

BONDING, LEWIS STRUCTURES

"There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions .And it is the Business of Experimental Philosophy to find them out." **Isaac Newton, 1717**

"Two atoms may conform to the rule of eight, or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons. These electrons which are held in common by two atoms may be considered to belong to the outer shells of both atoms." **Gilbert Newton Lewis, 1916**

"We shall say that there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species." **Linus Carl Pauling, 1939** (Nobel Prize in Chemistry in 1954 "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances" and Nobel Peace Prize in 1962.)

CLASSICAL DESCRIPTION OF BONDING AND PERIODICITY

Chemical bond – forces that hold a group of atoms together causing them to function as a unit and lowering the energy of the system

Experimental evidence:

ionization energy – minimum energy to remove an electron in the gas phase

electron affinity – energy change when an electron is added to a gaseous atom

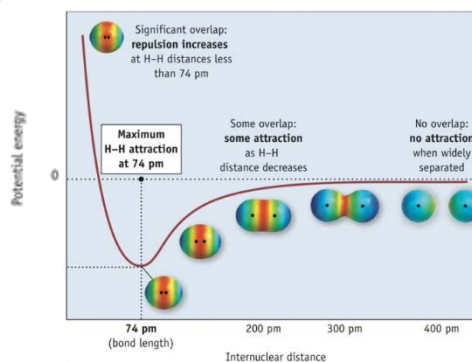
Idealized conceptual models:

1) **ionic bond** – e^- transferred

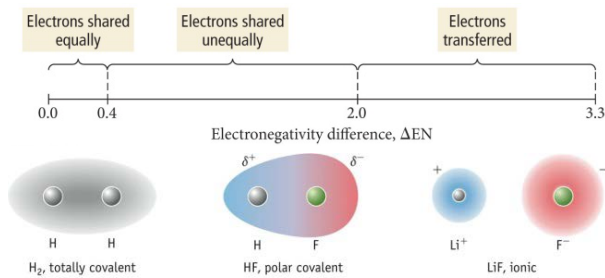
As **ion charge** increases, **force of attraction** increases

As **distance** increases, **force of attraction** decreases

2) **covalent bond** – e^- shared



3) **polar covalent bond** – partial transfer



Periodic Trends

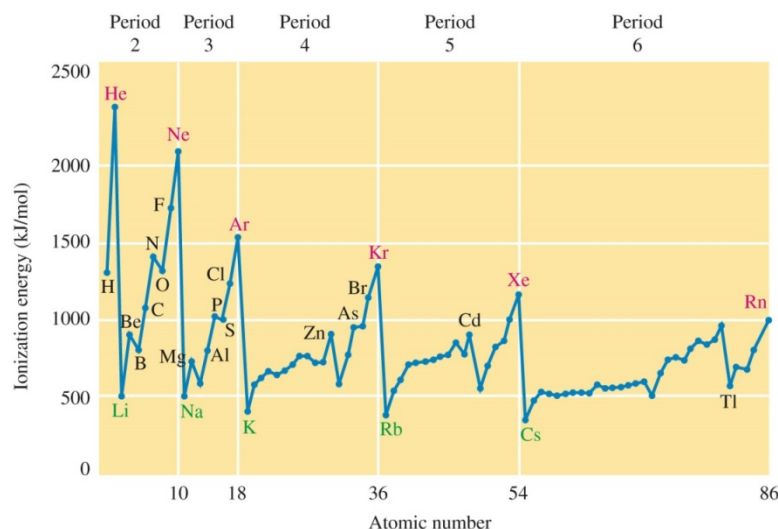
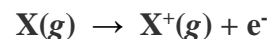


