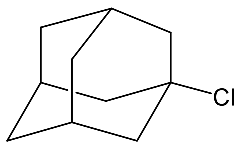
2016 Ch112 − Problem Set 1
Due: Thursday, October 6 – before class

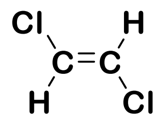
Note: Use of published character tables is not allowed for this problem set. You are welcome to check your solution with such tables after completion of the set.

Problem 1 (3 points)

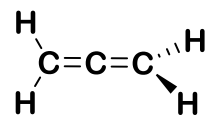
Part A.
Assign the point group of each molecule. Identify the location of the symmetry elements and determine if the molecule is chiral. If the molecule is achiral, clearly indicate the symmetry element that prevents it from being chiral. Treat all PMe_3 ligands, Me ligands, and SiR_3 substituents as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

1


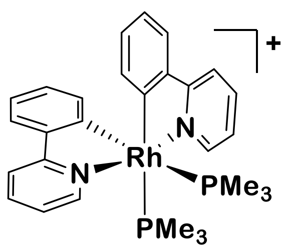
C_{3v}, achiral (σ_v)

2


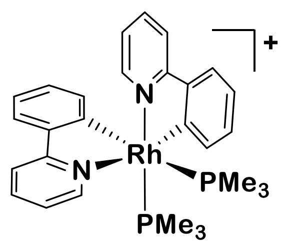
C_{2h}, achiral (i, σ_h)

3


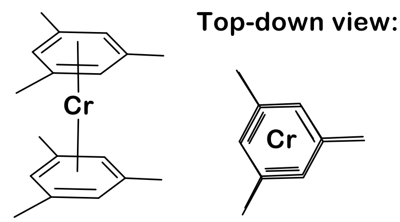
D_{2d}, achiral (S_4, σ_d)

4


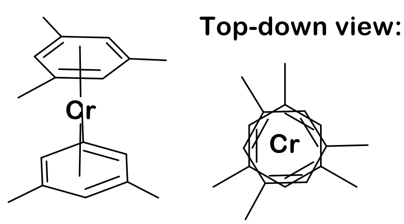
C_2, chiral

5


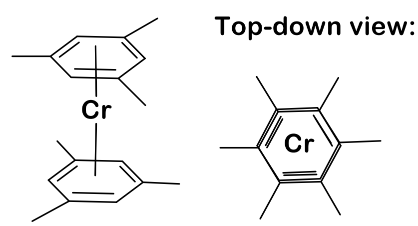
C_1, chiral

6


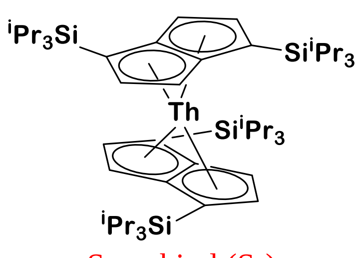
D_{3h}, achiral (S_3, σ_v, σ_d, σ_h)

7


D_3, chiral

8


D_{3d}, achiral (S_6, σ_d, i)

9


S_4, achiral (S_4)

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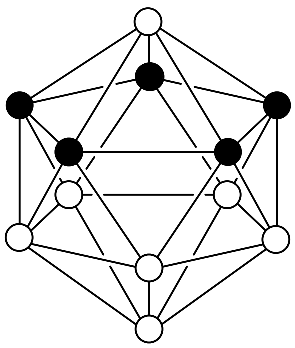
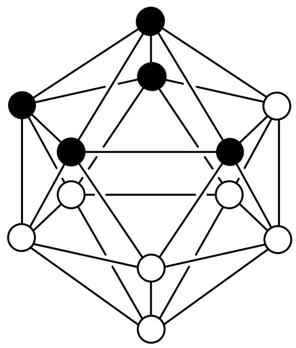
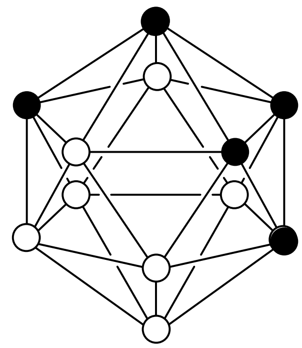
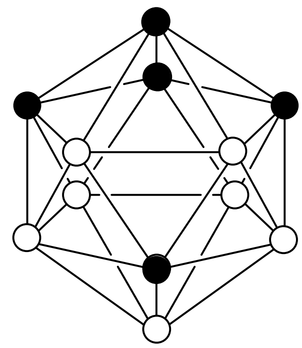
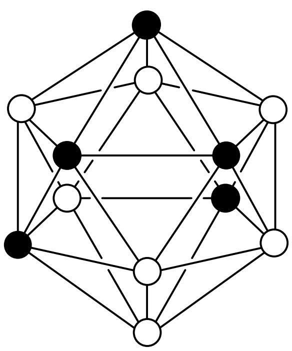
Part C.
Carboranes derived from $[B_{12}H_{12}]^{2-}$ were discussed in class. Replacement of 5 BH moieties with 5 CH moieties results in the $[B_7C_5H_{12}]^{3+}$ trication. Using the representations below by darkening the circles corresponding to CH groups, provide one structure each for isomers that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

