CHAPTER-4

GROUP & ITS PROPERTIES

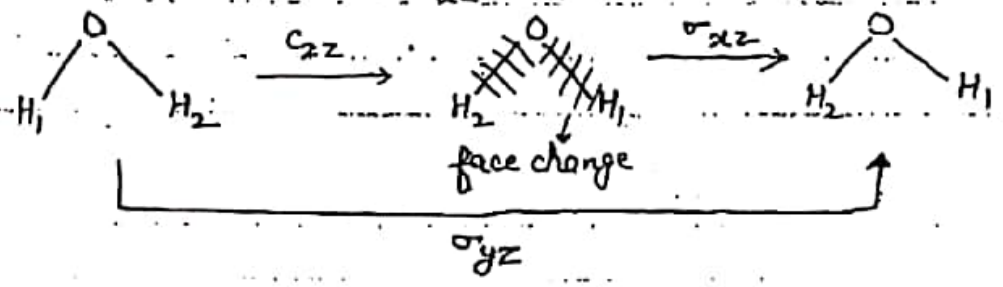
Collection of elements of symmetry is defined as Group

⇒ General Properties of Group:

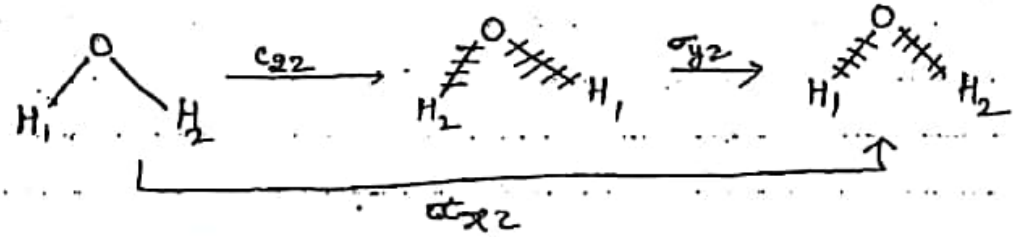
Property: The multiplication of effect of two elements in a group and square of any element in a group will be equal to effect of member of same group.

