

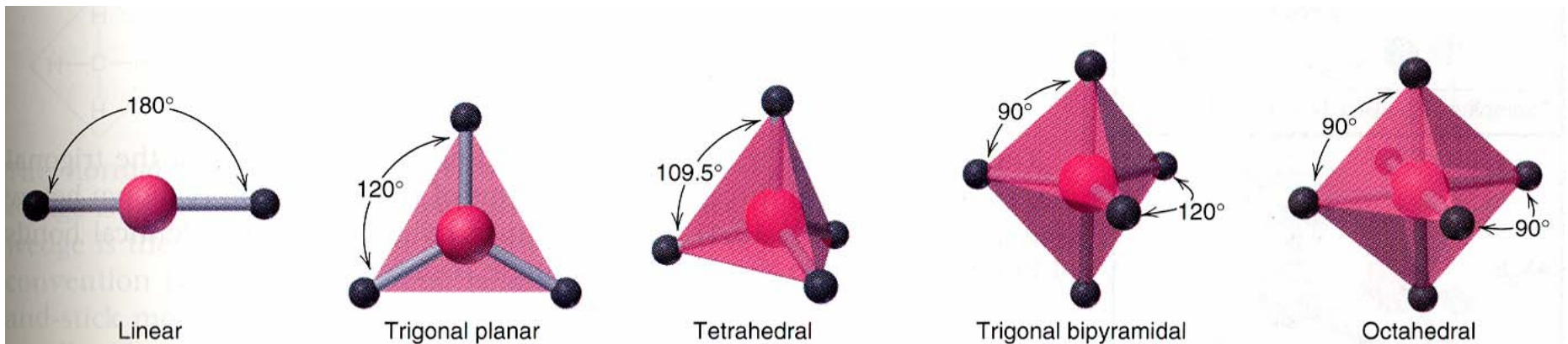
Molecular Geometry

Valence Shell Electron Pair repulsion

- The valence shell electron pair repulsion model (VSEPR model) assumes that **electron pairs repel one another**.
- (VSEPR) model gives helps determine the correct placement of atoms and nonbonding electrons in the molecule based on the repulsions of electrons in the molecule.
- The most stable conformation for a molecule is the one which has the electron pairs as far away from each other as possible.
- This produces a set of geometries which depend only on the number of valence shell electron pairs and not on the atoms present.

Predicting molecular geometry

- To determine the molecular geometry
 - Find number of valence electrons
 - Draw the Lewis structure
 - Count the number of electron pairs (bond pairs and lone pairs but count multiple bonds as one pair)
 - Arrange electron pairs to minimise repulsion
 - Name the geometry from the atom positions



Why study molecular geometry?

- **molecular geometry is vital in order to understand the polarity of molecules**
- **crucial to understanding reactions in organic, inorganic and biochemistry.**
- **Some sites on the molecule are more open to reaction than other sites – helps in deducing reaction mechanism, with information about the correct orientation of the atoms in the molecule.**

Example



C: 1s² 2s² 2p²: 4 valence electrons

H: 1s¹: 1 valence electron

(and there are 4 H's)

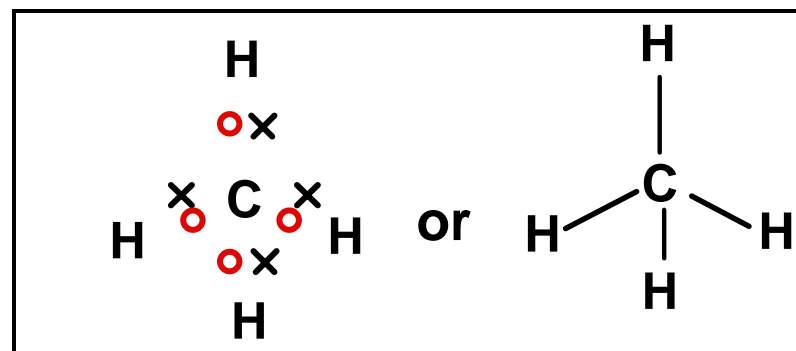
Total of 8 valence e's

Hence 4 pairs, tetrahedral pairs

There are 4 bonds (no lone pairs)

