Chemistry 322  
Inorganic Chemistry  
Spring 2007

**Problem Set 1**

*In solving the problems for this class, I encourage you to work together using whatever resources you need. Please answer the questions fully; use prose, calculations, figures and references as appropriate to communicate your understanding. The organization and comprehensibility of your answer is one basis for its evaluation. As always, the written work that you hand in should be your own.*

1. Determine the symmetry elements and assign the point group of the following molecules or ions. You will need to consult a general chemistry textbook if you do not remember how to use VSEPR to obtain the correct structure of the molecules.

   a. \( \text{NH}_3\text{Cl}^+ \)
   b. \( \text{BF}_4^+ \)
   c. \( \text{PF}_3 \)
   d. \( \text{PF}_5 \)
   e. \( \text{PBr}_3\text{F}_3 \)
   f. \( \text{PBr}_3\text{F}_2 \)
   g. \( \text{SF}_4 \)
   h. \( \text{Cl}_3\text{PO} \)
   i. \( \text{XeF}_4 \)
   j. Tetrachloroallene \( \text{Cl}_2\text{C}==\text{C}==\text{CCl}_2 \)
   k. Eclipsed Ferrocene (assume the rings are static) (see pg. 526)
   l. \( \text{NO}_2 \)

   3 pts total (0.25 pts each)  
   - take off 1 pt if no work  
   (must show/state some symmetry elements)

2. For trans-1,2-dibromo-1,2-dichloroethylene, of \( C_{2h} \) symmetry,

   a. List all the symmetry operations for the molecule.
   b. Write a set of transformation matrices that describe the effect of each symmetry operation in the \( C_{2h} \) point group on a set of coordinates \( x, y, z \) for a point. (Your answer should consist of four \( 3 \times 3 \) matrices.)
   c. Using the terms along the diagonal, obtain as many irreducible representations as possible from the transformation matrices. (You should be able to obtain three irreducible representations in this way, but two will be duplicates.)
   d. Using the \( C_{2h} \) character table, verify that the irreducible representations are mutually orthogonal.

3. Problem 7.7 from Shriver and Atkins.

   0.5 pt for all correct (\( \frac{4}{5} \))
   1 pt for all correct (\( \frac{7}{8} \))
1a. \( \text{NH}_3 \text{Ce}^+ \)

- \( C_3 \)
- \( \sigma_v \)

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

1b. \( \text{BF}_4^+ \)

- \( E \)
- \( \sigma_h \)
- \( C_2 \)
- \( C_3 \)

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{B} \\
\text{F}
\end{array}
\]

1c. \( \text{PF}_3 \)

- \( E \)
- \( \sigma_h \)

\[
\begin{array}{c}
\text{F} \\
\text{P} \\
\text{F} \\
\text{F}
\end{array}
\]

1d. \( \text{PF}_5 \)

- \( E \)
- \( C_3 \)
- \( \sigma_h \)

\[
\begin{array}{c}
\text{F} \\
\text{P} \\
\text{F} \\
\text{F}
\end{array}
\]

(PREFERRED WAY TO DRAW TBP)

\[
\begin{array}{c}
\text{D}_{3h}
\end{array}
\]

(high symmetry)

\[
\begin{array}{c}
\text{E, \sigma_h, C_2, C_3, etc...}
\end{array}
\]

\[
\begin{array}{c}
\text{T}_d
\end{array}
\]
e. $PBr_2F_3$

f. $PBr_3F_2$

$g. SF_4$ (v.e. 34)

$h. Cl_3PO$ (v.e. 32)
1. $E \xrightarrow{\text{Xe}} F \ldots F$  
$\text{D}_{4h}$  
($\text{square planar}$)  
& preferred way to draw $\equiv$  

$\text{C}_4$  
\begin{align*} 
\perp \text{C}_2' \perp \text{C}_2'' \\
\sigma_h (\sigma_v'') \\
\end{align*}$


2. $E \xrightarrow{\text{Cl}} C = C = C \xrightarrow{\text{Cl}} \text{Cl}$  
$\text{D}_{2d}$  
$C_L \perp C_2$ (hard to see)  
$\sigma_{dl}$  
(Also has $S_4$)

$\text{E}$  
$\sigma_v (+ \sigma''_v)$


3. $\text{NO}_2$ (17 v.e.)  
\begin{align*} 
\text{E} & \xrightarrow{\text{C}_2} \text{C}_2 \\
\sigma_v' & \sigma_v'' \\
\text{resonance} & \equiv \\
\end{align*}$
Chapter 4 Symmetry and Group Theory

4-10 a. \( p_z \) has \( C_{6v} \) symmetry. Ignoring the difference in sign between the two lobes, it is \( D_{6h} \).

b. \( d_y \) has \( D_{2h} \) symmetry. Ignoring the signs, it is \( D_{4h} \).

c. \( d_{x^2-y^2} \) has \( D_{2h} \) symmetry. Ignoring the signs, it is \( D_{4h} \).

d. \( d_z \) has \( D_{4h} \) symmetry.

4-11 The superimposed octahedron and cube show the matching symmetry elements. The descriptions below are for the elements of a cube; each element also applies to the octahedron.

- **E**: Every object has an identity operation.
- **8C_3**: Diagonals through opposite corners of the cube are \( C_3 \) axes.
- **6C_2**: Lines bisecting opposite edges are \( C_2 \) axes.
- **6C_1**: Lines through the centers of opposite faces are \( C_1 \) axes. Although there are only three such lines, there are six axes, counting \( C_2^3 \).
- **3C_2 (\( C_4^2 \))**: The lines through the centers of opposite faces are \( C_4 \) axes as well as \( C_2 \) axes.
- **i**: The center of the cube is the inversion center.
- **6S_4**: The \( C_4 \) axes are also \( S_4 \) axes.
- **8S_6**: The \( C_3 \) axes are also \( S_6 \) axes.
- **3n**: These mirror planes are parallel to the faces of the cube.
- **6n**: These mirror planes are through two opposite edges.

4-12 a. \( C_2 \) molecules have \( E, C_2, i, \) and \( \sigma \) operations.

![C2 molecule diagram]

b. 

\[
\begin{bmatrix}
E & C_2 & i & \sigma_h & \sigma_v \\
1 & 0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

These matrices can be block diagonalized into three \( 1 \times 1 \) matrices, with the representations shown in the table.

<table>
<thead>
<tr>
<th>( \chi(E) )</th>
<th>( \chi(C_2) )</th>
<th>( \chi(i) )</th>
<th>( \chi(\sigma_h) )</th>
<th>( \chi(\sigma_v) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

from the \( x \) and \( y \) coefficients

\[
\chi \text{ 'accidentally' the same}
\]

The total is \( \Gamma = 2B_v + A_v \).

d. Multiplying \( B_v \) and \( A_v \):

\[
1 \times 1 + (-1) \times 1 + (-1) \times (-1) + 1 \times (-1) = 0,
\]
proving they are orthogonal.
MA₂B₂C₂

None chiral; all have σ planes

D₂h

Chiral; enantiomers to each other