CHEM 205 section 03

LECTURE #24 Tues. April 01, 2008

ASSIGNED READINGS:

TODAY'S CLASS: finish Ch.9

NEXT CLASS: Ch.10.1 & 10.2

9.9 Molecular Shapes: the VSEPR model

- SHAPE is very useful information:
  - Start with Lewis structure: predict 3-D shape of molecule
  - Analyze bond dipoles: predict interactions between molecules
    ⇨ predict substance's physical & chemical properties!

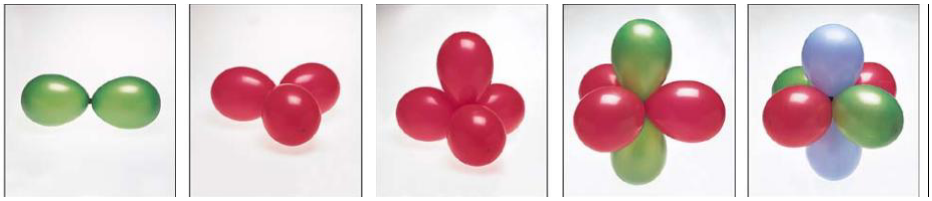
A model for molecular geometries: VSEPR
the Valence Shell Electron Pair Repulsion model

- Ron Gillespie (McMaster University…)
- The structure around a given atom is determined *principally* by minimizing repulsions between electron pairs in the valence shell

i.e., molecules adopt geometries with
bonds & lone pairs are as far apart as possible

In Ch.10: See how this actually does use our atomic orbitals…

3-D geometries that minimize repulsions between e^- pairs…



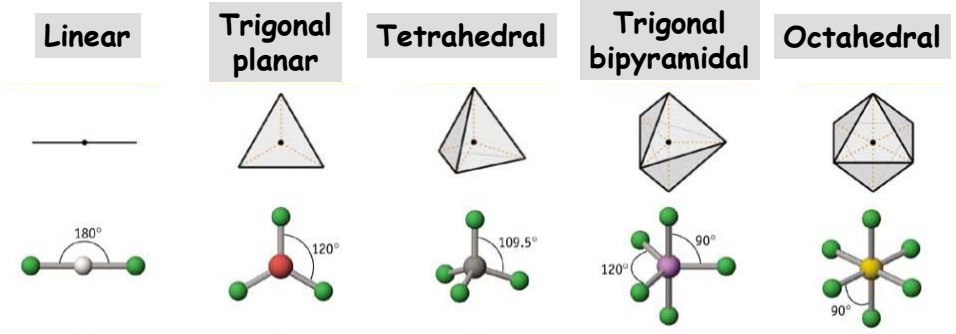
Linear | Trigonal planar | Tetrahedral | Trigonal bipyramidal | Octahedral

" electron-pair geometries "
OR " basic geometries "

(3)

See Figure 9.7

When central atom's e^- pairs are ALL IN BONDS… (Fig.9.8)
…molecular geometry is SAME as e^--pair (basic) geometry



"AB_2" | "AB_3" | "AB_4" | "AB_5" | "AB_6"

BeF_2 | BF_3 | CCl_4 | PBr_5 | SF_6

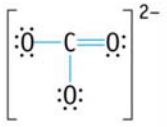
(4) *Draw these examples (Lewis structures) yourselves to verify this…*

Molecules with multiple bonds…

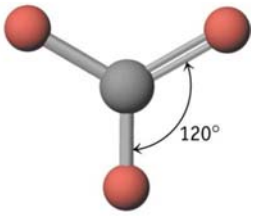
For predicting geometry:
treat multiple bonds like a single bonding pair of e⁻s

double bond = 4e⁻ (2 pairs)
triple bond = 6e⁻ (2 pairs)

e- PAIRS BEING SHARED BETWEEN SAME TWO ATOMS MUST POINT BETWEEN THEM!

