

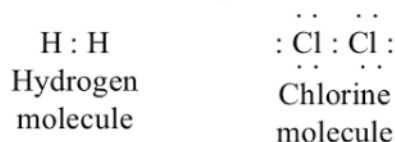
2.8 POLARITY OF BONDS

Covalent bonds are of two types:

- (i) Non-polar covalent bond. (ii) Polar covalent bond.

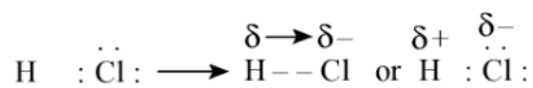
(i) **Non-polar covalent bond:** In the non-polar covalent bonds, the two atoms have equal electronegativity, i.e., equally attract the pair of shared electrons.

Thus, the electron pair is shared equally between two atoms, e.g., the covalent bond in H_2 and Cl_2 is non-polar. As a result, the molecule is neutral or non-polar.



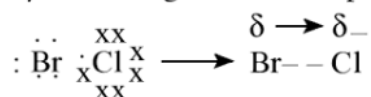
(ii) **Polar covalent bond:** In the case of polar covalent bonds, the two atoms have unequal electronegativities or the electron pair is shared unequally. For example, in HCl , the electron pair is more attracted or displaced towards chlorine, as it is more electronegative than hydrogen. Due to this, chlorine end of the molecule appears negative and the hydrogen end appears positive. Such molecules having the oppositely charged poles are called **polar molecules** and the bond is said to be a **polar covalent bond**.

Displaced to Cl atom



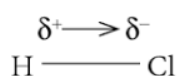
Similarly, $BrCl$ molecule is a polar molecule, as chlorine is more electronegative than bromine. The shared electron pair is more attracted towards chlorine than towards bromine. As a result, the chlorine end of the molecule is negative and the bromine end is positive.

If there is a single bond in a molecule, the molecular dipole moment is the same as that of the individual bond, e.g., molecular dipole moment of HCl is the same as that of single HCl bond, i.e., 1.03 D. In case of the molecule having more than one polar bond, the molecular dipole moment is not measured by the values of individual bonds but by the arrangement of the polar bonds in space.



2.8.1 Polar Character of Covalent Bond

When a covalent bond is formed between two dissimilar atoms, one of which has larger value of electronegativity and the bonding pair of electrons is displaced towards the more electronegative atom. In other words, electron cloud containing the bonding electrons gets distorted and the charge density gets concentrated around the more electronegative atom and it acquires a partial negative charge (indicated by δ^-), where as less electronegative atom acquires a partial positive charge (indicated as δ^+). Such a bond is called a polar covalent bond and it develops a partial ionic character. It is represented by an arrow pointing towards the more electronegative atom as shown in the case of hydrochloric acid



Whereas the covalent bond between two similar atoms is called *non-polar covalent bond*, as the shared pair of electrons lies midway between the nuclei of two atoms (Fig. 2.12).

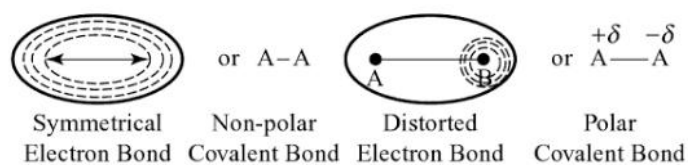


Figure 2.12 Polarity of covalent bond

The extent of ionic character in a covalent bond depends upon the difference of electronegativities of the atoms forming a covalent bond. A bond is considered to be ionic if it has more than 50% ionic character. If the difference in electronegative values of the two bonded atoms is more than 2, it is primarily ionic. The difference of about 1.17 gives 50% ionic character.

2.9 DIPOLE MOMENT

The degree of polarity developed in polar molecule is expressed in terms of dipole moment.

Dipole moment may be defined as the product of the magnitude of charge on either atom and the distance between the centres of the nuclei of bonding atoms forming a polar covalent bond.

