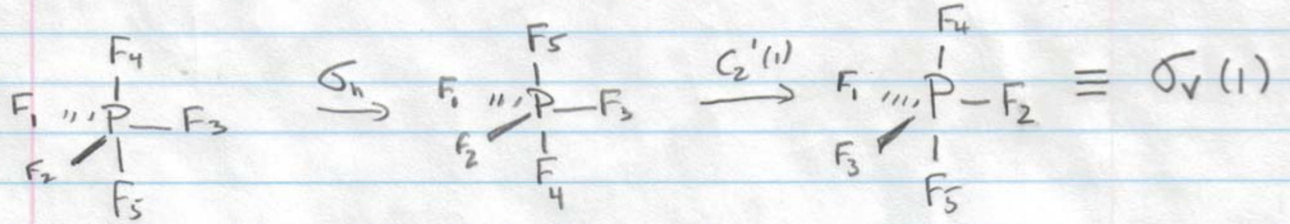
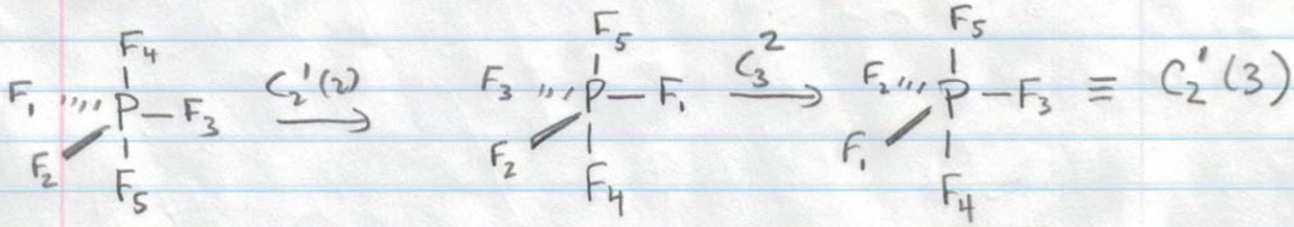
C734b 2008

Solutions : Problem Set #2

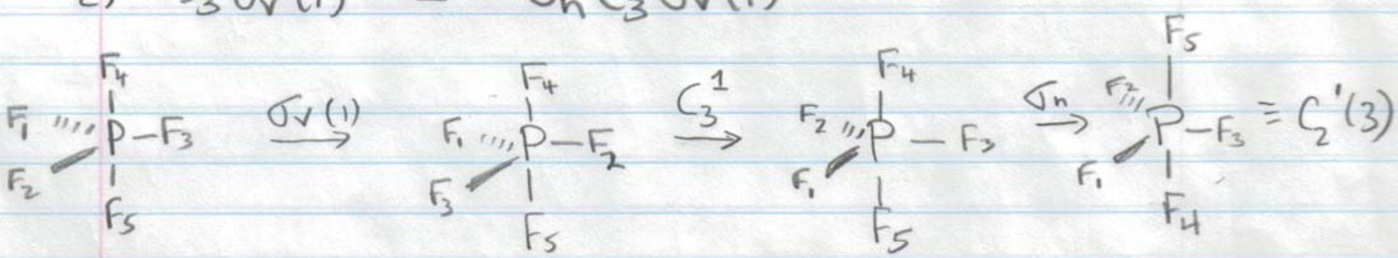
1. a) $C_2'(1)\,\sigma_h$.



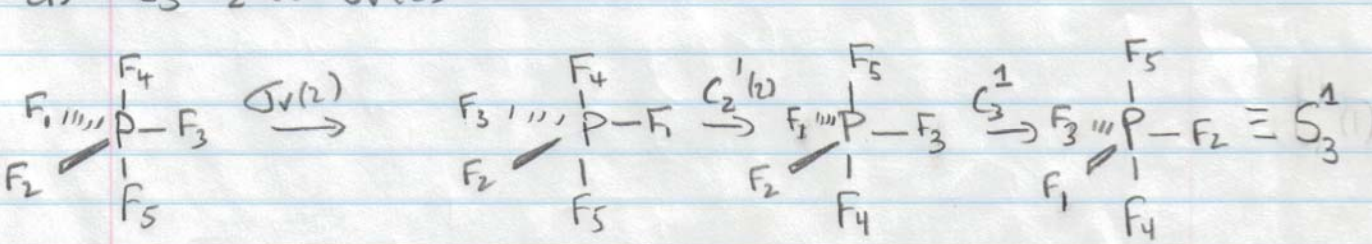
b) $C_3^2\,C_2'(2)$



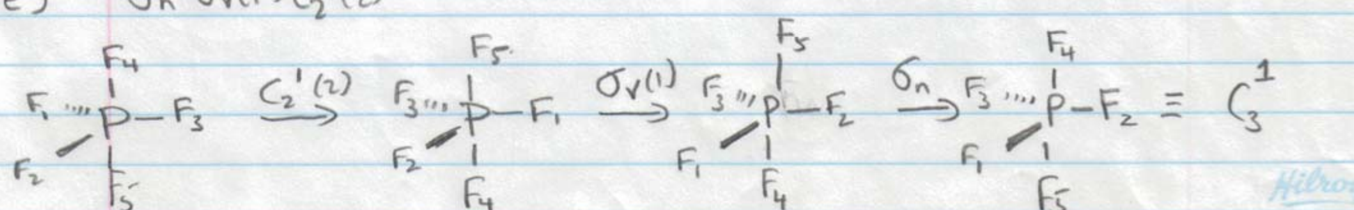
c) $S_3^1\,\sigma_v(1) \equiv \sigma_h\,C_3^1\,\sigma_v(1)$



d) $C_3^1\,C_2'(2)\,\sigma_v(2)$

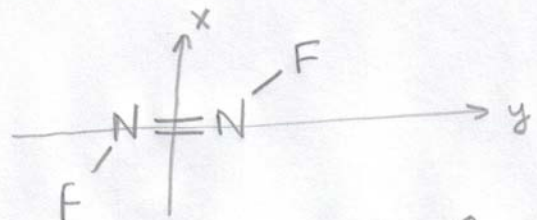


e) $\sigma_h\,\sigma_v(1)\,C_2'(2)$



1.

