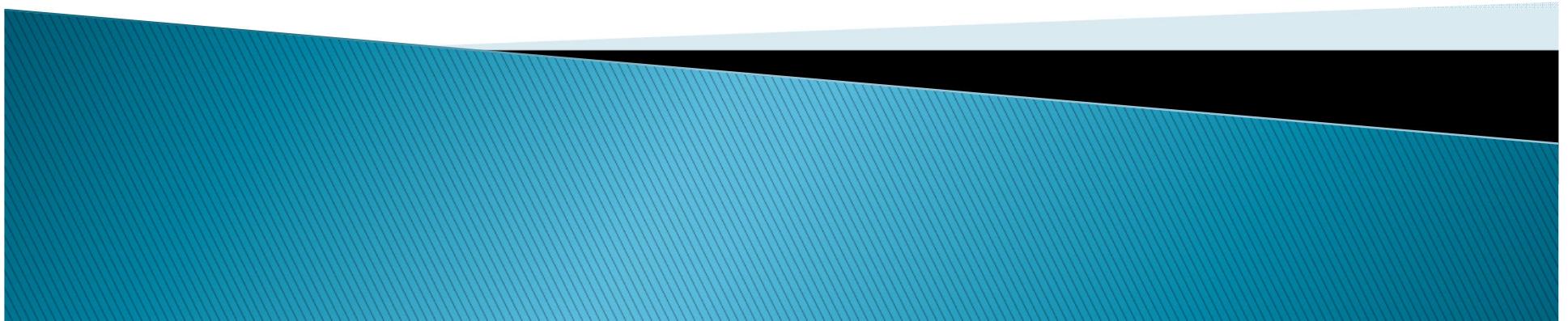


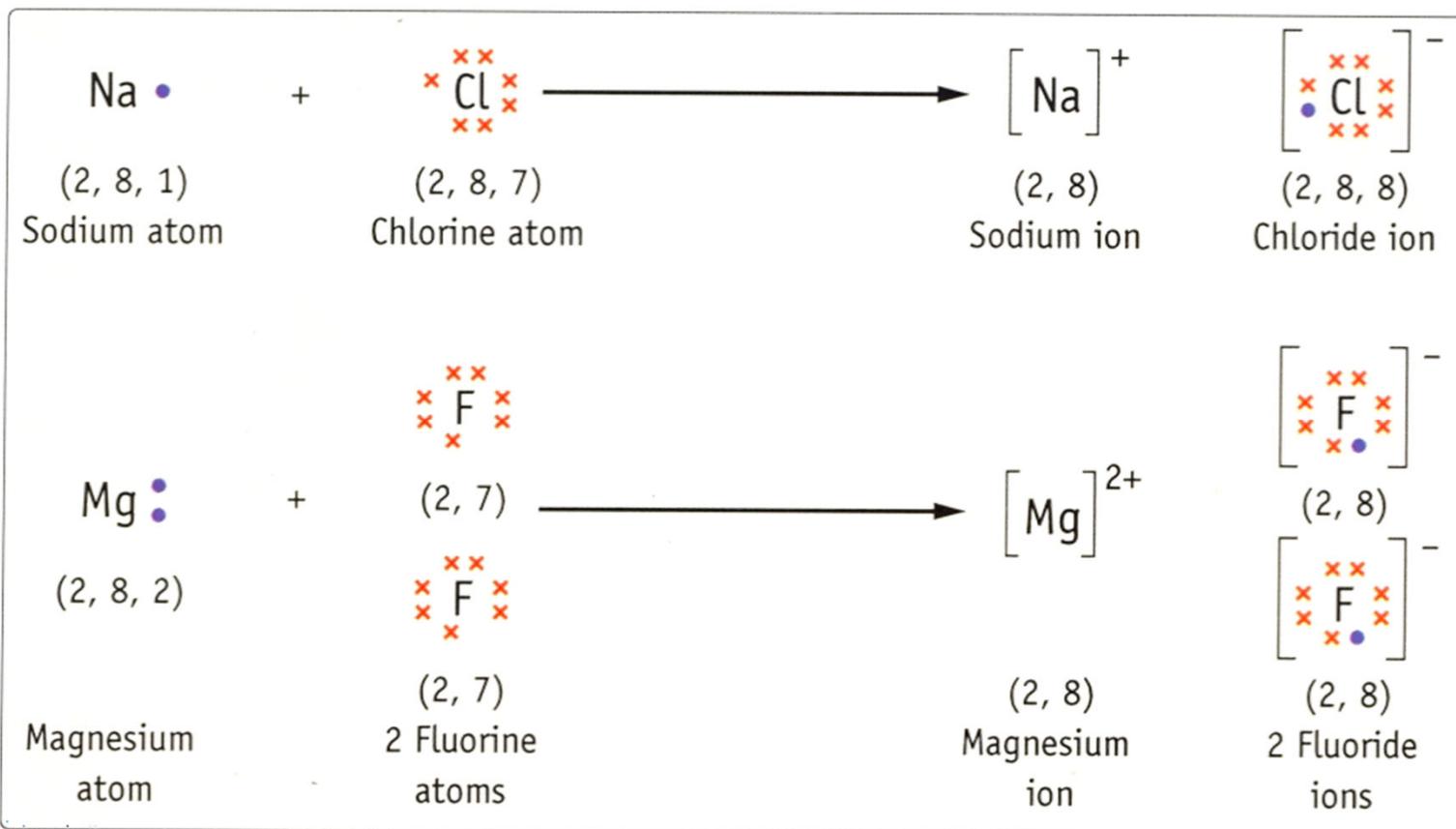
TOPIC 3

CHEMICAL BONDING



Dot and cross diagram

► Ionic Compound :



Dot and cross diagram

- ▶ Covalent compound :



Examples

- ▶ Ammonia, NH_3
- ▶ Carbon dioxide, CO_2
- ▶ Water, H_2O
- ▶ Nitrogen, N_2



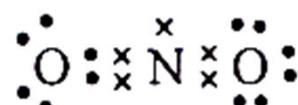
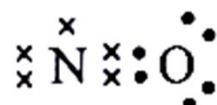
- ▶ Examples :
- ▶ CO_3^{2-}

- ▶ SO_3^{2-}

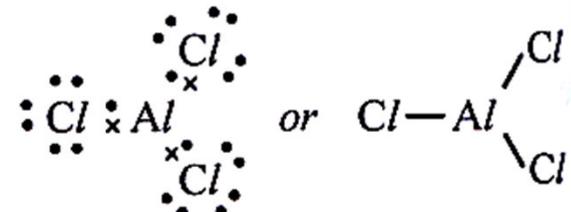
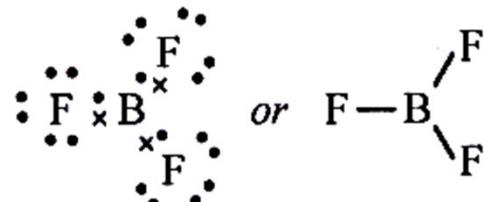
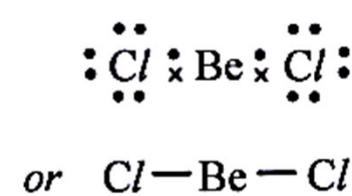


Exception to Octet Rule

- ▶ Compounds with odd number electrons.



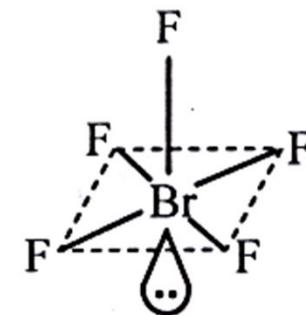
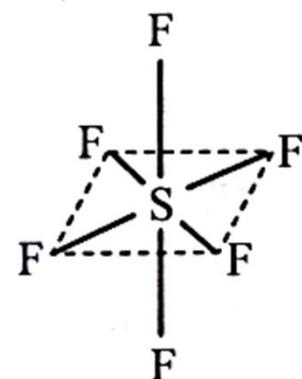
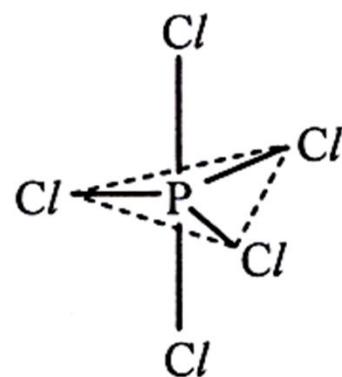
- ▶ Compounds with less than 8 valence electrons.



Exception to Octet Rule

- ▶ Compounds with more than 8 valence electrons.

e.g.



- ▶ The central atoms are able to bond with the side atoms by forming dative covalent bond.
- ▶ The central atoms have empty d orbitals that are able to accept electrons.

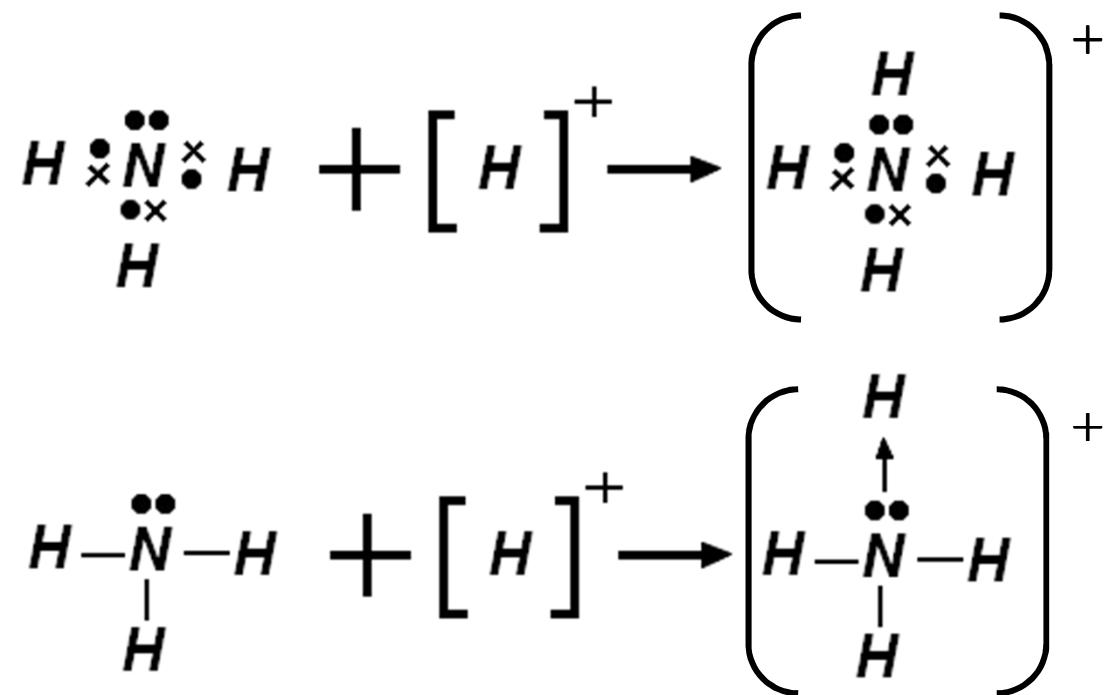
Co-ordinate Bond

- ▶ Also called a dative covalent bond.
- ▶ Is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom (donor atom).
- ▶ Donor atom possess a lone pair of electron and acceptor atom must have empty orbitals to accommodate the electron lone pair.