Dipole moment is represented by Greek letter μ and is expressed as:

$$\text{Dipole moment, } = e \times d \quad (2.21)$$

where e is the charge on either atom and d is the distance between them.

2.9.1 Unit of Dipole Moment

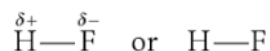
Since charge is of the order of 10^{-10} esu and distance is of the order of 10^{-8} cm, dipole moment is of the order of 10^{18} esu-cm and this unit is known as Debye unit (D), i.e.

$$1 \text{ D} = 10^{-18} \text{ esu-cm}$$

In S.I. system, the unit of dipole moment is coulomb metre, C-m.

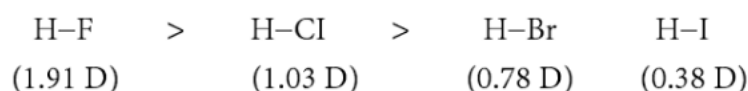
$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C-m.}$$

Dipole moment is a vector quantity and can be determined experimentally. It can be represented by an arrow pointing towards negative charge with a small tail at the positive charge, e.g.,

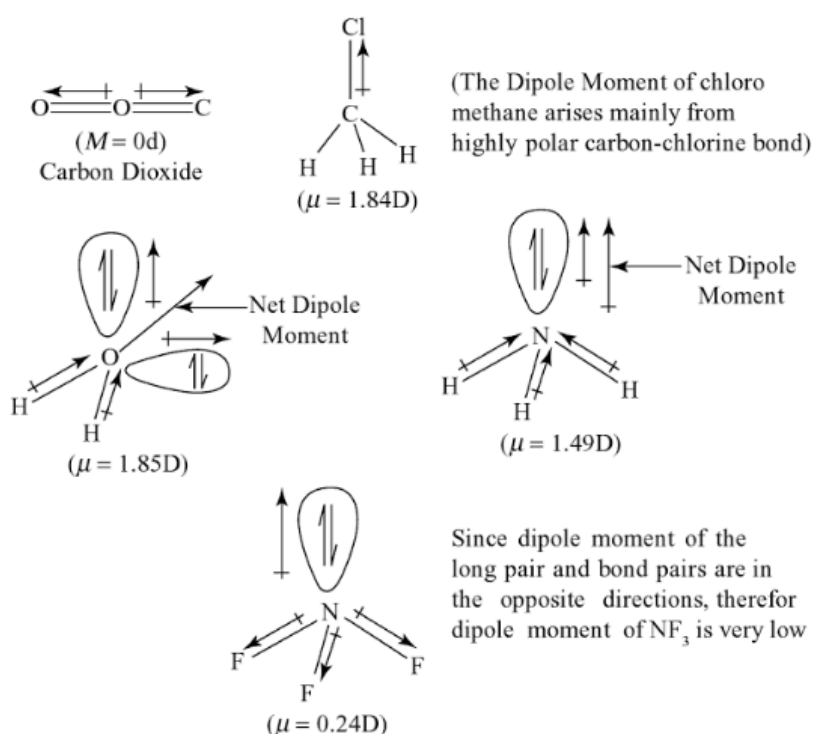


2.9.2 Dipole Moment and Molecular Structure

- (i) **Diatomic molecules:** Dipole moment is a vector quantity, i.e., it has magnitude as well as direction. As a polar diatomic molecule has only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond. Thus, the greater the electronegativity difference between the bonded atoms is, the greater is the dipole moment. For example, the dipole moments of hydrogen halides are in the order:



