CH 612 Advanced Inorganic Chemistry – Structure and Reactivity

Exam # 2 10/25/2010

***Print name:* ____________________________**

1. (25 points)

a) Given the set of operations C_4 , σ_h determine the other operations that must be present to form a complete point group.

If C_4 exists C_4^2 (= C_2), C_4^3 and C_4^4 (= E) also exist.

$C_4 \sigma_h = S_4$

$C_2 \sigma_h = S_2 = i$

$C_4^3 \sigma_h = S_4^3$

b) Identify the point group for the complete set of operations.

C_{4h} : E C_4 C_4^3 C_2 i S_4 S_4^3 σ_h

c) What is the order of the group?

$h = 8$

d) Name at least three possible sub-groups?

Possible subgroups have g = 4,2,1.

$g = 4$

C_4 {E, C_4 , C_4^3 , C_2}

S_4 {E, C_2 , S_4 , S_4^3}

C_{2h} {E, C_2 , i, σ_h}

$g = 2$

C_2 {E, C_2}

C_i {E, i}

C_s {E, σ_h}

$g = 1$

C_1 {E}

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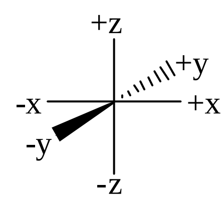
2. (25 points)

Complete the D_{2h} multiplication table below.
Verify that any **one** of its reflection operations does not belong to the same class as any other reflection.

D_{2h}	E	$C_{2(z)}$	$C_{2(y)}$	$C_{2(x)}$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
E	E	$C_{2(z)}$	$C_{2(y)}$	$C_{2(x)}$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
$C_{2(z)}$	$C_{2(z)}$	E	$C_{2(x)}$	$C_{2(y)}$	$\sigma_{(xy)}$	i	$\sigma_{(yz)}$	$\sigma_{(xz)}$
$C_{2(y)}$	$C_{2(y)}$	$C_{2(x)}$	E	$C_{2(z)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	i	$\sigma_{(xy)}$
$C_{2(x)}$	$C_{2(x)}$	$C_{2(y)}$	$C_{2(z)}$	E	$\sigma_{(yz)}$	$\sigma_{(xz)}$	$\sigma_{(xy)}$	i
i	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	E	$C_{2(z)}$	$C_{2(y)}$	$C_{2(x)}$
$\sigma_{(xy)}$	$\sigma_{(xy)}$	i	$\sigma_{(yz)}$	$\sigma_{(xz)}$	$C_{2(z)}$	E	$C_{2(x)}$	$C_{2(y)}$
$\sigma_{(xz)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	i	$\sigma_{(xy)}$	$C_{2(y)}$	$C_{2(x)}$	E	$C_{2(z)}$
$\sigma_{(yz)}$	$\sigma_{(yz)}$	$\sigma_{(xz)}$	$\sigma_{(xy)}$	i	$C_{2(x)}$	$C_{2(y)}$	$C_{2(z)}$	E

The multiplication table is efficiently completed by considering the operator matrices for each operation and how they transform the **x**, **y**, **z** vectors :



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

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

$$[C_{2(x)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\-y\\-z\end{bmatrix}$$

$$[\sigma_{(xy)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\y\\-z\end{bmatrix}$$

$$[C_{2(y)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-x\\y\\-z\end{bmatrix}$$

$$[\sigma_{(xz)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\-y\\z\end{bmatrix}$$

$$[C_{2(z)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-x\\-y\\z\end{bmatrix}$$

$$[\sigma_{(yz)}]\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-x\\y\\z\end{bmatrix}$$

The operator matrices can be summarized as the reducible representation Γ_m

D_{2h}	E	$C_{2(z)}$	$C_{2(y)}$	$C_{2(x)}$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_m	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}$	$\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$	$\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$

Multiplication of each operation *A* by the identity *E* results in the identical operation *A*, e.g.

$$[E][C_{2(x)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(x)}]$$

…etc.

Self binary combinations of each operation results in the identity operation E, e.g.

$$[\sigma_{(xy)}][\sigma_{(xy)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [E]$$

…etc.

The following binary combinations need then to be considered:

$$[C_{2(z)}]\,[C_{2(y)}] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(x)}]$$

$$[C_{2(z)}]\,[C_{2(x)}] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(y)}]$$

$$[C_{2(y)}][C_{2(x)}] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [C_{2(z)}]$$

$$[\sigma_{(xy)}]\,[\sigma_{(xz)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(x)}]$$

$$[\sigma_{(xy)}]\,[\sigma_{(yz)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(y)}]$$

$$[\sigma_{(xz)}]\,[\sigma_{(yz)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [C_{2(z)}]$$

$$[C_{2(z)}][i] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [\sigma_{(xy)}]$$

$$[C_{2(y)}][i] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [\sigma_{(xz)}]$$

$$[C_{2(x)}][i] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [\sigma_{(yz)}]$$

$$[\sigma_{(xy)}][i] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [C_{2(z)}]$$

$$[\sigma_{(xz)}][i] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(y)}]$$

$$[\sigma_{(yz)}][i] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [C_{2(x)}]$$

$$[\sigma_{(xy)}][C_{2(z)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = [i]$$

$$[\sigma_{(xz)}][C_{2(z)}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [\sigma_{(yz)}]$$

$$[\sigma_{(yz)}][C_{2(z)}] = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = [\sigma_{(xz)}]$$

