MSc SEMISTER II

Core Course- VI

Inorganic Chemistry II

UNIT-III,Symmetry in chemistry

Proper axis of symmetry:

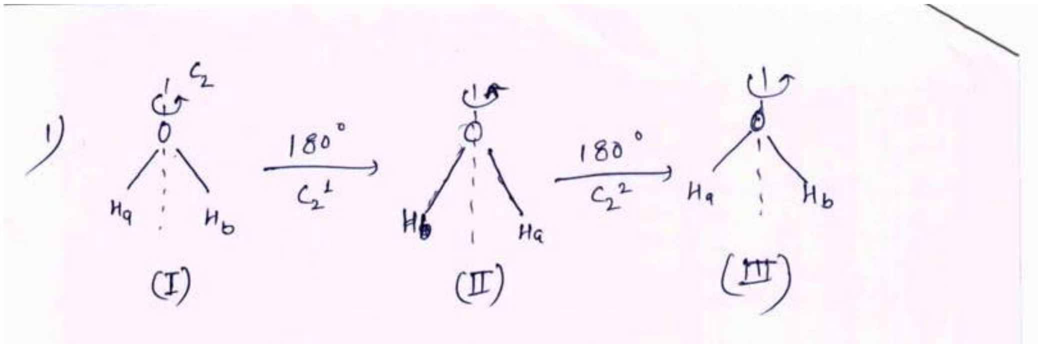
It is an imaginary axis around which the rotation carried out on the molecule, which takes the molecule from one orientation to the other equivalent indistinguishable orientation. The proper axis of symmetry is represented by C_n. And the operations generated by this are represented by C_n^m.

Where n= order of the axis
m = no. of times the operation is carried out
The order of axis is defined as the number of times an operation is to be carried out so as to get an identical configuration.

$$n = \frac{2\pi}{\theta}$$

θ = angle by which rotation is carried out

Let us consider the example of H_2O molecule.



We observe that rotation by 180° about the axis takes molecule I into II. Since the two hydrogen atoms are indistinguishable. This rotation is a symmetry operation, however we note that two atoms have been interchanged (since we have labeled them as H_a & H_b) and hence the configuration II is not exactly same as I or identical to I but it is equivalent to I. If we rotate it once more we get the configuration III, which is exactly the same as I or identical to I.

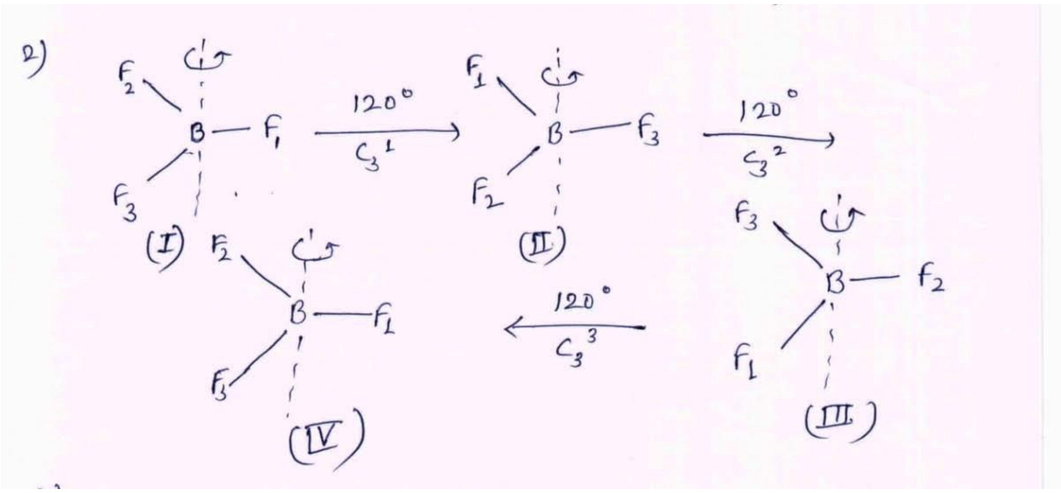
Here rotation is carried out by 180°, so according to the formula:

$$n = \frac{2\pi}{\theta}$$

$$n = \frac{360}{180} = 2$$

So order of axis is 2, and axis of symmetry is represented by C_2. As it is clear from the above figure that after rotating water molecule 2 times by 180° we are getting an identical configuration.