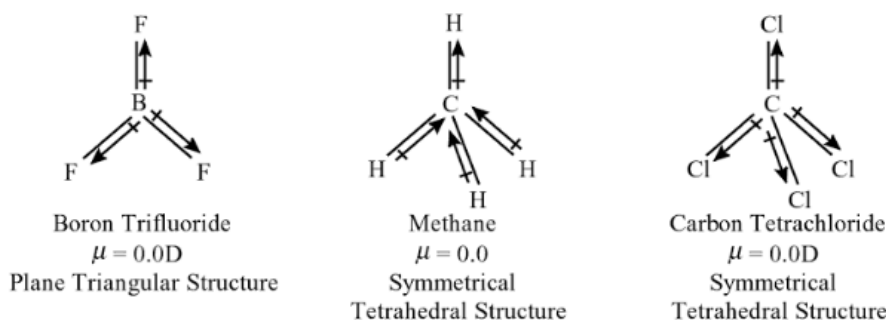
- (2) **Polyatomic molecules:** As polyatomic molecule has more than one polar bond, the dipole moment of the molecule is equal to the resultant dipole moment of all the individual bonds (called *bond moments*). The dipole moments of lone pairs also make their contribution to the resultant dipole moment. The magnitude of the resultant dipole moment not only depends upon the values of individual moments but also on their arrangements in space i.e shape. For example, CO_2 has linear structure because the dipole moment of one $\text{C}=\text{O}$ and is cancelled by that of the other $\text{C}=\text{O}$ bond. Water has angular V-shaped structure. It has a net value of dipole moments ($= 1.85 \text{ D}$), which the resultant of two $\text{O}-\text{H}$ bonds. The effect of two lone pairs on the oxygen atom is cancelled mutually. Ammonia molecule has pyramidal shape and has a net resultant value of dipole moment ($= 1.46 \text{ D}$) due to unsymmetrical structure.



2.9.3 Application of Dipole Moments

- (i) **To distinguish polar and non-polar molecules:** The molecules having zero dipole moment are non-polar, e.g., O_2 , CO_2 , CCl_4 , CH_4 , CS_2 , SiF_4 , SnCl_4 and BF_3 . The bonds of such molecules may be polar or non-polar. The molecules having dipole moments are polar, e.g., NH_3 , H_2O and HF .

- (ii) **To predict degree of polarity:** Dipole moments help in determining the degree of polarity developed in molecules. More the dipole moment is, the more will be the degree of polarity in molecules. For example, HF has more dipole moment than HCl. Thus, HF is more polar than HCl.
- (iii) **To predict the shape or the symmetry of molecules:** Dipole moment helps to determine the shape of the molecules. Tri and polyatomic molecules having zero double moment have **symmetrical structure**.

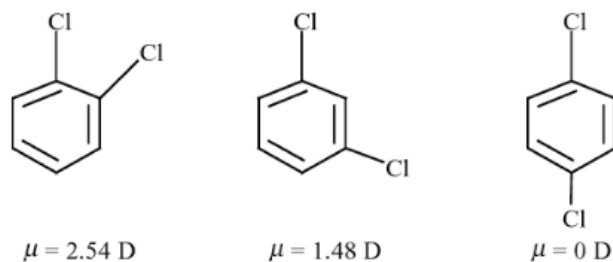


The bonds in such molecules (being polar in nature) have some dipole moment. However, the resultant dipole moment becomes zero due to symmetrical structure.

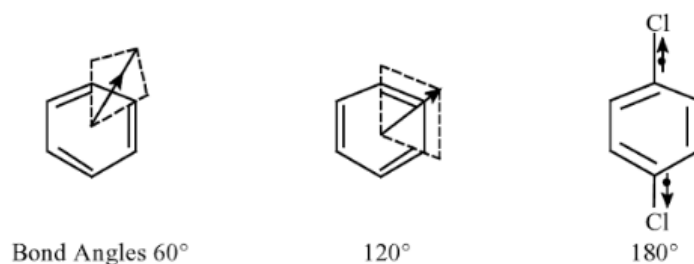
- (iv) **To distinguish *cis*- and *trans*-isomers:** *Trans*-isomer has almost zero dipole moment, whereas *cis*-isomer has significant dipole moment, e.g.,



- (v) **To distinguish *ortho*-, *meta*- and *para*-isomer:** The position of the two electronegative atoms/groups in the benzene ring, i.e., *o*-, *m*- and *p*-isomers.