Likewise

$[\sigma_{(xy)}][C_{2(y)}] = [\sigma_{(yz)}]$ $[\sigma_{(xy)}][C_{2(x)}] = [\sigma_{(xz)}]$

$[\sigma_{(xz)}][C_{2(y)}] = [i]$ $[\sigma_{(xz)}][C_{2(x)}] = [\sigma_{(xy)}]$

$[\sigma_{(yz)}][C_{2(y)}] = [\sigma_{(xz)}]$ $[\sigma_{(yz)}][C_{2(x)}] = [i]$

As the point group D_{2h} is an Abelian group all of the above combinations *commute* allowing us to easily fill the remaining of the multiplication table.

To verify that $\sigma_{(xy)}$ does not belong to the same class of $\sigma_{(xz)}$ or $\sigma_{(yz)}$ it similarity transforms must be derived using all of the symmetry operations of D_{2h}

$E\,\sigma_{(xy)}\,E = E\,\sigma_{(xy)} = \sigma_{(xy)}$

$C_{2(z)}\,\sigma_{(xy)}\,C_{2(z)} = C_{2(z)}\,i = \sigma_{(xy)}$

$C_{2(y)}\,\sigma_{(xy)}\,C_{2(y)} = C_{2(y)}\,\sigma_{(yz)} = \sigma_{(xy)}$

$C_{2(x)}\,\sigma_{(xy)}\,C_{2(x)} = C_{2(x)}\,\sigma_{(xz)} = \sigma_{(xy)}$

$i\,\sigma_{(xy)}\,i = i\,C_{2(z)} = \sigma_{(xy)}$

$\sigma_{(xy)}\,\sigma_{(xy)}\,\sigma_{(xy)} = \sigma_{(xy)}\,E = \sigma_{(xy)}$

$\sigma_{(xz)}\,\sigma_{(xy)}\,\sigma_{(xz)} = \sigma_{(xz)}\,C_{2(x)} = \sigma_{(xy)}$

$\sigma_{(yz)}\,\sigma_{(xy)}\,\sigma_{(yz)} = \sigma_{(yz)}\,C_{2(y)} = \sigma_{(xy)}$

Thus, there are no other operations in the same class as $\sigma_{(xy)}$.

3. (20 points)

Predict the representative character for the following combination of Mulliken symbols and symmetry class for the given point groups.

	point group	*Mulliken symbol*	*class*	*character*
(a)	D_{5d}	A_{2g}	i	1
(b)	C_8	B	C_8	-1
(c)	D_2	B_2	$C_{2(x)}$	-1
(d)	C_{6v}	A_2	σ_v	-1
(e)	D_{3h}	A_2'	σ_h	1
(f)	C_{6v}	E_2	C_3	-1
(g)	C_{6v}	E_2	E	2
(h)	C_{5h}	A''	σ_h	-1

4. (20 points)

Reduce the following representation into its component irreducible representations:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_c	5	2	1	3	0	3

Using the following formula we can carry out a systematic reduction to determine how many times (*n*) each irreducible representation contributes to the reducible representation.

$$n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Σ	Σ/h	$h = 12$
Γ_r	5	2	1	3	0	3			
A_1'	5	4	3	3	0	9	24	2	
A_2'	5	4	-3	3	0	-9	0	0	
E'	10	-4	0	6	0	0	24	2	
A_1''	5	4	3	-3	0	-9	0	0	
A_2''	5	4	-3	-3	0	9	12	1	
E''	10	-4	0	-6	0	0	0	0	

Thus, the reducible representation Γ_r is composed of the following irreducible components:

$$\Gamma_r = 2\,A_1' + E' + A_2''$$

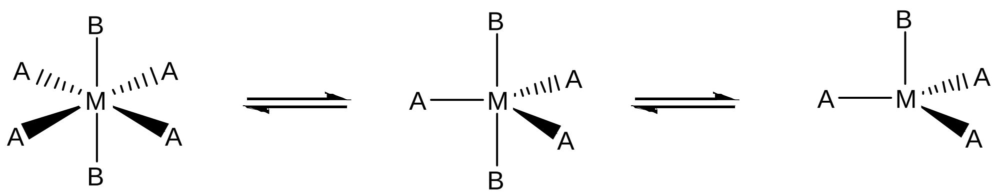
To check our answer the dimension of Γ_r must be calculated.

$$d_r = (2)(1) + (1)(2) + (1)(1) = 5$$

i.e., $d_r = 5$ which is the dimension of its character for the identity operation in Γ_r.

