A DOT STRUCTURE FOR A LARGER MOLECULE

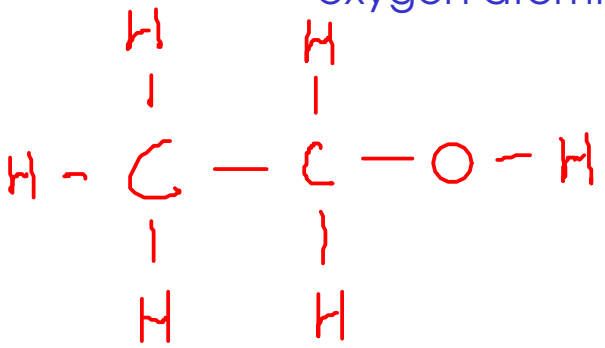
CH_3CH_2OH ETHANOL!

C : 4 x 2 = 8
H : 1 x 6 = 6
O : 6 x 1 = 6
| 20

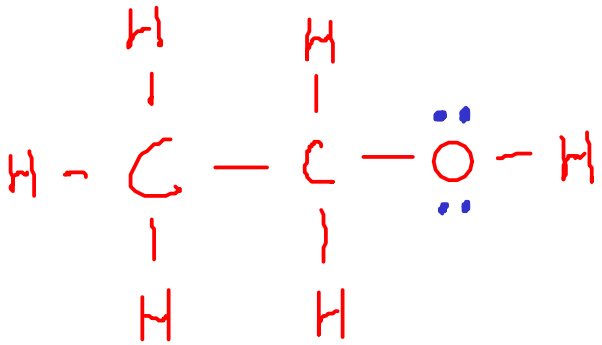
This formula gives us a hint to the structure of the molecule. Ethanol has THREE centers: the two carbon atoms and the oxygen atom.

1. Count valence electrons

2. Pick central atom and draw skeletal structure
   - central atom is usually the one that needs to gain the most electrons!
   - skeletal structure has all atoms connected to center with single bonds



3. Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.



The hydrogen atoms can only take TWO electrons, so the remaining four must go onto the oxygen atom.

4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS

O: 3 x 6 = 18

See text, 9.7 p 350-352

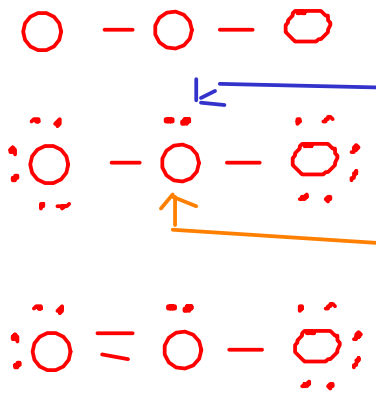
O_3 (OZONE)

1. Count valence electrons

2. Pick central atom and draw skeletal structure
   - central atom is usually the one that needs to gain the most electrons!
   - skeletal structure has all atoms connected to center with single bonds

3. Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

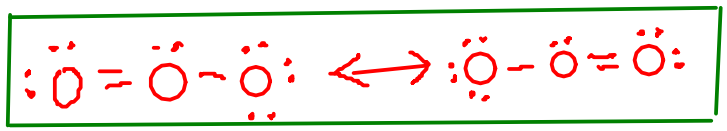


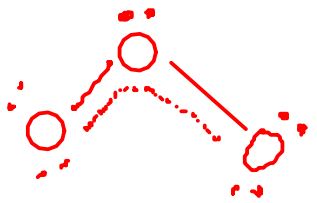
All atoms have a share in eight electrons!

The structure we drew implies that one of the outer oxygen atoms is closer to the central oxygen atom than the other one.

Experimentally, though, we find the two oxygen atoms to be the SAME distance from the center.

In the ozone molecule, electrons are actually being shared between ALL THREE oxygen atoms at the same time. This is called a DELOCALIZED BOND.





The structures in the green box are called RESONANCE STRUCTURES. The "real" structure of ozone is an "average" of the two resonsnce structures. The "double bond" electrons in these structures are actually shared between all three oxygen atoms

A DOT STRUCTURE FOR A POLYATOMIC ION

1. Count valence electrons

2. Pick central atom and draw skeletal structure
   - central atom is usually the one that needs to gain the most electrons!
   - skeletal structure has all atoms connected to center with single bonds

3. Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

4. Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

NH_4^+

N: 1 x 5 = 5

H: 4 x 1 = 4

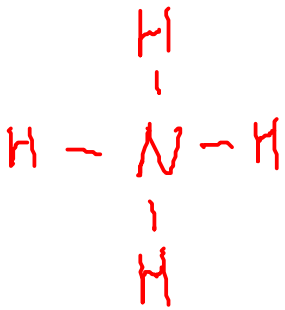
9

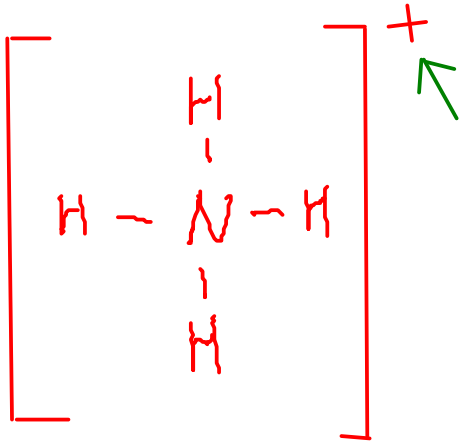
−1

8

An odd number of electrons? Lewis structures for molecules generally involve PAIRS of electrons!

To get a charge of +1 for the molecule, it has to have lost a single electron!



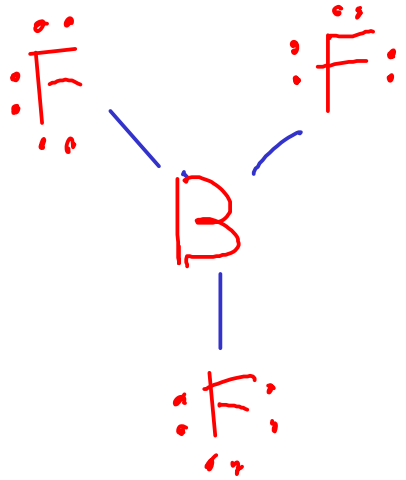


Draw brackets around the structure of an ion, then indicate the ion's charge in the upper right hand corner - just as we normally do with ions!

