Unit 4 - Bonding

Ionic, Covalent, Metallic, Molecular Shapes, Hybridization, Delocalization of E^-, IMFs

Bonding Review

what do you know?

Ionic

- metal & non-metal
- transfer of electrons
- held together by opposite charge ions
- combine in lowest whole number ratio
- have a lattice structure

Covalent

- NM & NM
- sharing of electrons
- forms a molecule

Lewis Structures

- Must include ALL electrons (including all lone pairs)
- if it's an ion must use brackets with a charge
- should be able to draw all of these...
    - HF, CF_3Cl, C_2H_6, NO_3^-, SO_2, C_2H_4, C_2H_2, NO^+

Dative Bonds

- aka "coordinate" bonds
- one atom 'donates' a whole lone pair to be shared between the two atoms
- examples: H_3O^+, NH_4^+, CO

Bond Length...

whats the relationship between length and strength??

- shorter the bond, stronger the attraction
- check out bond length vs. bond enthalpy in your data booklet - Tables 10&11

Bond Order

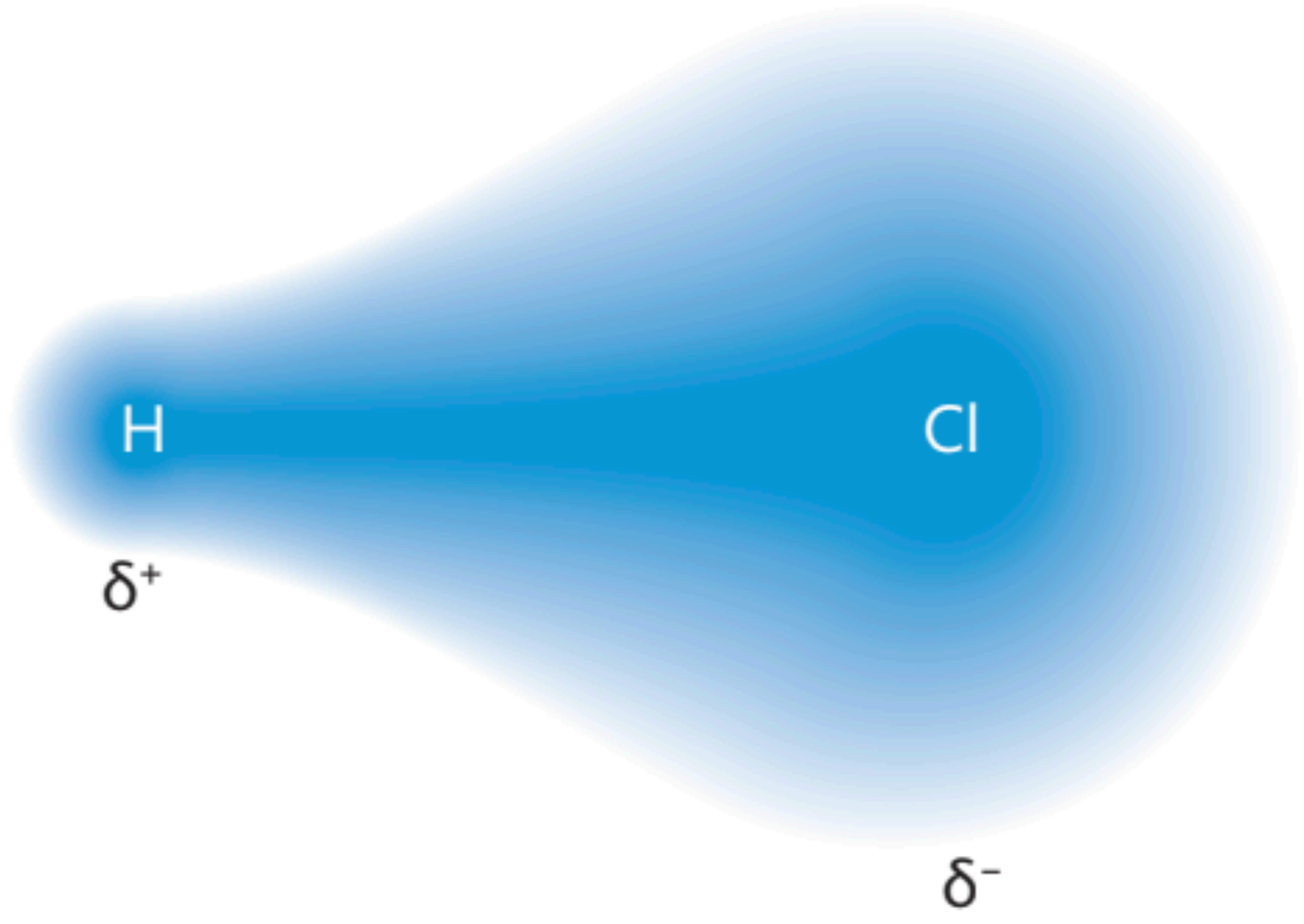
Single bond = 1

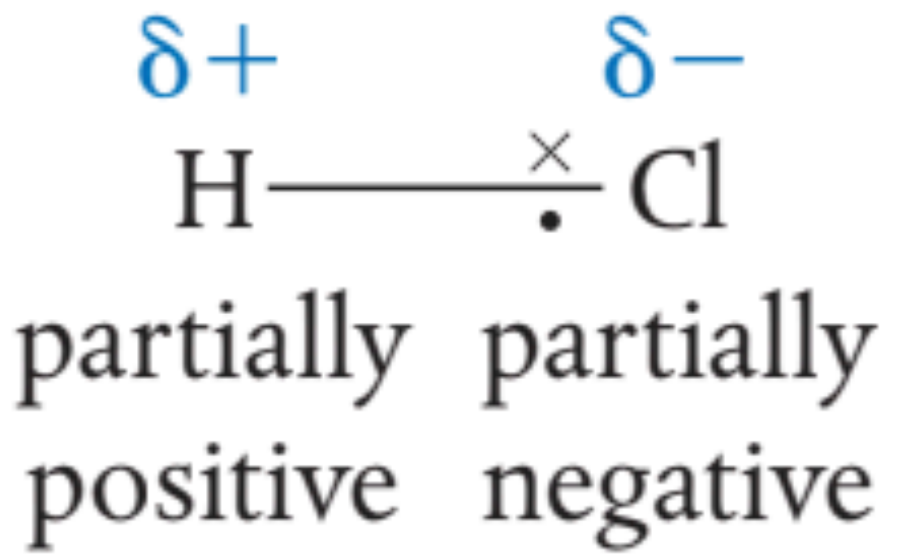
Double bond = 2

Triple bond = 3

Polar Bonds

- results from unequal sharing of electrons...
    - how do we tell???
    - Electronegativity!!
    - introduces some ionic nature into covalent bonds
- Non-Polar: almost no difference...Polar: up to about 1.8
- Ionic: more than about 1.8



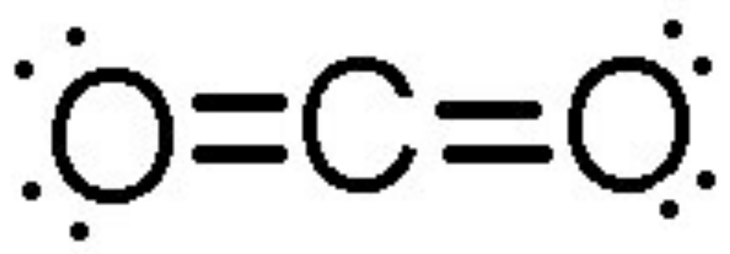


VSEPR theory

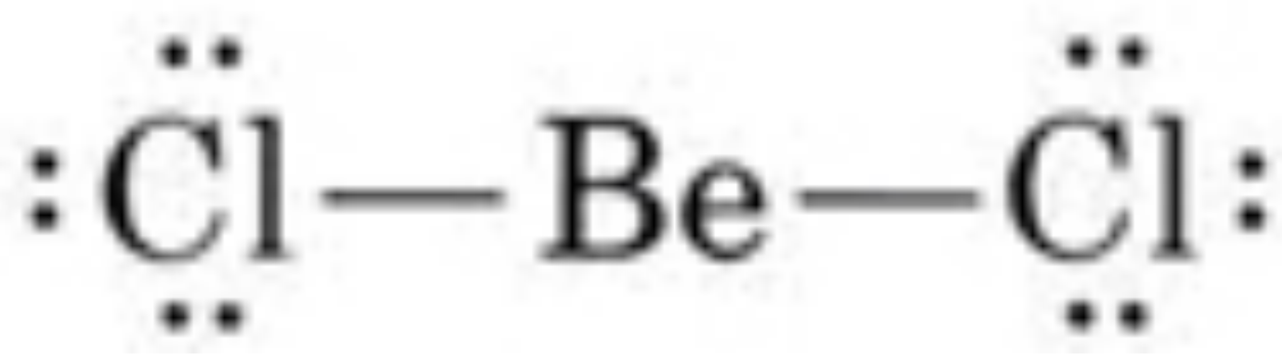
- shape of a molecule is determined by the repulsion between electron pairs
- **V**alence **S**hell **E**lectron **P**air **R**epulsion
  - applies to both bonding and non-bonding electrons
  - double and triple bonds are oriented together (single charge centre)
  - total # of <u>charge centres</u> (electron domains) around the atom determines shape
  - shape of molecules is determined by the angles between bonded atoms
  - non-bonding electrons have a higher concentration of charge (more repulsion)...repulsion decreases in this order:
    - lone-lone > lone-bonding > bonding-bonding

2 Charge Centers (draw Lewis structures)

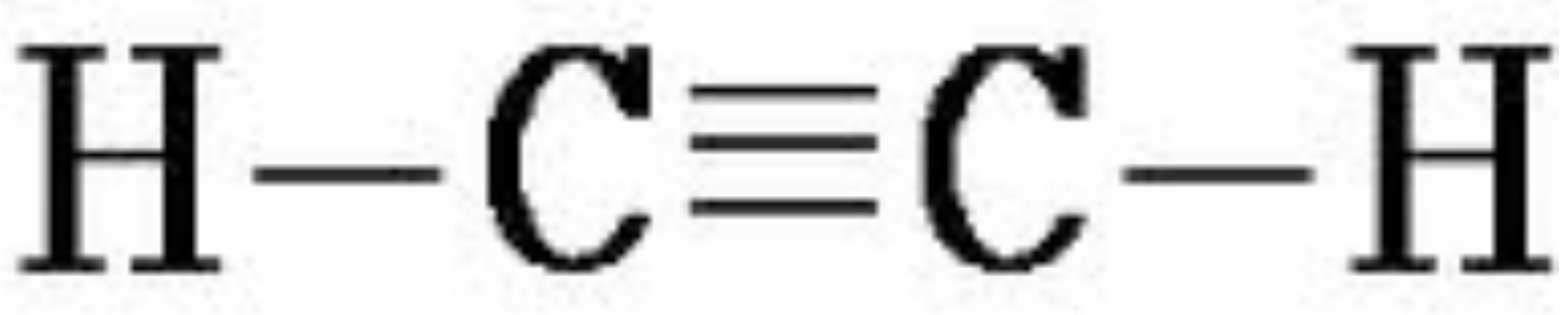
- CO_2



- $BeCl_2$



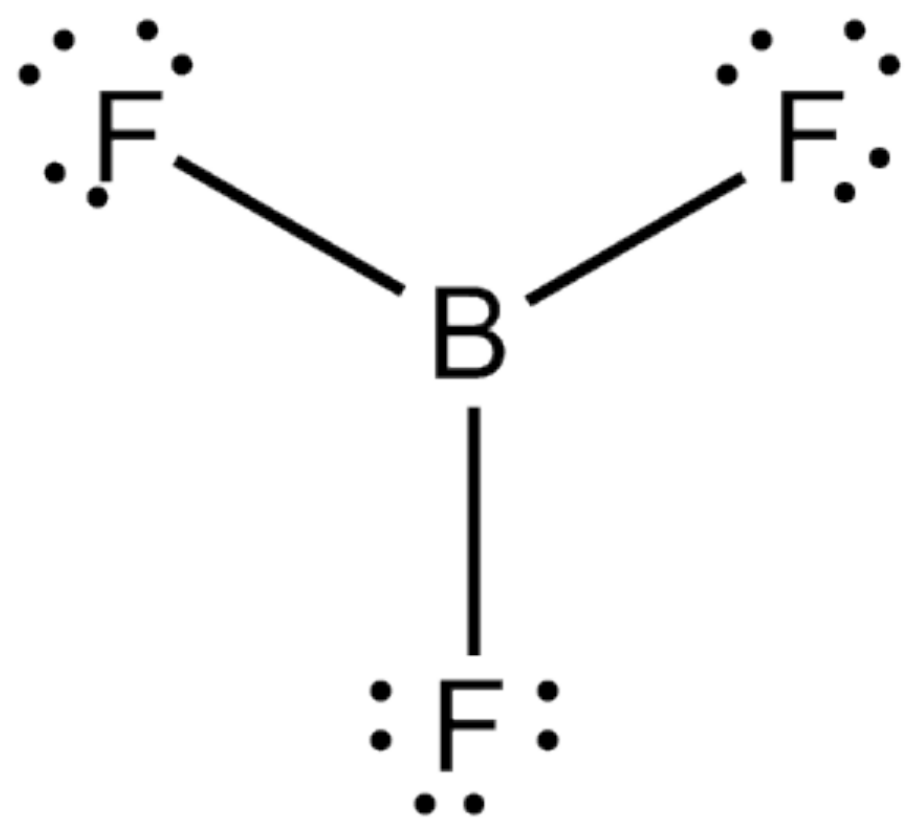
- C_2H_2



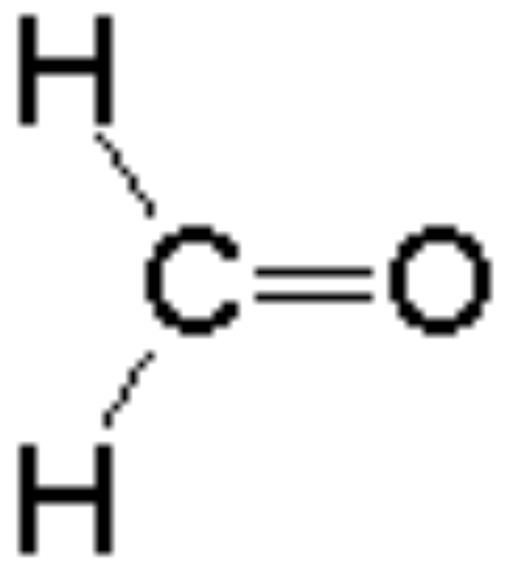
2 bonding pairs: 0 non-bonding pairs

3 Charge Centers

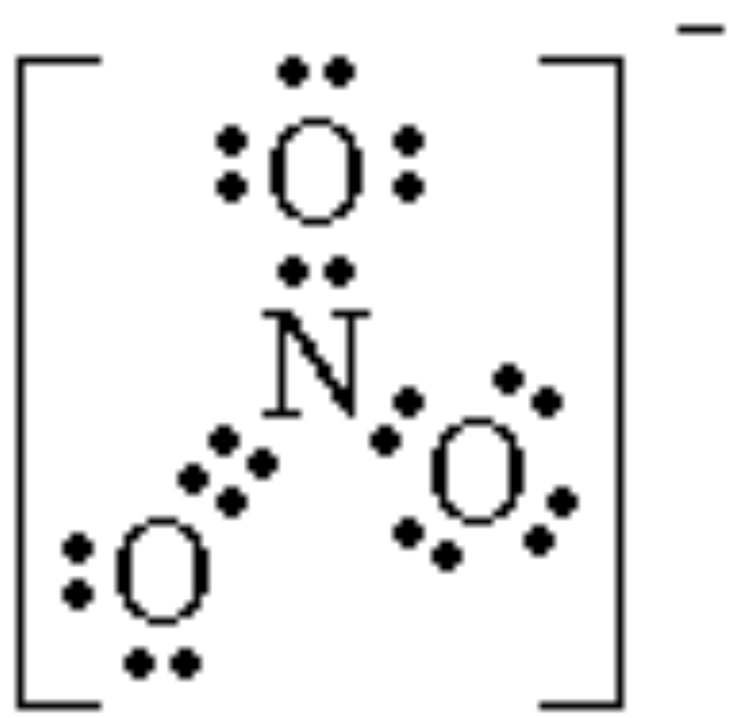
- BF_3



- HCHO



- NO_3^-



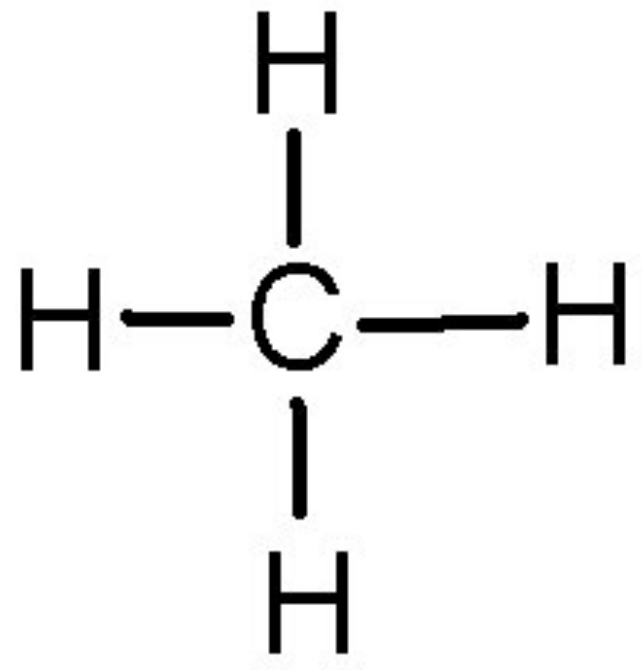
3 bonding pairs: 0 non-bonding pairs

Warm-up...

- Predict the bond angles for the following compound (you might need to draw a lewis structure...)
  - $AlCl_3$
  - CS_2
  - SiH_4
- Answers...
  - 120°
  - 180°
  - 109.5°