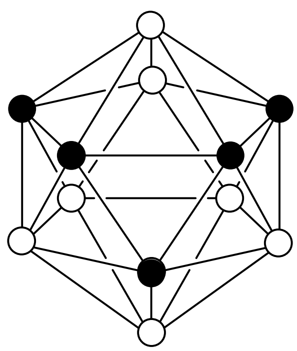

C_{5v}, 1 signal

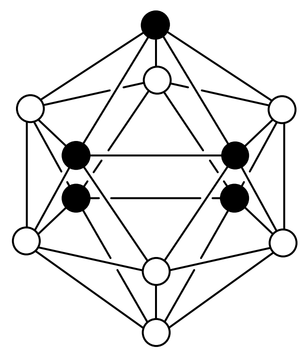

C_s, 3 signals

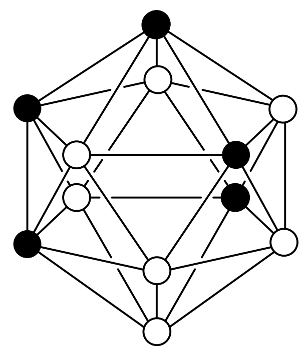

C_s, 4 signals

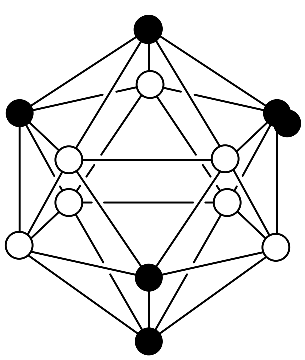

C_s, 4 signals

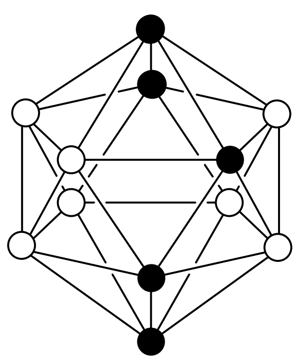

C_s, 4 signals

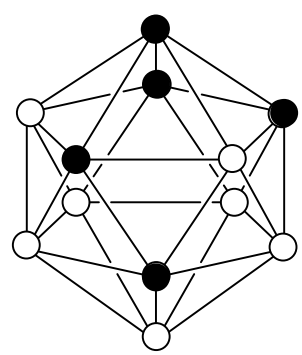

C_s, 3 signals

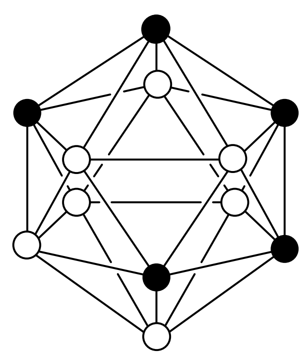

C_s, 3 signals


C_s, 3 signals


C_s, 4 signals


C_s, 3 signals


C_1, 7 signals


C_1, 7 signals

Ch112 − Problem Set 1, Answer Key

Problem 2 (2 points)

Part A.

1. σ_v(xz), reflection through the xz plane

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2. σ_v(yz), reflection through the yz plane

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Part B.

1.

C_{2v}	E	C_2	σ_v(xz)	σ_v(yz)
Γ	3	−1	1	1

Add the elements of the matrix in the diagonal from upper left to bottom right.

2.

C_{2v}	E	C_2	σ_v(xz)	σ_v(yz)	Coordinates used
Γ_1	1	−1	1	−1	x
Γ_2	1	−1	−1	1	y
Γ_3	1	1	1	1	z
Γ_4	1				
Γ	3	−1	1	1	

The x, y, z coordinates are independent of each other. Each matrix is block diagonalized into 1×1 matrices. Each element along the diagonal is a character under the corresponding class.

3.

C_{2v}	E	C_2	σ_v(xz)	σ_v(yz)	Coordinates used
Γ_1	1	−1	1	−1	x
Γ_2	1	−1	−1	1	y
Γ_3	1	1	1	1	z
Γ_4	1	1	−1	−1	
Γ	3	−1	1	1	

The sum of the squares under E equals the order of the group. Find the rest of the characters using the orthogonality principle between Γ_1, Γ_2, and Γ_3.