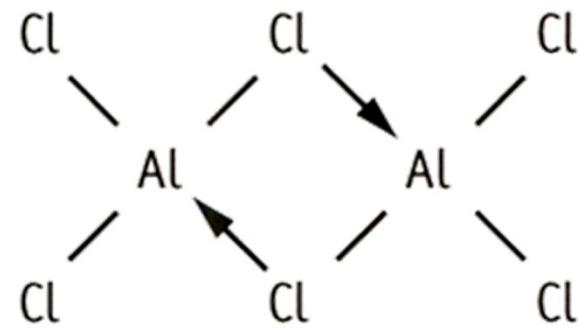
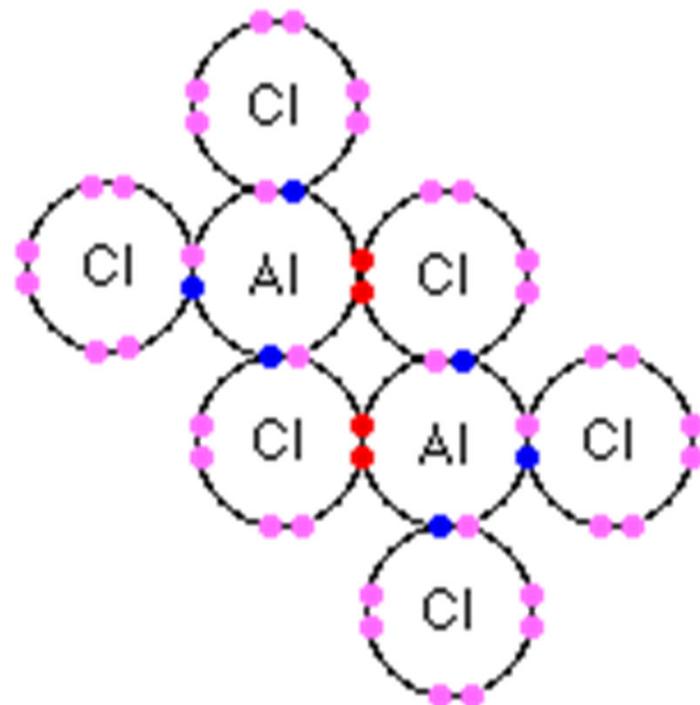


Co-ordinate Bond

► E.g : Formation of ammonium ion:



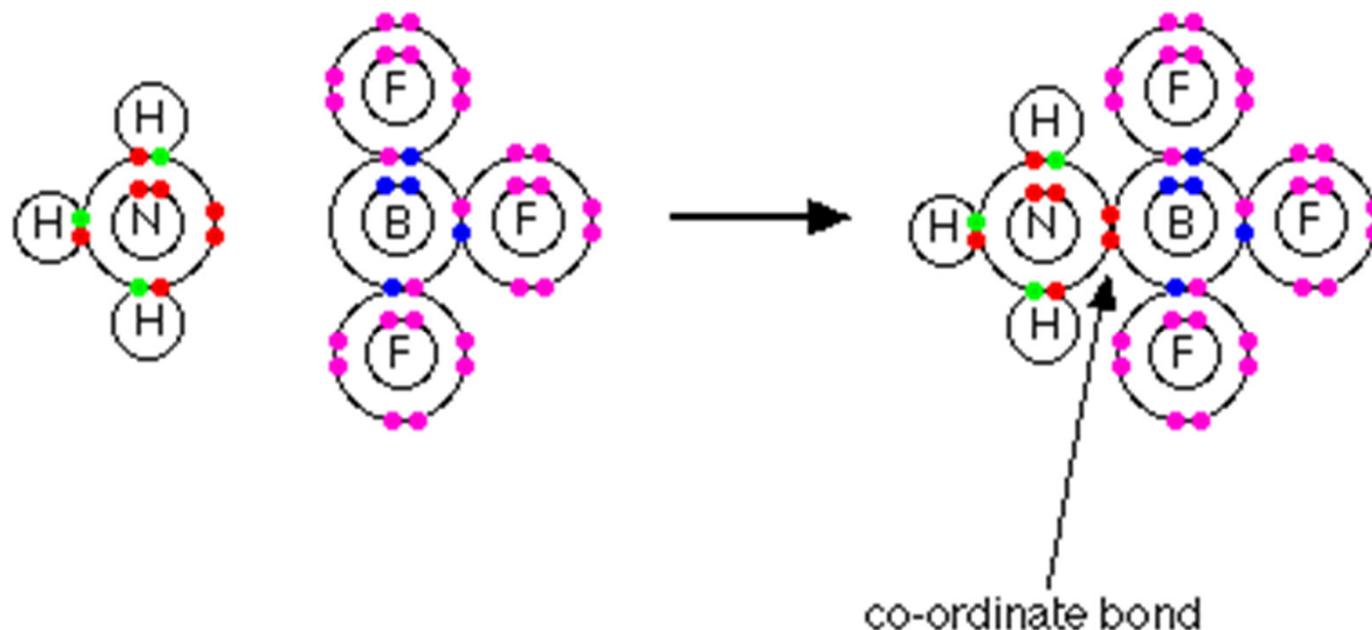
Co-ordinate Bond



- Cl has lone pairs of electrons.
- Al has empty orbitals.

Co-ordinate Bond

- Dative covalent bond in $\text{BF}_3 \cdot \text{NH}_3$



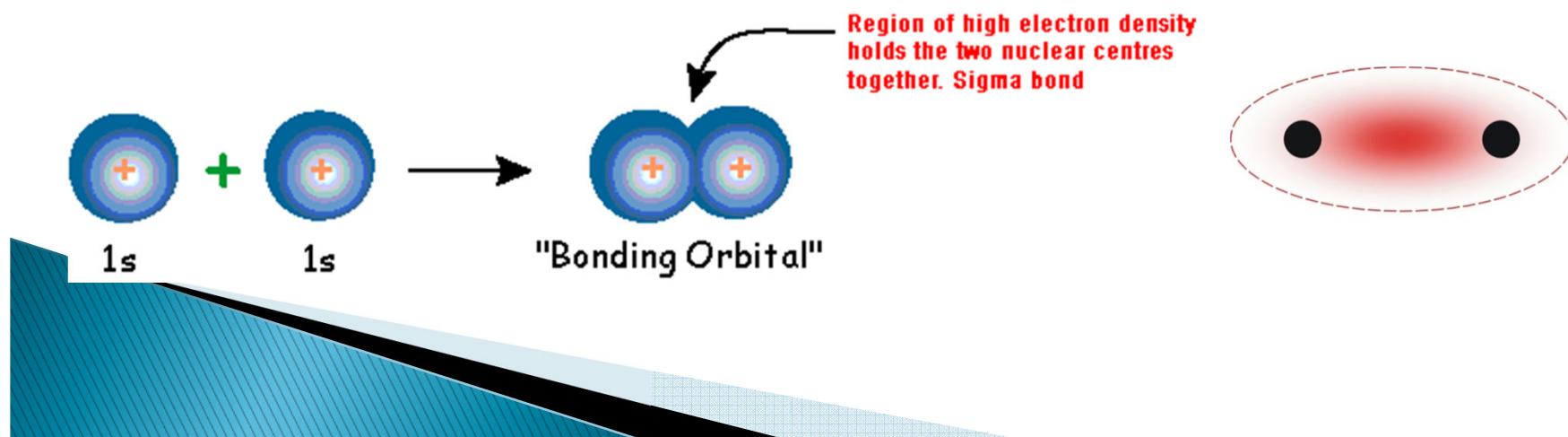
Pi and Sigma Bonds

- ▶ covalent bonds are formed when the orbitals of two neighbouring atoms overlap so that both nuclei attract the pairs of electrons between them.
- ▶ This can happen in two different ways making two different kinds of covalent bonds → sigma and pi bonds

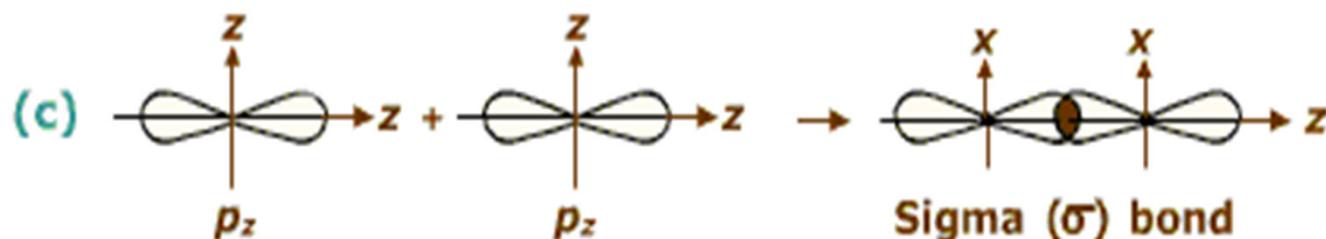
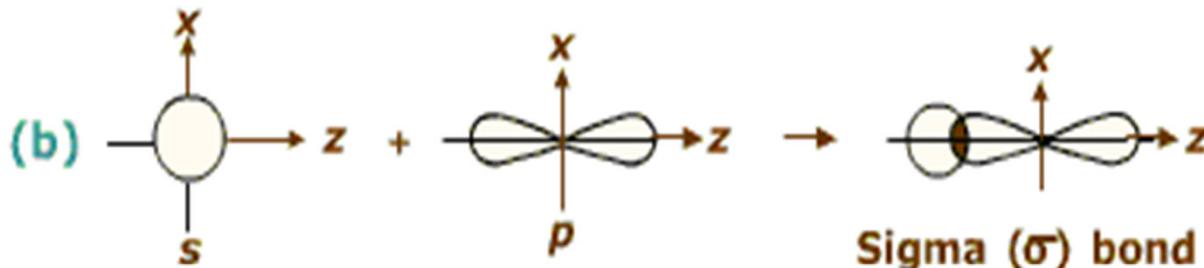
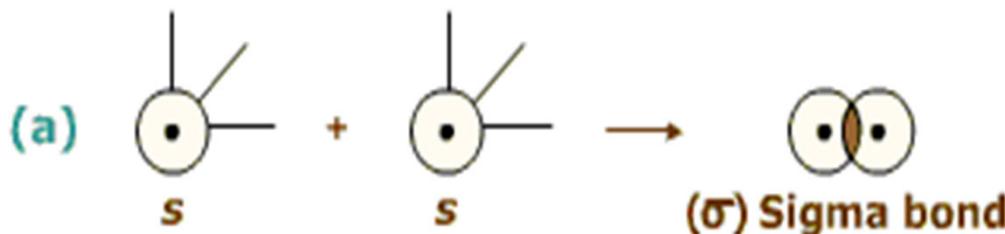


Sigma Bond

- ▶ Sigma bond (σ bond)
 - orbitals overlap head-on / direct overlapping.
 - can be rotated without breaking the bond.
 - eg. H_2 , HCl , Cl_2



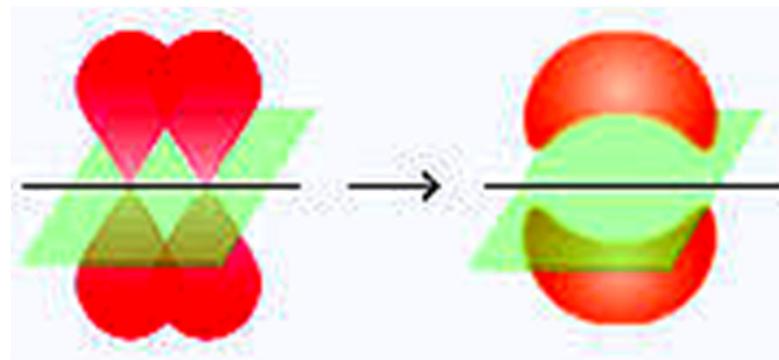
Sigma Bond



Formation of a sigma bond due to (a) The s - s overlap
(b) The s - p overlap (c) The p_z - p_z overlap

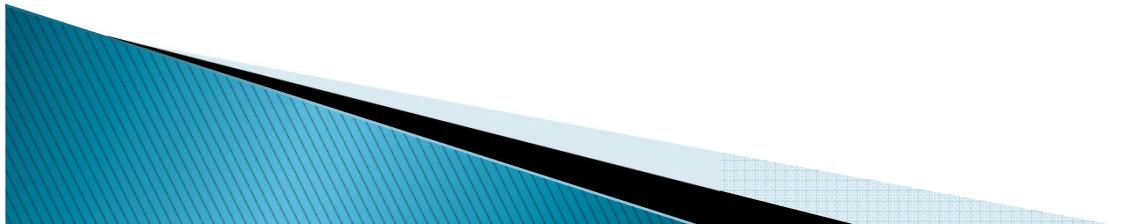
Pi – Bond

- ▶ orbitals overlap sideways.
- ▶ weaker than sigma bond.
- ▶ Electron density concentrated above and below the line joining the two nuclei.



