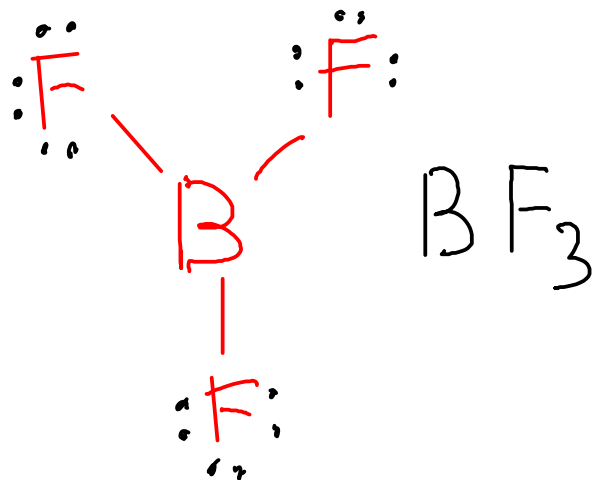


¹⁷⁵ EXPANDED VALENCE and other exceptions to the "octet rule"

- Some atoms do not always obey the octet rule. A few, like BORON, will bond in such a way that they end up with LESS than eight electrons.



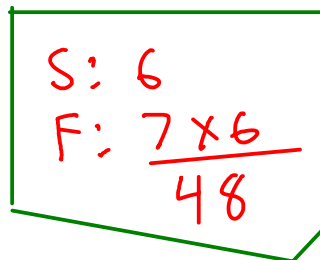
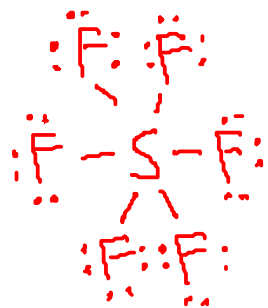
... but many more bond in such a way that they end up with a share in MORE THAN EIGHT electrons!

- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

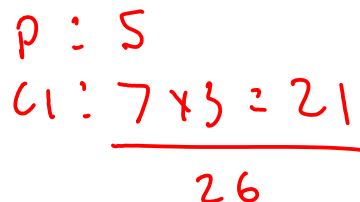
... these atoms have unfilled "d" orbitals that may participate in bonding!

- All noble gas compounds (example: XENON compounds with oxygen and fluorine) exhibit this behavior!

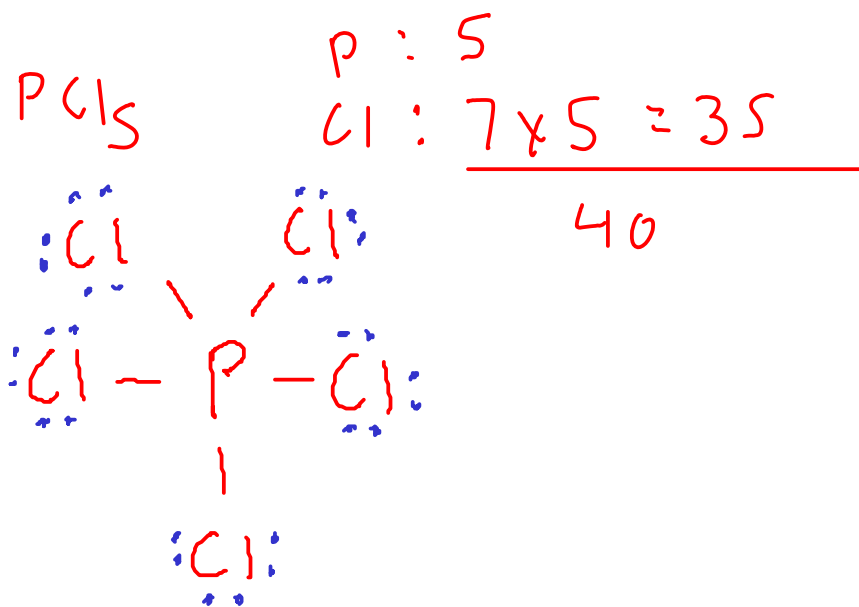
EXAMPLES:



- The central SULFUR atom has a share in TWELVE total electrons, not eight!
- The SHAPE of the sulfur hexafluoride molecule in three dimensions agrees with the picture of six fluorine atoms each sharing a pair of electrons with a sulfur center.



This structure obeys the octet rule.



This molecule does NOT obey the octet rule. Phosphorus ends up with ten electrons instead of eight.

FORMAL CHARGE

- You can sometimes draw more than one structure for a molecule that appears correct. How can you determine which one is more likely?

- USE FORMAL CHARGE!

- Formal charge is a hypothetical charge on each atom in a structure. It assumes:

- ① All bonding electrons are shared EQUALLY between atoms
- ② Lone pairs are NOT shared.

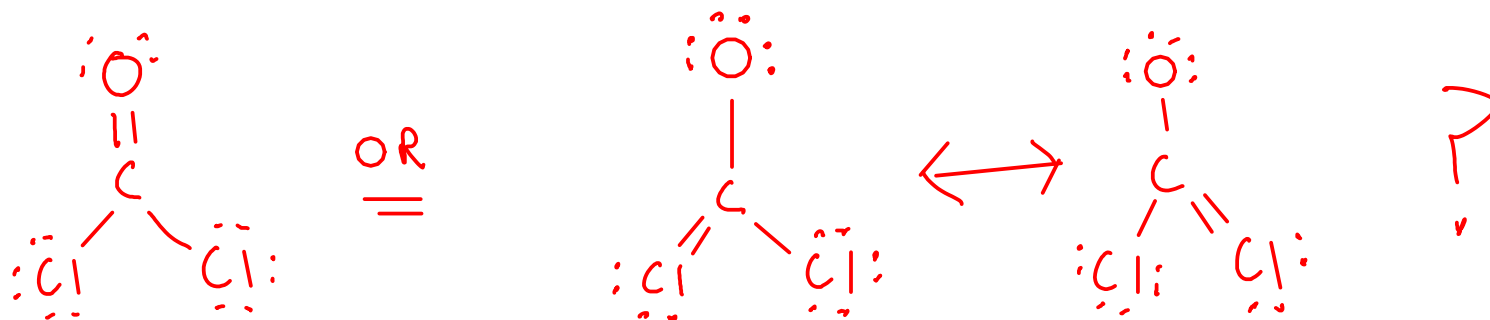
$$\text{FORMAL CHARGE} = \text{ORIGINAL \# OF VALENCE ELECTRONS} - \text{NUMBER OF BONDS} - \text{NUMBER OF UNSHARED ELECTRONS}$$

* The sum of the formal charges of all atoms in a structure should equal to the charge of the molecule (0 for neutral molecules)

The "better" Lewis structure will have:

- Lower magnitudes of formal charge (0 is better than +2 -2)
- Negative formal charges on ELECTRONEGATIVE atoms, or positive formal charges on atoms that are less electronegative.