4.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	Coordinates used
B_1	1	−1	1	−1	x
B_2	1	−1	−1	1	y
A_1	1	1	1	1	z
A_2	1	1	−1	−1	
Γ	3	−1	1	1	

A → symmetric with respect to the principal rotation axis.
B → antisymmetric with respect to the principal rotation axis.

Subscript 1 → symmetric with respect to the reflection plane $\sigma_v(xz)$.
Subscript 2 → antisymmetric with respect to the reflection plane $\sigma_v(xz)$.

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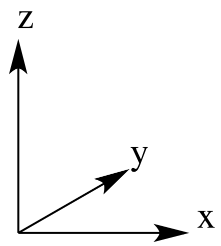
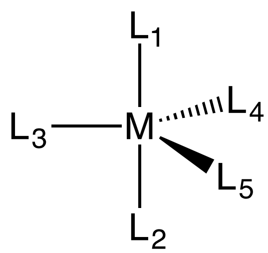
Problem 3 (3 points)

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

$$\begin{bmatrix} \cos(2\pi/3) & -\sin(2\pi/3) & 0 \\ \sin(2\pi/3) & \cos(2\pi/3) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2. σ_h

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

3. S_3 along the z axis Note, $S_3 = \sigma_h \cdot C_3$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} \cos(2\pi/3) & -\sin(2\pi/3) & 0 \\ \sin(2\pi/3) & \cos(2\pi/3) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos(2\pi/3) & -\sin(2\pi/3) & 0 \\ \sin(2\pi/3) & \cos(2\pi/3) & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

4. C_2 along the x axis

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

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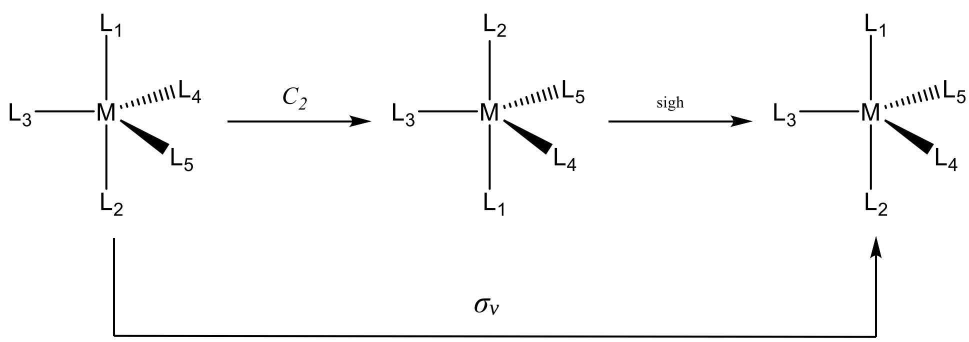
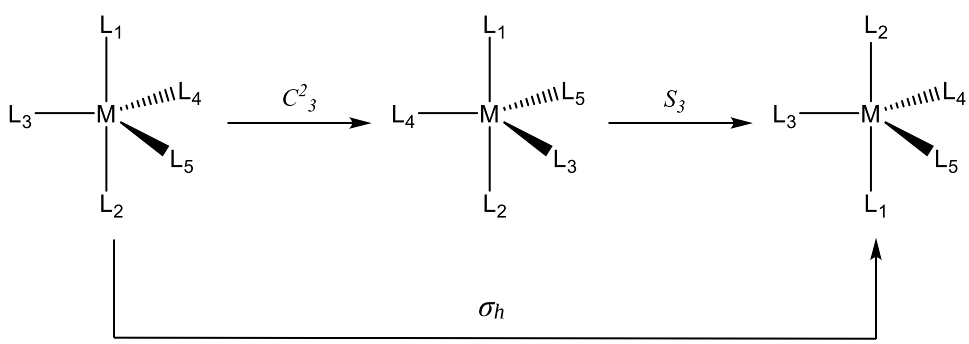
In addition to the operations described above, two more classes are present in the D_{3h} point group. Find them by performing the operation multiplications below. Draw and label the molecule to illustrate these operations and clearly label the symmetry elements.