Pi – Bond

- ▶ cannot be rotated.
- ▶ s-orbital cannot overlap sideways.
- ▶ eg. C=C bond in ethene



Bond Energy and Bond Lengths

- ▶ Bond energy → the energy required to break one mole of a covalent bond between two atoms in the gaseous state.
- ▶ $A-B(g) \rightarrow A(g) + B(g)$
 $\Delta H = +x \text{ kJmol}^{-1}$

Bond	Bond Length	Bond Energy/kJ mol ⁻¹
Cl–Cl	0.199	244
Br–Br	0.228	193
I–I	0.266	151
C–C	0.154	350
C=C	0.133	610
C≡C	0.120	840

Bond Length

- ▶ The distance between the nuclei of the two atoms joined by a covalent bond (and hence, depends on the size of the atoms)
- ▶ Bond length and bond energy gives an indication of the strength of a covalent bond.
- ▶ the shorter the bond length, the stronger is the bond.
- ▶ the greater the bond energy, the stronger is the bond.



- ▶ Eg. Cl-Cl > Br-Br > I-I

bond strength decrease/increase?

- ▶ C≡C > C=C > C-C

bond strength decrease/increase?

- ▶ Very large bond energy makes molecules unreactive. Eg. N₂



Shape of Molecules

- ▶ the electron pairs around the central atom of a molecule dictate the shape of the molecule.
- ▶ the shape of a molecule can be worked out using the electron pair repulsion model.



Valence Shell Electron Pair Repulsion(VSEPR)

- ▶ Lone pair-lone pair repulsion is greater than lone pair-bond pair repulsion which is greater than bond pair-bond pair repulsion.
- ▶ electron pairs in a molecule (both bond pairs and lone pairs) repel each other and so move as far apart as possible.
- ▶ the repulsion between electron pairs is increased by the increase in electronegativity of the central atom.

The Shapes of Molecules

Central atom without lone pairs:

- ▶ Linear
- ▶ Trigonal planar
- ▶ Tetrahedral
- ▶ Trigonal bipyramidal
- ▶ Octahedral

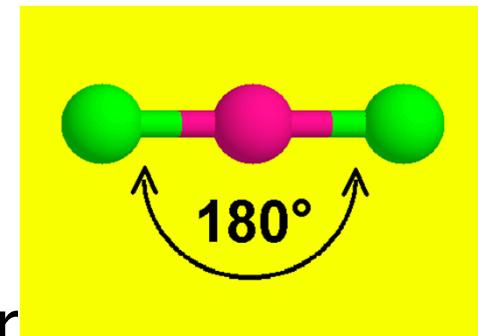


Central atom with lone pairs:

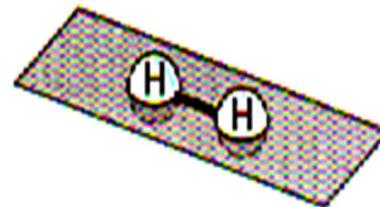
- ▶ V- shape (bent)
- ▶ Trigonal pyramidal

Linear Molecules

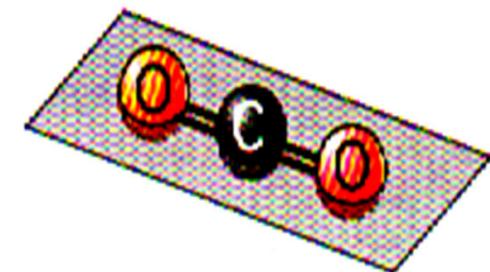
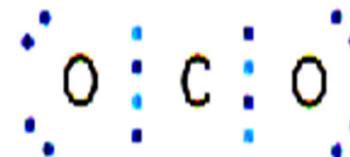
- ▶ Examples: H_2 , CO_2 , BeCl_2
- ▶ H_2 : 1 bonding pair, 0 lone pairs.
- ▶ For CO_2 , the 2 bonding pairs in the double bond is considered as 1 bonding pair.
- ▶ Bond angles are equal, 180°



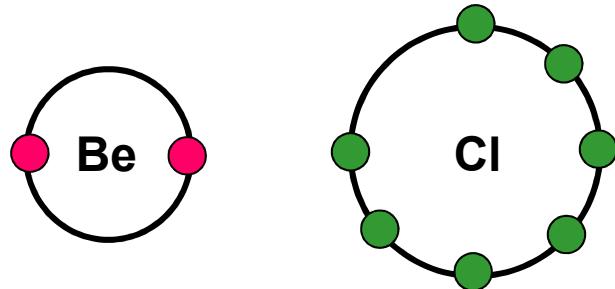
(a)



(b)

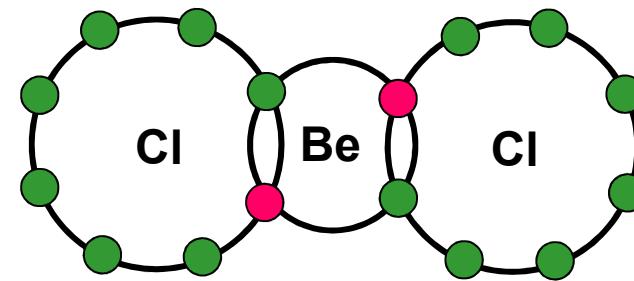


BERYLLIUM CHLORIDE



Beryllium - has two electrons to pair up

Chlorine - needs 1 electron for 'octet'



Two covalent bonds are formed

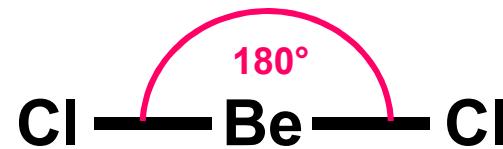
Beryllium still has an incomplete shell

BOND PAIRS 2

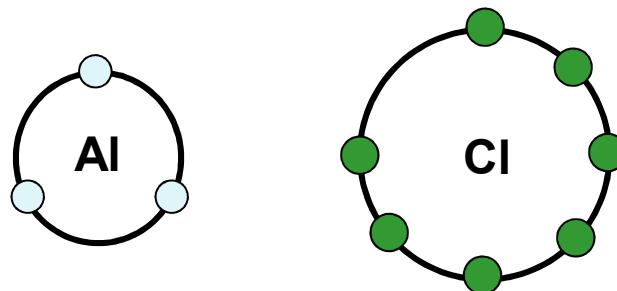
LONE PAIRS 0

BOND ANGLE... **180°**

SHAPE... **LINEAR**



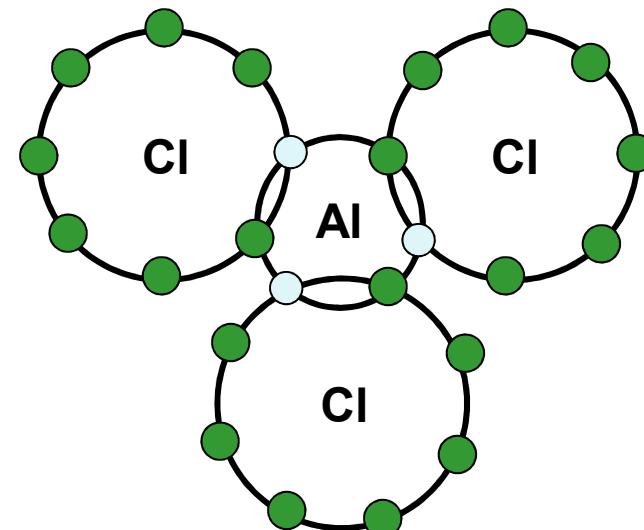
ALUMINIUM CHLORIDE



Aluminium - has three electrons to pair up

Chlorine - needs 1 electron to complete 'octet'

Three covalent bonds are formed; aluminium still has an incomplete outer shell.

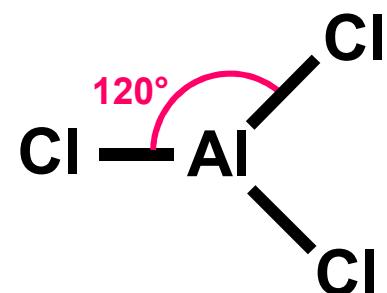


BOND PAIRS 3

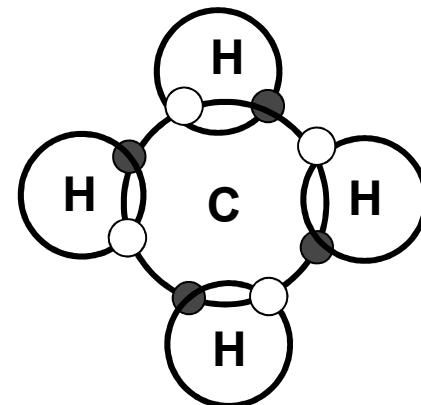
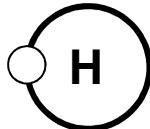
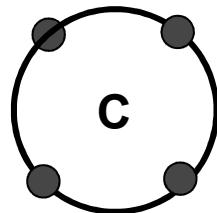
LONE PAIRS 0

BOND ANGLE... **120°**

SHAPE... **TRIGONAL PLANAR**



METHANE



Carbon - has four electrons to pair up

Hydrogen - 1 electron to complete shell

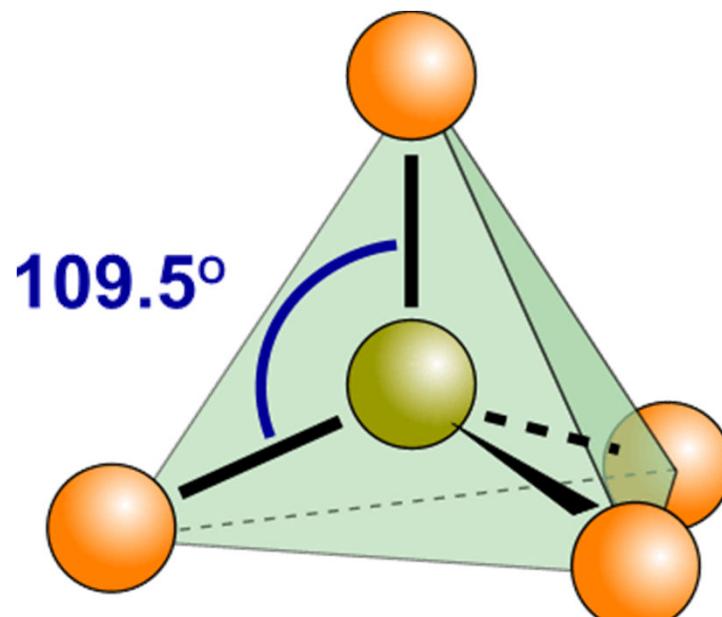
Four covalent bonds are formed

C and H now have complete shells

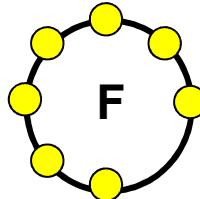
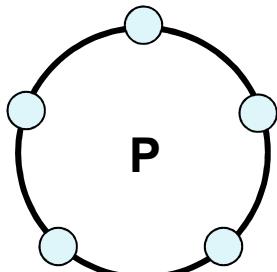
BOND PAIRS	4
LONE PAIRS	0