Hence bonds are also tetrahedral:

molecular geometry is tetrahedral



Example

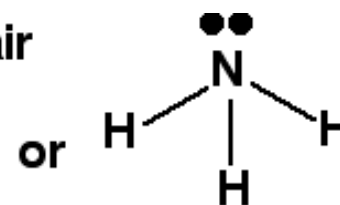


N: $1s^2 2s^2 2p^3$: 5 valence electrons

H: $1s^1$: 1 valence electron

(and there are 3 H's)

Total of 8 valence e's

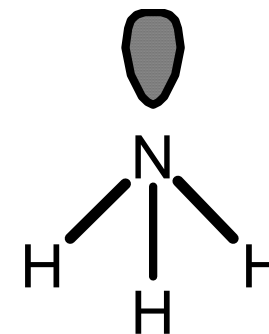


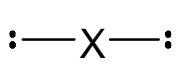
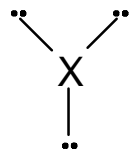
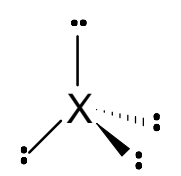
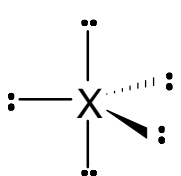
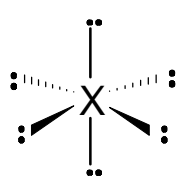
Hence 4 pairs, tetrahedral pairs

There are 3 bonds + 1 lone pair

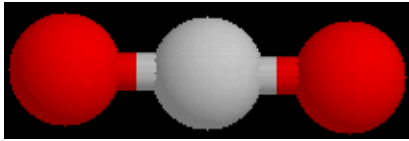
Hence bonds are trigonal pyramidal:

molecular geometry is trigonal pyramidal

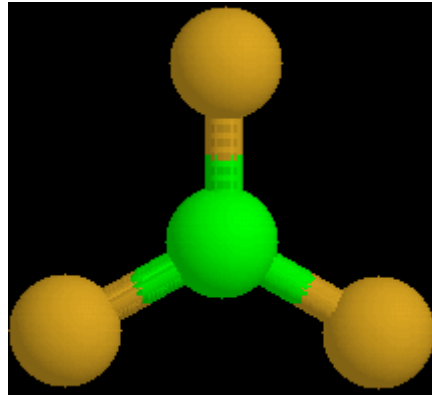


No# e ⁻ Pairs	Arrangement of Electron Pairs	No# of σ Bond Pairs	No# of Lone Pairs	Molecular geometry	Examples
2		2	0	Linear	CO ₂ , N ₃ ⁻
3		3	0	Trigonal planar	SO ₃ , CO ₃ ²⁻
		2	1	Bent	SO ₂ , O ₃ , NO ₂ ⁻
4		4	0	Tetrahedral	CH ₄ , NH ₄ ⁺ , PO ₄ ³⁻
		3	1	Trigonal pyramid	H ₃ O ⁺ , NH ₃
		2	2	Bent	H ₂ O, NH ₂ ⁻ , ClO ₂ ⁻
5		5	0	Trigonal bipyramid	PCl ₅ , SF ₅ ⁻
		4	1	"See-saw"	SF ₄ , PBr ₄ ⁻
		3	2	T-shaped	ClF ₃ , XeF ₃ ⁺
6		2	3	Linear	ICl ₂ ⁻ , XeF ₂
		6	0	Octahedral	SF ₆ , SiF ₆ ²⁻ , AsF ₆ ⁻
		5	1	Square pyramidal	IF ₅ , SF ₅ ⁻ , SbF ₅ ²⁻
		4	2	Square planar	ICl ₄ ⁻ , XeF ₄

