INTER-HALOGEN COMPOUNDS

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Introduction:

Halogen elements have different electro-negativity. Due to this they combine with each other to form covalent compounds (binary).

"The binary compounds formed by halogens amongst themselves are known as Inter-halogen compounds". These compounds have general formula; XY_n, where n = 1, 3, 5 & 7.

Ternary compounds of halogens are not known; as such a complex molecule might be unstable.

Classification:

Table 3.1 Various types of inter-halogen compounds

Element	Fluoride	Chloride	Bromide	Iodide
Fluorine	------	------	------	------
Chlorine	ClF, ClF_3, ClF_5	------	------	------
Bromine	BrF, BrF_3, BrF_5	$BrCl$	------	------
Iodine	IF, IF_3, IF_5, IF_7	ICl, ICl_3	IBr	------

From table 3.1, the following points may be noted.

- The inter-halogen compounds may be regarded as the halide of the more electronegative halogen. Thus, since the electro positive character of halogens is in the order $F < Cl < Br < I$, fluorine cannot form any inter-halogen compounds, while iodine has the maximum tendency to form inter-halogen compounds.
- Since F has the least electropositive character, amongst inter-halogen compounds, the fluorides are maximum in number.
- Inter-halogens can be grouped into four categories: XY, XY_3, XY_5, and XY_7. Here X halogen atom is more electropositive and larger in size than Y halogen atom.
- The oxidation state of atom X in XY, XY_3, XY_5, and XY_7 molecules is equal to +1, +3, +5 and +7 respectively.
- As the ratio between the radii of X and Y atoms increases, the number of halogen atoms per molecule increases.

I. Inter-halogen compounds of XY type(Diatomic inter-halogens):

Preparation:

- These are generally prepared by the direct combination of halogens e.g.,

$Br_{2\,(g)} + F_{2\,(g)} \rightarrow 2\,BrF$; $Br_2 + Cl_2 \rightarrow 2\,BrCl$

$I_2 + Cl_2\,(l)$ (in equal amount) $\rightarrow 2\,ICl$; $I_2 + F_2 \rightarrow 2\,IF$ (at -45^0C)

$$Cl_2 + F_2 \text{ (in equal amounts)} \xrightarrow[\text{Cu-vessel}]{250^0\,C} 2\,ClF$$

- Some of them can be prepared by other methods,

$$Cl_2 + ClF_3 \xrightarrow{300^0\,C} 3\,ClF$$

$Cl_2 + ClF_3 \xrightarrow{300^0\,C} 3\,ClF$; $Br_2 + BrF_3 \longrightarrow 3BrF$

$I_2 + AgF \longrightarrow IF + AgI$; $I_2 + KClO_3 \xrightarrow{\Delta} ICl + KIO_2$

Properties:

i. These are covalent gases because of small difference in electro-negativities between the two halogen atoms.

ii. *Stability:* They differ in thermal stability. For example, ClF is extremely stable and dissociate when heated strongly:

$2\,ClF \rightarrow Cl_2 + F_2$, while IBr dissociate to a small extent into I_2 and Br_2 when heated.

BrF and IF are unstable and undergo disproportionation rapidly.

$3\,BrF \rightarrow Br_2 + BrF_3$; $5\,IF \rightarrow 2\,I_2 + IF_5$

The stability of XY type inter-halogen compounds with respect to disproportionation is in the order:

ClF > ICl > IBr > BrCl >BrF

iii. *Hydrolysis:* Generally hydrolysis of these compounds give oxy acids and hydrohalic acid. For example:

$BrCl + H_2O \rightarrow HOBr + HCl$

$5ICl + 3H_2O \rightarrow HIO + 5HCl + 2I_2$; $ICl + H_2O \rightarrow HOI + HCl$

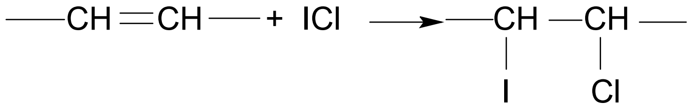
iv. *Action of metals and non-metals:*

$Se + 4\,ClF \rightarrow SeF_4 + 2\,Cl_2$; $ICl + 2Na \rightarrow NaI + NaCl$

$W + 6\,ClF \rightarrow WF_6 + 3\,Cl_2$

v. *Action of alkali metal halides and olefins:* With alkali metal halides, polyhalides are formed while inter-halogens add to olefins at double bond sites.

$KCl + ICl \rightarrow K[ICl_2]$; $NaBr + IBr \rightarrow Na[IBr_2]$



$$—CH{=}CH— + ICl \longrightarrow —\underset{I}{CH}—\underset{Cl}{CH}—$$

vi. *Lewis acid strength:* The Lewis acid strength of these compounds decreases in the order: ICl >> BrCl > IBr > I_2 *Reactivity:* These compounds are more reactive than each of the halogen molecules because X-Y bond dissociation energy is less than that of X-X bond.

1. Iodine monochloride, ICl:

Pretaration:

- It is formed by mixing I_2 and Cl_2 in equal amounts.

  $I_2 + Cl_2$ (equal amounts) $\rightarrow 2\,ICl$
- By heating I_2 with $KClO_3$

  $KClO_3 + I_2 \rightarrow KIO_3 + ICl$
- By heating ICl_3 at 68^0 C

Properties:

i. It is dark liquid with b. p. 97.4^0 C.

ii. ICl exists in two solid form as given below:

- Solid form: This form melts at 27.2^0 C and is obtained as needle like crystals on cooling the liquid rapidly.
- Metastable form: This form melts at 14^0 C and is obtained as a black solid on cooling the liquid slowly at 100^0 C.

iii. Hydrolysis: ICl dissolve in water and gets hydrolyzed as:

$ICl + H_2O \rightleftharpoons IOH + HCl$

$3\,ICl + 3\,H_2O \rightleftharpoons HIO_3 + 3\,HCl + 3\,HI$

$5\,ICl + 3\,H_2O \rightleftharpoons HIO_3 + 5\,HCl + 2\,I_2$

The hydrolysis can be prevented adding HCl

iv. ICl decomposed by excess of KOH as:

$3\,ICl + 6\,KOH \rightarrow 3\,KCl + 2\,KI + KIO_3 + 3\,H_2O$

v. In liquid state ICl undergoes auto-ionization as:

$2\,ICl \rightleftharpoons I^+$ (Solvent cation) + ICl_2^- (Solvent anion)

Metal halide give I^+ ions in liquid ICl hence it behaves as Lewis acid.

$AlCl_3 + ICl \rightleftharpoons I^+ + AlCl_4^-$; $TiCl_4 + ICl \rightleftharpoons I^+ + TiCl_5^-$

$MCl_5 + ICl \rightleftharpoons I^+ + MCl_6^-$; (M=Sb, Rb)

Alkali metal chloride gives ICl_2^- ion in liquid ICl and therefore acts as bases.

$MCl + ICl \rightleftharpoons M^+ + ICl_2^-$, (M=K, Rb)

vi. Bromide like KBr, $[(CH_3)_4N]Br$ etc. , reacts with ICl, polyhalide ion is produced.

$ICl + KBr \rightleftharpoons K^+[ClBrI]^-$

$ICl + [(CH_3)_4N]Br \rightleftharpoons [(CH_3)_4N]^+[ClBrI]^-$

vii. Excess of Cl_2 convert ICl into ICl_3

Cl_2 (excess) + $ICl \rightarrow ICl_3$

viii. When molten ICl is electrolyzed, a mixture of I_2 and Cl_2 is liberated at anode and I_2 is liberated at cathode. This suggests that ICl ionizes as:

$2\,ICl \rightleftharpoons I^+$ (Solvent cation) + ICl_2^- (Solvent anion)

Reaction at cathode: $2I^+ + 2\,e^- \rightarrow I_2$ (reduction)

Reaction at anode : $2\,ICl_2^- \rightarrow I_2 + 2\,Cl_2 + 2\,e^-$ (oxidation)

Uses:

- A solution of ICl is used as catalyst in the oxidation of As(III) oxide by ceric sulphate and for preparation of polyhalides.
- The solution of ICl in glacial acetic acid is used for determining the iodine value of oil by Wiz's method.

2. Chlorine monofluoride, ClF:

Preparation:

- It is prepared by the action of Cl_2 on F_2 or ClF_3.

$Cl_2 + F_2 \xrightarrow{250^0\,C} 2\,ClF$; $Cl_2 + ClF_3 \xrightarrow{300^0\,C} 3\,ClF$

Properties:

i. It is colourless gas having m. p. -156^0 C.

ii. On heating it dissociate as: $2ClF \rightleftharpoons Cl_2 + F_2$

iii. *Fluorination reactions:* Metals are converted in their fluorides.

$Se + 4\,ClF \rightarrow SeF_4 + 2\,Cl_2$; $W + 6\,ClF \rightarrow WF_6 + 3\,Cl_2$

iv. ClF acts as a *chorofluorinating agent* as under.

$CO + ClF \rightarrow COFCl$; $SF_4 + ClF \rightarrow SF_5Cl$

$SO_2 + ClF \rightarrow SO_2FCl$

3. Iodinemonobromide, IBr:

Preparation:

➢ It is prepared by direct combination of the elements.