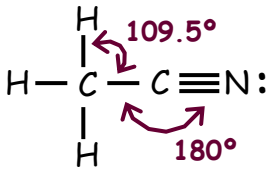


1 of 3 equivalent resonance structures of carbonate



Molecular structure, trigonal planar

Another example: predict geometries & identify bond angles…



←Acetonitrile, a common organic solvent

VSEPR strategy for determining molecular geometry

DRAW LEWIS STRUCTURE ↔ Show all bonds (—) & lone pairs (:)

↓

Determine central atom's electron-pair geometry

- Multiple bonds' pairs remain together, between the two atoms bonded:
  double bond = 2 pairs
  triple bond = 3 pairs
  } treat as 1
- Place central atom's e⁻ pairs as far apart as possible (in 3-d)

↓

Determine molecular geometry based on positions of atoms

- Identify lone *vs.* bonding pairs
- Place lone pairs:
  - in most spacious positions
  - as far from each other as possible

LONE PAIRS TAKE UP MORE SPACE…

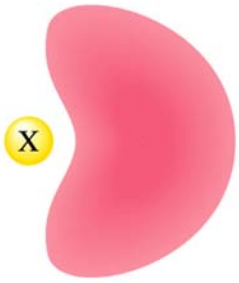
Zumdahl's Figure 8.18:

(a) **A BONDING PAIR:**

e⁻s shared between two nuclei
= attracted to two + centres
→ "stretched out" between them

(b) **A LONE PAIR:** ***larger*** !

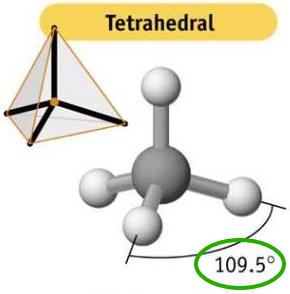
both electrons attracted to only one nucleus
→ spread out a bit more…



When central atom has lone pairs… (Fig.9.9)
…molecular geometry NOT same as e⁻pair (basic) geometry

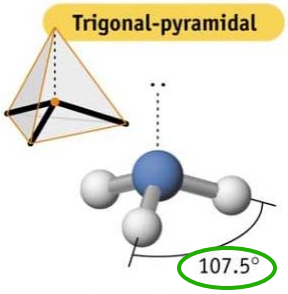
FOUR ELECTRON PAIRS
Electron Pair Geometry = tetrahedral

Molecular geometry affected by lone pairs:



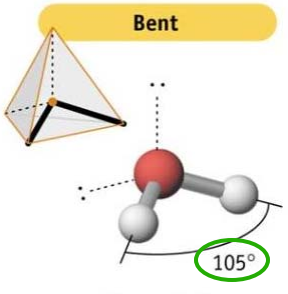
Methane, CH_4

A true tetrahedral ("Td") arrangement of e- pairs



Ammonia, NH_3

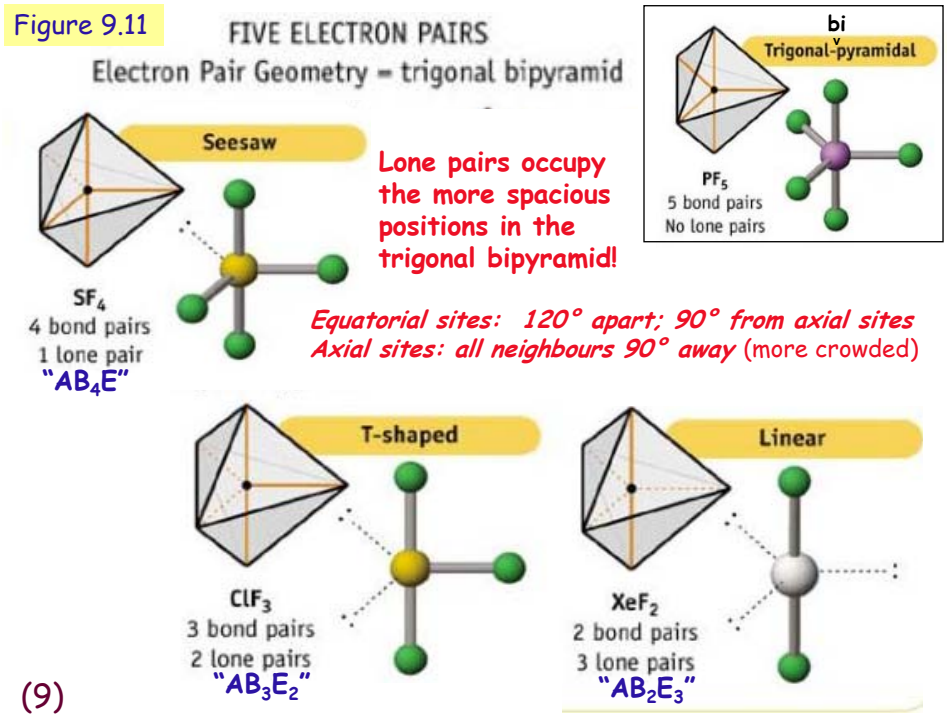
Lone pair squeezes H's closer together
→ Lower bond angle!



