**2019 Ch112 – Problem Set 1**
**Due: Thursday, October 10 – before class**

**ANSWER KEY**

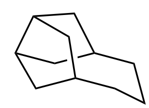
**Note: Use of published character tables is not allowed for this problem set. You are welcome to check your solution with such tables after completion of the set.**

**Problem 1 (3 points)**

Part A.

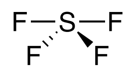
Assign the point group of each molecule. Identify the location of the symmetry elements and determine if the molecule is chiral. If the molecule is achiral, clearly indicate the symmetry element that prevents it from being chiral. Treat all Me ligands, L ligands, $SiR_3$ substituents, and $^tBu$ substituents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

1



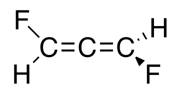
$C_s$, achiral ($\sigma_h$)

2



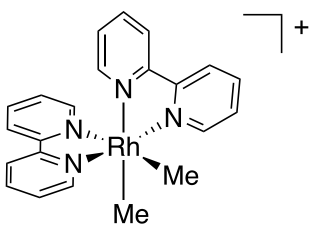
$C_{2v}$, achiral (two $\sigma_v$'s)

3



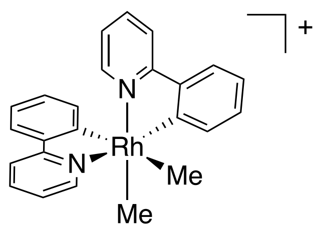
$C_2$, chiral

4



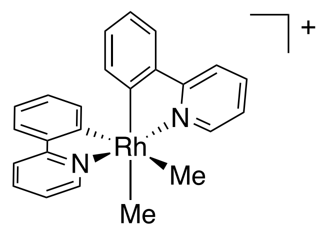
$C_2$, chiral

5



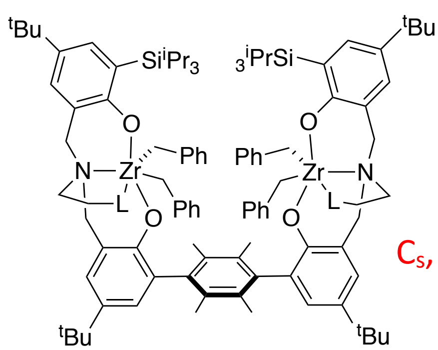
$C_1$, chiral

6



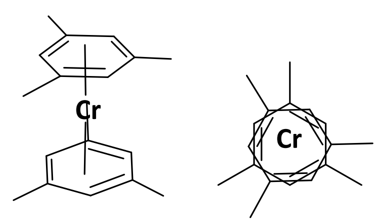
$C_2$, chiral

7



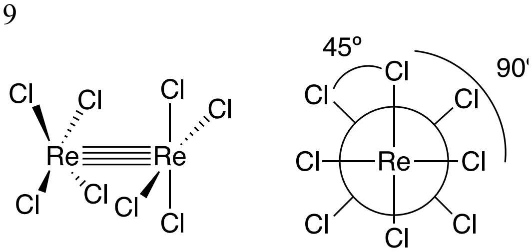
$C_s$, achiral $\sigma_h$ along Zr-Zr vector

8



$D_3$, chiral

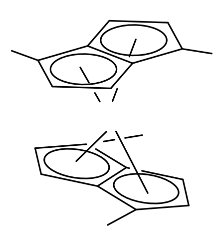
9



View along Re-Re bor

$D_{4d}$, achiral 4 $\sigma_h$'s

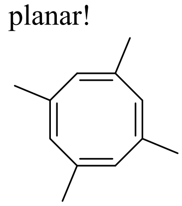
10



$S_4$, achiral, contains an $S_4$ symmetry operation

11

Hint: This molecule is not planar!



$S_4$, achiral, contains an $S_4$ symmetry operation

Part B.