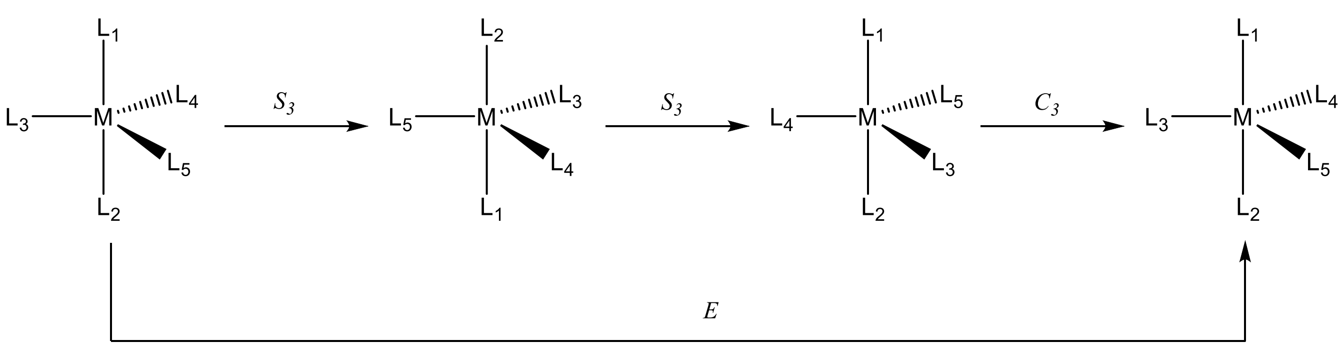
1. $C_2 \bullet \sigma_h =$

2. $C_3^2 \bullet S_3 =$

3. $S_3 \bullet S_3 \bullet C_3 =$







Problem 4 (2 points)

Group order 8.

There is always a totally symmetric irreducible representation: characters of A_1 are all 1.

Function z transforms as A_2: apply symmetry operations on z for characters of A_2.

Mulliken symbols give the dimensions of the irreducible representation. All characters under the identity function can be found in this way.

Using A or B, the characters under the principal axis (C_4) can be found.

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	
A_1	1	1	1	1	1	
A_2	1	1	1	−1	−1	z
B_1	1	−1	A	1	B	
B_2	1	−1	C	−1	D	
E	2	E	F	G	H	(x, y)

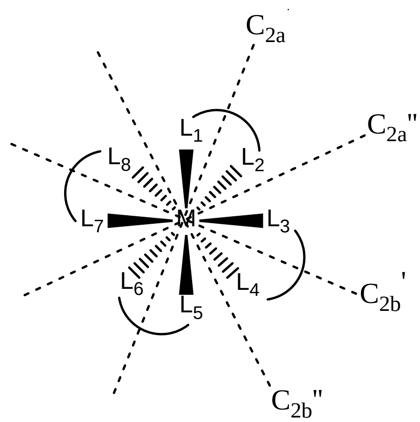
Find A, B, C, D using the orthogonality property.

Orthogonality between A_1 and B_1 and between A_2 and B_1 gives: A = 1 and B = −1

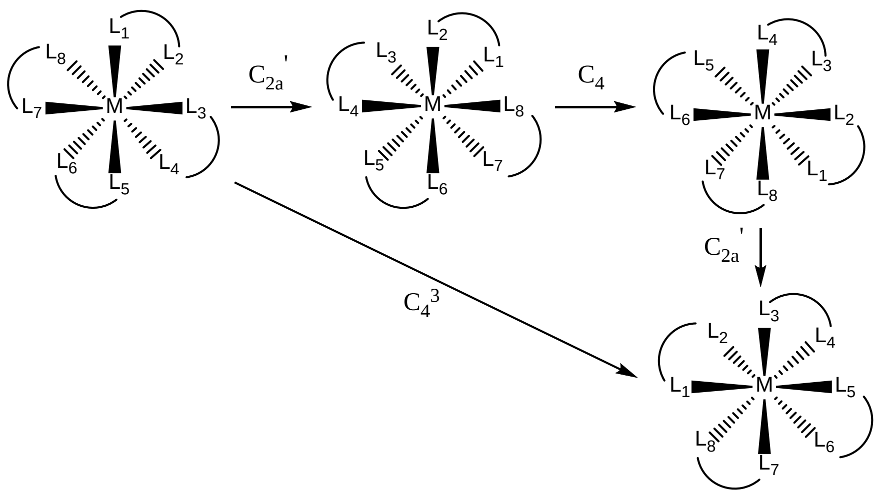
Orthogonality between A_1 and B_2 and between A_2 and B_2 gives: C = 1 and D = 1

Find E, F, G, H, by using the orthogonality property between E and all other irreducible representations: E = 0, F = −2, G = 0, H = 0
Alternatively, transform (x, y) to obtain the characters under each class.

Defining the symmetry elements as illustrated below, it can be shown that:



$C_{2a}' \cdot C_4 \cdot C_{2a}' = C_4^3$



Note that C_{2a}' is the inverse of itself. Hence, C_4 and C_4^3 belong to the same class.

Similarly,
$C_{2b}'' \cdot C_{2a}' \cdot C_{2b}'' = C_{2b}'$
Hence, C_{2a}' and C_{2b}' belong to the same class.

Similarly,
$C_{2b}' \cdot C_{2a}'' \cdot C_{2b}' = C_{2b}''$
Hence, C_{2a}'' and C_{2b}'' belong to the same class.