Chem 370 - Spring, 2019
Assignment 3 – Solutions

1. (a) By considering whether each vector is shifted into the negative of itself or remains nonshifted, we can obtain the following characters for the unit vector transformations:

C_{2h}	E	C_2	i	σ_h	
Γ_x	1	-1	-1	1	$\Rightarrow B_u$
Γ_y	1	-1	-1	1	$\Rightarrow B_u$
Γ_z	1	1	-1	-1	$\Rightarrow A_u$

Note that both **x** and **y** vectors transform by the same species (B_u) but are *not* degenerate, because the irreducible representation B_u is nondegenerate ($d_i = 1$). There are no degenerate representations in the group C_{2h}, and therefore there can be no degenerate properties.

(b) By considering the effect of each operation on the direction of rotation of each vector, we can obtain the following characters for the rotational vectors:

C_{2h}	E	C_2	i	σ_h	
Γ_{Rx}	1	-1	1	-1	$\Rightarrow B_g$
Γ_{Ry}	1	-1	1	-1	$\Rightarrow B_g$
Γ_{Rz}	1	1	1	1	$\Rightarrow A_g$

2. (a) The 3 x 3 transformation matrices that comprise Γ_m for the general vector **v** are

C_{2h}	E	C_2	i	σ_h	
Γ_m	$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$	$\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$	$\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$	$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$	$\begin{matrix} \Rightarrow B_u \\ \Rightarrow B_u \\ \Rightarrow A_u \end{matrix}$

(b) As shown above, by block diagonalization, the elements c_{11} comprise B_u, the elements c_{22} also comprise B_u, and the elements c_{33} comprise A_u. Given the results for unit vector transformations in problem 1, this is an expected result.

(c) From the traces of the 3 x 3 matrices we obtain the following characters:

C_{2h}	E	C_2	i	σ_h
Γ_v	3	-1	-3	1

(d)

C_{2h}	E	C_2	i	σ_h
B_u	1	-1	-1	1
B_u	1	-1	-1	1
A_u	1	1	-1	-1
Γ_v	3	-1	-3	1

(e) The multiplication table for C_{2h} is shown below:

C_{2h}	E	C_2	i	σ_h
E	E	C_2	i	σ_h
C_2	C_2	E	σ_h	i
i	i	σ_h	E	C_2
σ_h	σ_h	i	C_2	E

The group is Abelian, so we only need to look at one sense of combination for any pair of operations. Moreover, any combination between the identity matrix (for which all elements are given by $c_{ij} = \delta_{ij}$) and a second matrix will give the second matrix. Therefore we only need to consider the binary self-products and one direction of combination of all the binary cross products. For $C_2 \times C_2$ we obtain

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

which gives the matrix for E.

For $i \times i$ we obtain

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

which is also E.

For $\sigma_h \times \sigma_h$ we obtain

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

which is also E.

For the product $C_2 \times i = i \times C_2$ we obtain

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

which is the expected matrix for σ_h.

For $C_2 \times \sigma_h = \sigma_h \times C_2$ we obtain

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

which is the expected matrix for i.

And finally, for $\sigma_h \times i = i \times \sigma_h$ we obtain

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

which is the expected matrix for C_2. All of these results are consistent with the multiplication table above.

3. (a) MX_2 linear, $D_{\infty h}$ — $z = \Sigma_u^+$; $(x, y) = \Pi_u$

(b) MX_2 bent, C_{2v} — $x = B_1$; $y = B_2$; $z = A_1$

(c) MX_3 trigonal planar, D_{3h} — $(x, y) = E'$; $z = A_2''$

(d) MX_3 pyramidal, C_{3v} — $(x, y) = E$; $z = A_1$

(e) MX_3 T-shaped, C_{2v} — $x = B_1$; $y = B_2$; $z = A_1$ [same as (b)]

(f) MX_4 tetrahedral, T_d — $(x, y, z) = T_2$

(g) MX_4 square planar, D_{4h} — $(x, y) = E_u$; $z = A_{2u}$

(h) MX_4 irregular tetrahedron, C_{2v} — $x = B_1$; $y = B_2$; $z = A_1$ [same as (b)]

(i) MX_5 square pyramidal, C_{4v} — $(x, y) = E$; $z = A_1$

(j) MX_5 trigonal bipyramid, D_{3h} — $(x, y) = E'$; $z = A_2''$ [same as (c)]

(k) MX_6 octahedral, O_h — $(x, y, z) = T_{1u}$

4. Take all the similarity transforms on any one of the reflections (here σ_1).

$E\sigma_1 E = \sigma_1$
$C_3^2\sigma_1 C_3 = C_3^2\sigma_2 = \sigma_3$
$C_3\sigma_1 C_3^2 = C_3\sigma_3 = \sigma_2$
$\sigma_1\sigma_1\sigma_1 = \sigma_1 E = \sigma_1$
$\sigma_2\sigma_1\sigma_2 = \sigma_2 C_3 = \sigma_3$
$\sigma_3\sigma_1\sigma_3 = \sigma_3 C_3^2 = \sigma_2$

All transforms give σ_1, σ_2, or σ_3, indicating that all three reflection operations are in the same class.