BOND ANGLE... **109.5°**

SHAPE... **TETRAHEDRAL**



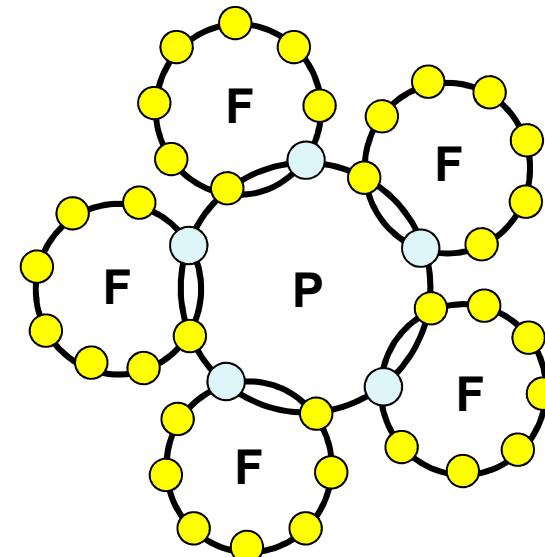
PHOSPHORUS(V) FLUORIDE



Phosphorus - has five electrons to pair up

Fluorine - needs one electron to complete 'octet'

Five covalent bonds are formed; phosphorus can make use of d orbitals to expand its 'octet'

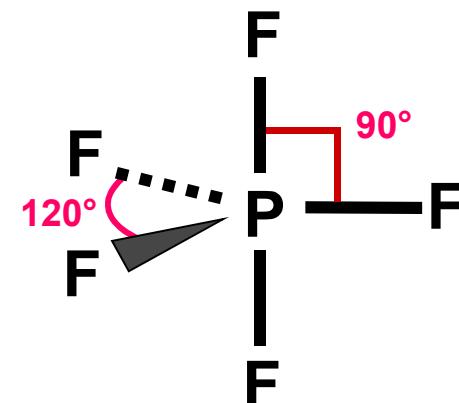


BOND PAIRS 5

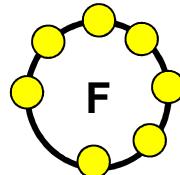
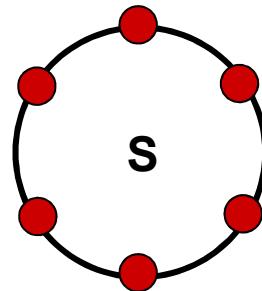
LONE PAIRS 0

BOND ANGLE... **120° & 90°**

SHAPE... **TRIGONAL BIPYRAMIDAL**



SULPHUR(VI) FLUORIDE



Sulphur - has six electrons to pair up

Fluorine - needs one electron to complete 'octet'

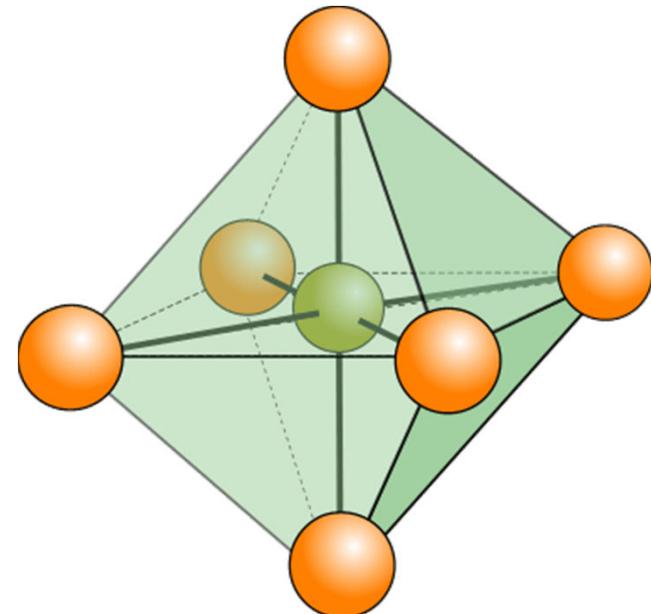
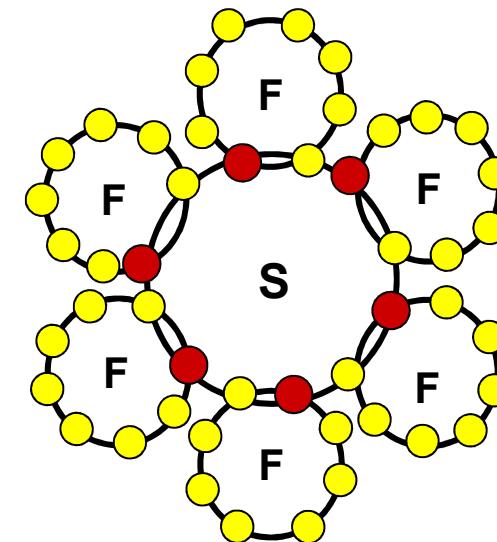
Six covalent bonds are formed; sulphur can make use of d orbitals to expand its 'octet'

BOND PAIRS 6

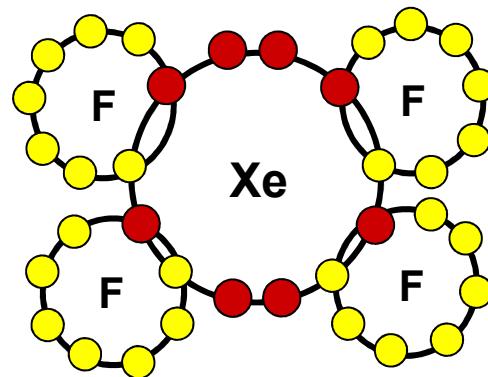
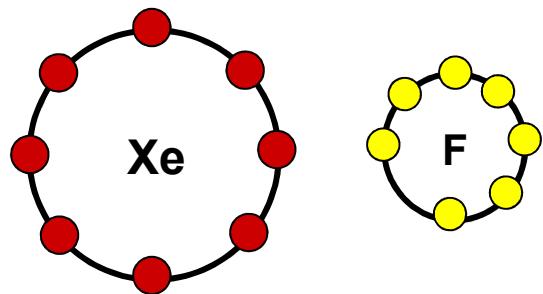
LONE PAIRS 0

BOND ANGLE... 90°

SHAPE... OCTAHEDRAL

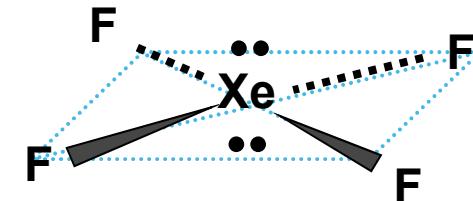
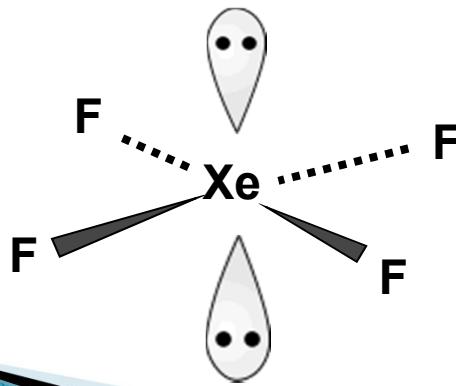


XENON TETRAFLUORIDE



BOND PAIRS	4
LONE PAIRS	2
TOTAL PAIRS	6

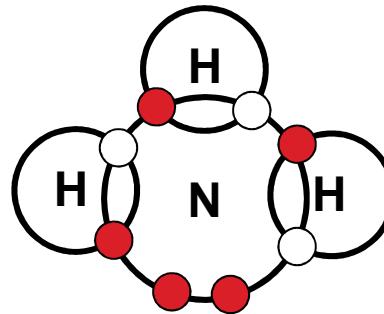
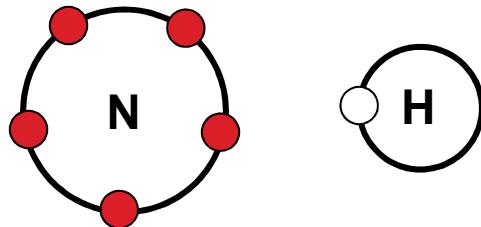
- As the total number of electron pairs is 6, the shape is BASED on an octahedron
- There are two possible spatial arrangements for the lone pairs
- The preferred shape has the two lone pairs opposite each other



ANGLE... **90°**

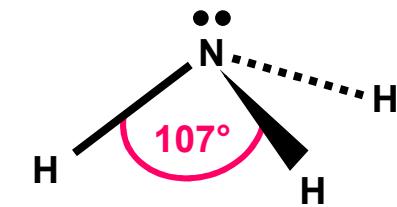
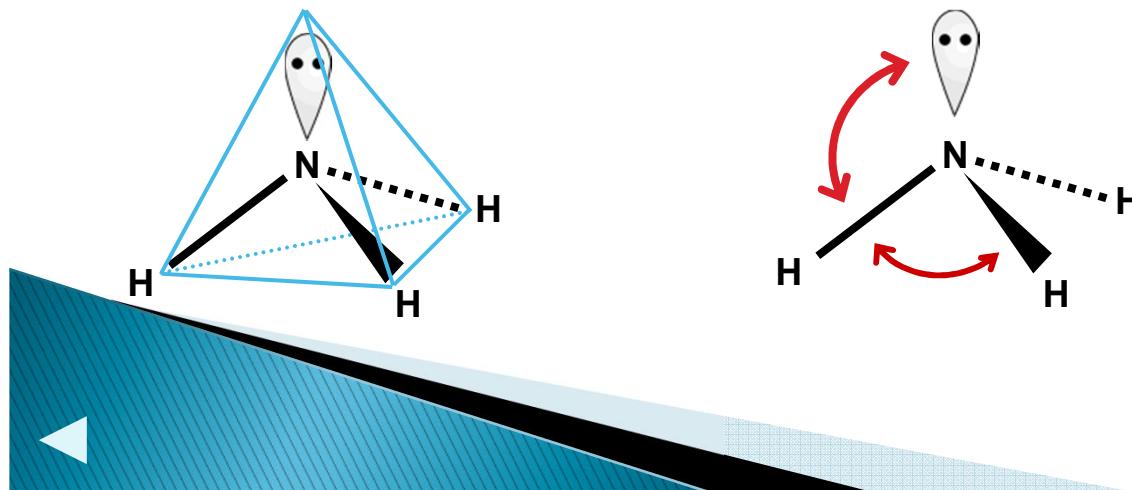
SHAPE... **SQUARE PLANAR**

AMMONIA



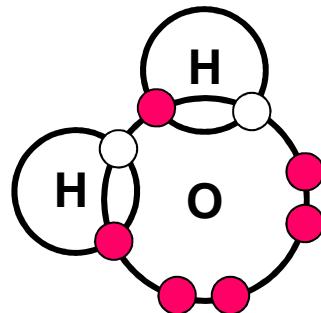
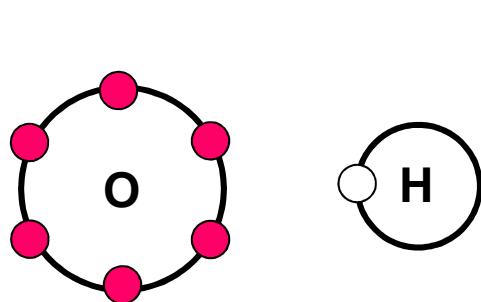
BOND PAIRS	3
LONE PAIRS	1
TOTAL PAIRS	4

- The shape is based on a tetrahedron but not all the repulsions are the same
- LP-BP REPULSIONS > BP-BP REPULSIONS**
- The N-H bonds are pushed closer together
- Lone pairs are **not included** in the shape



