

contain carbon, that is it is chiefly, the study of compounds where carbon is covalently bonded to carbon, hydrogen, halogens, oxygen, nitrogen and sulfur. The following text is devoted to the study of structure, bonding and physical nature of these classes of organic compounds.

1.2 ELECTRONIC STRUCTURE AND CHEMICAL BONDING IN ORGANIC COMPOUNDS

We presume that you are already familiar with fundamentals of electronic structure of atoms and therefore, the keypoints of electronic structure of an atom are enumerated in this section.

- (1) The simplest picture of an atom is represented by a nucleus (protons and neutrons) with a positive charge surrounded by negatively charged electrons. In a neutral atom, the number of electrons is equal to number of protons. When two atoms approach each other, the electrons of one are attracted by the nucleus of second atom and viceversa. Coulomb's law best describes the forces of attraction and repulsion and is given by

$$F = \frac{kq_1q_2}{r^2}$$

where, q_1 and q_2 are two charges separated by distance r .

If q_1 and q_2 are opposite charges then F is the force of attraction and if q_1 and q_2 are similar charges then F is the force of repulsion.

- (2) Electrons occupy the region of space called principal energy levels, identified by **principal quantum numbers** 1, 2, 3 and so on. Each principal energy level can contain upto $2n^2$ electrons, where n is the principal quantum number. Thus, the first energy level can contain 2 electrons, second 8 electrons, the third 18 electrons, fourth 32 electrons and so on.
- (3) Each principal energy level is subdivided into region of space called **orbitals**; each orbital can contain maximum two electrons with spin $+\frac{1}{2}$ and $-\frac{1}{2}$ (**Pauli exclusion principle**).
- (4) The first principal energy level contains single orbital, called 1s orbital. The second principal energy level contains one s orbital and three p orbitals; these orbitals are called $2s$, $2p_x$, $2p_y$, and $2p_z$. The third principal energy level contains one 3s orbital, three 3p orbitals, and five 3d orbitals.
- (5) A set of orbitals which have equivalent energies are said to be **degenerate orbitals**. For example, three p orbitals are degenerate and similarly, set of five d orbitals are also degenerate, as they are equivalent in energies.
- (6) According to **Hund's rule**, when a number of degenerate orbitals are available, they are first filled singly and then pairing of electrons takes place.
- (7) The filling of electrons in atomic orbitals is done according to the **Aufbau Principle**, that is, electrons occupy the orbitals successively in order of increasing energy.

1.3 LEWIS STRUCTURE AND CHEMICAL BONDS

Lewis structure represents the valence electrons (electrons in the outermost shell) of an atom by placing dots around the symbol of an atom, as represented in Table 1.1.

Table 1.1 Lewis structure representation and filling up of orbitals of some elements

Element	Atomic number	Electronic configuration (Valence shell electrons in bold)	Lewis structure	Electronic distribution in orbitals	Filling up of the S and p orbitals				
					1s	2s	2p _x	2p _y	2p _z
H	1	1	·H	1s ¹	↑				
He	2	2	:He	1s ²	↑↓				
Li	3	2,1	·Li	1s ² 2s ¹	↑↓	↑			
Be	4	2,2	:Be	1s ² 2s ²	↑↓	↑↓			
B	5	2,3	·B·	1s ² 2s ² 2p ¹	↑↓	↑↓	↑		
C	6	2,4	·C·	1s ² 2s ² 2p ²	↑↓	↑↓	↑	↑	
N	7	2,5	·N·	1s ² 2s ² 2p ³	↑↓	↑↓	↑	↑	↑
O	8	2,6	:O:	1s ² 2s ² 2p ⁴	↑↓	↑↓	↑↓	↑	↑
F	9	2,7	:F·	1s ² 2s ² 2p ⁵	↑↓	↑↓	↑↓	↑↓	↑
Ne	10	2,8	:Ne:	1s ² 2s ² 2p ⁶	↑↓	↑↓	↑↓	↑↓	↑↓

The Lewis structure of a compound, also known as the *electron-dot* formula, involves the representation of symbols of elements surrounded by dots, which indicates the electrons taking part in the bond formation as well as the non-bonding (or free) electrons. In accordance with Lewis model, during bond formation each atom attains a complete valence shell (either *two* (as in He) or *eight* electrons (referred as octet)) resembling that of its nearest noble gas configuration. This can be achieved by transfer of electrons (ionic bond) or by mutual sharing of electrons (covalent bond).

1.3.1 Electronegativity

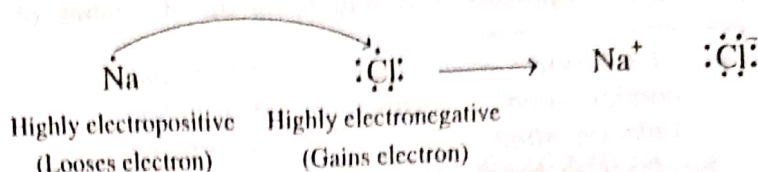
Electronegativity is a measure of the tendency of an atom to attract the electrons it shares with another atom. It is a periodic property, which increases from left to right in a period and decreases on moving down a group. Fluorine is the most electronegative element. Similarly, lithium and sodium with low electronegativity values of 1.0 and 0.9 respectively are often termed as *electropositive elements*. Table 1.2 illustrates the electronegativity values of some elements.