FIG I – First Ionization Energies (IE) of the Elements:



shell structure

noble gas configuration

good metals

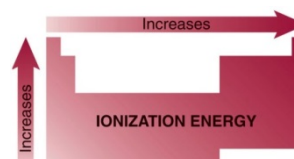


FIG II – Size of Atoms and Ions

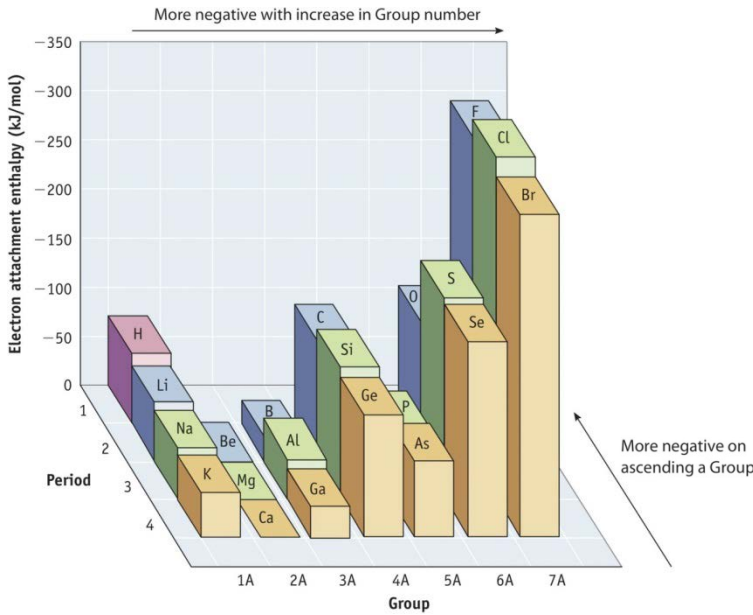
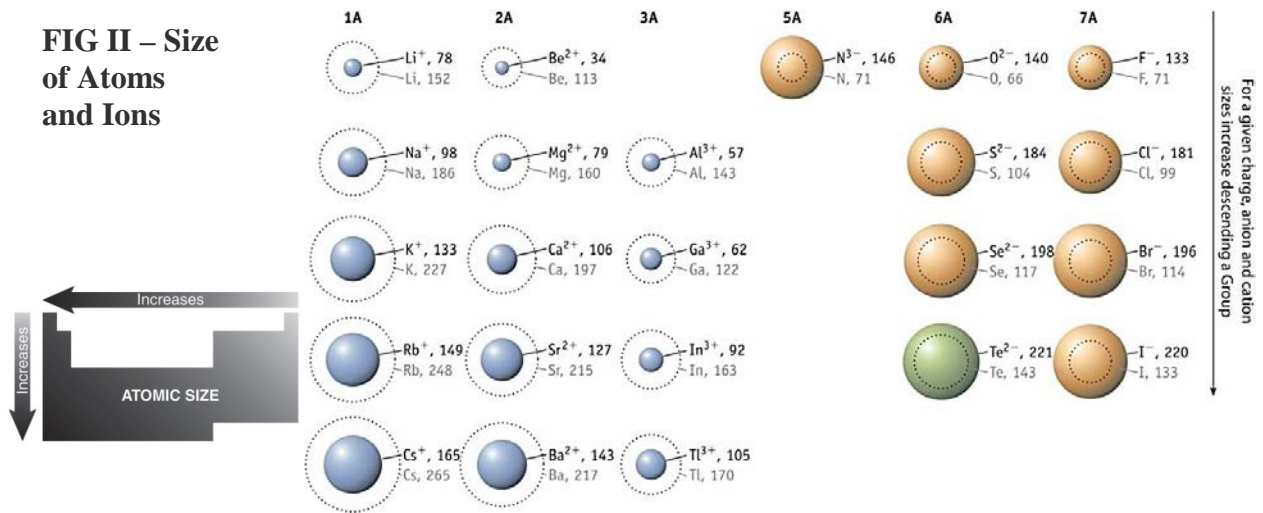
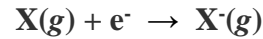