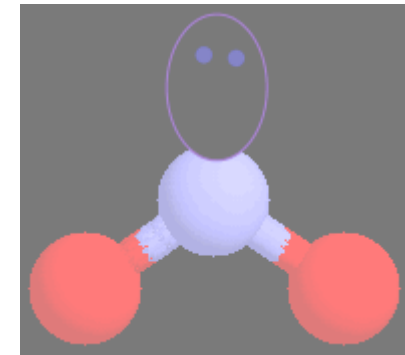
Molecular Geometry



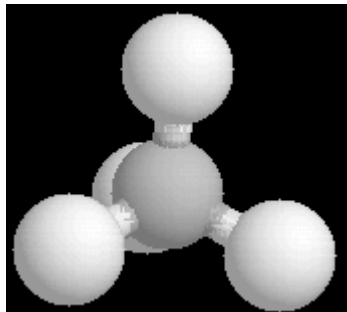
Linear



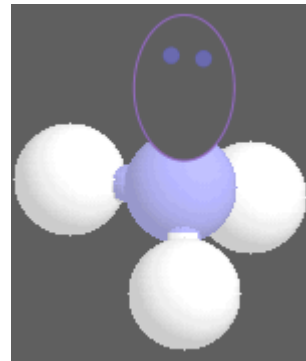
Trigonal planar



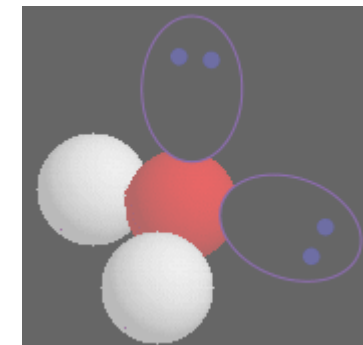
Bent(1 l.p., 2b.p.)



Tetrahedral

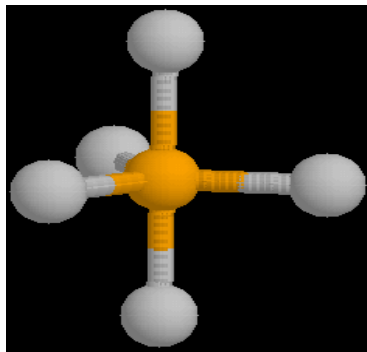


Trigonal pyramidal

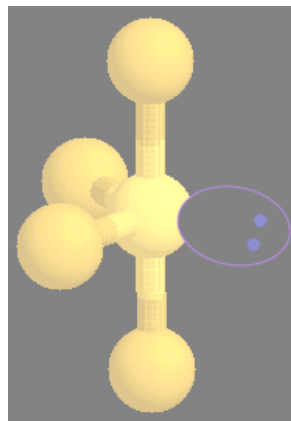


Bent (2 l.p., 2b.p.)