EXAMPLE: COCl_2



... calculate formal charges to tell which structure is more likely!

$$\text{O}: 6 - 2 - 4 = 0$$

$$\text{C}: 4 - 4 - 0 = 0$$

$$\text{Cl}: 7 - 1 - 6 = 0$$

$$\text{Cl}: 7 - 1 - 6 = 0$$

$$\text{O}: 6 - 1 - 6 = -1$$

$$\text{C}: 4 - 4 - 0 = 0$$

$$=\text{Cl}: 7 - 2 - 6 = +1$$

$$-\text{Cl}: 7 - 1 - 6 = 0$$

Based on formal charge, the structure on the LEFT is preferred ... lower magnitudes of formal charge.



... we can determine which of these structures is more likely by calculating \ formal charges!

$$\text{H: } 1 - 1 - 0 = 0$$

$$\text{C: } 4 - 3 - 2 = -1$$

$$\text{N: } 5 - 4 - 0 = +1$$

$$\text{H: } 1 - 1 - 0 = 0$$

$$\text{C: } 4 - 4 - 0 = 0$$

$$\text{N: } 5 - 3 - 2 = 0$$

Which structure is more likely?

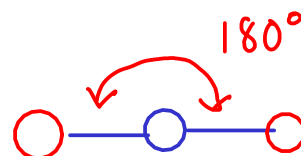
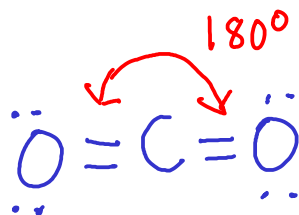
Based on formal charge, the structure on the RIGHT is preferred. The HCN version has lower magnitude of formal charge.

PREDICTING MOLECULAR SHAPE

The shape of simple molecules (and parts of larger molecules) can be easily predicted using the VSEPR model

VSEPR = Valence Shell Electron Pair Repulsion Model

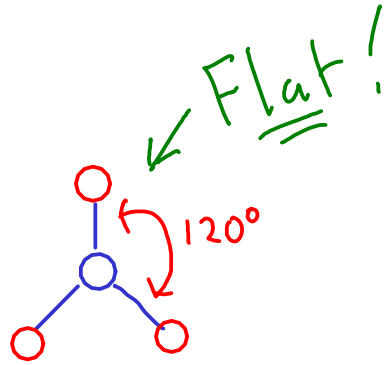
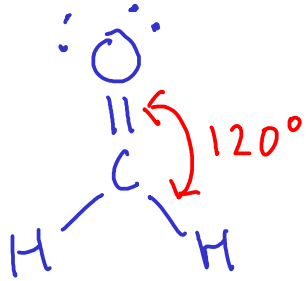
- Each BOND or LONE PAIR OF ELECTRONS around an atom will try to move itself as far away from other bonds or lone pairs as possible!



For the two red circles to be farthest apart, they must be 180 degrees apart

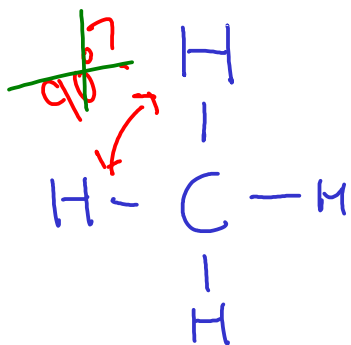
LINEAR MOLECULES

ANY diatomic (two-atom) molecule is linear, but only some three-atom molecules are!



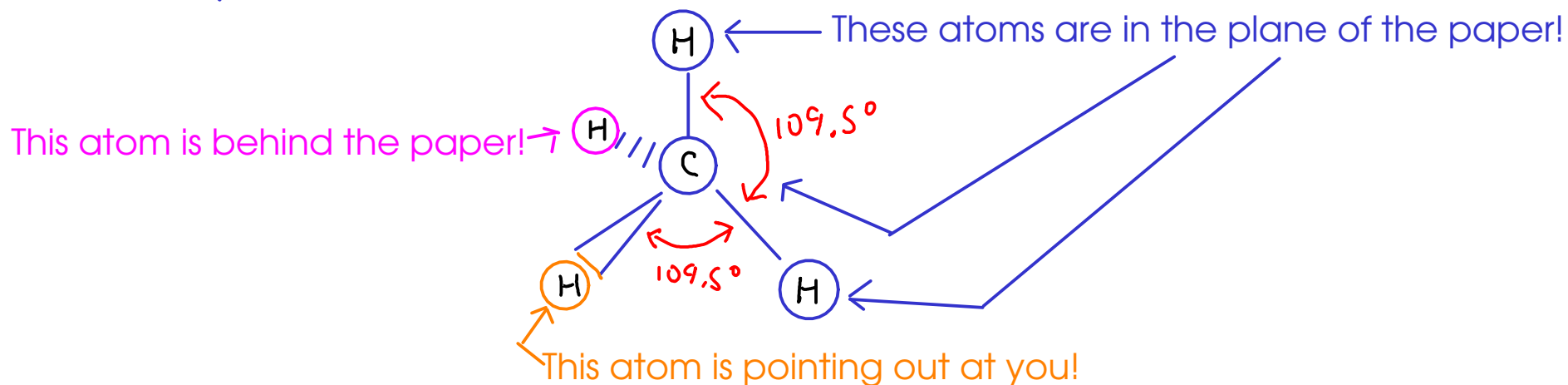
For the three red circles to be farthest apart, they spread out so that each is 120 degrees from the others!