FIG III – Electron Affinities (EA) of the Elements



noble gases have positive EAs

reveals

shell, subshell structure
noble gas configuration

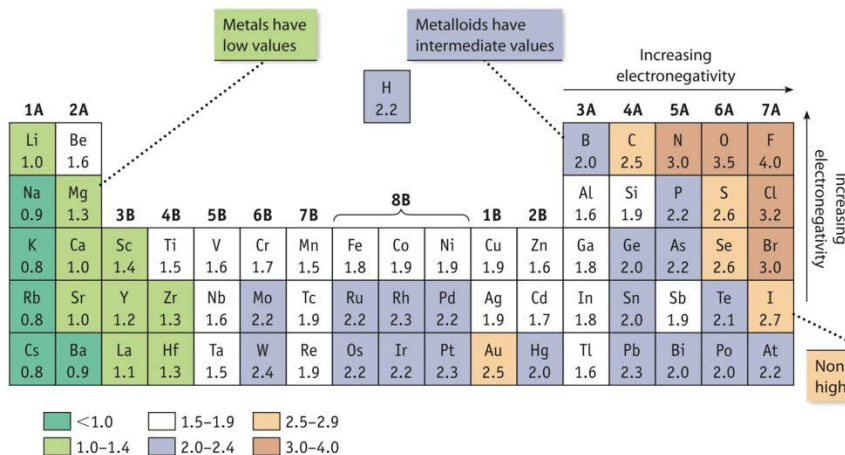
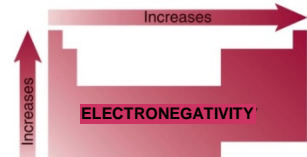


FIG IV – Electronegativities (EN) of the Elements

ability of an atom in a molecule to attract shared electrons to itself

combines IE and EA into one property



Seven SIMPLE BONDING CONCEPTS

1) Lewis structures – guidelines (13.10 – 13.12)

- determine total **number of valence electrons** from group numbers (GN); most atoms obey **octet rule** – exceptions to octet rule:

2 – H, He

4 – Be

6 – B, Al

species with odd number of electrons

some species with an element beyond 2nd period

- draw structure with all bonding pairs and lone pairs using symmetry
- show all **resonance structures** (atoms do not move)
- determine **formal charge** (FC) on all atoms having any

FC = GN – number of lone pair electrons – 1/2 number of bonding pair electrons

- **valence shell expand** (VSE) if atom is beyond 2nd period and 1) has a formal charge separation or 2) octet rule gives insufficient number of bonding electrons; VSE to minimize FC separation while maximizing number of resonance structures (VSE for Week 6)

1. NH₃

2. C₂H₆

3. C₂H₂

4. N₂

5. NaOH

6. S₂O

2) **resonance** – all resonance structures have same number of bonds and lone pairs

3) **formal charge** – usually more electronegative element has negative charge; consider CO

VSEPR THEORY

Z Ch 13.13

"... the size of the valency group ... assume that the electron pairs occupy much the same positions whether they are shared or not ... determines, the type of spatial arrangement adopted ... With a quartet of electron, the molecule is linear (as in Cl-Hg-Cl). With a sextet, the arrangement is planar, and the valency angles 120° , giving with a covalency of 3 the plane symmetrical molecule (as in BF_3) and where it is 2-covalent, as in SnCl_2 a triangular molecule. With an octet there appear[s] ... the tetrahedron ..., the 2-covalent being triangular and the covalent pyramidal ... The decet when fully shared (5-covalent) gives the trigonal [bi]pyramid ... The 2-covalent decet is ... linear, as if derived from the trigonal bipyramid by removing all three equatorial groups. The duodecet when fully shared (6-covalent) is octahedral ... The 4-covalent form is ... square, and so to be derived from the octahedron by removing two trans groups."

Nevil V. Sidgwick and Herbert M. Powell, 1940

"The stereochemistry of an atom in any particular molecule depends on the number of pairs of electrons in its valency shell ... The general arrangement of the valencies around any atom is determined by the fact that the lone pairs ... arrange themselves as far apart as possible ... A more detailed and exact description of the shapes of molecules can be given if it is assumed ... that a lone pair repels other electron pairs more than a bonding pair of electrons ..."

Ronald J. Gillespie and Ronald S. Nyholm, 1957

"We were concerned about how to best give students some understanding of the shapes of inorganic molecules ... We found that we could explain the shapes of essentially all molecules of the type AX on the basis that the electron pairs in the valence shell of a central atom keep as far apart as possible. Moreover, by making allowances for the differences between bonding and nonbonding electron pairs, we could account for small deviations from the basic idealized shapes ..."

