P.G. Sem. II[nd] Core course – VI Unit – III
Inorg. chem.

Point Groups and Character Table

Symmetry operations and matrices :-
In which we will see how the symm. operations change the co-ordinates of a molecule and what is the effect of combining two or more symmetry operations.

Let us consider the effect of the operations on the co-ordinates of a C_{2v} molecule H_2O.

On performing E operation x, y and z remain unchanged.

$$x \xrightarrow{\quad E \quad} x$$
$$y \xrightarrow{\quad E \quad} y$$
$$z \xrightarrow{\quad E \quad} z$$

On performing C_2, σ_{xz} and σ_{yz} operation following effects will arise —

$$\begin{matrix} x \\ y \\ z \end{matrix} \xrightarrow{C_2} \begin{matrix} -x \\ -y \\ z \end{matrix} \qquad \begin{matrix} x \\ y \\ z \end{matrix} \xrightarrow{\sigma_{xz}} \begin{matrix} +x \\ -y \\ z \end{matrix} \qquad \begin{matrix} x \\ y \\ z \end{matrix} \xrightarrow{\sigma_{yz}} \begin{matrix} -x \\ y \\ z \end{matrix}$$

Combination of two operations can be shown as following -

$$\begin{matrix} x \\ y \\ z \end{matrix} \xrightarrow{C_2} \begin{matrix} -x \\ -y \\ z \end{matrix} \xrightarrow{\quad \sigma_{xz} \quad} \begin{matrix} -x \\ y \\ z \end{matrix}$$

Another way of representing the operation is in the form of matrices.

Matrix → Matrix is combination of numbers, arranged in a rectangular array, and combined with another matrix with the certain general rule. A general representation of the matrix will be as follows: with n number of columns and m number of rows.

$$
\begin{array}{c|c}
 & \begin{array}{ccccc} \text{1st column} & \text{2nd ,,} & \text{3rd} & & \end{array} \\
\begin{array}{c} \text{1st row} \\ \text{2nd ,,} \\ \text{3rd ,,} \\ \text{4th ,,} \\ \\ \end{array} &
\begin{bmatrix}
a_{11} & a_{12} & a_{13} & a_{14} & \cdots & a_{1n} \\
a_{21} & a_{22} & a_{23} & a_{24} & & a_{2n} \\
a_{31} & a_{32} & a_{33} & a_{34} & & a_{3n} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
a_{m1} & a_{m2} & a_{m3} & a_{m4} & & a_{mn}
\end{bmatrix}
\end{array}
$$

$m \times n$ matrix

m - row

n - column

Square Matrix → If the number of row (m) is equal to the number of column (n), matrix is called Square matrix.

Representation of elements in the matrix →

An elemented a_{ij}, ~~represent~~ belongs to ith row and jth column.

a_{ij}: i → row, j → column $\qquad$ a_{23}: 2 → row, 3 → column

Digonal matrix → The elements which have $i = j$ are situated on the digonal ~~matrix~~ of the matrix and are called digonal matrix. For example a_{11}, a_{22}, a_{33} are digonal elements.

Unit matrix → The matrices in which ~~all~~ ~~eleme~~ digonal elements are 1 and other elements are zero, are called, unit matrices. For example

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\quad 3 \times 3
$$

Unit matrix

~~Sometimes~~ Some matrix have only one ~~row~~ column ~~and~~ or only one ~~column~~ row. These are called only single column or single row matrices. The vectors are ~~represente~~ normally represented as single column matrices and here single column matrices are called vector matrix.

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The combination (multiplication) of two matrices is carried out in the following way →

$$\begin{bmatrix} 2 & 1 \\ 0 & 3 \end{bmatrix} \times \begin{bmatrix} 4 & 2 \\ 3 & 1 \end{bmatrix} = \begin{bmatrix} 2\times4+1\times3 & 2\times2+1\times1 \\ 0\times4+3\times3 & 0\times2+3\times1 \end{bmatrix}$$

$$= \begin{bmatrix} 11 & 5 \\ 9 & 3 \end{bmatrix}$$

(Combination of matrices are possible only if the number of row in one are equal to number of column in another.)

Representation of Symm. operations in the matrix form →

⟹ . Symm. ~~operations~~ operations can be represented as matrices in the following way.

$$\begin{bmatrix} & & \\ & E & \\ & & \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \quad \begin{bmatrix} & & \\ & C_2 & \\ & & \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}.$$

↳ oper ↳ column matrix

combination of the single column matrix with E leaves it ~~ch~~ unchanged. Hence the matrix representation of E must be

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Combination can be shown as follows —

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} (x\times1)+(y\times0)+(z\times0) \\ (x\times0)+(y\times1)+(z\times0) \\ (x\times0)+(y\times0)+(z\times0) \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Matrix representation of other operations can be similarly worked out.

$$[C_2]\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix} \quad \text{hence} \quad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Similarly —

$$\sigma_{vxz}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix} \text{ hence } C_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{and } \sigma_{vyz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{bmatrix}.$$

Character → The summation of the digonal elements of matrix is called its charater. Thus character of the matrices of the different operations in C_{2v} point symmetry are.

E	C_2	σ_{vxz}	σ_{vyz}	← operations
3	−1	1	1	Character

combination of two operations can be shown as the combinatio of their matrices →

$$C_2 \times \sigma_{vxz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

i.e. σ_{vyz}.

combination of different matrices can be shown in the form of ~~ta~~ table →

Table

	E	C_2	σ_{vxz}	σ_{vyz}
E	E	C_2	σ_{vxz}	σ_{vyz}
C_2	C_2	E	σ_{vyz}	σ_{vxz}
σ_{vxz}	σ_{vxz}	σ_{vyz}	E	C_2
σ_{vyz}	σ_{vyz}	σ_{vxz}	C_2	E

The symm operations can be considered as elements. The ~~a~~ molecule can be considered to be a set of elements