(2)

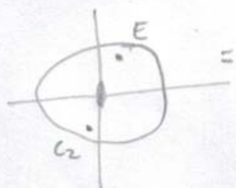
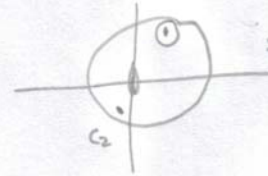


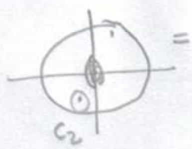
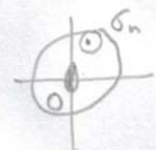
Symmetry operators : E (always), C_{2z} , i , σ_h

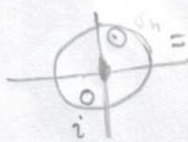
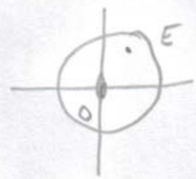
(C_{2h} point group).

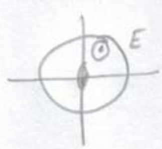
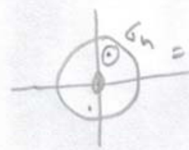
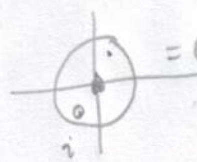
$E C_{2z} = C_{2z} E = C_{2z}$; $E i = i E = i$; $E \sigma_h = \sigma_h E = \sigma_h$.

$EE = E$

$C_{2z} C_{2z}$  $= E$; $i C_{2z}$  $= \sigma_h$

$\sigma_h C_{2z}$  $= i$; $C_{2z} \sigma_h$  $= i$

$C_{2z} i$  $= \sigma_h$; $i i$  $= E$

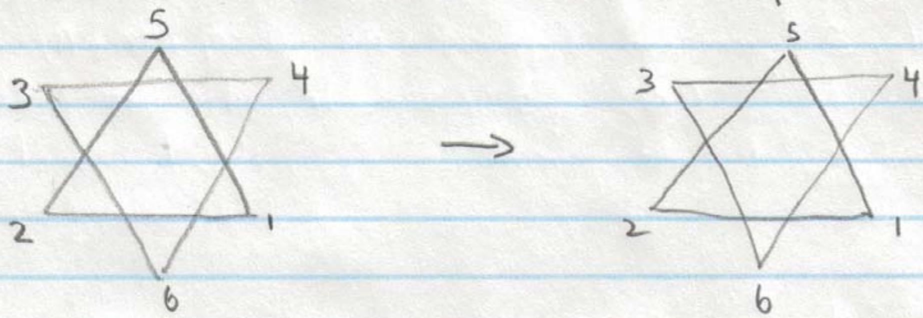
$\sigma_h \sigma_h$  $= E$; $i \sigma_h$  $= C_{2z}$; $\sigma_h i$  $= C_{2z}$

Table

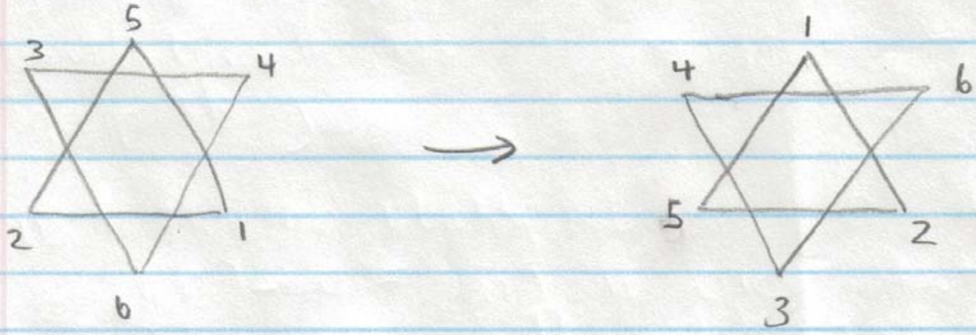
	E	C_{2z}	i	σ_h
E	E	C_{2z}	i	σ_h
C_{2z}	C_{2z}	E	σ_h	i
i	i	σ_h	E	C_{2z}
σ_h	σ_h	i	C_{2z}	E

(3) a) First consider what each operation does.