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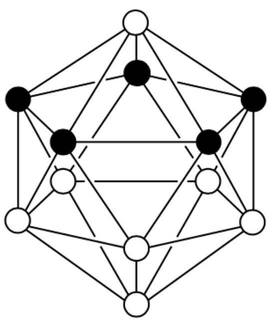
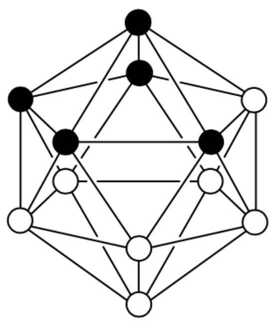
One of the handouts for the first lecture lists all point group classes. Provide an example of molecule for each of the 15 point group types listed. Answers will vary

Part C.

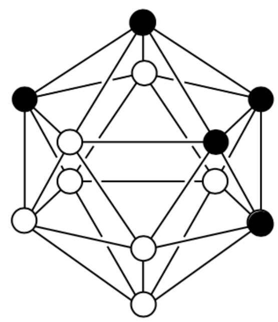
Carboranes derived from $[B_{12}H_{12}]^{2-}$ can be synthesized by replacement of BH moietes with CH moieties. Replacement of 5 BH moieties with 5 CH moieties results in the $[B_7C_5H_{12}]^{3+}$ trication. Using the representations below by darkening the circles corresponding to CH groups, provide 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.



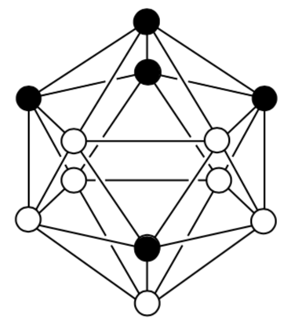
$C_{5v}$, 1 signal



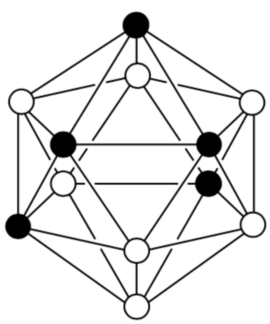
$C_s$, 3 signals



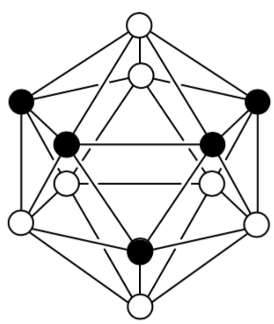
$C_s$, 4 signals



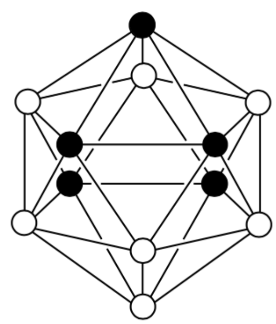
$C_s$, 4 signals



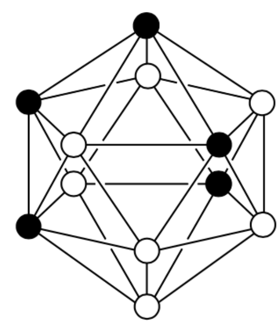
$C_s$, 4 signals



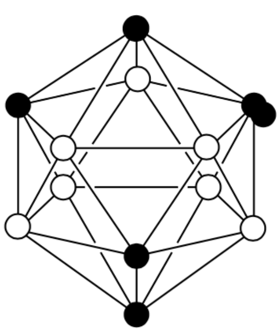
$C_s$, 3 signals



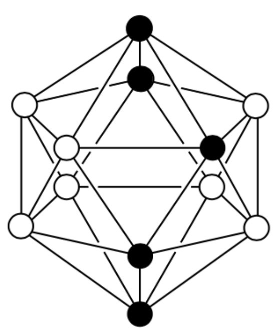
$C_s$, 3 signals



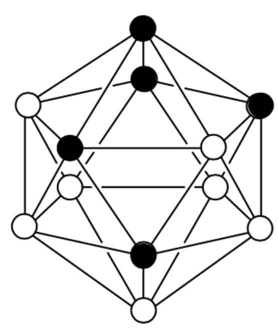
$C_s$, 3 signals



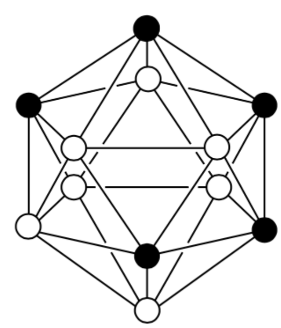
$C_s$, 4 signals



$C_s$, 3 signals



$C_1$, 5 signals



$C_1$, 5 signals

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**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]