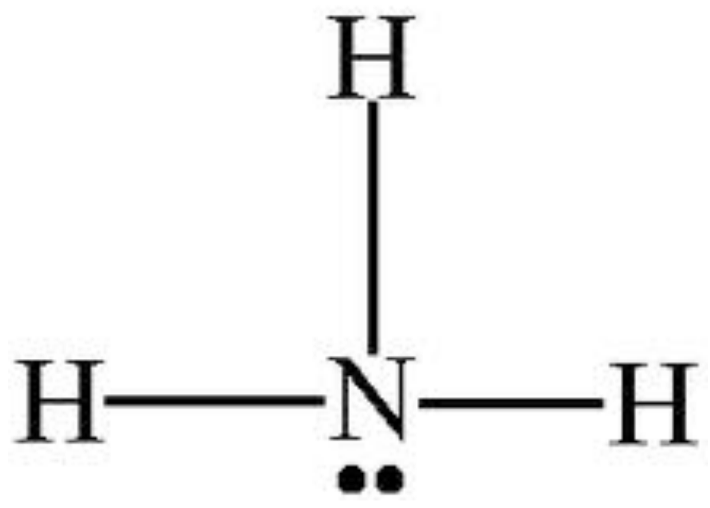
Four Charge Centres

- CH_4



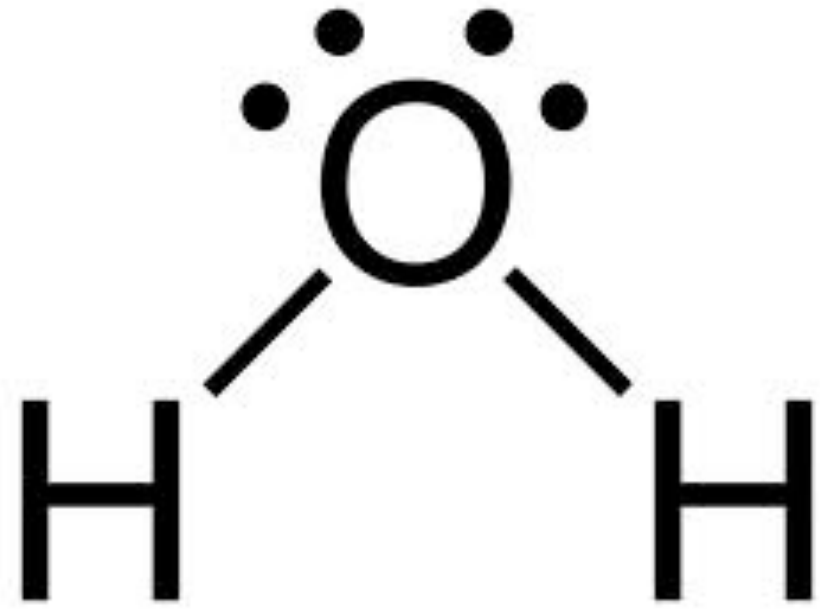
4 bonding pairs: 0 non-bonding pairs

- NH_3



3 bonding pairs: 1 non-bonding pair

- H_2O



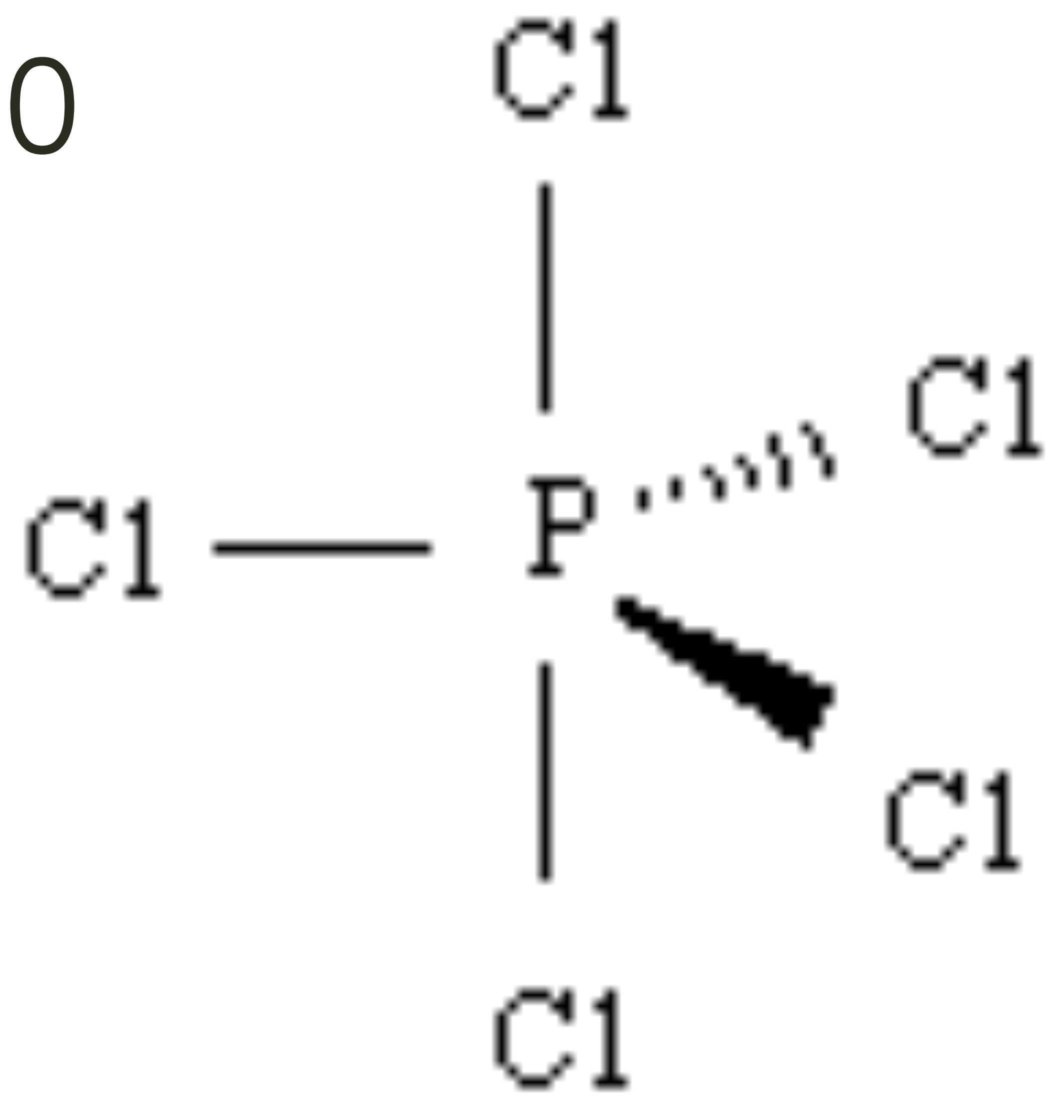
2 bonding pairs: 2 non-bonding pairs

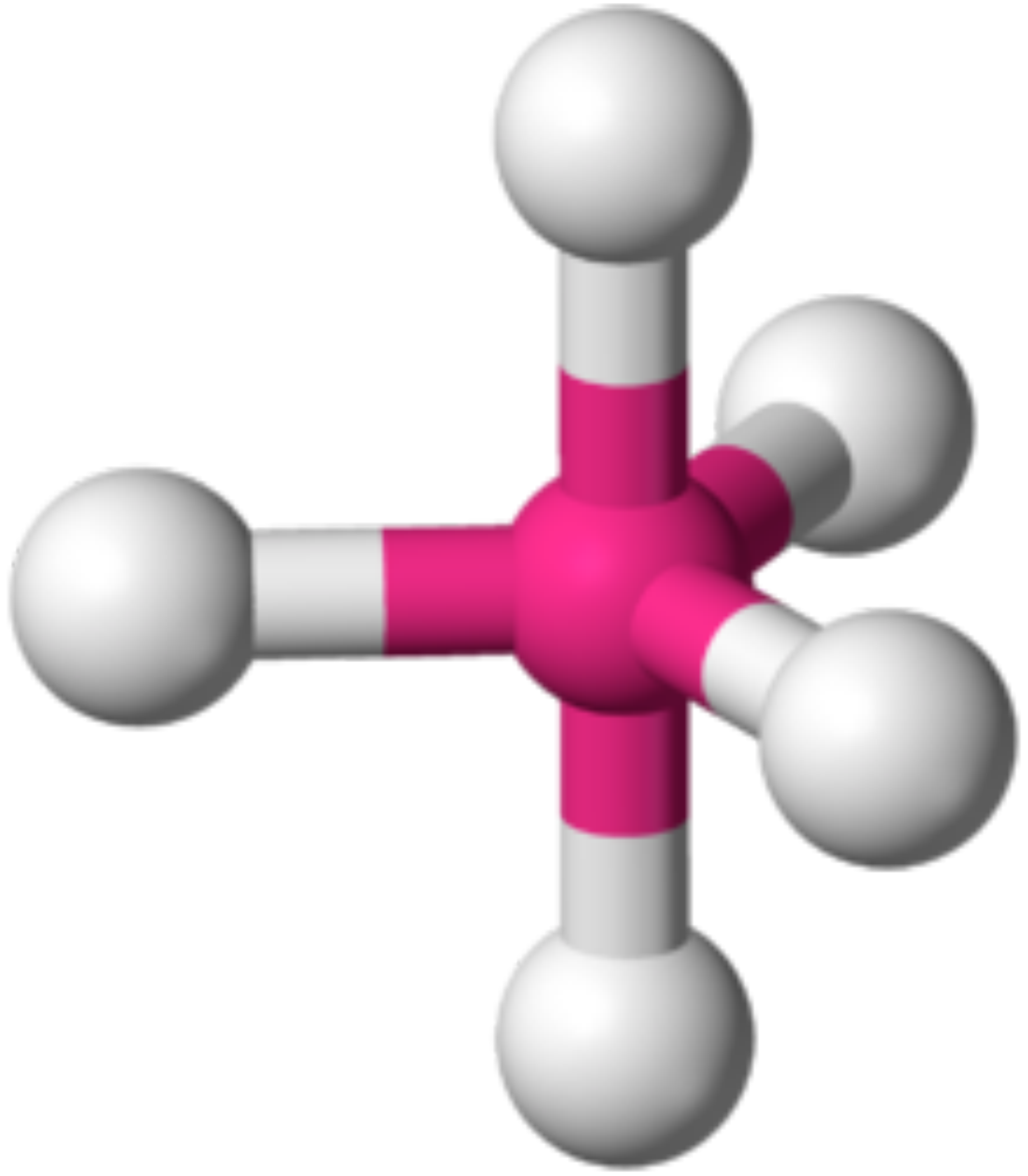
Molecules with Expanded Octets

- What does that mean?
  - Yes....more than 8 electrons around the central atom
  - This is possible because of the d-block electrons being involved with the bonding and the similar relative energies of the p and d orbitals
  - possible to have 5 or 6 charge centres

Five charge centres

- If all 5 charge centres are from bonding electrons…the shape is **trigonal bipyramidal**
- 3 different bond angles…90, 120 and 180
- Where are they?



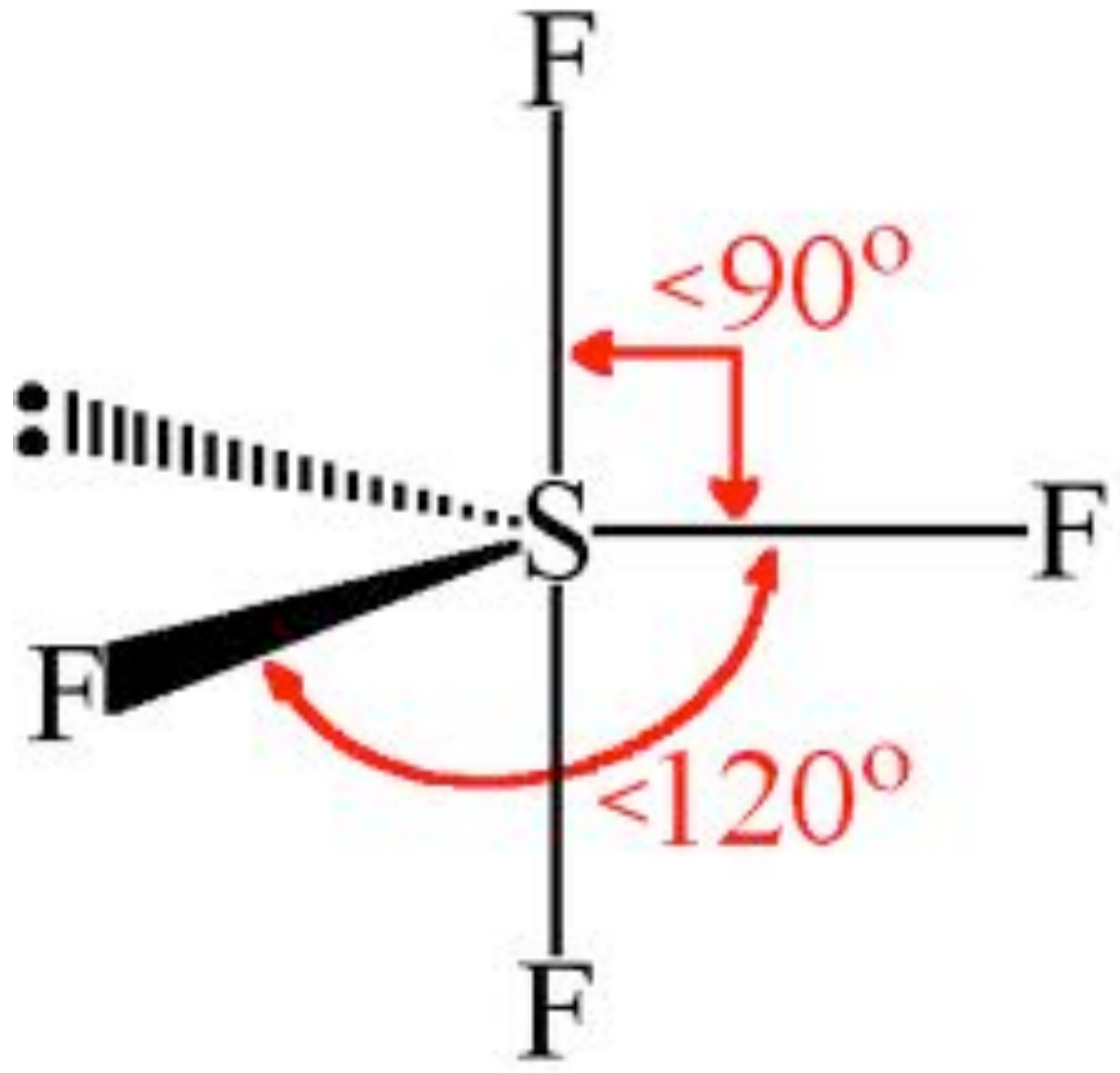


Example: PCl_5

5 bonding pairs: 0 non-bonding pairs

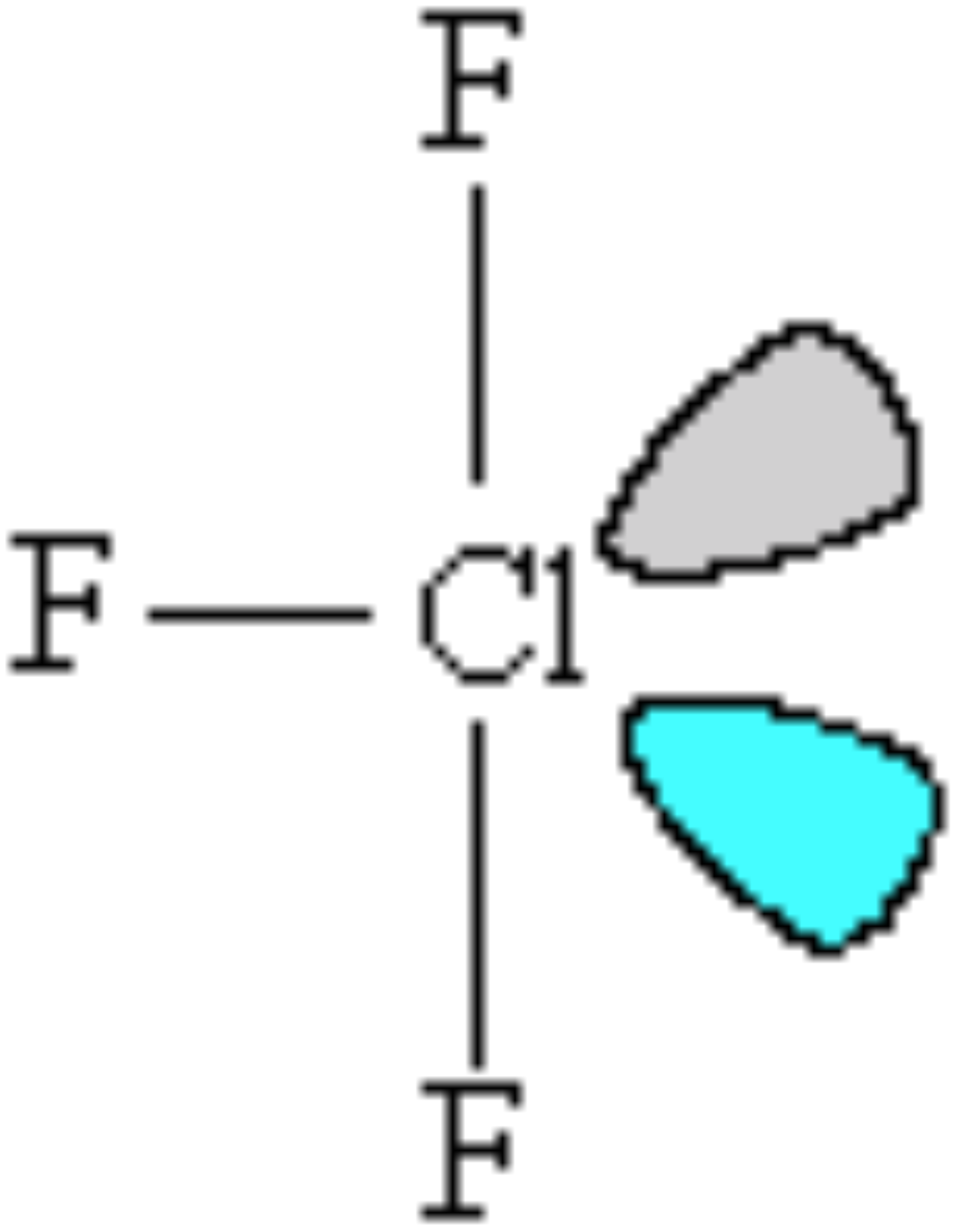
5 Centres…continued

- SF_4
- unsymmetrical tetrahedron or ‘see saw’
- **4 bonding pairs: 1 non-bonding pair**