Ronald J. Gillespie, 1984

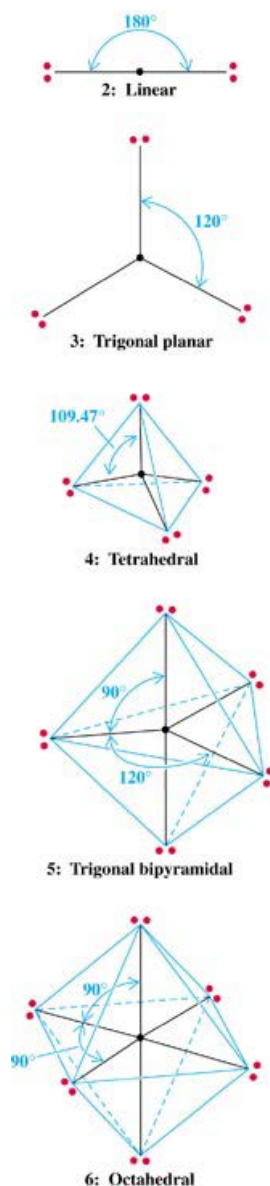


FIG V – Electron Pair Geometries

4) Valence Shell Electron Pair Repulsion (VSEPR) Theory

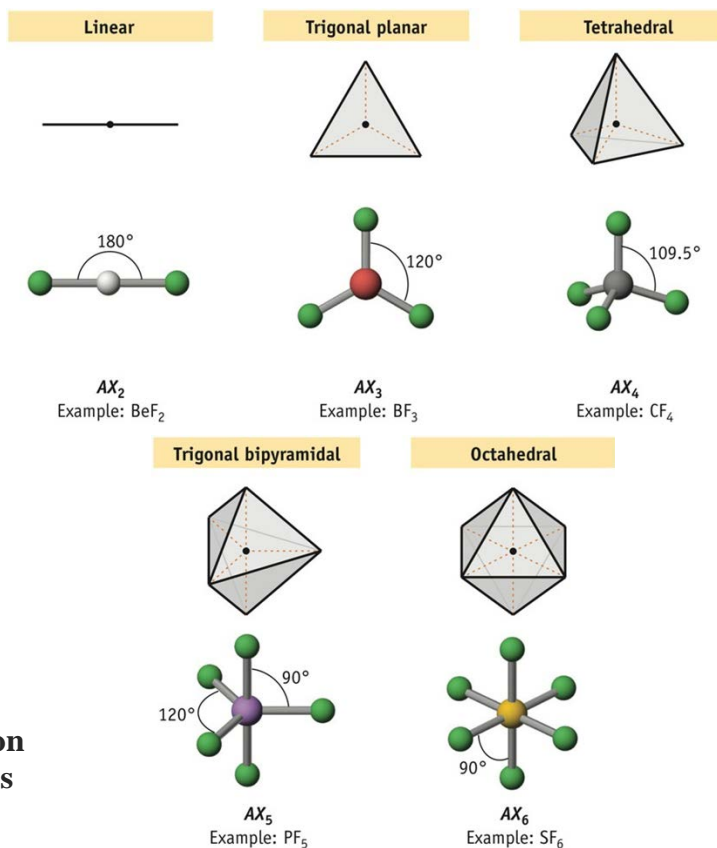
repulsions: BP/BP < BP/LP < LP/LP

steric number (number of electron pairs) => **electronic geometry**
molecular geometry (shape) => bond angles, distortions

electronegativity => bond polarity

molecular polarity => dipole moment

FIG VI – Various Geometries Predicted by VSEPR



linear, bent, and trigonal planar geometries for two and three electron pairs (steric number = 2, 3)