TRIGONAL
PLANAR
MOLECULES



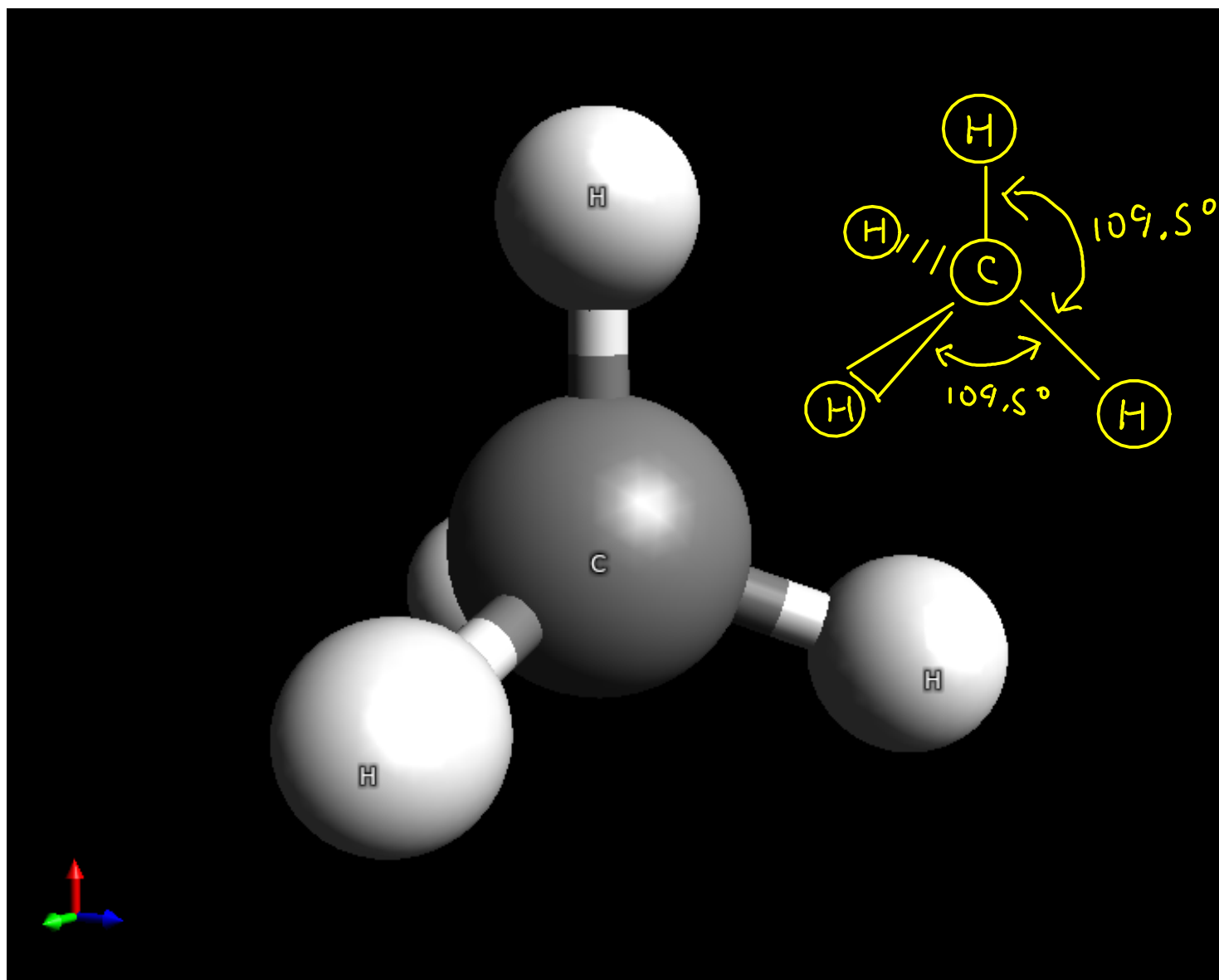
These hydrogen atoms might appear at first glance to be 90 degrees apart, but remember that molecules exist in THREE DIMENSIONS, not two!

Each hydrogen atom is actually 109.5 degrees apart, forming a TETRAHEDRON.



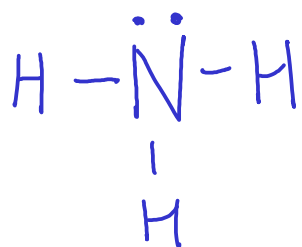
To see the tetrahedron in three dimensions WITHOUT buying a molecular model kit, just take four balloons, blow them up, and then tie them together. The knot will be the central atom, and the balloons will line themselves up to be 109.5 degrees apart.

Here's a computer ball-and-stick rendering of the methane molecule.



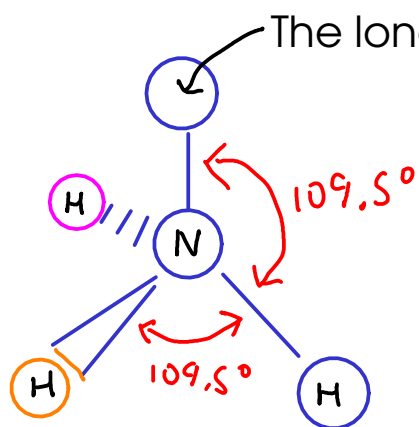
DERIVATIVES OF THE TETRAHEDRON

- What if there are lone pairs? The way the shape of a molecule is described depends on the ATOMS in the molecule, even though lone pairs play a role in the positions of the atoms.

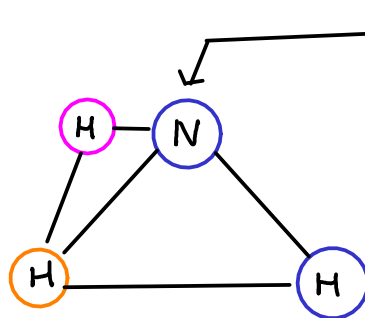


Since there are four "things" around the nitrogen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT ... only three of these things are atoms.

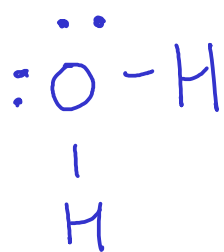
The atoms are arranged in a PYRAMID shape, so we call this molecule PYRAMIDAL!