Table 1.2 Electronegativity values (on Pauling scale) for selected elements

Element	H	Li	Na	C	N	O	F	Cl	Br	I
Electronegativity	2.1	1.0	0.9	2.5	3.0	3.5	4.0	3.0	2.8	2.5

1.3.2 Ionic Bond

An ionic bond is formed when atoms participating in bond formation involve transfer of electrons from one atom to the other. The transfer of electron(s) results in the formation of ions. The electrostatic force of attraction holds these oppositely charged ions close together resulting in the formation of a strong **ionic bond**. For example,



The ionic bond is formed between atoms having an appreciable difference in electronegativities.

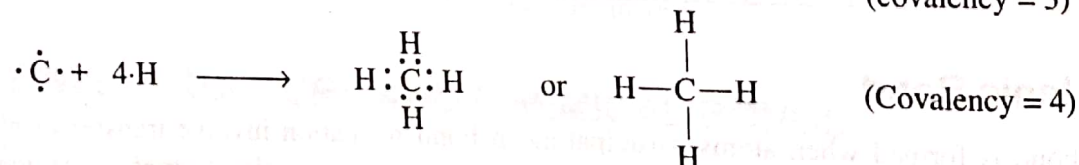
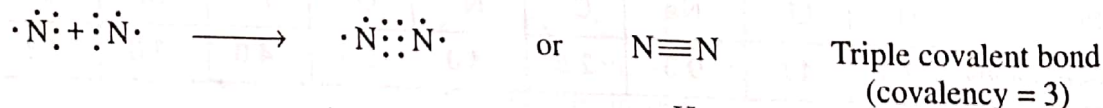
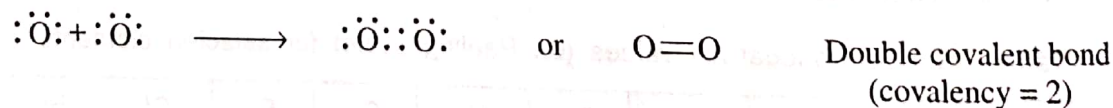
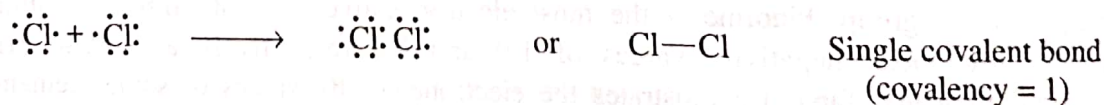
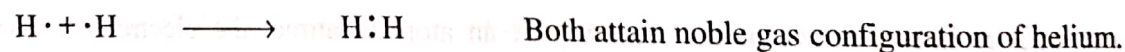
1.3.3 Covalent Bond

Two atoms which have same electronegativity or a small difference in electronegativity involve mutual sharing of electrons to form a bond known as **covalent bond**. In general, Lewis structure is used for the representation of a covalent bond. The shared pair of electrons is represented by a dash (—) between two atoms and represents a bond. The bond formed between atoms of similar electronegativities is a *non-polar covalent bond* such as H_2 , Cl_2 , O_2 , N_2 , CH_4 , and so on. The bond formed between atoms having a small difference in electronegativities is a *polar covalent bond* such as HCl , H_2O and so on. The *degree of ionic or covalent character* can be predicted from electronegativities of the involved atoms by the formula:

$\% \text{ Ionic character} = \frac{\text{Electronegativity of more electronegative atom} - \text{Electronegativity of less electronegative atom}}{\text{Electronegativity of more electronegative atom}} \times 100$

For example, the calculations using this formula (refer to Table 1.2 for electronegativity) indicate that the covalent bond in HCl possesses 30% ionic character.

Depending upon the number of shared electron pairs, the covalent bond may be characterized as a single, double or triple covalent bond.



1.3.4 Atomic Radius, van der Waals Radius, Bond Length, and Bond Angle

Atomic radius. The distance from the nucleus of the atom to the outermost electrons is known as the radius of an atom. The atomic radius is the half of the closest distance of the approach of

the atoms in the structure of symmetrical molecule. For covalent molecules such as H-H and Cl-Cl, the atomic radius is often termed as *covalent radius*.

van der Waals radius. The distance from the nucleus of an atom beyond which the approach of another atom causes repulsion is known as van der Waals radius of that atom. If two atoms are brought closer than the sum of their van der Waals radii, they repel each other and this phenomenon is known as *van der Waals repulsion*.

Bond length. In a covalently bonded molecule, the distance between the nuclei of the two atoms is known as bond length. Atomic radii and bond lengths are measured in angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$) units.

Bond angle. In a covalently bonded molecule having more than two atoms, the bonds form an angle with each other, which is termed as bond angle.