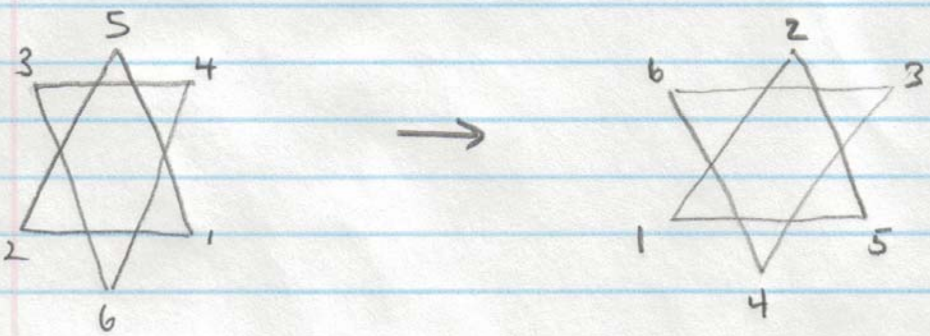
E



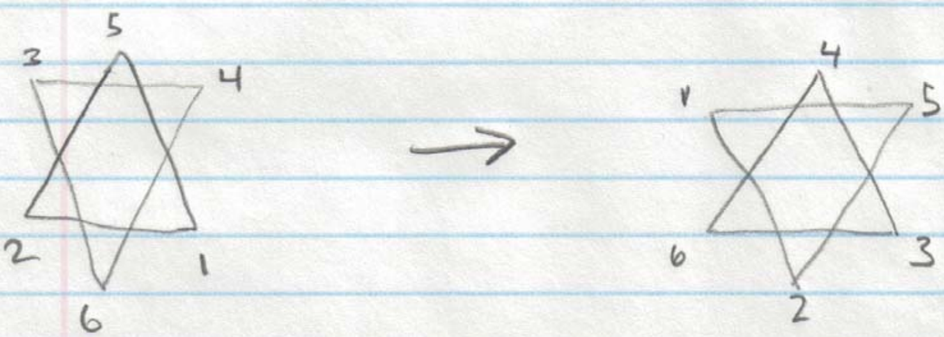
C_3



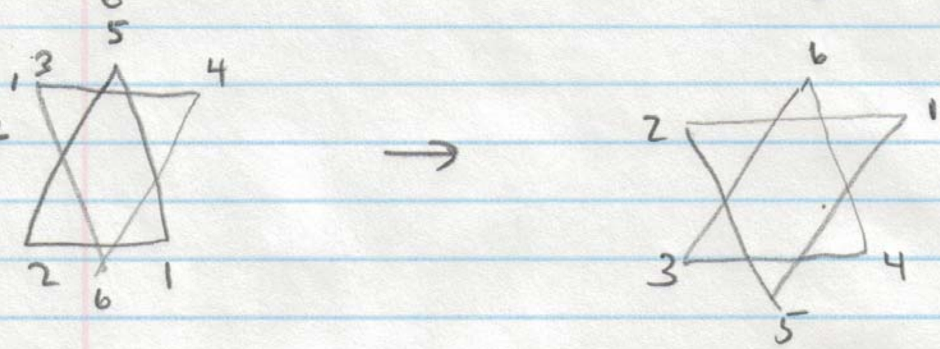
C_3^2

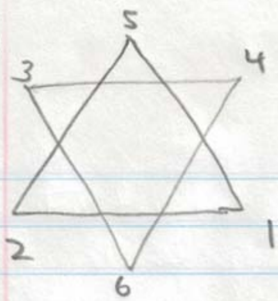
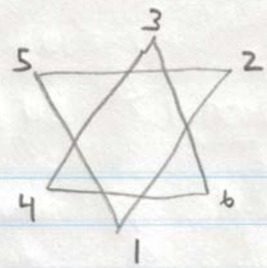


C_2



C_2'



C_2''  $\longrightarrow$ 

Products $= 36$

Clearly 1.) $EE = E$

2.) + 3.) $EC_3 = C_3E = C_3$

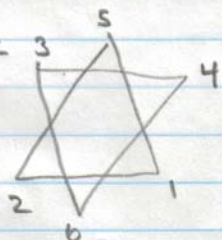
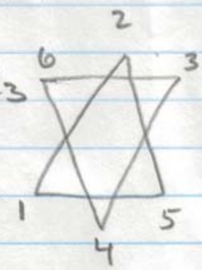
4.) + 5.) $EC_3^2 = C_3^2E = C_3^2$

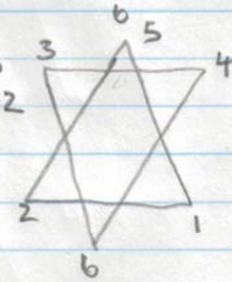
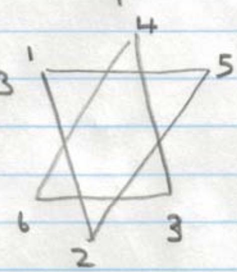
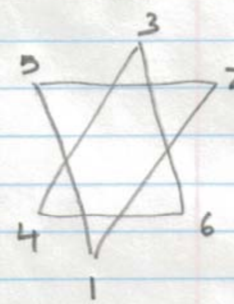
6.) + 7.) $EC_2 = C_2E = C_2$

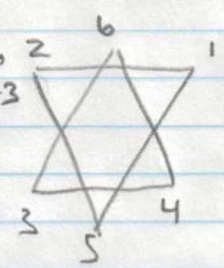
8.) + 9.) $EC_2' = C_2'E = C_2'$

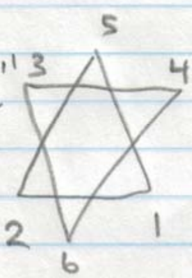
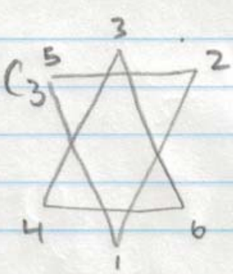
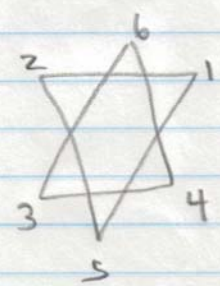
10.) + 11.) $EC_2'' = C_2''E = C_2''$

Consider additional products.