$I_2 + Br_2 \rightarrow 2\,IBr$

Properties:

i. It is hard crystalline solid of grey-violet colour.

ii. Its vapour dissociate to small extent on heating:

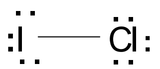
$2\,IBr \rightleftharpoons I_2 + Br_2$

iii. IBr is an electrical conductor in molten state.

$IBr \rightarrow I^+ + Br^-$

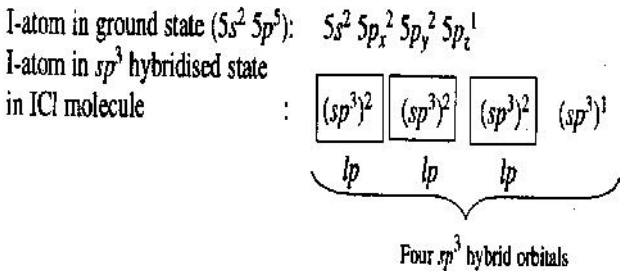
Structure and geometry of XY type Inter-halogen compounds:

Examples of such compounds are ClF, BrF, IF, BrCl, ICl abd IBr. Let us consider example of ICl molecule in which I-atom is the central atom. All these molecules have *linear geometry* which arises because of sp^3 hybridisation of the central halogen atom, iodine.



Lewis strucure of ICl molecule

Lewis structure of this molecule shows that the central I-atom is surrounded by three lone pairs of electrons ane one σ-bonding elctron pair. Thus I-atom is *sp^3* hybridised in ICl molecule.



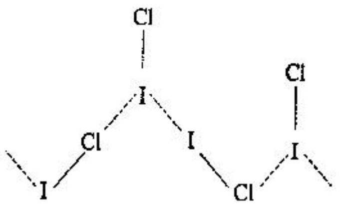


Fig. 3.1 Zig-zag chain of ICl molecule in its α and β–form

I-Cl σ-bond results by the head-to-head overlap between the singly-filled $3p_z$ orbital of Cl-atom and singly filled sp^3 hybrid orbital on I-atom. Although the spatial arrangement of 4-electron pairs round I-atom is tetrahedral, due to the presence of three lone pairs of electrons, the shape of ICl molecule gets distorted and becomes linear. ICl molecule form zig-zag chains in both α and β-form. Both forms differ only whether Cl-branches are cis (α) or trans (β).

II. Inter-halogen compounds of XY_3 type (Tetra-atomic inter-halogens):

Preparation:

➢ These are generally prepared by direct combination of elements under suitable conditions.

$$Cl_2 + 3\,F_2\,(\text{excess}) \xrightarrow{200\text{-}300^0\,C} 2\,ClF_3;$$

$$Br_2\,(\text{vapour}) + 3\,F_2 \xrightarrow{\text{In presence of } N_2} 2\,BrF_3\,;$$

$$3\,Cl_2\,(\text{excess}) + I_2 \xrightarrow{100^0\,C} 2\,ICl_3$$

- Some of them may be prepared by other methods like:
  $ClF_3 + Br_2 \rightarrow BrF_3 + BrCl$; $ICl + Cl_2 \rightarrow ICl_3$

$$3\,BrF \xrightarrow[\text{rtionation}]{\text{Dispropo-}} BrF_3 + Br_2;\quad I_2O_5 + 10\,HCl \xrightarrow{\Delta} 2\,ICl_3 + 5\,H_2O$$

Properties: Among these compounds, ClF_3 is the most reactive. All have high electrical conductivity and hence undergoes self-ionisation

$2\,ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$; $2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$

1. Chlorine trifluoride, ClF_3:

Preparation:

- It is prepared by action of Cl_2 and F_2 at 200-300^{0}C in Cu vessel.

$Cl_2 + 3\,F_2\,(\text{excess}) \rightarrow 2\,ClF_3$

Properties:

i. It is colourless gas which condenses to give a pale green liquid of b. p. -12^0 C.

ii. It is the most reactive of all XY_3 type compounds and reacts with inert substance also. It ignites material like wood, asbestos etc.

iii. Liquid ClF_3 is electrical conductor which suggest its auto-ionisation.
   $2\,ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$
   It is obvious from the following reaction that MF_5 (M=As, Sb, V) acts as an acid in liquid ClF_3.
   $MF_5 + ClF_3 \rightleftharpoons ClF_2^+\,(\text{Solvent cation}) + MF_6^-$
   It acts as fluorinating agent as follow.

$$U_{(s)} + 3\,ClF_3 \xrightarrow{50\text{-}90^0\,C} UF_6(l) + 3\,ClF$$

   $6\,NiO + 4\,ClF_3 \rightarrow 6\,NiF_2 + 2\,Cl_2 + 3\,O_2$
   $2\,AgCl + ClF_3 \rightarrow 2\,AgF + Cl_2 + ClF$

v. It hydrolysed by water, forming ClOF.
   $ClF_3 + H_2O \rightarrow ClOF + 2\,HF$

vi. It produced HF with NH_3 and N_2H_4.
   $2\,NH_3 + 2\,ClF_3 \rightarrow 6\,HF + N_2 + Cl_2$;
   $2\,N_2H_4 + 4\,ClF_3 \rightarrow 12\,HF + 3\,N_2 + 2\,Cl_2$

vii. With F_2 gives higher inter-halogens.

$$ClF_3 + F_2 \xrightarrow{h\nu} ClF_5$$

Uses: ClF_3 is used as fluorinating agent for preparation of number of metal fluoride, for preparation of metallic polyhalides and in cutting oil well tubes.

2. Iodine trichloride, ICl_3:

Preparation:

- It is obtained by action of excess of Cl_2 on I_2 or on ICl at 100^0 C.
  $3Cl_2\text{ (excess)} + I_2 \rightarrow 2\,ICl_3$; $Cl_2\text{ (excess)} + ICl \rightarrow ICl_3$
- It is formed when dry ICl gas reacts with heated I_2O_5
  $I_2O_5 + 10\,HCl \rightarrow 2\,ICl_3 + 5\,H_2O + 2\,Cl_2$

Properties:

i. It is lemon-yellow solid which fumes readily, soluble in organic solvent, liquid NH_3 and liquid SO_2.

ii. With metal halide it gives crystalline additive products.
$MCl + ICl_3 \rightleftharpoons MICl_4$

iii. With alkali halide it gives polyhalides of $MICl_3F$ type.

iv. ICl_3 is completely hydrolysed by water.
$2\,ICl_3 + 3\,H_2O \rightarrow 5\,HCl + HIO_3 + ICl$

v. It dissociate at 68^0 C giving ICl and Cl_2.
$ICl_3 \rightarrow ICl + Cl_2$

vi. Molten ICl_3 has high electrical conductivity. The liberation of I_2 and Cl_2 at both electrodes indicates that ICl_3 is ionized into ICl_2^+ and ICl_4^- ions as follow.
$2\,ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$
Reaction at anode : $2\,ICl_4^- \rightarrow I_2 + 4Cl_2 + 2e^-$ (oxidation)
Reaction at cathode: $2ICl_2^+ + 2\,e^- \rightarrow I_2 + 2\,Cl_2$ (reduction)

Uses: Used in medicines and for preparation of polyhalides.

3. Bromine trifluoride, BrF_3:

Preparation:

- It is obtained by mixing Br_2 vapour with F_2 in presence of N_2

$$Br_2(g) + 3\,F_2 \xrightarrow{N_2} 2\,BrF_3$$

- By action of ClF_3 on Br_2 at 10^0 C.

$$ClF_3 + Br_2 \xrightarrow{10^0\,C} BrF_3 + BrCl$$

Properties:

i. It is fuming liquid with b. p.125.8^0 C, is very reactive and non corrosive liquid.

ii. It reacts with Br_2 to form BrF : $BrF_3 + Br_2 \rightarrow 3\,BrF$

iii. *Auto-ionisation:* $2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$
The substance making available BrF_2^+, due to above mode of auto-ionisation; acts as acids.
Examples: $AuF_3 + BrF_3 \rightleftharpoons BrF_2^+ + AuF_4^-$
MF_4 (M=Ge, Sn, Ti) + $2\,BrF_2^+ \rightleftharpoons 2\,BrF_2^+ + MF_6^{2-}$
The substance making available BrF_4^- acts as bases.
Examples: MF (M=Li, K, Ag) + $BrF_3 \rightleftharpoons M^+ + BrF_4^-$

iv. *Neutralisation reactions:* These reactions are those in which a compound containing BrF_2^+ ion reacts with that having BrF_4^- ion and salt and solvent are formed.

Acid	Base	Salt	Solvent

$[BrF_2]_2^+[SnF_6]^{2-} + 2\,Ag^+[BrF_4]^- \rightarrow Ag_2[SnF_6] + 4\,BrF_3$

$[BrF_2]_2^+[VF_6]^{2-} + K^+[BrF_4]^- \rightarrow K[VF_6] + 4\,BrF_3$

$[BrF_2]_2^+[AuF_6]^{2-} + Ag^+[BrF_4]^- \rightarrow Ag[AuF_4] + 3\,BrF_3$

VF_5 (Acidic anhydride) + $Ag^+[BrF_4]^-$ (base)

$\rightleftharpoons$ $Ag^+[VF_6]$ (salt) + BrF_3 (solvent)

v. BrF_3 is useful *fluorination agent* as follow.