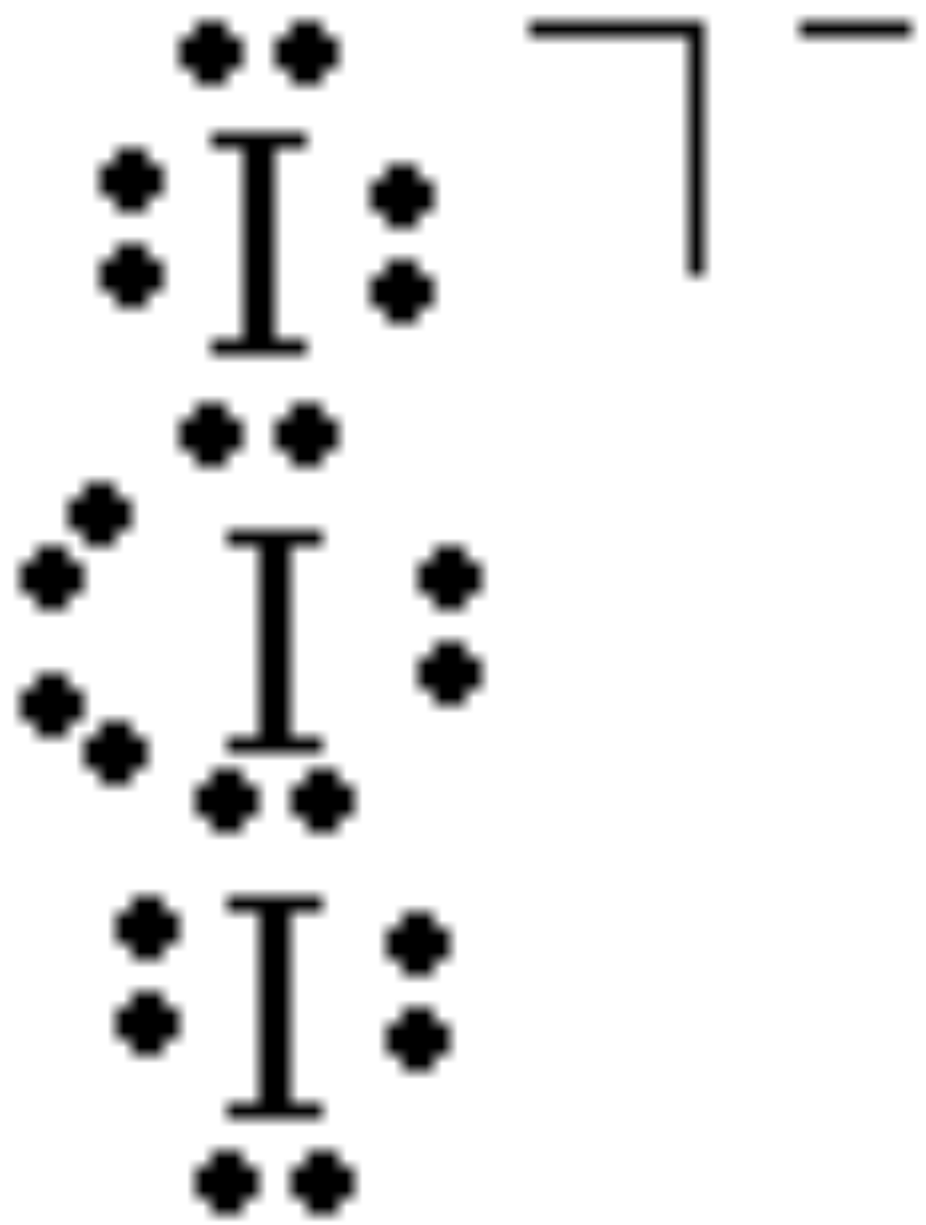
5 Centres…continued

- ClF_3
- T-shaped structure
- **3 bonding pairs: 2 non-bonding pairs**

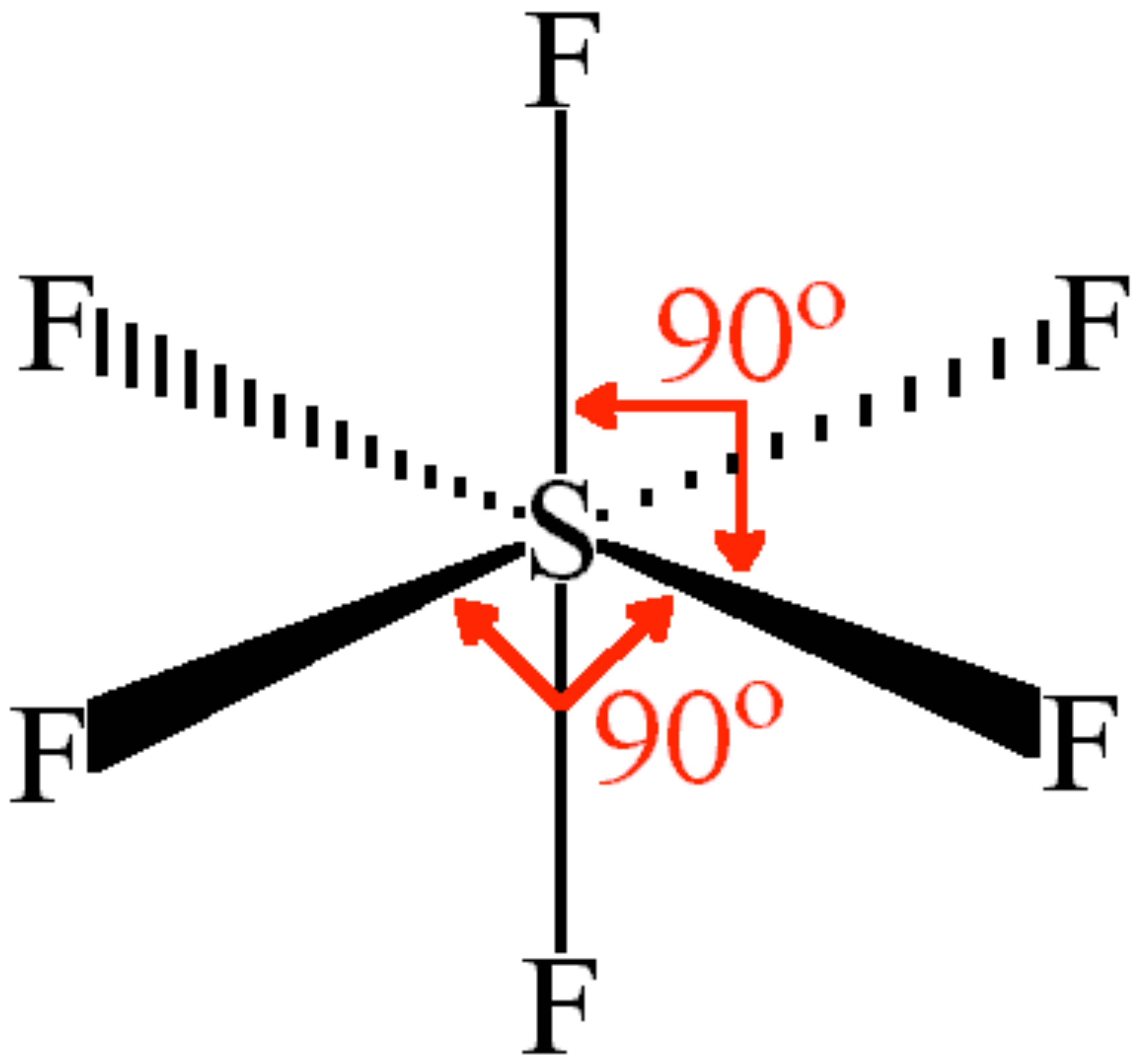


5 Centres…continued

- I_3^-
- linear
- **2 bonding pairs: 3 non-bonding pairs**



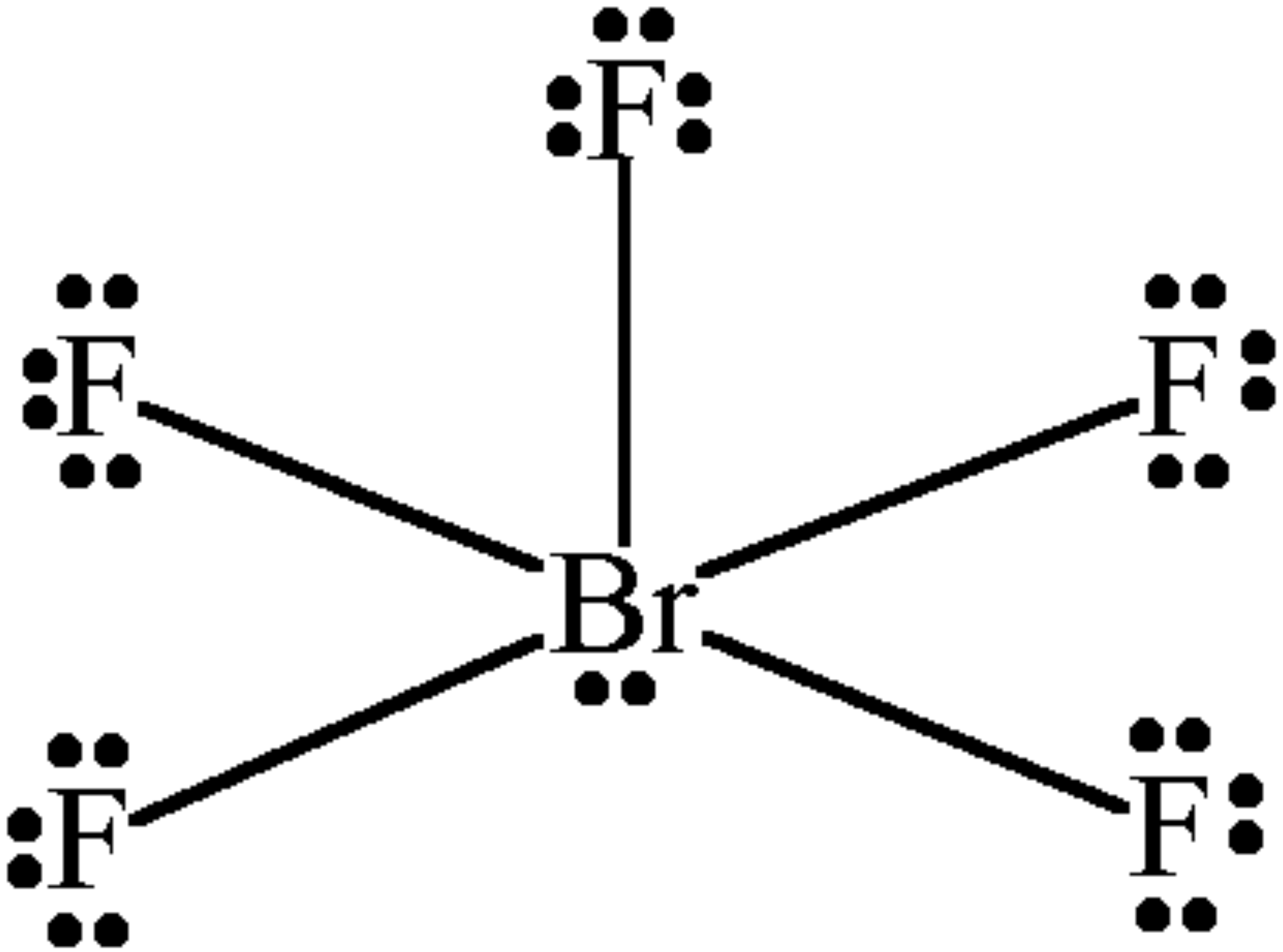
Six Charge Centres



- SF_6
- octahedral
- **6 bonding pairs: 0 non-bonding pairs**

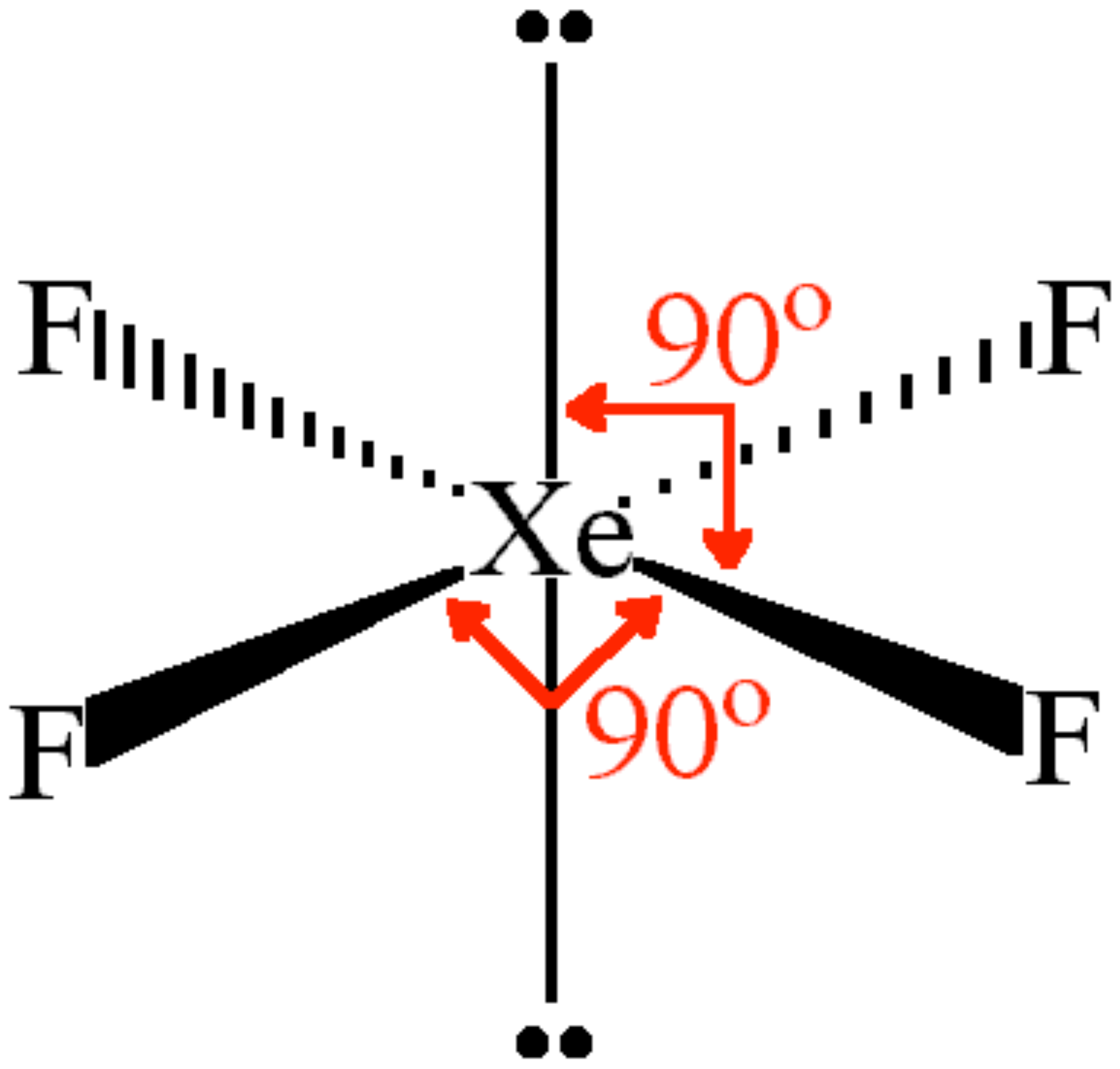
6 Charge Centres…continued

- BrF_5
- square pyramidal
- **5 bonding pairs: 1 non-bonding pair**



6 charge centres…continued

- XeF_4
- square planar
- **4 bonding pairs: 2 non-bonding pairs**



Overview…

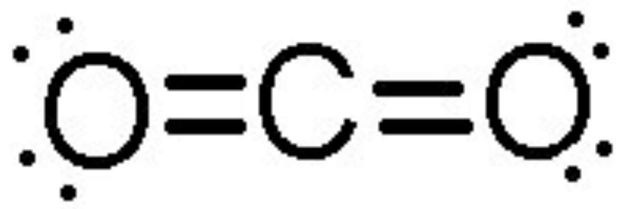
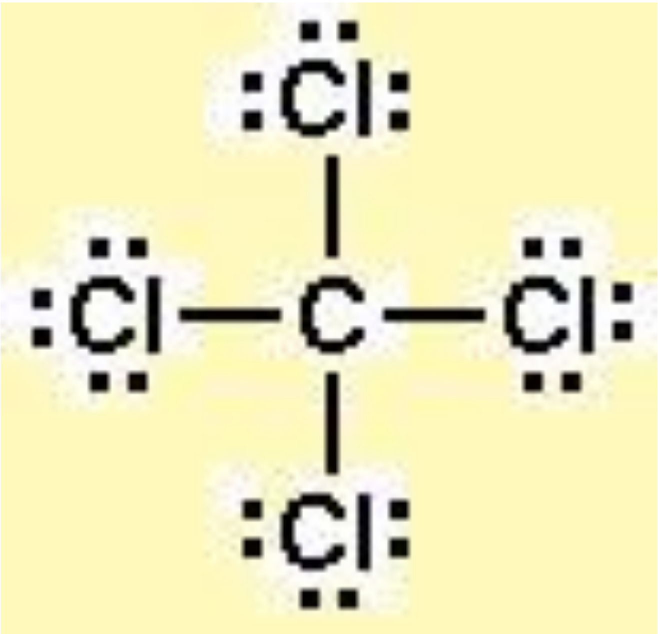
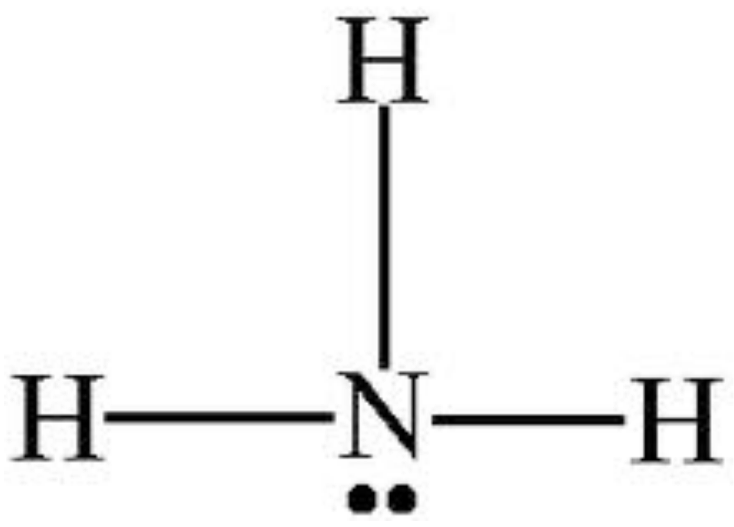
- page 189 in your book
- Also (p. 162):

1. *Draw the Lewis Structure*
2. *Electron domains around central atom*
3. *Geometry (electron domains)*
4. *Molecular geometry (bonding domains)*
5. *Consider extra repulsion*

Bond Polarity vs. Molecular Polarity

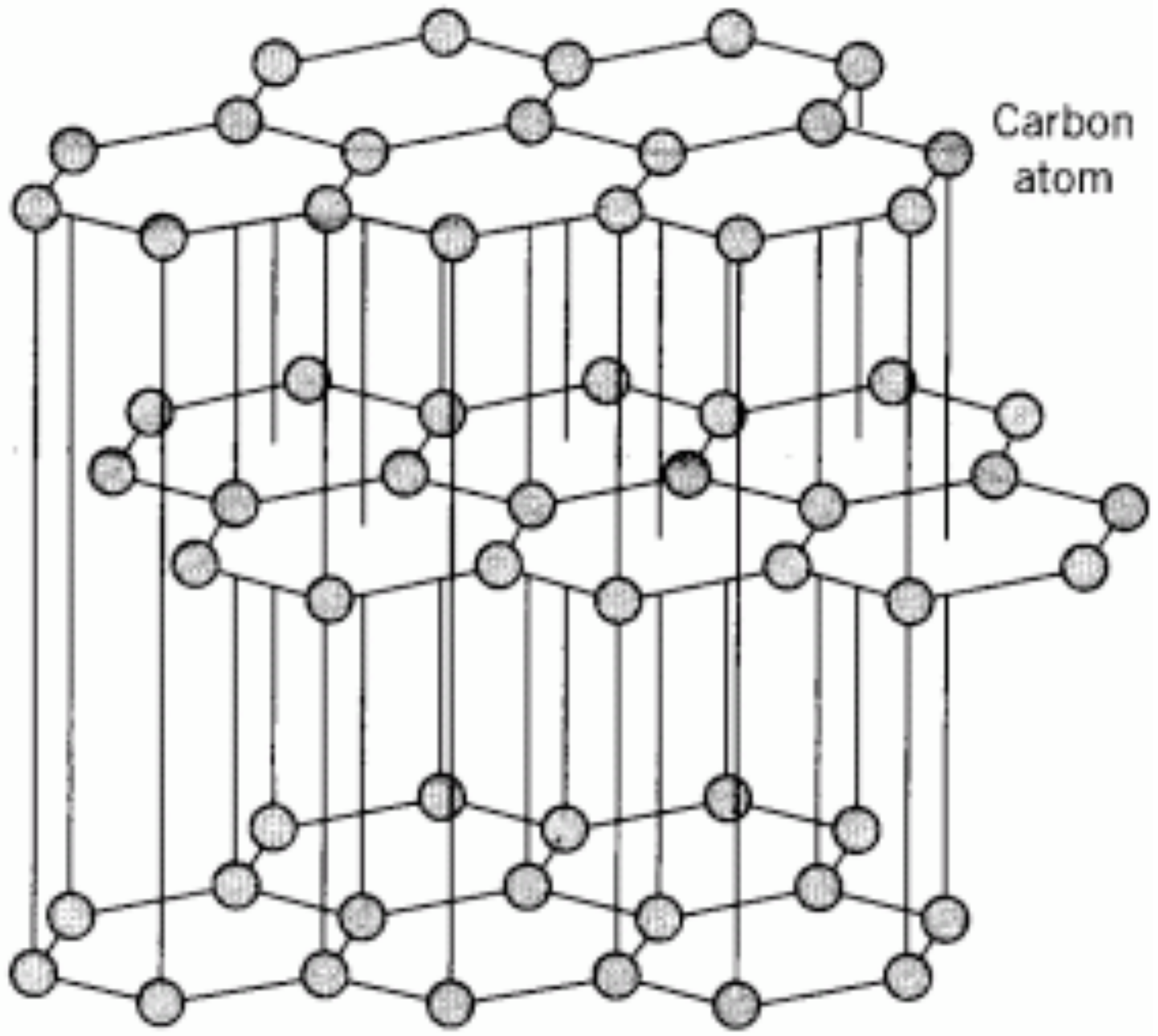
- You know about electronegativity…this deals with BOND polarity
- Molecular polarity depends on the way the polar bonds are oriented within the molecule

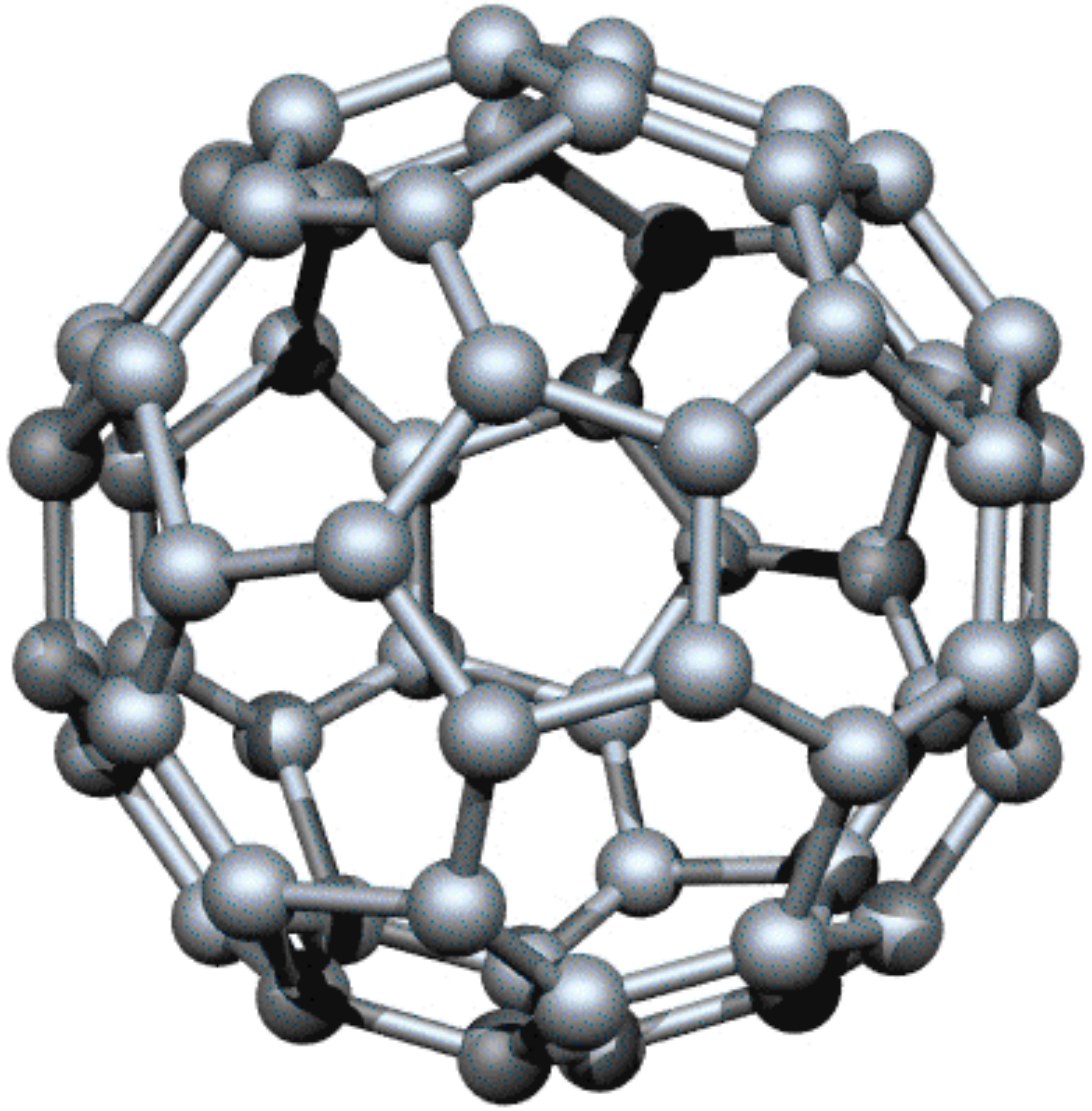
Polar or Non-polar?