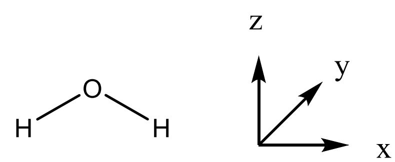
For a basis set of (x, y, z) coordinates, the transformation matrix of the *E* is given as:

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

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

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

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

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

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:

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

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

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

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 |
|---|---|---|---|---|---|
| $B_1$ $\Gamma 1$ | 1 | −1 | 1 | -1 | x, $R_y$ |
| $B_2$ $\Gamma 2$ | 1 | −1 | -1 | 1 | y, $R_x$ |
| $A_1$ $\Gamma 3$ | 1 | 1 | 1 | 1 | z |
| $A_2$ $\Gamma 4$ | 1 | 1 | -1 | -1 | $R_z$ |
| $\Gamma_{x,y,z}$ | 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 $\sigma_v(xz)$.

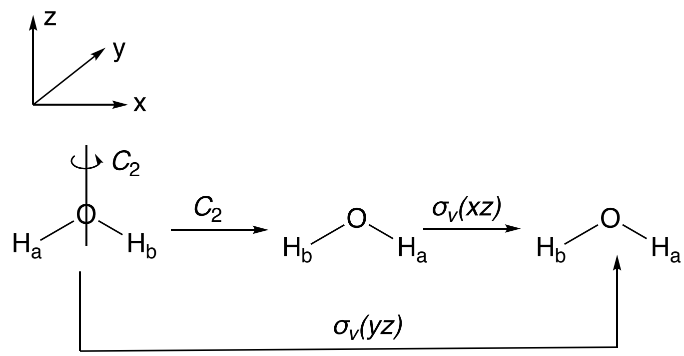
Subscript 2→antisymmetric with respect to the reflection plane $\sigma_v(xz)$.

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.

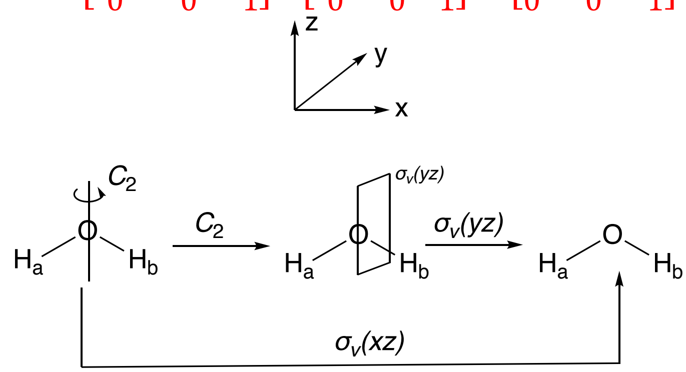
5. Define how rotation about the x, y, and z axes (e.g. $R_x$, $R_y$, $R_z$) transform in $C_{2v}$ and place them in the right-most column in the character table above.
6. Show using both the geometric manipulations of the $H_2O$ molecule and the matrix representations generated above that the following requirements for a group are met:
    a. All binary products must be members of the group

E multiplied by any other symmetry operation will result in that particular symmetry operation (e.g., E * $C_2 = C_2$)