$6\,M + 2\,BrF_3 \rightarrow 6\,MF + Br_2$; $3\,MCl + BrF_3 \rightarrow 3\,MF + BrCl_3$

$WO_3 + 4\,BrF_3 \rightarrow 2\,WF_6 + 2\,Br_2 + 3\,O_2$

$6\,CuO + 4\,BrF_3 \rightarrow 6\,CuF_2 + 3\,Br_2 + 3\,O_2$

vi. Redox reactions and complex formation:

$3\,K + 4\,BrF_3 \rightarrow 3\,K^+[BrF_4]^- + \frac{1}{2}\,Br_2$

zxc

vii. *Solvolysis reaction:* In these reaction the concentration of $[BrF_2]^+$ and $[BrF_4]^-$ is increased.

$4\,BrF_3(l) + K_2[TiF_6] \rightleftharpoons [BrF_2]_2[TiF_6] + 2\,K[BrF_4]$

$2\,BrF_3(l) + K[PF_6] \rightleftharpoons [BrF_2][PF_6] + K\,[BrF_4]$

viii. Formation of adducts:

$XeF_2 + MF_5 \rightarrow XeF_2.MF_5$ (In BrF_3 solution)

BrF_3 hydrolysed by water with formation of bromine oxy-fluoride.

$BrF_3 + H_2O \rightarrow BrOF_3 + H_2$

Uses:

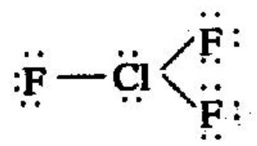
- For preparation of polyhalides.
- For preparation of complex compounds by acid-base reaction, are difficult to prepare by other methods.
- As fluorinating agent.
- For preparation of fluorocomplexes of many metals like Au, Ge, As etc.

Structure and geometry of XY_3 type Inter-halogen compounds:

Examples of such compounds are ClF_3, BrF_3 and IF_3. All these molecules have bent *T-shaped structure* which is due to sp^3d hybridization of the central bigger atom.

Let us discuss the geometry of ClF_3 molecule in which Cl-atom is the central atom. Lewis structure of ClF_3 molecule shows that the central Cl-atom is surrounded by three σ-bps and two lone pairs of electrons and hence Cl-atom is sp^3d hybridized in ClF_3 molecule.

Each of the three Cl-F σ-bonds results by the overlap of singly-filled sp^3d hybrid orbital on Cl-atom and singly-filled $2p_z$ orbital of F-atom.



Lewis structure of ClF_3 molecule

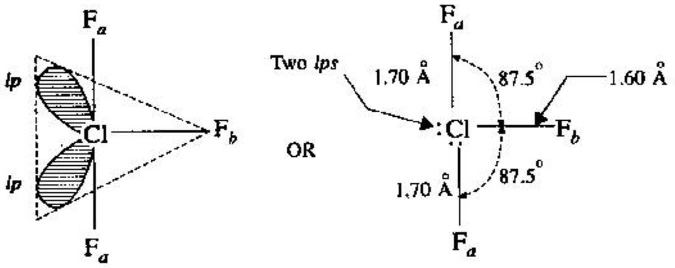


Fig. 3.2 Bent T-shaped structure of ClF_3 molecule

Cl-atom in ground state ($3s^2\ 3p^5\ 3d^0$) : $3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1\ 3d_{z^2}^0$

Cl-atom in excited state ($3s^2\ 3p^4\ 3d^1$) : $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1\ 3d_{z^2}^1$

Cl-atom in sp^3d hybridised state in ClF_3 molecule : $\underbrace{\underset{lp}{\boxed{(sp^3d)^2}}\ \underset{lp}{\boxed{(sp^3d)^2}}\ (sp^3d)^1\ (sp^3d)^1\ (sp^3d)^1}_{\text{Five } sp^3d \text{ hybrid orbitals}}$

Although the spatial arrangement of five electron pairs round the central Cl-atom in space is *trigonal bipyramidal,* due to presence of two lone-pairs of electrons, the shape of ClF_3 molecule gets distorted and becomes *slightly bent T-shaped*. The repulsion between two lps of electrons reduces $F_{(a)}$-Cl-$F_{(b)}$ bond angle from 90^0 to 87.5^0. The basal Cl-$F_{(b)}$ bond length is equal to 1.60 A^0 while each of two axial Cl-$F_{(a)}$ bond length is equal to 1.70 A^0.

Structure of $(ICl_3)_2$ dimeric molecule: ICl_3 is dimeric molecule $(ICl)_2$, in the solid state and has a chlorine-bridged structure in which Cl-atom makes a bridge between two ICl_2 units. It may be seen from strucure that each I-atom is surrounded by four σ-bps and two lps and is sp^3d^2 hybridized.

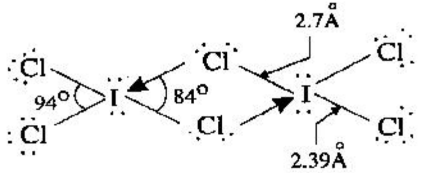


Fig. 3.3 Chlorine-bridged structure of $(ICl_3)_2$ dimer

Two lps of electrons are residing in the axial sp^3d^2 hybrid orbital of the octahedron. Each of the three Cl-I σ-bonds results from the overlap between the singly-filled $3p_z$ orbital of Cl-atom and singly filled sp^3d^2 hybrid orbital on I-atom while Cl→I bond arises by the do--nation of an electron pair on bridging Cl-atom to vacant sp^3d^2 hybrid orbital on I-atom. Formation of 8 bonds between two I-atoms and six Cl-atom in $(ICl_3)_2$ dimeric molecule has been shown in fig. 3.4.

I-atom in ground state

$(5s^2\,5p^5\,5d^0)$: $5s^2\,5p_x^2\,5p_y^2\,5p_z^1\,5d_{z^2}^0\,5d_{x^2-y^2}^0$

I-atom in excited state

$(5s^2\,5p^4\,5d_{z^2}^1,\,5d_{x^2-y^2}^0)$: $5s^2\,5p_x^2\,5p_y^1\,5p_z^1\,5d_{z^2}^1\,5d_{x^2-y^2}^0$

I-atom in sp^3d^2 hybridised state in ICl_4 unit : $\underbrace{\underset{lp}{(sp^3d^2)^2}\ \underset{lp}{(sp^3d^2)^2}\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^0}_{\text{Six } sp^3d^2 \text{ hybrid orbitals}}$

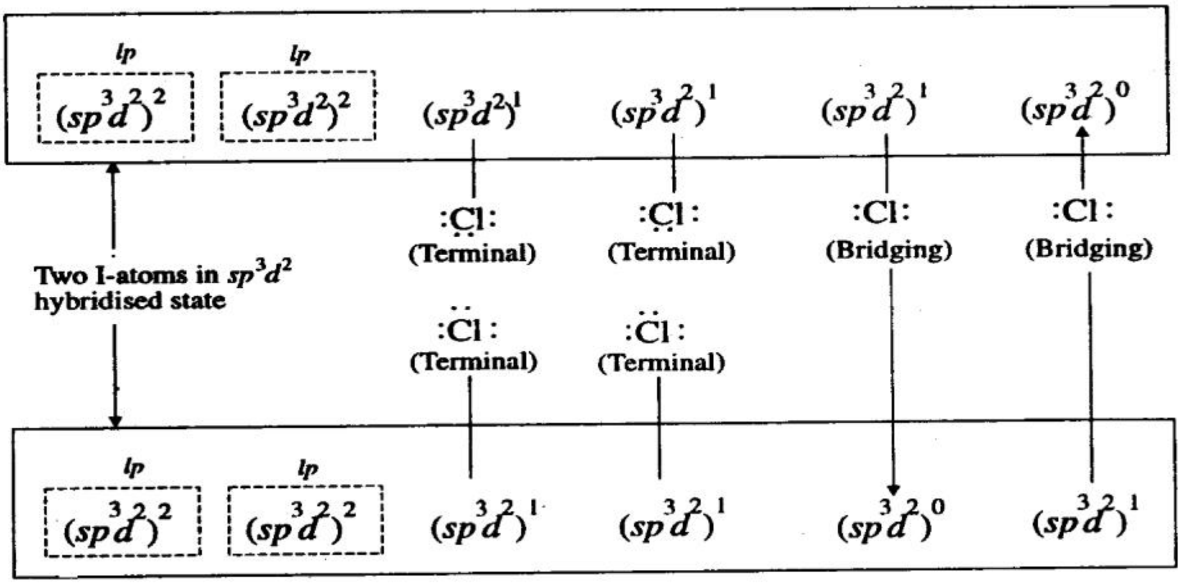


Fig. 3.4 Formation different bonds in dimeric $(ICl_3)_2$ molecule.