5. (a) Use **z** as a basis for the representation A_1. The transformations effected by C_3 and C_3^2 can both be represented by the expression $[+1]\mathbf{z} = \mathbf{z}$. The 1×1 transformation matrix in each case has a character $\chi = 1$.

(b) Use the degenerate pair of vectors (**x**, **y**) as a basis for the representation E. In effect, we will describe the transformation of a vector $\mathbf{v}_{x,y}$ in the xy plane, whose base is at 0,0,0 and whose tip is initially at $(x, y, 0)$. The following 2×2 matrix expressions describe the transformations of C_3 and C_3^2:

$$C_3: \quad \begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos 2\pi/3 & -\sin 2\pi/3 \\ \sin 2\pi/3 & \cos 2\pi/3 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

$$C_3^2: \quad \begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos 2\pi/3 & \sin 2\pi/3 \\ -\sin 2\pi/3 & \cos 2\pi/3 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

In both cases the character of the transformation matrix is $\chi = -1$.

6. (a) A_g in C_{2h}: symmetric to C_2; symmetric to i. [Totally symmetric representation]

(b) B_2 in C_{4v}: anti-symmetric to C_4; anti-symmetric to σ_v.

(c) E in D_3: doubly degenerate.

(d) A_1'' in D_{3h}: symmetric to C_3; symmetric to $3C_2$; anti-symmetric to σ_h.

(e) E' in D_{3h}: doubly degenerate; symmetric to σ_h.

(f) B_{1g} in D_{4h}: anti-symmetric to C_4; symmetric to $2C_2'$; symmetric to i.

(g) E_u in D_{4h}: doubly degenerate; anti-symmetric to i.

(h) T_g in T_h: triply degenerate; symmetric to i.

7. (a) $i + (-i) = 0$

C_4	E	C_4	C_2	C_4^2
$\{E\}$	2	0	-2	0

(b) Let $c = 2 \cos 2\pi/6 = 2 \cos \pi/3$

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5
$\{E_1\}$	2	c	$-c$	-2	$-c$	c
$\{E_2\}$	2	$-c$	$-c$	2	$-c$	$-c$

(c) Let $c = 2 \cos 2\pi/5$ and $c^2 = 2 \cos 4\pi/5$.

C_5	E	C_5	C_5^2	C_5^3	C_5^4
$\{E_1\}$	2	c	c^2	c^2	c
$\{E_2\}$	2	c^2	c	c	c^2

(d) Let $c = 2 \cos 2\pi/7$, $c^2 = 2 \cos 4\pi/7$, and $c^3 = 2 \cos 6\pi/7$.

C_7	E	C_7	C_7^2	C_7^3	C_7^4	C_7^5	C_7^6
$\{E_1\}$	2	c	c^2	c^3	c^3	c^2	c
$\{E_2\}$	2	c^2	c^3	c	c	c^3	c^2
$\{E_3\}$	2	c^3	c	c^2	c^2	c	c^3

8. (a) $\Gamma_a = A_1 + B_2 + E$

(b) $\Gamma_b = 3A_1 + A_2 + 4E$

(c) $\Gamma_c = 2A_1' + E' + A_2''$

(d) $\Gamma_d = A_1 + E + T_1 + 3T_2$

(e) $\Gamma_e = 2A_1' + E_1' + E_2' + A_2''$

9. (a) $\Gamma_a = 4A + 3B + 4\{E\}$

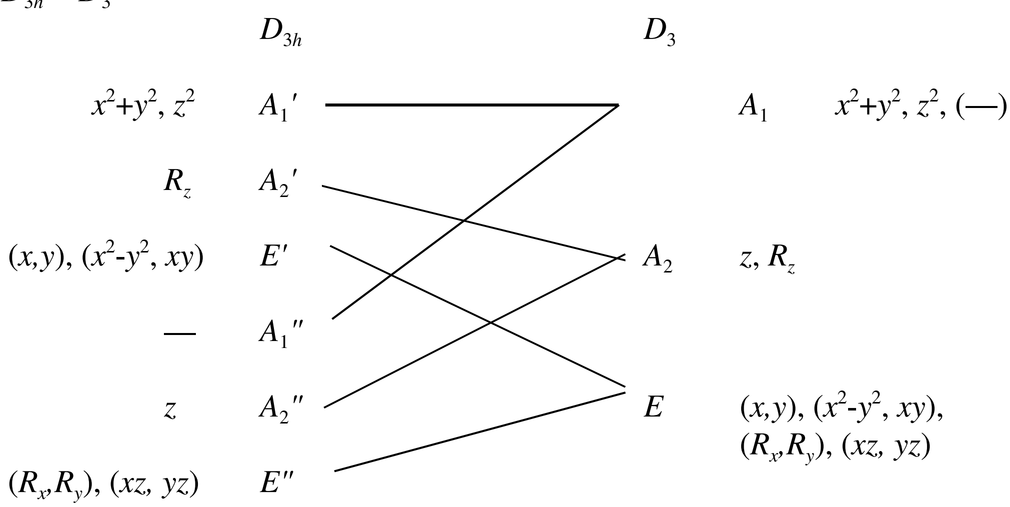
(b) $\Gamma_b = 4A' + 5\{E'\} + 3A'' + 2\{E''\}$ [Note: $\varepsilon + \varepsilon^* = 2 \cos 2\pi/3 = 2(-0.5) = -1$]