The role of bond angle in the dipole moment is explained as



Bond angle in *ortho*-derivative is less than that of *meta*-isomer. From the above examples of *o*-, *m*- and *p*-dichlorobenzenes, it is clear that **as the angle between the polar bonds increase, the dipole moment decreases.**

- (vi) **Calculation of percentage ionic character:** This may be illustrated by taking an example of HCl. The dipole moment of HCl is 1.03 D and its bond length is 1.275 Å. If the bond in HCl were 100% ionic, its dipole moment would have been

$$= (4.8 \times 10^{-10}) \times (1.275 \times 10^{-8}) \text{ esu-cm}$$

where 4.8×10^{-10} esu is one unit charge which would have been present on end in case the molecule was 100% ionic.

$$= 6.11 \times 10^{-18} \text{ esu-cm} = 6.11 \text{ D}$$

Actual dipole moment of HCl = 1.03 D

$$\text{Hence, percentage ionic character} = \frac{1.03}{6.11} \times 100$$

$$= 17\% \text{ (approximately)}$$

- (vii) **Bond moments:** The contribution of an individual bond towards the dipole moment of a polyatomic molecule is called bond moment. This can be calculated as illustrated below by taking an example of water molecule.

The dipole moment of water as found experimentally is 1.85 Debyes. This value of dipole moment is supposed to be the vectorial sum of the individual bond moments of the two –OH bonds directed at an angle of 104.5° (see Fig. 2.13).

Thus, the dipole moment of water is given by,

$$\mu_{\text{observed}} = 2\mu_{\text{OH}} \cos \frac{104.5}{2}$$

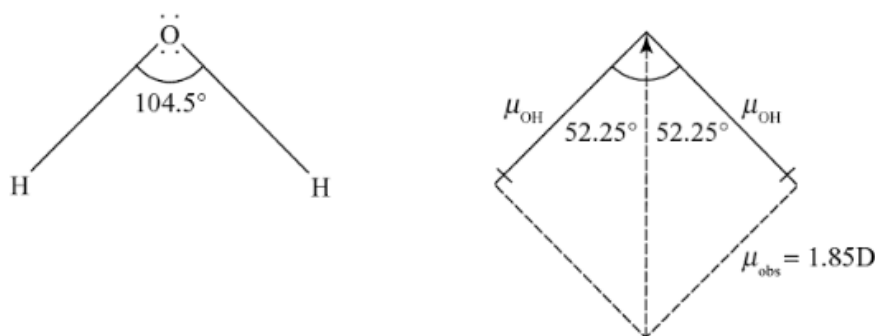


Figure 2.13 Calculation of bond moment

$$\mu_{\text{observed}} = 2\mu_{\text{OH}} \cos 52.25^\circ$$

$$\mu_{\text{observed}} = 2\mu_{\text{OH}} \times 0.6129$$

However, μ_{observed} in case of water = 1.85 D

$$\therefore 1.85 = 2\mu_{\text{OH}} \times 0.6129$$

or
$$\mu_{\text{OH}} = \frac{1.85}{2 \times 0.6129} = 1.51 \text{ Debyes}$$

The values of calculated bond moments of some bonds are given in Table 2.6.

Table 2.6 Bond moments of some common bonds.