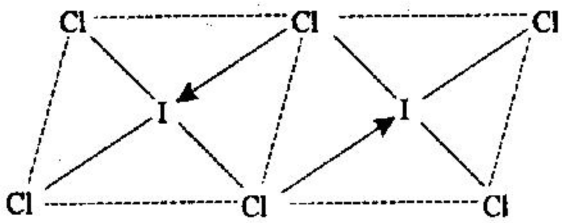


Fig. 3.5 Two ICl_4 squares sharing two bridging Cl-atom in the structure of $(ICl_3)_2$ dimer

Due to presence of two lps in axial position of the octahedron, each ICl_4 unit has square planar structure as shown in fig. 3.5

III. Inter-halogen compounds of XY_5 type (Hexa-atomic inter-halogens):

Preparation:

- These are prepared by direct combination of elements, e.g.,

$$Cl_2 + 5\,F_2 \xrightarrow[250\text{ atm.}]{350^0\text{ C}} 2\,ClF_5; \qquad Br_2 + 5\,F_2\,(\text{excess}) \xrightarrow{>150^0\text{ C}} 2\,BrF_5$$

$I_2 + 5\,F_2$ (excess) → $2\,IF_5$

- These can also be prepared by other methods, e.g.,

$$ClF_3 + F_2 \xrightarrow{h\nu} ClF_5\,; \qquad KBr + 3\,F_2 \xrightarrow{25^0\text{ C}} KF\,(s) + BrF_5$$

1. Chlorine pentafluoride(ClF_5) and bromine pentafluoride(BrF_5):

Preparation:

i. ClF_5 is prepared by the action of F_2 on Cl_2 or ClF_3

$$Cl_2 + 5\,F_2 \xrightarrow[250\text{ atm.}]{350^0\text{ C}} 2\,ClF_5; \qquad ClF_3 + F_2 \xrightarrow{h\nu} ClF_5$$

ii. BrF_5 is obtained by the action of F_2 on Br_2 or KBr.

$$Br_2 + 5\,F_2\text{ (excess)} \xrightarrow{\geq 150^0\text{ C}} 2\,BrF_5\ ; \quad KBr + 3\,F_2 \xrightarrow{25^0\text{ C}} KF\text{ (s)} + BrF_5$$

Properties:

i. ClF_5 is gas having m. p.= -103^0 C. It is *fluorinating agent* and hydrolyzed by water to liberate HF and $FClO_2$.
$ClF_5 + 2\,H_2O \rightarrow FClO_2 + 4\,HF$
ClF_5 ionises as: $2\,ClF_5 \rightleftharpoons ClF_4^+ + ClF_6^-$

ii. *With AsF_5 and SbF_5 it form adducts:* $ClF_5.AsF_5$ and $ClF_5.SbF_5$ which are ionic.

iii. BrF_5 reacts very violently. Therefore, generally it is diluted with N_2. BrF_5 is hydrolysed by water as:
$BrF_5 + 3\,H_2O \rightarrow 5\,HF + HBrO_3$

Uses:

- BrF_5 is used in organic synthesis.
- It is also recommended as an oxidizer for propellants.

2. Iodine pentafluoride, IF_5:

Preparation:

- It is formed by direct combination of I_2 and F_2 (excess):
  $I_2 + 5\,F_2\text{ (excess)} \rightarrow 2\,IF_5$
- By the action of F_2 on I_2O_5: $10\,F_2 + 2\,I_2O_5 \rightarrow 4\,IF_5 + 5\,O_2$
- By heating I_2 with AgF: $I_2 + 10\,AgF \rightarrow 2\,IF_5 + 10\,Ag$

Properties:

i. It is courless liquid with m. p. = 9.6^0 C.

ii. It is good conductor of electricity as it ionizes as:
$2\,IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

Thus, the substances that give IF_4^+ ions in liquid IF_5, acts as acid and those which produce IF_6^- ions behave as bases in this solvent. The following acid-base reaction takes place in liquid IF_5.

$$[IF_4]^+[SbF_6]^-\text{(Acid)} + K[IF_6]^-\text{ (Base)} \rightleftharpoons K^+[SbF_6]^-\text{ (Salt)} + 2\,IF_5\text{ (Solvent)}$$

iii. IF_5 reacts with I_2O_5 to form iodine oxy-fluoride, IOF_5 which is solid and decomposes on heating at 110^0 C.

$$3\,IF_5 + I_2O_5 \longrightarrow 5\,IOF_3; \quad 2\,IOF_3 \xrightarrow{\Delta} IF_5 + IO_2F$$

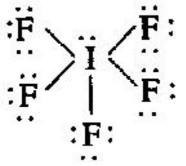
i. Hydrolysis of IF_5 gives halogen acid and oxy-halic acid.
$IF_5 + 3\,H_2O \rightarrow 5\,HF + HIO_3$

v. With F_2 at 250^0-300^0 C temperature gives IF_7.

$$IF_5 + F_2 \xrightarrow{250^0\text{-}300^0\ C} IF_7$$

Structure and geometry of XY_5 type Inter-halogen compounds:

Examples of such compounds are ClF_5, BrF_5 and IF_5. All these molecules have *distorted octahedral (square pyramidal) structure* which arises from sp^3d^2 hybridization of the central atom. Let us discuss the shape of IF_5 molecule in which bigger I-atom is the central atom. The Lewis structure of this molecule shows that the central I-atom is surrounded by five σ–bps and one lp of electrons hence I-atom is sp^3d^2 hybridized in IF_5 molecule.



Out of six sp^3d^2 hybrid orbitals, one axial hybrid orbital contains lone pair of electrons while remaining five orbitals are singly-filled. The lone pair occupies the axial orbital, since in this case (lp-lp) repulsion is minimum. Each of five F-I σ-bonds result by the overlap of singly-filled sp^3d^2 hybrid orbital in Cl-atom and singly-filled $2p_z$ orbital of F-atom.

Although the spatial arrangement of six electrons pairs round I-atom in space is octahedral, due to the presence of one lone pair electrons the shape of molecule gets distorted and hence IF_5 assumes square pyramidal shape.

A recent study of this molecule shows that all four basal F-atom are slightly displaced up wards from the base of the square pyramid and hence molecule assume the structure as shown in fig. 3.5

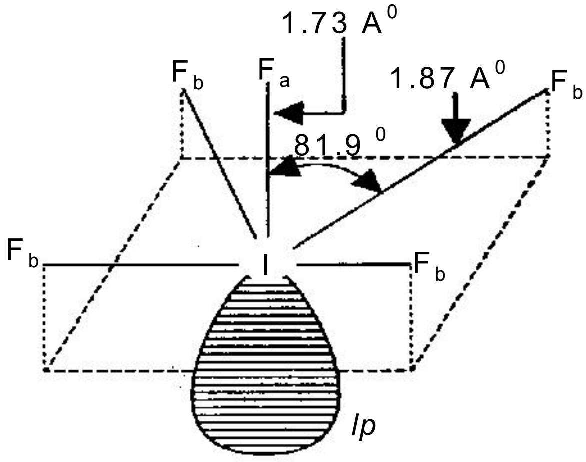


Fig. 3.6 Square pyramid structure of IF_5 molecule

I-atom in ground state
($5s^2\ 5p^3\ 5d^0$) : $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d_{z^2}^0\ 5d_{x^2-y^2}^0$
I-atom in the excited state
($5s^2\ 5p^3\ 5d^1\ 5d^1$) : $5s^2\ 5p_x^1\ 5p_y^1\ 5p_z^1\ 5d_{z^2}^1\ 5d_{x^2-y^2}^1$
I-atom in sp^3d^2 hybridised state
in IF_5 molecule : $\underbrace{\underset{lp}{\boxed{(sp^3d^2)^2}}\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1}_{\text{Six } sp^3d^2 \text{ hybrid orbitals}}$

IV. Inter-halogen compounds of XY_7 type (Octa-atomic inter -halogens):

Only one compound, IF_7 of this type has been found and characterized. The reason is that an iodine atom has largest size among halogens, while F-atom has the smallest size.

Iodine heptafluoride, IF_7:

Preparation:

It is prepared by the action of F_2 on IF_5, KI or PbI_2.

$$F_2 + IF_5 \xrightarrow{250^0\text{-}300^0\,C} IF_7; \qquad 4\,F_2 + KI \xrightarrow{250^0\,C} KF + IF_7$$

$$8\,F_2 + PbI_2 \longrightarrow PbF_2 + 2\,IF_7$$

Properties:

i. It is gas at room temperature and highly reactive.

ii. At 250^0 C, with SiO_2 and Pyrex glass it gives SiF_4.
$IF_7 + SiO_2 \rightarrow 2\,IOF_5 + SiF_4$

iii. Vapour of IF_7 hydrolyzed by water, giving HF and H_5IO_6
$IF_7 + 6\,H_2O \rightarrow H_5IO_6 + 7\,HF$

i. It form adducts with SbF_5 and AsF_5. These adducts are ionic compounds having the structure $[IF_6]^+[SbF_6]^-$ and $[IF_6]^+[AsF_6]^-$ respectively.

Structure and geometry of XY_7 type Inter-halogen compounds:

IF_7 is the only inter-halogen compound of this type. The Lewis structure of this molecule shows that the central I-atom is surrounded by seven σ-bps and hence I-atom in its excited state is sp^3d^3 hybridized in IF_7 molecule.

