

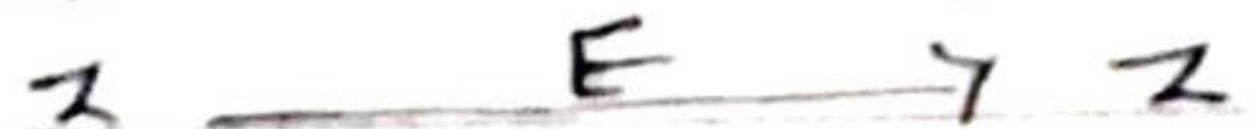
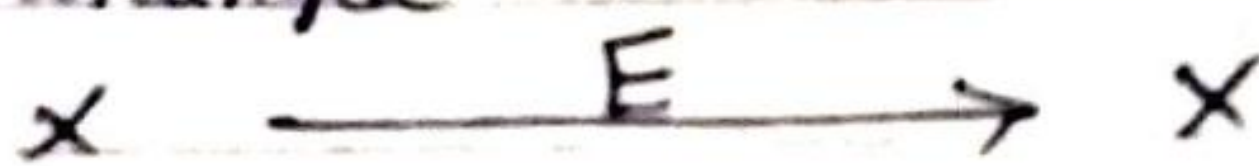
## Point Groups and Character Table

Symmetry operations and matrices :-

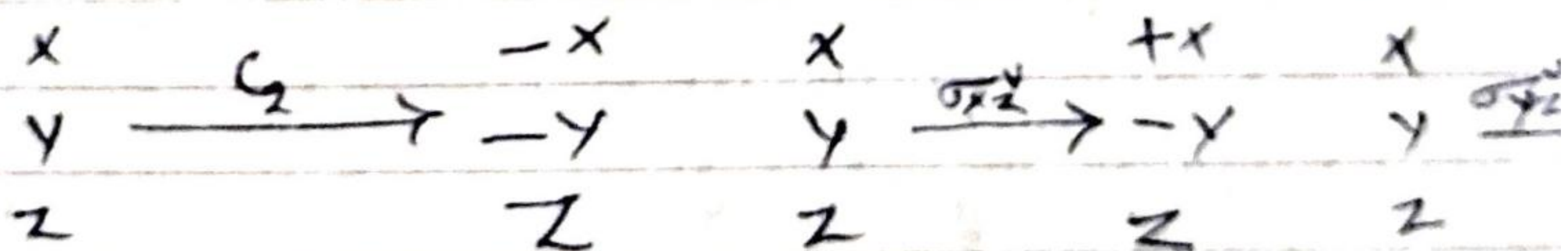
in which we will see how the symmetry operations change the co-ordinates of a molecule and to the effect of combining two or more symmetry operations.

Let us consider the effect of the operation on the co-ordinates of a  $\text{C}_{2v}$  molecule  $\text{H}_2\text{O}$ .

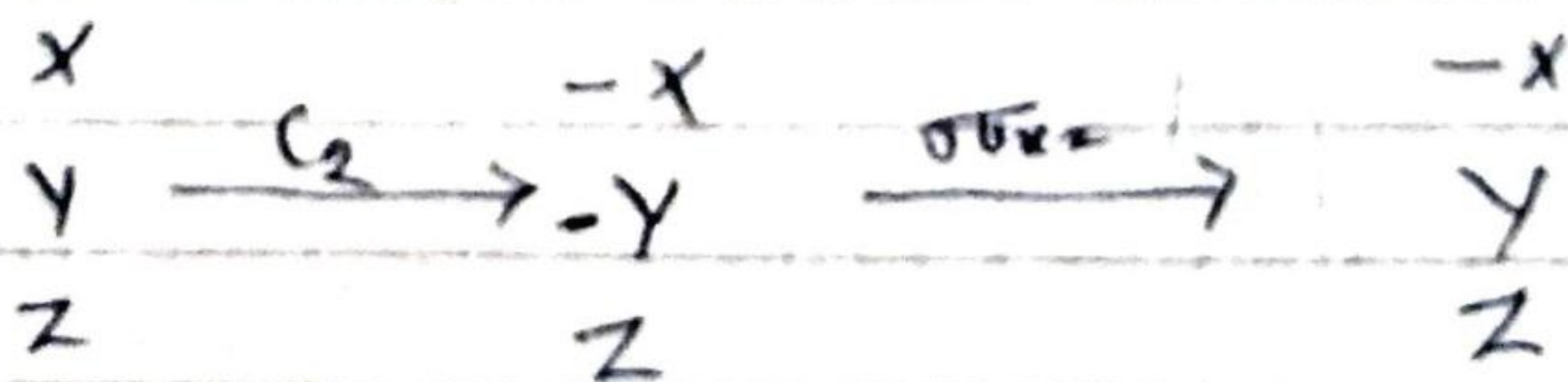
On performing E operation x, y and z are unchanged.