(c) $\Gamma_c = 3A + \{E_1\} + \{E_2\}$ [Note: $\varepsilon + \varepsilon^* = 2 \cos 2\pi/5 = 0.6180$, and $\varepsilon^2 + \varepsilon^{*2} = 2 \cos 4\pi/5 = -1.6180$]

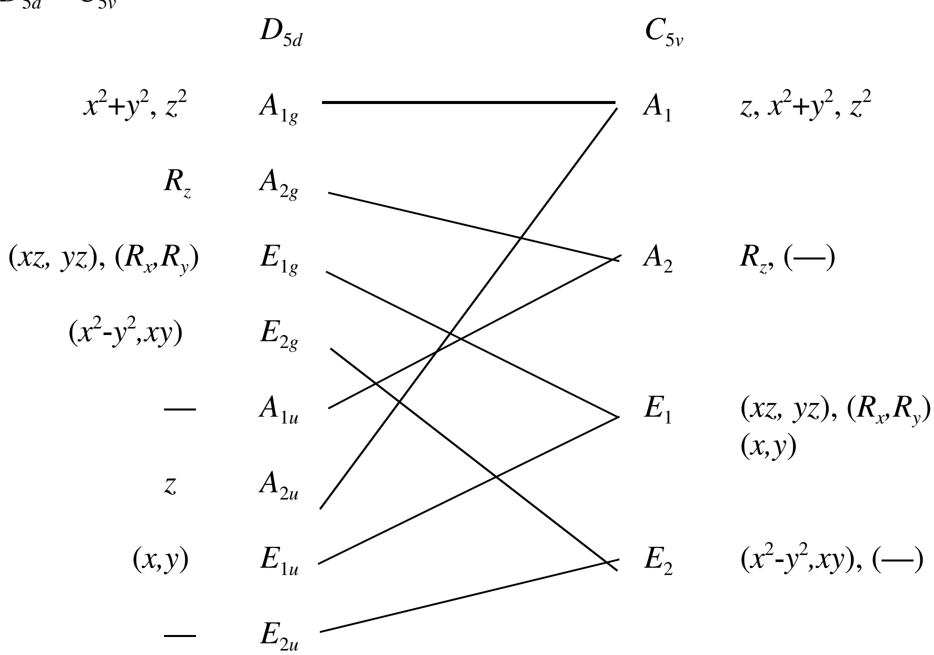
10. (a) $C_{4v} \rightarrow C_4$

	C_{4v}	C_4	
z, x^2+y^2, z^2	A_1	A	z, x^2+y^2, z^2, R_z
R_z	A_2		
x^2-y^2	B_1	B	x^2-y^2, xy
xy	B_2		
$(x,y), (R_x,R_y), (xz, yz)$	E	$\{E\}$	$(x,y), (R_x,R_y), (xz, yz)$

(b) $D_{3h} \rightarrow D_3$



(c) $D_{5d} \rightarrow C_{5v}$



11. For both of these, use the appropriate correlation table shown on the following page, which was presented in class (also appended here).

(a) In C_{2v}, $\Gamma_a = 5A_1 + 5B_1 + 5B_2$, from which it follows in $C_{\infty v}$, $\Gamma_a = 5\Sigma^+ + 5\Pi$.

(b) In D_{2h}, $\Gamma_b = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$, from which it follows in $D_{\infty h}$, $\Gamma_b = \Sigma_g^+ + \Pi_g + 2\Sigma_u^+ + 2\Pi_u$.

Partial Correlation Tables for $C_{\infty v}$ and $D_{\infty h}$

$C_{\infty v}$	C_{2v}
$A_1 = \Sigma^+$	A_1
$A_2 = \Sigma^-$	A_2
$E_1 = \Pi$	$B_1 + B_2$
$E_2 = \Delta$	$A_1 + A_2$

$D_{\infty h}$	D_{2h}
Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g} + B_{3g}$
Δ_g	$A_g + B_{1g}$
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u} + B_{3u}$
Δ_u	$A_u + B_{1u}$