Each of the seven I-F σ-bonds is formed by the overlap between the singly-filled sp^3d^3 hybrid orbital on I-atom and singly-filled $2p_z$ orbital in F-atom. Since there is no lone pair of electrons in any of the hybrid orbital, IF_7 molecule has expected pentagonal bipyramidal shape. IF_7 molecule has two equal axial, I-Fa bonds and

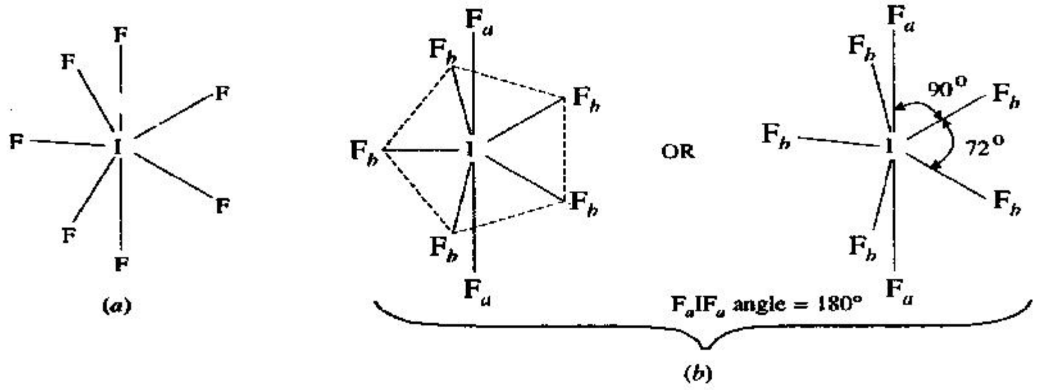
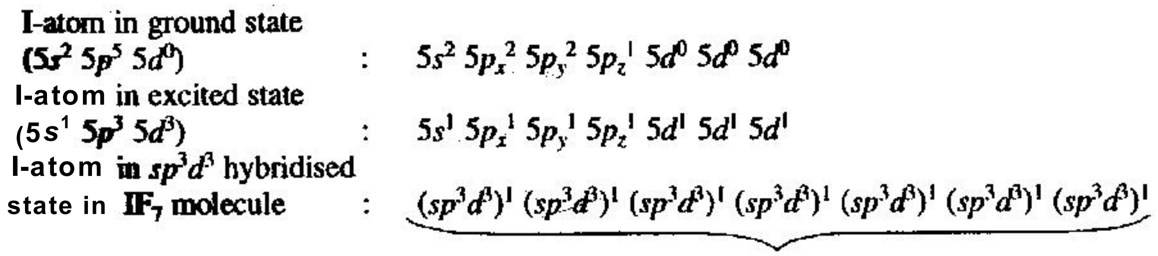


Fig. 3.8 (a) Lewis structure of IF_7 (b) Pentagonal bipyramida geometry of IF_7 molecule



I-atom in ground state
($5s^2\ 5p^5\ 5d^0$) : $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d^0\ 5d^0\ 5d^0$
I-atom in excited state
($5s^1\ 5p^3\ 5d^3$) : $5s^1\ 5p_x^1\ 5p_y^1\ 5p_z^1\ 5d^1\ 5d^1\ 5d^1$
I-atom in sp^3d^3 hybridised
state in IF_7 molecule : $\underbrace{(sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1}$

Seven sp^3d^3 hybrid orbitals

five equal equatorial, I-Fb bonds. I-Fa bond length is longer than I-Fb bond length.

Polyhalide ions and Polyhalides:

What are polyhalide ions and polyhalides?

The ions (catons or anions) composed of similar halogen atoms (e.g., Cl_2^+, Br_2^+, I_5^+ etc.) or dissimilar halogen atoms (e.g., ICl_2^+, $IBrCl^-$ etc.) are called polyhalide ions. These ions may be regarded as positively or negatively charged inter-halogen ions.

The formation of these ions observed during self-ionization of some inter-halogen compounds,e.g.,

$2\ ICl \rightleftharpoons I^+ + ICl_2^-$ $2\ BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$
$2\ ClF_5 \rightleftharpoons ClF_4^+ + ClF_6^-$ $2\ ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$
$IF_7 \rightleftharpoons IF_6^+ + F^-$ $2\ IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

The ionic compounds containing either polyhalide cations or polyhalide anions are called polyhalides.

Examples of polyhalides, containing polyhalide anions, are:
$K^+[Cl_3]^-$, $NH_4^+[I_5]^-$, $Cs^+[ClBrI]^-$, $[N(C_2H_5)_4]^+[I_3]^-$, $[As(C_6H_5)_4]^+[I_3]^-$, $Na^+[IBr_2]^-$, $H^+[ICl_4]^-.4\ H_2O$ etc.

Examples of polyhalides, containing polyhalide cations, are:
$[X_2]^+[Sb_3F_{16}]^-$, (X=Cl,Br, I); $[Cl_3]^+[AsF_6]^-$, $[BrF_2]^+[SbF_6]^-$ (M=Sb, As).

Iodine has maximum tendency to form polyhalide ions. Cl, Br and I-atoms can form triatiomic anions, while F-atom is not able to form F_3^- ion.

Preparation:

i. By direct action of halogen on metallic halides or on other polyhaide.
$Cl_2 + KCl \rightarrow K[Cl_3]$; $Br_2 + KBr \rightarrow K[Br_3]$
$I_2 + KI \rightarrow K[I_3]$ $2\ I_2 + NH_4I \rightarrow NH_4[I_5]$
$Cl_2 + K[ICl_2] \rightarrow K[ICl_4]$; $Cl_2 + K[IBr_2] \rightarrow K[ICl_2] + Br_2$

ii. By the action of inter-halogens on metals, metallic halides or other polyhalides.
$4\ BrF_3 + 3\ K \rightarrow 3\ K[BrF_4] + ½\ Br_2$
$ICl + MCl$ (M=K, Rb, NH_4^+) $\rightarrow M[ICl_2]$; $ICl + KCl \rightarrow K[ICl_2]$
$ICl + KBr \rightarrow K[ClBrI]$; $BrCl + CsI \rightarrow Cs[IBrCl]$
$BrF_3 + MF$ (M=Li, K, Ag) $\rightleftharpoons M[BrF_4]$;
$ClF_5 + AsF_5 \rightarrow [ClF_4]^+[AsF_6]^-$
$IF_7 + MF_5$ (M=As, Sb) $\rightarrow [IF_6]^+[MF_6]^-$
$ICl + K[ClBrI] \rightarrow K[ICl_2] + IBr$

iii. By action of I_2 or Cl_2 on solution of metallic chlorides in HCl.
$I_2 + 3\ Cl_2 + 2\ MCl$ (Li, Na) $\rightarrow 2\ M^+[ICl_4]^-$

$I_2 + Cl_2 + 2\,RbCl \text{ (in HCl)} \rightarrow 2\,Rb^+[ICl_2]^-$

iv. By action of an appropriate gaseous halogen on metallic halide in absence of solvent.

$F_2 + CsCl \rightarrow Cs[ClF_4]$

v. I_2 dissolve in highly acidic oxidizing media to give I_2^+ ion. The salts of X_2^+ are best prepared by action of $S_2O_6F_2$ on X_2 molecule and then SbF_5 is added.

$X_2 + S_2O_6F_2 \text{ (then add } SbF_5) \rightarrow [X_2]^+[Sb_3FI_6]^-$

vi. Salts of X_3^+ ions can be prepared by a number of methods. For example:

$2\,I_2 + ICl + AlCl_3 \rightarrow [I_5]^+[AlCl_4]^-$

$$Cl_2 + ClF + AsF_5 \xrightarrow{-78^0\,C} [Cl_3]^+[AsF_6]^-$$

$$3\,I_2 + 3\,AsF_5 \xrightarrow{\text{in } SO_2} 2\,[I_3]^+[AsF_6]^- + AsF_3$$

Properties:

i. All polyhalides are coloured compounds and depth of colour increases with the increase of the atomic number of halogen atoms.

ii. Polyhalides are highly soluble in water and get dissociated in water. The stability of metallic trihalides of MX_3 type having the same cation in the same oxidation state is in the order: $MI_3 > MBr_3 > MCl_3$. And the stability of metallic trihalides, having the same trihalide anion and different cation increases with the increase in size of the cation. For example:

$NaI_3 < KI_3 < RbI_3 < CsI_3$.

The polyhalides, containing ICl_4^- anion, dissociate in aqueous solution followed by hydrolysis to iodate, IO_3^-.