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.

BF_3



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

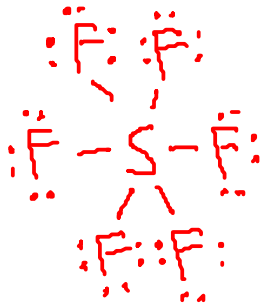
- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

... 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:

SF_6



S: 6
F: 7 x 6
48

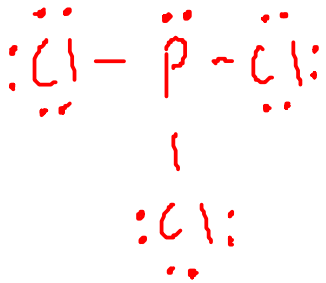
- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- 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.

PCl_3 vs PCl_5

PCl_3

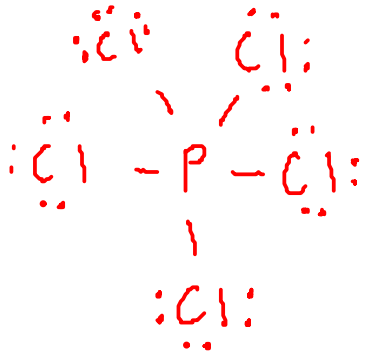
P : 5
Cl : 7 x 3 = 21
26



This structure obeys the octet rule.

PCl_5

P : 5
Cl : 7 x 5 = 35
40



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

FORMAL CHARGE

- You can often 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.

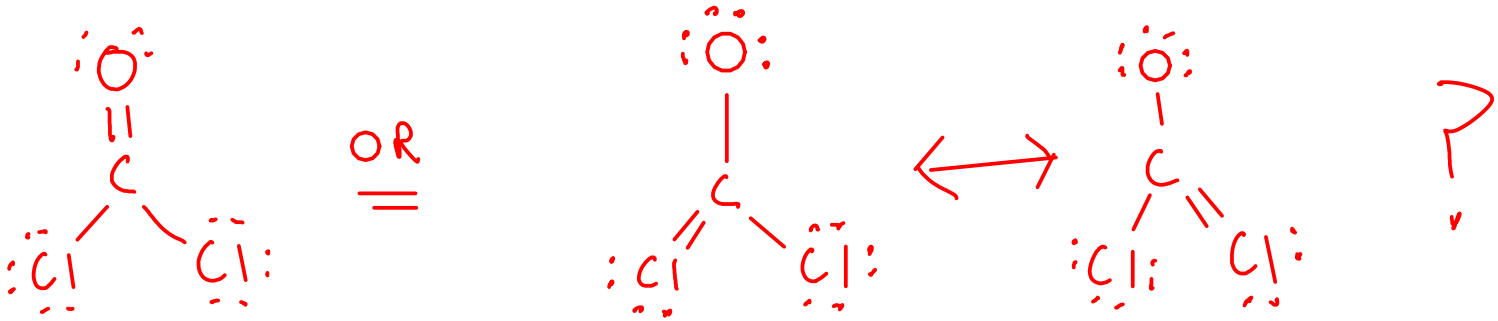
FORMAL CHARGE = ORIGINAL # OF VALENCE ELECTRONS − NUMBER OF BONDS − NUMBER OF UNSHARED ELECTRONS

* 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 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!

O: 6 − 2 − 4 = 0

C: 4 − 4 − 0 = 0

Cl: 7 − 1 − 6 = 0

Cl: 7 − 1 − 6 = 0

O: 6 − 1 − 6 = −1

C: 4 − 4 − 0 = 0

=Cl: 7 − 2 − 4 = +1

−Cl: 7 − 1 − 6 = 0

the structure on the LEFT is preferred, since it has lower formal charges than the resonance structures on the right. We predict that the OXYGEN will have a double bond.

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

H: 1 – 1 – 0 = 0

C: 4 – 3 – 2 = –1

N: 5 – 4 – 0 = +1

H: 1 – 1 – 0 = 0

C: 4 – 4 – 0 = 0

N: 5 – 3 – 2 = 0

Which structure is more likely?

* The HCN structure is more likely. It has lower formal charges than the HNC structure.

* The HNC structure has a positive formal charge on electronegative NITROGEN (and a negative charge on CARBON). We don't think that carbon would be able to pull electrons away from nitrogen!