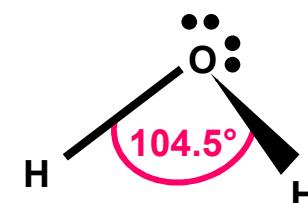
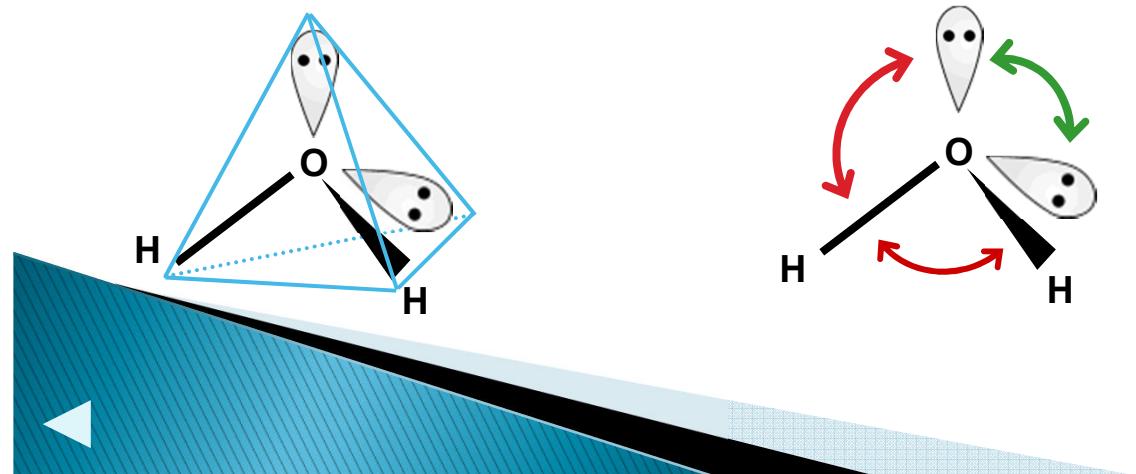
ANGLE ... 107°
SHAPE ... PYRAMIDAL

WATER



BOND PAIRS	2
LONE PAIRS	2
TOTAL PAIRS	4

- The shape is based on a tetrahedron but not all the repulsions are the same
- LP-LP REPULSIONS > LP-BP REPULSIONS > BP-BP REPULSIONS**
- 2 lone pair exist which gives stronger repulsion than the bonding pairs
- The O-H bonds are pushed even closer together
- Lone pairs are not included in the shape



ANGLE ... **104.5°**

SHAPE ... **ANGULAR**

Predict the Shape of Molecules

- ▶ Steps to follow:-
- ▶ Decide which atom is at the centre of the molecule (usually the atom of which there is only one or least)
- ▶ Determine the number of electron pairs around the central atom :
- ▶ 1. Look up number of valence electrons in central atom
- ▶ 2. Add e^- if particle is negatively charged or subtract e^- if particle is positively charged.



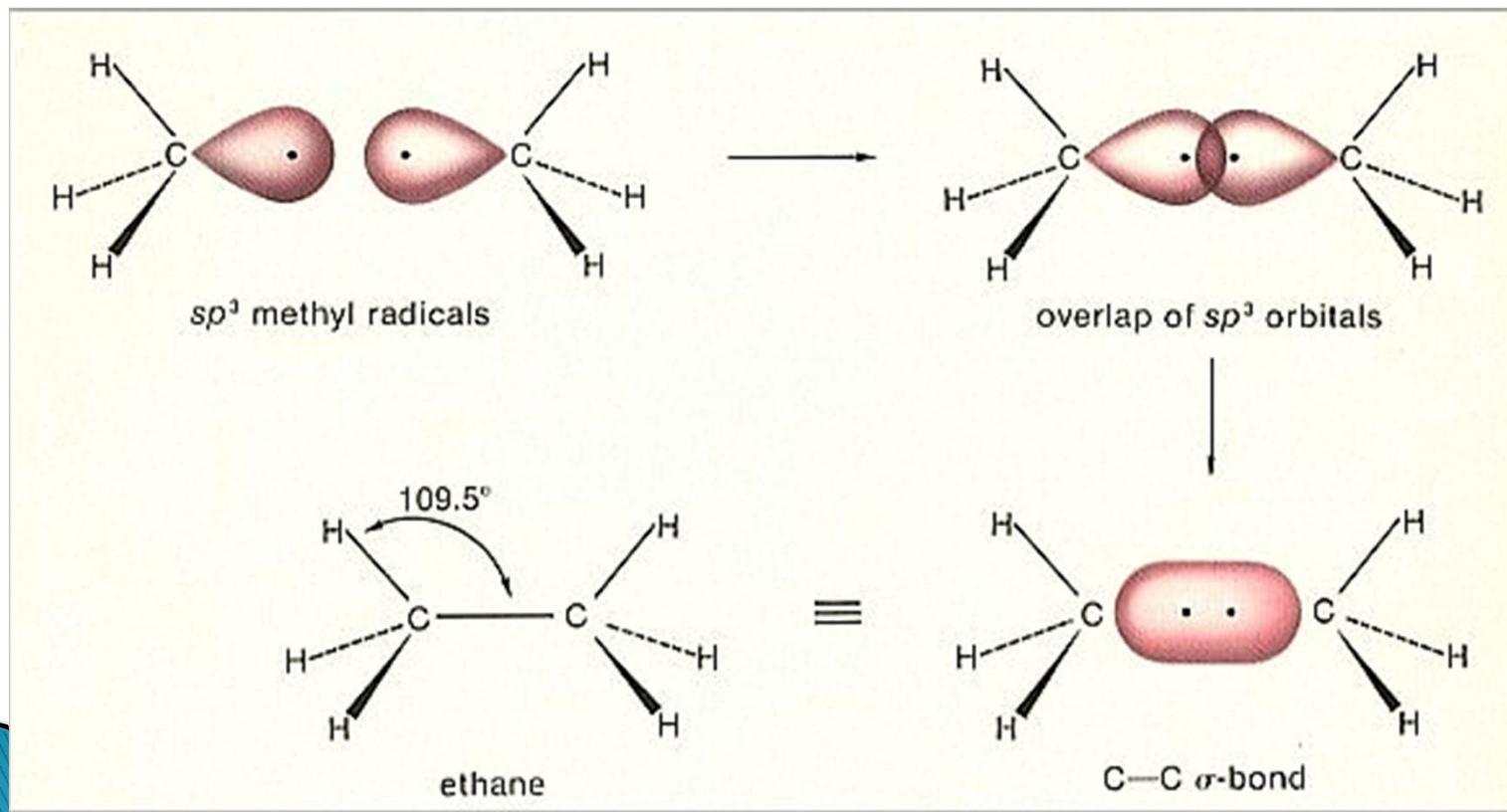
Predict the Shape of Molecules

- ▶ 3. Draw the dot and cross diagram.
- ▶ 4. Determine the number of bond pairs and lone pairs and hence, the shape of the molecules.
- ▶ 5. The repulsion between lone pairs and bond pairs determines the bond angle.



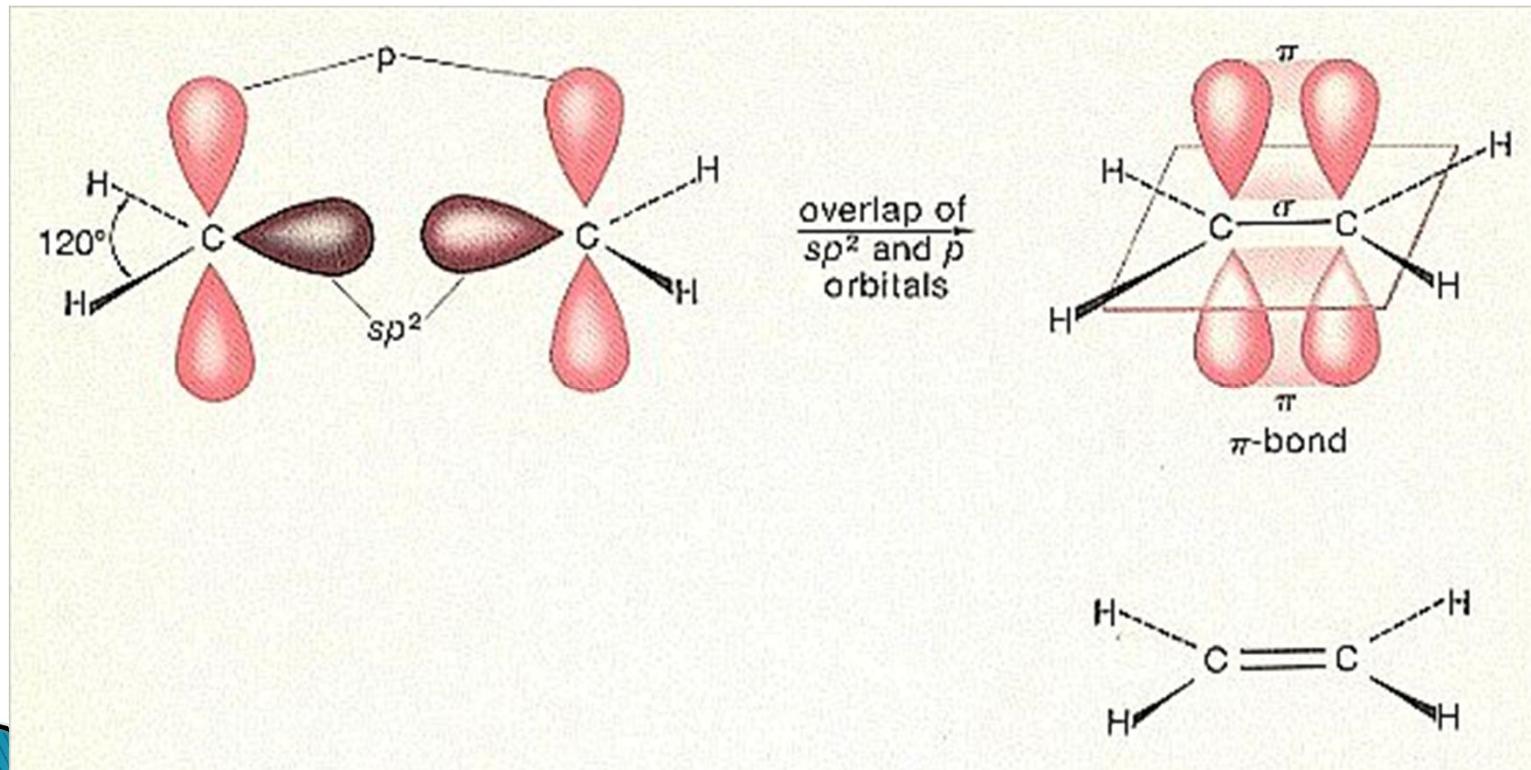
Angles in ethane molecule

- ▶ The ethane molecule is a non-planar molecule.
- ▶ All bond angles = 109.5°



Angles in ethene molecule

- ▶ Ethene molecule is a planar molecule.
- ▶ All bond angles = 120°



Shapes of Molecules summary

Total no. of electron pairs	No. of bonding pair	No. of lone pair	Shape
1 or 2	1 or 2	0	Linear
3	3	0	Trigonal planar
4	4	0	Tetrahedral
4	3	1	Trigonal pyramidal
4	2	2	V-shape (bent)
5	5	0	Trigonal bipyramidal
6	6	0	Octahedral

Bond Polarity

- ▶ A polar covalent bond is formed between atoms of different electronegativities.
- ▶ Electronegativity is a measure of the relative tendency of an atom in a covalent bond to attract a bonding pair of electrons.
- ▶ The more electronegative atom pulls the electrons of the covalent bond towards itself → acquires a partial negative charge(δ^-)
- ▶ while the less electronegative atom acquires a partial positive charge(δ^+)
- ▶ This unequal sharing of electrons is known as polarisation.



Bond Polarity

- ▶ The covalent is said to be polarised and has dipole (i.e. there are two separate regions of charge).
- ▶ Eg. H-Cl bond is polar; the bonding pair of electrons in the covalent bond is attracted towards the more electronegative Cl atom.
- ▶ a covalent bond between two identical atoms (eg. two Cl atoms in a molecule of Cl_2) is not polarised since the electrons are equally shared.