The lone pair takes one position in the tetrahedron



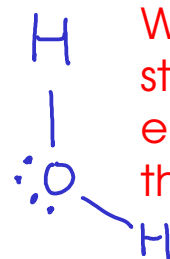
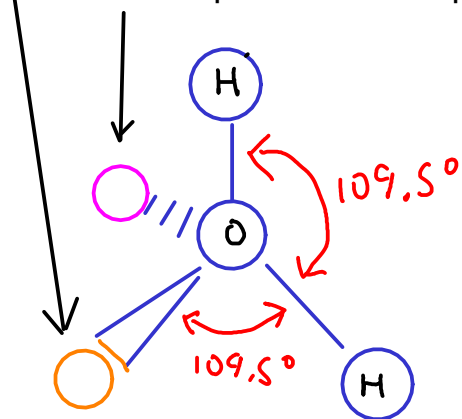
By just looking at the atoms, you can see the pyramid - with the central nitrogen atom as the top and the hydrogen atoms forming the base of the pyramid.



Since there are four "things" around the oxygen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT... only two of these things are atoms.

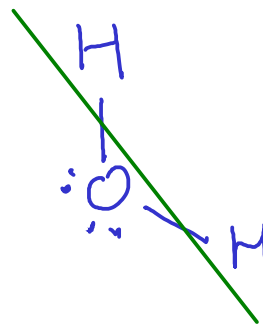
The atoms are all in a single plane, but they are not lined up in a straight line. We call this shape "BENT".

Lone pairs take up two positions in the tetrahedron



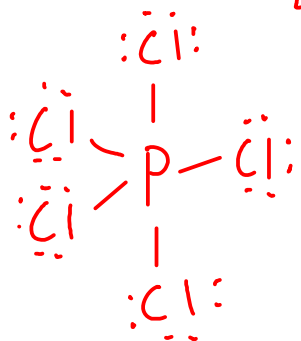
We sometimes draw the Lewis structure of water this way to emphasize the "bent" nature of the molecule!

Notice that this molecule has two "sides", one with the oxygen atom and one with hydrogen atoms.

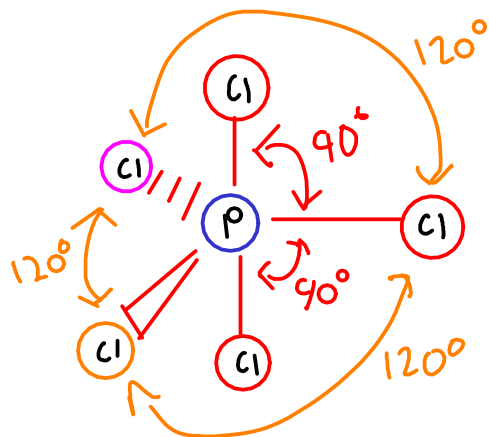


* These atoms are in the same plane, like carbon dioxide. But they are not arranged linearly!

186 SHAPES OF EXPANDED VALENCE MOLECULES

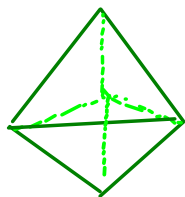


There are five atoms bonded to the central phosphorus atom, and they will attempt to get as far apart as possible from one another!



The top and bottom atoms are 90 degrees apart from the atoms around the center.

The atoms around the center are 120 degrees apart from each other.

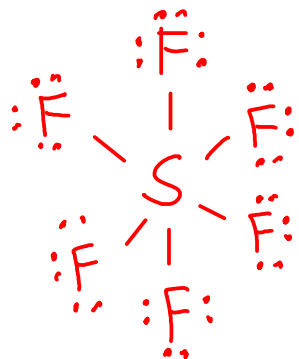


There are actually two DIFFERENT bond angles in this structure. It's called TRIGONAL BIPYRAMIDAL.

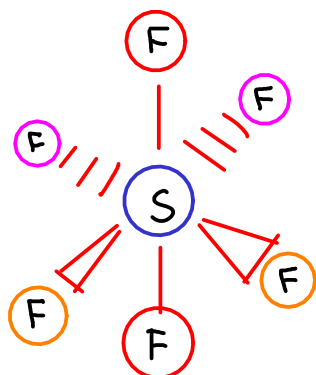
There are several derivatives of the trigonal bipyramidal shape (like the tetrahedral shape) - depending on how many things around the central atom are atoms!



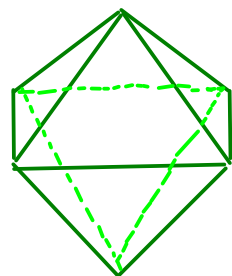
$$\begin{array}{r} S: 6 \\ F: 7 \times 6 \\ \hline 48 \end{array}$$



There are six atoms bonded to the central sulfur atom, and they will attempt to get as far apart as possible from one another!