Water, H_2O

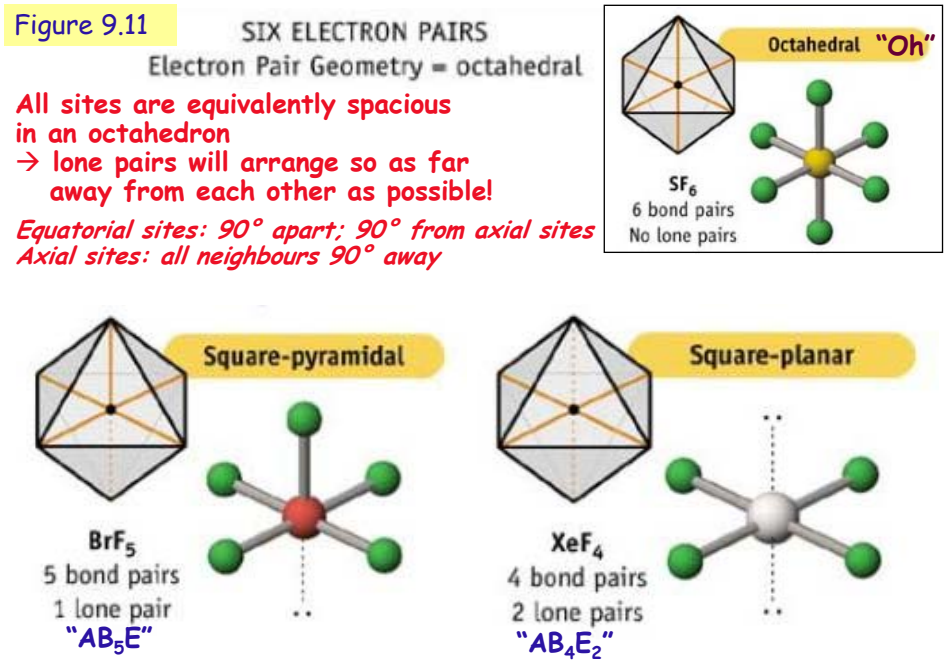
2 lone pairs. Even smaller bond angle!

Figure 9.11



(9)

Figure 9.11



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Molecular geometry: summary of strategy & names

DRAW LEWIS STRUCTURE ⟷ Show all bonds (—) & lone pairs (:)

↓

Determine central atom's basic e⁻-pair geometry ⟷ Place central atom's e⁻ pairs as far apart as possible (in 3-d)

2 pairs: linear
3 pairs: trigonal planar
4 pairs: tetrahedral
5 pairs: trigonal bipyramidal
6 pairs: octahedral

↓

Determine molecular geometry based on positions of atoms ⟷ Determine impact of lone pairs on observed shape of molecule…

2 pairs: linear
3 pairs: trigonal planar, bent
4 pairs: tetrahedral, trigonal pyramidal, bent…
5 pairs: trigonal bipyramidal, see-saw, T-shaped, linear…
6 pairs: octahedral, square pyramidal, square planar, T-shaped, linear…

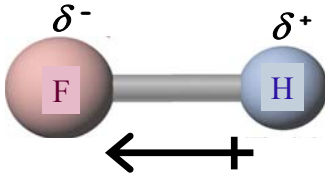
9.8 Charge distribution in covalent bonds & molecules

Formal charges: how charge is "explained" when FULL charges are present (*e.g.*, in polyatomic ions)

BUT: What happens when bonded atoms unequally share e⁻s ?