Bond	Dipole Moment (Debye)	Bond	Dipole Moment
H-F	1.9	F-Cl	0.9
H-Cl	1.0	F-Br	1.3
H-Br	0.8	Br-Cl	0.6
H-I	0.4	C-H	0.4
H-O	1.5	C-F	1.4
H-N	1.3	C-Cl	1.5
H-P	0.4	C-Br	1.4
P-Cl	0.8	C-I	1.2
P-Br	0.4	C-O	0.7
As-F	2.0	C-N	0.2
As-Cl	1.6	C-O	2.3
AS-Br	1.3	C-NO ₂	3.54

Lorentz – Lorenz Equation

A light wave is electromagnetic in nature, *i.e.*, it has rapidly changing electric and magnetic fields associated with it. The electric field of the light wave polarizes the medium through which it passes, pulling the electrons back and forth rapidly. Maxwell in his electromagnetic theory of light showed that at optical frequencies the dielectric constant (*i.e.*, relative permittivity) and the refractive index of the medium are related as follows :

$$\epsilon_r \approx n_r^2 \quad \dots(29)$$

This relation, known as the **Maxwell relation**, holds only when the permanent dipole moment of a molecule does not contribute to ϵ_r and hence to P_m .

Thus, at optical frequencies, substitution of the Maxwell relation into the Clausius-Mosotti equation (Eq. 14) yields

$$P_m = R_m = \frac{n_r^2 - 1}{n_r^2 + 2} V_m = \frac{N_A \alpha_d}{3\epsilon_0} \quad \dots(30)$$

where R_m is called *molar refraction*. Eq. 30 is known as the **Lorentz-Lorenz equation**. Using this equation, one can determine induced polarizations from the refractive index measurements. If these data are combined with dielectric data, the dipole moment can be determined from the Debye equation.

Eq. 30 can also be inverted to give an expression for the refractive index of a medium :

$$n_r = \left(\frac{V_m + 2R_m}{V_m - R_m} \right)^{1/2} \quad \dots(31)$$

Eq. 30 can be rearranged to yield an expression for distortion polarizability, α_d :

Symmetry Elements in Crystal Systems

Besides the interfacial angles, another important property of crystals is their *symmetry*. There are various types of symmetry, only three of which will be described here. These are : (i) *Plane of Symmetry* (ii) *Axis of Symmetry* and (iii) *Centre of Symmetry*.

Plane of Symmetry. When an imaginary plane can divide a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a **plane of symmetry**.

Axis of Symmetry. An axis of symmetry is a line about which the crystal may be

rotated such that it presents the same or similar appearance more than once during the complete revolution.

For example, in the case of a **cube**, an axis passing perpendicularly through the centre is such that when the cube is rotated it presents similar appearance in three rotations of 90° each and the same appearance after the fourth rotation. Such an axis is called a **four-fold** or a **tetrad axis** (Fig. 3a). If the same or similar appearance is repeated after an angle of 180° , the axis is called a **two-fold** or a **diad axis** (Fig. 3b). In the same way, if the same or similar appearance is repeated after an angle of 120° , the axis is called a **three-fold** or **triad axis** (Fig. 3c). If the same or similar appearance is repeated after an angle of 60° , as in the case of a hexagonal crystal, the axis is called a **six-fold** or **hexad axis** (Fig. 3d). In general, if the same or similar appearance of a crystal is repeated on rotation through an angle of $360^\circ/n$, around an imaginary axis, the axis is called an **n-fold axis**. A crystal can have only 2-fold, 3-fold, 4-fold and 6-fold axes of rotation. The angle through which the crystal will have to be rotated to get the same or similar appearance, evidently, will be 180° , 120° , 90° and 60° , respectively.