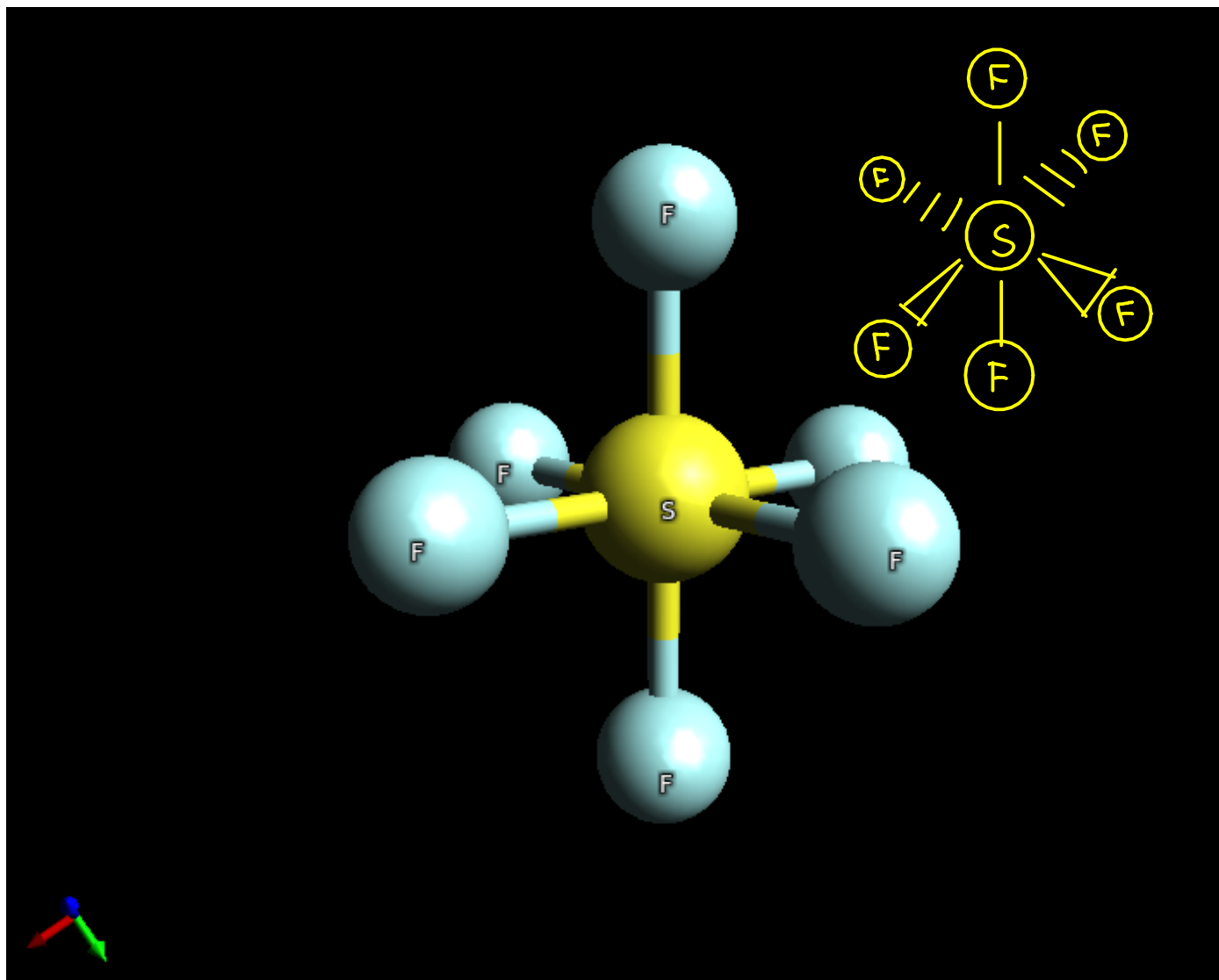
All bond angles in this arrangement are 90 degrees!



This shape is called OCTAHEDRAL, since it has eight sides.

Like the tetrahedral and trigonal bipyramidal arrangements, there are several derivatives of the octahedron - depending on how many of the six things around the center are atoms!

Here's a ball-and-stick rendering of the sulfur hexafluoride molecule:



POLARITY

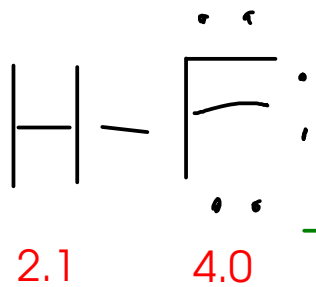
- When atoms share electrons, the electrons might not be EVENLY shared. Shared electrons may spend more time around one atomic nucleus than the other.
- When electrons are shared UNEVENLY, this results in a POLAR BOND.

... but how can we tell whether or not a bond will be POLAR? Use ELECTRONEGATIVITY!
Usually no actual calculation is required - trends are often good enough to see whether a bond is polar.

REMINDER: ELECTRONEGATIVITY

- A number that describes how tightly an atom will hold shared electrons
- A bond where there is a LARGE electronegativity difference between atoms will be either POLAR or (for very large differences) IONIC!
- A bond with little or no electronegativity difference between atoms will be NONPOLAR

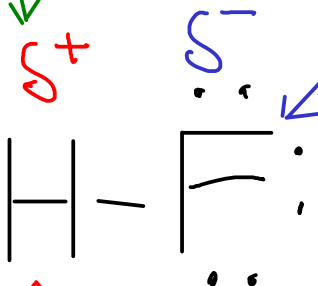
¹⁹⁰ ELECTRONEGATIVITY EXAMPLE



Electronegativity values
Difference = 1.9

Fluorine is much more electronegative than hydrogen. This is a POLAR BOND, and the shared electrons will be held more closely to FLUORINE!

δ means "small" here



This end of the molecule will have a slight NEGATIVE charge, since the shared electrons are closer to FLUORINE!

This end of the molecule will have a slight POSITIVE charge, since the shared electrons are pulled away from HYDROGEN!

POLARITY OF MOLECULES

So what can a molecule's LEWIS STRUCTURE, SHAPE, and the POLARITY of its bonds tell us?

... the POLARITY of the overall molecule, which will tell us (among other things) what a given molecule will mix with or dissolve in!

POLAR MOLECULES

- Will dissolve in or dissolve other polar molecules
- Will dissolve some ionic compounds
- Will NOT easily dissolve nonpolar molecules

Example:
WATER

NONPOLAR MOLECULES

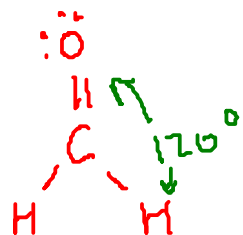
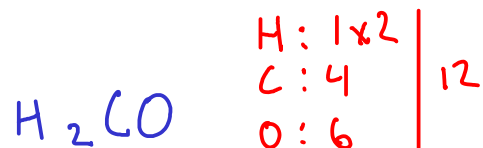
- Will dissolve in or dissolve other nonpolar molecules
- Will NOT easily dissolve polar molecules or ionic compounds

Example:
OILS

For a molecule to be polar, it must ...