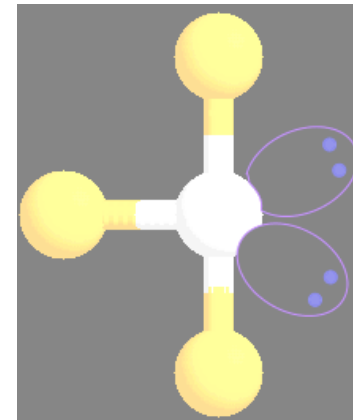
Molecular Geometry



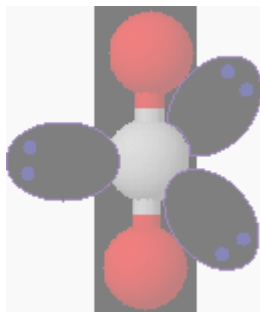
Trigonal-bipyramidal



Seesaw

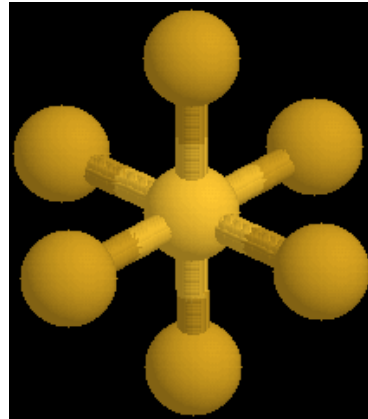


T-shaped

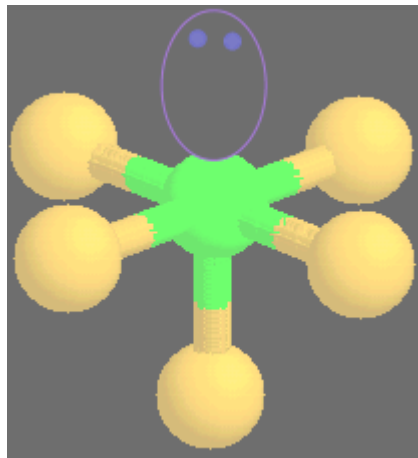


Linear

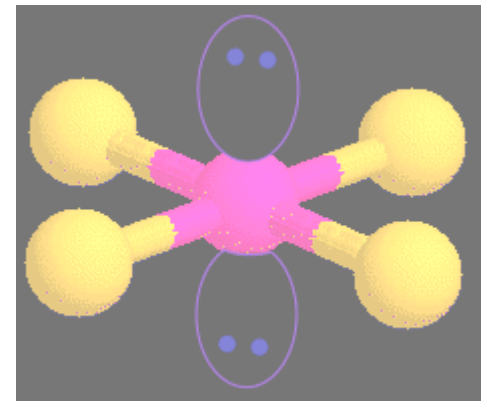
Molecular Geometry



Octahedral

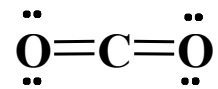


Square pyramidal

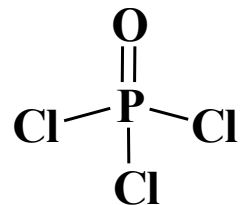


Square planar

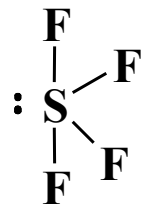
Examples



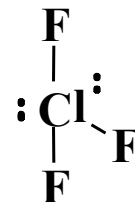
Linear



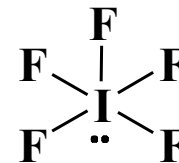
Tetrahedral



'See-saw'



'T'-shaped



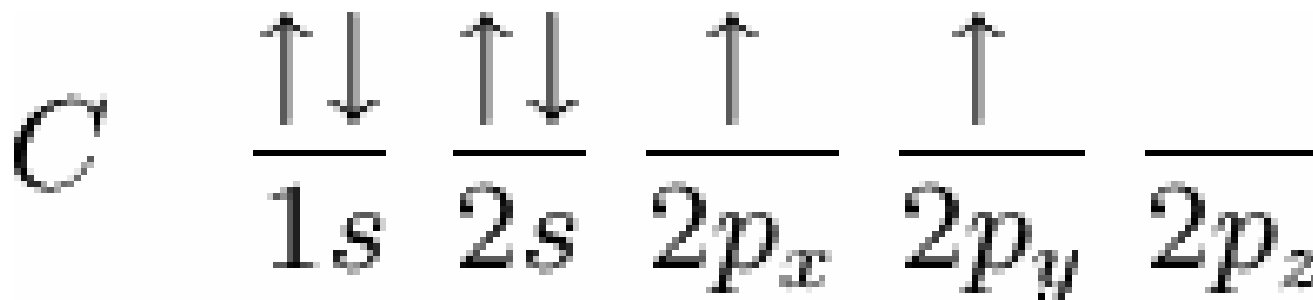
Square pyramid

Hybridisation

- Hybridization is the concept of mixing atomic orbitals to form new *hybrid orbitals* suitable for the qualitative description of atomic bonding properties.
- Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules.
- It is an integral part of valence bond theory.
- Valence bond and hybridization are in fact not related to the VSEPR model, however the spatial orientation in each type of hybrid orbital corresponds with the common electron group arrangements predicted by VSEPR theory.
- hybridisation theory was promoted by chemist Linus Pauling in order to explain the structure of molecules such as methane (CH₄).