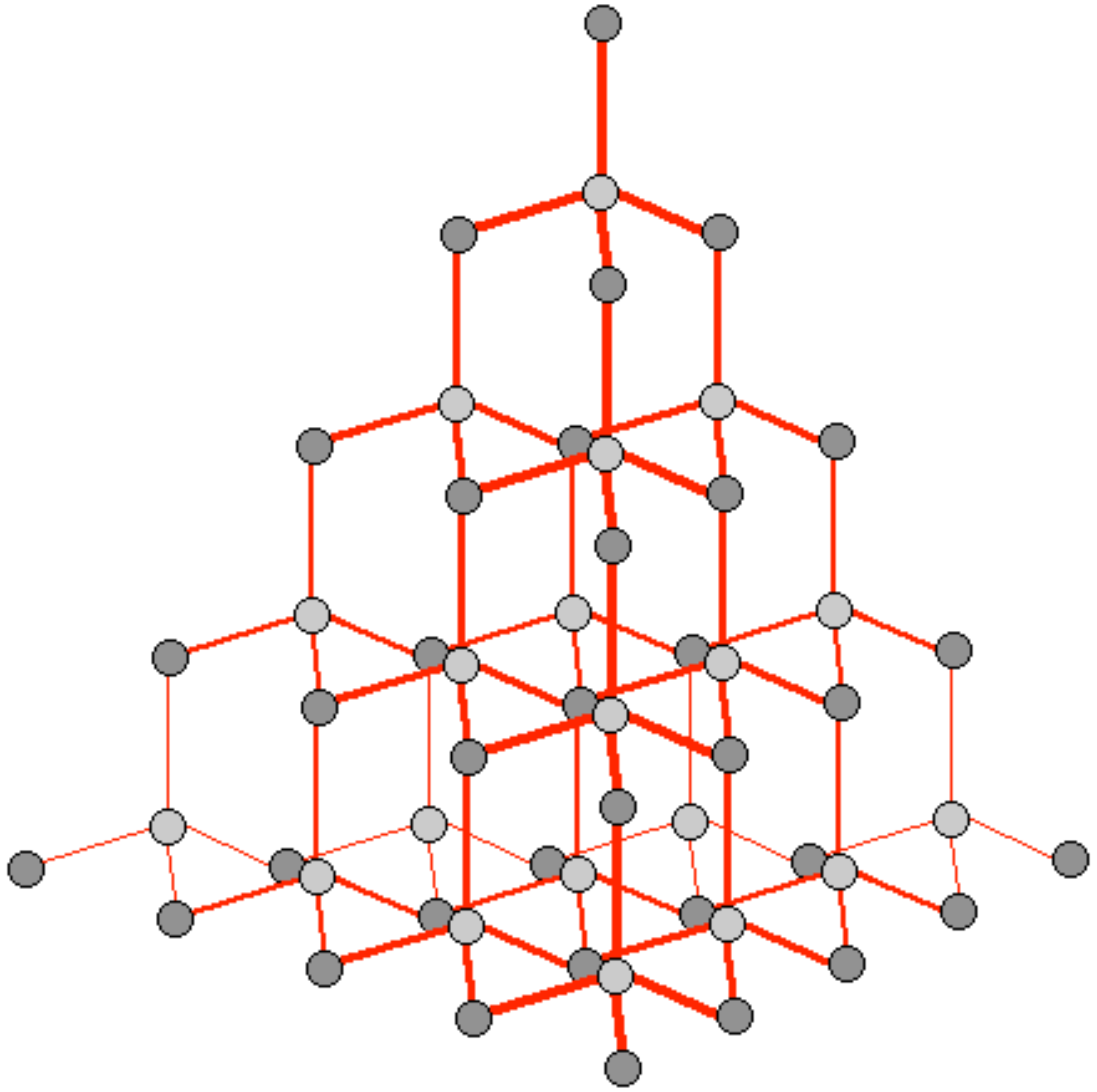
		POLAR?
CO_2		NO!
CCl_4		NO!
NH_3		YES!

Covalent Crystalline Solids

- Allotropes of Carbon…



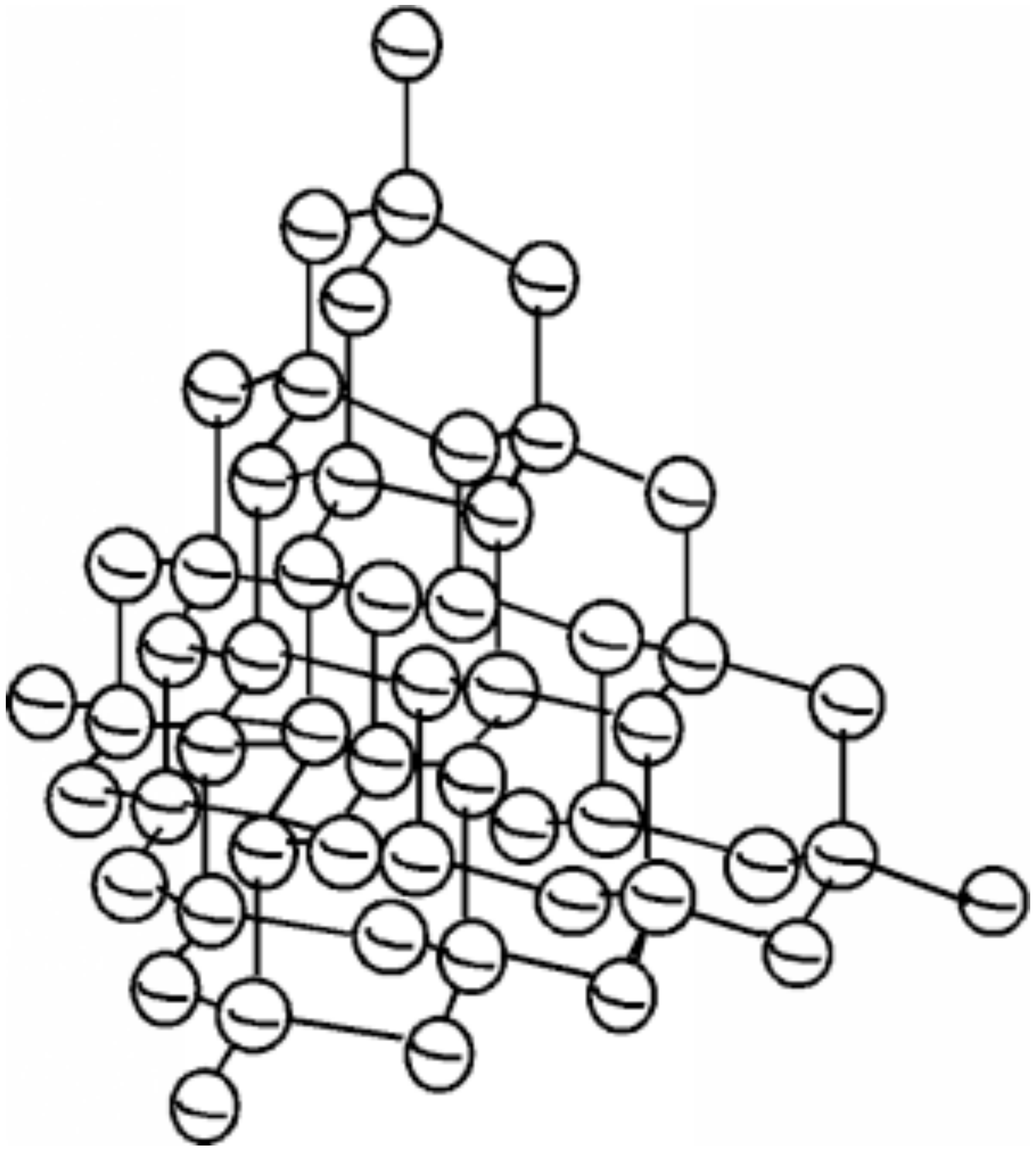


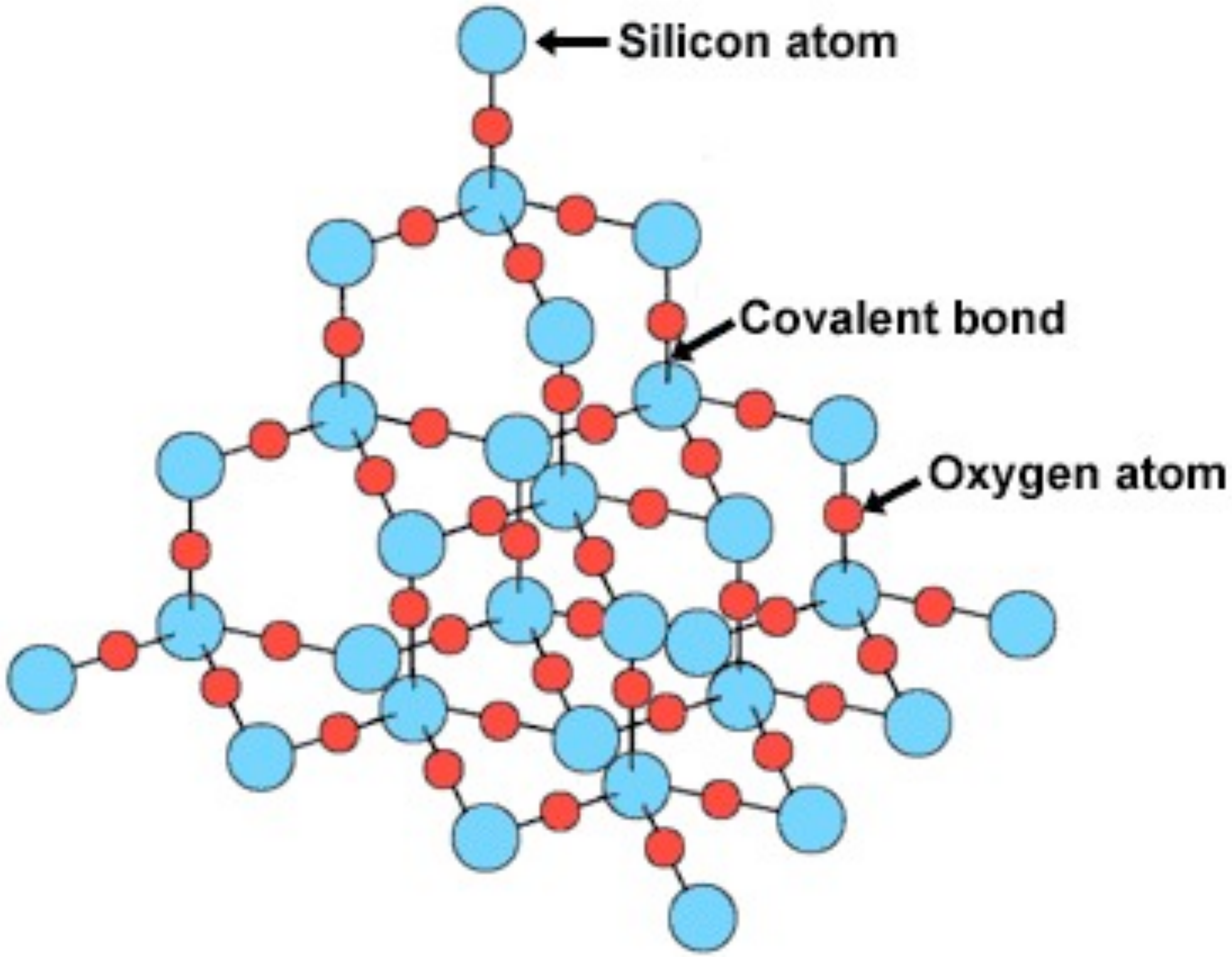


Graphene

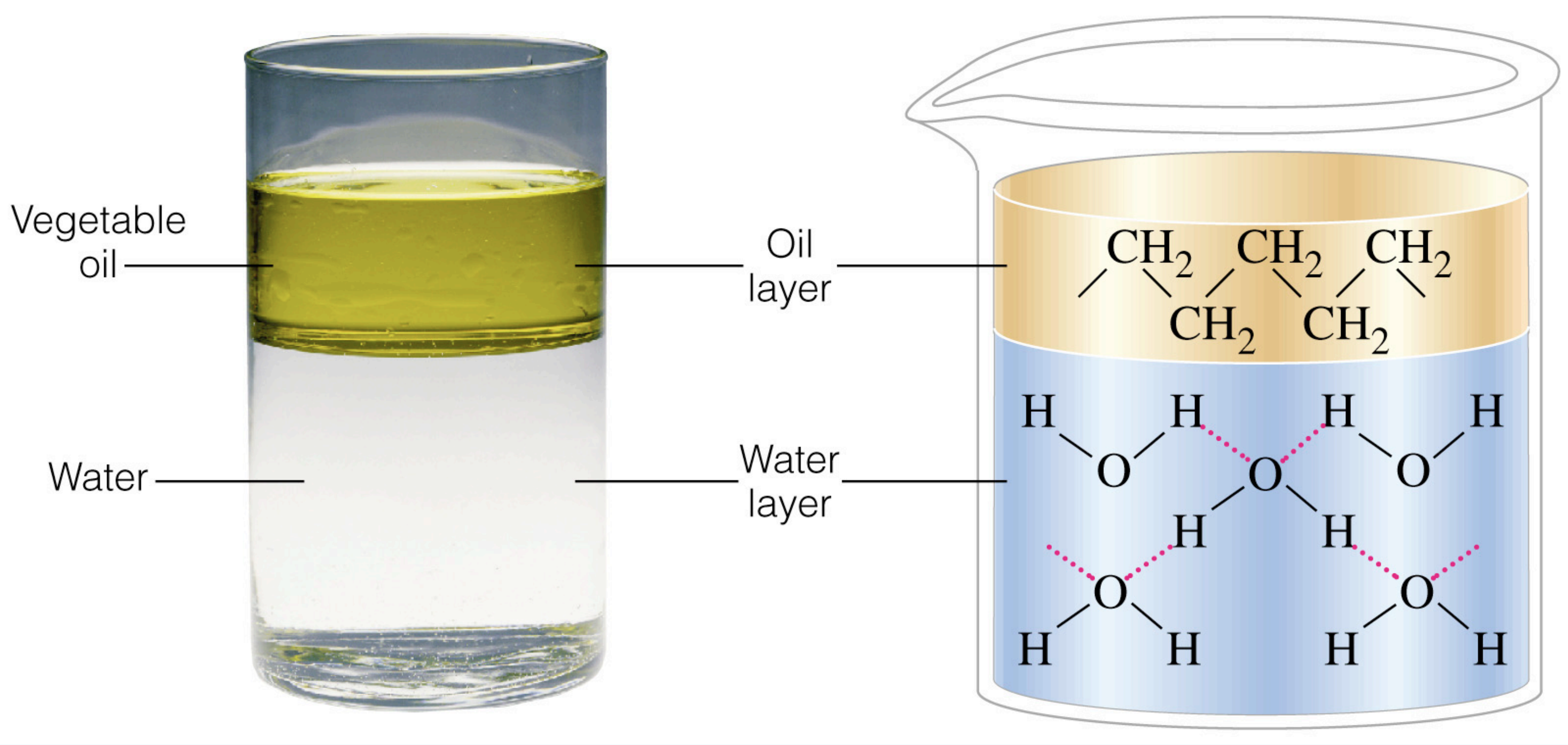
- Single layer of C atoms covalently bonded to 3 others (120* bond angles)
- Good electrical conductor
- Thinnest material to exist but 100 times stronger than steel
- Flexible and high MP

Si and SiO_2





Intermolecular Forces

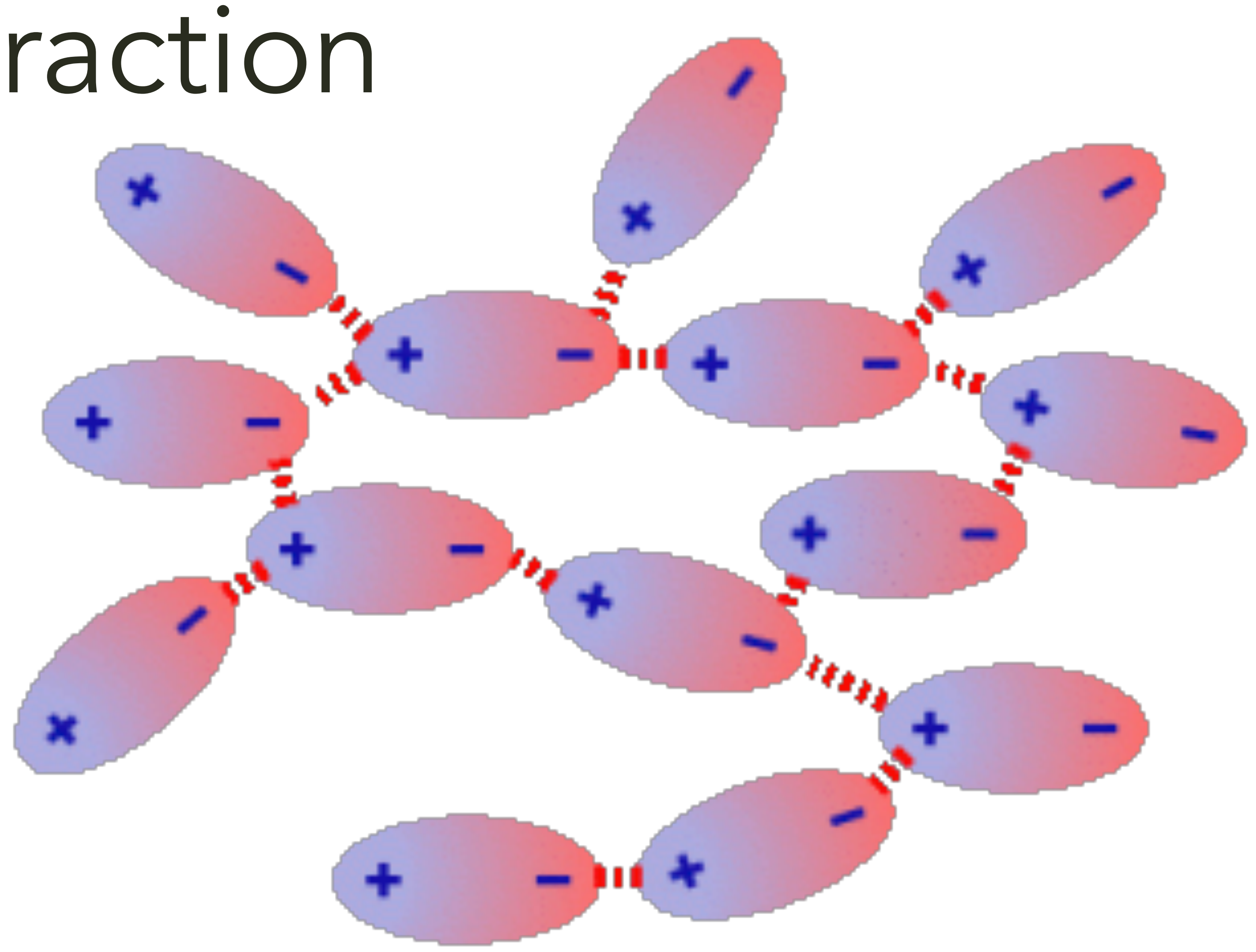


What IMFs do you know?

- Van der Waals' Forces
- Dipole-Dipole attraction
- Hydrogen Bonding

London Dispersion Forces (VdW)

- temporary
- the clouds of negative electrons surrounding the molecule causes temporary partial dipoles
- one atom has this temporary charge and induces another to have the temporary charge and this ends in a temporary attraction
- strength increases as # of electrons increase

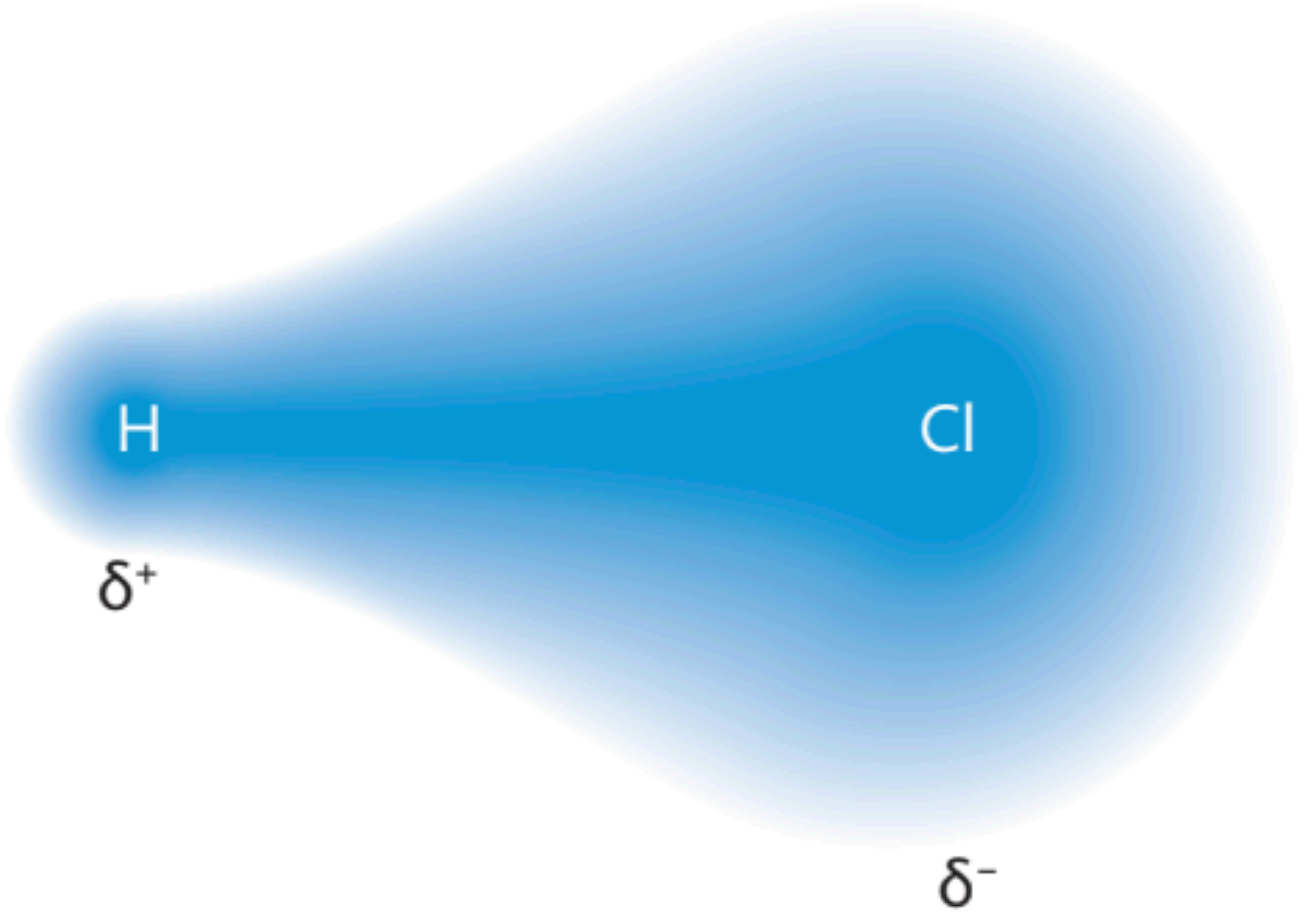


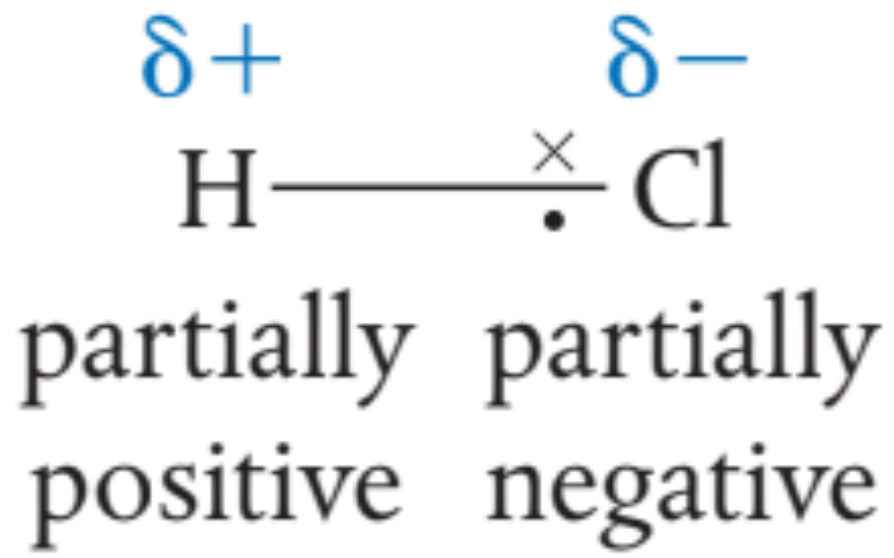
London Dispersion Forces (VdW)