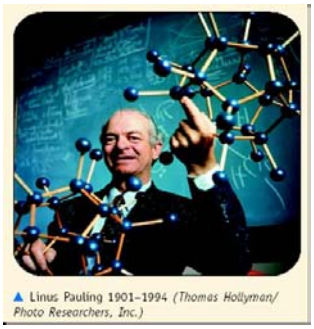
COVALENT BONDING	POLAR COVALENT BONDING	IONIC BONDING
Equal sharing **no separation of charge**	**Unequal sharing** partial separation of charge	No sharing **complete separation of charges**

F has stronger pull (Z_{eff}) on e⁻s than H…
⇨ shared e⁻s spend more time closer to **F**'s nucleus



- ***Polar bond*** *(dipolar)*
- Polarity labeled via:
  1.) δ^+ & δ^- *OR*
  2.) dipole arrow

Linus Pauling (1930's): "electronegativity" (χ)



▲ Linus Pauling 1901–1994 (Thomas Hollyman/ Photo Researchers, Inc.)

Linus Pauling (1901-1994)
Nobel prize in Chemistry
& Nobel Peace prize

= the ability of an atom <u>in a molecule</u> to attract <u>shared electrons</u> to itself

- highest for nonmetals
- lowest for metals

- Numerical values of Pauling's electronegativities often found on periodic table…
- Calculated from experimental bond energy data: difference between expected (if nonpolar covalent) *and* observed…

<u>EXPLAINED</u> USING Z^*: atom's pull on valence e^-s…

↳ nuclear charge felt by valence e^-s + valence-nucleus distance

(13)

Electronegativity (χ): ↑ across a period… ↓ down a group

Metals: Not good at holding e^-s…

Nonmetals: Pull strongly…

												H 2.1				
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

Useful: ↑ Electronegativity difference ($\Delta\chi$) ⇨ ↑ bond polarity

Nonmetals: F > O > N, Cl > Br > I, S, C > H, P

Rank according to polarity of bonds: H_2O, HF, H_3N, HI

1st: use logic (trends)…

2nd: calculate $\Delta\chi$

Fig.9.14

MOLECULES
lets us predict many of its properties! (more in Chem206)

Polar molecules:
- Interact strongly with each other because of electrostatic attractions

RESULT: polar substances…
- Have higher melting points and boiling points
- Have high surface tension, and tend to resist flowing
- Interact with electric fields
- Dissolve well in other polar substances!

EXAMPLES:
water, alcohols, ammonia, sugar ($C_6H_{12}O_6$)…

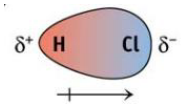
Nonpolar molecules:
- Interact only weakly with each other

RESULT: nonpolar substances…
- Are easier to melt, boil…
- Have lower surface tension & flow easily
- Dissolve in other nonpolar substances only
  → oil & water don't mix well!

EXAMPLES:
CCl_4, benzene (C_6H_6), paint thinner (C_6H_{12}), vegetable oil, waxes…

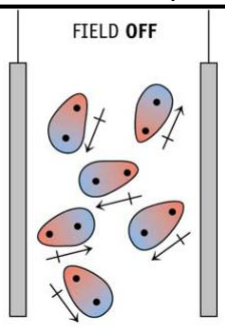
9.9 Determining molecular polarity: vector sum of bond dipoles

- If bond dipoles don't cancel ⇨ yield δ+ & δ- regions of molecule
  ⇨ molecule has net dipole moment
- polar molecules interact with: charged species, electric fields…



= basis of liquid crystal displays!
Special molecules block light when all lined up…

Field OFF: molecules are randomly oriented



Field ON: molecules line up
- **negative ends toward +ve plate**
- **positive ends toward -ve plate**

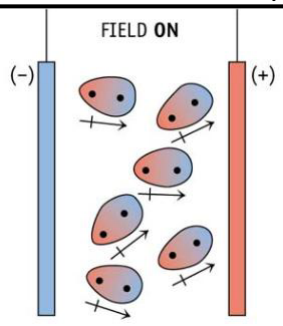


Fig.9.15

Table 9.10 • Dipole Moments of Selected Molecules — Determined by EXP'T!