12) $C_3C_3^2$  $= C_3$  $=$  $\equiv E$

13) C_3C_2  $= C_3$  $=$  $= C_2''$

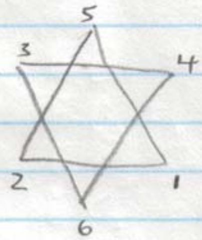
14) C_3C_2  $= C_3$  $=$  $= C_2$

15) C_3C_2''  $= C_3$  $=$  $= C_2'$

16) $C_3^2 C_3 = C_3^3 = E$

17.) $C_3^2 C_3^2 = C_3^4 = C_3$

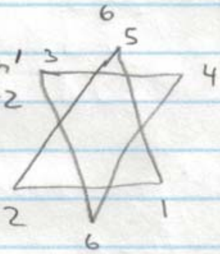
property of rotational group elements

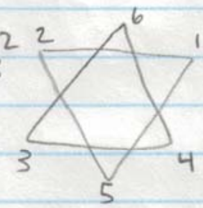
18.) $C_3^2 C_2$ 

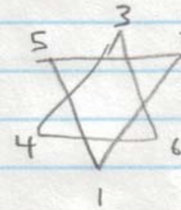
$= C_3^2$ 

$=$ 

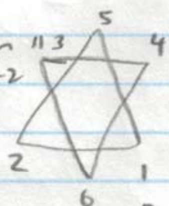
$= C_2'$

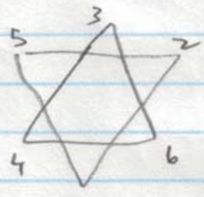
19.) $C_3^2 C_2'$ 

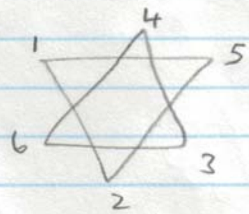
$= C_3^2$ 

$=$ 

$= C_2''$

20.) $C_3^2 C_2''$ 

$= C_3^2$ 

$=$ 

$= C_2$

21.) $C_2 C_3$ 

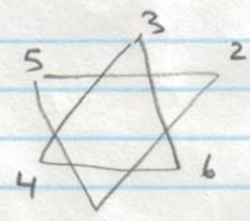
$= C_2$ 

$=$ 

$= C_2'$

22.) $C_2 C_3^2$ 

$= C_2$ 

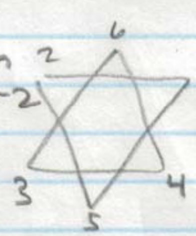
$=$ 

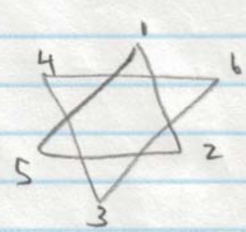
$= C_2''$

property of binary rotations

23.) $C_2 C_2 = E$ 24.) $C_2' C_2' = E$ 25.) $C_2'' C_2'' = E$

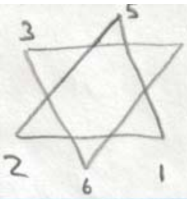
26) $C_2 C_2'$ 

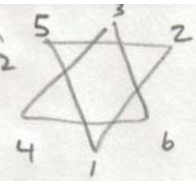
$= C_2$ 

$=$ 

$= C_3$

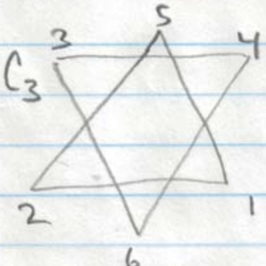
Hilroy

27) $C_2 C_2''$ 

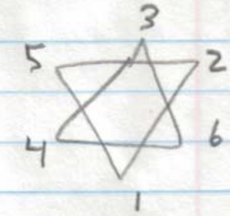
$= C_2$ 

$=$ 

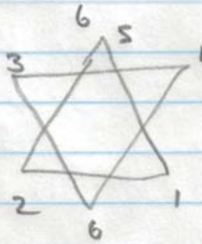
$= C_3^2$

28.) $C_2' C_3$ 

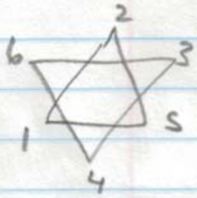
$= C_2'$ 

$=$ 

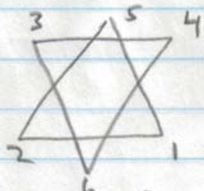
$= C_2''$

29.) $C_2' C_2$ 

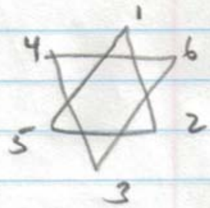
$= C_2'$ 

$=$ 

$= C_3^2$

30.) $C_2' C_2''$ 

$= C_2'$ 

$=$ 

$= C_3$

31.) $C_2' C_3^2$ 

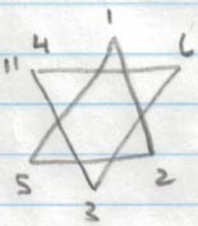
$= C_2'$ 

$=$ 

$= C_2$

32.) $C_3 C_3 = C_3^2$

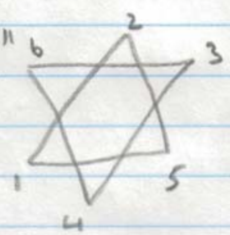
33.) $C_2'' C_3$ 

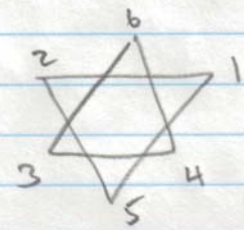
$= C_2''$ 

$=$ 

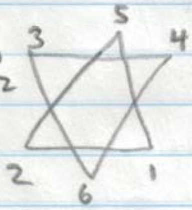
$= C_2$

34.) $C_2'' C_3^2$ 

$= C_2''$ 

$=$ 

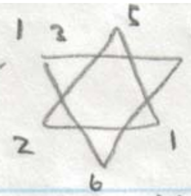
$= C_2'$

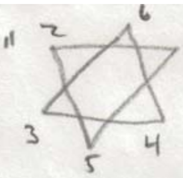
35.) $C_2'' C_2$ 

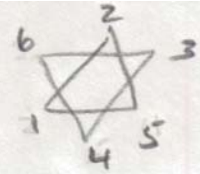
$= C_2''$ 

$=$ 

$= C_3$

36.) $C_2''C_2'$ 

$=$ C_2'' 

$=$ 

$= C_3^2$

Multiplication Table

	E	C_3	C_3^2	C_2	C_2'	C_2''
E	E	C_3	C_3^2	C_2	C_2'	C_2''
C_3	C_3	C_3^2	E	C_2'	C_2''	C_2
C_3^2	C_3^2	E	C_3	C_2''	C_2	C_2'
C_2	C_2	C_2''	C_2'	E	C_3^2	C_3
C_2'	C_2'	C_2	C_2''	C_3	E	C_3^2
C_2''	C_2''	C_2'	C_2	C_3^2	C_3	E

note: rearrangement theorem works (as it must).

b) First find inverses.

$$E^{-1} = E$$
$$C_3^{-1} = C_3^2$$
$$C_3^{-2} = C_3$$
$$C_2^{-1} = C_2$$
$$C_2'^{-1} = C_2'$$
$$C_2''^{-1} = C_2''$$

i) E is in its own class (always).

ii) $\underline{\underline{C_3}}$

$$E^{-1} C_3 E = E C_3 E = C_3$$
$$C_3^{-1} C_3 C_3 = C_3^2 C_3 C_3 = C_3^4 = C_3$$
$$C_3^{-2} C_3 C_3^2 = C_3 C_3^3 = C_3^4 = C_3$$
$$C_2^{-1} C_3 C_2 = C_2 C_3 C_2 = C_2 C_2'' = C_3^2$$
$$C_2'^{-1} C_3 C_2' = C_2' C_3 C_2' = C_2' C_2 = C_3^2$$
$$C_2''^{-1} C_3 C_2'' = C_2'' C_3 C_2'' = C_2'' C_2' = C_3^2$$

$\therefore \{C_3, C_3^2\}$ form a class.

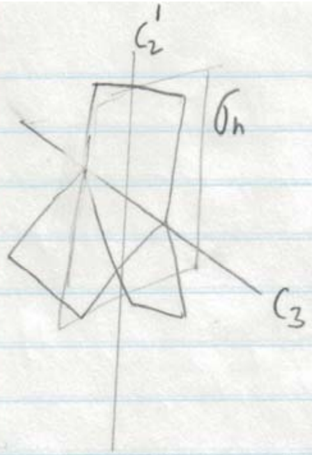
$\underline{\underline{C_2}}$

$$E^{-1} C_2 E = E C_2 E = C_2$$
$$C_3^{-1} C_2 C_3 = C_3^2 C_2 C_3 = C_3^2 C_2' = C_2''$$
$$C_3^{-2} C_2 C_3^2 = C_3 C_2 C_3^2 = C_3 C_2'' = C_2'$$
$$C_2^{-1} C_2 C_2 = C_2 C_2 C_2 = C_2 E = C_2$$
$$C_2'^{-1} C_2 C_2' = C_2' C_2 C_2' = C_2' C_3 = C_2''$$
$$C_2''^{-1} C_2 C_2'' = C_2'' C_2 C_2'' = C_2'' C_3^2 = C_2'$$

$\therefore \{C_2, C_2', C_2''\}$ form a class.

