General Chemistry-I

Unit-3 Covalent bonding

Hybridization

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Hybridization

Aim:

- Making the students to understand the basic concepts hybridization.
- Understanding the need of concept of hybridization in the view of bonding.

Objective:

- Learning the concepts of ground and excited states
- Understanding the mixing of atomic orbitals to different extents and their shapes/ orientations

Prerequisite

- The forces and bonds between molecules; Van der Waals, dipole-dipole and hydrogen bonding
- Covalent bond and its types
- Atomic orbitals
- VSEPR theory

Outcome

- Able to identify and name hybrid orbitals (sp3)
- Able to distinguish between the occurrence and shape of atomic orbitals and hybrid orbitals.
- Able to Understand the bond angles found in different molecules with hybrid orbitals
- Distinguish between sigma and pi bonds in both geometry and strength.

sp^3 Hybridization of carbon

Let us consider the electronic configuration of carbon in its ground or atomic state.

$$\textbf{C (Ground state)} = 1s^2\ \underbrace{2s^2\ 2p_x^1 2p_y^1 2p_z^0}_{\text{Valence shell}}$$

In terms of energy level diagram, this electron configuration may be represented as in Figure. Since there are only two unpaired electrons (half-filled orbitals), it might be expected that only two single covalent bonds will be formed.

On this basis, carbon would combine with two hydrogen atoms ($H=1s^1$) to form a molecule CH_2. The two C-H bonds would be formed by overlap of the 2p orbitals (p_x and p_y) with the 1s orbital of each hydrogen atom. Since the angle separating the p orbitals is 90º, the C-H bonds would be at right angles to each other. But from chemical analysis we know that the simplest stable compound that carbon forms with hydrogen is methane (CH_4) and this compound contains four identical C-H bonds.

Now let us assume that one of the 2s electrons in the ground state is moved or promoted to the empty p_z orbital. Since $2p_z$ orbital is at a higher energy level than the 2s orbital. This promotion process would require input of energy. This energy is supplied in the form of heat or light. This new state of carbon is referred to as the excited state. The electronic configuration of carbon in its excited state is:

$$\textbf{C (Excited state)} = 1s^2\ \underbrace{2s^2\ 2p_x^1 2p_y^1 2p_z^1}_{\text{Valence shell}}$$

In terms of energy level diagram, this electron configuration may be represented as in Figure. Since there are four unpaired electrons (half-filled orbitals) in the valence shell of the carbon atom in its excited state, it might be expected that four covalent bonds will be formed. On this basis, carbon would combine with four hydrogen atoms to form a molecule CH_4. The three C-H bonds would be formed by the overlap of three 2p orbitals (p_x, p_y, and p_z) with the 1s orbital of each hydrogen atom. The fourth C-H bond will be formed by the overlap of the 2s orbital of carbon with the 1s orbital of a hydrogen atom. Since the angle separating the p orbitals in an atom is 90º, the three C-H bonds may be expected to be at right angles to each other. The fourth C-H bond involving the overlap of s orbitals will not have any directional characteristics because s orbitals are spherically symmetrical. This implies that two different types of C-H bonds are involved in the formation of methane molecule. This is not true. Experimentally, methane has been shown to contain four identical C-H bonds that are directed towards the corners of a regular tetrahedron.

To form four identical bonds, carbon must contribute a set of four equivalent orbitals. This can be achieved if the 2s and the three 2p orbitals (p_x, p_y, and p_z) in the excited state are mixed or hybridized to give four new equivalent orbitals. These new orbitals are known as sp^3 hybrid orbitals or simply sp^3 orbitals because they are formed by the interaction of one s and three p orbitals. The process of mixing of pure orbitals to give a set of new equivalent orbitals is termed Hybridization and the carbon is said to be in Hybridized state. The electronic configuration of carbon in its sp^3 hybridized state is:

$$\textbf{C (Excited state)} = 1s^2\ \underbrace{2(sp^3)^1 2(sp^3)^1 2(sp^3)^1 2(sp^3)^1}_{\text{Valence shell}}$$

In terms of energy level diagram, the above electronic configuration may be represented as figure.

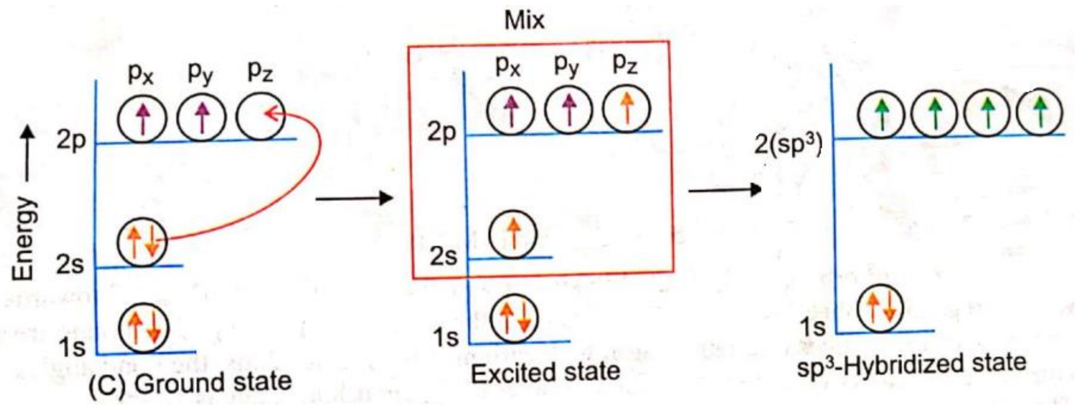
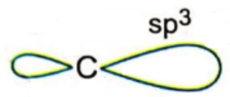
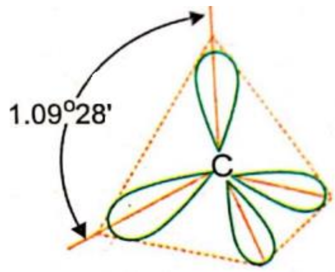