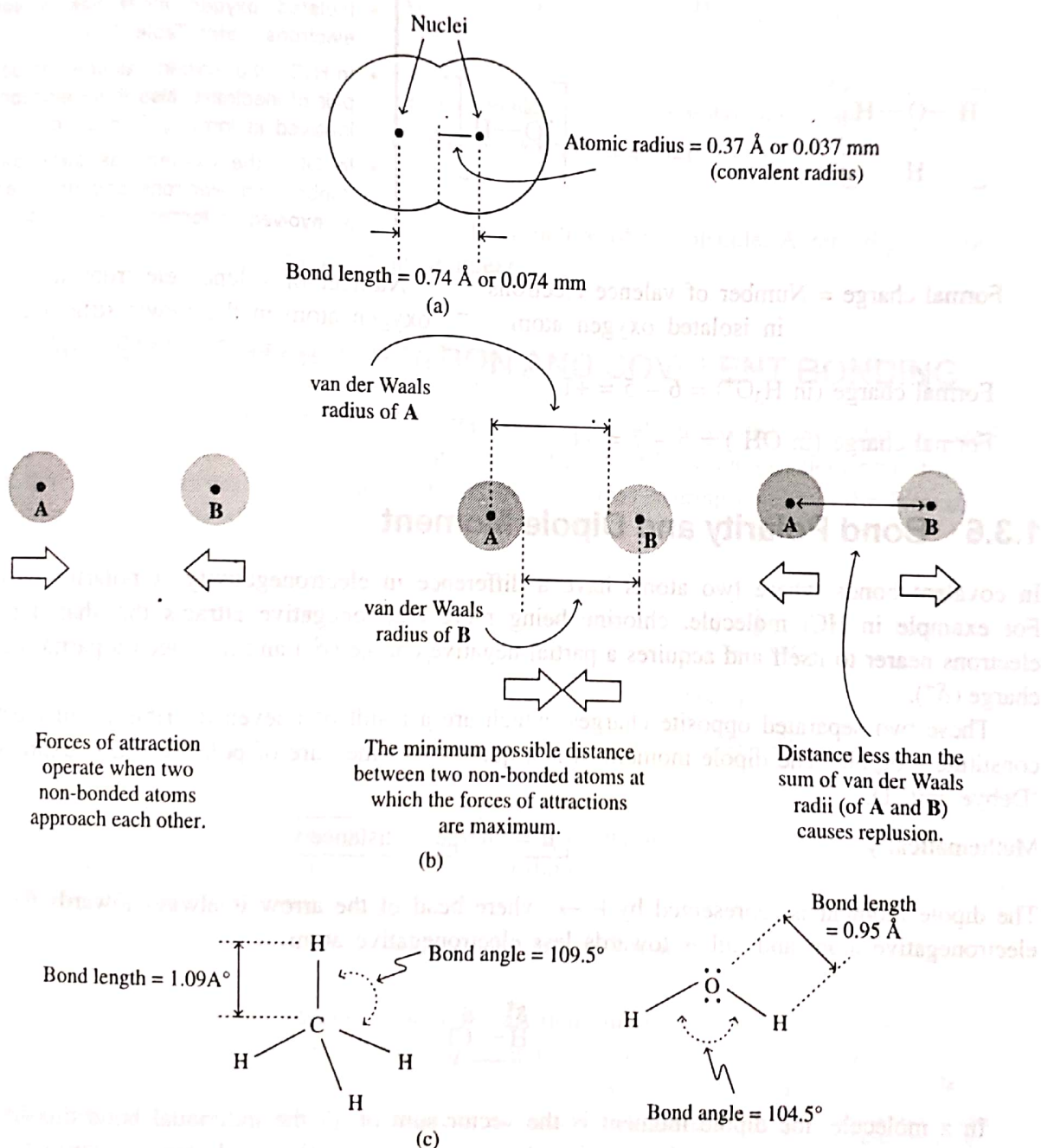


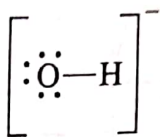
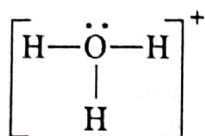
Fig. 1.1 (a) Atomic radius and bond length in hydrogen; (b) van der Waals radii of atoms; (c) bond angles, and bond lengths in methane and water molecule.

1.3.5 Formal Charge

The charge present on an atom, in a molecule or in an ion is known as formal charge. The formal charge is calculated by taking into consideration, the number of valence electrons of the Lewis structure as follows.

$$\text{Formal charge} = \text{Number of valence electrons in an isolated atom} - \text{Number of valence electrons assigned to atom in the Lewis structure}$$

As an example, let us calculate the formal charge on oxygen in H_3O^+ and OH^- . The Lewis structure for these species are



- Isolated oxygen atom has 6 valence electrons (refer Table 1.1)
- In H_3O^+ , the oxygen has one non bonding pair of electrons, also three electrons are involved in forming O-H bonds.
- In OH^- , the oxygen has three pairs of nonbonding electrons and one electron is involved in forming O-H bond.

$$\text{Formal charge} = \text{Number of valence electrons in isolated oxygen atom} - \text{Number of valence electrons in oxygen atom in the Lewis structure}$$

$$\text{Formal charge (in } \text{H}_3\text{O}^+) = 6 - 5 = +1$$

$$\text{Formal charge (in } \text{OH}^-) = 6 - 7 = -1$$

1.3.6 Bond Polarity and Dipole Moment

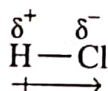
In covalent bonds where two atoms have a difference in electronegativity, a polarity develops. For example in HCl molecule, chlorine being more electronegative attracts the shared pair of electrons nearer to itself and acquires a partial negative charge (δ^-) and hydrogen a partial positive charge (δ^+).

These two separated opposite charges, which are a result of uneven distribution of electrons, constitute a dipole. The dipole moment, μ is a quantitative measure of polarity and is expressed in 'Debye unit' D.