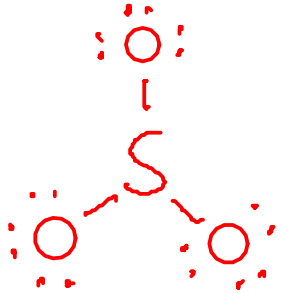
Let's look at sulfur trioxide. SO_3

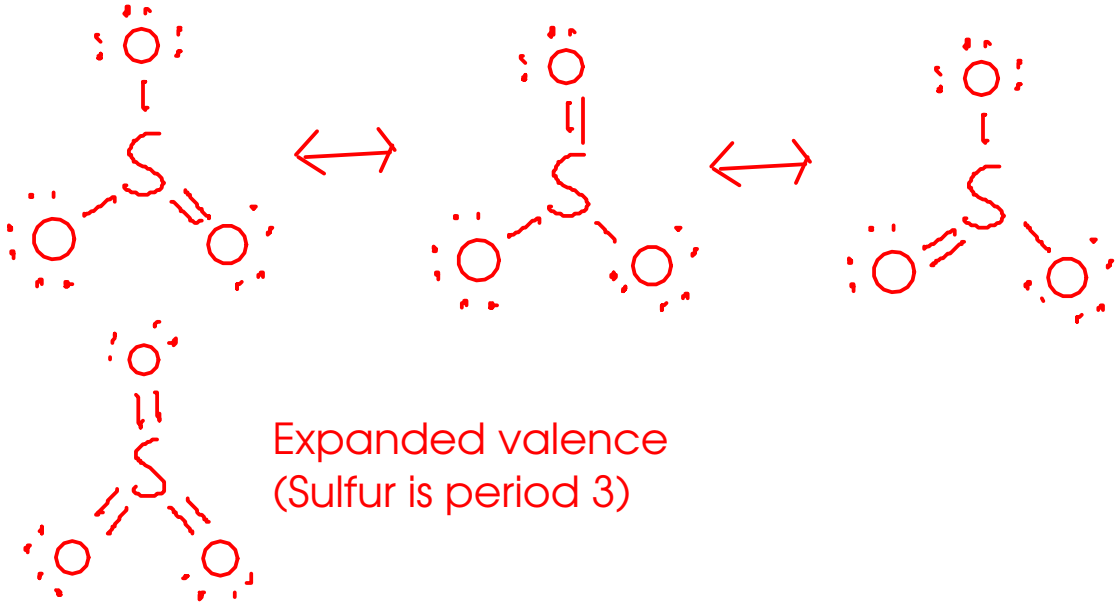
S: 6

O: 6 x 3 = 18

24 e⁻

Skeletal structure:

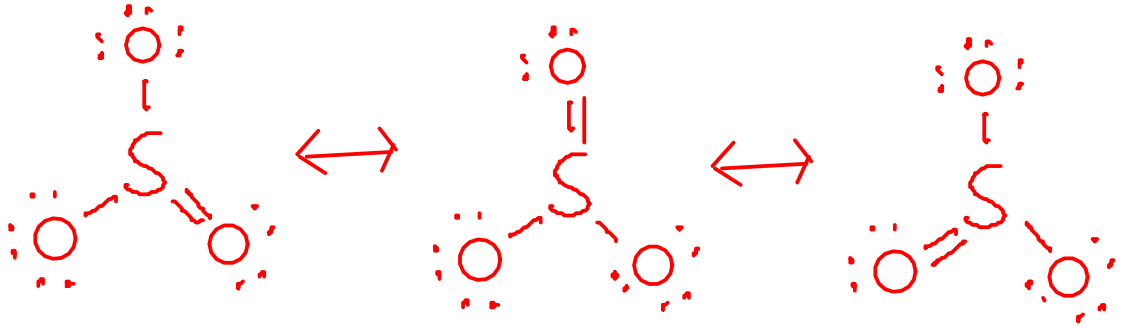




Resonance structures.

Expanded valence
(Sulfur is period 3)

To decide which structure is preferred, let's look at formal charges.



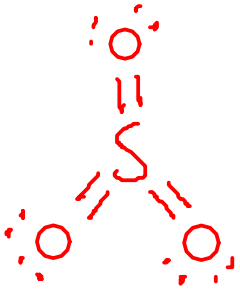
Resonance structures.

S: 6 − 4 − 0 = +2

O−: 6 − 1 − 6 = −1

O−: 6 − 1 − 6 = −1

O=: 6 − 2 − 4 = 0



Expanded valence
(Sulfur is period 3)

S: 6 − 6 − 0 = 0

O=: 6 − 2 − 4 = 0

O=: 6 − 2 − 4 = 0

O=: 6 − 2 − 4 = 0

BASED ON FORMAL CHARGE, the expanded valence structure is preferred.

The correct (as in, agrees with experimental data) structure is typically the one with minimized formal charges - EVEN IF that structure does not obey the octet rule!

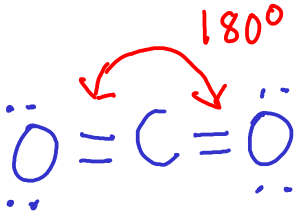
REMEMBER: Period 2 atoms never end up with more than eight electrons1

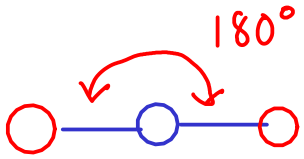
PREDICTING MOLECULAR SHAPE

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!

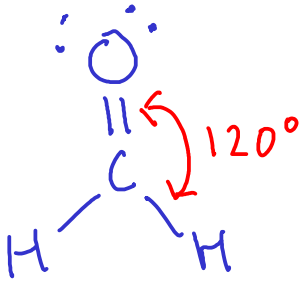


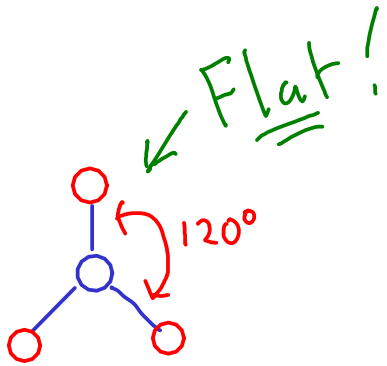


For the two red circles to be farthest apart, they must be 180 degrees apart

LINEAR MOLECULES

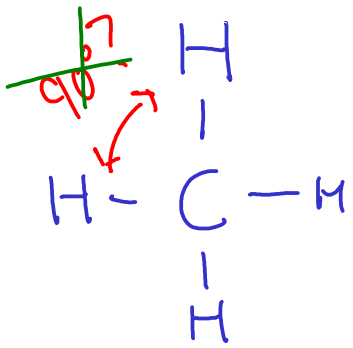
ANY diatomic (two-atom) molecule is linear, but only some three-atom molecules are!