Hybridization

- covalent bonding requires a consideration of valence shell atomic orbitals. For second period elements eg. carbon, nitrogen and oxygen, these orbitals have been designated 2s, 2p_x, 2p_y & 2p_z.



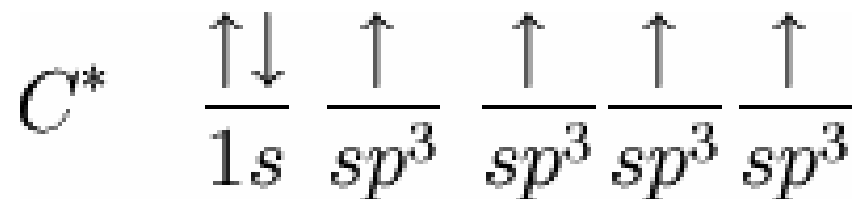
Ground state electronic configuration of methane

- The valence shell electron configuration of carbon is.....
- If this was the configuration used in covalent bonding, carbon would only be able to form **two bonds**.

sp^3 hybridization in methane

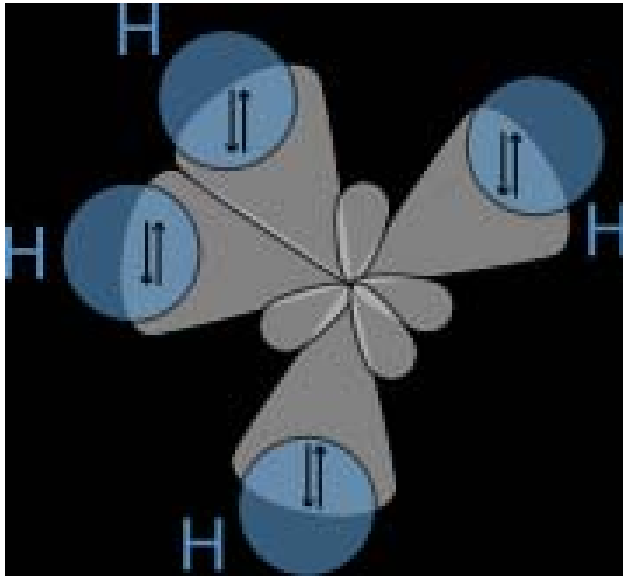
Carbon attempting to bond with four hydrogens, needs four orbitals. Therefore, the $2s$ orbital (core orbitals are almost never involved in bonding) mixes with the three $2p$ orbitals to form four sp^3 hybrids (read as *s-p-three*).

The four equivalent hybrid atomic orbitals, each having 25% s and 75% p character, have a specific orientation, and the four are naturally oriented in a tetrahedral fashion.

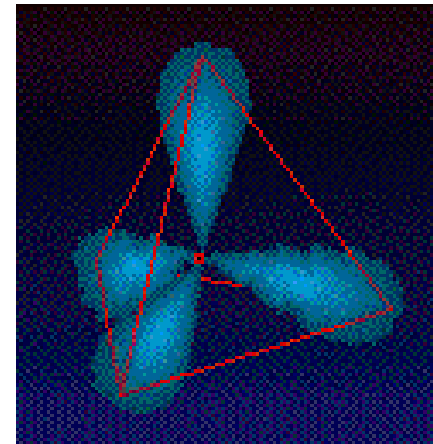
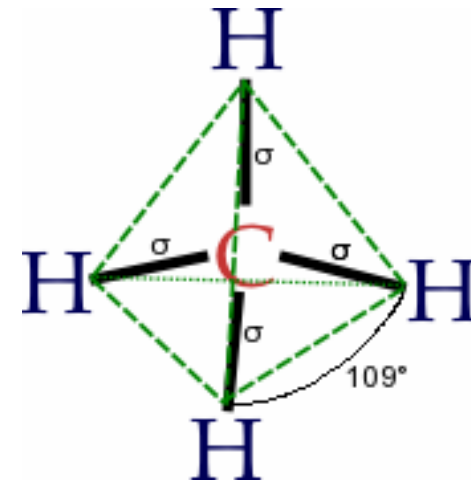


four sp^3 hybridised orbitals are overlapped by hydrogen's $1s$ orbital, yielding four σ (sigma) bonds. The four bonds are of the same length and strength.