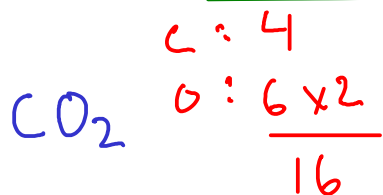
- ① Have polar bonds! (Any molecule that contains no polar bonds must be nonpolar!)
- ② Have polar bonds arranged in such a way that they don't balance each other out! (This is why you need to know the structure and shape of the molecule)

Examples:



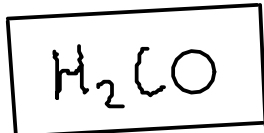
Shape? This molecule is TRIGONAL PLANAR. There are THREE THINGS around the central carbon: =O, -H, and -H

Polar? 1) Polar bonds? YES ... C=O is polar. C-H is nonpolar
2) Arrangement? Electrons are pulled towards the oxygen end of the molecule, making the H side positive, so POLAR.

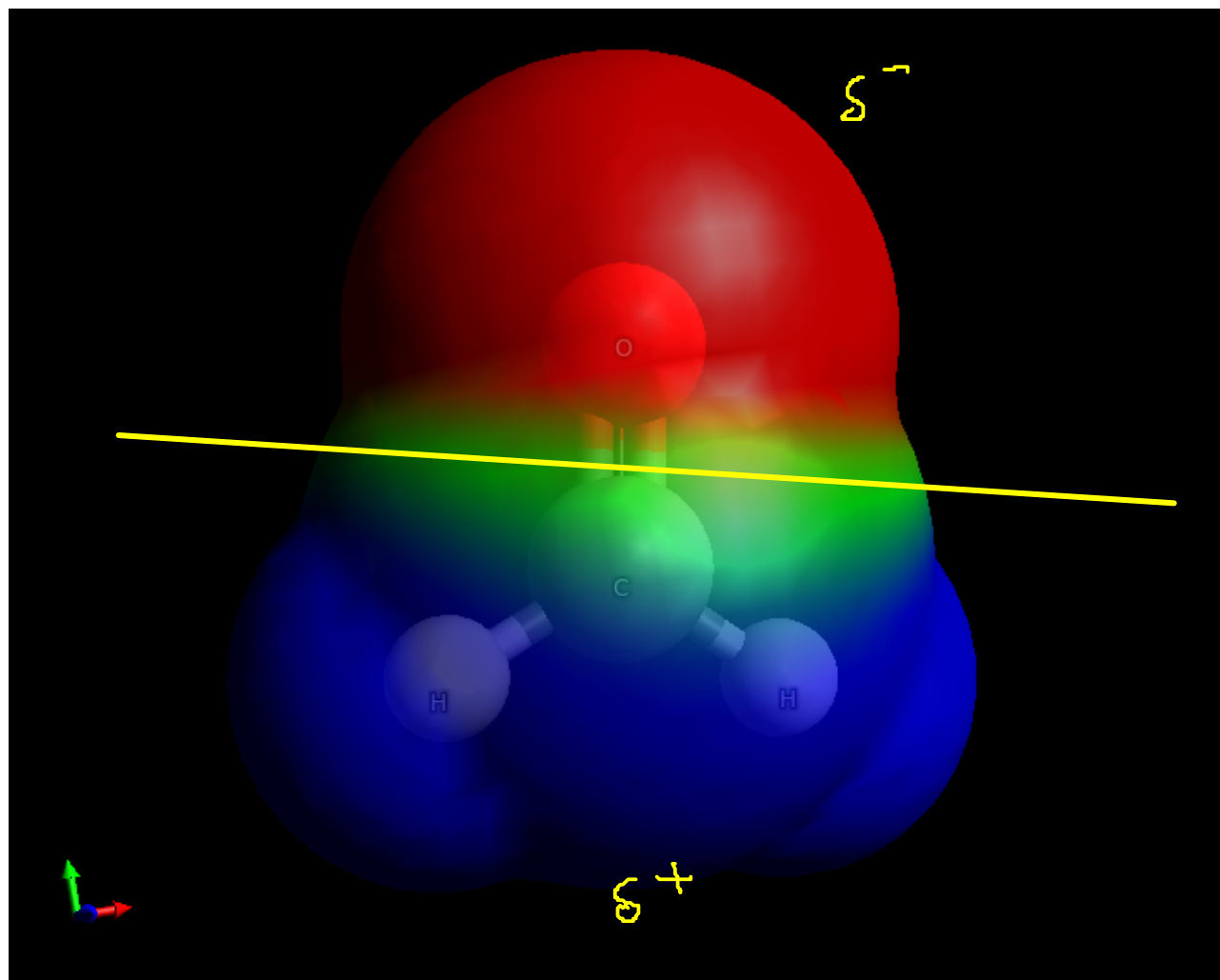


Shape? LINEAR. There are only two things around carbon, and they will be 180 degrees apart.

Polar? 1) Polar bonds? C=O bonds are polar.
2) Arrangement? The oxygen atoms are electronegative, but are on opposite sides of the molecule, so there's no negative "side". This is a NONPOLAR molecule.