Molecule (AB)	Moment (μ, D)	Geometry
HF	1.78	linear
HCl	1.07	linear
HBr	0.79	linear
HI	0.38	linear
H_2	0	linear

Molecule (AB_2)	Moment (μ, D)	Geometry
H_2O	1.85	bent
H_2S	0.95	bent
SO_2	1.62	bent
CO_2	0	linear

Molecule (AB_3)	Moment (μ, D)	Geometry
NH_3	1.47	trigonal-pyramidal
NF_3	0.23	trigonal-pyramidal
BF_3	0	trigonal-planar

Molecule (AB_4)	Moment (μ, D)	Geometry
CH_4	0	tetrahedral
CH_3Cl	1.92	tetrahedral
CH_2Cl_2	1.60	tetrahedral
$CHCl_3$	1.04	tetrahedral
CCl_4	0	tetrahedral

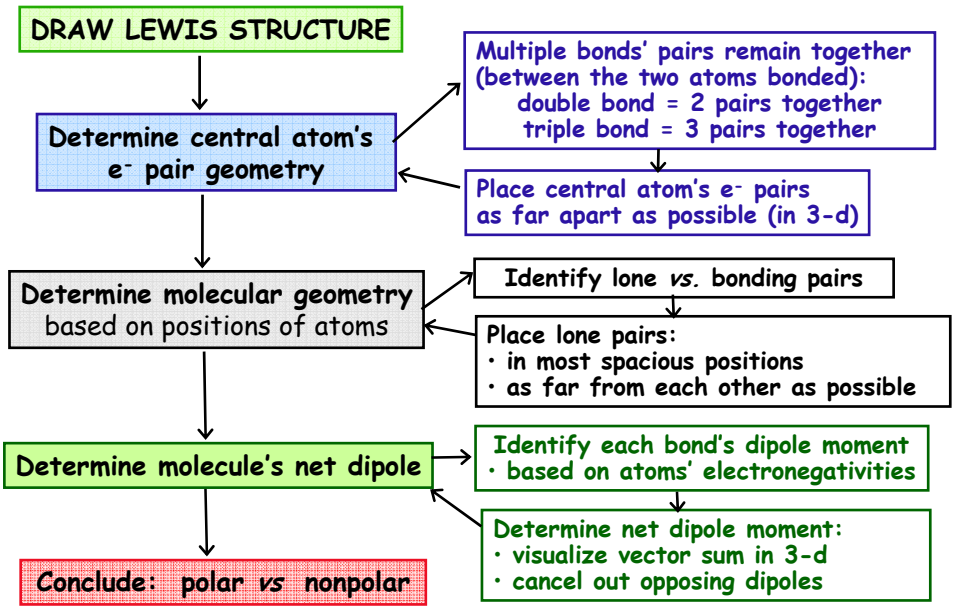
Draw/analyze these yourselves

Dipole moments (μ) measured in "Debyes" (D; 1 D = 3.34×10^{-30} C·m)
Based on strength of interaction with an applied electric field

Magnitude of dipole moment determined by:
1. **polarity of bonds** (electronegativity difference between atoms)
2. **molecule's geometry** (how much of each bond dipole is canceled by others)

(17)

STRATEGY FOR DETERMINING GEOMETRY & POLARITY



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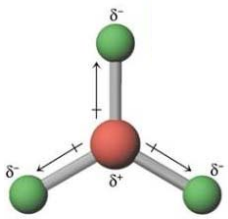
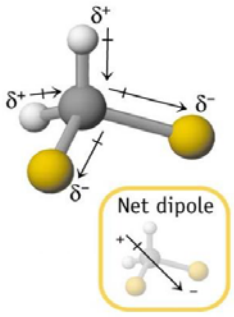
3-dimensional VECTOR SUM of bond dipoles yields NET dipole moment of molecule