Consider another example of boron trifluoride (BF_3). Now the rotation by 120° in anticlockwise direction about an axis passing through boron atom and perpendicular to plane of the paper brings the molecule from configuration I to II, which is equivalent to I. One more rotation coverts it from II to III. It is seen that the configuration I and IV are identical and to get an identical configuration o BF_3 molecule, the operations was carried out three times about the symmetry axis.



As the rotation is carried out by 120°, so order of axis is-

$$n = \frac{360}{120} = 3$$

So order of axis is 3 and axis is represented by C_3. The C_3 axis thus generated 3 operations C_3^1, C_3^2 and C_3^3. The operation C_3^4 will result in configuration I, which is equivalent to C_3^1. The C_3^3 results in identical configuration & we can write

$$C_3^3 = E$$

Where E represents identity

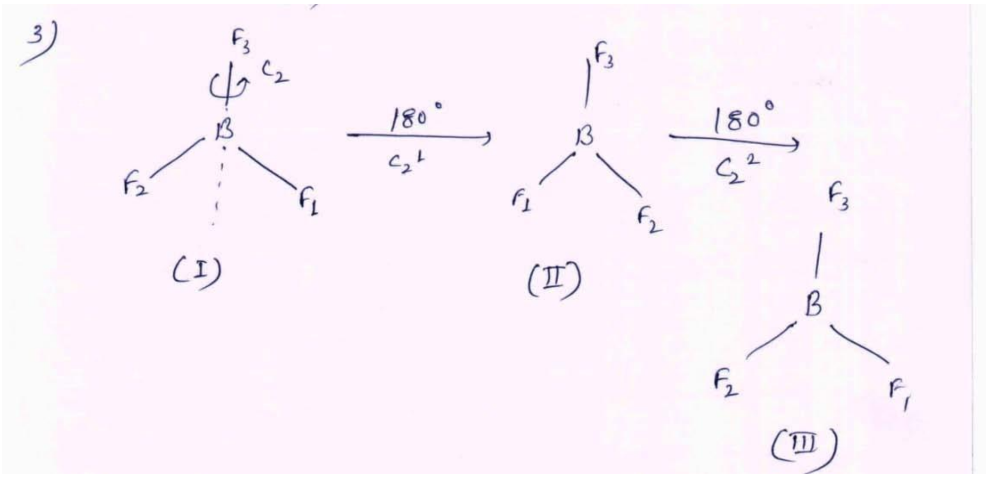
In general we can write

$$C_n^m = E \qquad \text{(When } n=m\text{)}$$

$$C_n^{m+1} = C_n^1$$

$$C_n^{m+2} = C_n^2 \quad \text{\& so on....}$$

A molecule can have more than one axis of symmetry. As in the last example suppose the rotation is being carried through each B-F bond by 180°. So BF_3 molecule contains three C_2 axis (C_2, C_2' and C_2'') along with C_3 axis.