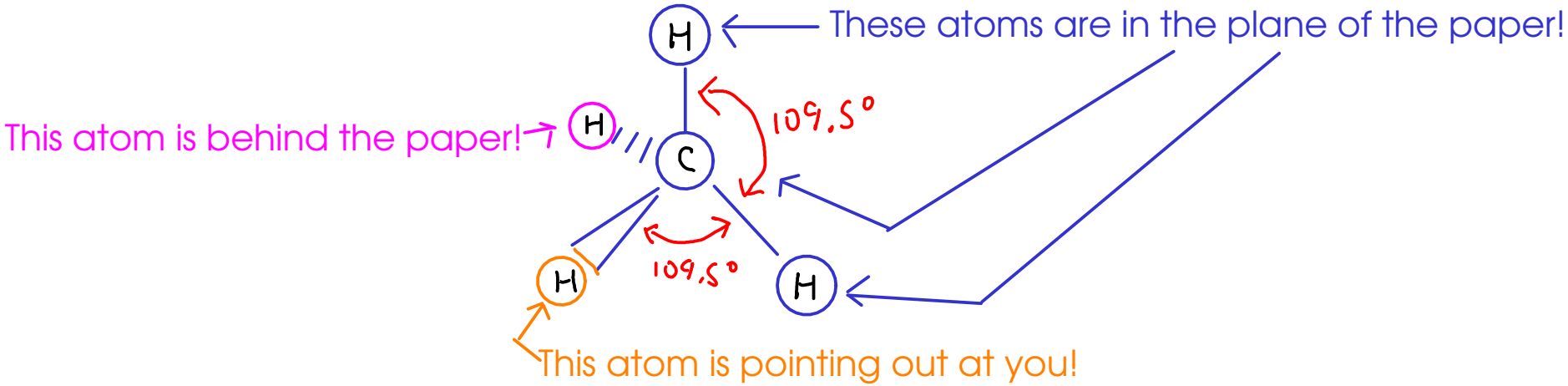
For the three red circles to be farthest apart, they spread out so that each is 120 degrees from the others!

TRIGONAL PLANAR MOLECULES



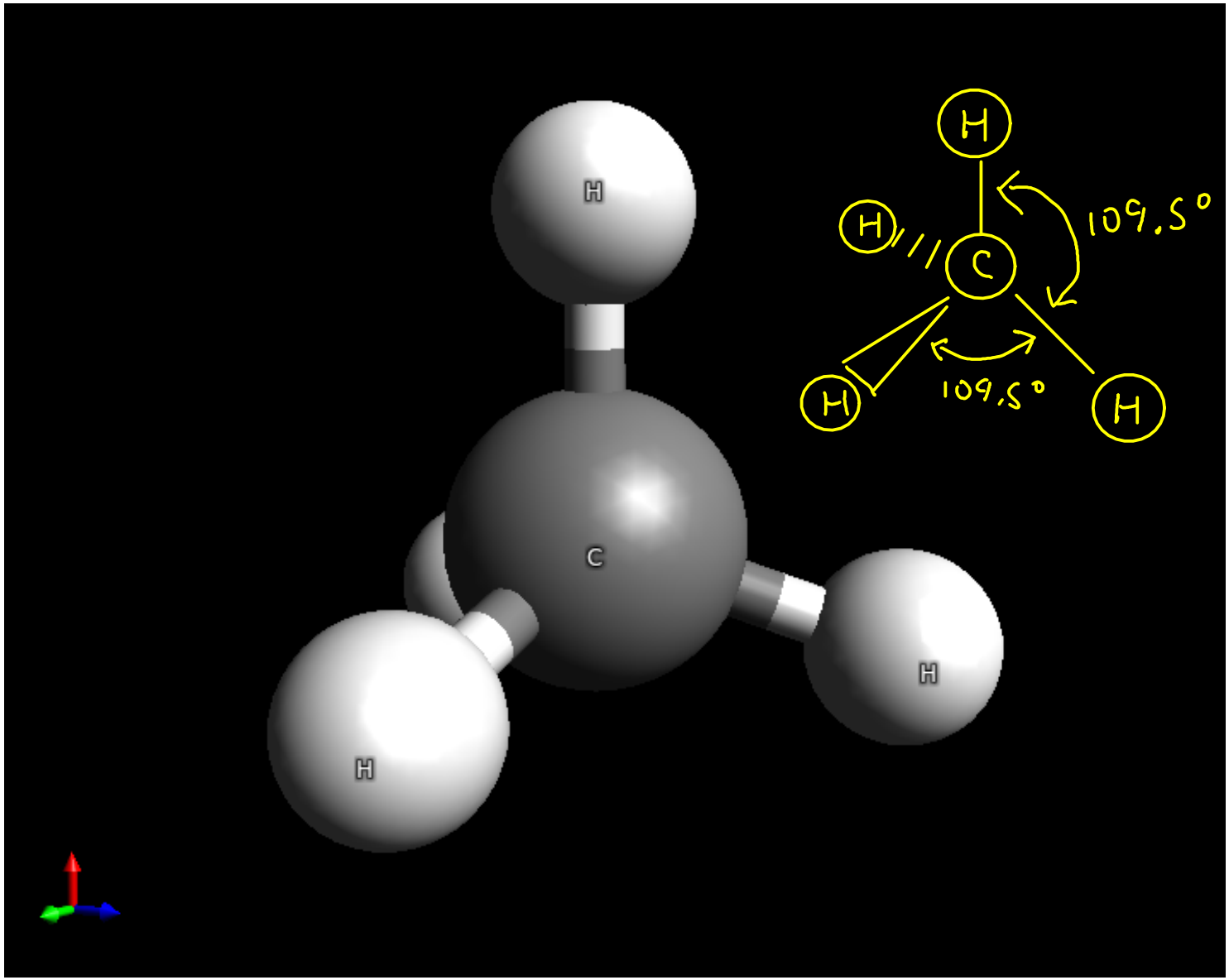
These hydrogen atoms might appear at first glance to be 90 degrees apart, but remember that molecules exist in THREE DIMENSIONS, not two!

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



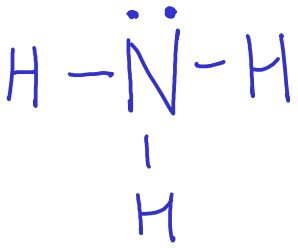
To see the tetrahedron in three dimensions WITHOUT buying a molecular model kit, just take four balloons, blow them up, and then tie them together. The knot will be the central atom, and the balloons will line themselves up to be 109.5 degrees apart.

