2016 Ch112 − Problem Set 1
Due: Thursday, October 6 – before class

Note: Use of published character tables is not allowed for this problem set. You are welcome to check your solution with such tables after completion of the set.

Problem 1 (3 points)

Part A.
Assign the point group of each molecule. Identify the location of the symmetry elements and determine if the molecule is chiral. If the molecule is achiral, clearly indicate the symmetry element that prevents it from being chiral. Treat all PMe_3 ligands, Me ligands, and SiR_3 substituents as spheres.

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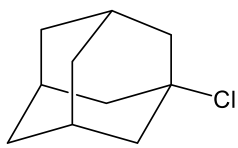

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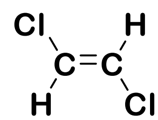

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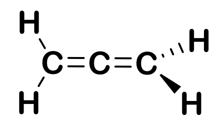

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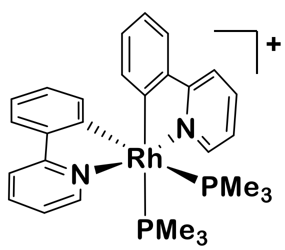

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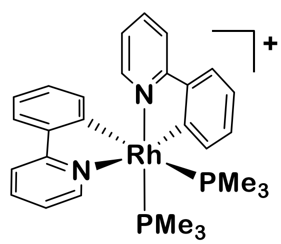

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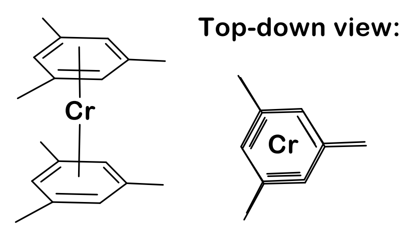

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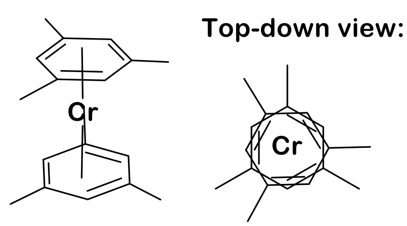

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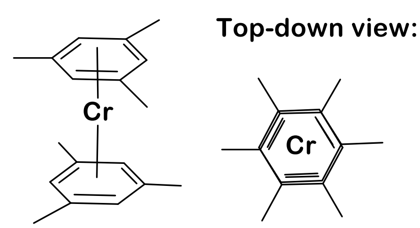

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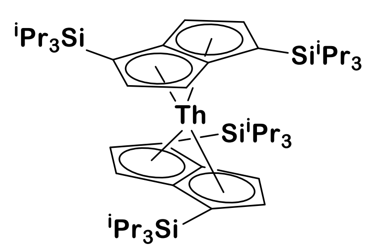

Part B.
One of the handouts for the first lecture lists all point group classes. Provide an example of molecule for each of the 15 point group types listed.

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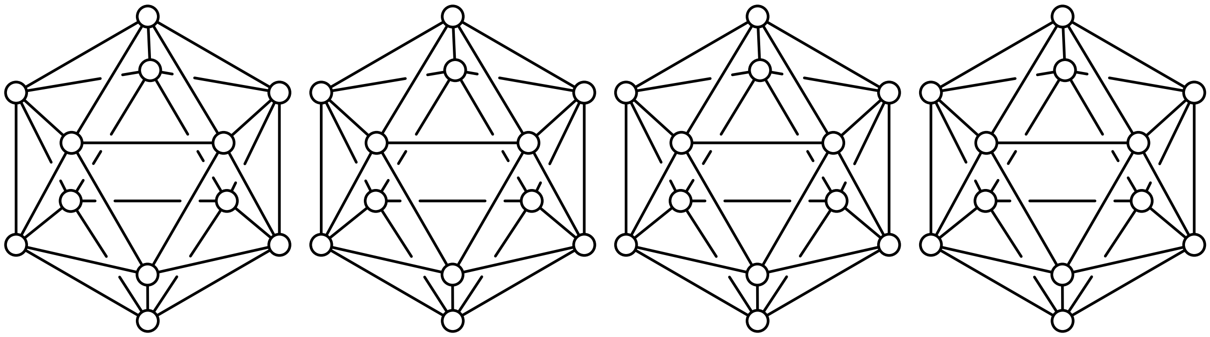
Part C.
Carboranes derived from $[B_{12}H_{12}]^{2-}$ were discussed in class. Replacement of 5 BH moieties with 5 CH moieties results in the $[B_7C_5H_{12}]^{3+}$ trication. Using the representations below by darkening the circles corresponding to CH groups, provide one structure each for isomers that are expected to display 1, 3, 4 and 5 peaks, respectively, in their ^{13}C NMR spectra. Assign the point group of each isomer.



