UNIT - 1A | PAPER - 1

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UNIT 1A - PAPER 1
DIFFERENT TYPES OF FORCES

1. Covalent Bond
2. Ionic Bond
3. Vander Walls
4. H-Bonding
5. VESPER Theory
6. Bent's Rule
7. M.O.T. (Homo & Hetero Nuclear)
8. Acid-Based Strength
9. HSAB Concept

UNIT - 1A | PAPER - 1

MOLECULAR GEOMETRY AND BONDING THEORIES

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MOLECULAR SHAPES

•Lewis structures give atomic connectivity: they tell us which atoms are physically connected to which.

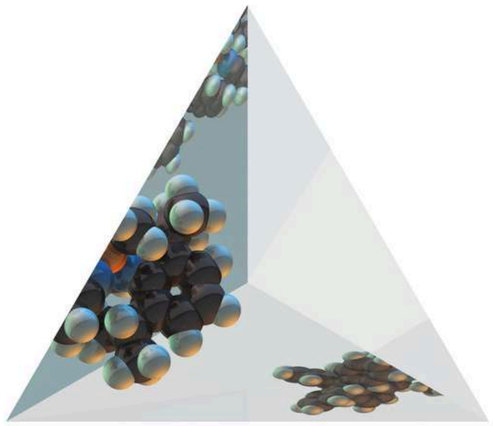
•The shape of a molecule is determined by its bond angles.

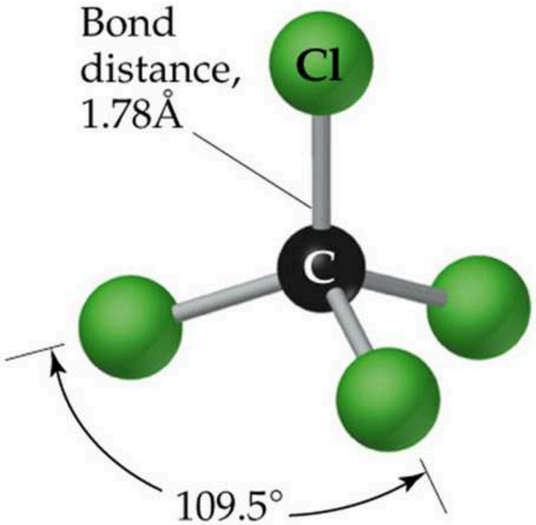
•Consider CCl_4: experimentally we find all Cl-C-Cl bond angles are 109.5°.

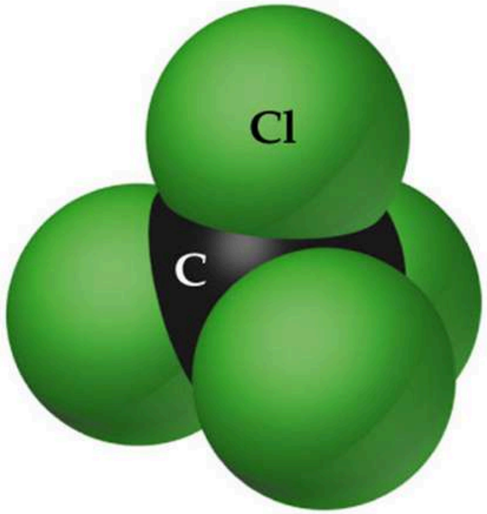
•Therefore, the molecule cannot be planar.

•All Cl atoms are located at the vertices of a tetrahedron with the C at its center.