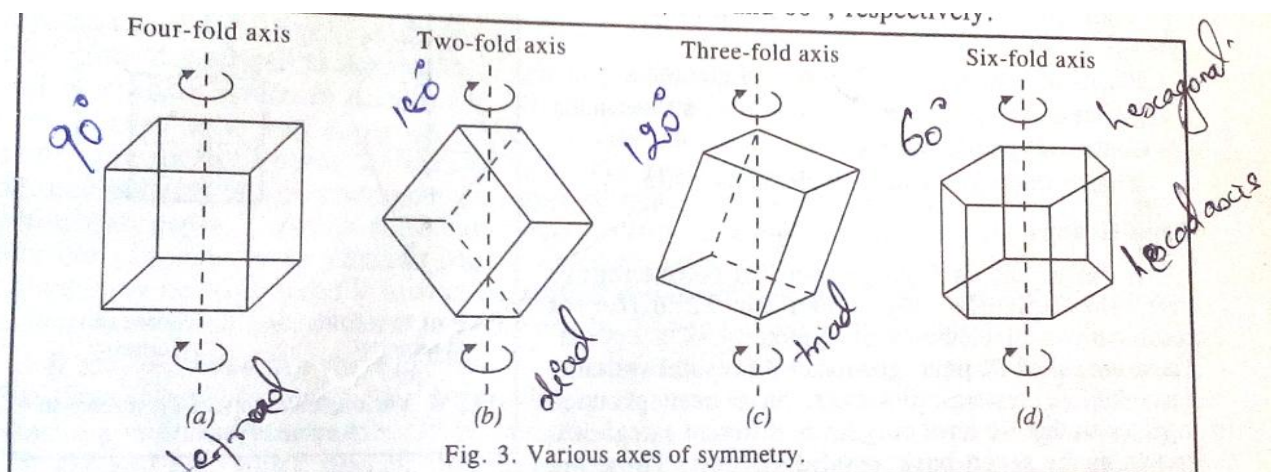


Fig. 3. Various axes of symmetry.

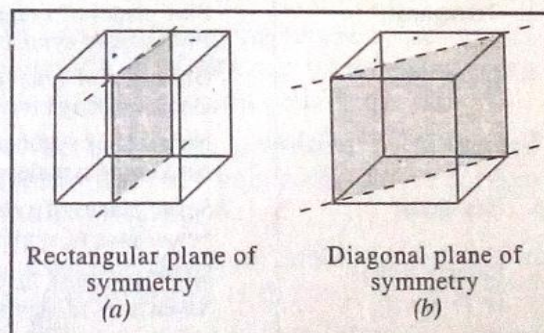
Centre of Symmetry. Centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions.

It may be pointed out that a crystal may have any number of planes or axes of symmetry but it has only **one** centre of symmetry.

Elements of Symmetry of a Crystal. As mentioned above, there are different types of symmetries which are possible in a crystal. A crystal may have different numbers of each type of symmetry. The total number of **planes, axes and centre of symmetries** possessed by a crystal is termed as **elements of symmetry** of the crystal. To explain this term further, we may consider the elements of symmetry possessed by a **cubic crystal**, such as NaCl crystal. A cubic crystal possesses a **total of 23 elements of symmetry**, as will be clear from the discussion given below. These elements of symmetry are :

a. Rectangular planes of symmetry. One rectangular plane of symmetry is shown in Fig. 4a. There will be two more such planes, each of which will be at right angles to the plane shown in the figure. Thus, there are 3 rectangular planes of symmetry in all.

b. Diagonal planes of symmetry. One plane passing diagonally through the cube is shown in Fig. 4b. There can be a total of 6 such planes passing diagonally through the cube, as a little reflection will show.



c. **Axes of four-fold symmetry.** One of the four-fold axes is shown in Fig. 4c. Evidently, there can be a total of 3 such four-fold axes at right angles to one another.

d. **Axes of three-fold symmetry.** One such axis passing through opposite corners is shown in Fig. 4d. There can be a total of 4 such three-fold axes.

e. **Axes of two-fold symmetry.** One such axis emerging from opposite edges is shown in Fig. 4e. There are, evidently, 6 such axes of two-fold symmetry.

f. **Centre of symmetry.** There is only one centre of symmetry lying at the centre of the cube (Fig. 4f).

Thus, the number of symmetry elements of various types in a cubic crystal are :

$$\text{Planes of symmetry} = 3 + 6 = 9 \text{ elements}$$

$$\text{Axes of symmetry} = 3 + 4 + 6 = 13 \text{ elements}$$

$$\text{Centre of symmetry} = 1$$

$$\text{Total number of symmetry elements} = 23$$