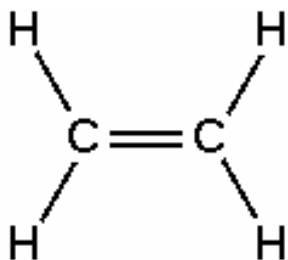
tetrahedral CH₄



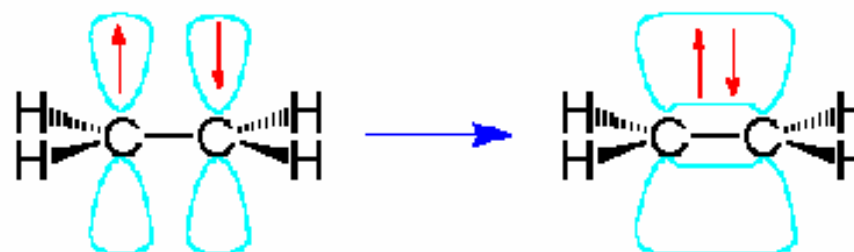
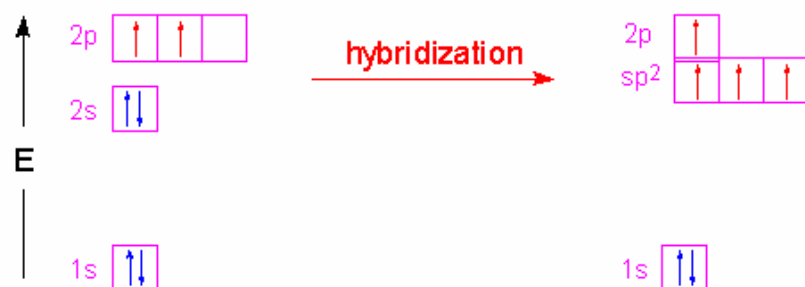
translates into



sp^2 hybridization in ethylene



- Lewis structure of ethene
- Shape – trigonal planar
- 2s-orbital combines with two of the available p-orbitals (sp^2) – they point towards the vertices of an equilateral triangle, with axes 120° apart.

