2. Consider unit Cartesian vectors located on each of the heavy atoms in the molecule drawn below – we can ignore the H atoms for the purpose of this question. (Line up the x-axis perpendicular to the molecular plane and the z-axis lies along the in-plane C₂ axis (as shown in the diagram below).

   (a) Determine the point group of this species, clearly identifying the symmetry elements on a picture of the molecule. (6 points)
(b) Calculate the characters of the reducible representation \( \chi_{\text{red}}( \hat{R} ) \) for all symmetry elements \( \hat{R} \) of an appropriate subgroup e.g. if the full point group is \( D_{6d} \) then you could use the \( D_6 \) subgroup etc. Show your reasoning. (10 points)

Use \( D_2 \) group.

\[
\begin{array}{cccc}
\hat{E} & \hat{C}_2(z) & \hat{C}_2(y) & \hat{C}_2(x) \\
24 & -4 & 0 & 0
\end{array}
\]

\( \chi_{\text{red}}( \hat{R} ) \)

Since on 3 axes on all 8 atoms (excluding the H's) are unchanged by this operation

\( 8 \times 3 \times 1 = 24 \)

Only 4 = 0 atoms remain unchanged

\( \Rightarrow 4 \times 2 = 8 \) axes unchanged

\( \Rightarrow 8 \times 4 \) axes reversed

\( \Rightarrow 4 \times 1 = +4 \)

\( 2 \times -1 = -8 \)

Total 4

(c) Calculate the number of times each irreducible representation appears in the reducible representation. (10 points)

\[
\begin{align*}
&\alpha_A = \frac{1}{4} \left[ (24)(1) + (-4)(1) \right] = 5 \\
&\alpha_{B_1} = \frac{1}{4} \left[ (24)(1) + (-4)(1) \right] = 5 \\
&\alpha_{B_2} = \frac{1}{4} \left[ (24)(1) + (-4)(1) \right] = 7 \\
&\alpha_{B_3} = \frac{1}{4} \left[ (24)(1) + (-4)(1) \right] = 7 
\end{align*}
\]

\( \Gamma_{\text{red}} = 5A \oplus 5B \oplus 7B_2 \oplus 7B_3 \)

If you used the full \( D_{6h} \) group this would further break down into (after a good bit more work!)

\[
\begin{align*}
4A_g & \oplus A_u \oplus B_g \oplus 4B_u \oplus 3B_{1g} \oplus 4B_{2g} \oplus 4B_{3g} \oplus 3B_{3u} \\
& \overset{\frac{\text{ie}}{\text{}}}{\begin{array}{cccccccc}
5A & 5B_1 & 7B_2 & 7B_3
\end{array}}
\end{align*}
\]
4. Using the character tables and direct product tables for the $C_{4v}$ group (attached), state whether you would expect the following integral to be zero or non-zero.

$$\int \psi_f^* \mu \psi_i \, d\tau.$$  (4 points)

$$B_2 \otimes (A_1 \otimes B_1) = (B_2 \otimes B_1) = A_2 \Rightarrow$$

expect zero for this integral

5. As we will see later in this course, the intensity of an infrared transition is proportional to the transition moment integral which has the form $$\int \psi_f^* \mu \psi_i \, d\tau,$$
where $\psi_i$ and $\psi_f$ are the wavefunctions for the initial and final states involved in the transition and $\mu$ is the transition dipole moment.

(a) For the $C_{4h}$ point group, if $\psi_i$ belongs to the $B_8$ irreducible representation and given that the $\mu_z$ dipole moment operator transforms the same as a translation in the $z$-direction, determine the symmetry of the upper state ($\psi_f$) required to make the transition moment integral non-zero. (6 points)

$$\int \psi_f^* \mu_z \psi_i \, d\tau = \otimes B_8 \otimes B_9 = \otimes B_u \text{ must equal } A_g$$

$$\Rightarrow \psi_f \text{ must belong to } B_u \text{ symmetry for non-zero integral.}$$

(b) Repeat part (a) using the $\mu_x$ dipole moment operator. (6 points)

$$\mu_x \text{ belongs } = E_u.$$ 

So $$\int \psi_f^* \mu_x \psi_i \, d\tau = \otimes E_u \otimes B_9 = \otimes E_u$$

Hence $\psi_f$ must belong to $E_u$ symmetry since $E_u \otimes E_u = A_g \otimes A_g \oplus B_9 \otimes B_9$

(c) Repeat using the $\mu_y$ dipole moment operator and the point group $D_{3h}$ assuming that the ground state wavefunction has $A_1''$ symmetry in this case. (6 points)

$$\mu_y \text{ has } E' \text{ symmetry under } D_{3h}.$$ 

$$\psi_f^* \mu_y \psi_i \downarrow \downarrow$$

$$\otimes E' \otimes A_1'' = \otimes E''$$

Hence $\psi_f$ must belong to $E''$

When $E'' \otimes E'' = A_1'' + A_2' + E'$

 totalmente symm.