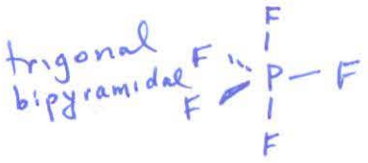
Name: _____

Group Theory Mini-Exam

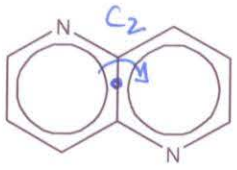
1. (10 pts) Please determine the **point group** for each molecule below.

a. PF_5



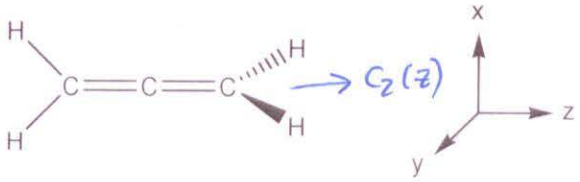
D_{3h}

b.



C_{2h}

2. (8 pts) Please generate the **transformation matrix** for the ***C₂(z)* operation** of the ***D₂d*** point group by operating on a point, (x, y, z). What is the **character** of the matrix? (It may help to consider allene, a molecule with D_{2d} symmetry, shown below.)



$z \rightarrow z$
$x \rightarrow -x$
$y \rightarrow -y$

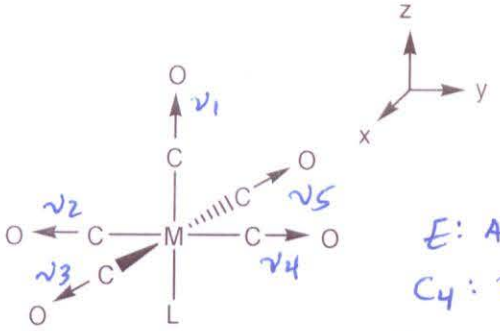
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$C_2(z)$

$\chi = -1 + (-1) + 1 = -1$

3. (10 pts) Consider the carbonyl stretches in $ML(CO)_5$, depicted with vectors below. Please **generate a reducible representation** (Γ_R) showing how these vectors transform under the operations of the C_{4v} point group. (This would be the first step toward predicting the number of C-O peaks in the IR spectrum.)

Hint: Recall that σ_v planes tend to contain the most bonds; σ_d planes tend to lie between bonds.



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
Γ_R	5	1	1	3	1	C-O stretches

$\{\nu_1 \rightarrow \nu_5\}$

Basis set = 5 C-O stretching vectors shown $\nu_1 \rightarrow \nu_5$

E: All 5 vectors stay the same. $\chi = 5$

C_4: ν_1 stays. Others interchange. $\chi = 1$

C_2: ν_1 stays. Others interchange. $\chi = 1$

σ_v: 3 vectors are in the plane and are unchanged. The other two switch places. $\chi = 3$

σ_d: Plane contains only ν_1. Others are reflected into each other. $\chi = 1$

4. (8 pts) Please **reduce the reducible representation (Γ_R)** below. Show your work and clearly indicate your final answer.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h=6$
Γ_R	12	0	2	
A_1	1	1	1	
A_2	1	1	−1	
E	2	−1	0	

$\#A_1 = \frac{1}{6}(12+0+6) = 3$

$\#A_2 = \frac{1}{6}(12+0-6) = 1$

$\#E = \frac{1}{6}(24+0+0) = 4$

$\Gamma_R = 3A_1 + 1A_2 + 4E$

5. (14 pts) The reducible representation in Question 4 represents all 3N molecular motions in ammonia, NH_3. Please use the C_{3v} character table and the irreducible representations from your answer above to complete the following questions.

   a. Which irreducible representation(s) describe(s) **translational** motions? $1A_1$ (z), $1E$ (x, y)

   b. Which irreducible representation(s) describe(s) **rotational** motions? $1A_2$ (R_z), $1E$ (R_x, R_y)

   c. Which irreducible representation(s) describe(s) **vibrational** motions? $2A_1$, $2E$

   d. How many **vibrations** are expected for NH_3? Are all of these represented in your answer to (c)? Explain briefly. $3N-6 = 3(4)-6 = 6$ vibn expected.
   $2A_1 + 2E = 2(1) + 2(2) = 6$ vibrations represented
   Each A_1 represents 1 vibration; each E represents 2 degenerate vibrations.

   e. How many **peaks** should be visible in the IR spectrum of ammonia? Briefly explain how you arrived at your answer.
   $2A_1 + 2E$ vibrations. All are IR-active - with same symmetry as translation (∴ net change of dipole moment).
   ↘ 4 peaks

   f. How many **peaks** should be visible in the Raman spectrum of ammonia? Briefly explain how you arrived at your answer.
   $2A_1 + 2E$ vibrations. All are Raman-active (same sym. as product terms, representing change in molecular polarizability). ⇒ 4 peaks