- explains the trend in boiling point in group 17
  - $F_2 < Cl_2 < Br_2 < I_2$ (gas to liquid to solid)
- explains the boiling point trend in the simple hydrocarbons
  - $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10}$

Dipole-Dipole Attraction

- permanent separation of charge
  - one end of molecule is partial positive (δ^+) and one end is partial negative (δ^-)
  - this is called a permanent dipole





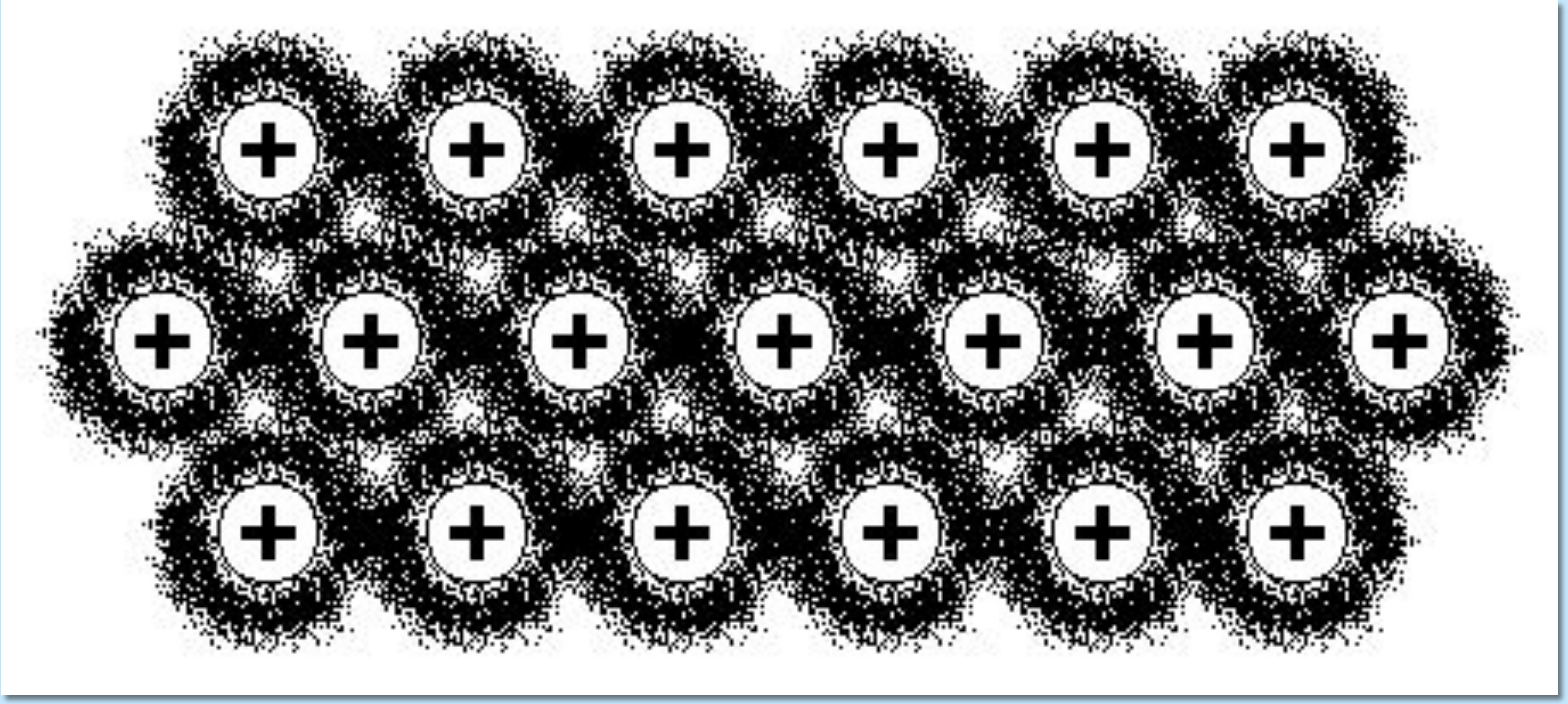
Hydrogen Bonding

- When a molecule contains hydrogen covalently bonded to a highly electronegative atom (F, O, N)
- large electronegativity difference causes the electrons to be pulled away from hydrogen and causes δ^+ and δ^-
- strongest form of IMF...Is NOT a bond
- responsible for H_2O's crazy properties - surface tension, density

Quick Question to See if You're Paying Attention

- Arrange these compounds in order of increasing boiling point...
  - CH_3CHO, CH_3CH_2OH, $CH_3CH_2CH_3$

Metallic Bonding

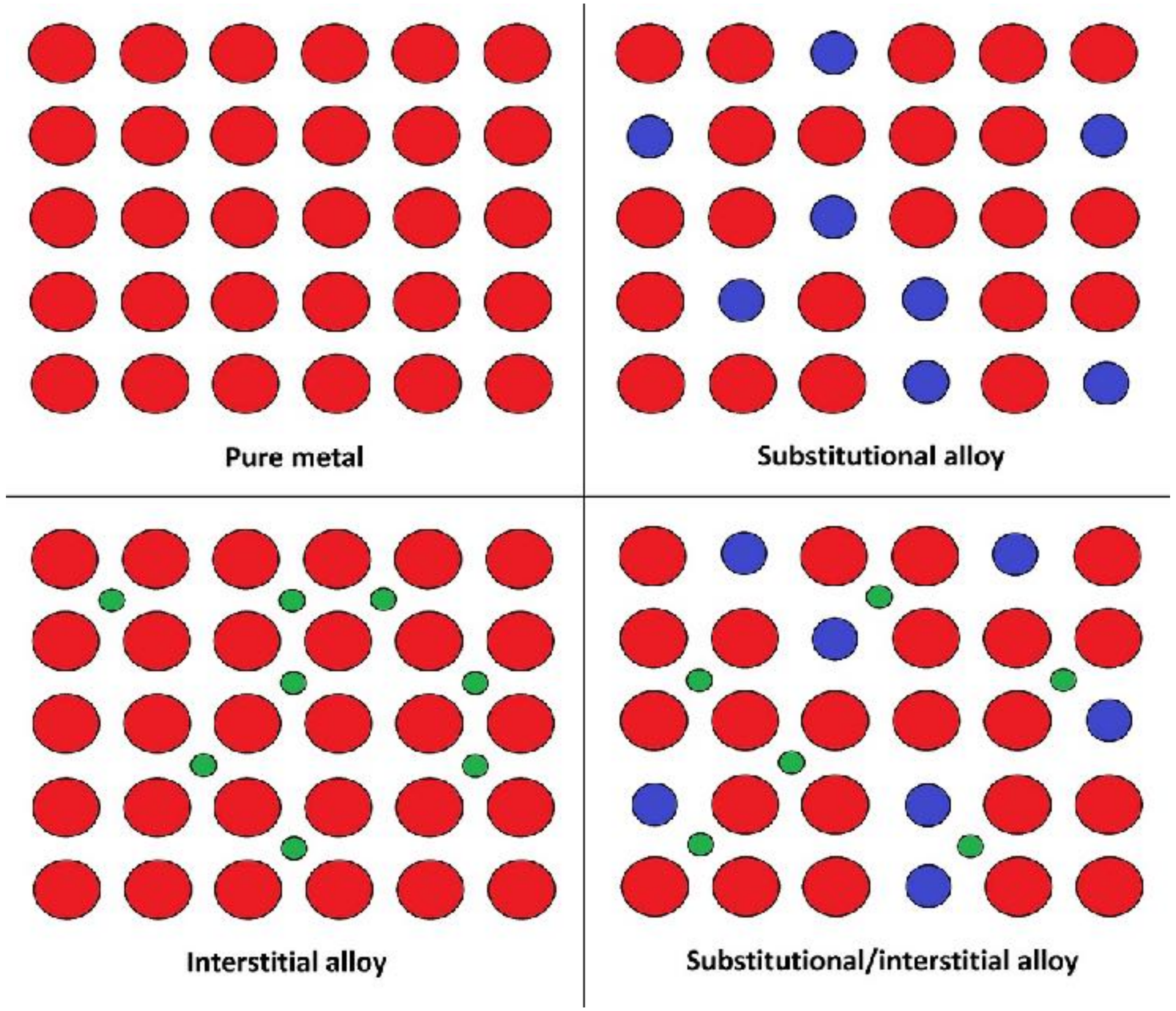


Metallic Bonding

- metals tend to lose electrons - when only metal atoms are present, these electrons become delocalized
- Non-directional nature of delocalized electrons “sea of electrons”
- responsible for properties of metals: malleable, ductile, conducts electricity and heat

Alloys

- Mixing of two or more metals in the molten state
- As mixture solidifies, the positive metallic ions are distributed throughout the lattice structure and bound by the non-directional, delocalized electrons (sea of mobile valence electrons)
- Have properties that are distinct from their component metals due to the different packing of the ions in the lattice



Common Alloys: Steel, Bronze, Brass, Rose Gold

Detective work...

- Using your skills, find the molecular shape for the following compounds (feel free to use your notes and your textbook) - you may also need to draw Lewis structures

- IF_4^+

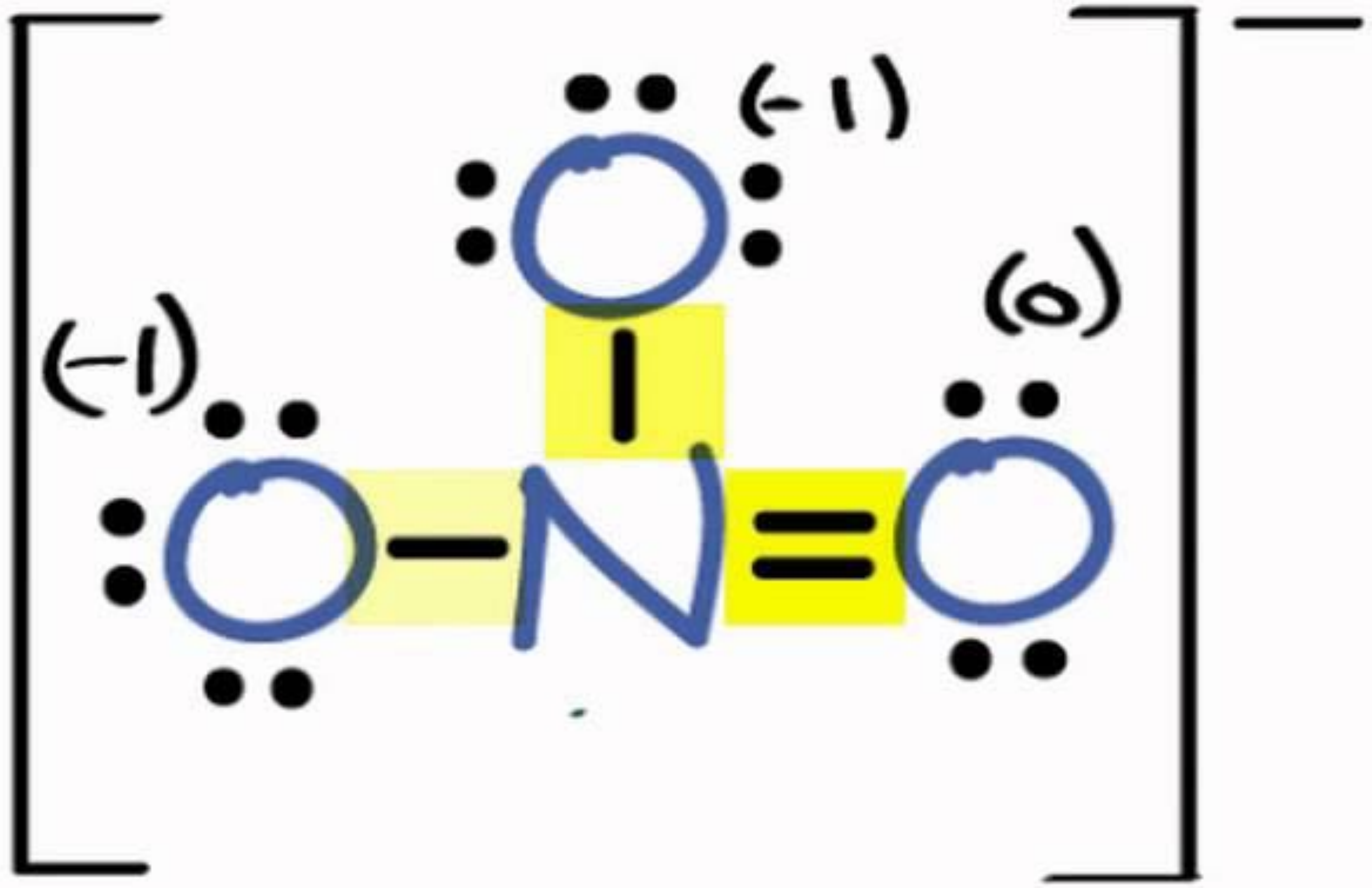
- OF_2

- What would you expect the O-Xe-O bond angle to be in the compound XeO_4?

Formal Charge

NO_3^-

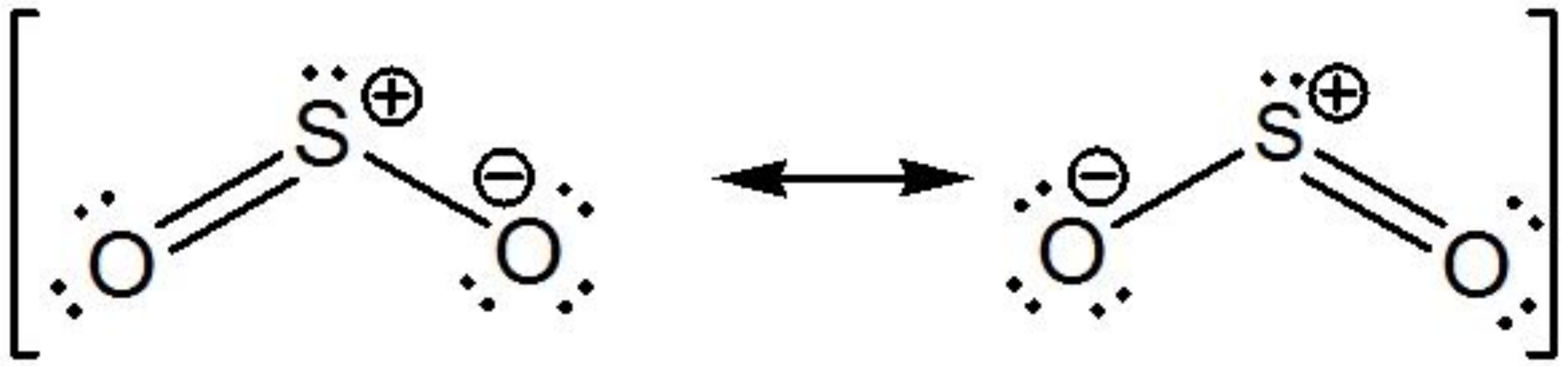
Formal Charges

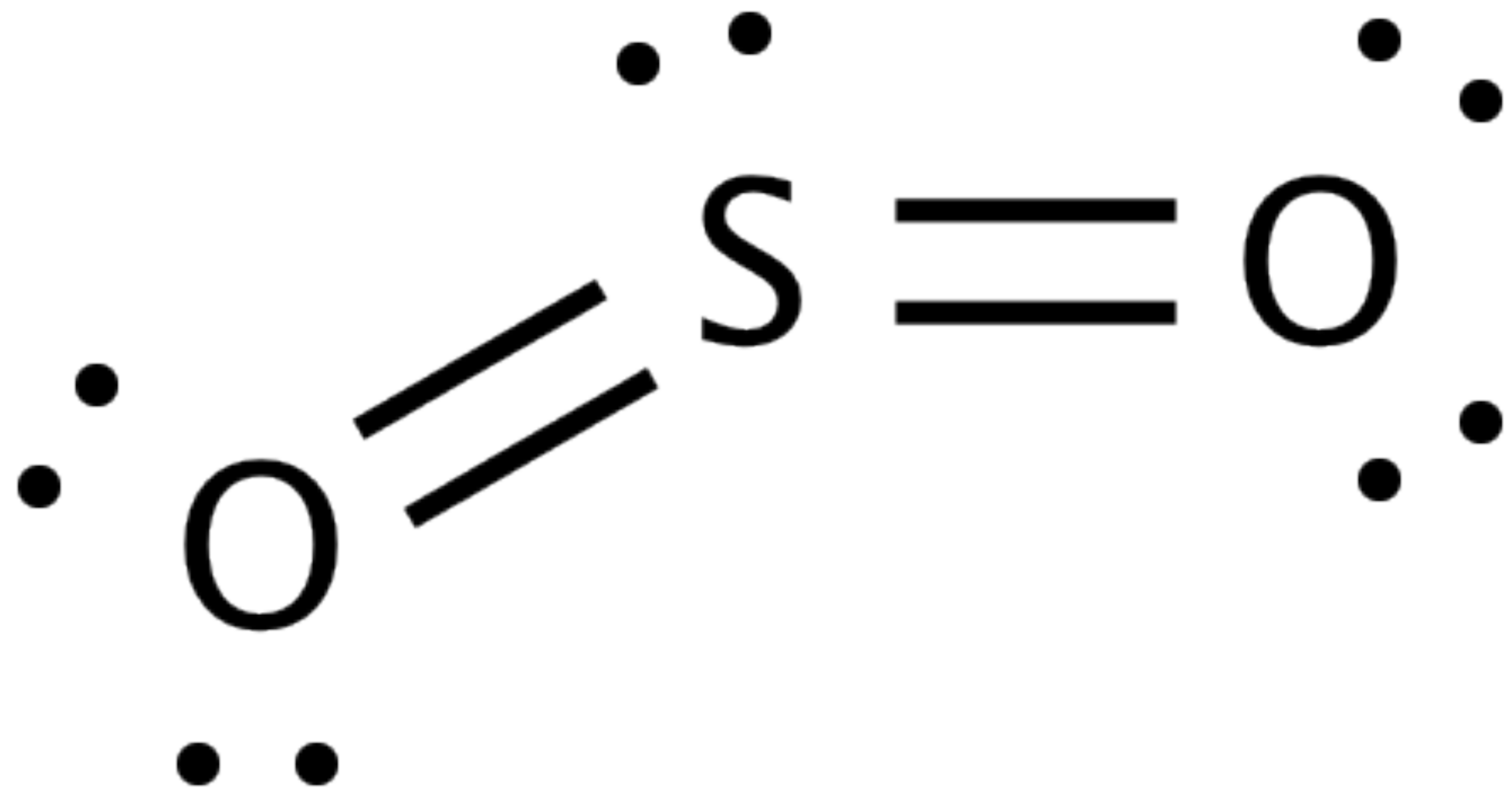


$$\textbf{Formal Charge} = \text{Valence Electrons} - \text{NonBonding Val Electrons} - \frac{\text{Bonding Electrons}}{2}$$