Figure - Formation of four equivalent sp^3 hybrid orbitals of carbon

Each sp^3 orbital contains one electron. Since each sp^3 orbital is obtained from one s and three p orbitals, it has 25 % s-character and 75% p-character. As indicated, each sp^3 orbitals has a large lobe and a small lobe.



Shape of an sp^3 hybrid orbitals



Orientation of four sp^3 hybrid orbitals

The four new sp^3 orbitals obtained above are identical (same energy and shape) but differ only in their orientation in space with respect to each other. The four sp^3 orbitals are arranged in such a way that their axes are directed towards the corners of a regular tetrahedron with carbon located at the centre. The angle between any two orbitals is therefore, 109º 28'. The orientation of sp^3 orbitals is shown in figure. The smaller lobes are not indicated because they do not extend sufficiently far from nucleus to participate in bond formation.

The tetrahedral arrangement is favoured because it allows the sp^3 orbitals to stay as far away from each other as possible and thereby reducing the electron-electron repulsion. This is in keeping with the fact that each sp^3 orbitals contains an electron, and electrons stay as far apart as possible because they have the same charge.

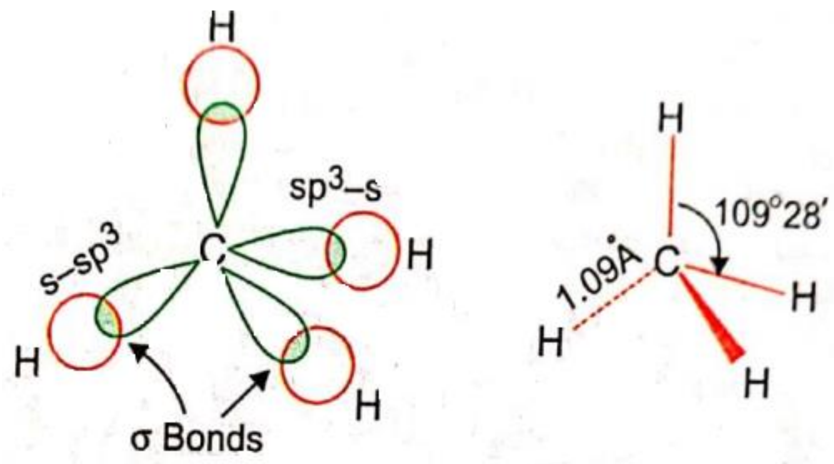
At this stage, the student should clearly understand that carbon does not necessarily undergo bond formation in its ground state. The electron configuration may change prior to bond formation and the final arrangement that it acquires would depend upon the number of other atoms or groups to which it is attached.

Whenever carbon is bonded to four other atoms or groups (as in methane), it uses sp^3 hybrid orbitals.

Bonding in Methane:

In methane carbon forms single covalent bonds with four hydrogen atoms. Since the carbon atom is attached to four other atoms it uses sp^3 orbitals to form these bonds. Figure shows how the bonds in methane are formed.

Each C-H covalent bonds is the result of the overlap of an sp^3 orbital from carbon and 1s orbital from hydrogen.



Bonding in methane

Since the four sp3 orbitals are oriented in such a way that their axes are directed towards the corners of a regular tetrahedron with carbon located at the centre, the resulting C-H bonds are also directed towards the vertices of a tetrahedron with carbon at the centre. Thus, the bond angles in methane are the same as the angles between the axes of the sp^3 orbitals that is 109º28'.

The covalent bonds formed by the overlap of sp^3 orbitals and s orbitals are sigma (σ) bonds because the electron density in each bond is symmetrical about the line joining the centres of two bonded atoms. Thus, all C-H bonds in methane are sigma bonds.

Electron diffraction and spectroscopic studies have shown that methane has as tetrahedral structure and all the C-H bonds are identical. They are the same length (1.09 Å). The energy required to break any of the four bonds is the same (102 Kcal). The angle between any pair of bonds is 109º28'.

Reference Books:

1. Bahl B.S. and Arun Bahl, Advanced Organic Chemistry, (12th edition), New Delhi, Sultan Chand & Co., (1997)
2. Morrison R.T. and Boyd R.N.,Organic Chemistry (6th edition), New York, Allyn & Bacon Ltd., (1976)

Short answer questions

1. Define hybridization.
2. What is the electronic configuration of hybridized state of CH_4?
3. Write short note on sp^3 hybridization.
4. Explain why four covalent bonds in methane are equivalent.
5. Find out the type of hybridization of CH_3CH_3.

Long answer questions

1. Explain the hybridization of the methane molecule
2. Explain the structure of methane using sp^3 hybridization.
3. Discuss the orbital structure of methane.