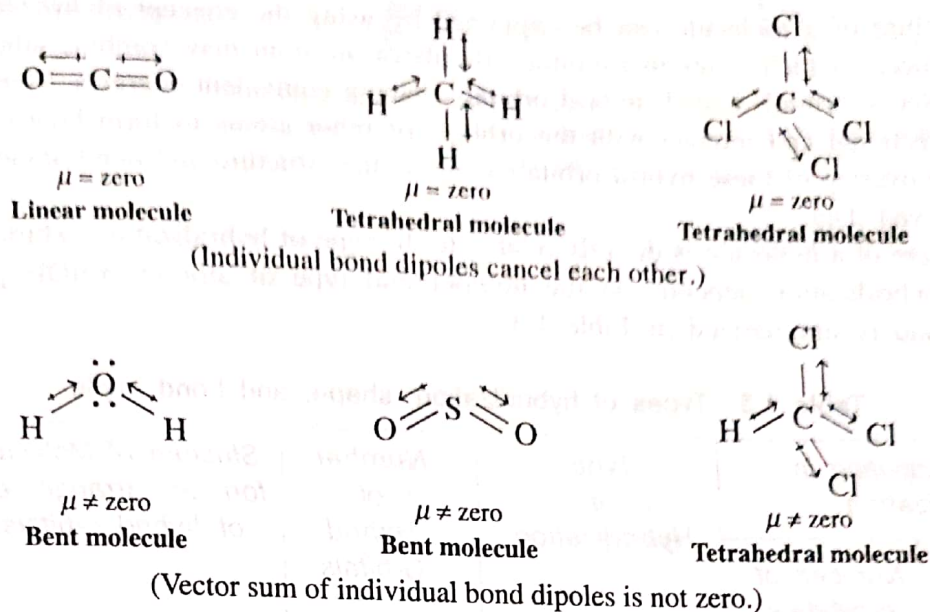
Mathematically

$$\mu = \text{charge} \times \text{distance}$$

The dipole moment is represented by \rightarrow , where head of the arrow is always towards the more electronegative atom and tail is towards less electronegative atom.



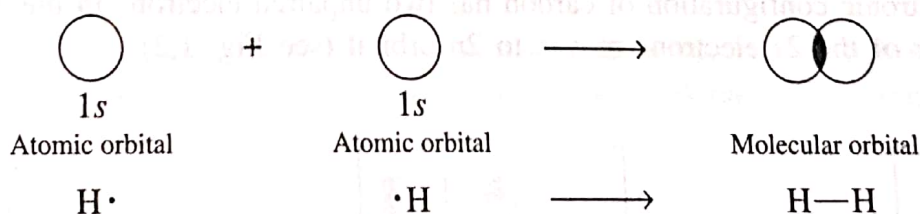
In a molecule, the dipole moment is the vector sum of all the individual bond dipoles. The individual bond dipole may not be zero but their vector sum on the whole may be zero since they cancel each other being vector quantities.



Dipole moment values give an idea about the structure of a molecule. A zero dipole moment indicates that the molecule is symmetrical or linear.

1.4 CONCEPT OF HYBRIDIZATION AND COVALENT BONDING

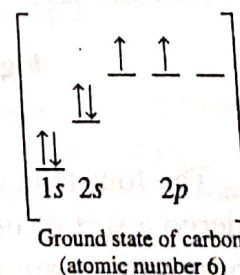
As mentioned earlier, an orbital describes the region in space which has the maximum probability of finding the electrons. In accordance with the modern theory of bonding, covalent bond formation between two atoms involves the overlap of atomic orbitals. This overlap results in the formation of new orbitals termed *molecular orbitals*.



As you already know that based on principal energy levels, the orbital may be *s*, *p*, *d*, or *f*. In present text our emphasis will be on *s* and *p* atomic orbitals as carbon (atomic number 6) involves atomic orbitals of second principal energy level.

The electronic configuration of carbon is $1s^2, 2s^2, 2p^2$ and is depicted as follows

As per this configuration, carbon should be divalent in nature (2 unpaired electrons in *p* orbitals) and since *p* orbitals are mutually perpendicular, the covalent bond formed using *p* orbitals should have bond angle $\sim 90^\circ$. In actual, carbon is tetravalent in nature and bond angles are never observed to be 90° .



The structure of a molecule can be explained by using the concept of *hybridization*. It is a theoretical concept, which states that atomic orbitals of an atom may combine among themselves to form new set of orbitals called 'hybrid orbitals' having equivalent energies. These new orbitals are highly directional and interact with the orbitals of other atoms to form bonds. The molecule formed by the overlap of these hybrid orbitals exhibits the structure and bond angle in accordance with the observed data.

The structure of a molecule is directly related to the type of hybridization exhibited by atom(s). The type of hybridization depends on the number and type of atomic orbitals participating in hybridization and is summarized in Table 1.3.

Table 1.3 Types of hybridization, shape, and bond angle

Orbitals participating in hybridization		Type of Hybridization	Number of Hybrid Orbitals	Structure of Molecule formed (arrangement of hybrid orbitals)	Bond angle
Number of s-orbitals	Number of p-orbitals				
1	3	sp^3	4	Tetrahedral	109.5°
1	2	sp^2	3	Trigonal planar	120°
1	1	sp	2	Linear	180°

1.4.1 sp^3 Hybridization

Structure of methane (CH_4)

Experimentally, it has been observed that methane (CH_4), the simplest carbon compound, has same bond length (1.09 Å) for all the four carbon-hydrogen bonds and has a bond angle of 109.5°. The ground state electronic configuration of carbon has two unpaired electrons in the 2p orbital. In the excited state, one of the 2s electrons moves to 2p orbital (see Fig. 1.2).