$$N = 5 - 0 - \square$$

SO_2



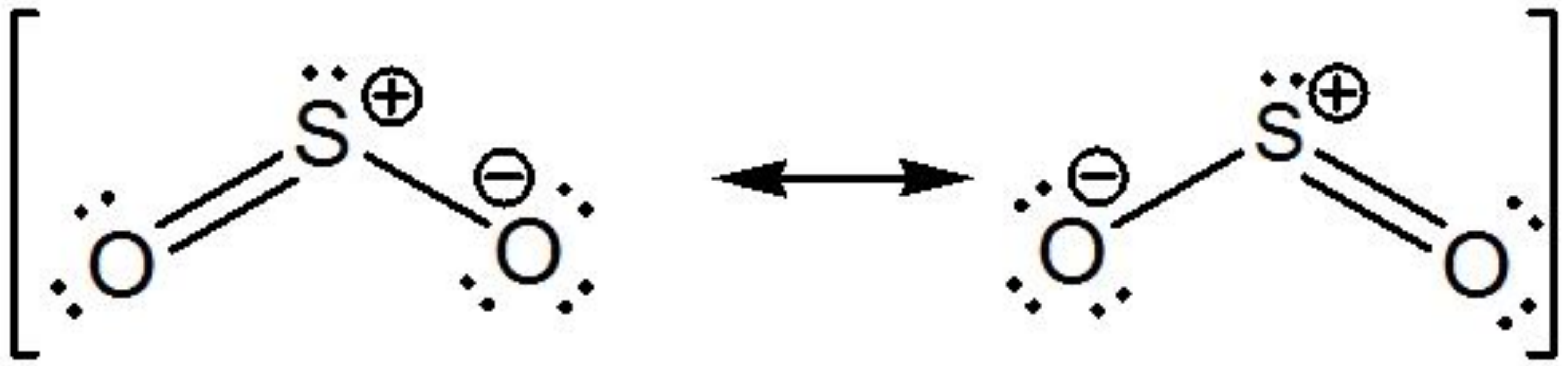


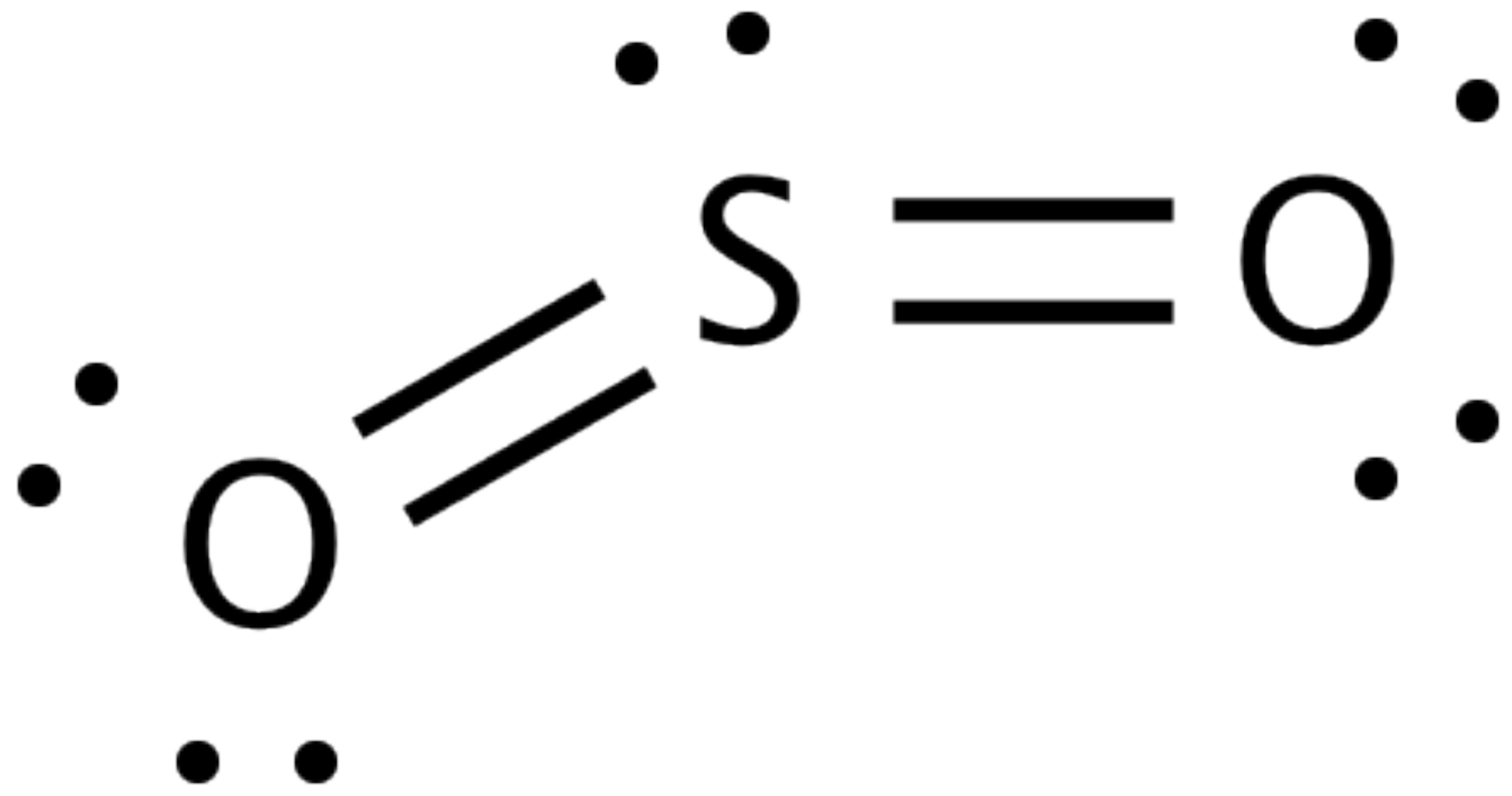
Formal charge

- FC = # valence electrons - # electrons assigned to atom in Lewis structure

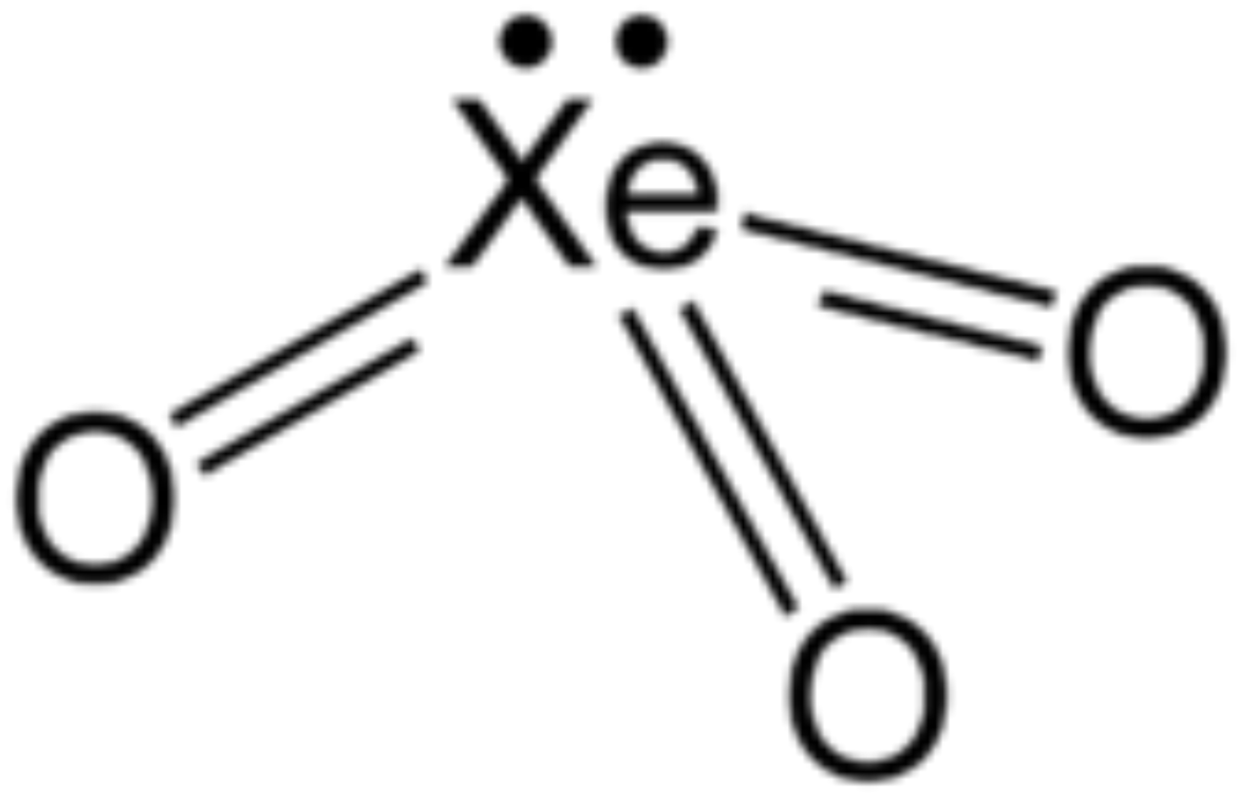
- FC = #v.e. - (1/2 bonding + # electrons in lone pairs)
- Low FC means less electron transfer has taken place and therefore is more stable and the preferred structure

SO_2





XeO_3



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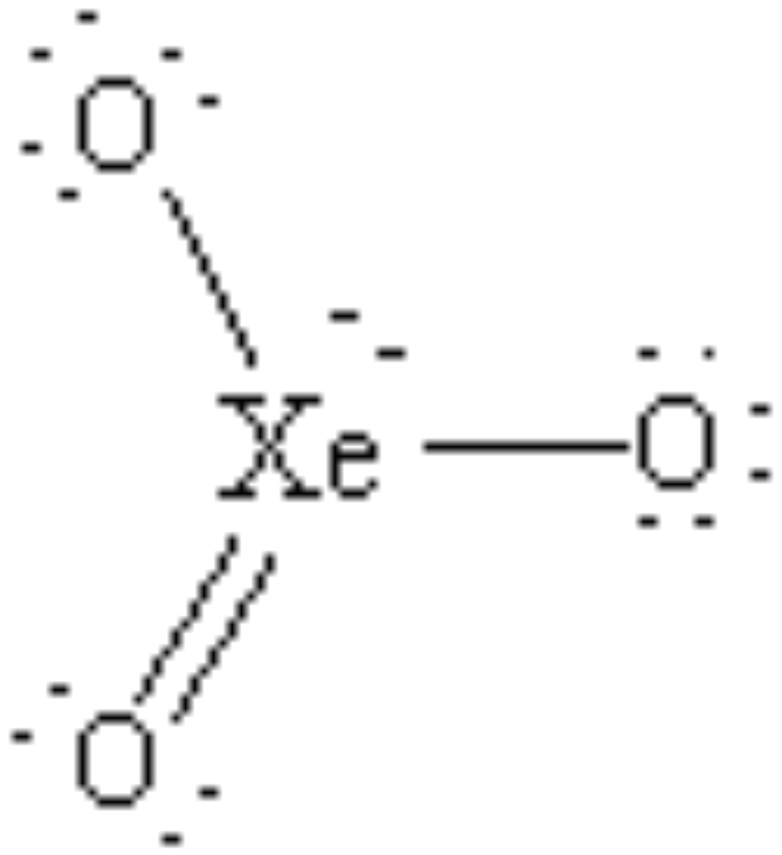
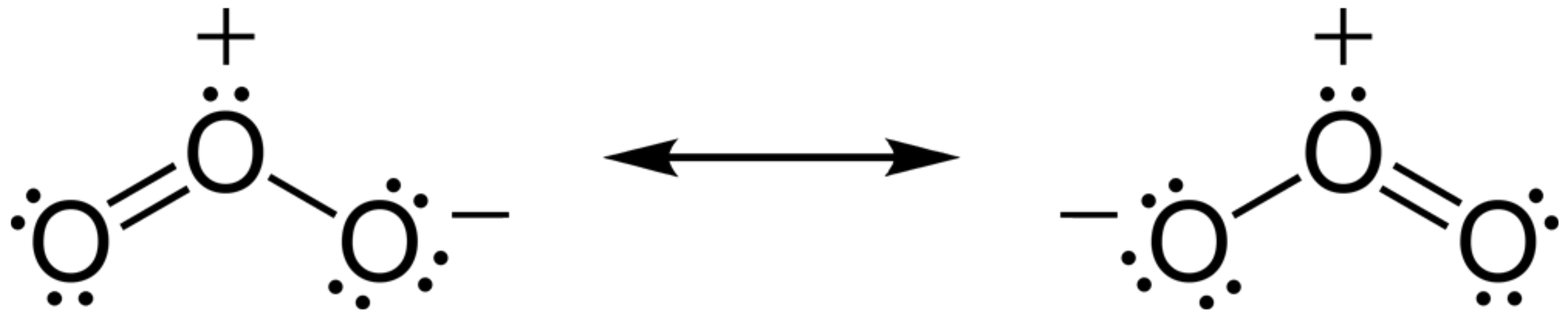


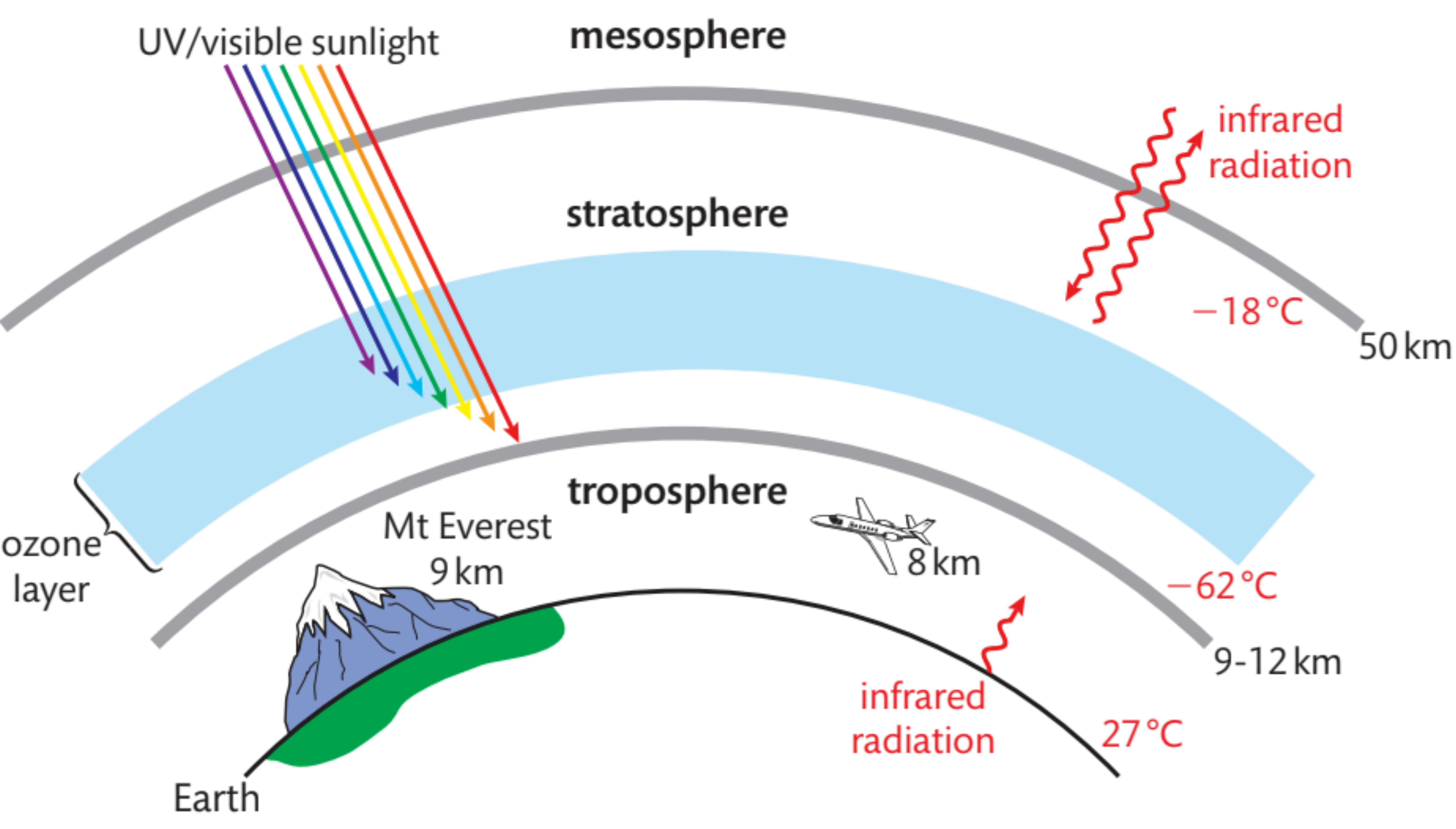
Ozone

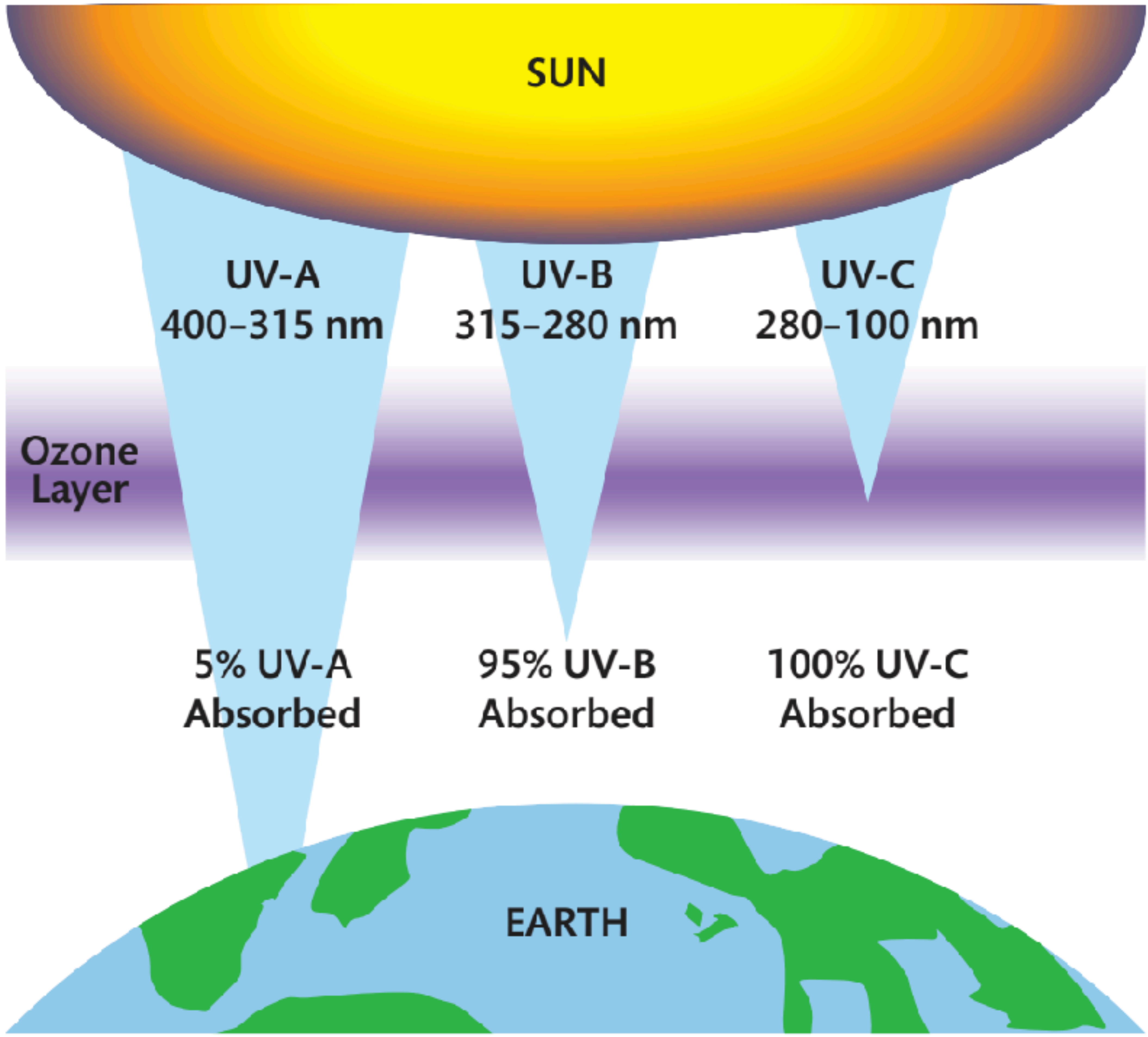


Ozone

- essential component of the atmosphere
- traps heat in order to maintain life while blocking some of the sun's radiation from reaching the Earth
- levels of about 10 ppm in the lower stratosphere maintained by a cycle of equations

Regions of the atmosphere



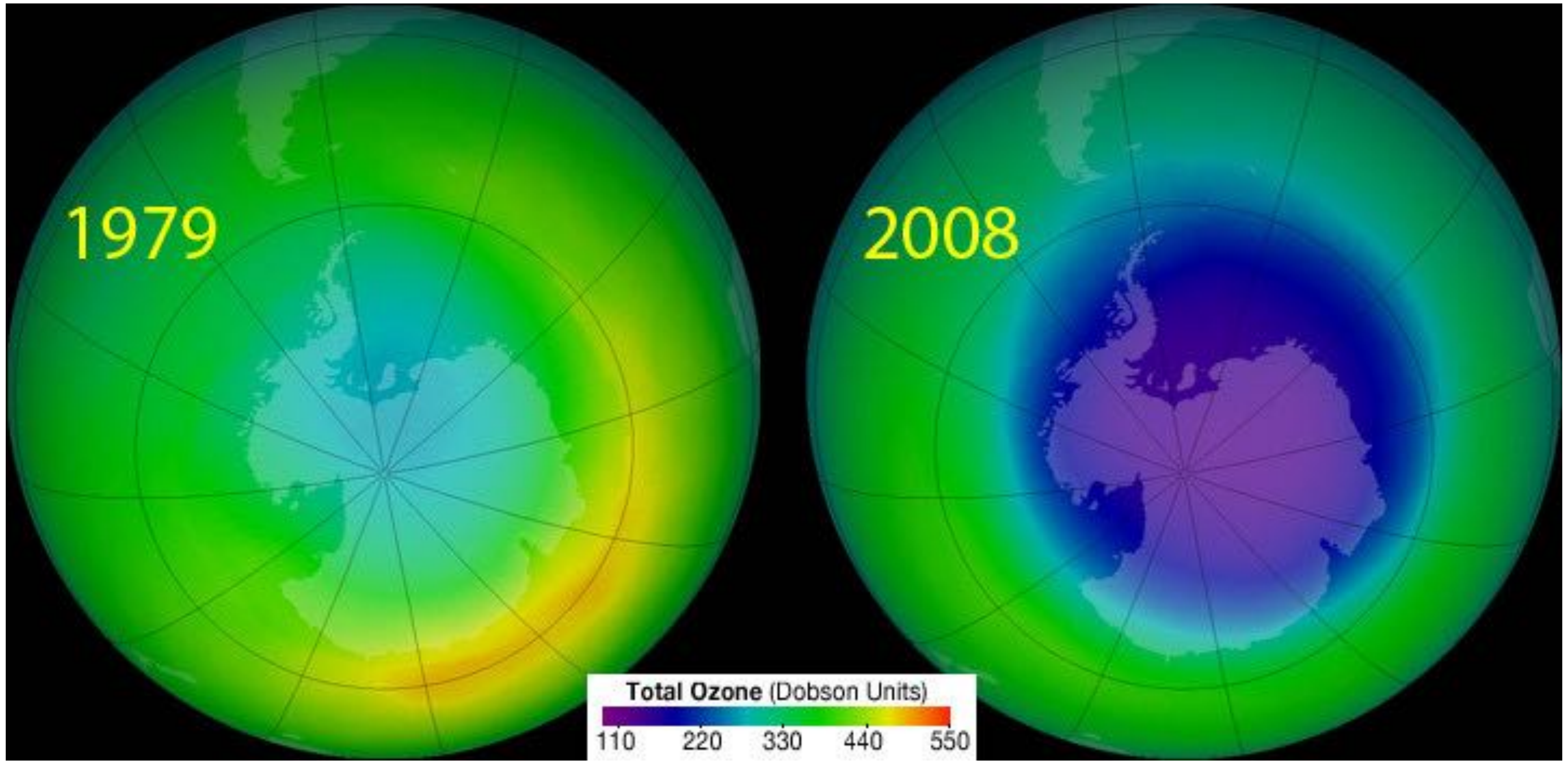


Free Radical Oxygen and Ozone Reactions

- Oxygen dissociation
  - $O_{2(g)}$ ---λ < 242nm---> $O\bullet_{(g)}$ + $O\bullet_{(g)}$ (free radical oxygens)
- Ozone Dissociation
  - Step 1: $O_{3(g)}$ ---λ < 330nm---> $O_{2(g)}$ + $O\bullet_{(g)}$ (Fast)
  - Step 2: $O_{3(g)}$ + $O\bullet_{(g)}$ ----> $2O_{2(g)}$ Exothermic (Slow)
- What type of energy is being absorbed by the O_2 and O_3?
- Why does it take a shorter wavelength to break the O_2 bond?