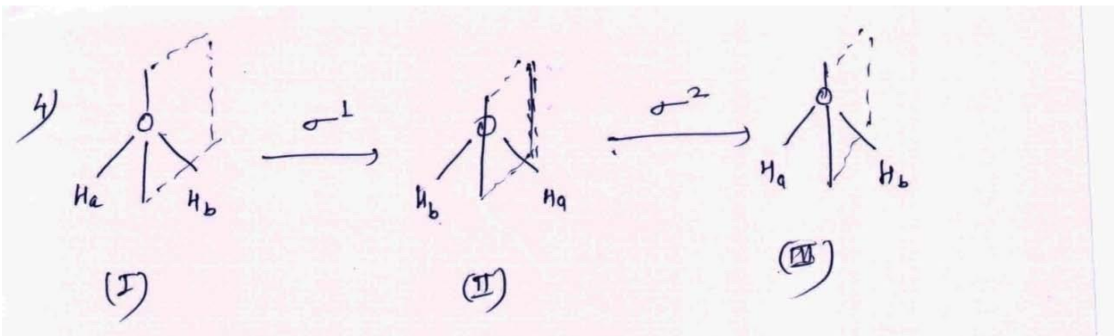


If there are several proper axis of rotation then the axis of highest order symmetry is called the principal axis and the lowest order symmetry is known as subsidiary axis. If the molecule has more than one axis of highest order, then the one that passes through maximum number of atom is the principal axis. In BF_3 molecule C_3 axis is principal axis.

a) Plane of Symmetry

It is an imaginary plane within the molecule which bisects it into two equal half which are mirror image s of each other. A plane of symmetry exists when a reflection through the plane gives an equivalent configuration. Plane of symmetry is represented by σ.

Let us consider the example of water molecule. There exists a plane of symmetry for this molecule which contains oxygen atom and bisect the angle HOH as shown in figure.



We can see that the configuration II is equivalent to I as the reflection through the plane results in the exchange of the two hydrogen atoms. The atom of oxygen which lies in the plane is not shifted. We get an identical configuration III after carrying out one more operation of reflection.

From the above example we also find that carrying out the operation of reflection twice results in an identical configuration. When the operation carried out one more time, we get the configuration II.

In general we write

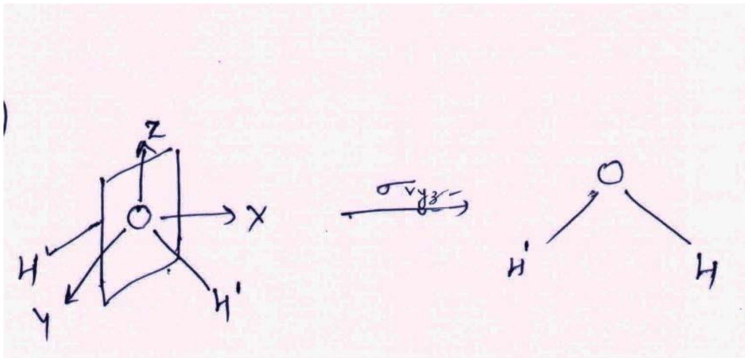
$\sigma^n = E$ {When n is even}

$\sigma^n = \sigma$ {When n is odd}

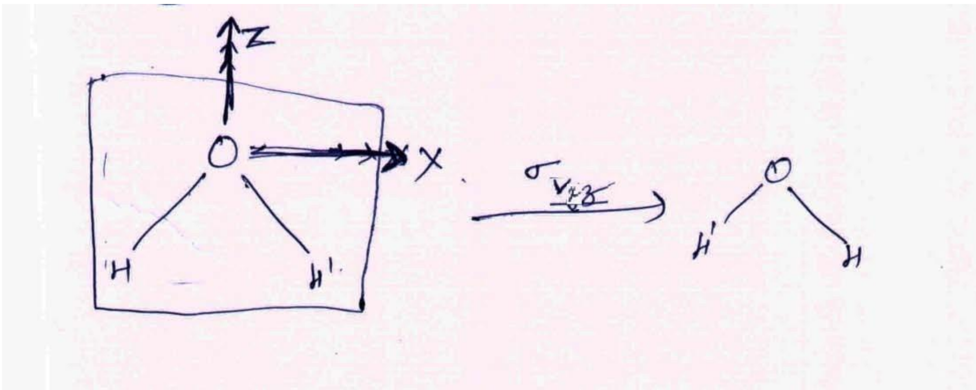
Types of plane of symmetry: the plane of symmetry can be divided into three types-

1) Vertical plane of symmetry (σ_v) - The plane passing through the principal axis and one of the subsidiary axis (If present) is called vertical plane of symmetry.
2) Horizontal plane of symmetry (σ_h) - The plane perpendicular to the axis is called horizontal plane of symmetry.
3) Dihedral plane of symmetry (σ_d) – The plane passing through principal axis but passing in between two subsidiary axes is called dihedral plane.