For example: H_2O

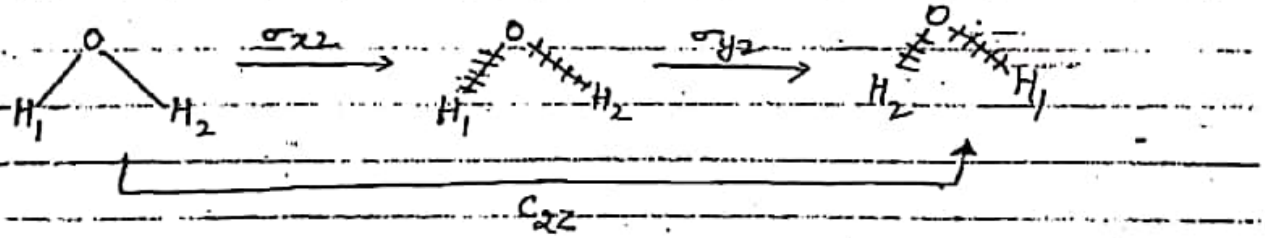
① $C_{2z} \cdot \sigma_{xz} =$



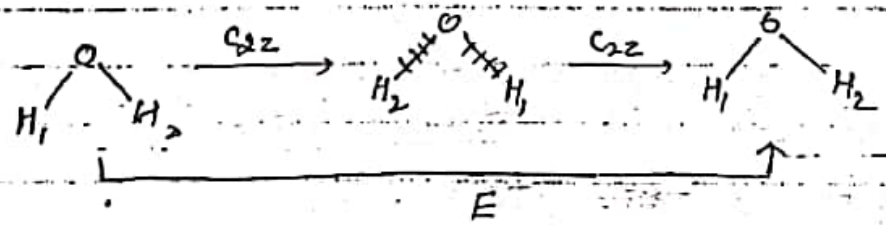
② $C_{2z} \cdot \sigma_{yz} =$

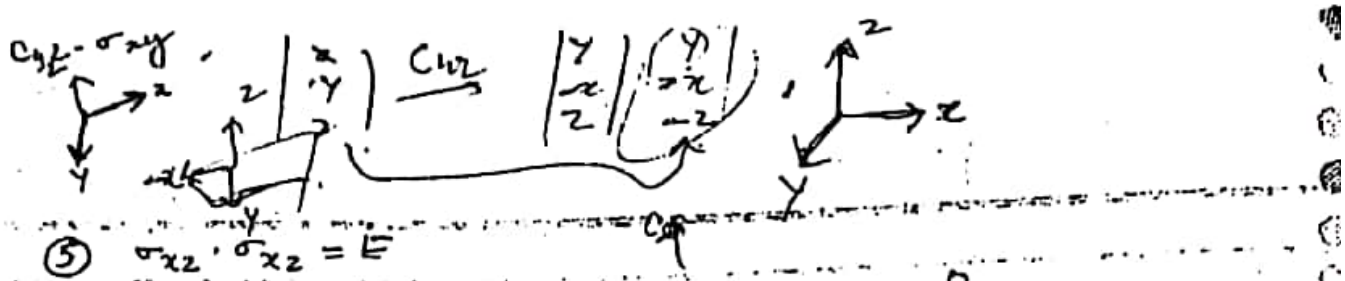


③ $\sigma_{xz} \cdot \sigma_{yz}$

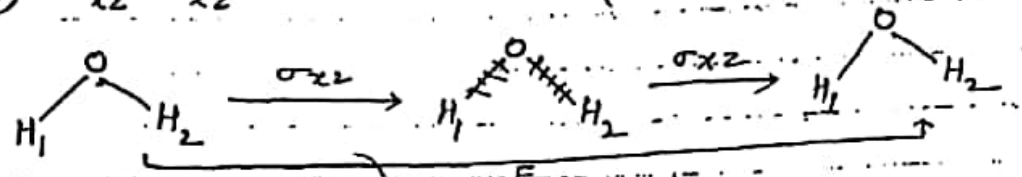


④ $C_{2z} \cdot C_{2z}$





⑤ $\sigma_{xz} \cdot \sigma_{xz} = E$



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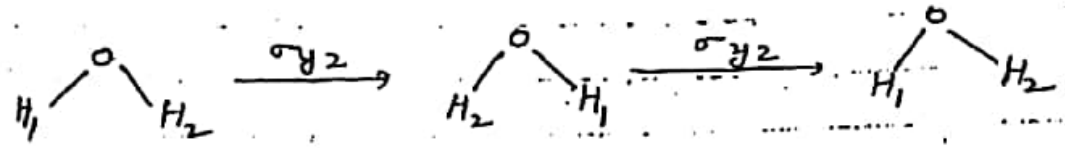


~~Proof~~

(2) Every element must have its reciprocal i.e. called inverse of that element and product of element with its inverse will be equal identity.

(a) Inverse of axis :-

$$C_b^a \longrightarrow C_b^{b-a}$$
$$(A) \qquad (A^{-1})$$

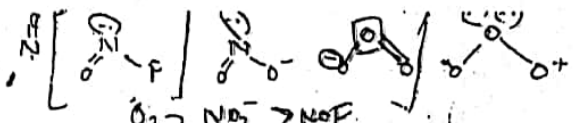
For example,

$$C_3^2 \rightarrow C_3^{3-2} = C_3^1$$
$$C_2^1 \rightarrow C_2^{2-1} = C_2^1$$
$$C_4^3 \rightarrow C_4^{4-3} = C_4^1$$
$$C_7^5 \rightarrow C_7^{7-5} = C_7^2$$

imp.

(b) Inverse of Improper axis :- S_b^a

Inverse	a	b	
S_b^{b-a}	even	even	e.g. $S_4^2 = S_4^{4-2} = S_4^2$
S_b^{b-a}	odd	even	e.g. $S_2^1 = S_2^{2-1} = S_2^1$
C_b^{b-a}	even	odd	e.g. $S_7^4 = S_8^{7-4} = C_8^3$
S_b^{2b-a}	odd	odd	e.g. $S_7^3 = S_7^{14-3} = S_7^{11}$



$O_3 > NO_2^- > NOF$

3. In every group, there is one element which commute with all other elements leaving them unchanged i.e. Identity Element (E).

