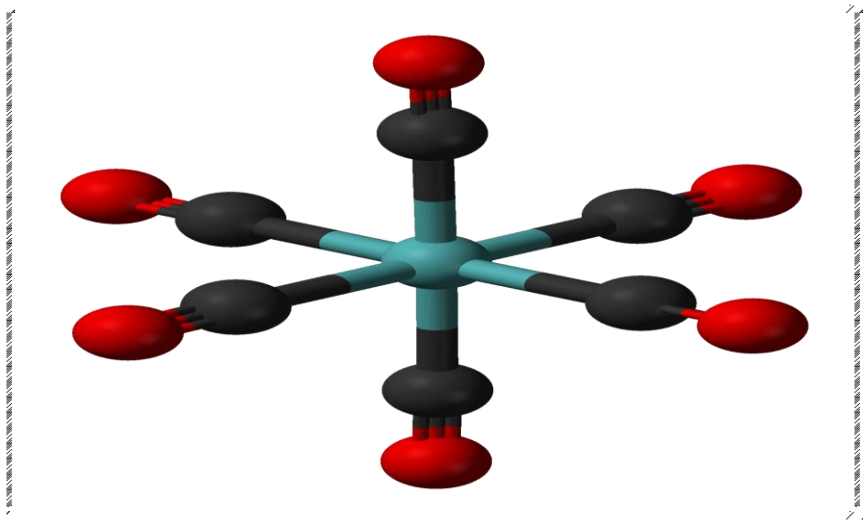
Molecular Symmetry



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***M**olecular symmetry in chemistry describes the symmetry present in molecules and the classification of molecules according to their symmetry. For qualitative refer to the shape of a molecule using terms such as tetrahedral, octahedral or square planar. It can be used to predict or explain many of a molecule's chemical properties, such as its dipole moment and its allowed spectroscopic transitions.

Symmetry is useful in the study of molecular orbital's, with applications such as the Hückel method, ligand field theory, and the Woodward-Hoffmann rules. Another framework on a larger scale is the use of crystal systems to describe crystallographic symmetry in bulk materials. Many techniques for the practical assessment of molecular symmetry exist, including X-ray crystallography and various forms of spectroscopy.

Types of molecules:-

1) Symmetry (H_2,CH_4,H_2O) **2)**Un Symmetry (HCl,CH_3Cl,HDO)

Forms of molecules

1) Linear (SP)[H_2,HCl], **2)** Trigonal planar (SP^2)[BF_3] **, 3)** Tetrahedral (SP^3) [CH_4]**, 4)** Square planar (dSP^2)[$PtCl_4$] , **5)** Octahedral (d^2SP^3)[$Co(NH_3)_6]^{2+}$

Symmetry operations and symmetry elements

A symmetry operation is an operation performed on an object which leaves it in a configuration that is indistinguishable from, and super imposable on, the original configuration.

Figure (1).. we applied **120°** rotations to **BF_3** and saw that each rotation generated a representation of the molecule that was indistinguishable from the first. Each rotation is an example of a **Symmetry operation**. The rotations described in Figure (1) were performed about an axis perpendicular to the plane of the paper and passing through the boron atom; the axis is an example of a **Symmetry element.**

Fig. (1) Rotation of the trigonal planar BF_3 molecule through 120^o generates

Symmetry element

The point group symmetry of a molecule can be described by **5 types** of symmetry elements.

<u>1)</u> Identity operator (E) :

All objects can be operated upon by the identity operator **E**. This is the simplest operator and effectively identifies the molecular configuration. The operator **E** leaves the molecule unchanged, which returns the molecule to its initial state. All molecules**(symmetrical and unsymmetrical)** in nature possess **(E).**

<u>2)</u> Rotation about an n-fold axis of Symmetry [(C)] {($C^{n^-}_n$) ,(C_1^1) ,(C_∞)}

a) In Symmetric molecules ($C^{n^-}_n$) except linear:

The symmetry(operation of rotation about an n-fold axis (the symmetry element) is denoted by the symbol $\mathbf{C_n}$, in which the angle of rotation is **(360 °/ n)**, **n** is an integer, e.g. **2, 3** or **4**. While (n^- =Rotation step number)

Example; this notation to the BF_3 molecule gives a value of **n** = **3**, and therefore we say that the BF_3 molecule contains a C_3 rotation axis; in this case, the axis lies perpendicular to the plane containing the molecule.$\mathbf{n^-}$ = **3**. Angle of rotation (**360** °/ **3=120**°), therefore the rotation axis for $\mathbf{BF_3=C^3_3}$. Some molecule can have more than one(**n**) symmetry axis; due to effect of the **free electronic pair**, for examples; the $\mathbf{C^2_2}$ and $\mathbf{C^4_4}$ axis in water**(H_2O)** and the $\mathbf{C^3_3}$ and $\mathbf{C^4_4}$ axis in ammonia **(NH_3)**.Therefore **($C^{n^-}_n$ = E)**.