Water molecule has 2 planes of symmetry one in passing through O and in between 2 H atoms that is in yz plane

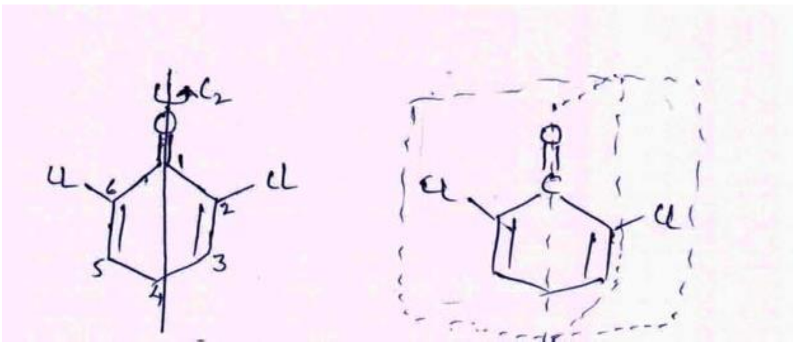


As this plane passes through C_2 axis which is principal axis in case of H_2O molecule so this plane is a vertical plane and it is represented as σv_{yz}. The other is the molecular plane passing through O and 2 H atoms in XZ plane. This plane also passes through C_2 axis so it is called as σv_{xz}.



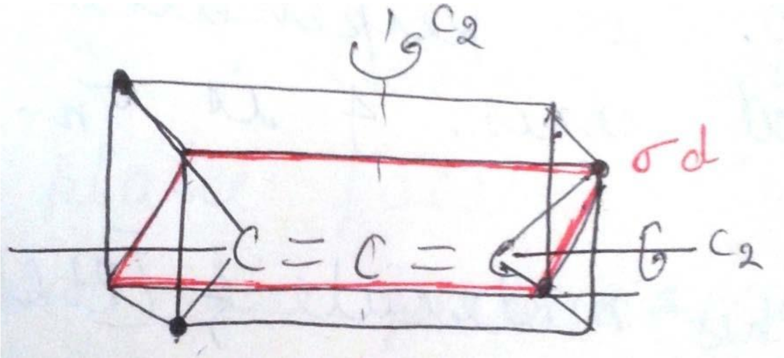
The ammonia molecule has three σ_v, each passing through N atom and one of the H atoms and bisects the H-N-H angle. The BF_3 molecule, with trigonal planar geometry has a C_3 axis and has four planes of symmetry. Out of these four planes three planes passing through C_3 axis and one of the C_2 axis, can be represented as σ_v. The molecule has also a plane of symmetry which is perpendicular to C_3 axis represented as σ_h.

Consider the example of 2,6- dichloro benzophenone.



As shown in figure the molecule possesses C_2 axis and it is the only axis of symmetry so it is principal axis. The two planes of symmetry the molecular plane and the plane containing the oxygen atom and bisects the angle between the carbon atom 2, 1 and 6 containing the principal axis and hence are vertical planes of symmetry σ_v. So in this molecule horizontal plane of symmetry is absent.

There is one more kind of plane of symmetry σ_d, The dihedral plane of symmetry. These are the planes which bisects the angle between two adjacent subsidiary axes. The molecule of allene as shown in figure has two dihedral planes of symmetry.



b) Improper Axis of Symmetry

An improper axis of rotation is said o exist when rotation about an axis followed by a reflection in a plane perpendicular to the axis of rotation results in an equivalent or identical configuration or in other words we can say that it is an imaginary axis on which the molecule has to be rotated and then reflected on a plane perpendicular to the rotation axis to get an equivalent or identical configuration.

The improper axis of rotation is represented by S_n. The operations generated by it are represented by S_n^m, where

n = order of axis and

m= no. of times the operation is being performed.