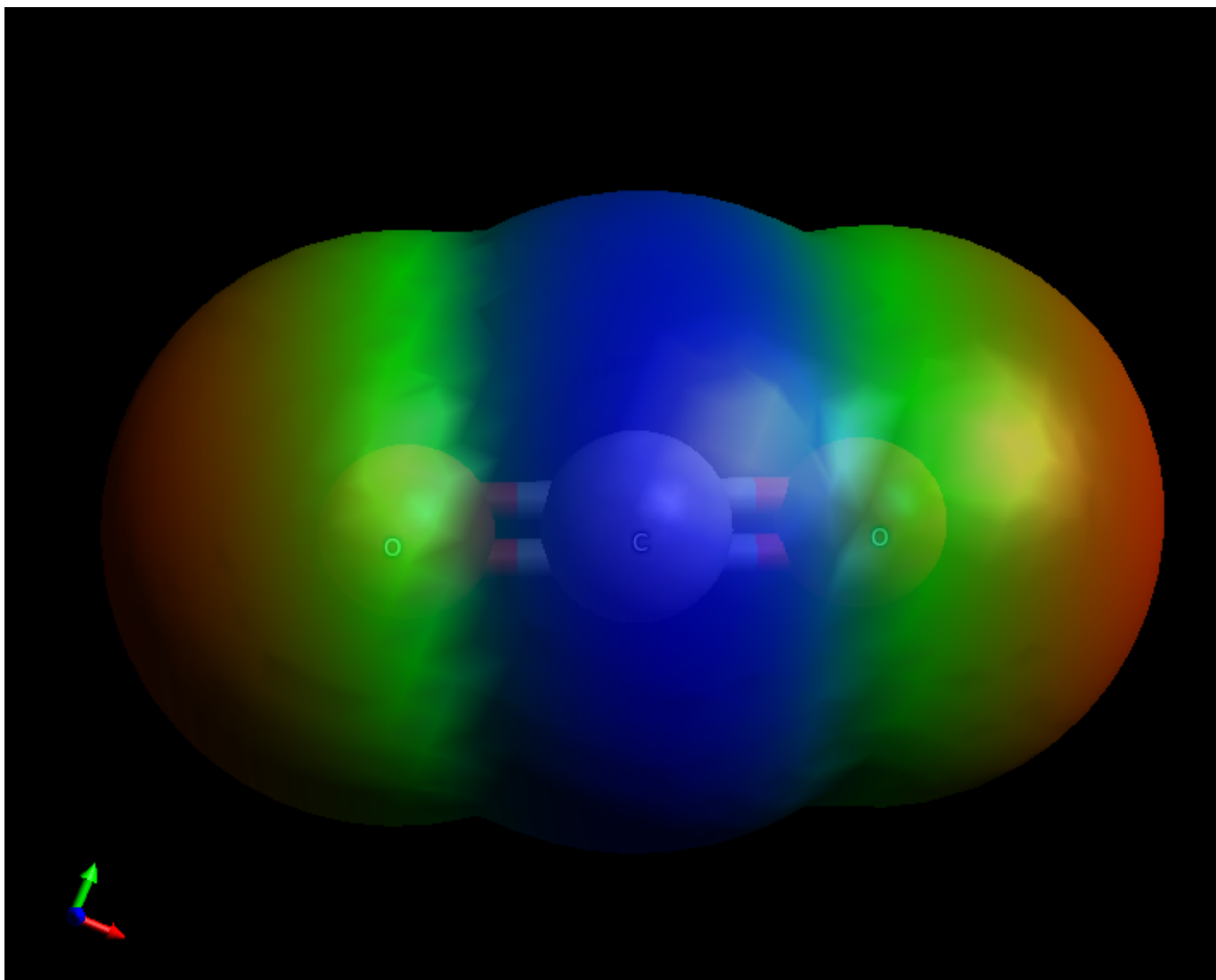
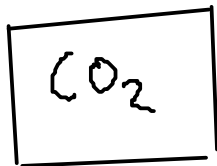


This ball-and-stick model shows electrostatic potential - red for more negative and blue for more positive



oxygen "side",
slightly negative

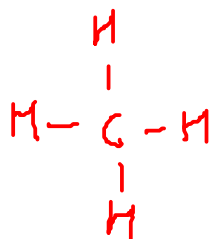
hydrogen "side",
slightly positive



This molecule is NONPOLAR. No positive "side" or negative "side"

methane, CH_4

C: 4

$$\begin{array}{r} \text{H: } 4 \times 1 \\ \hline 8 \end{array}$$


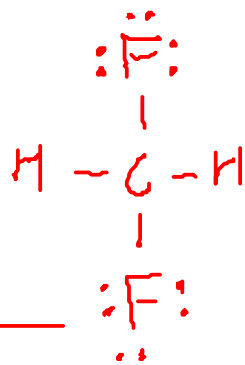
Shape? TETRAHEDRAL. Four atoms around the central carbon atom, all 109.5 degrees apart.

Polar? 1) Polar bonds? C-H bonds are nonpolar. **NONPOLAR MOLECULE.**

 CH_2F_2

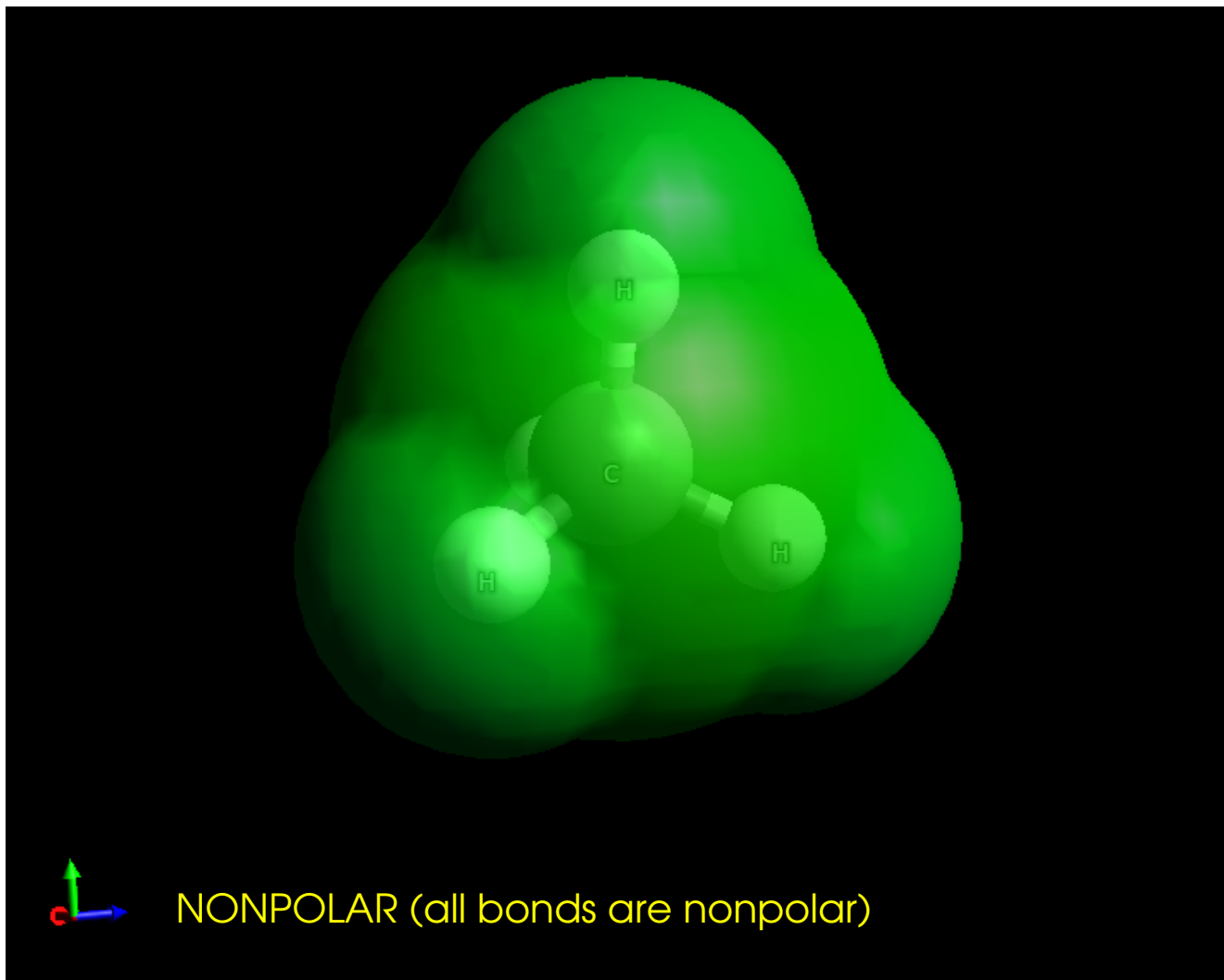
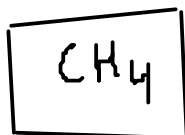
C: 4