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



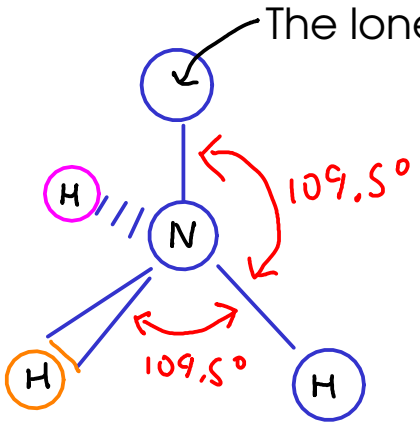
DERIVATIVES OF THE TETRAHEDRON

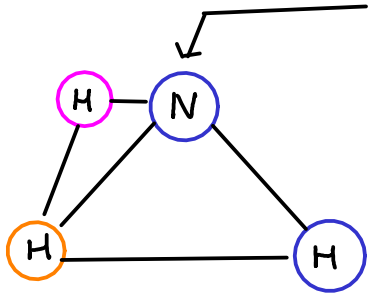
- What if there are lone pairs? The way the shape of a molecule is described depends on the ATOMS in the molecule, even though lone pairs play a role in the positions of the atoms.



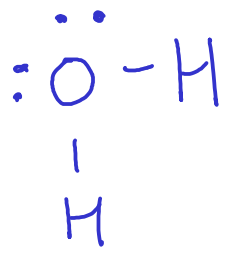
Since there are four "things" around the nitrogen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT ... only three of these things are atoms.

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





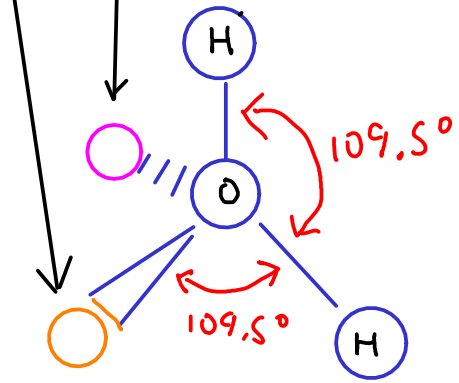
By just looking at the atoms, you can see the pyramid - with the central nitrogen atom as the top and the hydrogen atoms forming the base of the pyramid.

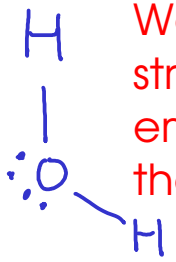


Since there are four "things" around the oxygen atom, we would expect them to be approximately 109.5 degrees apart (in other words, TETRAHEDRAL). BUT... only two of these things are atoms.

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

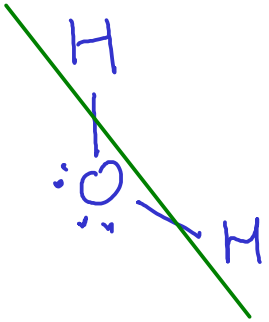
Lone pairs take up two positions in the tetrahedron





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

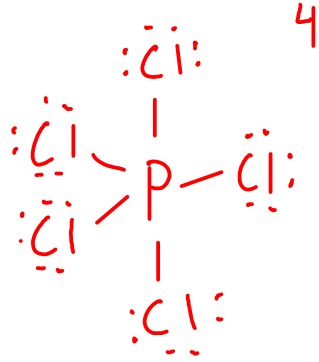
Notice that this molecule has two "sides", one with the oxygen atom and one with hydrogen atoms.



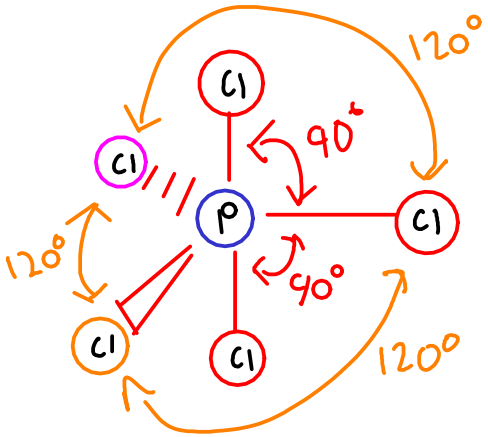
* These atoms are in the same plane, like carbon dioxide. But they are not arranged linearly!

SHAPES OF EXPANDED VALENCE MOLECULES

PCl_5 : P : 5
Cl : 7 × 5 = 40

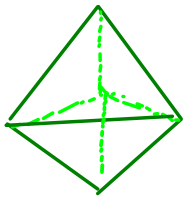


There are five atoms bonded to the central phosphorus atom, and they will attempt to get as far apart as possible from one another!



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.

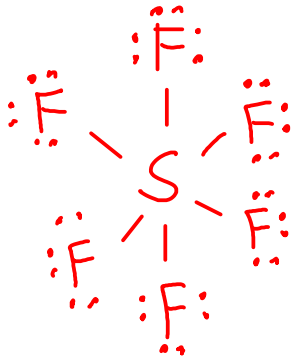


There are acually two DIFFERENT bond angles in this structure. It's called TRIGONAL BIPYRAMIDAL.

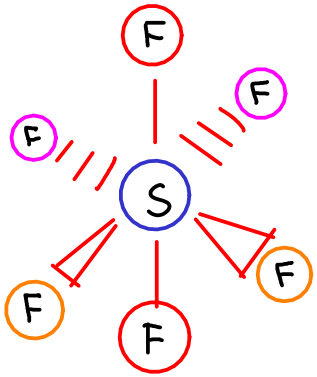
There are several derivatives of the trigonal bipyramidal shape (like the tetrahedral shape) - depending on how many things around the central atom are atoms!