4

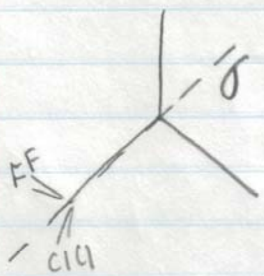
a)



C_3 axis but $\ngtr$ 1 C_3 axis
$3\,C_2'$ axes $\perp$ C_3, σ_h

$\Rightarrow$ D_{3h} point group

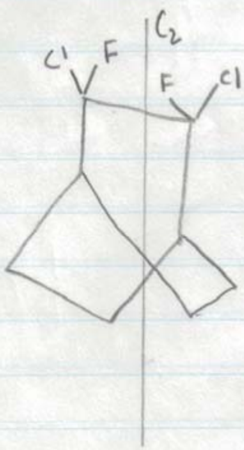
b) look down the "C_3" axis in example a)



no C_n axis save C_1, one plane, σ

$\Rightarrow$ C_s point group

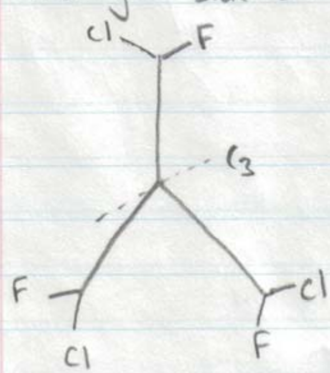
c)



one C_2 axis, but $\ngtr$ 1 C_3 axis
no C_2' axes $\perp$ C_2, no σ, no S_4 axis

$\Rightarrow$ C_2 point group

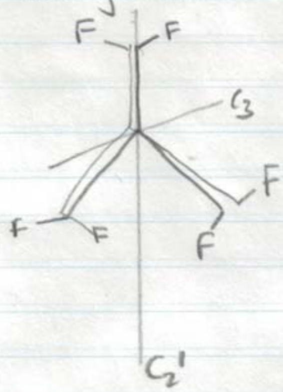
d) looking side-on.



one C_3 $\perp$ to plane of paper as drawn.
no C_2' axes $\perp$ C_3
no σ_h, or 3 σ_v's
no S_6

$\Rightarrow$ C_3 point group

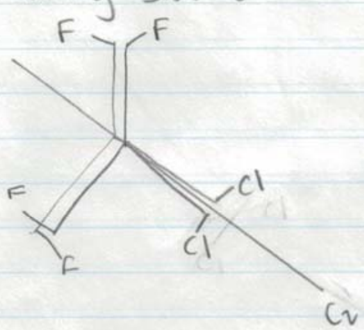
e) looking side-on



C_3 axis $\perp$ plane of paper as drawn
3 C_2' axes $\perp$ C_3
no σ_h, no σ_d

$\Rightarrow$ D_3 point group.

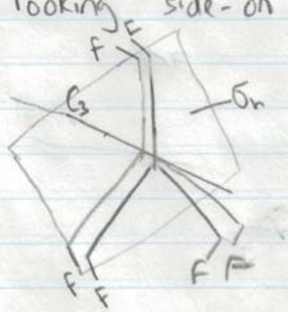
f) looking side-on



one C_2 axis indicated. no C_2' axes $\perp$ C_2 axis
no σ_h, σ_d, S_4 axis

$\Rightarrow$ C_2 point group.

g) looking side-on

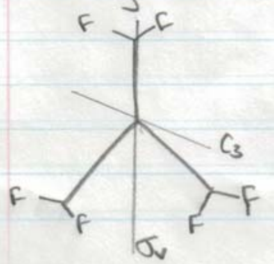


no C_3 axis $\perp$ plane of paper as shown
no C_2' axes $\perp$ C_3

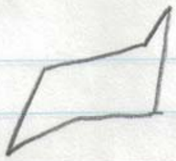
σ_h plane

$\Rightarrow$ C_s point group.

h). looking side-on



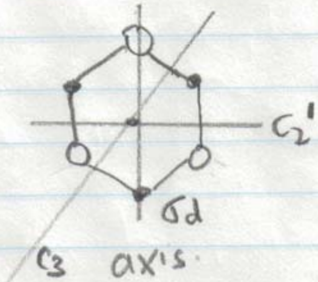
C_3 axis $\perp$ plane of paper as shown
no C_2' axes $\perp$ C_3
3 σ_v planes
$\Rightarrow$ C_{3v} point group.

i) 

looking down on plane of molecule.

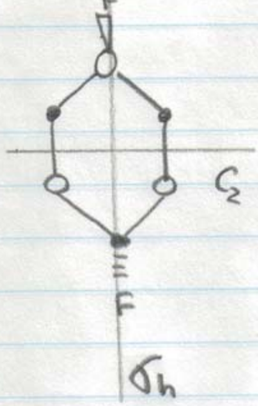
o ≡ below plane

• ≡ above plane.

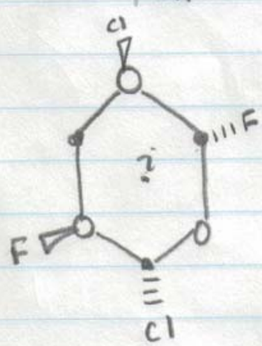


one C_3 axis.
3 C_2' axes $\perp$ C_3.
3 σ_d axes.

$\Rightarrow$ D_{3d} point group.

j) 

one C_2 axis., no C_2' axes $\perp$ C_2
one σ_h $\perp$ C_2
$\Rightarrow$ C_{2h} point group.