b) In Unsymmetrical molecules (C_1^1) except linear:

Molecules that appear to have no symmetry at all, must possess the symmetry element **E** and effectively possess at least one $\mathbf{C^1_1}$ axis of rotation. Therefore **(C^1_1 = E).**

Example; $\mathbf{BF_2Cl}$ molecule give a value of **n** = **1**, and therefore we say that the $\mathbf{BF_2Cl}$ molecule contains a $\mathbf{C_1}$ rotation axis; in this case, the axis lies perpendicular to the plane containing the molecule.$\mathbf{n^-}$ = **1**. Angle of rotation (**360** °/ **1=360**°), therefore the rotation axis for $\mathbf{BF_2Cl = C^1_1}$ .As well as isotope **molecules form C^1_1**,like **(HOD)**.

b) In linear molecules (C_∞)(symmetrical and unsymmetrical):

C∞ signifies the presence of an∞-fold axis of rotation, i.e. that possessed by a linear molecule. These criteria are met by symmetrical and asymmetrical di atomics such as H_2,Br_2,BeH_2, **HF, CO** and [**CN**]$^-$ and linear poly atomics mean a(species containing three or more atoms) that do not possess a centre of symmetry, e.g. **OCS** and **HCN**.

3) Reflection through a plane of symmetry(mirror plane) [(ϭ)] { (σv) ,(σh) ,(ϭ ∞)}

A plane of reflection through which an identical copy of the original molecule is generated. This is also called a mirror plane and abbreviated σ (sigma). Water has two of them: one in the plane of the molecule itself and one perpendicular to it. A symmetry plane parallel with the principal axis is dubbed vertical (**σv**) and one perpendicular to it horizontal (**σh**).

***In general,** the plane particles show a symmetry process of type (**σv**),while the non- plane molecules show a symmetry process of type (**σh). (ϭ ∞)** signifies the presence of an∞-fold axis of reflection, i.e. that possessed by a linear molecule(**in symmetric molecules).**

***In general,** the (**unsymmetrical molecules)** plane –non plan particles **as well as** asymmetric linearity do not show any kind of reflection, **{ (σv) ,(σh) and(ϭ ∞)}**.

4) Rotation about an axis, followed by reflection[(S_n^{n-})]

Rotation-reflection axis: an axis around which a rotation by {**360** °/ **n** } , followed by a reflection in a plane perpendicular to it, leaves the molecule unchanged. Also called an **n-fold** improper rotation axis, it is abbreviated S_n^{n-}. Examples are present in tetrahedral silicon tetra fluoride, species of the type XY_4 (all **Y** groups must be equivalent) possess three S_4 **axes**, and the operation **(S^4_4)** rotation–reflection in the SiF_4 molecule. As another example, in the case of SF_6 the operation rotation–reflection will be equal to **(S^6_6) .**

***In general,** the non- plane molecules only show a symmetry process of type (S_n^{n-}). While the (**unsymmetrical molecules)** non plan particles **did** not show any operation of S_n rotation–reflection, **{** S_n^{n-}**}**. Therefore **(**$S_n^{n-} = C^{n-}_n = E$**).**

5) Reflection through a centre of symmetry (inversion centre) [(n i)]

If reflection of all parts of a molecule through the centre of the molecule produces an indistinguishable configuration, the centre is a centre of symmetry, also called a centre of inversion; it is designated by the symbol **i**. Each of the molecules $PtCl_4$ **,trans-**N_2F_4, SF_6 and **benzene** possesses a centre of symmetry, but **H_2S**, **cis-N_2F_4** and **SiH_4** did not. **(i ∞)** signifies the presence of an∞- centre of inversion, i.e. that possessed by a linear molecule(**in symmetric molecules)** **,**for example the molecules **CO_2 ,Cl_2** and **BeF_2** possesses a centre of inversion will be equal to**(i ∞).** While the (**unsymmetrical molecules)** [non plan particles **as well as** asymmetric linearity do not show any kind of inversion, **{ (ni)** and **(i∞)}**, for example the molecules **Hl** and **trans-$N_2F_2Cl_2$** .

Factors affecting the presence of the free electronic pair

1) Increase symmetry**…..(H_2O..C^2_2,C^4_4)**
2) Minimize **of the angle** due to angular tensile between **the bonded bonds** and **the free electrons …….{CH_4 (109.5)…,NH_3 (107.3)..**and **H_2O (105.1)}.** All molecules are **tetrahedral,** but with the **free electronic pair** there is a **decrease** in **angle** value.

Point groups

Point groups ... represents the total number of operations experienced by Molecule during rotation.
*BF_3=[C_3^3,E,3σv]
*H_2O=[C_2^2,E,2 σv] , {C_4^4,E, σh,S_4^4}

Types of symmetry

1) Week symmetry ..... represents molecules that contain only **two** processes.
2) Moderate symmetry ...... represent molecules that contain **three** and **four** processes.
3) Strong or high symmetry ...... represent the molecules that contain **all** processes.