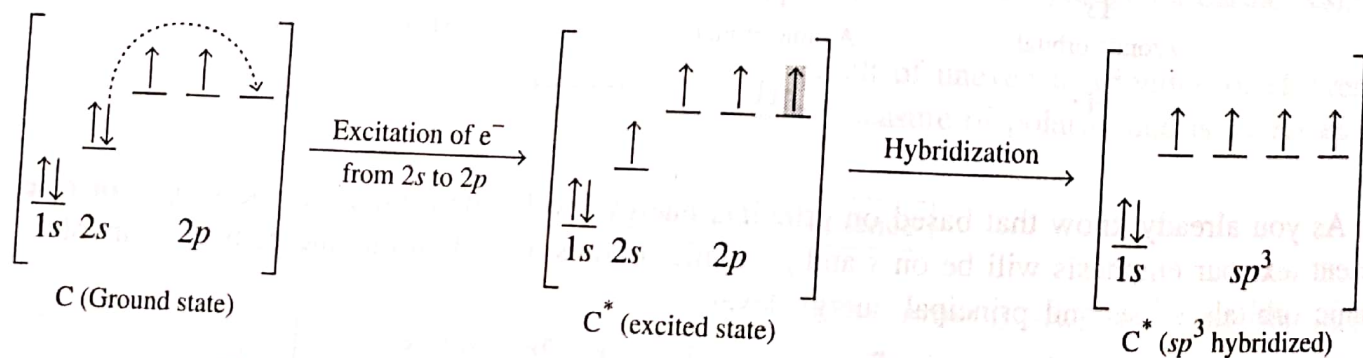
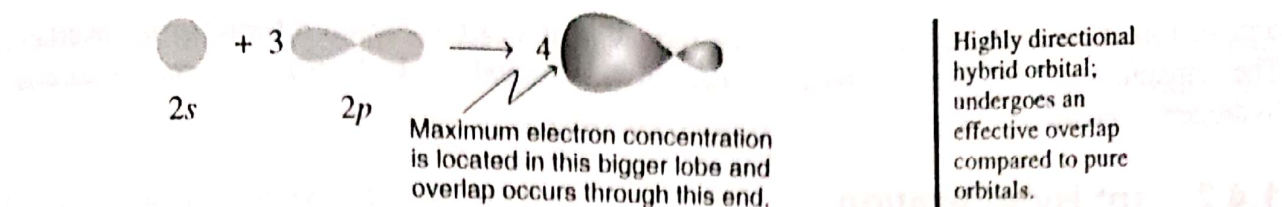


Fig. 1.2 Excitation and sp^3 hybridization of the atomic orbitals of carbon.

The four atomic orbitals of carbon which differ in their energies (one 2s and three 2p orbitals), undergo a sort of intermixing to form four new hybrid orbitals having equivalent energies. The new hybrid orbitals are highly directional in nature and are more effective in overlapping compared to pure atomic orbitals.



The four hybrid orbitals are arranged along the sides of a regular tetrahedron (bond angle 109.5°) to have minimum electronic repulsions.

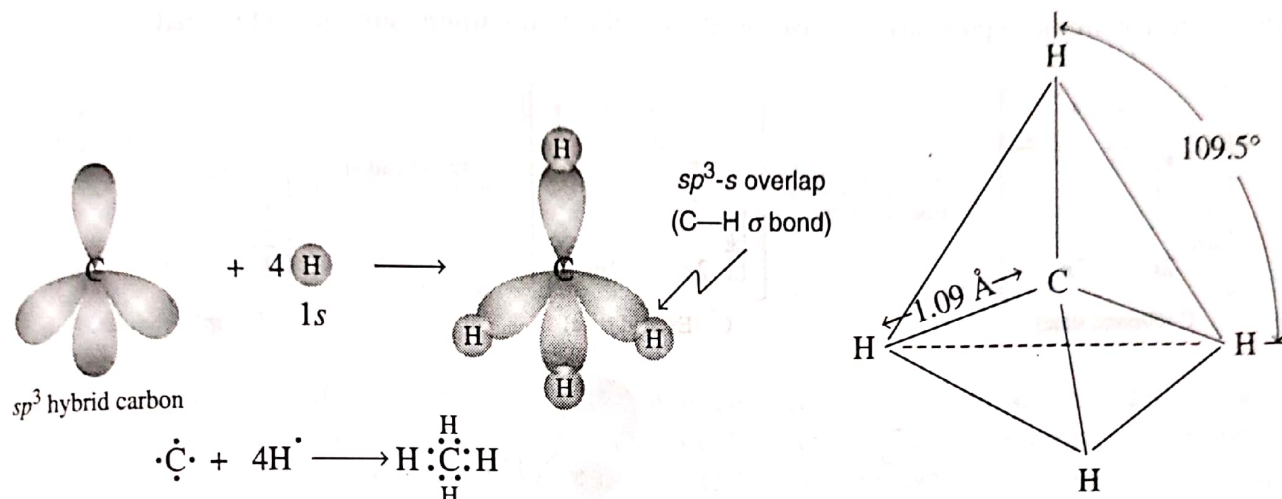


Fig. 1.3 Tetrahedral arrangement of four sp^3 hybrid orbitals of carbon and formation of methane.

The four sp^3 hybrid orbitals overlap with $1s$ orbital of four hydrogens to form four carbon-hydrogen σ bonds (sp^3-s overlap) with same bond lengths (1.09 Å) and same bond angle. The methane molecule is tetrahedral in shape.

Structure of ethane (C_2H_6)

In ethane, two carbons undergo sp^3 hybridization. Each carbon has four sp^3 hybrid orbitals arranged in tetrahedral manner, that is, in all, eight hybrid orbitals are available. The overlap of two sp^3 hybrid