On performing  $C_2$ ,  $\sigma_{xz}$  and  $\sigma_{yz}$  operation following effects will arise -



Combination of two operations can be as following -



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

representation of the matrix will be as follows

with  $n$  number of columns and  $m$  number of rows.

$$\begin{array}{l} \text{1st row} \\ \text{2nd } \\ \text{3rd } \\ \text{4th } \end{array} \left[ \begin{array}{cccccc} a_{11} & a_{12} & a_{13} & a_{14} & \dots & a_{1n} \\ a_{21} & a_{22} & a_{23} & a_{24} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33} & a_{34} & \dots & a_{3n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ a_{m1} & a_{m2} & a_{m3} & a_{m4} & \dots & a_{mn} \end{array} \right] \begin{array}{l} m \times n \text{ matrix} \\ m - \text{row} \\ n - \text{column} \end{array}$$

Square matrix  $\rightarrow$  If the number of row ( $m$ ) is equal to the number of column ( $n$ ) a matrix is called Square matrix.

Representation of elements in the matrix  $\rightarrow$   
An element  $a_{ij}$ , represents belongs to  $i$ th row and  $j$ th column.

$$\begin{array}{c} a_{ij} \\ \swarrow \quad \searrow \\ \text{row} \quad \text{column} \end{array} \qquad \begin{array}{c} a_{23} \\ \downarrow \quad \searrow \\ \text{row} \quad \text{column} \end{array}$$

Diagonal matrix  $\rightarrow$  The elements which have  $i=j$  are situated on the diagonal of the matrix and are called diagonal matrix. For example  $a_{11}, a_{22}, a_{33}$  are diagonal elements.

Unit matrix  $\rightarrow$  The matrices in which all diagonal elements are 1 and other elements are zero, are called, unit matrices. For example

$$\left[ \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right] \begin{array}{l} 3 \times 3 \\ \text{Unit matrix} \end{array}$$

Sometimes Some matrix have only one <sup>column</sup> ~~row~~ or only one ~~column~~ <sup>row</sup>. These are called only single column or single row matrices. The vectors are normally represented as single column matrices and hence single column matrices are called vector matrix.

The combination (multiplication) of two matrices is carried out in the following way  $\rightarrow$

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

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

(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

$\rightarrow$  Symm. operations can be represented as matrix in the following way.

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

combination of the single column matrix with E leaves it 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 —

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

Matrix representation of other operations can be similarly worked out.

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

Similarly -

$$\sigma_{yz} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix} \quad \text{Hence } \sigma_{yz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{and } \sigma_{xz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{bmatrix}$$

**Character**  $\rightarrow$  The summation of the diagonal elements of matrix is called its character. Thus character of the matrices of the different operations in  $C_{2v}$  point symmetry are.

Operations	Character
E	3
$C_2$	-1
$\sigma_{yz}$	1
$\sigma_{xz}$	1

Combination of two operations can be shown as the combination of their matrices  $\rightarrow$

$$C_2 \times \sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{i.e. } \sigma_{xz}$$

Combination of different matrices can be shown in the form of a table  $\rightarrow$

Table

	E	$C_2$	$\sigma_{yz}$	$\sigma_{xz}$
E	E	$C_2$	$\sigma_{yz}$	$\sigma_{xz}$
$C_2$	$C_2$	E	$\sigma_{xz}$	$\sigma_{yz}$
$\sigma_{yz}$	$\sigma_{yz}$	$\sigma_{xz}$	E	$C_2$
$\sigma_{xz}$	$\sigma_{xz}$	$\sigma_{yz}$	$C_2$	E

The symmetry operations can be considered as elements. Thus molecule can be considered to be a set of elements.