Catalytic Destruction of Ozone

- Ozone is unstable! (because it absorbs UV radiation)
- Reacts easily with compounds released by human activities
- Nitrogen oxides (NO_x) and CFCs



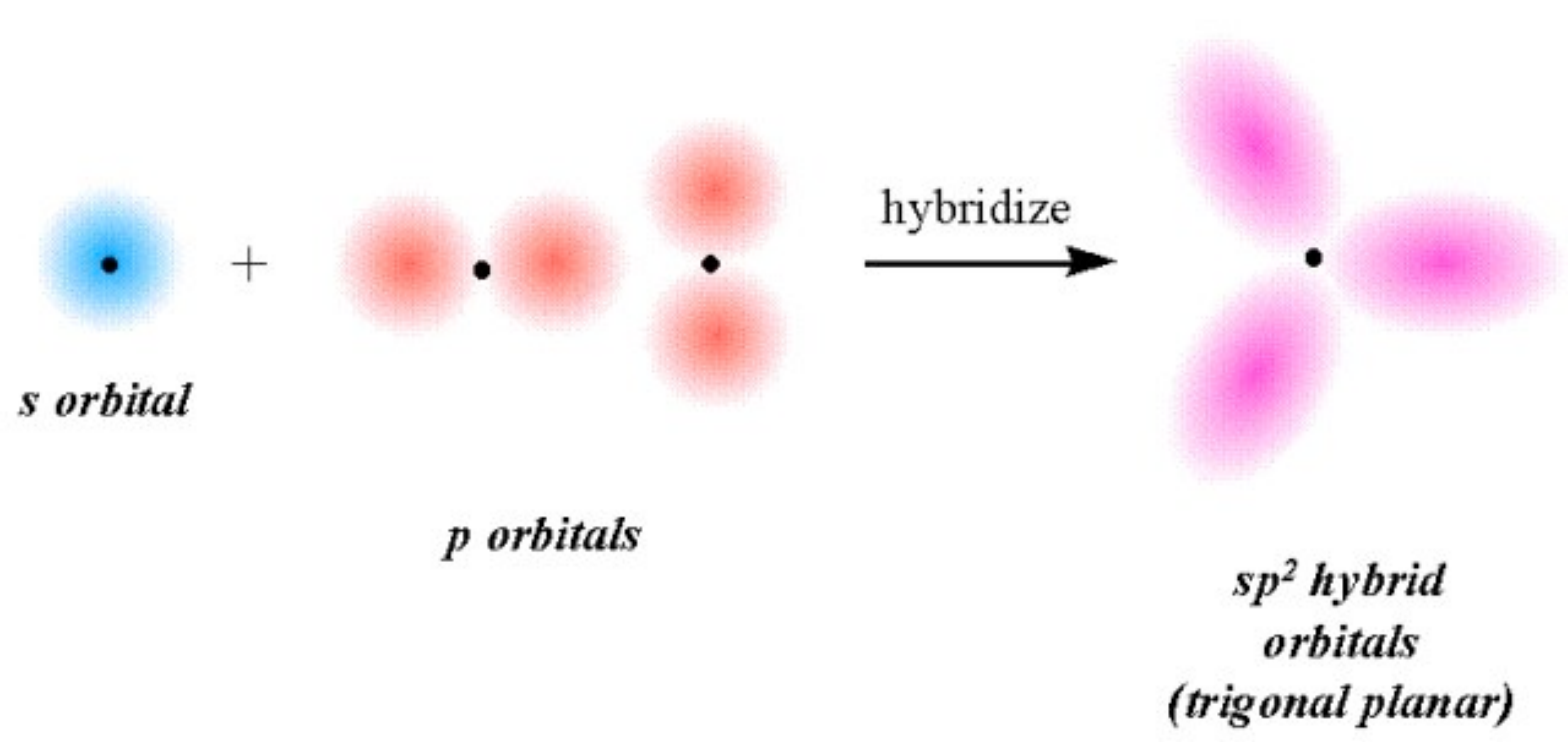
Reactions w/NO_x

- $NO\bullet$: created in vehicle engines @ high temp.
- free radical that will react w/ozone
  - $NO\bullet + O_3 \text{--->} NO_2\bullet + O_2$
  - $NO_2\bullet + O\bullet \text{--->} \bullet NO + O_2$
- Net Reaction:
  - $O_3 + O\bullet \text{--->} 2O_2$

Reactions w/CFCs

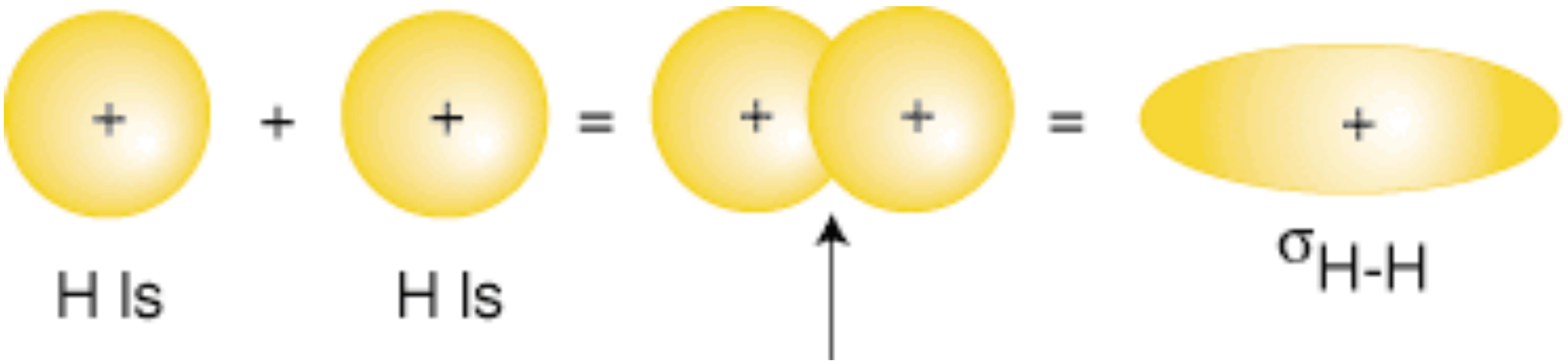
- CFCs used in refrigerants/aerosols/solvents/plastics
  - low reactivity (unless in stratosphere)
- CCl_2F_2 --> $\bullet CClF_2$ + $Cl\bullet$ (weaker C-Cl bond breaks 1st)
  - $Cl\bullet + O_3$ ---> $O_2 + ClO\bullet$
  - $ClO\bullet + O\bullet$ ---> $O_2 + Cl\bullet$
  - Net reaction? $O_3(g) + O\bullet$ --> $2O_2(g)$

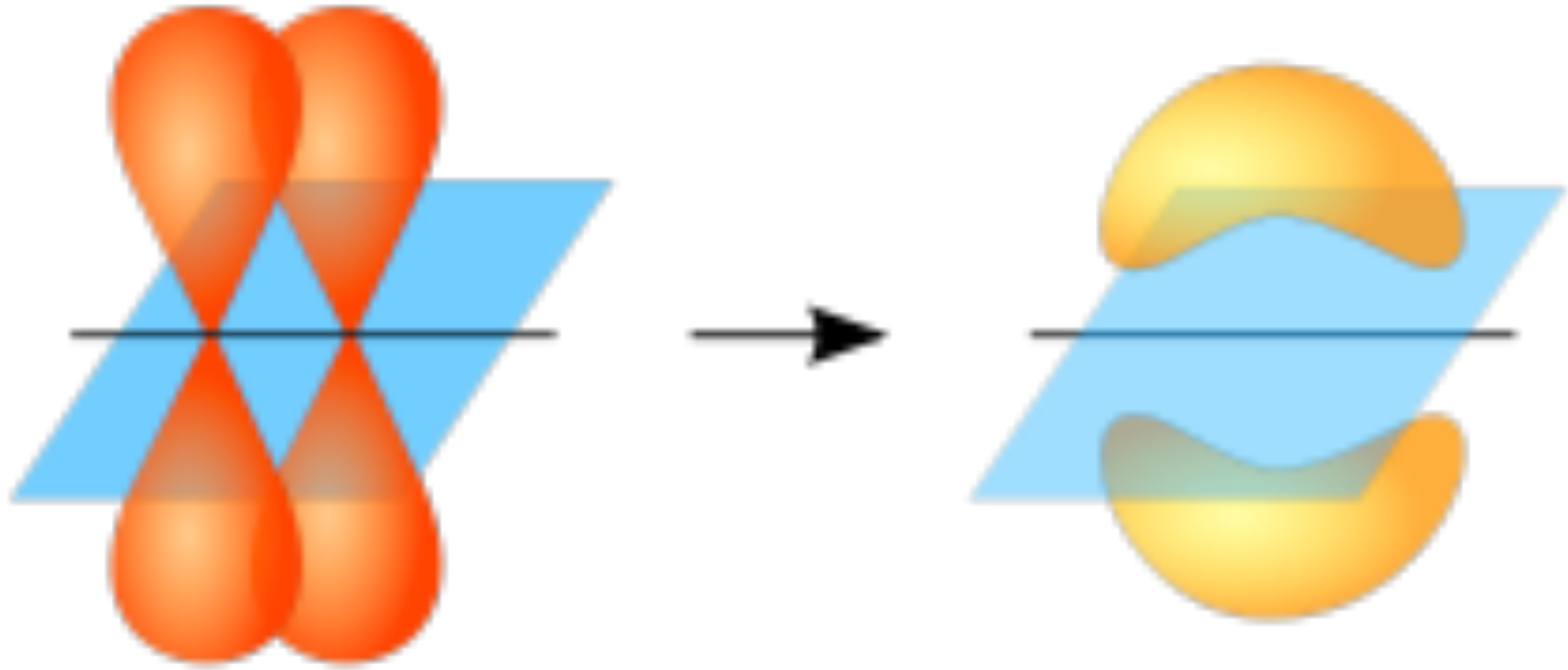
Hybridization



Bonding revisited

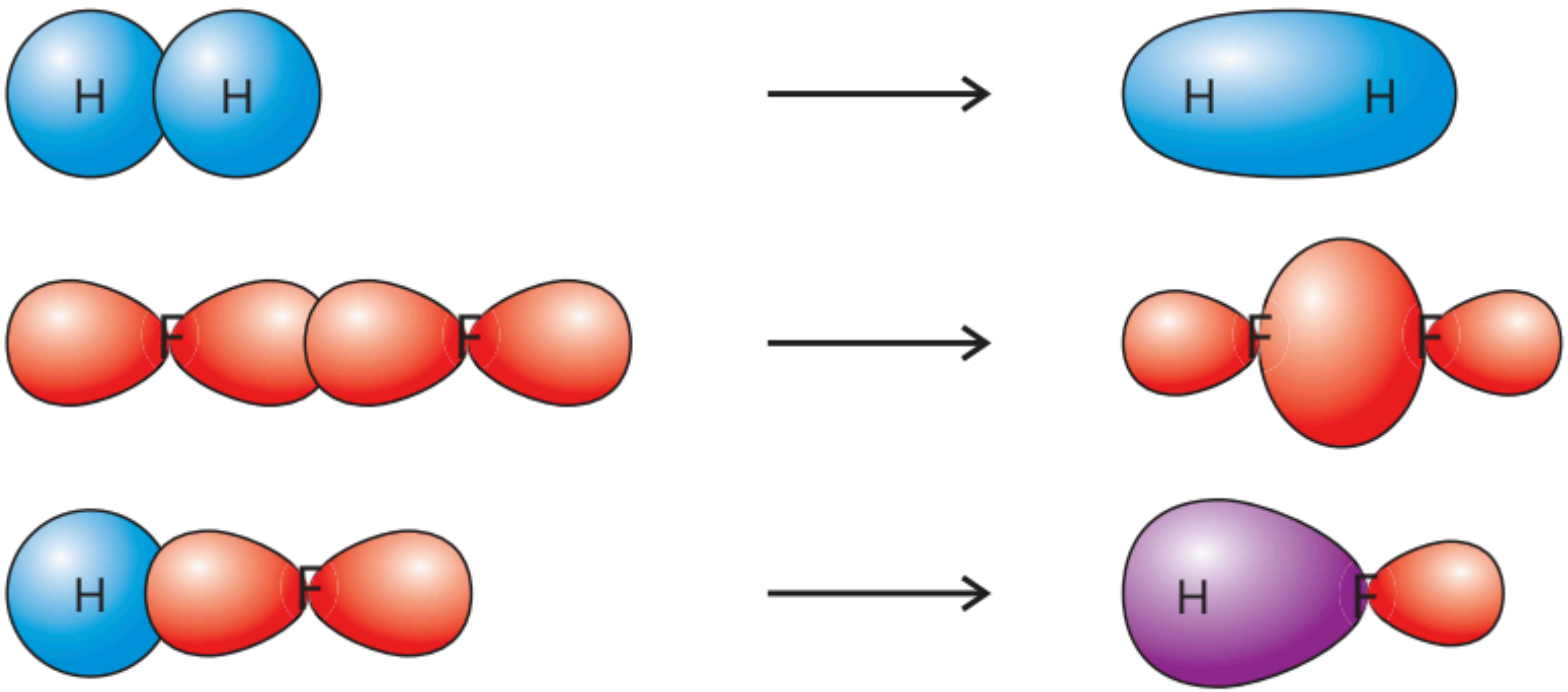
- How does bonding happen if electrons are in orbitals???
  - Overlap of different orbitals
  - can overlap end to end or side to side
- this overlap creates a new *molecular orbital* that is at a lower energy





the sigma (σ) bond

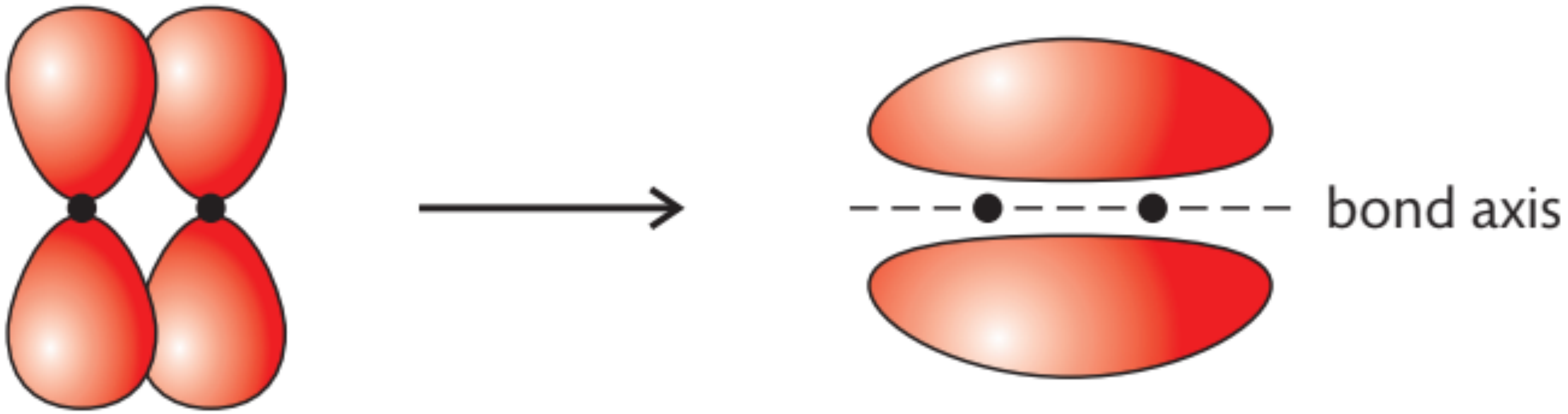
- when the overlap occurs along the bond axis (on a line between the two nuclei)
- can happen between two 's' orbitals, two 'p' orbitals or an s and p orbital
- the electron density lies between the two nuclei

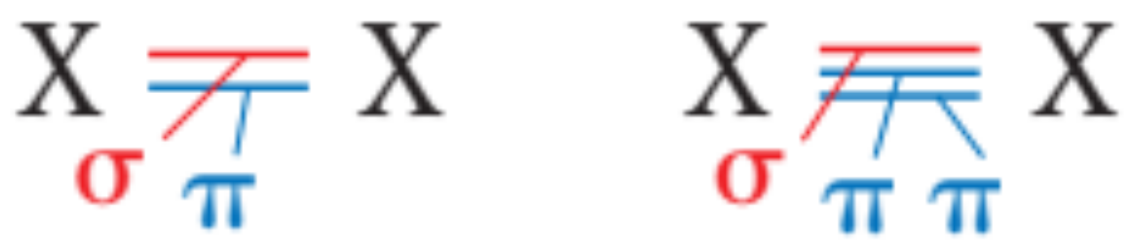


the pi (π) bond

- when two 'p' orbitals overlap sideways

- the electron density is concentrated in two places lies above and below the bond axis

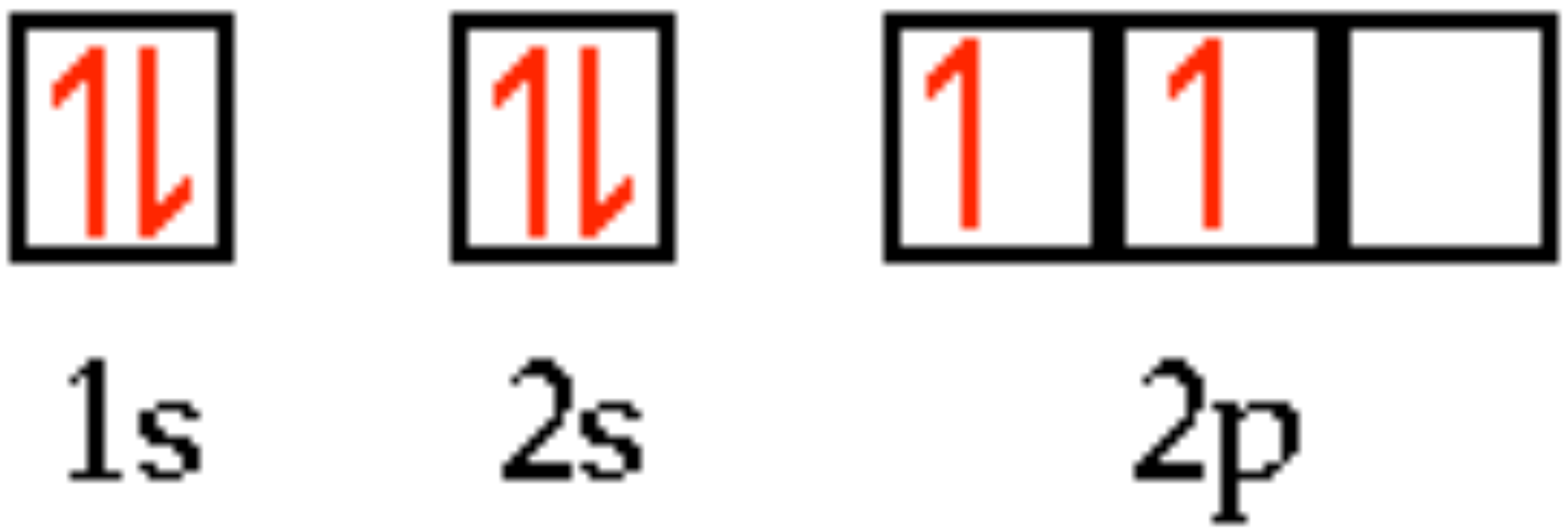




cannot have a pi bond, without having a sigma bond take place first; therefore, if a pi bond exists, it is a part of a double or triple bond.