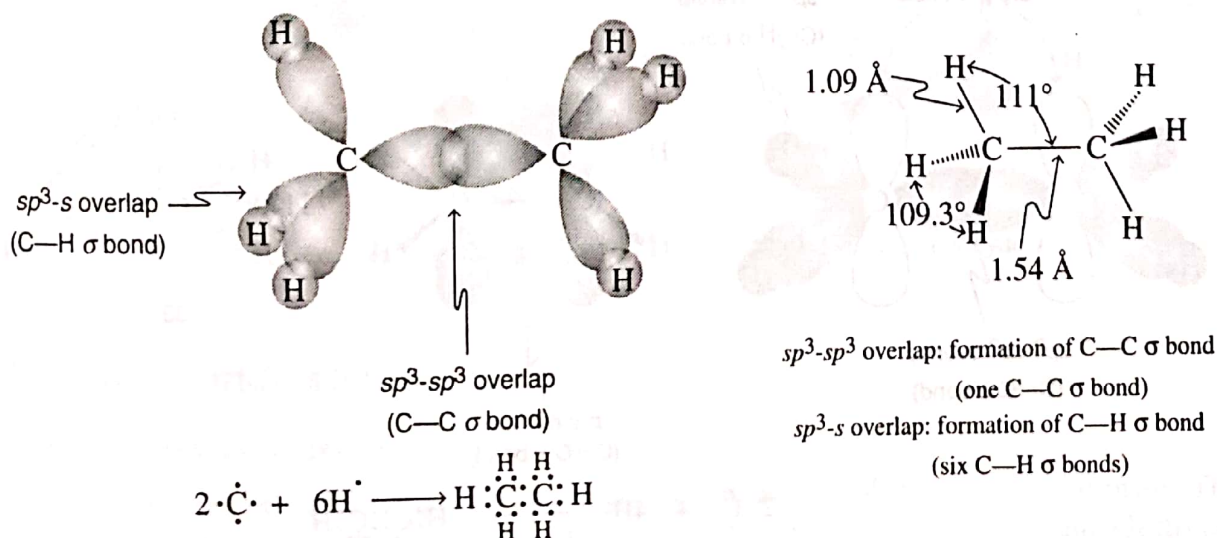


Fig. 1.4 Structure of ethane showing overlap of sp^3 hybrid orbitals of carbons.

orbitals (one from each carbon) results in the formation of a carbon-carbon σ bond (sp^3-sp^3 overlap). The remaining six sp^3 hybrid orbitals overlap with $1s$ orbitals of hydrogens to form six carbon-hydrogen σ bonds (sp^3-s overlap).

1.4.2 sp^2 Hybridization

Structure of ethene (C_2H_4)

The combination of one $2s$ and two $2p$ orbitals of carbon results in the formation of three sp^2 hybrid orbitals. These hybrid orbitals have trigonal planar arrangement (bond angle close to 120°) to minimize electronic repulsions. In case of ethene, the two carbons are sp^2 hybridized.

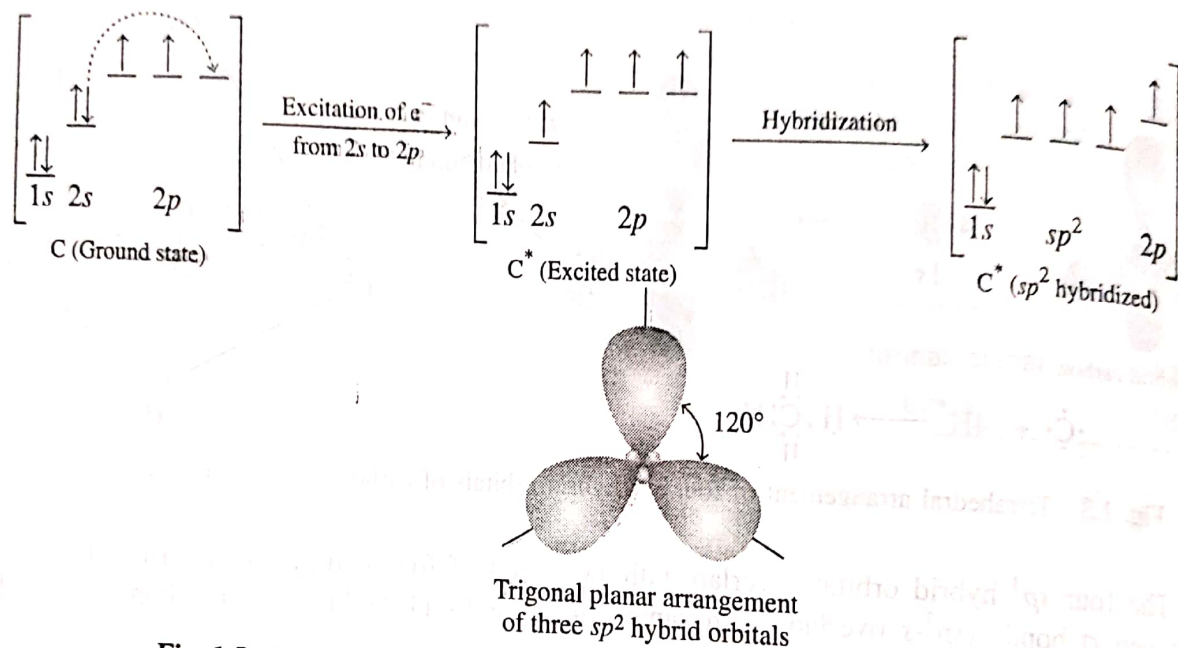


Fig. 1.5 Excitation and sp^2 hybridization of the atomic orbitals of carbon.

Each carbon has three planar sp^2 hybrid orbitals, that is, in all six hybrid orbitals are available. The sp^2-sp^2 overlap results in C-C σ bond formation and sp^2-s overlap results in four C-H σ bonds (1.08 \AA).