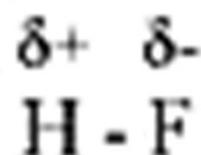


Bond polarity

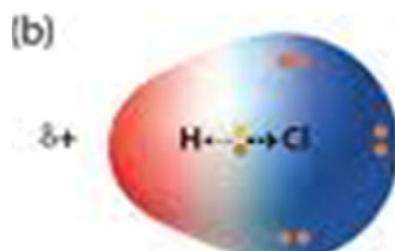
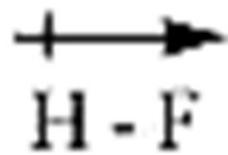


Nonpolar covalent bond

Bonding electrons shared equally between two atoms.
No charges on atoms.

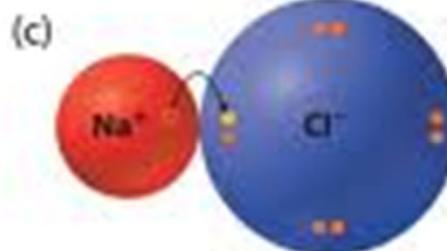


or



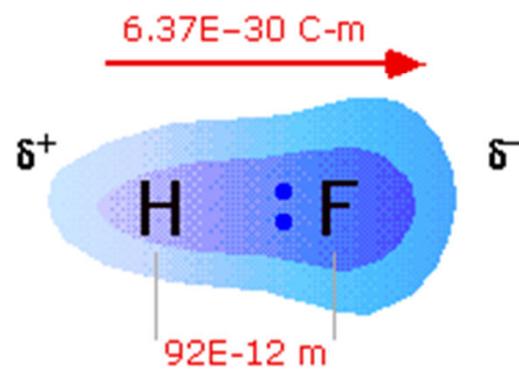
Polar covalent bond

Bonding electrons shared unequally between two atoms.
Partial charges on atoms.



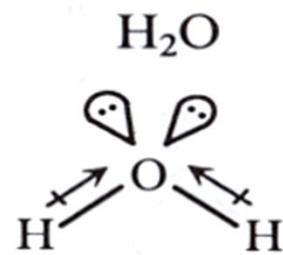
Ionic bond

Complete transfer of one or more valence electrons.
Full charges on resulting ions.

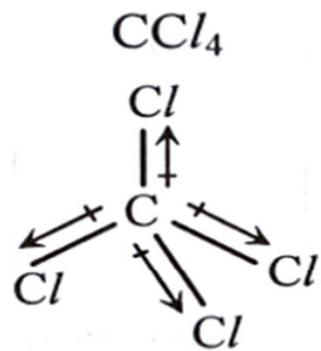


Polar Molecule

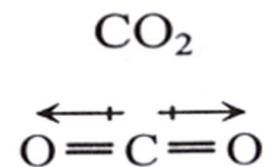
- ▶ A molecule is polar and thus, has a dipole moment if :
 - ❖ its bonds are polarised and
 - ❖ it is not symmetrical (i.e the individual dipoles do not cancel each other out)



Individual dipoles do **not** cancel out; so molecule has a dipole moment.



Individual dipoles cancel each other; so molecule has **no** dipole moment.



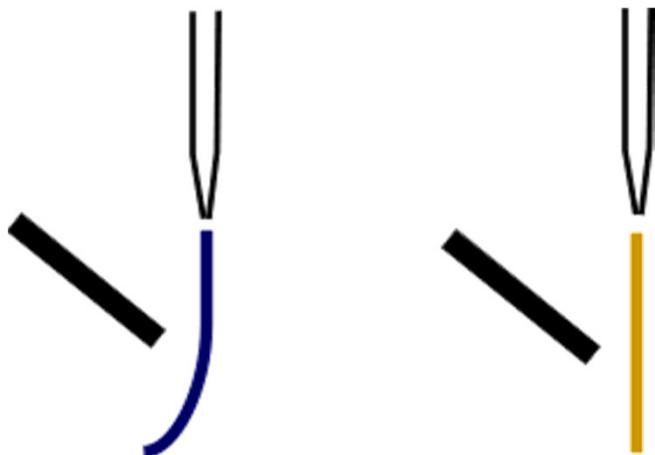
Individual dipoles cancel each other; so molecule has **no** dipole moment.

POLAR MOLECULES

Evidence

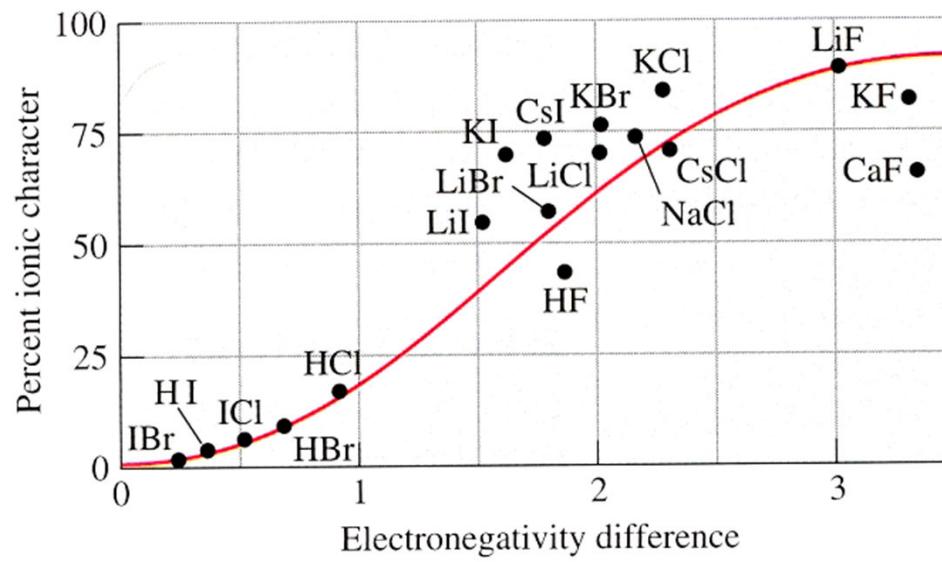
attraction

place a liquid in a burette allow it to run out place a charged rod alongside the stream of liquid
polar molecules will be attracted by electrostatic
non-polar molecules will be unaffected



Covalent compound with ionic character.

- ▶ Electronegativity decrease down the group, increase across the period.
- ▶ The higher the difference of electronegativity between the 2 covalent bonded atoms, the higher the percentage of ionic character.



Ionic compound with covalent character.

- ▶ Ionic bonds can have some covalent character
→ due to polarisation of ions.
- ▶ The cation attracts the negative charge of anion → distortion of anion charge cloud.
- ▶ The covalent character is higher when the cation has high charge density (high charge, small size.)

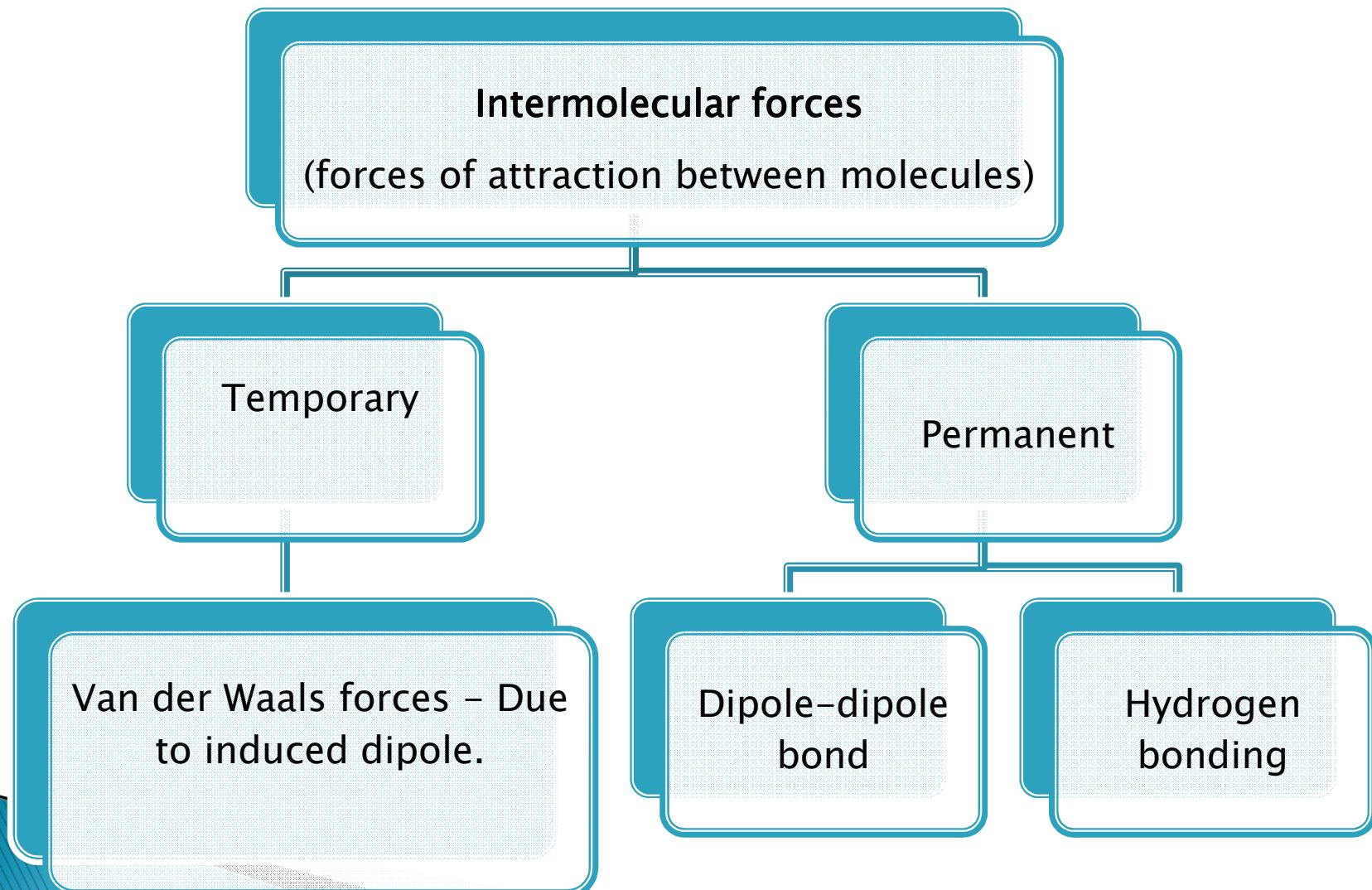


Ionic compound with covalent character.