SF_6:

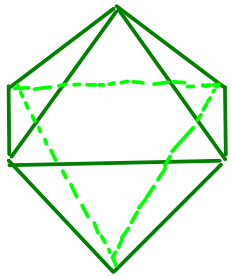
S: 6
F: 7x6
48



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



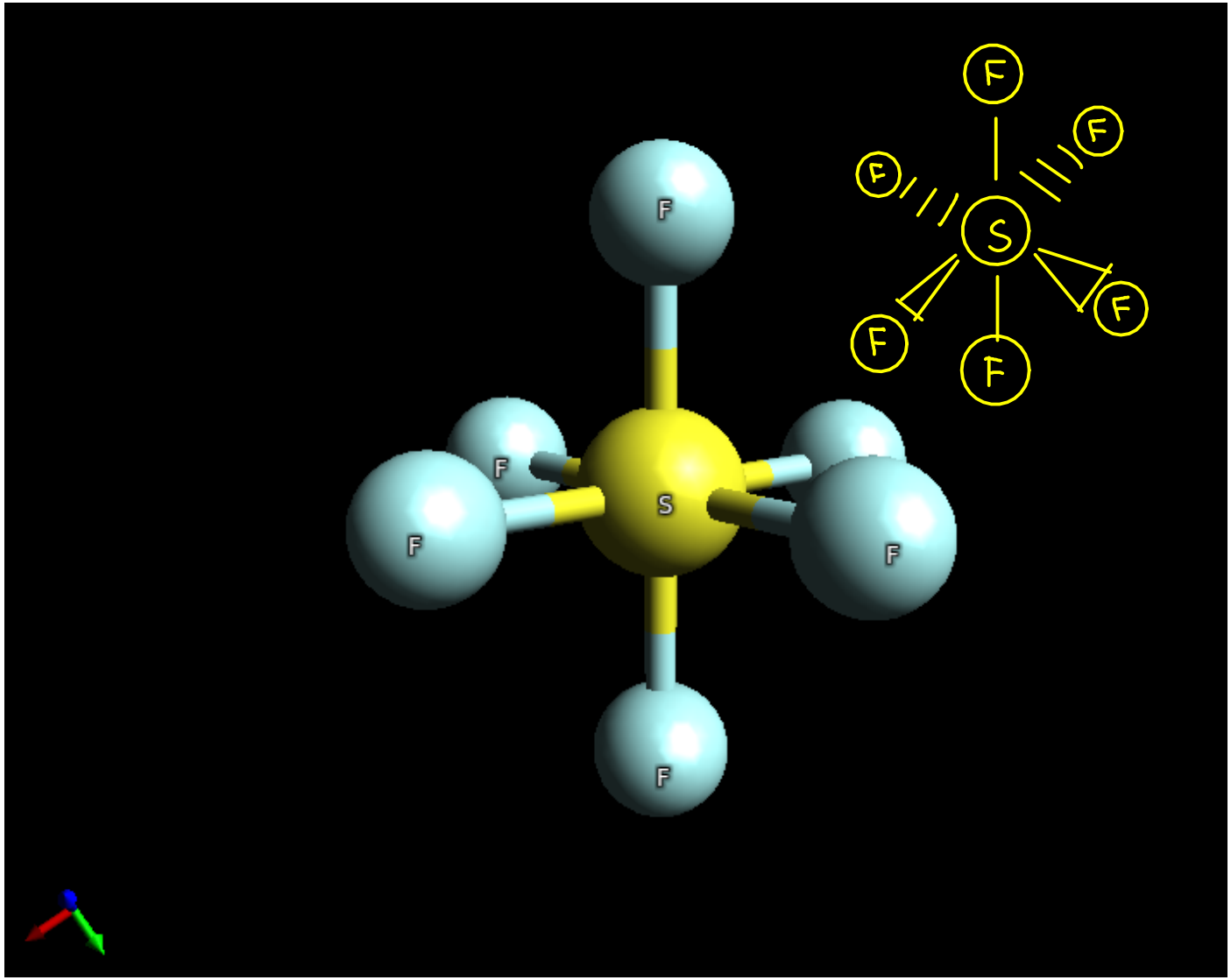
All bond angles in this arrangement are 90 degrees!



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 experimental data on ELECTRONEGATIVITY!

ELECTRONEGATIVITY:
-A measure of how closely to itself 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

ELECTRONEGATIVITY TRENDS (AGAIN!)

- You may look up elecronegativity data in tables, but it helps to know trends!

INCREASING ELECTRO-NEGATIVITY

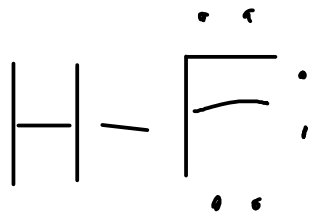
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA
2	Li	Be										B	C	N	O	F
3	Na	Mg										Al	Si	P	S	Cl
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
7	Fr	Ra	*Ac	Rf	Db	Sg	Bh	Hs	Mt								

*"inner" transition metals go here

Notes:

1. - FLUORINE is the most elecronegative element, while FRANCIUM is the least!
2. - All the METALS have low electronegativity, and metal/nonmetal combinations form IONIC bonds
3. - HYDROGEN is similar in electronegativity to CARBON, so C-H bonds are considered NONPOLAR

ELECTRONEGATIVITY EXAMPLE



2.1 4.0] – 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 ...

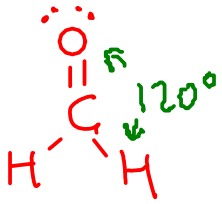
1. Have polar bonds! (Any molecule that contains no polar bonds must be nonpolar!)
2. Have polar bonds arranged in such a way that they don't balance each other out! (This is why you need to know the structure and shape of the molecule)

Examples:

H_2CO

H : 1x2
C : 4
O : 6
| 12

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

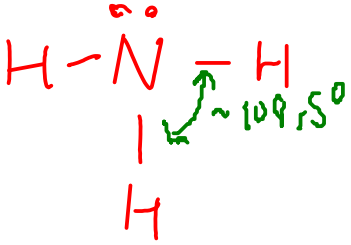


Polar? C-H bonds are nonpolar, but the C=O bond should be polar. Electrons are pulled towards the oxygen and this pull is not "cancelled" by the opposing hydrogen atoms (they're not very electronegative). POLAR MOLECULE.

NH_3

N : 5
H : 1 x 3
8

Shape? PYRAMIDAL. There are four things around the central nitrogen, but only three are atoms. Tetrahedral bond angles (109.5), but pyramidal shape.

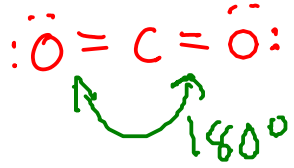


Polar? N-H bonds are polar, and since the molecule has nitrogen "side" (the top of the pyramid), the molecule is POLAR. The nitrogen end is slightly negative, while the hydrogen end is slightly positive.