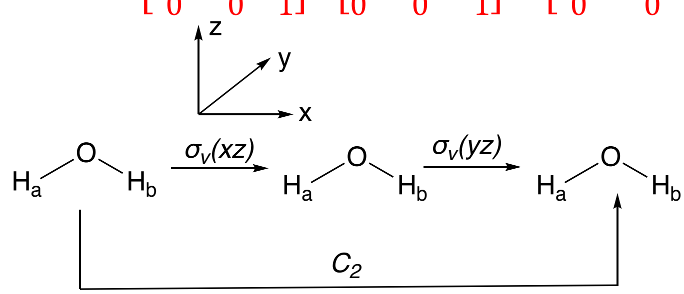
$$C_2 * \sigma_v(xz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \sigma_v(yz)$$




$$C_2 * \sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} * \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \sigma_v(xz)$$




$$\sigma_v(xz) * \sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_2$$



Note: Performing the multiplication in the reverse order will result in the same product since $C_{2v}$ is an Abelian group (the operators commute)

b. The associative law of multiplication holds
   i. A*(B*C) = (A*B)*C, where A, B, and C are symmetry operations

**Show that E*(C₂*$\sigma_v(xz)$) = (E*C₂)*$\sigma_v(xz)$:**

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\left\{\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}=\left\{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}*\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$$

Left-hand side:

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\left\{\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Right-hand side:

$$\left\{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}*\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Associative law of multiplication holds for these operators.

**Show that E*(C₂*$\sigma_v(yz)$) = (E*C₂)*$\sigma_v(yz)$**

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\left\{\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}\right\}=\left\{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Left-hand side:

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\left\{\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}\right\}=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$$

Right-hand side:

$$\left\{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$$

Associative law of multiplication holds for these operators.

**Show that E*($\sigma_v(xz)$*$\sigma_v(yz)$) = (E*$\sigma_v(xz)$)*$\sigma_v(yz)$**

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\left\{\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}\right\}=\left\{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}*\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\right\}*\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Left-hand side:

$$\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} * \left\{\begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}\right\} = \begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}$$

Right-hand side:

$$\left\{\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}\right\} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} = \begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}$$

Associative law of multiplication holds for these operators.

**Show that $C_2 * (\sigma_v(xz) * \sigma_v(yz)) = (C_2 * \sigma_v(xz)) * \sigma_v(yz)$:**

$$= \begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \left\{\begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}\right\}$$

$$= \left\{\begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}\right\} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$$

Right-hand side:

$$\left\{\begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}\right\} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$$

Left-hand side:

$$\begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \left\{\begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} * \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}\right\} = \begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$$

Associative law of multiplication holds for these operators.

c. Every member of the group has an inverse
   i. $A * A^{-1} = A^{-1} * A = E$, where E is the identity operation.

$C_2 * C_2 = E$

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

$(\sigma_v(xz) * \sigma_v(xz) = E$

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

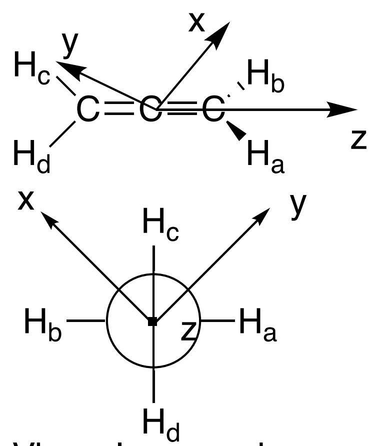
$(\sigma_v(yz) * \sigma_v(yz) = E$

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

Since the symmetry operations of a $C_{2v}$ point group involve either 180º rotation or reflection across a plane, then their inverses involve performing the operation a second time on the molecule/object. This results overall in the identity (E) operation.