- ▶ High covalent character in ionic bond exist when:
 - (a) cation is small
 - (b) anion is large
 - (c) cation has a high charge.
- ▶ E.g : Al_2O_3



Intermolecular forces



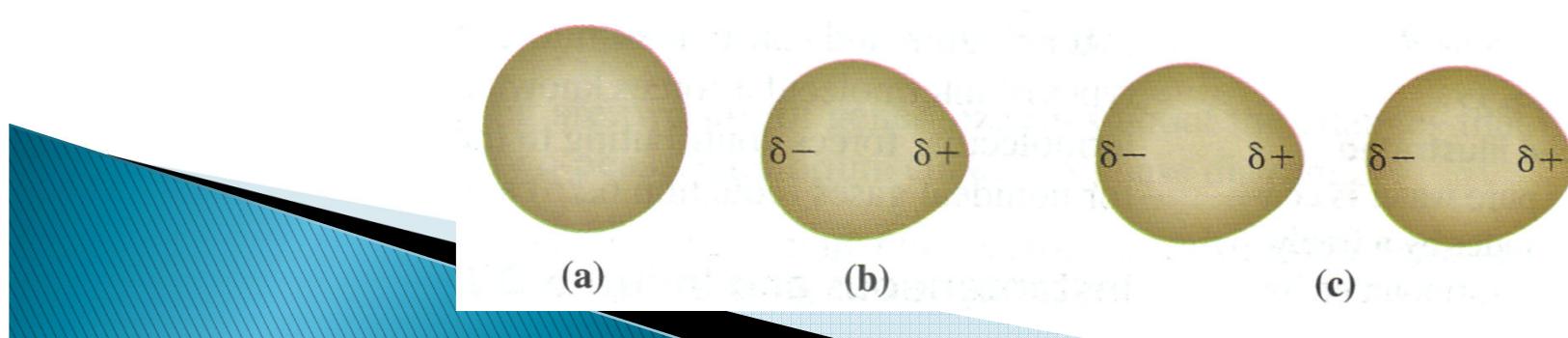
Van der Waals' Force

- ▶ forces of attraction between non-polar molecule (eg. Br_2) which arises due to induced/temporary dipole-dipole attraction.
- ▶ the electrons in a molecule can, at any moment, be unevenly distributed so that one side of the molecule is slightly positive and the opposite side is slightly negative.
- ▶ This is called an instantaneous dipole.



Van der Waals' Force

- ▶ an instantaneous dipole in one molecule can induce another dipole in a neighbouring molecule.
- ▶ the two molecules will then attract each other.
- ▶ these weak forces of attraction between all the molecules are called Van der Waals' forces.
- ▶ <http://chemmovies.unl.edu/ChemAnime/LONDOND.html>



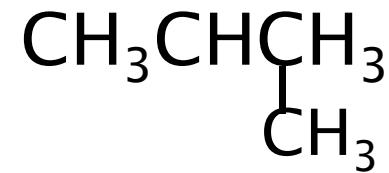
Factors affecting the strength of Van der Waals Forces

- ▶ 1. Number of electrons in the molecule
- ▶ the greater the number of electrons in the molecule, the stronger is the intermolecular Van der Waal's forces of attraction.
- ▶ this is shown by the higher melting and boiling points of the substances.



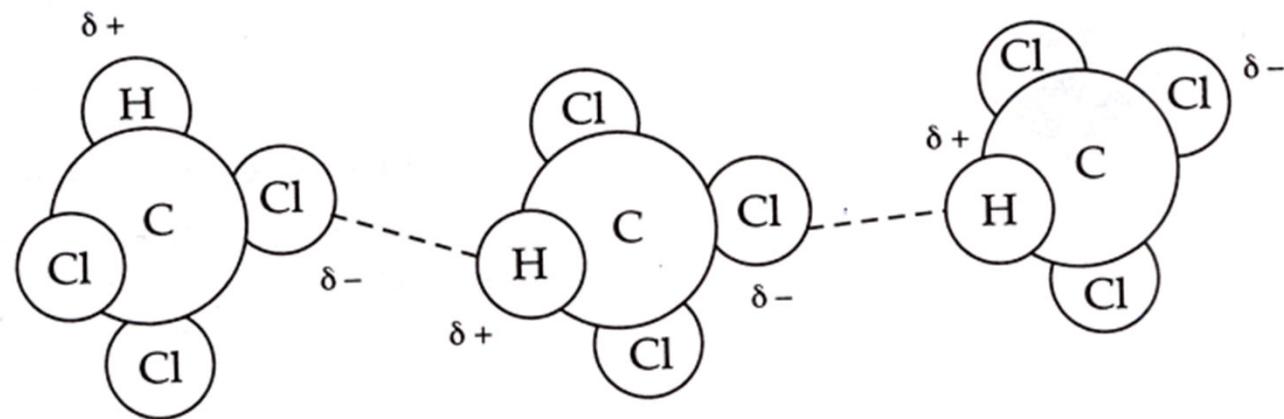
Factors affecting the strength of Van der Waals Forces

- ▶ 2. Shape of the molecule
- ▶ > in hydrocarbons, branching reduces the strength of Van der Waals' forces because the molecule is more spherical in shape and so, offers smaller surface areas of contact for Van der Waals' forces.



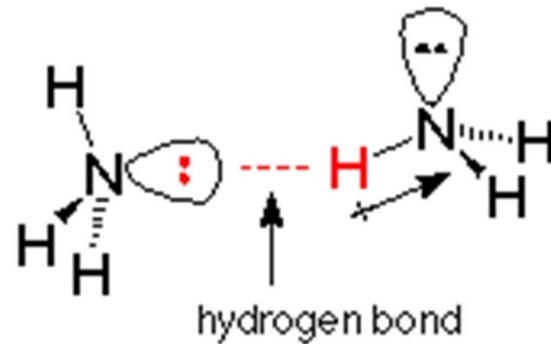
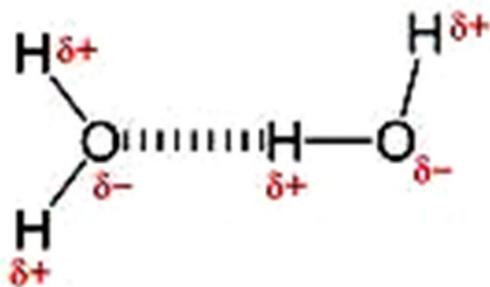
Permanent Dipole–Dipole forces

- ▶ forces of attraction between polar molecules (eg. HCl, CHCl₃).
- ▶ Molecules have permanent dipole moments.



Hydrogen bonding

- ▶ forces of attraction between an electron – deficient hydrogen bonded to a very electronegative atom (such as N, O and F)
- ▶ and the lone pair of a neighbouring very electronegative atom(such as N, O or F)



Hydrogen bonding

- ▶ Hydrogen bonds are stronger than ordinary dipole attraction, but weaker than normal covalent or ionic bonds.

Hydrogen bond

Intermolecular
(between atoms of
neighbouring
molecules)

Intramolecular
(between atoms in
same molecules)

Hydrogen bonding

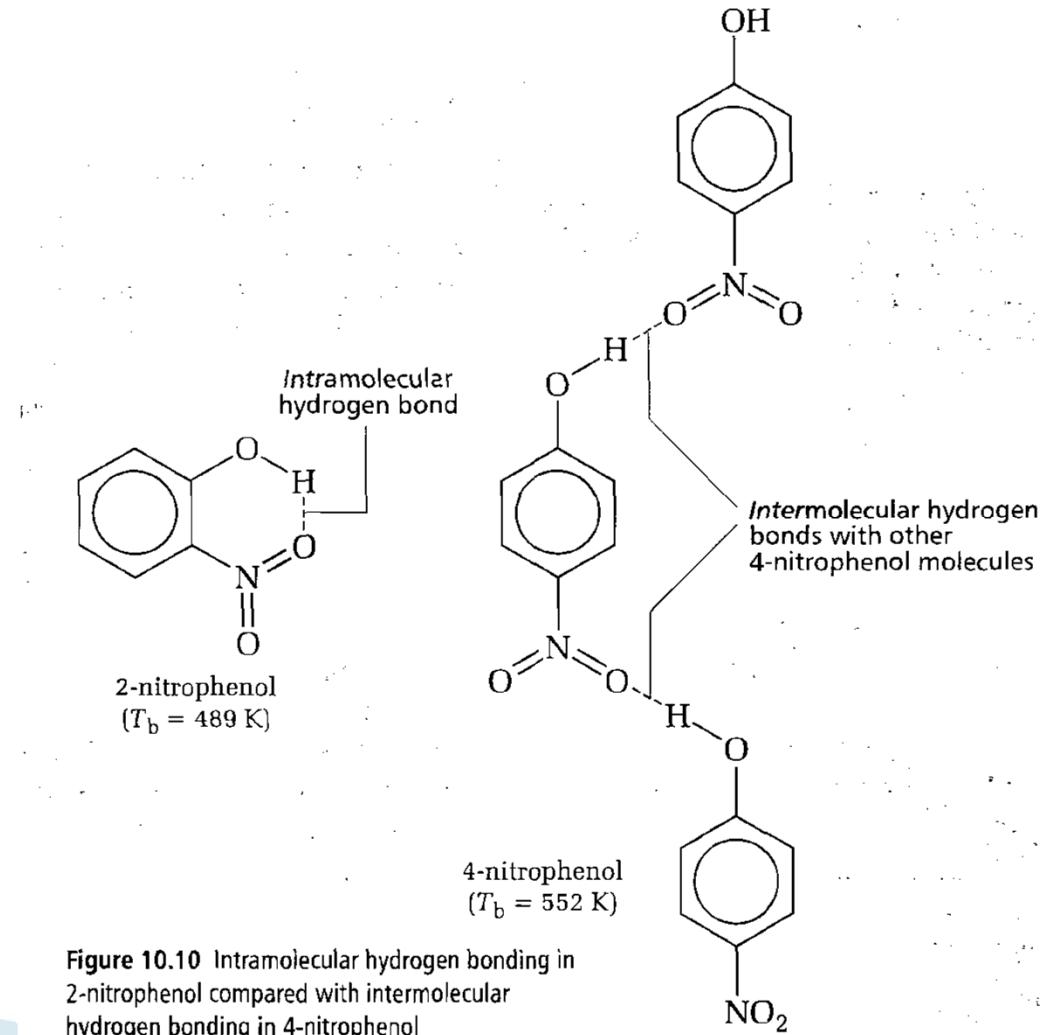


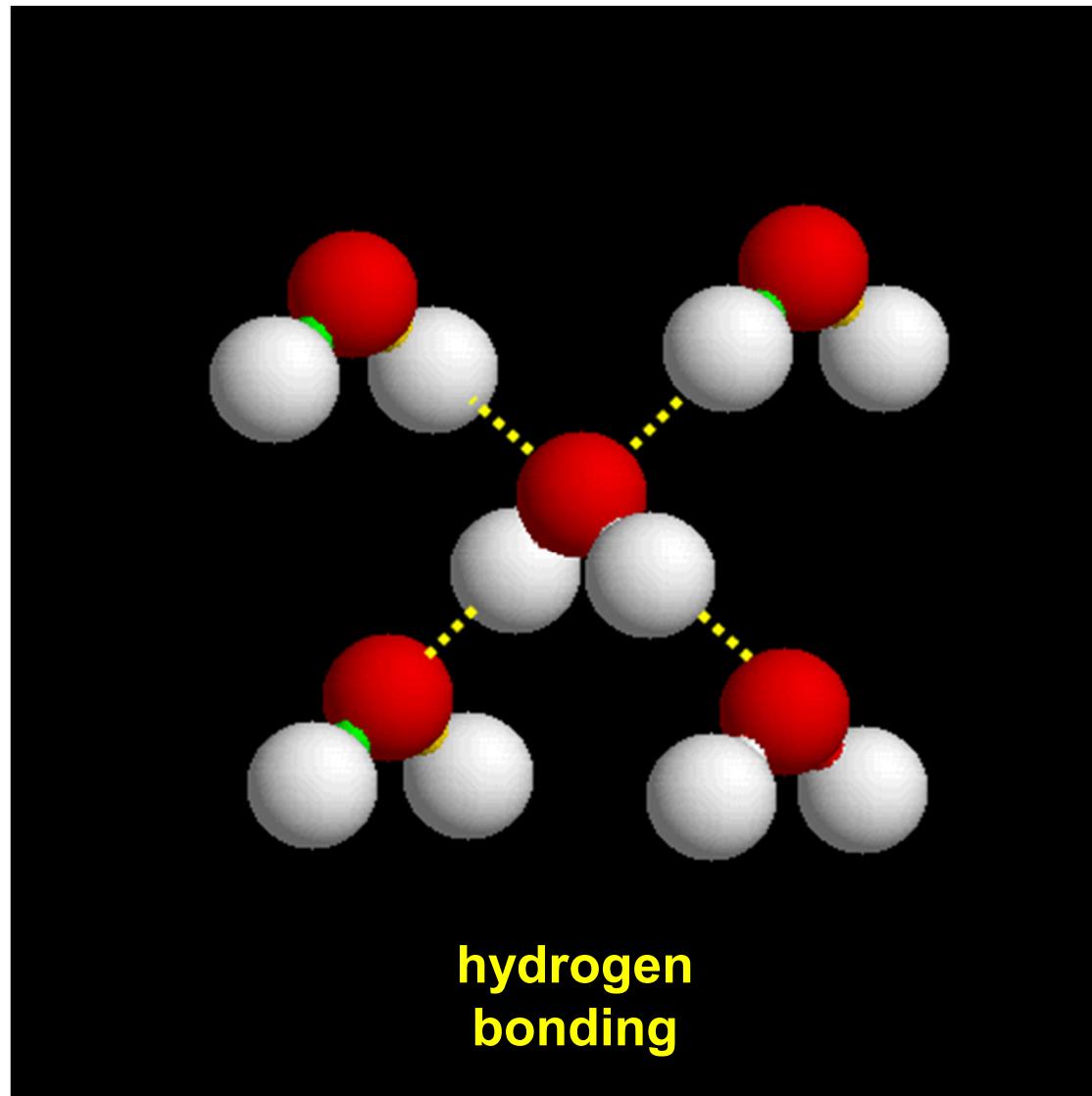
Figure 10.10 Intramolecular hydrogen bonding in 2-nitrophenol compared with intermolecular hydrogen bonding in 4-nitrophenol