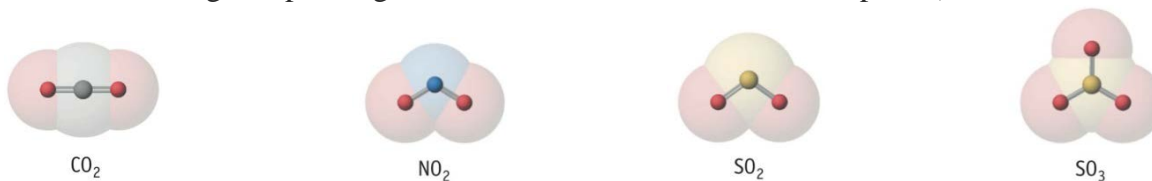
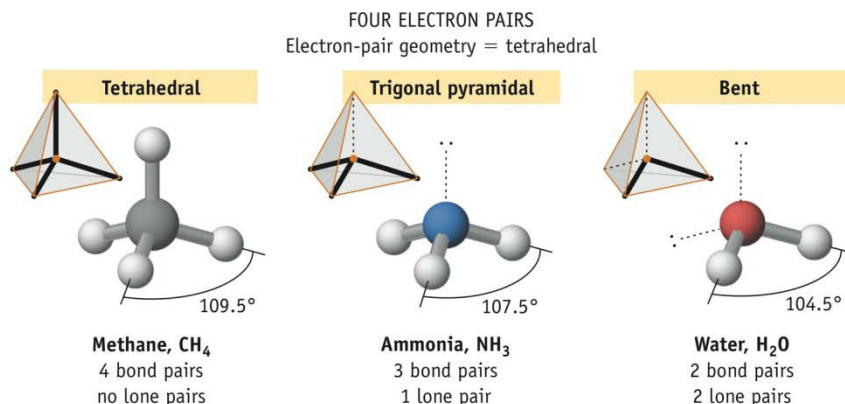


FIG VII – Molecular Geometries for Four Electron Pairs (Steric Number = 4)



5) valence shell expansion (VSE)

FIG VIII – Molecular Geometries for Five Electron Pairs (Steric Number = 5)

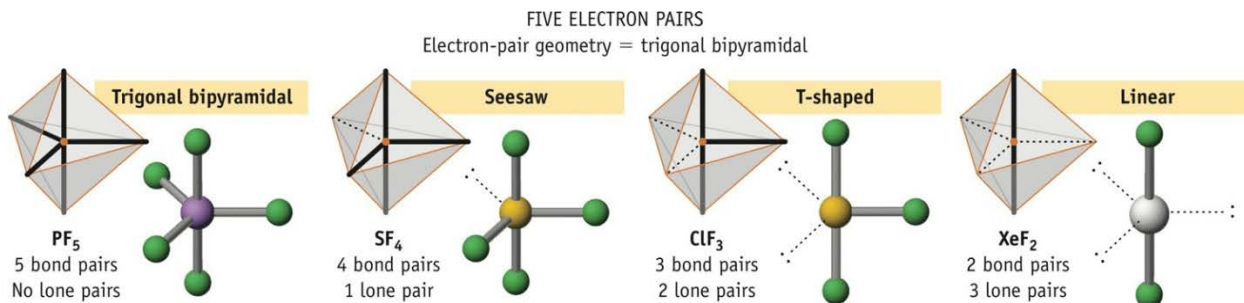


FIG IX – Placement of Lone Pairs of Electrons; Distortions from Perfect VSEPR Geometry