5. (30 points)

Consider the following sequential structural changes (I → II → III).



Indicate

a) The point group of each structure.

$$D_{4h} \rightleftharpoons D_{3h} \rightleftharpoons C_{3v}$$

b) Whether structures I and II of each series bear any group-subgroup relationship to each other.

D_{4h} and D_{3h} bear no group-subgroup relationship to each other.

c) Whether structures II and III of each series bear any group-subgroup relationship to each other.

C_{3v} is a subgroup of D_{3h}.

d) Whether each transition represents an *ascent* or *descent* in symmetry.

$$\underset{(h = 16)}{D_{4h}} \underset{\text{ascent}}{\overset{\text{descent}}{\rightleftharpoons}} \underset{(h = 12)}{D_{3h}} \underset{\text{ascent}}{\overset{\text{descent}}{\rightleftharpoons}} \underset{(h = 6)}{C_{3v}}$$

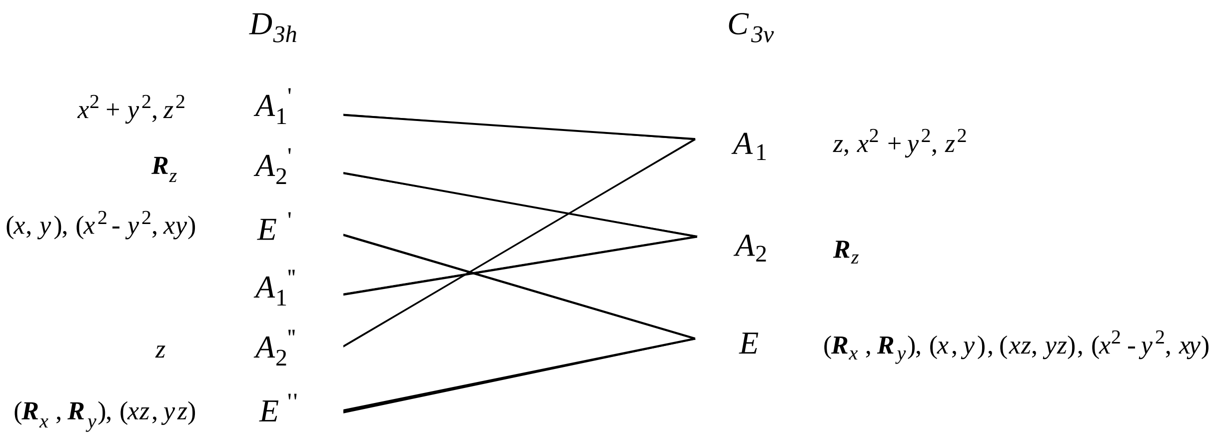
e) Specific symmetry elements lost *or* gained following the transition from II → III.

$$\underset{(h = 12)}{D_{3h}} \underset{\text{gained}}{\overset{\text{lost}}{\rightleftharpoons}} \underset{(h = 6)}{C_{3v}}$$

$$D_{3h} \quad E,\ C_3,\ C_3^2,\ \boxed{3C_2',\ S_3,\ S_3^2,}\ 3\sigma_v,\ \boxed{\sigma_h}$$

$$C_{3v} \quad E,\ C_3,\ C_3^2,\ \qquad\qquad\qquad\qquad 3\sigma_v$$

f) Construct a correlation table(s) for any group-subgroup pair present.



As the A_1'' representation in D_{3h} has no direct products associated with it, its correlating representation in C_{3v} must be identified using the characters of from each character table and their group-subgroup relationship.

	D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$	C_{3v}	
$x^2 + y^2, z^2$	A_1'	1	1	1	1	1	1	A_1	$z, x^2 + y^2, z^2$
$\boldsymbol{R}_z$	A_2'	1	1	-1	1	1	-1	A_2	$\boldsymbol{R}_z$
$(x, y), (x^2 - y^2, xy)$	E'	2	-1	0	2	-1	0	E	$(\boldsymbol{R}_x, \boldsymbol{R}_y), (x, y), (xz, yz), (x^2 - y^2, xy)$
	A_1''	1	1	1	-1	-1	-1	A_2	$\boldsymbol{R}_z$
z	A_2''	1	1	-1	-1	-1	1	A_1	$z, x^2 + y^2, z^2$
$(\boldsymbol{R}_x, \boldsymbol{R}_y), (xz, yz)$	E''	2	-1	0	-2	1	0	E	$(\boldsymbol{R}_x, \boldsymbol{R}_y), (x, y), (xz, yz), (x^2 - y^2, xy)$