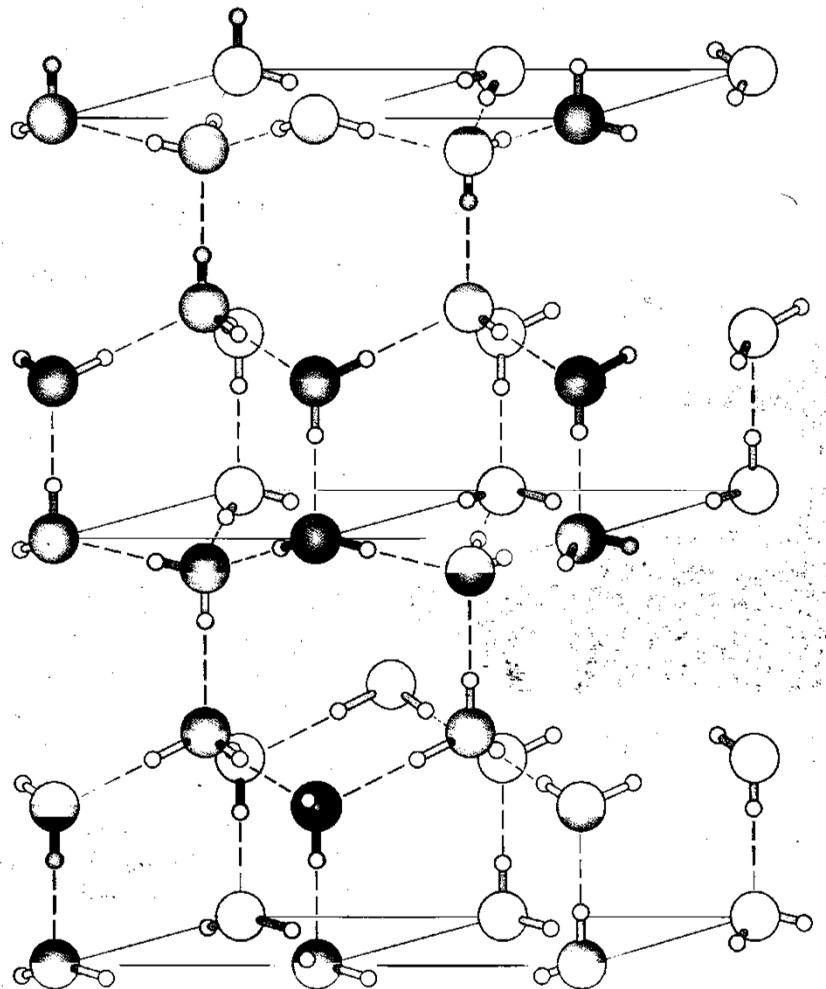
Properties of Hydrogen Bonding

1. Solubility of substance in water.
 - NH₃, alcohol, carboxylic acid, amines and sugar is soluble in water.
2. Anomalous behaviour of water.
 - Density of ice, H₂O(s) < density of water, H₂O(l)
 - water expands on freezing.
 - 1 water molecule held to 4 neighbours in a tetrahedral arrangement → called open structure.
 - density = mass/volume



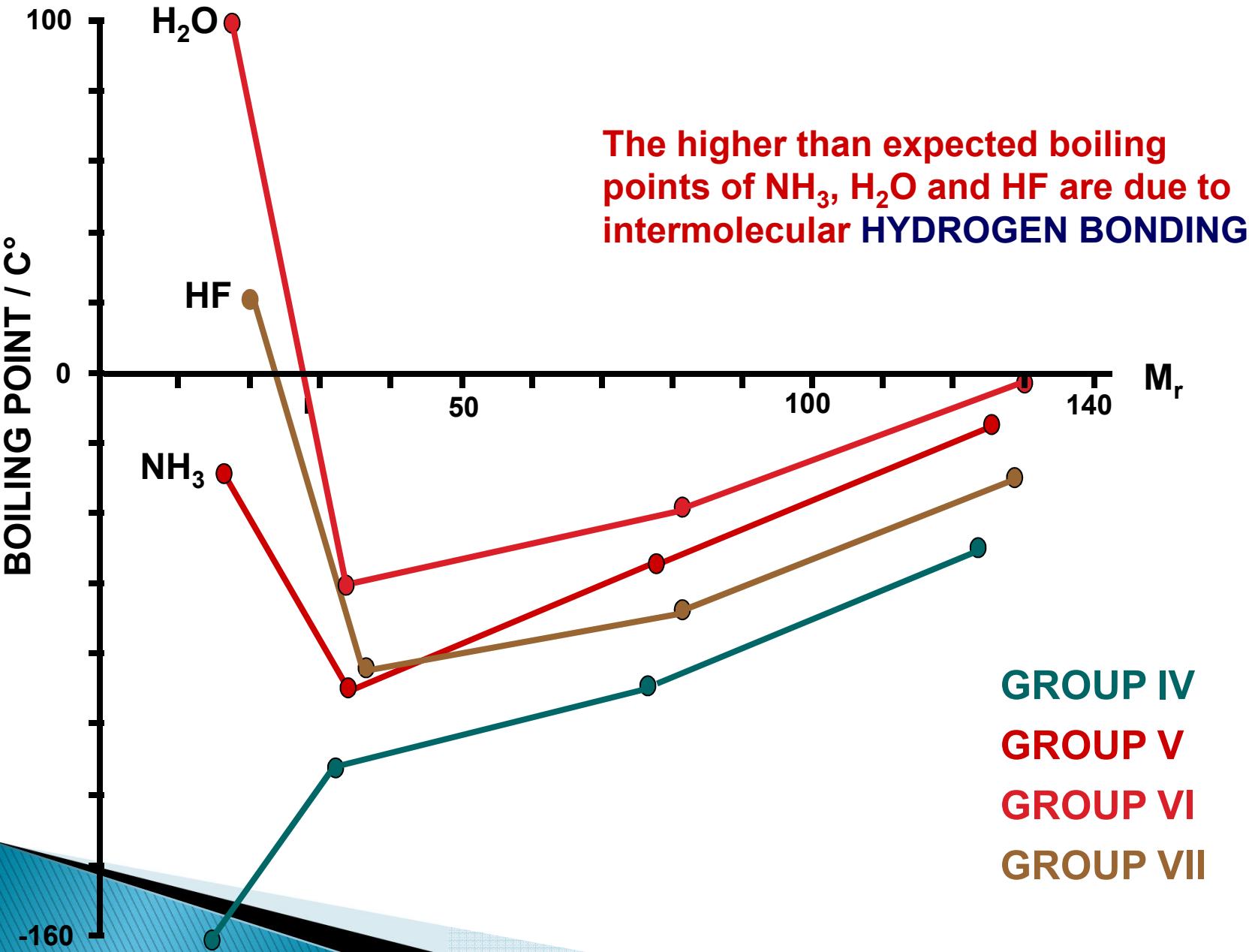
HYDROGEN BONDING – ICE





Rigid and open structure of ice gives ice a low density

BOILING POINTS OF HYDRIDES



Boiling points of hydrides cont.

Why boiling point of $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$?

state the no. of lone pairs, H atoms bonded to F,O, or N, and H-bond can be formed for each molecule in:

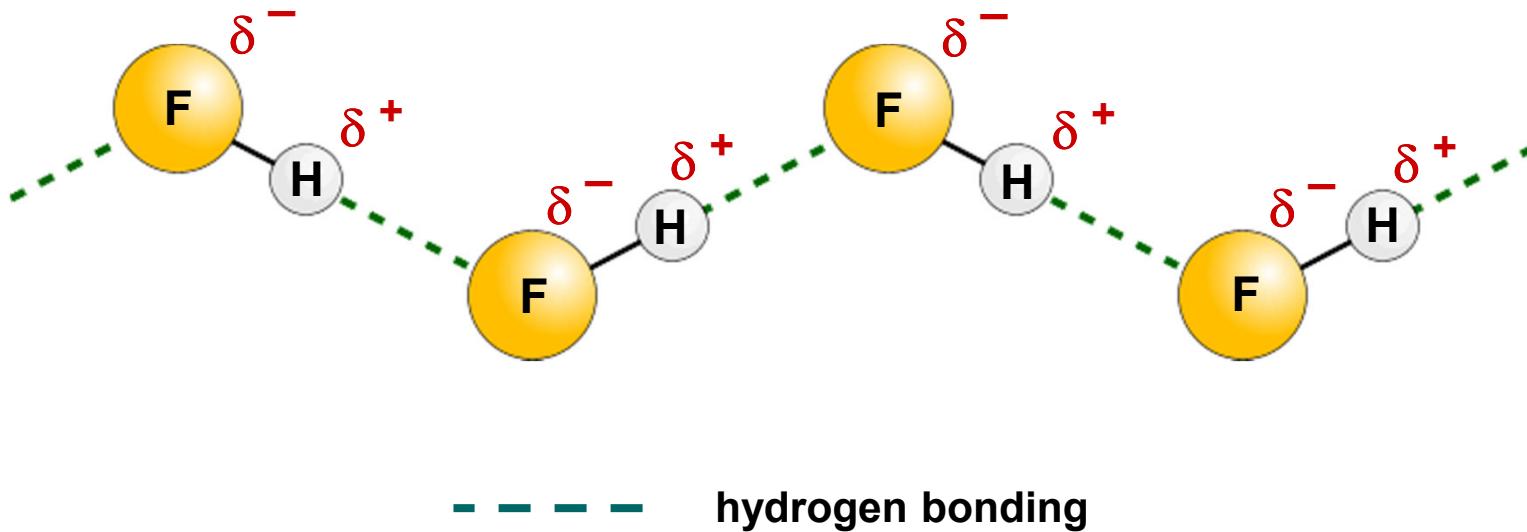
▶ H_2O

▶ HF

▶ NH_3



HYDROGEN BONDING – HF



Hydrogen fluoride has a much higher boiling point than one would expect for a molecule with a relative molecular mass of 20

Fluorine has the highest electronegativity of all and is a small atom so the bonding with hydrogen is extremely polar

4. Anomalous M_r

- ▶ E.g : Gaseous ethanoic acid
- ▶ Measured M_r from experiment = 120 g mol⁻¹
- ▶ Calculated M_r (theoretical value) = 60 g mol⁻¹
- ▶ Due to dimerisation through hydrogen bonding.