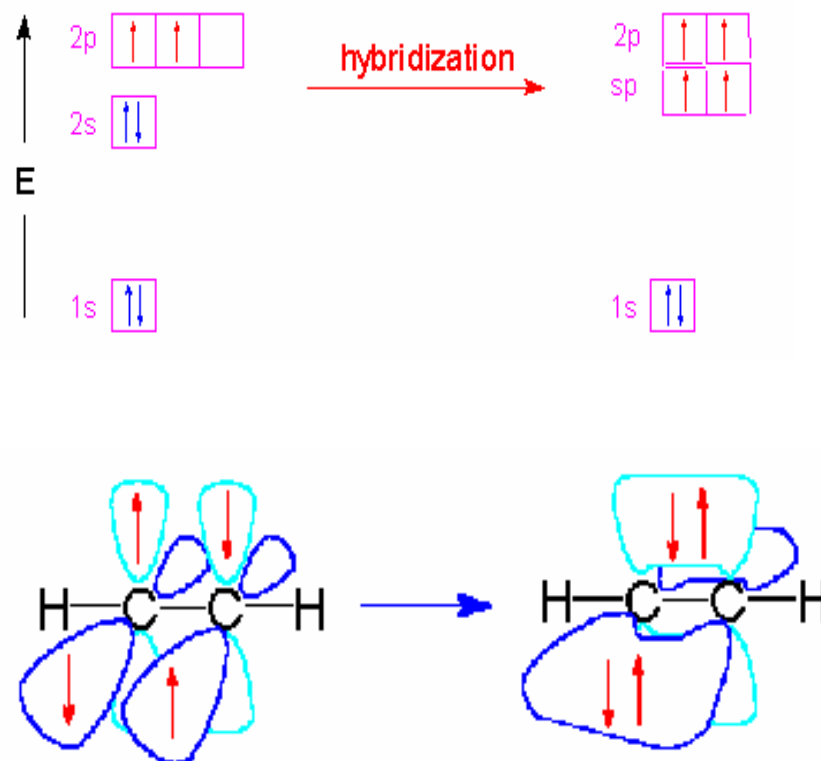


❖ the single bond, formed from the sp^2 orbitals, and π bond by parallel overlap of p-orbitals with bean-shaped probability areas above and below the plane of the six atoms.

sp hybridization in acetylene

- C_2H_2 (acetylene). Both carbon atoms will be sp hybridized (one s orbital mixing with one p orbital) and have one electron in each of two unhybridized p orbitals.

These p orbitals will undergo parallel overlap to form two pi-bonds at right angles to each other.



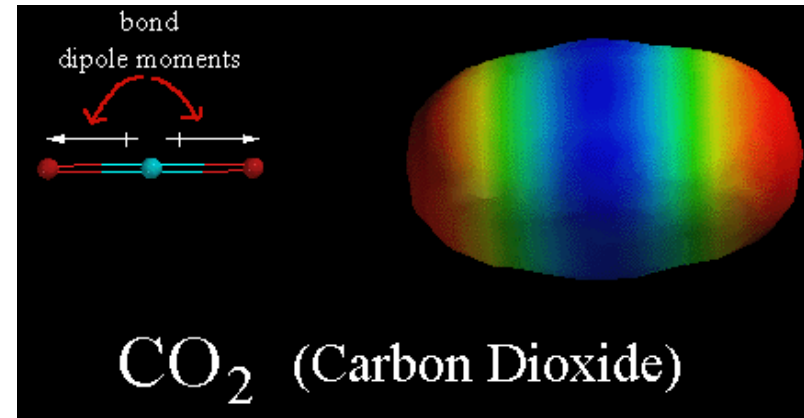
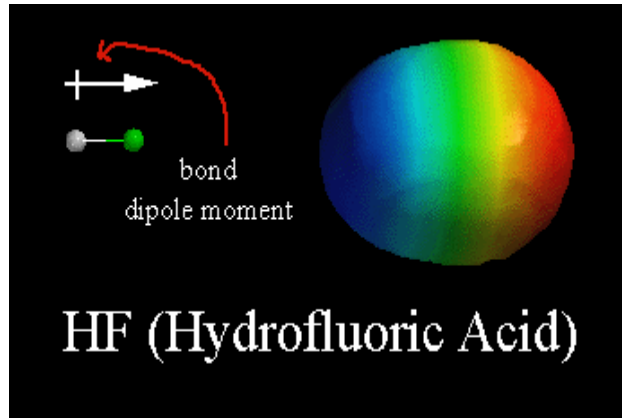
Dipole moment

- The **bond dipole moment** is a measure for the polarity of a chemical bond within a molecule. The bond dipole μ is given by:

$$\mu = \delta d$$

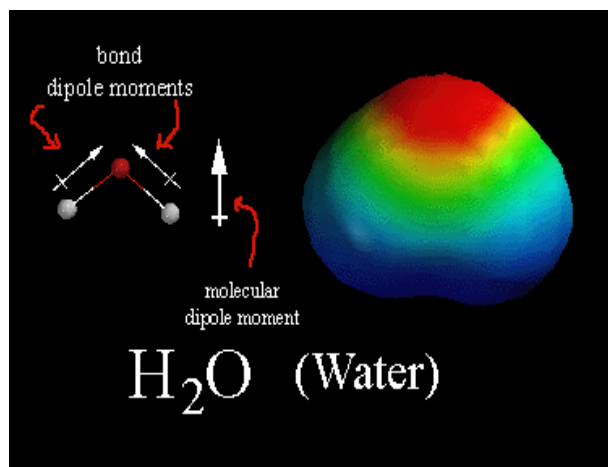
- Chemists generally measure electrical dipole moments in **debyes**, represented by the symbol **D**.
- The SI unit for dipole moment is the **coulomb-meter** ($1 \text{ C m} = 2.9979 \times 10^{29} \text{ D}$), δ is the amount of charge in coulombs, and d is in meters.
- For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