Problem 2 (2 points)

Part A.
Important information about the symmetry aspects of point groups is summarized in character tables, as described in class. Each symmetry operation in a point group may be expressed as a transformation matrix as follows:

[new coordinates] = [transformation matrix][old coordinates]

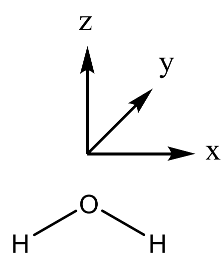
For a basis set of (x, y, z) coordinates, the transformation matrix of the *E* is given as:

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

For C_2 rotation with respect to the z axis:

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

Consider the water molecule:



H_2O is in the C_{2v} point group. Using the given coordinate system as the basis set, find transformation matrices for the following symmetry operations:

1. $\sigma_v(xz)$, reflection through the xz plane

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2. $\sigma_v(yz)$, reflection through the yz plane

Part B.

The *character* (or *trace*), defined for square matrices, is the sum of the numbers on the diagonal from upper left to lower right.

For the C_{2v} point group, the following characters can be obtained from the previous part with the basis set of (x, y, z) coordinates:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{x,y,z}$	3	−1		

1. Using the trace of the square matrices above, find the characters of $\sigma_v(xz)$ and $\sigma_v(yz)$.

This set of characters forms the reducible representation, $\Gamma_{x,y,z}$, of the (x, y, z) coordinates consisting of a combination of irreducible representations.

$$E = \begin{bmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{bmatrix}, C_2 = \begin{bmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

The transformation matrices derived for the (x, y, z) coordinates in the C_{2v} are block diagonalized. The characters in each of the smaller matrices form the basis of irreducible representations, shown below.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	Coordinates used
Γ_1	1	−1			x
Γ_2	1	−1			y
Γ_3	1	1			z
Γ_4					
$\Gamma_{x,y,z}$	3	−1			

2. Complete the first three irreducible representations from $\sigma_v(xz)$ and $\sigma_v(yz)$. The first three irreducible representations show how the x, y, and z axes transform under each symmetry operation, respectively.
3. Find the last irreducible representation using the properties of characters of point groups. (Show your work)
4. Give Mulliken symbols for each irreducible representation.

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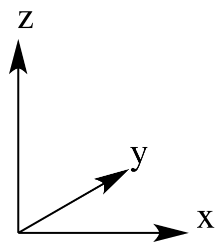
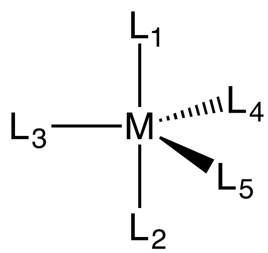
Problem 3 (3 points)

D_{3h} is a common point group that describes the symmetry of trigonal planar and trigonal bipyramidal complexes. Using the given coordinate system as the basis set, find transformation matrices for the following symmetry operations:





1. C_3 along the z axis

2. σ_h

3. S_3 along the z axis

4. C_2 along the x axis

In addition to the operations described above, two more classes are present in the D_{3h} point group. Find them by performing the operation multiplications below. Draw and label the molecule to illustrate these operations and clearly label the symmetry elements.

5. $C_2 \bullet \sigma_h =$

6. $C_3^2 \bullet S_3 =$

7. $S_3 \bullet S_3 \bullet C_3 =$

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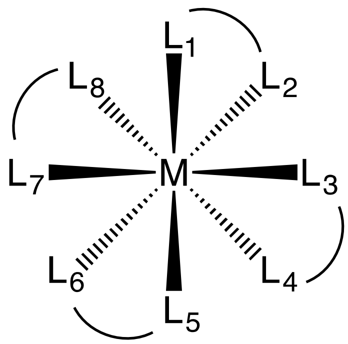
Problem 4 (2 points)

Shown below is an incomplete character table for the D_4 point group.

1. What is the order of the group?

2. Using the information contained within the Mulliken symbols and the functions shown to transform as the particular irreducible representations, complete the character table for the D_4 point group.

3. Using similarity transformations, show that the operations under the three classes with more than one member are conjugates. For graphic illustration of these operations use the following molecule:



D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	
A_1						
A_2						z
B_1				1		
B_2				−1		
E						(x, y)

Don't forget to email the TAs with your top three choices of project topic. Priority will be given in the order of email arrival.