K) 

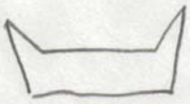
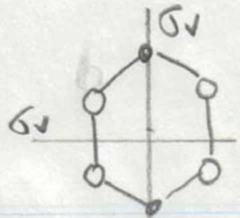
no C_n axis, n σ_h

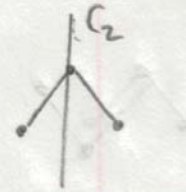
i exists $\Rightarrow$ C_i point group

l) 

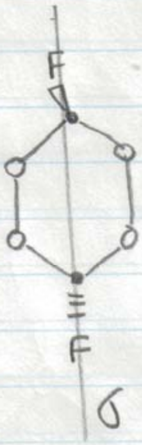
no C_n axis, one σ containing F and Cl groups

$\Rightarrow$ C_s point group

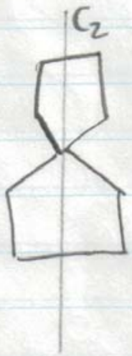
m)  $\equiv$ from top view 

; side view 

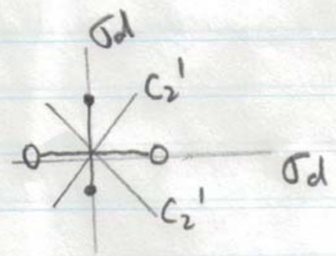
one C_2 axis , 2 σ_v planes , no $C_2{}'$ axis $\perp$ C_2
$\Rightarrow$ C_{2v} point group.

n) 

no C_n axis except C_1 ; one σ plane containing F's.
$\Rightarrow$ C_s point group.

o) 

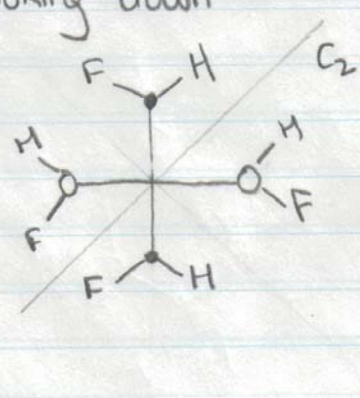
one C_2 axis.

looking down 

2 $C_2{}'$ axes $\perp$ C_2 axis
2 σ_d axes containing C_2

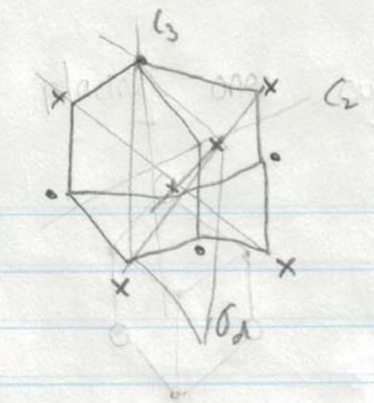
$\Rightarrow$ D_{2d} point group.

p). looking down

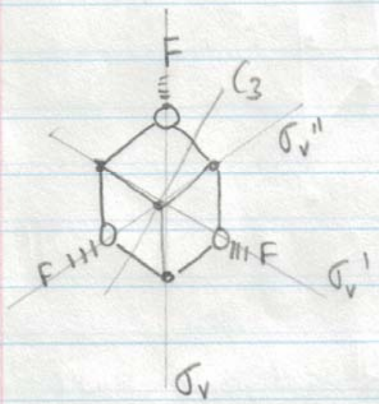


C_2 axis as shown
no $C_2{}'$ axes $\perp$ C_2
no σ's , no S_4 axes

$\Rightarrow$ C_2 point group.

q) 

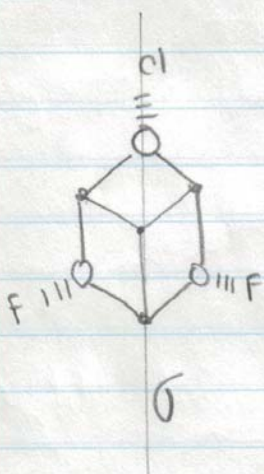
4 C_3 axes going through C's indicated by "•"
3 C_2 axes connecting "x" ⇒ 3 S_4 axes coincident
6 σ_d ⇒ T_d point group.

r) 

one C_3 axis ; no C_2' axes ⊥ C_3
3 σ_v planes containing C_3

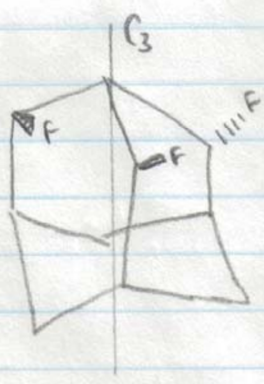
⇒ C_{3v} point group

O ≡ below plane
• ≡ above plane.

s) 

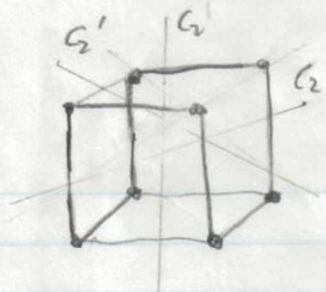
no C_n axis ; no C_2' axis
one σ-plane containing Cl atom

⇒ C_s point group

t) 

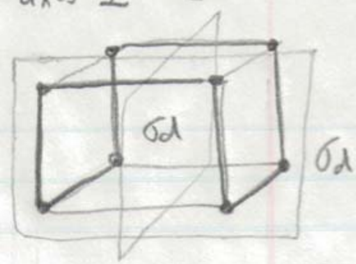
one C_3 axis ; no C_2' axes ⊥ C_3
no σ_h, no σ_v

⇒ C_3 point group.

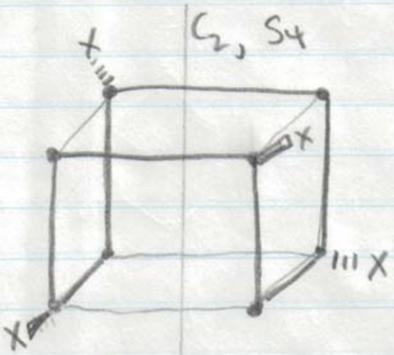
u) 

one C_2 axis, 2 C_2' axes $\perp$ C_2

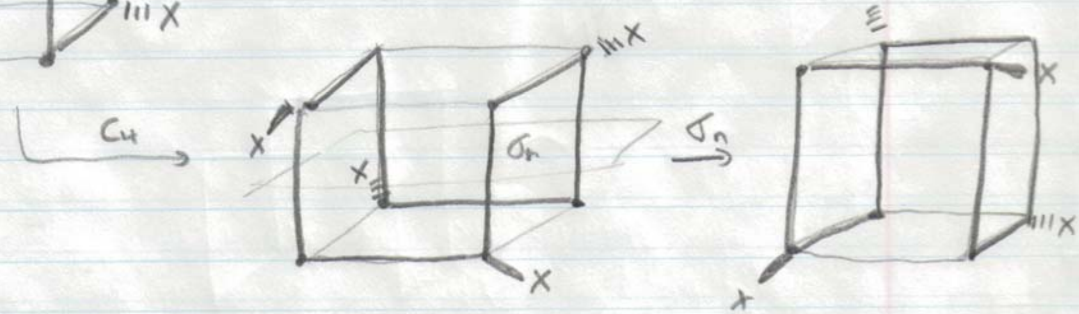
2 σ_d planes.