MOLECULAR SHAPES

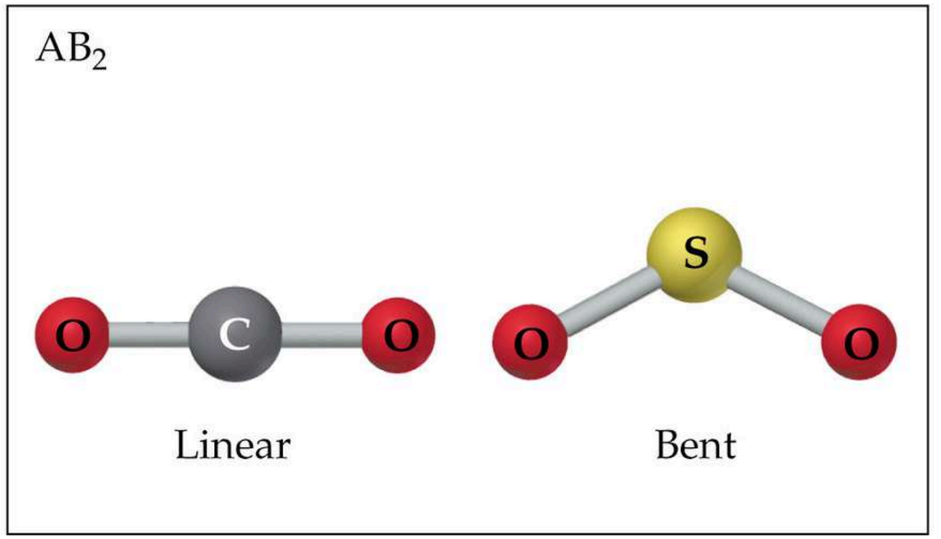


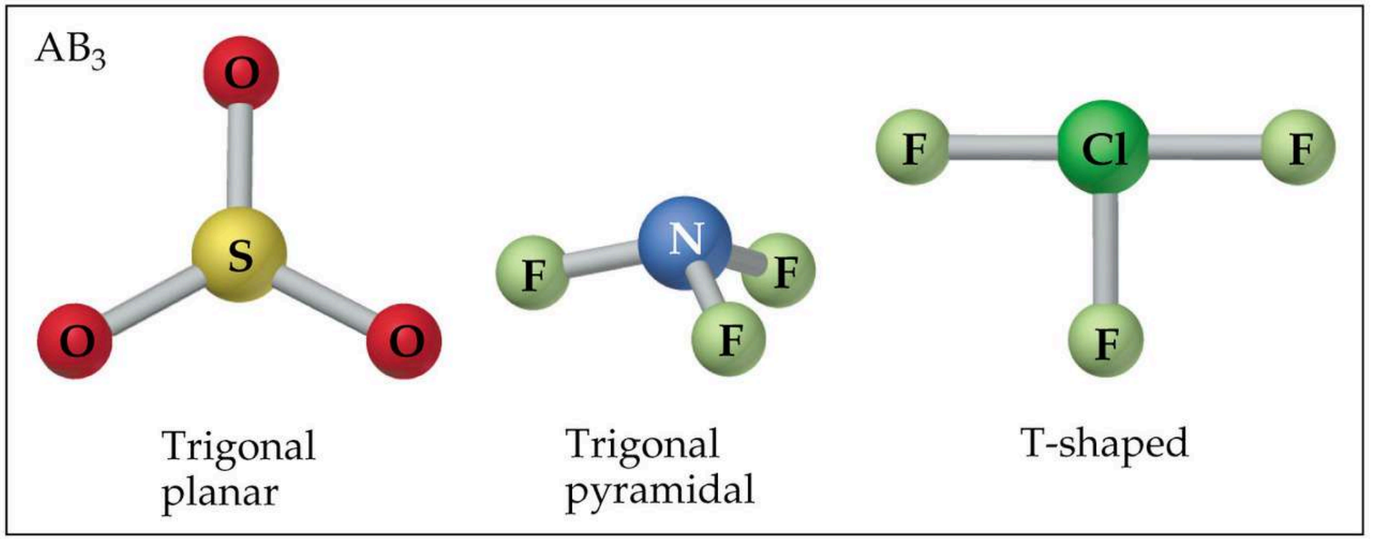




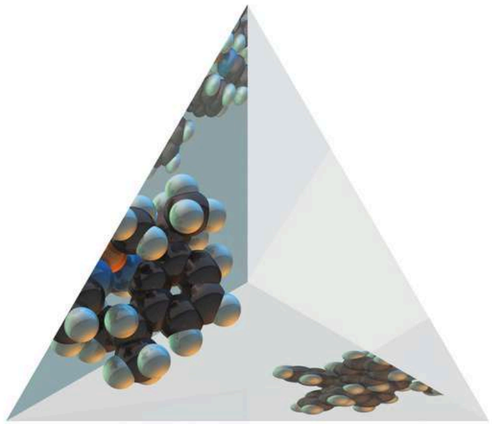
MOLECULAR SHAPES

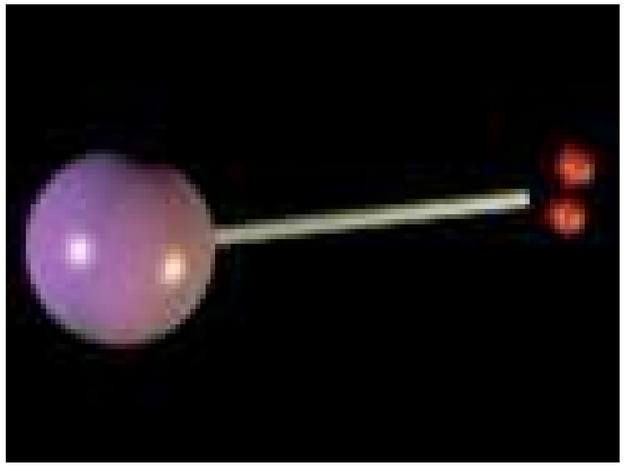
- In order to predict molecular shape, we assume the valence electrons repel each other. Therefore, the molecule adopts whichever 3D geometry minimized this repulsion.
- We call this process Valence Shell Electron Pair Repulsion (VSEPR) theory.
- There are simple shapes for AB2 and AB3 molecules.

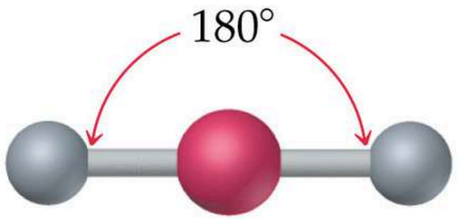




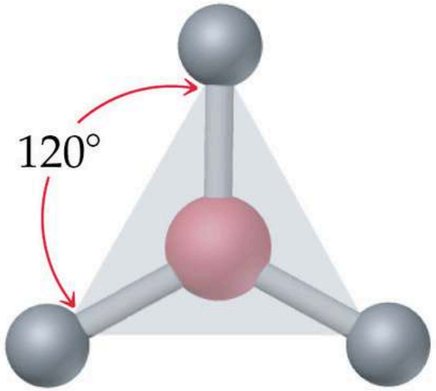
- There are five fundamental geometries for molecular shape:



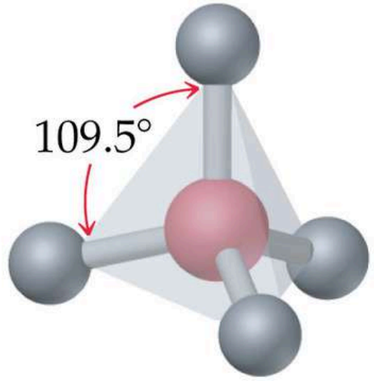




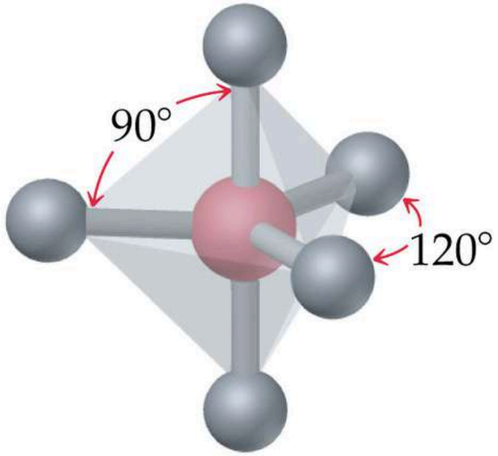
Linear



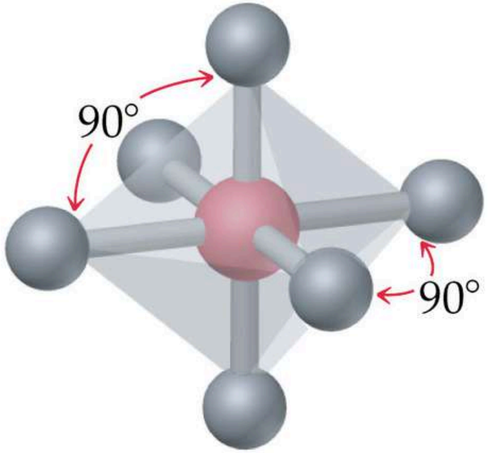
Trigonal planar



Tetrahedral

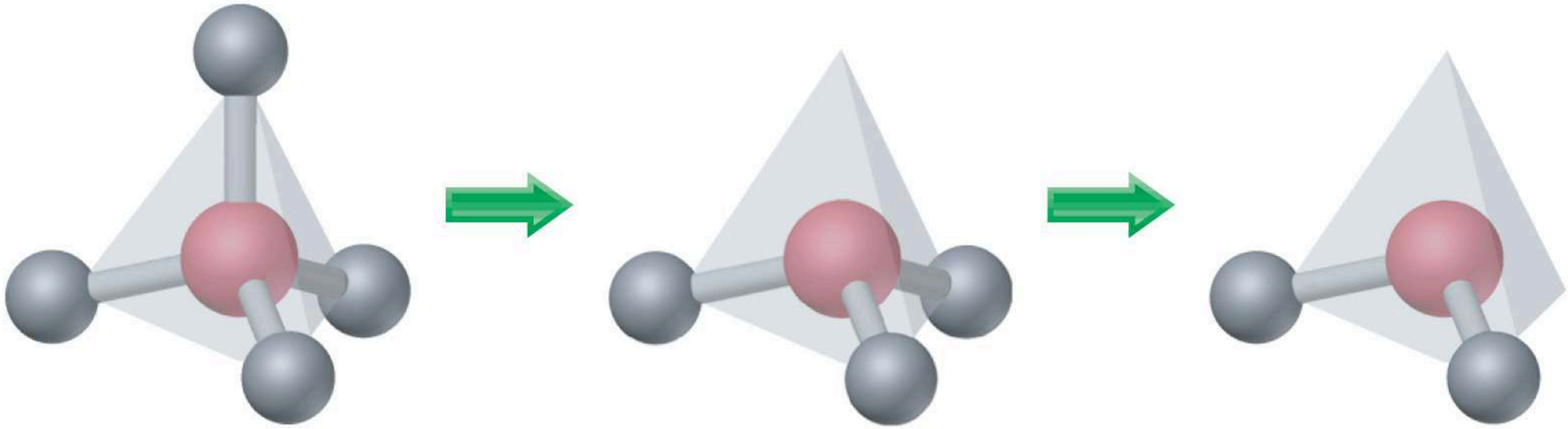


Trigonal bipyramidal



Octahedral

- When considering the geometry about the central atom, we consider all electrons (lone pairs and bonding pairs).
- When naming the molecular geometry, we focus only on the positions of the atoms.



Tetrahedral Trigonal pyramidal Bent

VSEPR MODEL

- To determine the shape of a molecule, we distinguish between lone pairs (or non-bonding pairs, those not in a bond) of electrons and bonding pairs (those found between two atoms).
- We define the electron domain geometry by the positions in 3D space of ALL electron pairs (bonding or non-bonding).
- The electrons adopt an arrangement in space to minimize e^-- e^- repulsion.

TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

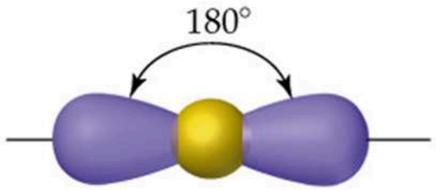
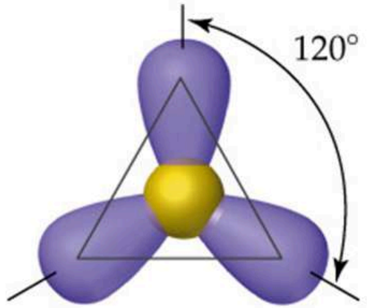
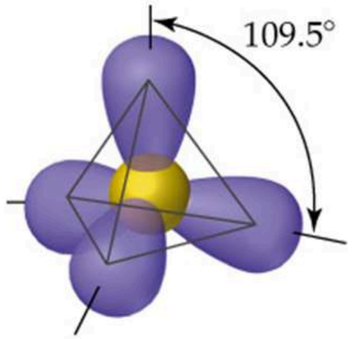
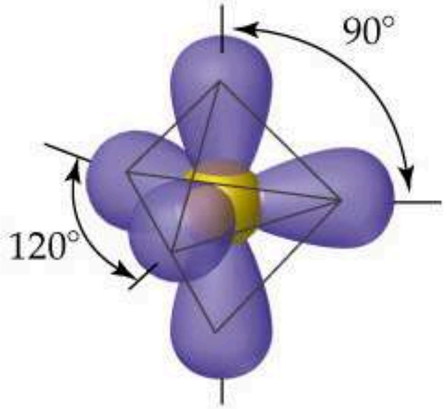
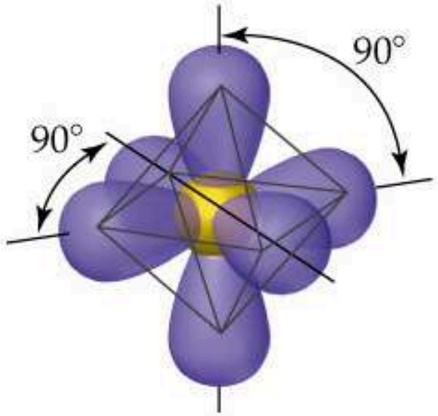
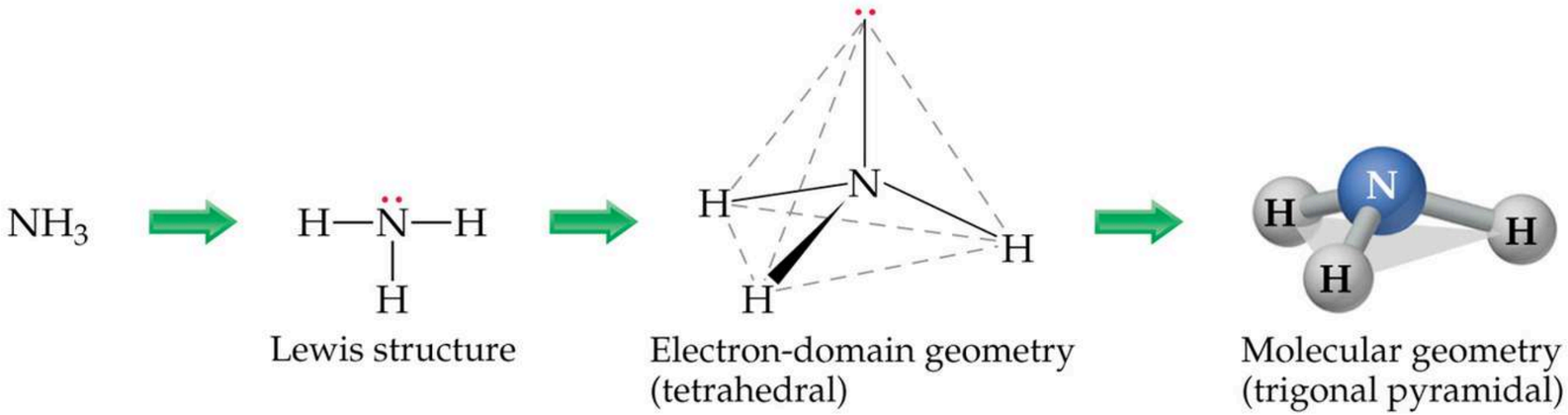
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

VSEPR MODEL

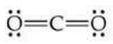
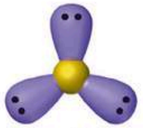
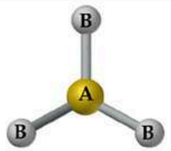
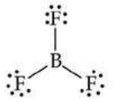
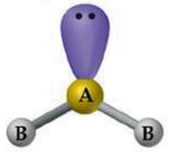
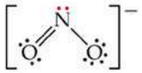
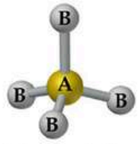
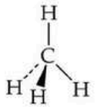
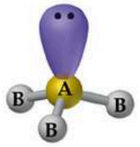
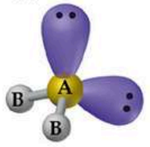
- To determine the electron pair geometry:
- draw the Lewis structure,
- count the total number of electron pairs around the central atom,
- arrange the electron pairs in one of the above geometries to minimize e^--e^- repulsion, and count multiple bonds as one bonding pair.