**Problem 3 (3 points)**

$D_{2d}$ is the point group that describes the symmetry of the molecule allene. Using the given coordinate system as the basis set, find transformation matrices for the following symmetry operations:



View along z-axis

Generally:

$$C_n = \begin{bmatrix} cos\theta & -sin\theta & 0 \\ sin\theta & cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$S_n = \begin{bmatrix} cos\theta & -sin\theta & 0 \\ sin\theta & cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\theta = 360/n$$

1. $C_2$ along the z axis

$$C_{2\,(z)} = \begin{bmatrix} cos\pi & -sin\pi & 0 \\ sin\pi & cos\pi & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2. $S_4$ along the z axis

$$S_4 = \begin{bmatrix} \cos\left(\frac{\pi}{2}\right) & -sin\left(\frac{\pi}{2}\right) & 0 \\ sin\left(\frac{\pi}{2}\right) & cos\left(\frac{\pi}{2}\right) & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Can also do $i \bullet C_4$

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

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

3. $C'_2$ along the x axis

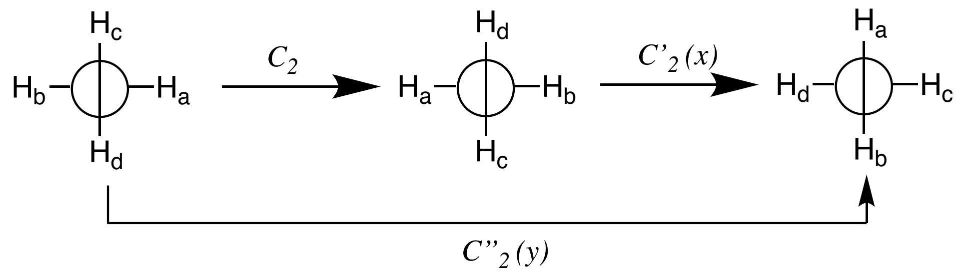
$$C'_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Since,

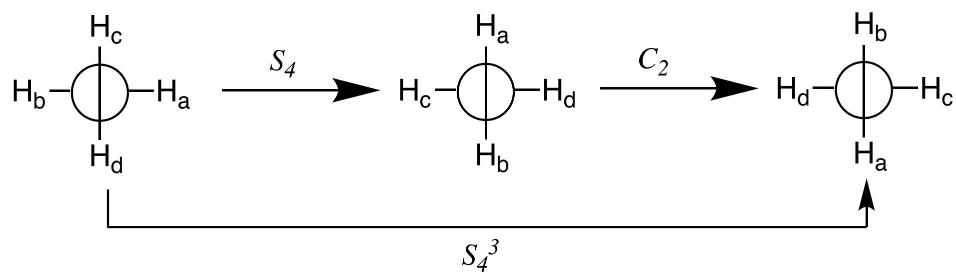
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ -z \end{bmatrix}$$

In addition to the operations described above, two more classes are present in the $D_{2d}$ point group. Find them by performing operation multiplications below. Draw and label the molecule (we recommend drawing them as Newman projections from the starting template shown above) to illustrate these operations and clearly label the symmetry elements. Finally, for each question, specify whether or not the operators commute with one another.

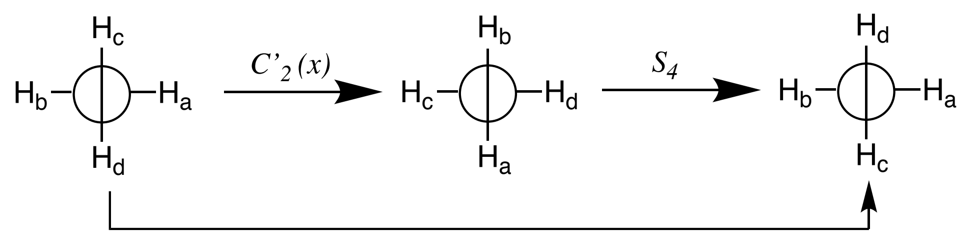
7.




8.




9.




$\sigma_d$ (horizontal plane coming into/out of page)

The new class discovered in this point group is $\sigma_d$, from performing the operations in (9.). Operations in (7.) and (8.) commute with one another, whereas those in (9.) do not.