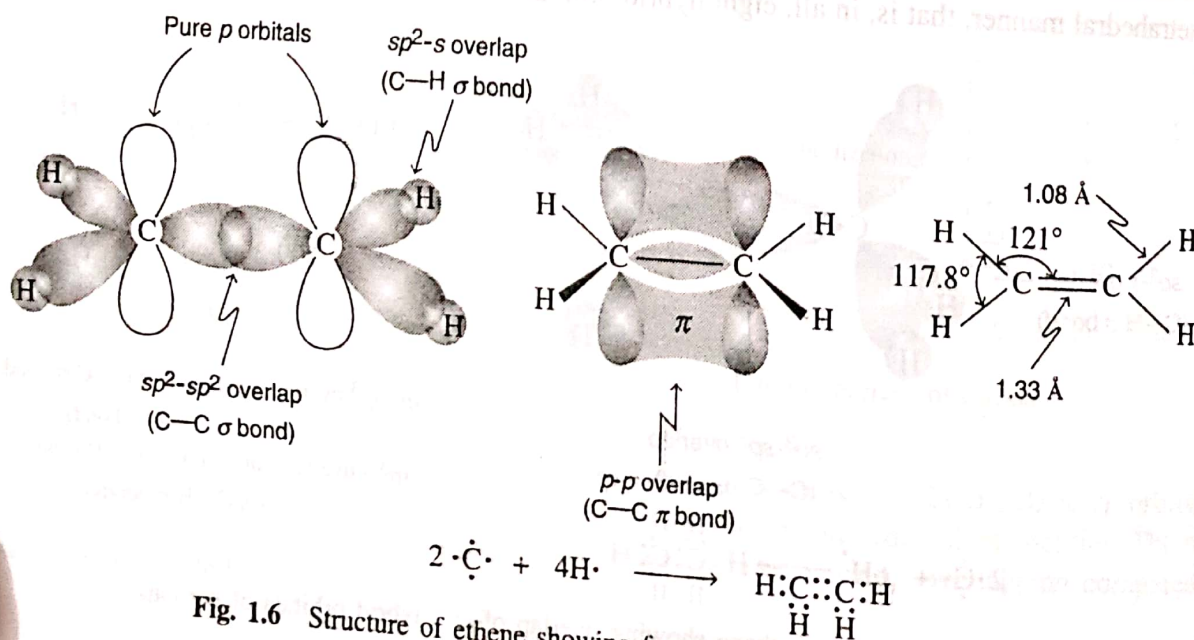
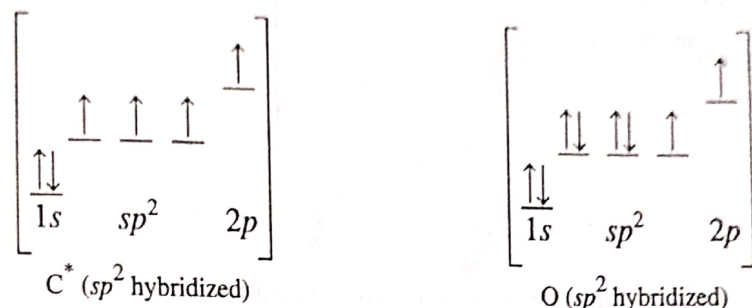


Fig. 1.6 Structure of ethene showing formation of σ and π bonds.

Each carbon has a pure p orbital (does not participate in hybridization) and overlap of these two p orbitals results in the formation of a π bond. Since π bond is formed by collateral (sideways) overlapping of p orbitals of carbon, it is relatively weaker than σ bond.

Structure of formaldehyde (CH_2O)

In general, sp^2 hybridization results in the formation of double bond. For example, formaldehyde ($\text{H}_2\text{C}=\text{O}$) where both carbon and oxygen are sp^2 hybridized.



Carbon has three hybrid orbitals (each having single electron). Oxygen too, has three hybrid orbitals (two having paired electrons and one with single electron). The carbon-oxygen σ bond is formed by the overlap of one of the sp^2 orbitals of carbon and sp^2 orbital of oxygen containing single electron. The remaining two sp^2 hybrid orbitals on carbon form two C-H σ bonds by overlapping with $1s$ orbitals of the two hydrogens. The hybrid orbitals of oxygen contain two lone pairs of electrons. The overlap of pure p orbitals of carbon as well as of oxygen forms a carbon-oxygen π bond.

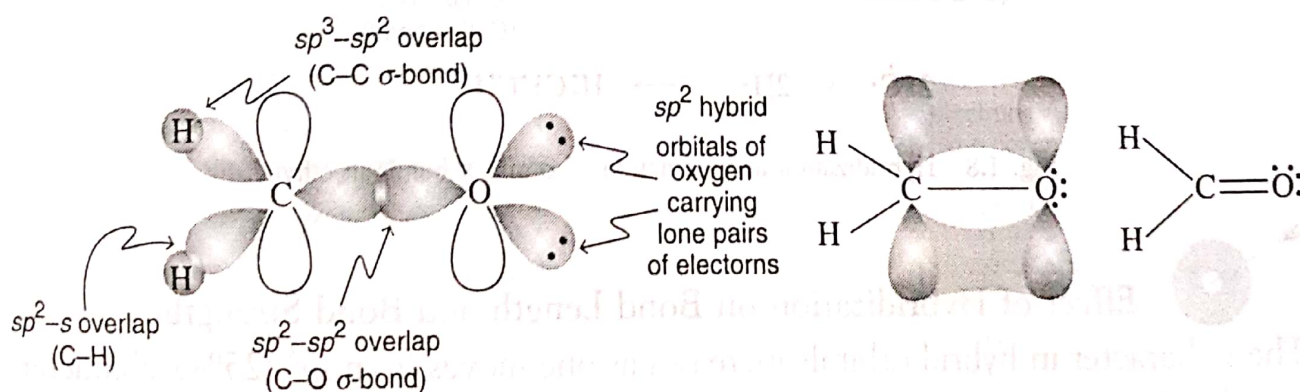


Fig. 1.7 Hybridization and formation of σ and π bond in formaldehyde.