Lewis structure | Electron-domain geometry (tetrahedral) | Molecular geometry (trigonal pyramidal)

VSEPR MODEL

TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom

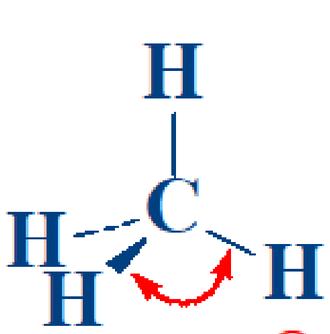
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

THE EFFECT OF NONBONDING ELECTRONS AND MULTIPLE BONDS ON BOND ANGLES

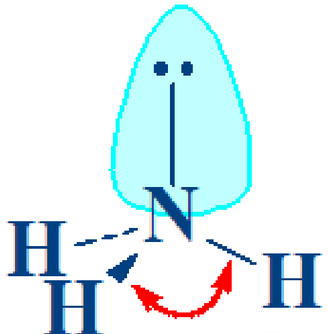
- The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles
- We determine the electron pair geometry only looking at electrons.
- We name the molecular geometry by the positions of atoms.
- We ignore lone pairs in the molecular geometry.
- All the atoms that obey the octet rule have tetrahedral electron pair geometries.

THE EFFECT OF NONBONDING ELECTRONS AND MULTIPLE BONDS ON BOND ANGLES

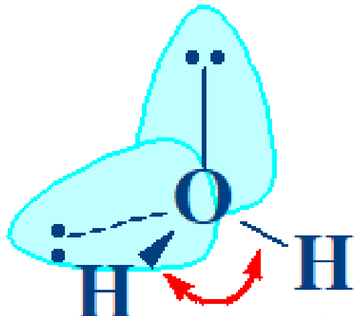
- By experiment, the H-X-H bond angle decreases on moving from C to N to O:



109.5^{O}



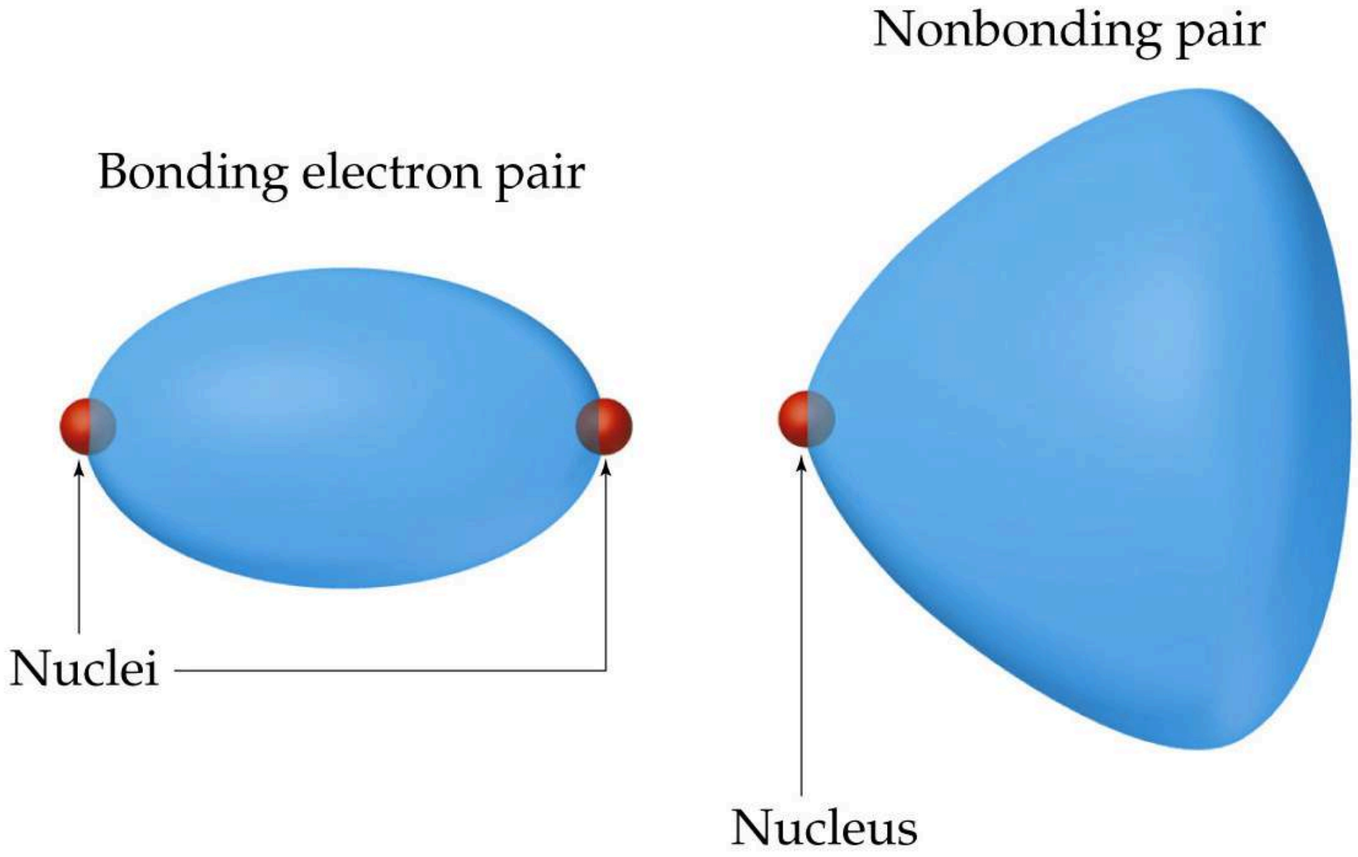
107^{O}



104.5^{O}

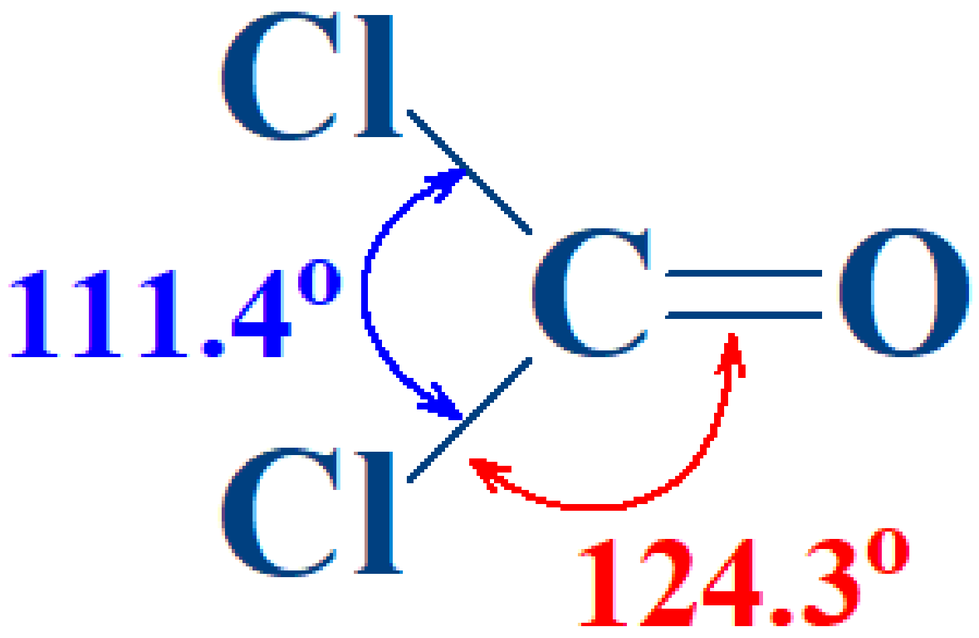
- Since electrons in a bond are attracted by two nuclei, they do not repel as much as lone pairs.
- Therefore, the bond angle decreases as the number of lone pairs increase.

THE EFFECT OF NONBONDING ELECTRONS AND MULTIPLE BONDS ON BOND ANGLES



THE EFFECT OF NONBONDING ELECTRONS AND MULTIPLE BONDS ON BOND ANGLES

- Similarly, electrons in multiple bonds repel more than electrons in single bonds.



MOLECULES WITH EXPANDED VALENCE SHELLS

- Atoms that have expanded octets have AB5 (trigonal bipyramidal) or AB6 (octahedral) electron pair geometries.
- For trigonal bipyramidal structures there is a plane containing three electrons pairs. The fourth and fifth electron pairs are located above and below this plane.
- For octahedral structures, there is a plane containing four electron pairs. Similarly, the fifth and sixth electron pairs are located above and below this plane.

TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

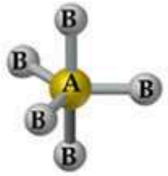
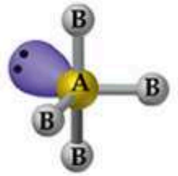
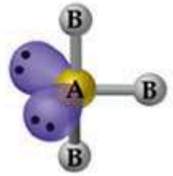
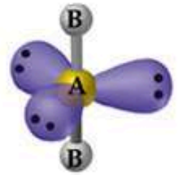
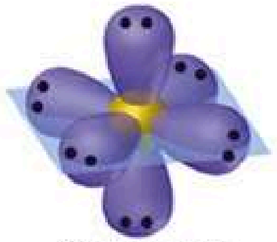
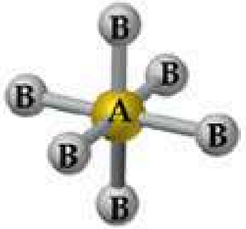
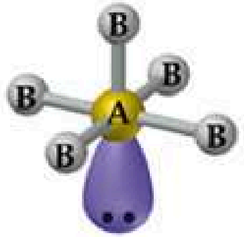
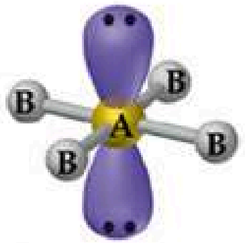
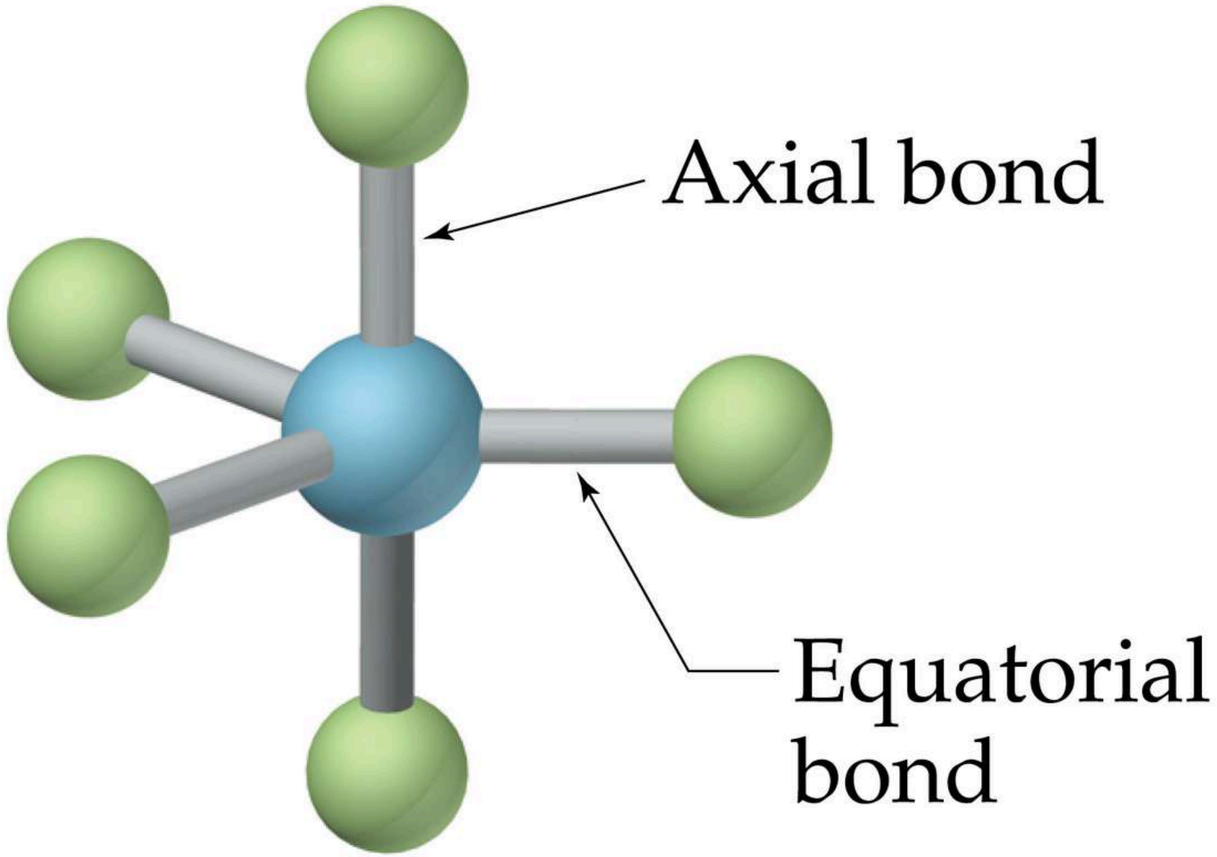
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