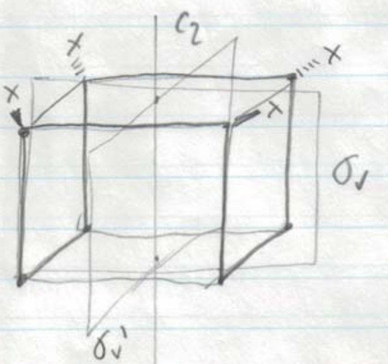


$\Rightarrow$ D_{2d} point group

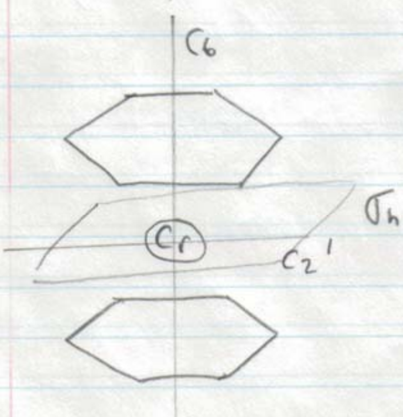
v) 

one C_2 axis, no C_2' axes $\perp$ C_2
one S_4 axis coincident with C_2
no σ $\Rightarrow$ S_4 point group.



w). 

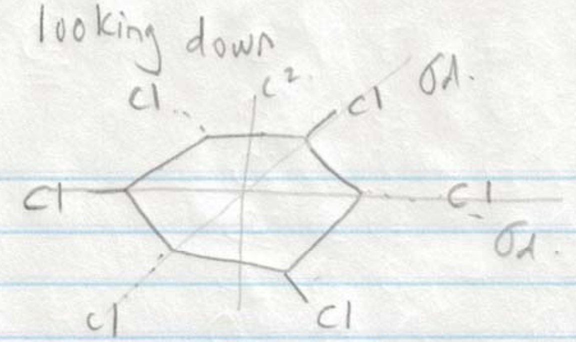
one C_2 axis, no C_2' axes $\perp$ C_2
2 σ_v containing C_2 $\Rightarrow$ C_{2v} point group

x) 

one C_6 axis, 6 C_2' axes $\perp$ C_6
σ_h $\perp$ C_6

$\Rightarrow$ D_{6h} point group.

y.) looking down

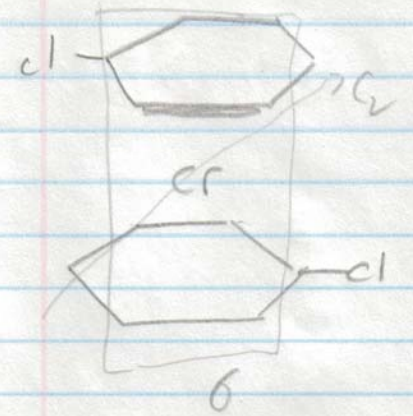


one C_3 axis $\perp$ plane of paper as drawn.

$3\,C_2'$ axes $\perp$ C_3

$3\sigma_d$, no σ_h

$\Rightarrow$ D_{3d} point group

z) 

one C_2 axis; no C_2' axes $\perp$ C_2

one σ containing Cl's

$\Rightarrow$ C_{2h} point group.

(5)

a) $$\tilde{A}+\tilde{B} = \begin{pmatrix} 1+1 & 2+0 & 3+1 \\ 2+3 & 1+(-1) & 23+(-2) \\ 4+2 & 3+3 & 2+2 \end{pmatrix} = \begin{pmatrix} 2 & 2 & 4 \\ 5 & 0 & 21 \\ 6 & 6 & 4 \end{pmatrix}$$

b) $$\tilde{A}-\tilde{B} = \begin{pmatrix} 1-1 & 2-0 & 3-1 \\ 2-3 & 1-(-1) & 23-(-2) \\ 4-2 & 3-3 & 2-2 \end{pmatrix} = \begin{pmatrix} 0 & 2 & 2 \\ -1 & 2 & 25 \\ 2 & 0 & 0 \end{pmatrix}$$

$$\tilde{A}\cdot\tilde{B} = \begin{pmatrix} (1)(1)+(3)(2)+(3)(2) & (1)(0)+(2)(-1)+(3)(3) & (1)(1)+(2)(-2)+(3)(2) \\ (2)(1)+(1)(3)+(23)(2) & (2)(0)+(1)(-1)+(23)(3) & (2)(1)+(1)(-2)+(23)(+2) \\ (4)(1)+(3)(3)+(2)(2) & (4)(0)+(3)(-1)+(2)(3) & (4)(1)+(3)(-2)+(2)(2) \end{pmatrix}$$

$$= \begin{pmatrix} 13 & 7 & 3 \\ 51 & 68 & 46 \\ 17 & 3 & 2 \end{pmatrix}$$

$$\tilde{B}\tilde{A} = \begin{pmatrix} 1 & 0 & 1 \\ 3 & -1 & -2 \\ 2 & 3 & 2 \end{pmatrix}\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 23 \\ 4 & 3 & 2 \end{pmatrix} = \begin{pmatrix} (1)(1)+0\cdot 2+1\cdot 4 & 1\cdot 2+0\cdot 1+1\cdot 3 & 1\cdot 3+0\cdot 23+1\cdot 2 \\ 3\cdot 1+-1\cdot 2+-2\cdot 4 & 3\cdot 2+-1\cdot 1+-2\cdot 3 & 3\cdot 3+-1\cdot 23+-2\cdot 2 \\ 2\cdot 1+3\cdot 2+2\cdot 4 & 2\cdot 2+3\cdot 1+2\cdot 3 & 2\cdot 3+3\cdot 23+2\cdot 2 \end{pmatrix}$$