$5\,[ICl_4]^- \rightarrow 5\,Cl^- + 5\,ICl_3$

$\underline{5\,ICl_3 + 9\,H_2O \rightarrow 3\,H^+ + 3\,IO_3^- + 15\,H^+ + 15\,Cl^- + I_2}$

$5\,[ICl_4]^- + 9\,H_2O \rightarrow 20\,Cl^- + 18\,H^+ + 3\,IO_3^- + I_2$

iii. Polyhalide ions form complexes with organic donor molecules. Examples: $LiI_3.4\,C_6H_5CN$, $MI_3.2\,C_6H_5CN$ (M=Na or K)

iv. They undergo thermal decomposition when heated. The ease of dissociation decreases with the increase of the size of the cation. On thermal dissociation, the polyhalides give metal monohalides and halogen molecule or inter-halogen molecule.

$$CsI_3 \xrightarrow{\Delta} CsI + I_2; \qquad RbICl_2 \xrightarrow{\Delta} RbCl + ICl$$

The stability of trihalide ions formed by the same metal, decrea -ses in the order: $I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_2^- > BrCl_2^- > Br_2Cl^-$

v. When polyhalide is allowed to react with halogen molecule, it undergoes substitution reaction.

$KIBr_2 + Cl_2 \rightarrow KICl_2 + Br_2; \qquad CsBr_3 + I_2 \rightarrow CsIBr_2 + IBr$

Sometimes a higher polyhalide is formed. $KICl_2 + Cl_2 \rightarrow KICl_4$

vi. Polyhalides may dissolve in liquid halogen or in inter-halogen to give solution from which original polyhalide may be crystallised by evaporation.

Structure of Polyhalide ions:

1. Geometry of Tri-atomic inter-halogen cations:

I-atom in ground state ($5s^2\ 5p^5$): $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1$

I^+ ion in ground state ($5s^2\ 5p^4$): $5s^2\ 5p_x^2\ 5p_y^1\ 5p_z^1$

I^+ ion in sp^3 hybridised state in ICl^+ ion :

$$\underbrace{\underset{lp}{\boxed{(sp^3)^2}}\ \underset{lp}{\boxed{(sp^3)^2}}\ (sp^3)^1\ \ (sp^3)^1}_{\text{Four } sp^3 \text{ hybrid orbitals}}$$

Examples of such cations are: ICl_2^+, IBr_2^+, BrF_2^+, ClF_2^+ etc. All these cations have angular (V-shaped) geometry which arises from sp^3 hybridisation of central positively-charged bigger halogen atom and due to presence of two lps of electrons on the central atom.

Let us discuss the geometry of ICl_2^+ ion. Here positively-charged I-atom is the central atom and is surrounded by two σ-bps and two lps and is sp^3 hybridised as shown above.

Although the spatial arrangement of four sp^3 hybrid orbitals is tetrahedral, due to presence of two lone pairs of electrons, ICl_2^+ ion assumes angular shape as shown in fig. 3.9

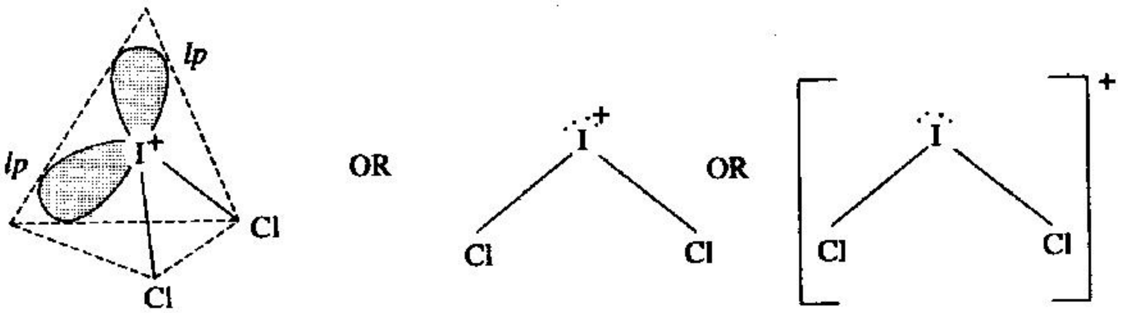
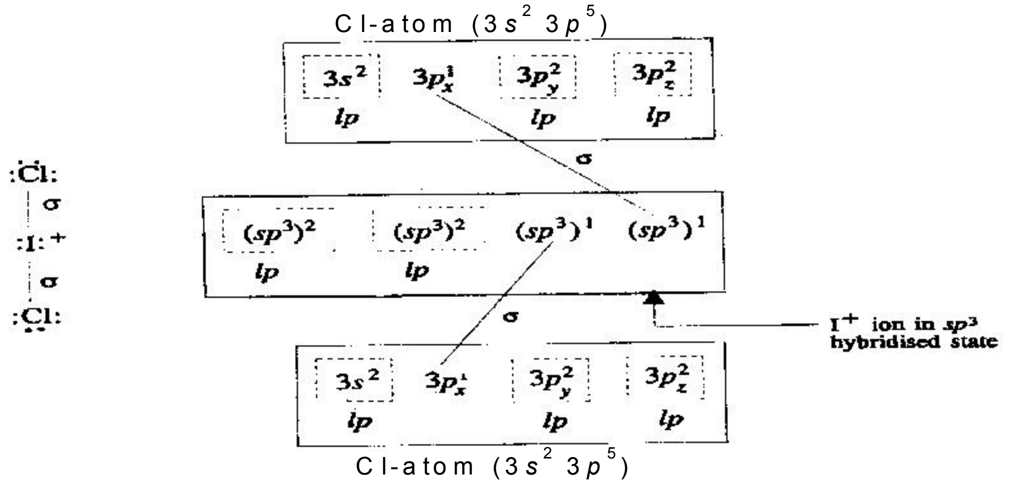


Fig. 3.9 : Angular (V-shaped) structure of ICl_2^+ ion



(a) (b)

Fig. 3.8 : (a) Lewis structure of ICl_2^+ ion, (b) sp^3 hybridisation of I^+ in ICl_2^+ ion and formaton of different bonds.

2. Geometry of Penta-atomic inter-halogen cations:

Examples of such cations are: IF_4^+, ClF_4^+, BrF_4^+ etc. All these cations have distorted-tetrahedral or see-saw structure. This structure arises from sp^3d hybridisation of central positively-charged bigger halogen atom and due to presence of one lone pair of electrons on the central atom.

Let us discuss the geometry of IF_4^+ ion. Here positively-charged I-atom is the central atom and is surrounded by four σ-bps and one lone pair and is sp^3d hybridised as shown below.

The Lewis structure of ICl_4^+ ion can be written as shown in fig. 3.10 (a). Sp^3d hybridisation scheme indicate that ICl_4^+ ion is AB_4(lp)

I-atom in ground state ($5s^2\ 5p^5\ 5d^0$) : $5s^2\ 5p^5\ 5d_{z^2}^0$

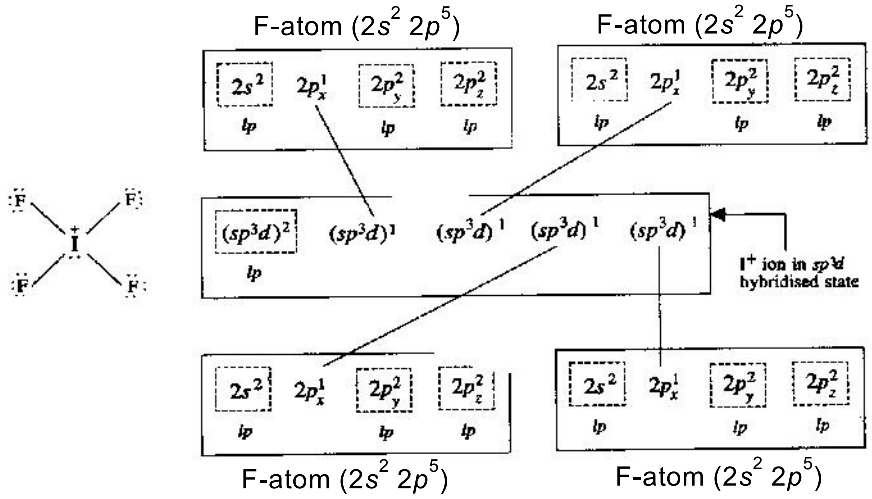
I^+ ion in ground state ($5s^2\ 5p^4\ 5d^0$) : $5s^2\ 5p_x^2\ 5p_y^1\ 5p_z^1\ 5d_{z^2}^0$

I^+ ion in the excited state ($5s^2\ 5p^3\ 5d^1$) : $5s^2\ 5p_x^1\ 5p_y^1\ 5p_z^1\ 5d_{z^2}^1$

I^+ ion in sp^3d hybridised state in IF_4^+ ion. : $\underbrace{\underset{lp}{\boxed{(sp^3d)^2}}\ (sp^3d)^1\ (sp^3d)^1\ (sp^3d)^1\ (sp^3d)^1}_{\text{Five } sp^3d \text{ hybrid orbitals}}$

type species. Formation of four (I^+-F) σ-bonds have been shown at fig. 3.10 (b).

As discuss earlier the lone pair prefer to occupy the basal hybrid orbital and due to the presence of lone pair in the basal position, the shape of ICl_4^+ gets distorted and becomes distorted octahedral or see-saw (fig. 3.11).