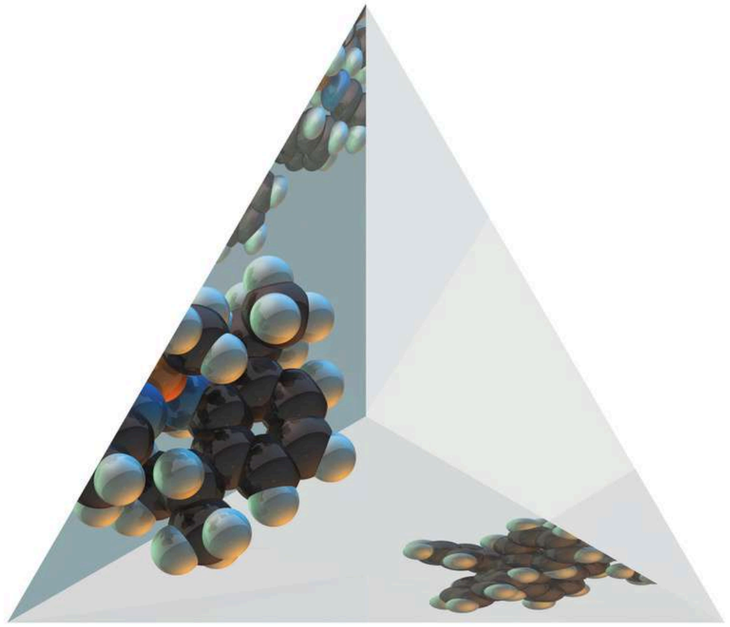
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

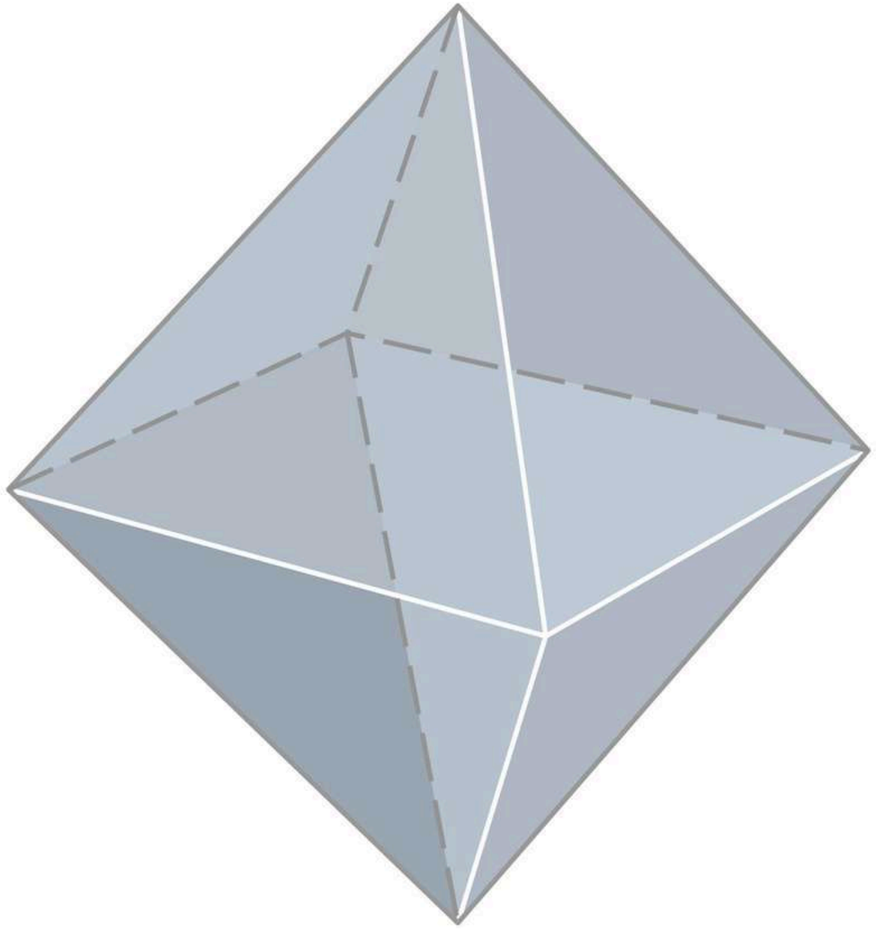
MOLECULES WITH EXPANDED VALENCE SHELLS

- To minimize e^-- e^- repulsion, lone pairs are always placed in equatorial positions.