$$= \begin{pmatrix} 5 & 5 & 5 \\ -7 & -1 & -18 \\ 16 & 13 & 71 \end{pmatrix} \neq \tilde{A}\tilde{B}.$$

b) $$(\tilde{A}\cdot B)^T = \begin{pmatrix} 13 & 51 & 17 \\ 7 & 68 & 3 \\ 3 & 46 & 2 \end{pmatrix} \text{ from part a)}$$

$$\tilde{B}^T\cdot\tilde{A}^T = \begin{pmatrix} 1 & 3 & 2 \\ 0 & -1 & 3 \\ 1 & -2 & 2 \end{pmatrix}\begin{pmatrix} 1 & 2 & 4 \\ 2 & 1 & 3 \\ 3 & 23 & 2 \end{pmatrix}$$

$$= \begin{pmatrix} 1\cdot 1+3\cdot 2+2\cdot 3 & 1\cdot 2+3\cdot 1+2\cdot 23 & 1\cdot 4+3\cdot 3+2\cdot 2 \\ 0\cdot 1-1\cdot 2+3\cdot 3 & 0\cdot 2+-1\cdot 1+3\cdot 23 & 0\cdot 4-1\cdot 3+3\cdot 2 \\ 1\cdot 1-2\cdot 2+2\cdot 3 & 1\cdot 2+-2\cdot 1+2\cdot 23 & 1\cdot 4-2\cdot 3+2\cdot 2 \end{pmatrix}$$

$$= \begin{pmatrix} 13 & 51 & 17 \\ 7 & 68 & 3 \\ 3 & 46 & 2 \end{pmatrix} = (\tilde{A}\cdot\tilde{B})^T.$$

c) $$\det(\tilde{A}) = (+1)\begin{vmatrix} 1 & 23 \\ 3 & 2 \end{vmatrix} - 2\begin{vmatrix} 2 & 23 \\ 4 & 2 \end{vmatrix} + 3\begin{vmatrix} 2 & 1 \\ 4 & 3 \end{vmatrix}$$

$$= (1)(2-69) - (2)(4-92) + (3)(6-4)$$

$$= -67 + 176 + 6 = 115.$$

$$\det(\tilde{B}) = (1)\begin{vmatrix} -1 & -2 \\ 3 & 2 \end{vmatrix} + (0)\begin{vmatrix} 3 & -2 \\ 2 & 2 \end{vmatrix} + (1)\begin{vmatrix} 3 & -1 \\ 2 & 3 \end{vmatrix}$$

$$= (1)(-2+6) + 0 + (1)(9+2) = 4 + 11 = 15$$

$$\det(\tilde{A}\tilde{B}) = (13)\begin{vmatrix} 68 & 46 \\ 3 & 2 \end{vmatrix} - (7)\begin{vmatrix} 51 & 46 \\ 17 & 2 \end{vmatrix} + (3)\begin{vmatrix} 51 & 68 \\ 17 & 3 \end{vmatrix}$$

$$= (13)(136 - 138) - (7)(102 - 782) + (3)(153 - 1156)$$

$$= -26 + 4760 - 3009 = \boxed{1725}$$

$$\det(\tilde{B}\tilde{A}) = (5)\begin{vmatrix} -1 & -18 \\ 13 & 79 \end{vmatrix} - (5)\begin{vmatrix} -7 & -18 \\ 16 & 79 \end{vmatrix} + (5)\begin{vmatrix} -7 & -1 \\ 16 & 13 \end{vmatrix}$$

$$(5)(-79 + 234) - (5)(-553 + 288) + (5)(-91 + 16)$$

$$= 775 + 1325 - 375 = \boxed{1725} = \det(\tilde{A}\tilde{B})$$

d) $\tilde{A} \otimes \tilde{B} =$

$$\begin{pmatrix} (1)\tilde{B} & (2)\tilde{B} & (3)\tilde{B} \\ (2)\tilde{B} & (1)\tilde{B} & (23)\tilde{B} \\ (4)\tilde{B} & (3)\tilde{B} & (2)\tilde{B} \end{pmatrix}$$

$$= \left(\begin{array}{ccc|ccc|ccc} 1 & 0 & 1 & 2 & 0 & 2 & 3 & 0 & 3 \\ 3 & -1 & -2 & 6 & -2 & -4 & 9 & -3 & -6 \\ 2 & 3 & 2 & 4 & 6 & 4 & 6 & 9 & 6 \\ \hline 2 & 0 & 2 & 1 & 0 & 1 & 23 & 0 & 23 \\ 6 & -2 & -4 & 3 & -1 & -2 & 69 & -23 & -46 \\ 4 & 6 & 4 & 2 & 3 & 2 & 46 & 69 & 46 \\ \hline 4 & 0 & 4 & 3 & 0 & 3 & 2 & 0 & 2 \\ 12 & -4 & -8 & 9 & -3 & -6 & 6 & -2 & -4 \\ 8 & 12 & 8 & 6 & 9 & 6 & 4 & 6 & 4 \end{array}\right)$$

6. Using diagrams C_3^2 operator takes $1 \to 3$, $2 \to 1$, $3 \to 2$

$$\therefore C_3^2 \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 3 \\ 1 \\ 2 \end{pmatrix}$$

E: "do nothing operator" $\Rightarrow E\begin{pmatrix}1\\2\\3\end{pmatrix}=\begin{pmatrix}1\\2\\3\end{pmatrix} \Rightarrow E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$

σ_v operator takes $1\to1$ (atom 1 in plane), $2\to3$, $3\to2$

$\therefore \sigma_v\begin{pmatrix}1\\2\\3\end{pmatrix}=\begin{pmatrix}1\\3\\2\end{pmatrix} \Rightarrow \sigma_v=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}$

σ_v' operator takes $1\to3$, $2\to2$ (atom 2 in plane), $3\to1$

$\therefore \sigma_v'\begin{pmatrix}1\\2\\3\end{pmatrix}=\begin{pmatrix}3\\2\\1\end{pmatrix} \Rightarrow \sigma_v'=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}$

σ_v'' takes $1\to2$, $2\to1$, $3\to3$ (atom 3 in plane)

$\therefore \sigma_v''\begin{pmatrix}1\\2\\3\end{pmatrix}=\begin{pmatrix}2\\1\\3\end{pmatrix} \Rightarrow \sigma_v''=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$.

C_3 already done in problem set handout.