1.4.3 sp Hybridization

Structure of ethyne (acetylene, C_2H_2)

The combination of one s and one p orbital results in the formation of two sp hybrid orbitals. The two sp hybrid orbitals are linearly arranged (bond angle 180°) to have minimum electronic

repulsion. In acetylene, the two carbons are sp hybridized. Each carbon has two hybrid orbitals, the sp - sp overlap from each carbon results in carbon-carbon σ bond formation whereas sp - s overlap results in the formation of two C-H σ bonds. Each carbon has two pure p orbitals (mutually perpendicular) and their overlap results in the formation of two π bonds.

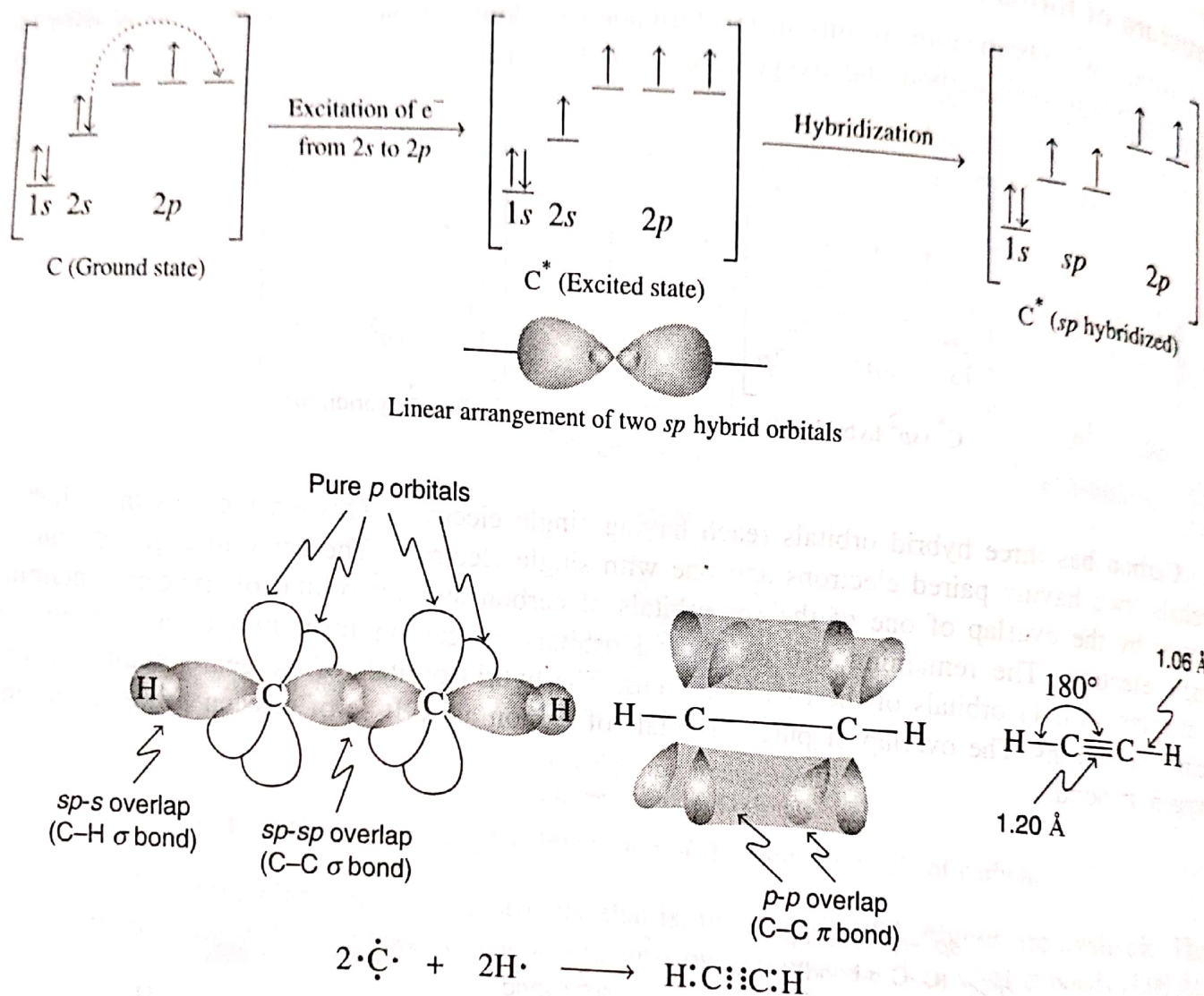


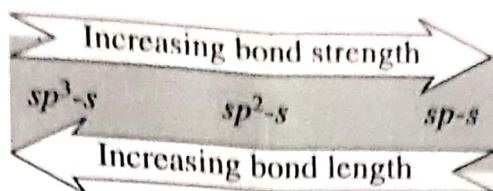
Fig. 1.8 Hybridization and formation of σ and π bonds in ethyne.



Effect of Hybridization on Bond Length and Bond Strength

The s character in hybrid orbitals increases as one moves from sp^3 (25% s character) to sp^2 (33% s character) to sp (50% s character). The s orbitals are spherical and electrons are closer to nucleus. Thus, the higher the s character of hybrid orbital, more effective its overlap with the other atomic orbitals or hybrid orbitals is. This causes an increase in bond strength and decrease in the bond length of the system with an increase in ' s ' character of overlapping orbitals.

Order of bond strength and bond length of C-H bond



Order of bond strength and bond length of C-C bond

