Bond characteristics.

(1) Bond length

"The average distance between the centre of the nuclei of the two bonded atoms is called bond length".

It is expressed in terms of Angstrom (1 Å = 10–10 m) or picometer (1pm = 10–12 m). It is determined experimentally by X-ray diffraction methods or spectroscopic methods. In an ionic compound, the bond length is the sum of their ionic radii (d = r++ r–) and in a covalent compound, it is the sum of their covalent radii (e.g., for HCl, d = rH + rCl).

Factors affecting bond length

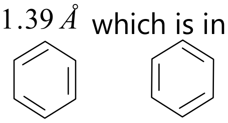
(i) Size of the atoms : The bond length increases with increase in the size of the atoms. For example, bond length of $H-X$ are in the order , $HI > HBr > HCl > HF$

(ii) Electronegativity difference : $\text{Bond length} \times \frac{1}{\Delta \text{EN}}$.

(iii) Multiplicity of bond : The bond length decreases with the multiplicity of the bond. Thus, bond length of carbon–carbon bonds are in the order , $C \equiv C < C = C < C - C$

(iv) Type of hybridisation : As an s-orbital is smaller in size, greater the s-character shorter is the hybrid orbital and hence shorter is the bond length. For example,
$sp^3\ C-H > sp^2\ C-H > sp\ C-H$

(v) Resonance : Bond length is also affected by resonance as in benzene and CO_2. In benzene bond length is $1.39\,\mathring{A}$ which is in between $C-C$ bond length $1.54\,\mathring{A}$ and C = C bond length $1.34\,\mathring{A}$



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In CO_2 the C-O bond length is 1.15 $\mathring{A}$.

(In between $C \equiv O$ and $C = O$)

$O = C = O \leftrightarrow \overline{O} - C \equiv \overset{+}{O} \leftrightarrow \overset{+}{O} \equiv C - \overline{O}$

(vi) Polarity of bond : Polar bond length is usually smaller than the theoretical non-polar bond length.

(2) Bond energy

“The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation energy or simply bond energy”. Greater is the bond energy, stronger is the bond.

Bond energy is usually expressed in $kJ\,mol^{-1}$.

Factors affecting bond energy

(i) Size of the atoms : Bond energy $\propto \frac{1}{\text{atomic size}}$ Greater the size of the atom, greater is the bond length and less is the bond dissociation energy i.e. less is the bond strength.

(ii) Multiplicity of bonds : For the bond between the two similar atoms, greater is the multiplicity of the bond, greater is the bond dissociation energy. This is firstly because atoms come closer and secondly, the number of bonds to be broken is more, $C-C < C=C < C \equiv C$, $C \equiv C < C \equiv N < N \equiv N$

(iii) Number of lone pairs of electrons present : Greater the number of lone pairs of electrons present on the bonded atoms, greater is the repulsion between the atoms and hence less is the bond dissociation energy. For example for a few single bonds, we have

Bond	C – C	N – N	O – O	F – F
Lone pair of electrons	0	1	2	3
Bond energy (kJ mol–1)	348	163	146	139

(iv) Percentage s–character : The bond energy increases as the hybrid orbitals have greater amount of s orbital contribution. Thus, bond energy decreases in the following order, $sp > sp^2 > sp^3$

(v) Bond polarity : Greater the electronegativity difference, greater is the bond polarity and hence greater will be the bond strength i.e., bond energy, $H-F > H-Cl > H-Br > H-I$,

(vi) Among halogens Cl – Cl > F – F > Br – Br > I – I, (Decreasing order of bond energy)

(vii) Resonance : Resonance increases bond energy.

(3) Bond angle

In case of molecules made up of three or more atoms, the average angle between the bonded orbitals (i.e., between the two covalent bonds) is known as bond angle θ.

Factors affecting bond angle

(i) Repulsion between atoms or groups attached to the central atom : The positive charge, developed due to high electronegativity of oxygen, on the two hydrogen atoms in water causes repulsion among themselves which increases the bond angle, H–O–H from 90º to 105º.

(ii) Hybridisation of bonding orbitals : In hybridisation as the s character of the s hybrid bond increases, the bond angle increases.

Bond type	sp3	sp2	sp
Bond angle	109º28′	120o	180o

(iii) Repulsion due to non-bonded electrons : Bond angle $\propto \frac{1}{\text{No. of lone pair of electrons}}$. By increasing lone pair of electron, bond angle decreases approximately by 2.5%.

	CH4	NH3	H2O
Bond angle	109º	107o	105o

(iv) Electronegativity of the atoms : If the electronegativity of the central atom decreases, bond angle decreases.

	H_2O	$> H_2S$	$> H_2Se$	$> H_2Te$
Bond angle	104.5^o	92.2^o	91.2^o	89.5^o

In case the central atom remains the same, bond angle increases with the decrease in electronegativity of the surrounding atom, e.g.

	PCl_3	PBr_3	PI_3 ,	$AsCl_3$	$AsBr_3$	AsI_3
Bond angle	100^o	101.5^o	102^o	98.4^o	100.5^o	101^o

Example: Energy required to dissociate 4 grams of gaseous hydrogen into free gaseous atoms is 208 kcal at 25oC the bond energy of H–H bond will be

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(a) $104\ Kcal$ (b) $10.4\ Kcal$ (c) $20.8\ Kcal$ (d) $41.6\ Kcal$

Answer: (a) 4 gram gaseous hydrogen has bond energy 208 kcal

So, 2 gram gaseous hydrogen has bond energy $= \frac{208}{2} kcal$ = 104 kcal.

Important Tips

More directional the bond, greater is the bond strength and vice versa. For example :

$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp > p - p > s - p > s - s$

The hybrid orbitals with more p-character are more directional in character and hence of above order.

The terms 'bond energy' and 'bond dissociation' energy are same only for di-atomic molecules.

The order of O–O bond length in O2, H2O2 and O3 is H2O2 > O2 > O3

Because of higher electron density and small size of F atom repulsion between electron of it two F atoms, weakens the F-F bond.

The bond length increases as the bond order decreases.

Carbon monoxide (CO) has the highest bond energy(1070 $kJmol^{-1}$) of all the diatomic molecules. Bond energy of $N_2(946\,kJmol^{-1})$ and that of H2(436 kJmol-1) are other diatomic molecules with very high bond energies.