CO_2

C : 4
O : 6x2
16

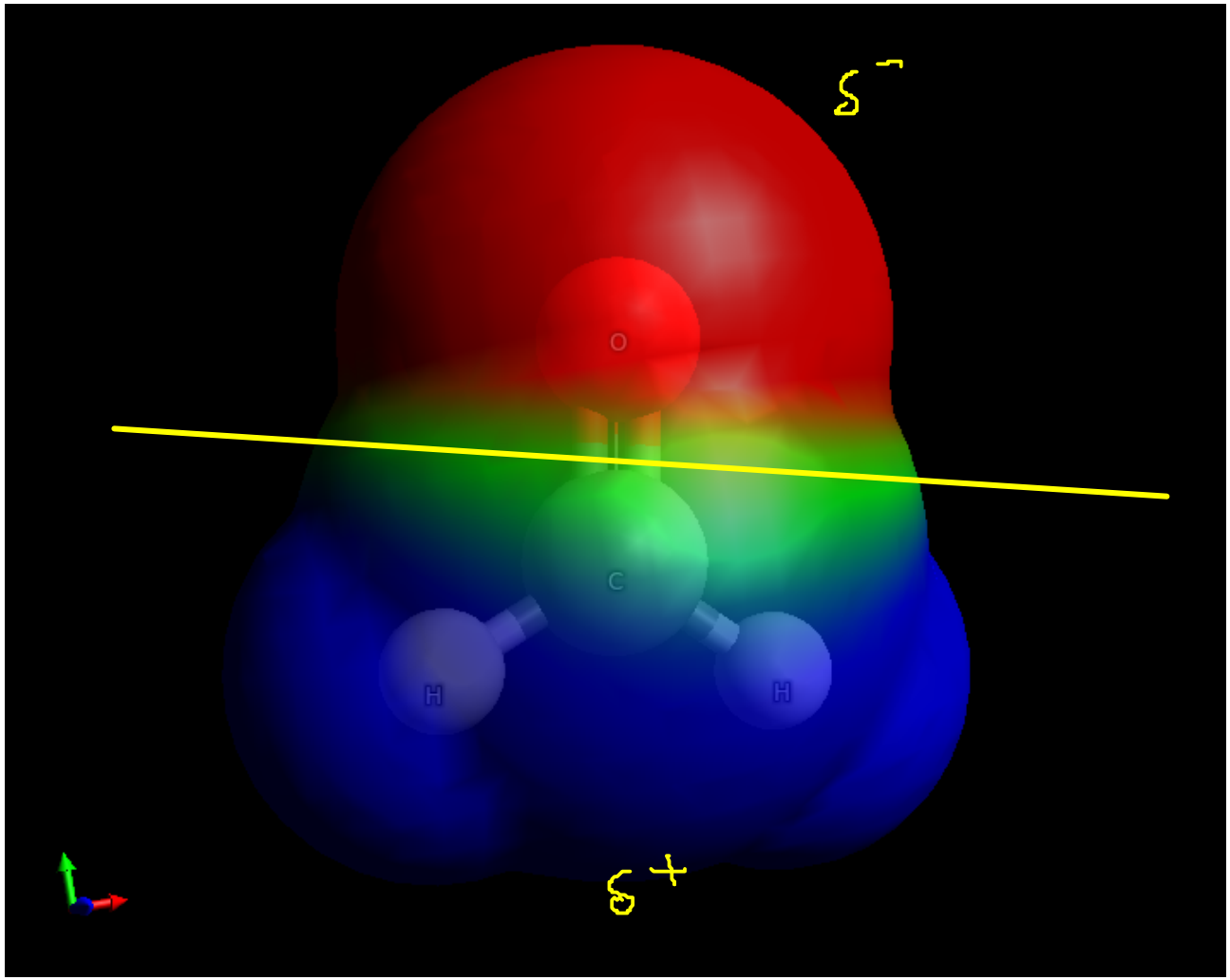
Shape: LINEAR. Only two groups attached to carbon.



Polar? C=O bonds should be polar, but took at the arrangement! The molecule is NONPOLAR, since the oxygens directly oppose one another!