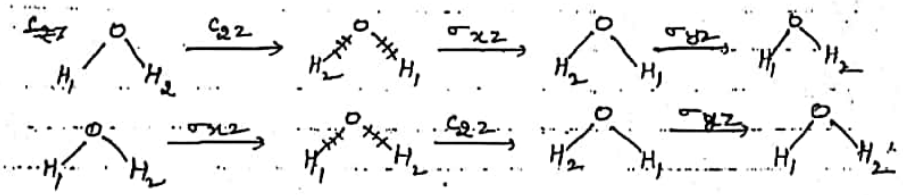
4. The associative law of multiplication must hold good for every group.

$A(BC) = (AB)C = B(AC)$

★ Prove it for water. $A = C_{2z}$, $B = \sigma_{xz}$, $C = \sigma_{yz}$

$A(BC) = C_{2z}(\sigma_{xz} \cdot \sigma_{yz}) = C_{2z} \cdot C_{2z} = E$

$B(AC) = \sigma_{xz}(C_{2z} \cdot \sigma_{yz}) = \sigma_{xz} \cdot \sigma_{xz} = E$



★ **Representation of Group :-**

Representation of group is defined as set of matrices each corresponding to single operation in the group, that can be combined among themselves in a manner parallel to the way in which group elements are combined.

(a) Every element (like C_{2z}, σ, S_2, S_3) can be expressed in form of matrix.

(b) Multiplication of these matrices of these elements can be combined in the same manner as elements are combined. Group of these matrices is defined as representation of group.

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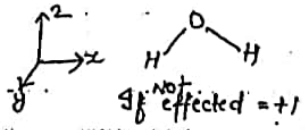
Representation of Group

- **Reducible Representation**
  - (a) 3 cartesian coordinates
  - (b) 3N cartesian " where N is no. of atoms
  - (c) Bond vector
  - (d) Bond angle
- **Irreducible Rep^n** ← derived by
  - * GOT Theorem
  - (GREAT ORTHOGONALITY TH)

REDUCIBLE REPRESENTATION :-

1. Derivation of Reducible Representation using 3 cartesian coordinates :-

C_{2v}	E	C_{2z}	σ_{xz}	σ_{yz}
x	1	−1	1	−1
y	1	−1	−1	1
z	1	1	1	1
Red. Rep^n	3	−1	1	1



If not effected = +1
If effected = −1

(Gate-2009)

Qo-55. Reducible rep^n in C_{2v} point gp. corresponding to 3-translational deg. of freedom is

(a) 3, 1, 1, 1
(b) 3, −1, 1, 1
(c) 3, −1, −1, −1
(d) 3, +1, −1, −1

Ans. (b) 3, −1, 1, 1

Representation of Group

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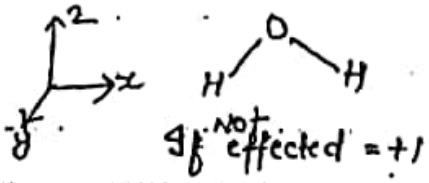

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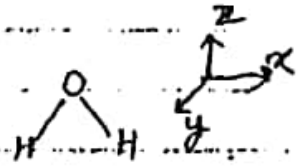
② Derivation of Reducible Representation using 3N cartesian coordinates :-

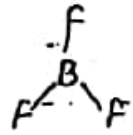
Shortcut Method



C_{2v}	E	C_{2z}	σ_{xz}	σ_{yz}
No. of Unshifted Atoms	3	1	3	1
Contribution per atom	3	-1	1	1
Reducible Repⁿ	9	-1	3	1

⇒ From character table

* Derive the reducible repⁿ of D_{3h} point group using BF_3 as a molecule and 3N cartesian coordinates as basis set.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
No. of Unshifted atoms	4	1	2	4	1	2
Contribution per atom	3	0	-1	1	-2	1
R.R.	12	0	-2	4	-2	2

* Derive reducible repⁿ of tetrahedral point group using CH_4 as example and 3N-cartesian coordinate as basis set.

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
No. of unshifted Atoms	5	2	1	1	3
Contribution per atom	3	0	-1	-1	1
R.R.	15	0	-1	-1	3

S_4 $C_4 + \perp$