(a) (b)

Fig. 3.10 : (a) Lewis structure of IF_4^+ ion (b) Formatin different bonds in IF_4^+ion

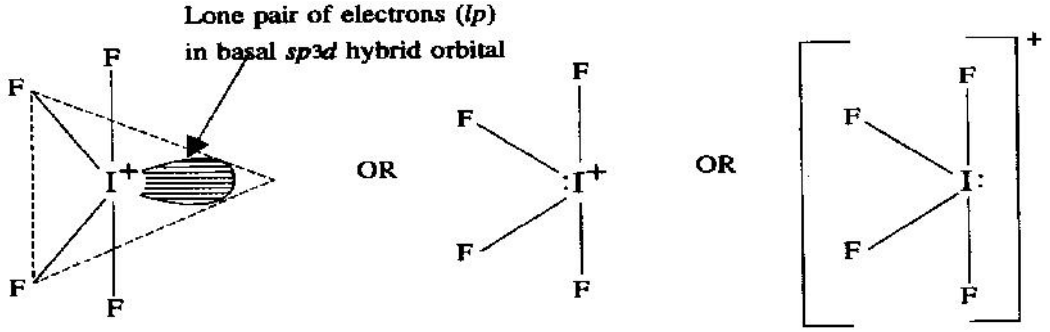
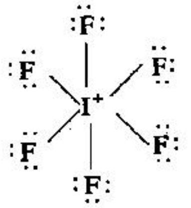


Fig. 3.11 : Distorted tetrahedral or see-saw structure of IF_4^+ ion

3. Geometry of Hepta-atomic inter-halogen cations:



Lewis structure of IF_6^+

Examples of such cations are: IF_6^+, BrF_6^+ etc. All these ions have octahedral structure corresponding to sp^3d^2 hybridisation of the central positively-charged bigger halogen atom and due to absence of lp of electrons on the central atom.

Let us discuss the geometry of IF_6^+ ion. Lewis structure of IF_6^+ shows that the central atom is surrounded by six σ-bps and is sp^3d^2 hybridised as shown below.

Sp^3d^2 hybridisation scheme given above shows that IF_6^+ ion has no lone pair of electrons and hence this ion has octahedral geometry as shown below in fig. 3.12

I-atom in ground state ($5s^2\ 5p^5\ 5d^0$) : $5s^2\ 5p^5\ 5d^0_{z^2}\ 5d^0_{x^2-y^2}$

I^+ ion in ground state ($5s^2\ 5p^4\ 5d^0$) : $5s^2\ 5p^4\ 5d^0_{z^2}\ 5d^0_{x^2-y^2}$

I^+ ion in doubly-excited state ($5s^1\ 5p^3\ 5d^2$) : $5s^1\ 5p^3\ 5d^1_{z^2}\ 5d^1_{x^2-y^2}$

I^+ ion in sp^3d^2 hybridised state in IF_6^+ ion : $\underbrace{(sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1}_{\text{Six singly-filled } sp^3d^2 \text{ hybrid orbitals}}$

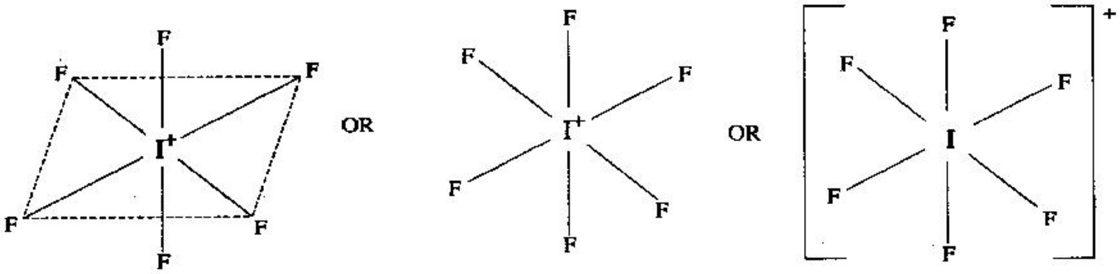
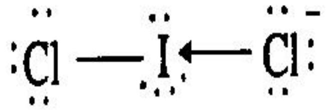


Fig. 3.12 : Octahedral structure of IF_6^+ ion

4. Structure of Tri-atomic inter-halogen anions:

Examples of such anions are: ICl_2^-, IBr^-, $BrCl_2^-$, ClF_2^-, I_3^-, $ClBrI^-$ etc. All these ions have linear structure which due to sp^3d hybridisation of central atom and presence of three lps of electrons on the central atom. Let us discuss the structure and geometry of ICl_2^- and I_3^- ions.

(a) Structure and geometry of ICl_2^- ion: The negative charge on this ion shows that the central I-atom is surrounded by two σ-bps and three lps of electrons and hence I-atom is sp^3d hybridised as shown below.



Lewis structure of ICl_2^-

I-atom in ground state ($5s^25p^55d^0$) : $5s^2\ 5p^5\ 5d^0_{z^2}$

I-atom in sp^3d hybridised state in ICl_2^- ion. : $\underbrace{\underset{lp}{(sp^3d)^2}\ \ \underset{lp}{(sp^3d)^2}\ \ \underset{lp}{(sp^3d)^2}\ \ (sp^3d)^1\ (sp^3d)^0}_{\text{Five } sp^3d \text{ hybrid orbitals}}$

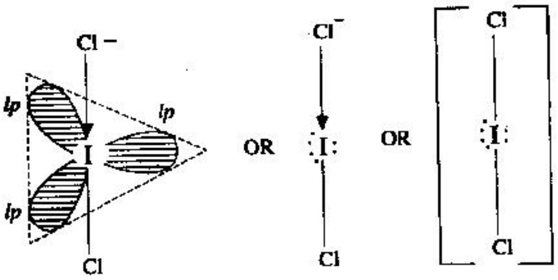
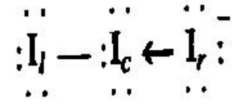


Fig. 3.13 : Linear shape of ICl_2^- ion

The sp^3d hybrid orbital which is vacant forms $Cl^- \longrightarrow I$ coordinate bond. Hybridisation scheme shows that ICl_2^- ion is $AB_2(lp)_3$ type species and three lps prefer to sit at the basal position of the tbp, since in this case the repulsion between electron pairs are minimum. Due to the presence of three lps in the basal positions, the shape of ICl_2^- gets distorted and becomes linear as shown in fig. 3.13

(b) Structure of I_3^- : This ion also have linear structure in which I-atom undergoes sp^3d hybridisation. In order to differntiate three I-atom, they have been designated as: Ic = Central I-atom, I_l = I-atom lying to the left of Ic-atom and Ir = I-atom lying to the right of Ic-atom.



Lewis structure of I_3^- ion

Molecular Orbital treatment of I_3^- ion:

If we take linear combination of the two singly-filled 5*p* orbitals of two I-atoms ($I=5s^2\ 5p^2\ 5p^2\ 5p^1$) and one completely-filled 5*p* orbital of central I^- ion ($I^-=5s^2\ 5p^2\ 5p^2\ 5p^2$) gives three molecular orbitals which are bonding molecular orbital (ψ^b), non-bonding molecular orbital (ψ^{nb}) and antibonding molecular orbital (ψ^*). The MO-digram of I_3^- ion is shown below in fig. 3.14

The electrons involved in bond formation are occupy BMO (ψ^b) which spreads out on either side of the negatively-charged central I-atom and thus two equivalent bonds are formed.

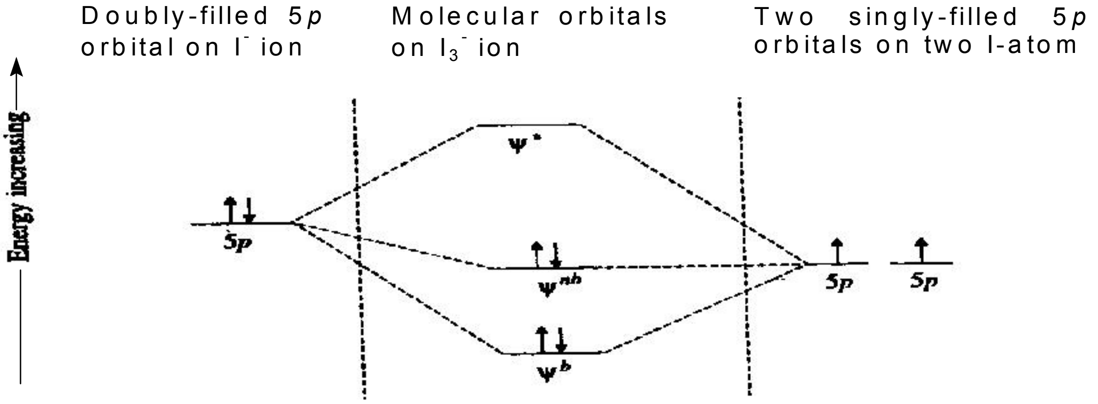
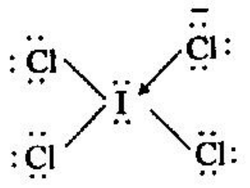


Fig. 3.14 : MO-energy level diagram of I_3^- ion

5. Structure of Penta-atomic inter-halogen anions:

Examples of such anions are: ICl_4^-, BrF_4^-, I_5^- etc. All these ions have square planar geometry which arises due to sp^3d^2 hybridisation of central atom and presence of two lps of electrons on this atom.