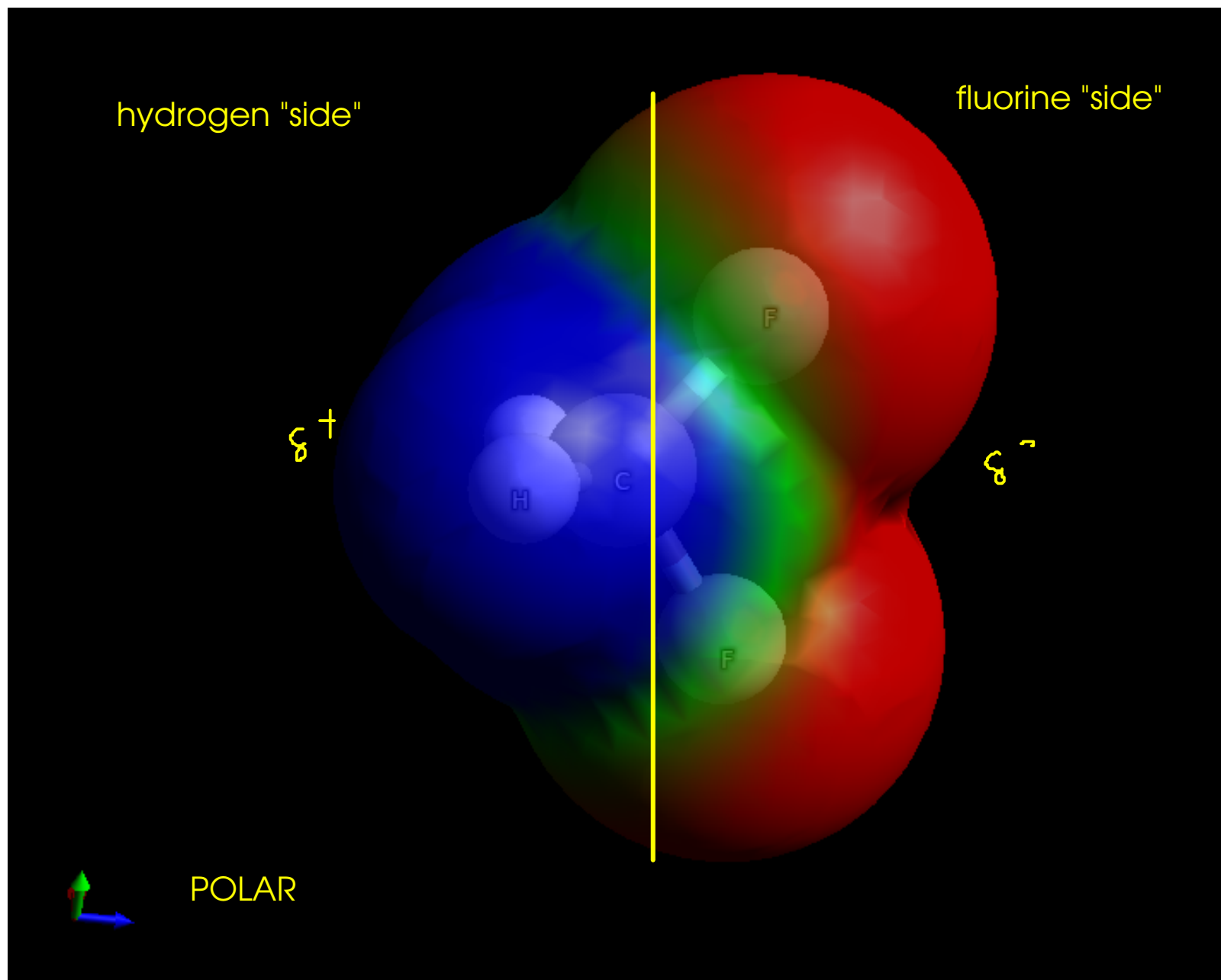
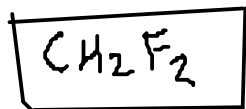
H: $2 \times 1 = 2$ F: $2 \times 7 = 14$

$$\hline 20$$


Shape? TETRAHEDRAL. Four atoms around the central carbon atom, just like methane.

Polar? 1) Polar bonds? YES ... C-F is polar
2) Arrangement? We have an uneven tetrahedron, which has a fluorine side and a hydrogen side, so the molecule is **POLAR.**





POLARITY AND MOLECULAR PROPERTIES

- POLAR MOLECULES have
 - higher boiling points and melting points that comparably sized nonpolar molecules.
 - higher solubility in polar solvents like water than nonpolar molecules

"LIKE DISSOLVES LIKE"

- NONPOLAR MOLECULES have
 - lower boiling points and melting points that comparably sized polar molecules.
 - higher solubility in nonpolar solvents like carbon tetrachloride or oils