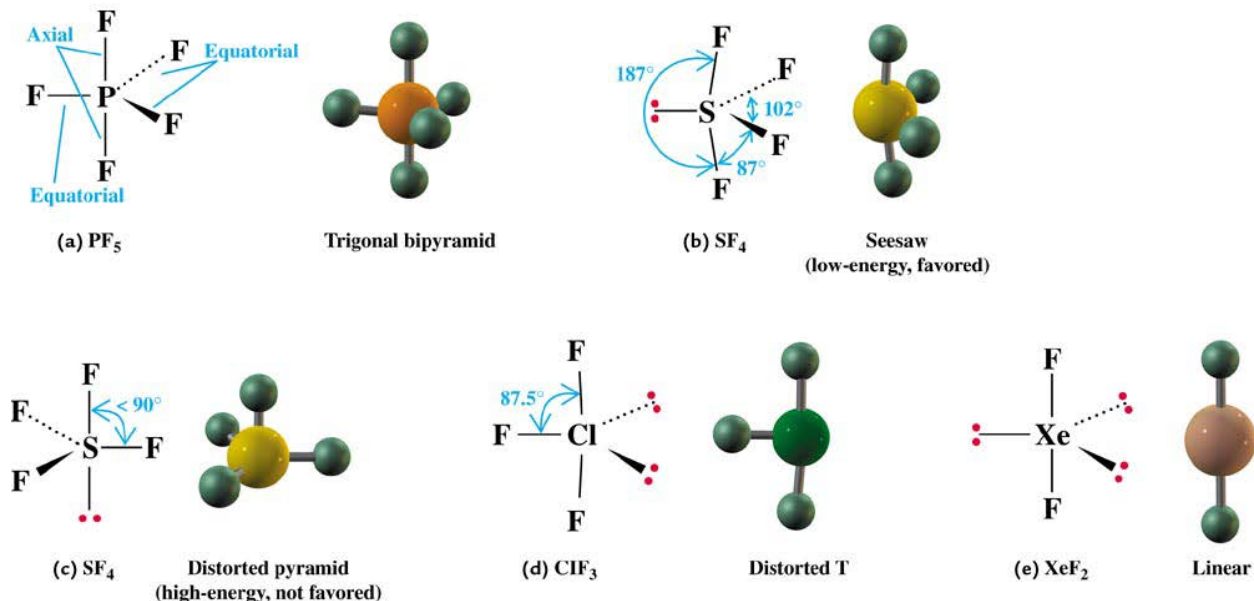
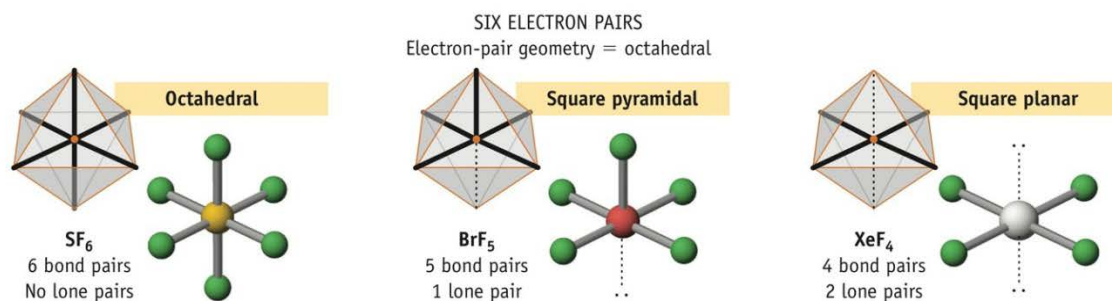


FIG X – Molecular Geometries for Six Electron Pairs (Steric Number = 6)



Bond Polarity and Electronegativity (13.3, 13.13)

6) for molecular polarity the molecule must have a **dipole moment**:

1. have a polar bond
2. vector addition of bond dipoles is nonzero

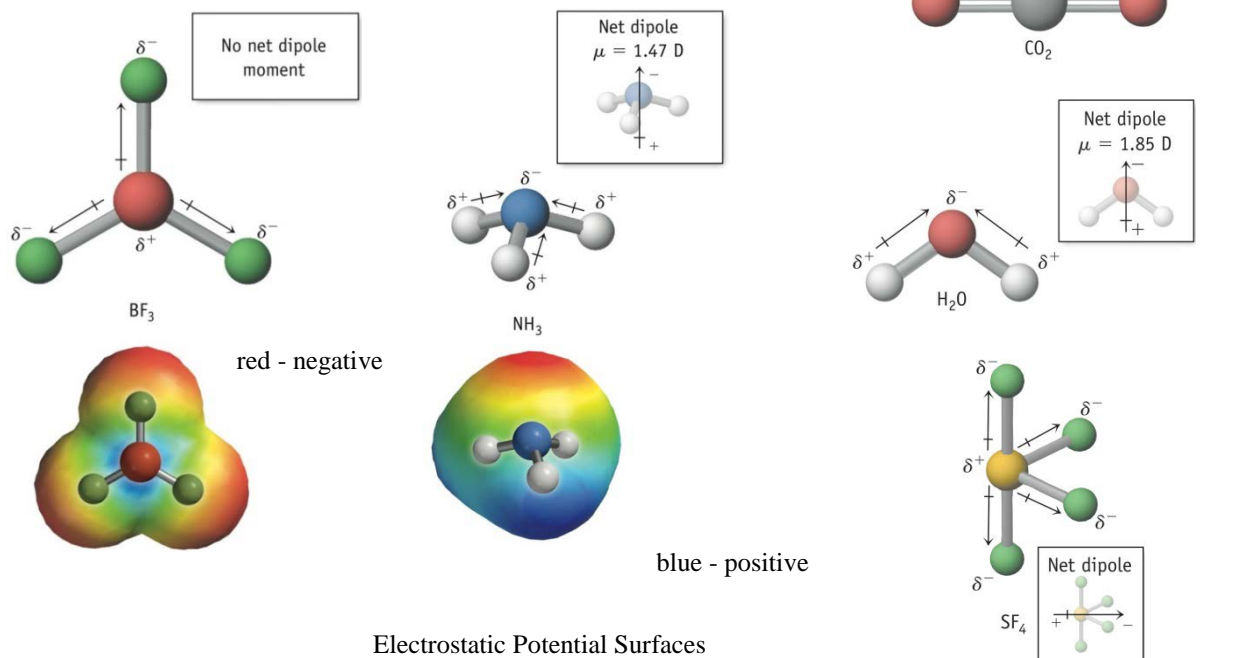
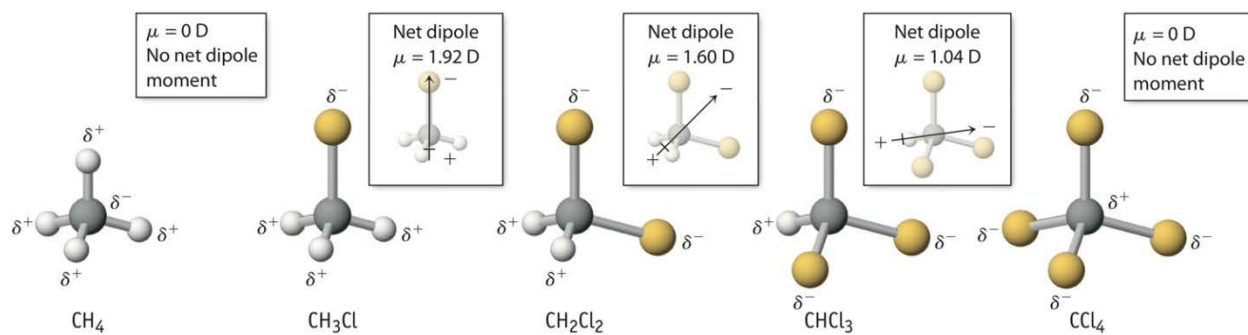
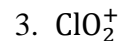
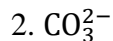


FIG XI – Polarity of Some Tetrahedral Molecule



Give all resonance structures, formal charges, and bond angles for



7) electronegativity and atomic size effects

Many bond angles can be rationalized on the basis of electronegativity or size arguments.

In a bond between elements of differing electronegativity, the more electronegative element pulls the bonding pair electrons more strongly to itself. If a central atom is surrounded by atoms of large electronegativity, the bonding electrons are drawn away from the central atom, reducing the repulsive effect of these electrons and leading to smaller bond angles. On the other hand, if the central atom has a large electronegativity, bonding electrons are pulled toward it, increasing electronic repulsions and a larger bond angle results.

In comparing a bond containing a larger atom to one containing a smaller atom, the bond with the larger atom naturally has its bonding pair of electrons further removed from it just due to its size. So a molecule with a large central atom would tend to have smaller bond angles than a smaller central atom.

when is electronegativity the more important effect

when is size the more important effect

The effect of electronegativity and size revealed by the periodic table:

EX 1. Determine the stronger acid in the following pairs and explain why.

- a) H_3PO_3 or H_3PO_4
- b) CH_4 or NH_3
- c) H_2AsO_4^- or HAsO_4^{2-}
- d) HIO or HClO
- e) H_2Se or H_2Te

EX 2. Which compound has the smallest bond angle in each series? Why?

- a) PI_3 AsI_3 SbI_3
- b) SbI_3 SbBr_3 SbCl_3