Let us discuss the geometry of ICl_4^- ion. The negative charge on this ion is supposed to be present on one of the four Cl-atoms. Thus Lewis structure of this ion can be written as given in the margine.



Lewis structure ICl_4^- ion

Thus, Lewis structure shows that the central I-atom is surrounded by four σ-bps and two lps. So I-atom is sp^3d^2 hybridised. One of the six sp^3d^2 hybrid orbital is vacant and hence accepts an electron pair donated by Cl^- ion and $Cl^- \rightarrow I$ coordinate bond is established.

I-atom in ground state $(5s^25p^55d^0)$: $5s^2\ 5p^5\ 5d_{z^2}^0\ 5d_{x^2-y^2}^0$

I-atom in excited state $(5s^25p^4\ 5d^1)$: $5s^2\ 5p^4\ 5d_{z^2}^1\ 5d_{x^2-y^2}^0$

I-atom in sp^3d^2 hybridised state in ICl_4^- ion :

$$\underbrace{\underset{lp}{\boxed{(sp^3d^2)^2}}\ \underset{lp}{\boxed{(sp^3d^2)^2}}\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^0}_{\text{Six } sp^3d^2 \text{ hybrid orbitals}}$$

sp^3d^2 hybridisation scheme shows that ICl_4^- ion is $AB_4(lp)_2$ type species.

Experiments have shown that the two lps prefer to sit in the axial positions of the octahedron, since in this case (lp-lp) repulsion is minimum. Although the spatial arrangement of six electron pairs round the central I-atom is octahedral, due to presence of two lps, the shape of ICl_4^- ion becomes square planar as shown in fig. -3.15

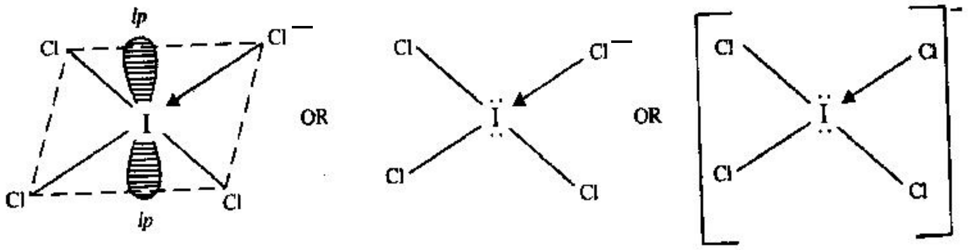
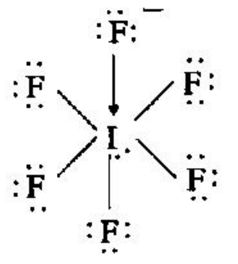


Fig. 3.15 - Square planar geometry on ICl_4^-

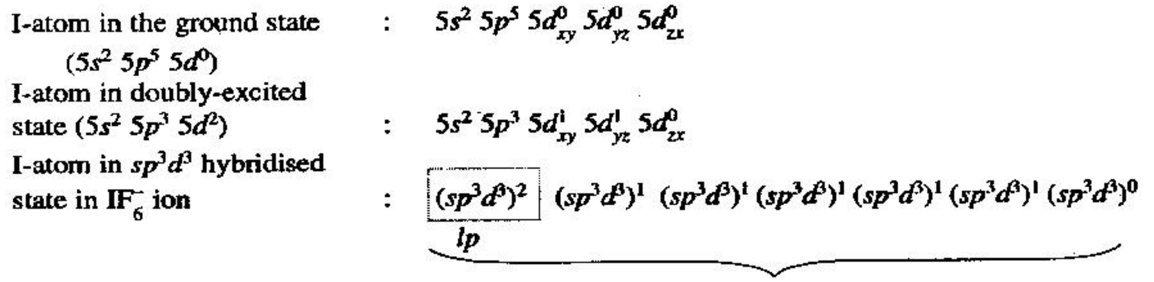
6. Structure of Hepta-atomic inter-halogen anions:

Examples of such anions are: IF_6^-, BrF_6^- etc. These ions have distorted octahedral structure which is because of sp^3d^3 hybridisation of central atom and presence of one lone pair of electrons on the central atom.



Lewis structure of IF_6^- ion

Let us discuss the structure and geometry of IF_6^- ion. The negative charge on IF_6^- may be supposed to be present on one of the six F-atoms. Thus, Lewis structure of this ion is given in the margine. This structure shows that the central I-atom is surrounded by six σ-bps and one lone pair of electrons and is sp^3d^3 hybridised.

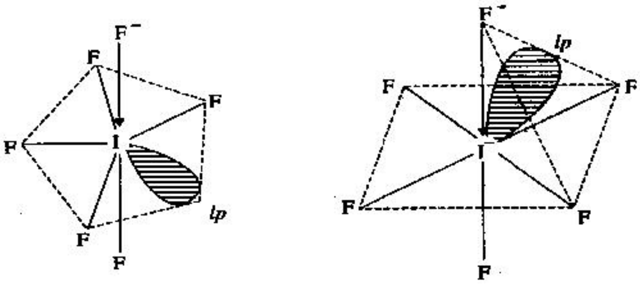


I-atom in the ground state ($5s^2\ 5p^5\ 5d^0$) : $5s^2\ 5p^5\ 5d^0_{xy}\ 5d^0_{yz}\ 5d^0_{zx}$

I-atom in doubly-excited state ($5s^2\ 5p^3\ 5d^2$) : $5s^2\ 5p^3\ 5d^1_{xy}\ 5d^1_{yz}\ 5d^0_{zx}$

I-atom in sp^3d^3 hybridised state in IF_6^- ion : $\underbrace{\underset{lp}{\boxed{(sp^3d^3)^2}}\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^0}_{\text{seven } sp^3d^3 \text{ hybrid orbitals}}$

One of the seven hybrid orbital is vacant and hence accepts an electron pair donated by F^- ion ($F=2s^2\ 2p^2\ 2p^2\ 2p^2$) to form $F^- \rightarrow I$ coordinate bond. sp^3d^3 hybridisation of I-atom can be shown as above.



(a) (b)

Fig. 3.16 : (a) Distorted pentagonal bipyramidal structure of IF_6^- ion (wrong), (b) Distorted octahedral structure of IF_6^- ion (correct)

Theoretically the lone pair of electrons should occupy one of the five basal position of pentagonal bipyramidal as shown at fig. 3.16 (a). However, experiment have shown that distorted pentagonal bipyramidal structure of IF_6^- ion is wrong. It is believed that IF_6^- ion has distorted octahedral structure in which the six positions of octahedron are occupied by six F-atoms and the lone pair of electrons is directed towards the centre of one of the eight triangular face of octahedron as shown in fig. 3.16 (b).

7. Structure of I_8^{2-} ion:

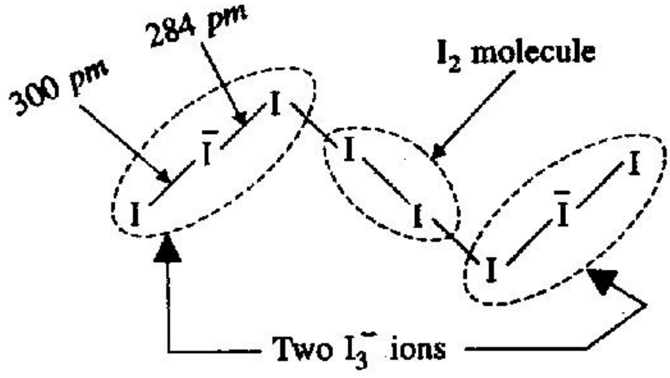
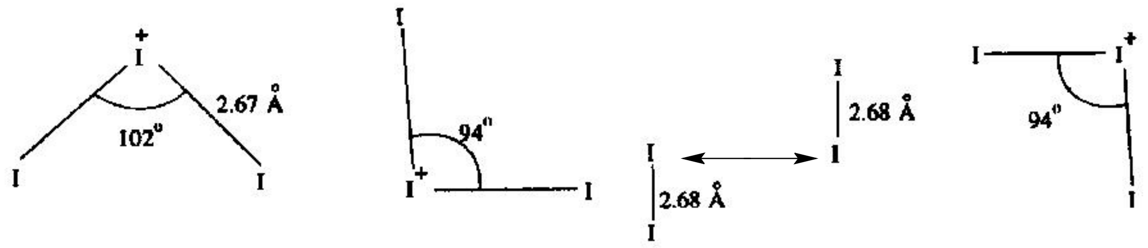


Fig. 3.17 : Zig-zag chain structure of I_8^{2-} ion

This ion is found in $[Cs^+]_2[I_8]^{2-}$ which. I_8^{2-} ion contains two I_3^- which are linked together into zig-zag chain by one I_2 molecule as shown in fig. 3.17

8. Structure of I_3^+ and I_5^+ ions:

The structure of I_3^+ is bent as shown in fig. 3.19 (a) and that of I_5^+ ion is said to be resonance hybrid of the two structures as shown in fig. 3.19



(a) (b)

Fig. 3.19 : (a) Bent structure of I_3^+ ion, (b) Resonance in I_5^+ ion