**Problem 4 (2 points)**

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

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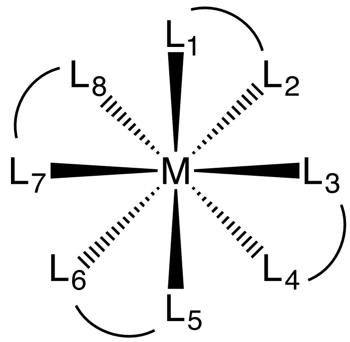
1. What is the order of the group? 8

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:

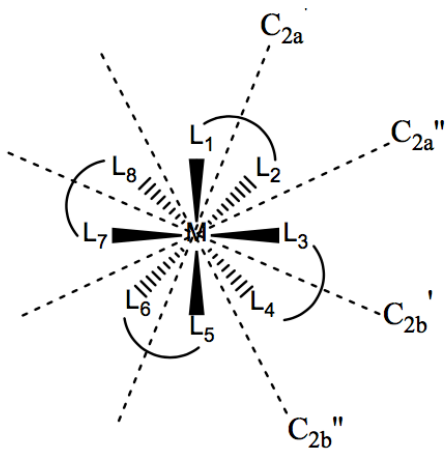



| $D_4$ | $E$ | $2C_4$ | $C_2$ | $2C_2'$ | $2C_2''$ | |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 | |
| $A_2$ | 1 | 1 | 1 | -1 | -1 | z |
| $B_1$ | 1 | -1 | 1 | 1 | -1 | |
| $B_2$ | 1 | -1 | 1 | −1 | 1 | |
| E | 2 | 0 | -2 | 0 | 0 | (x, y) |

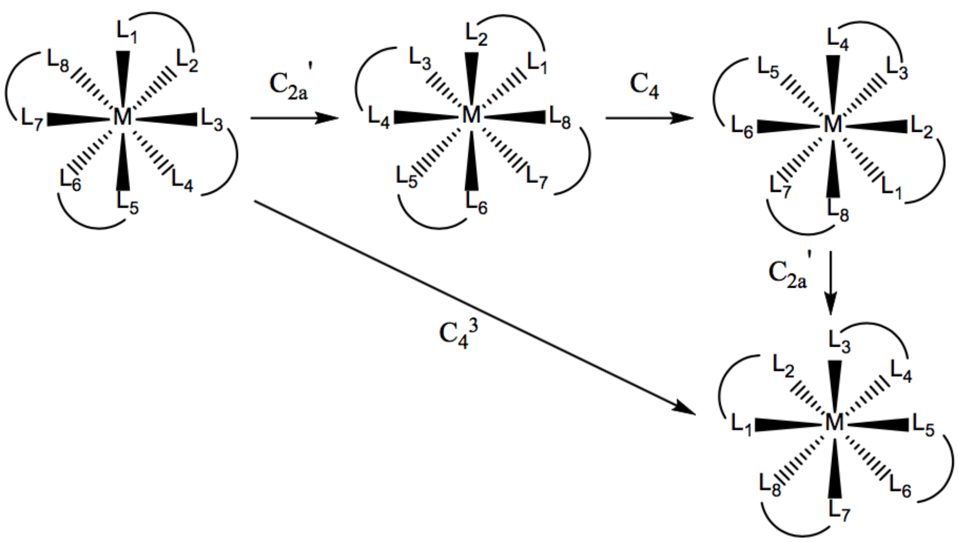
There is always a totally symmetric irreducible representation: characters of $A_1$ are all 1. Function z transforms as $A_2$: apply symmetry operations on z for characters of $A_2$.
Mulliken symbols give the dimensions of the irreducible representation. All characters under the identity function can be found in this way. Using A or B, the characters under the principal axis ($C_4$) can be found.

Character under $C_4$ for E irreducible representation is 0 from property 2
Find A, B, C, D using the orthogonality property.
$A_1 \perp B_1$ and $A_2 \perp B_1 \rightarrow$ for $B_1$: $C_2 = 1$ and $C_2'' = -1$
$A_1 \perp B_2$ and $A_2 \perp B_2 \rightarrow$ for $B_2$ $C_2 = 1$ and $C_2'' = 1$
For E, find $C_2$, $C_2'$, $C_2''$, by applying property 2 on each column. $C_2 = -2$, $C_2' = 0$, $C_2'' = 0$

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.

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