BF_3: no lone pairs on B



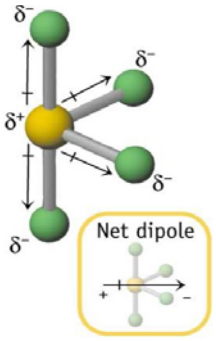
Dipoles cancel out
Overall: no net dipole
NONPOLAR

CH_2Cl_2: no lone pairs on C



POLAR

SF_4: 1 lone pair on S



POLAR

1. Determine structure & molecular geometry
   - After determining geometry: ignore lone pairs
2. Determine which dipole components add *vs.* cancel

FYI - Lone pairs influence geometry, not net dipole

Formal charges take bonding and lone pairs into account

- Is there an extra or missing e- on atom in current bonding environment compared to a "free atom" ?
- **Calculated by treating all bonds as nonpolar (which isn't true…).**
- **Book-keeping, but not necessarily realistic…**

Bond dipoles take only shared (bonding) pairs into account

- Is there a build up of partial charge because e⁻s are shared unevenly between atoms with different electronegativity?
- **Realistic view of how bonding e⁻s are distributed between atoms**
- **Regardless of presence of lone pairs on either atom**

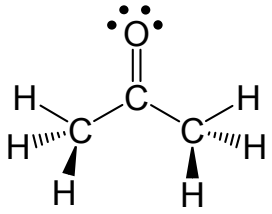
NOTE: Sometimes formal charges and bond polarities are opposite to each other

e.g., CO ⇨ bond really is polarized with bonding e⁻s closer to O…but not overall –ve on oxygen…

Determine the polarity of: **thionyl chloride, $SOCl_2$**
(very reactive, used in organic synthesis)

Central atom

Determine the polarity of: **acetone** (nail-polish remover)



What are the bond angles?

How might it interact with water?

ASSIGNED READINGS

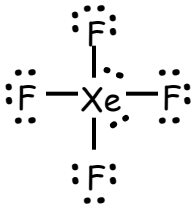
BEFORE NEXT CLASS:

read rest of Ch.9

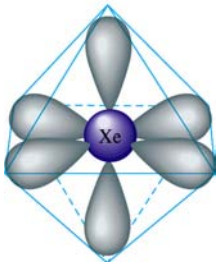
PRACTICE: Lewis structures → geometries → polarities

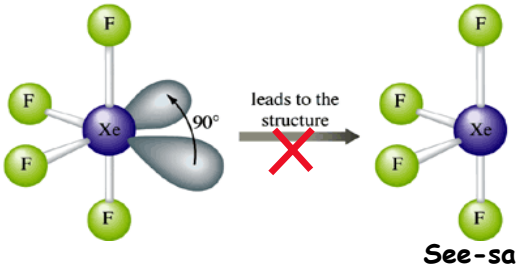
What is the molecular shape of XeF_4? Zumdahl's Figure 8.19

To draw Lewis structure: $8e^-$ (Xe) + $28e^-$ (4F) = $36e^-$

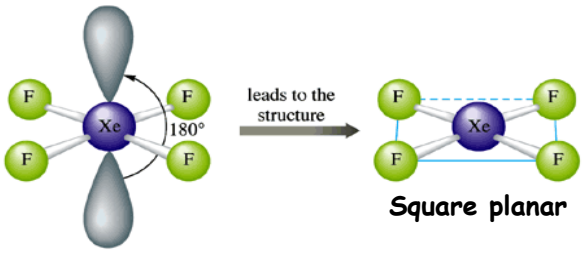


Around Xe: $6e^-$ pairs
⇨Oh e^--pair geometry



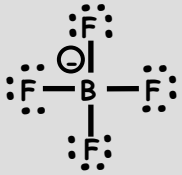
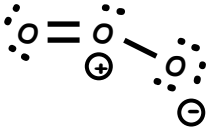
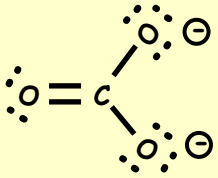


See-saw



Square planar

On your own: determine geometry around central atom…

Species	BF_4^-	O_3	CO_3^{2-}
Representative structure (not including resonance)			
# e^- pairs on central atom			
Electron-pair geometry			
# lone pairs			
Molecular geometry			
Hybridization of central atom			

See Ch.10.2