Dipole moment

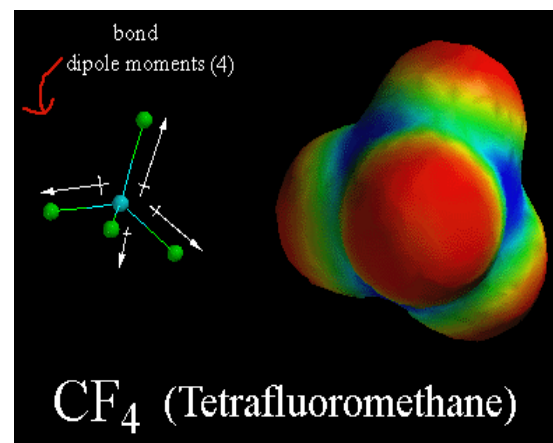


- Δ E.N. is huge, so that the majority of electron density in the hydrogen-fluorine bond ends up on the much more E.N. fluorine. Resulting bond- Polar covalent with a dipole moment.
- *Blue - partial positive charge on hydrogen atom; red- partial negative charge on fluorine atom.*
- Carbon dioxide has two polar covalent C-O bonds. However, the bond dipole moments exactly cancel each other since they are pointing in exactly opposite directions.
- What is the hybridisation of carbon atom in CO₂?
Hint: consider shape

Dipole moments



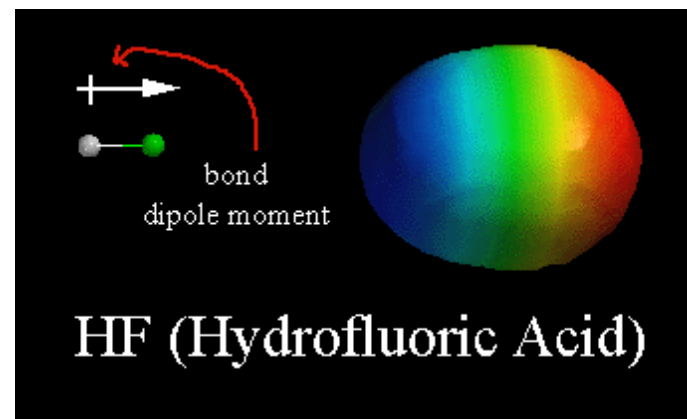
- **Shape – bent**
- **Hybridisation – sp³**
- **two very polar covalent bonds between oxygen and hydrogen.**
- **the two bond dipole moments add up to give water a relatively large molecular dipole moment.**



- **CF₄ has four polar covalent bonds.**
- **they are arranged in a symmetrical tetrahedral array**
- **all of the bond dipole moment vectors exactly cancel**
- **Net dipole moment/ molecular dipole moment = 0**

Dipole moments

- Do HF, HCl, HBr, HI have bond and molecular dipole moments?



- A molecule that possesses a measurable molecular dipole will be called a polar molecule.
- Molecules whose bond dipoles cancel each other out will have no resulting molecular dipole and therefore will be called non-polar molecules.
- Compounds that are composed of only carbon and hydrogen (hydrocarbons) will have weak bond dipoles between carbon and hydrogen atoms that will cancel each other. Thus, they are non-polar.
- Oxygen (or Nitrogen) containing organic compounds (amines, ethers, alcohols, ketones, aldehydes, carboxylic acids, esters, etc) will be polar molecular substances because of the high Δ E.N.