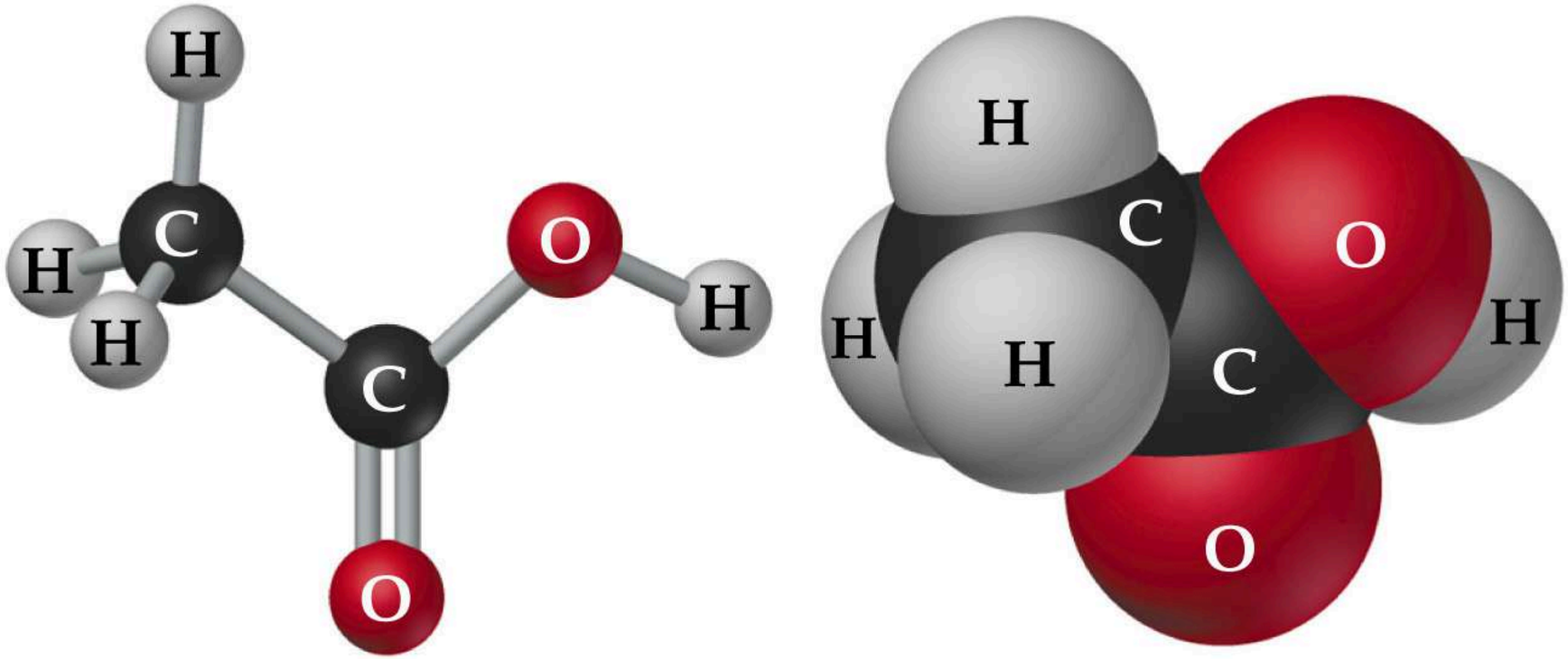
MOLECULES WITH EXPANDED VALENCE SHELLS





SHAPES OF LARGER MOLECULES

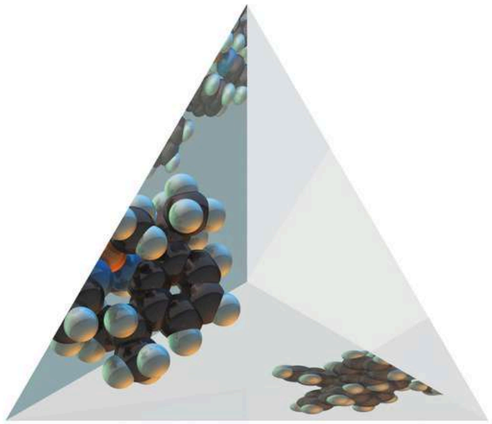
- In acetic acid, CH_3COOH, there are three central atoms.
- We assign the geometry about each central atom separately.

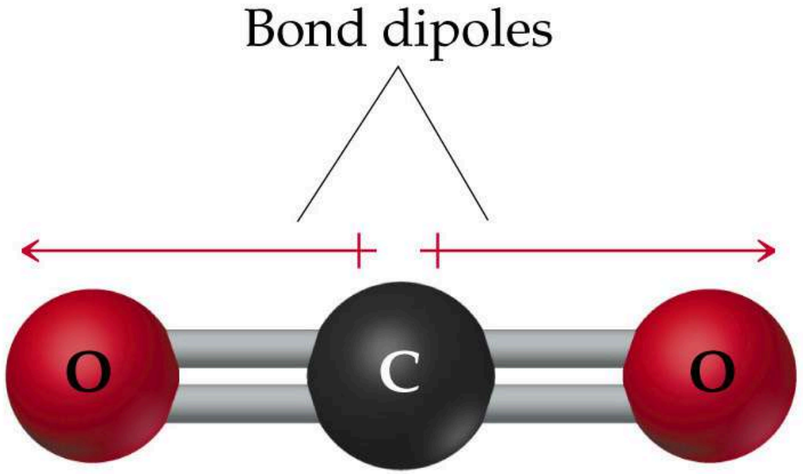


MOLECULAR SHAPE AND MOLECULAR POLARITY

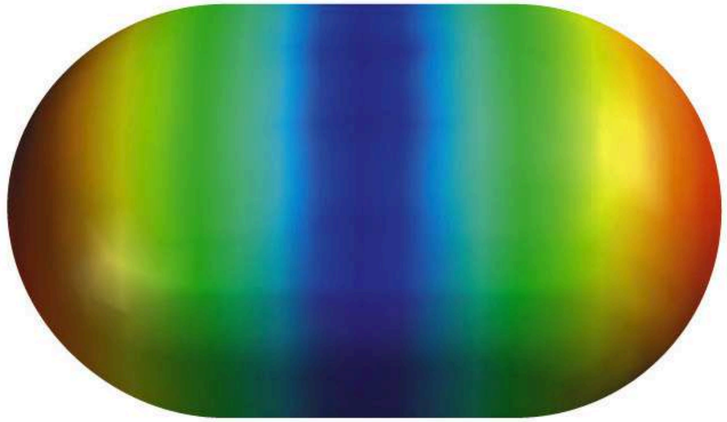
- When there is a difference in electronegativity between two atoms, then the bond between them is polar.
- It is possible for a molecule to contain polar bonds, but not be polar.
- For example, the bond dipoles in CO_2 cancel each other because CO_2 is linear.