H_2CO

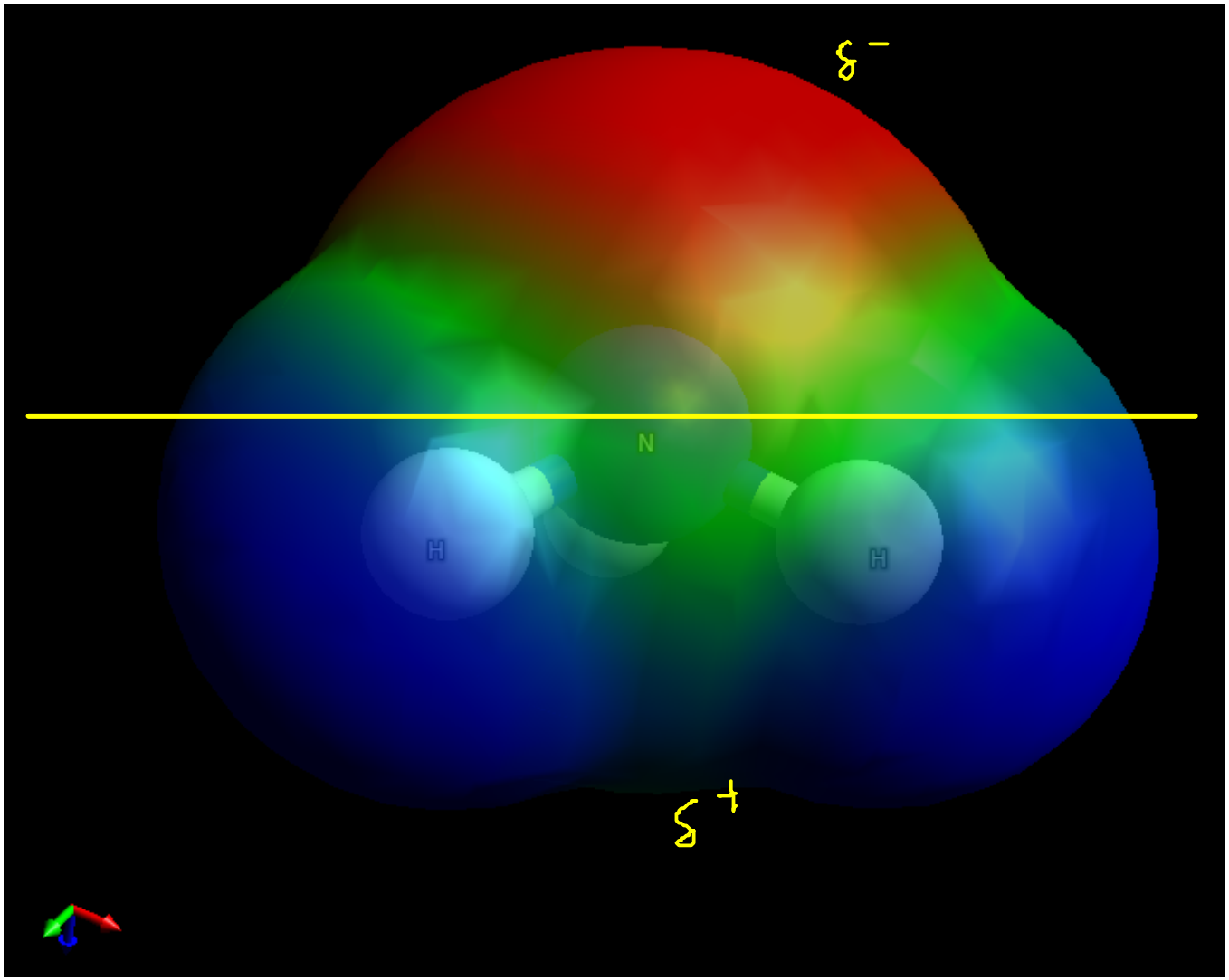
This ball-and-stick model shows electrostatic potential - red for more negative and blue for more positive



oxygen "side", slightly negative

hydrogen "side", slightly positive

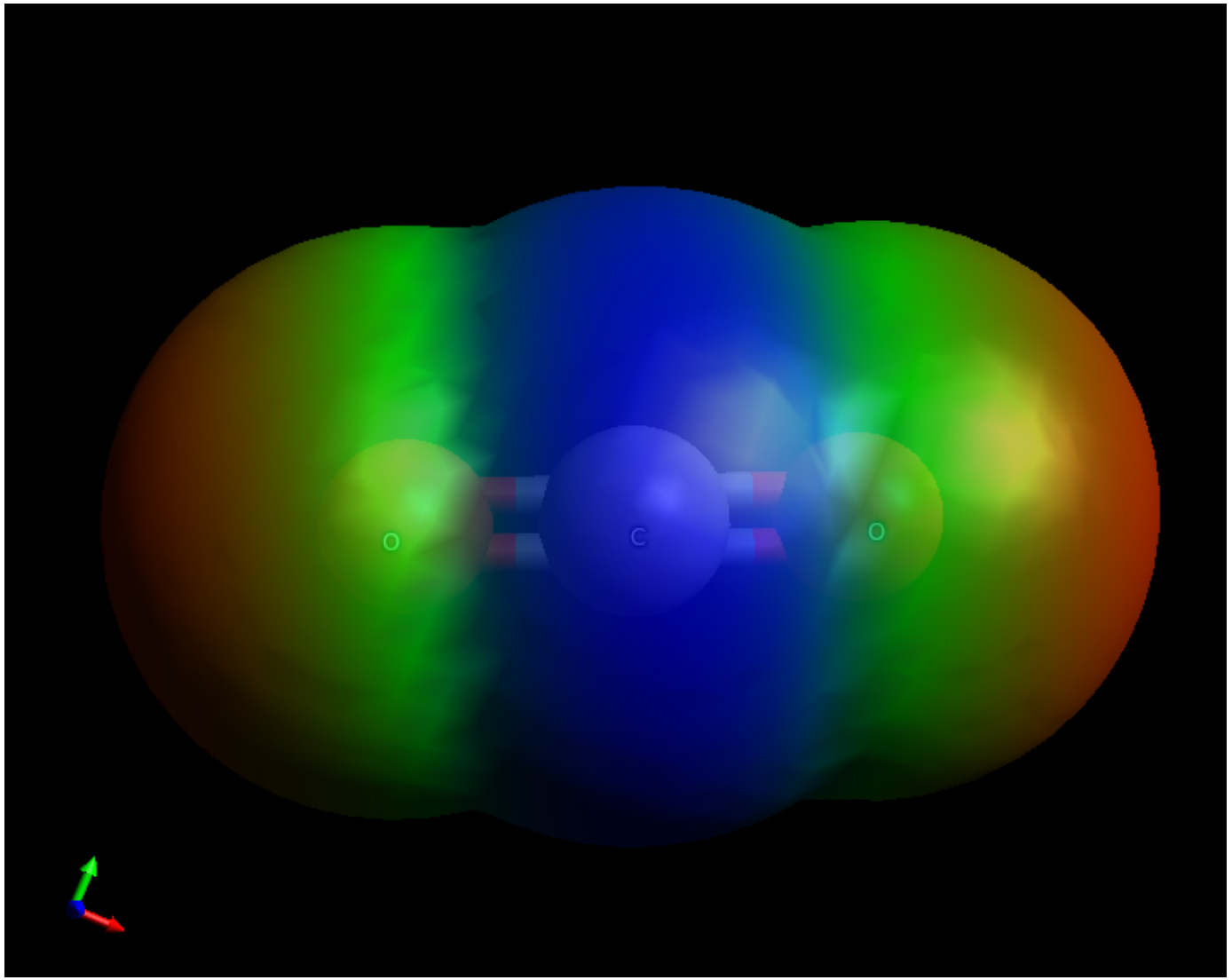
NH_3



nitrogen "side"
slightly negative

hydrogen "side"
slightly positive

CO_2



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