MOLECULAR SHAPE AND MOLECULAR POLARITY



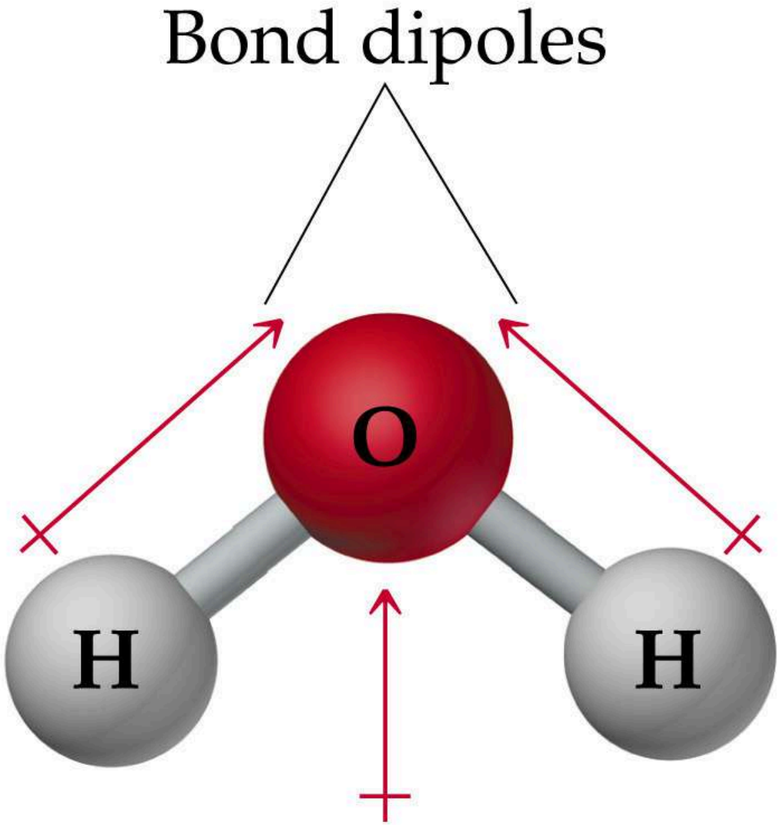


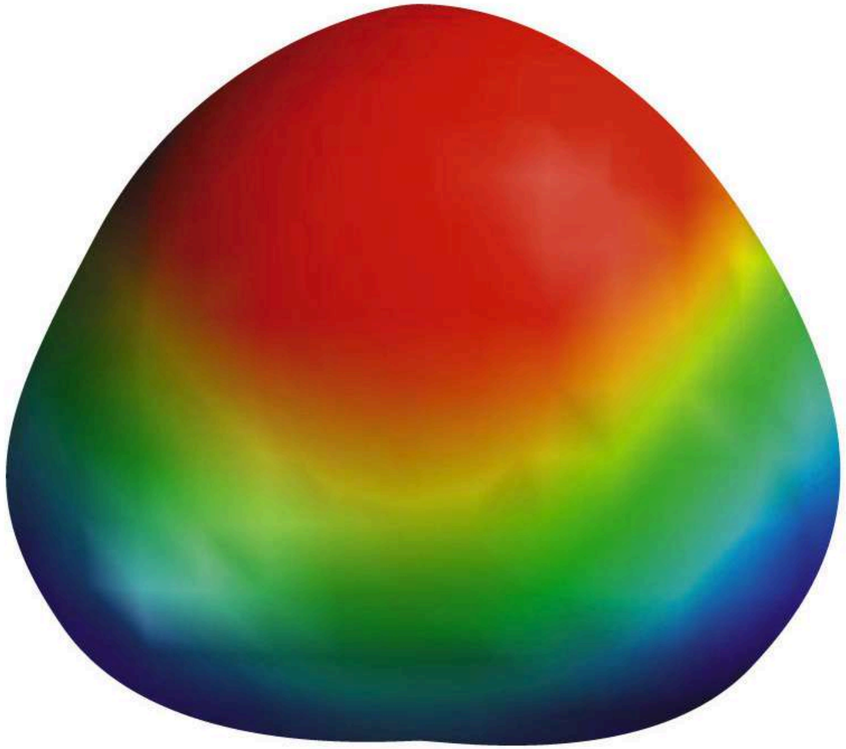
Overall dipole moment = 0



MOLECULAR SHAPE AND MOLECULAR POLARITY

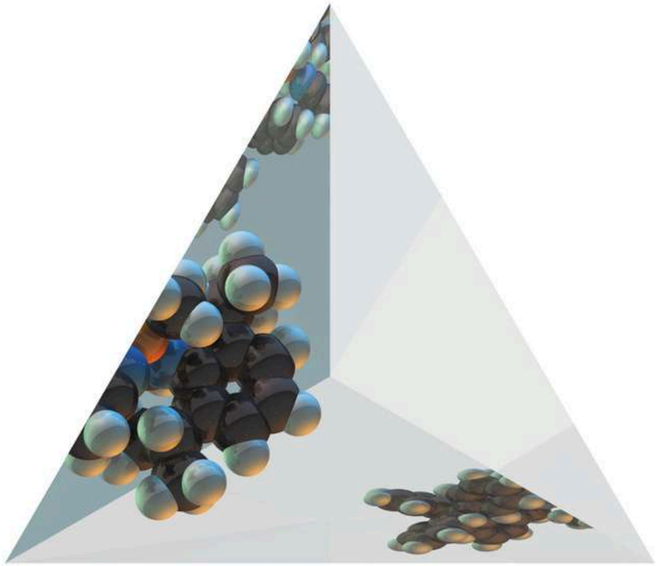
- In water, the molecule is not linear and the bond dipoles do not cancel each other.
- Therefore, water is a polar molecule.



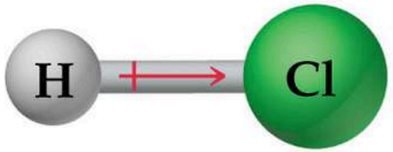


MOLECULAR SHAPE AND MOLECULAR POLARITY

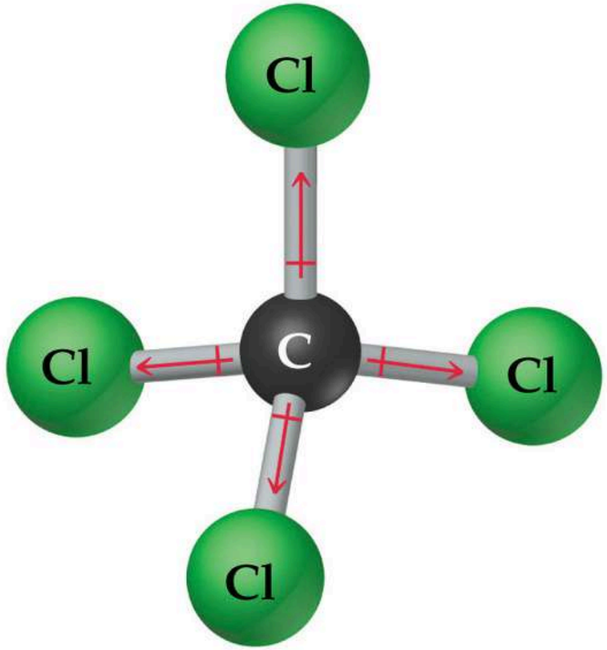
- The overall polarity of a molecule depends on its molecular geometry.



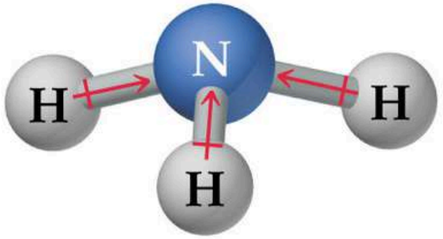
MOLECULAR SHAPE AND MOLECULAR POLARITY



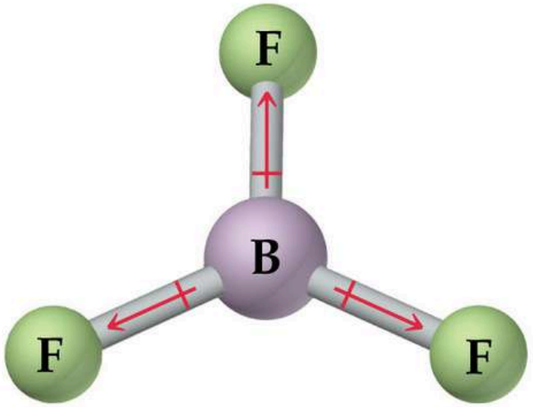
Polar



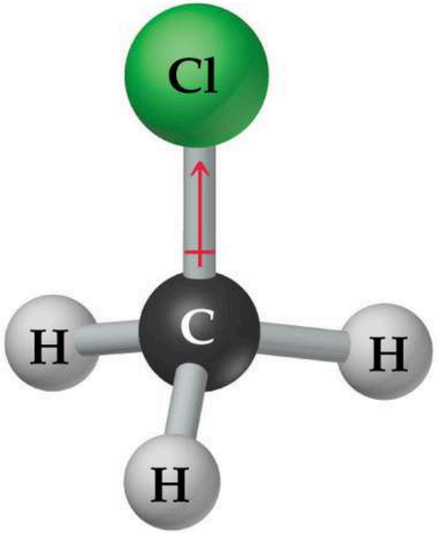
Nonpolar



Polar



Nonpolar



Polar

COVALENT BONDING AND ORBITAL OVERLAP

- Lewis structures and VSEPR do not explain why a bond forms.
- How do we account for shape in terms of quantum mechanics?
- What are the orbitals that are involved in bonding?
- We use Valence Bond Theory:
- Bonds form when orbitals on atoms overlap.
- There are two electrons of opposite spin in the orbital overlap.

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