Carbon, building block of life…but a weirdo…

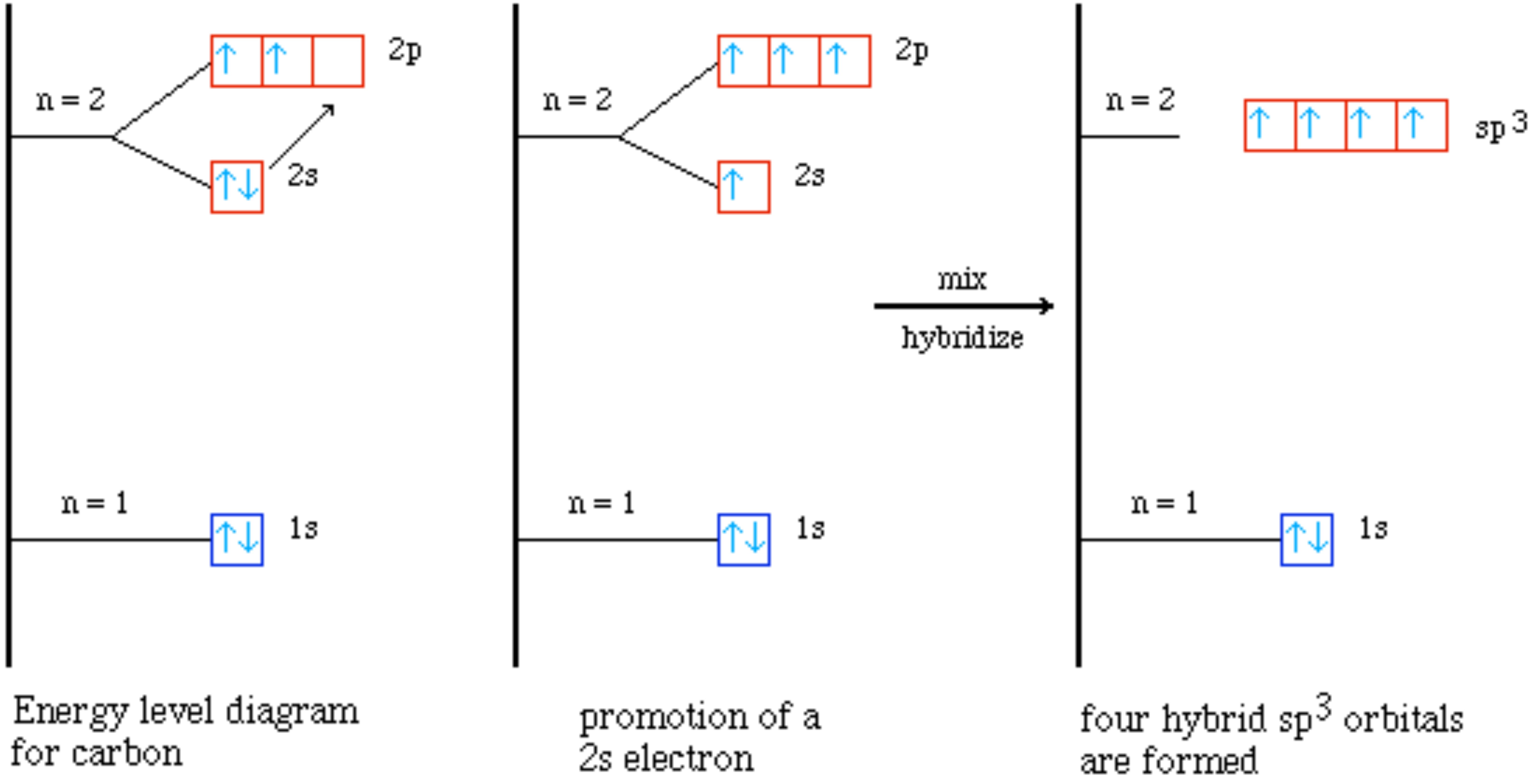
- What is carbon’s electron configuration?
- Draw its electron in a box diagram…



- How many bonds does carbon generally form?
- Does this make sense? What must happen?

sp^3 hybridization

- when carbon forms 4 single bonds



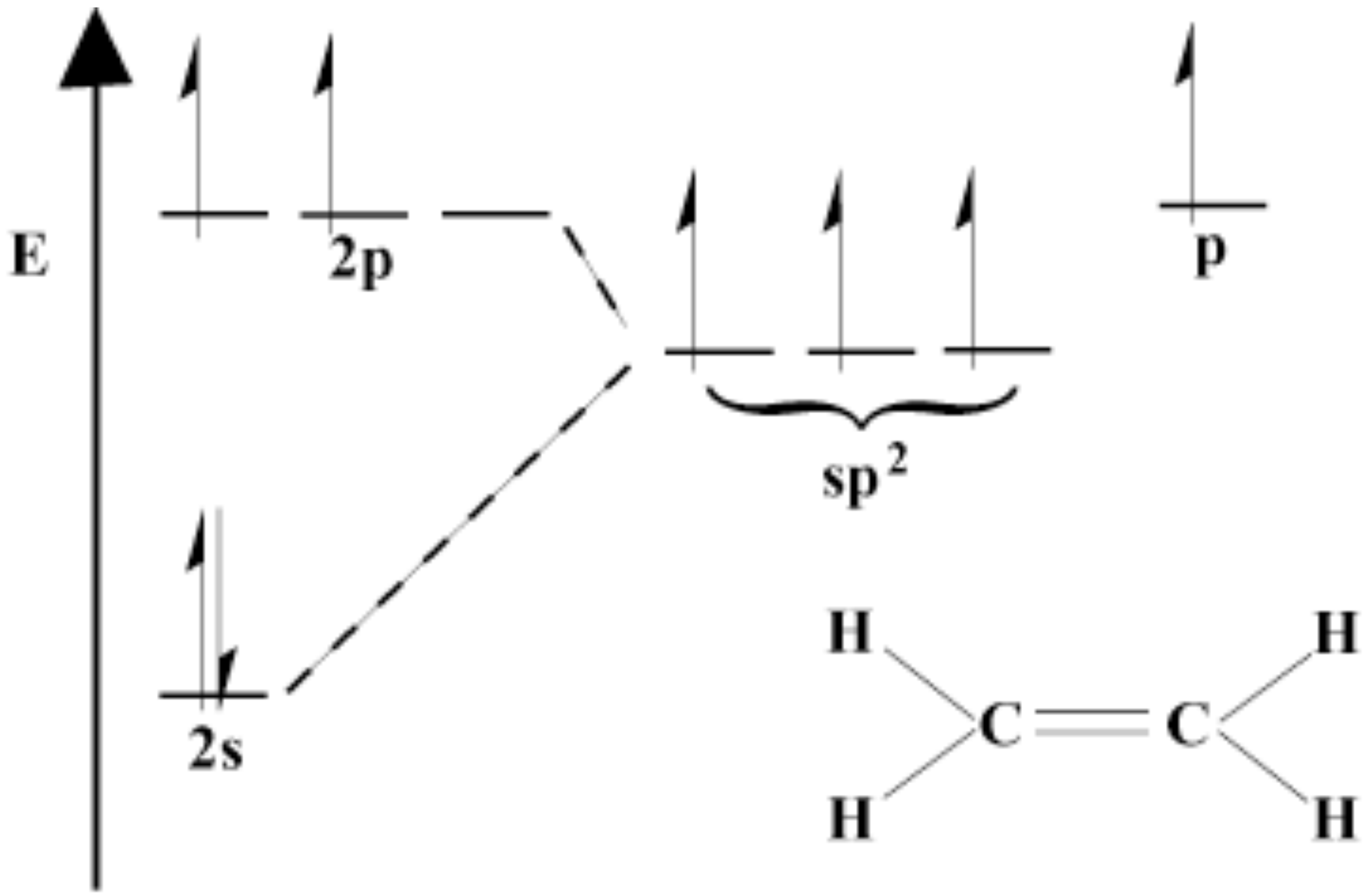
- each hybrid orbital overlaps with the atomic orbital of another atom, causing 4 sigma bonds

sp^2 hybridization

- occurs when carbon forms a double bond
- forms 3 sp^2 orbitals and one unhybridized p orbital

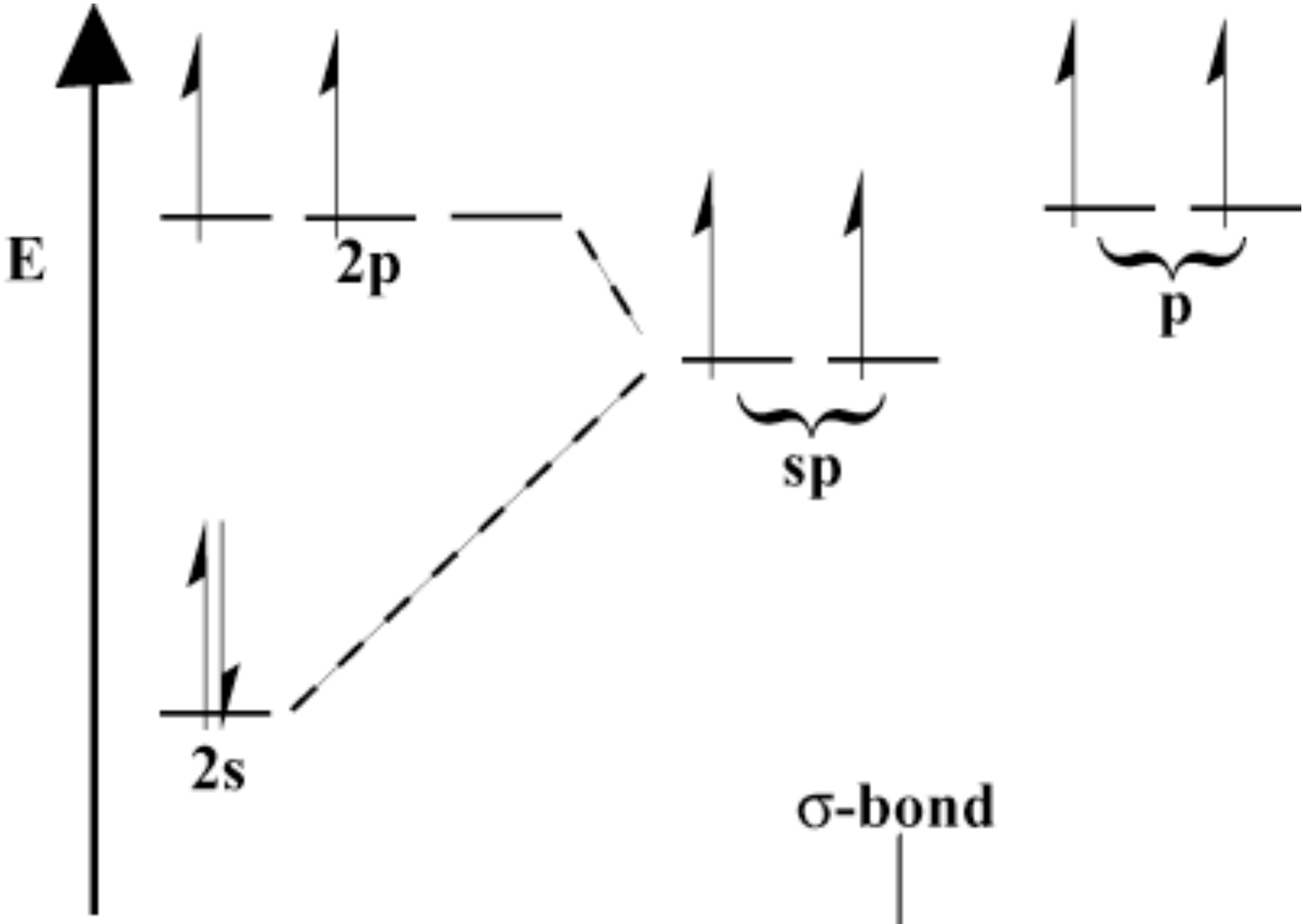
the unhybridized p-orbital is available to form a pi bond between the carbon atoms:

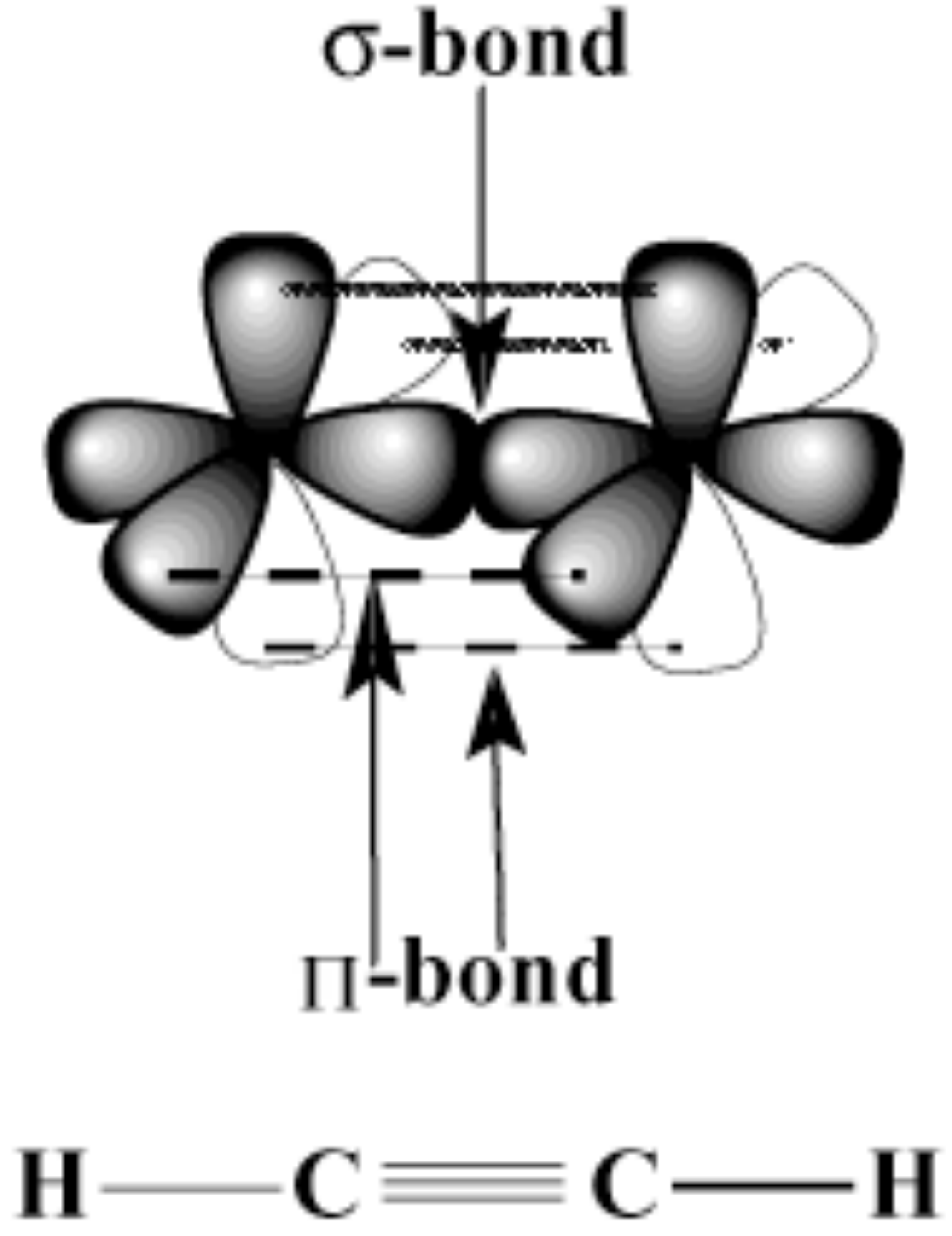
3 sp^2 sigma bonds and 1 pi bond



sp hybridization

- when carbon forms a triple bond, it undergoes sp hybridization
- the 2 hybrid orbitals form sigma bonds (one between them and one with another atom)
- the two other orbitals (unhybridized p's) will form the two other bonds between the atoms --> pi bonds





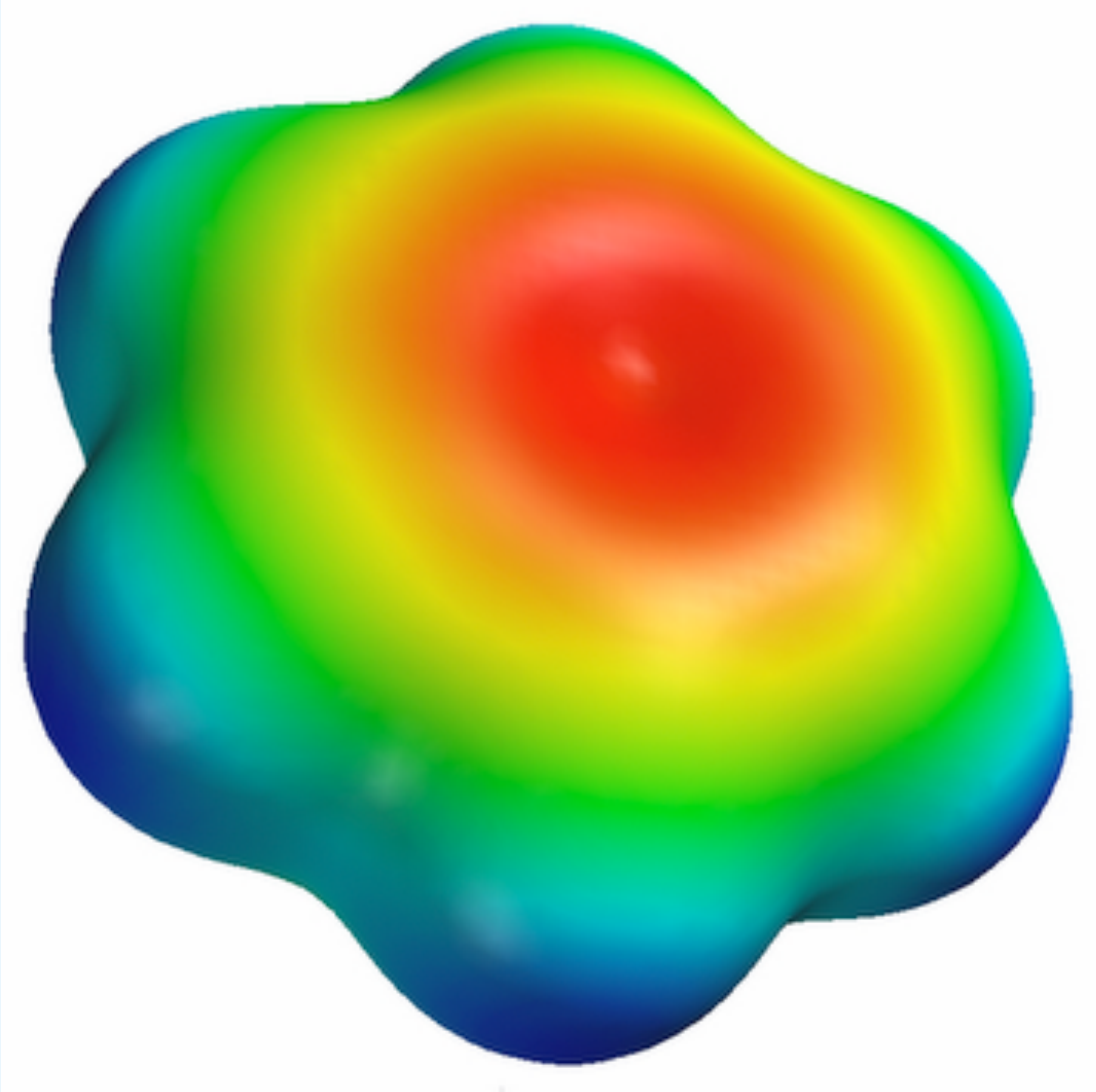
Predicting molecular shape..

- Please predict the molecular shape of a molecule that undergoes hybridization:
  - sp^3
  - sp^2
  - sp

these are all related...

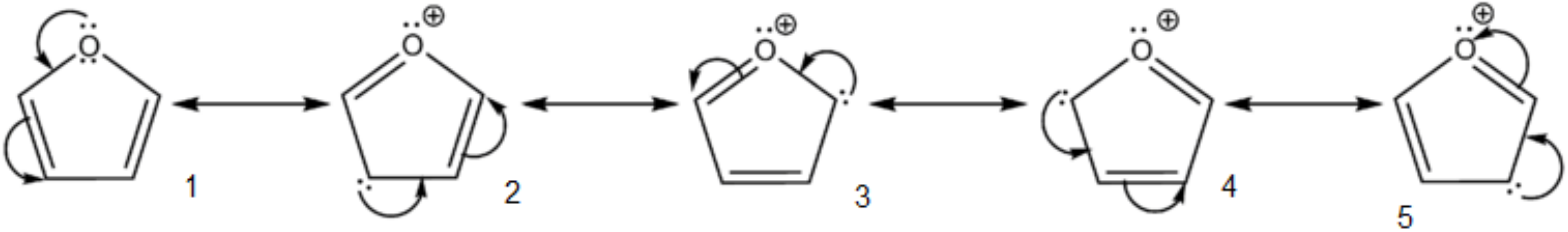
number of charge centres ↔ shape of the molecule ↔ hybridization

Delocalization of Electrons



What is it?

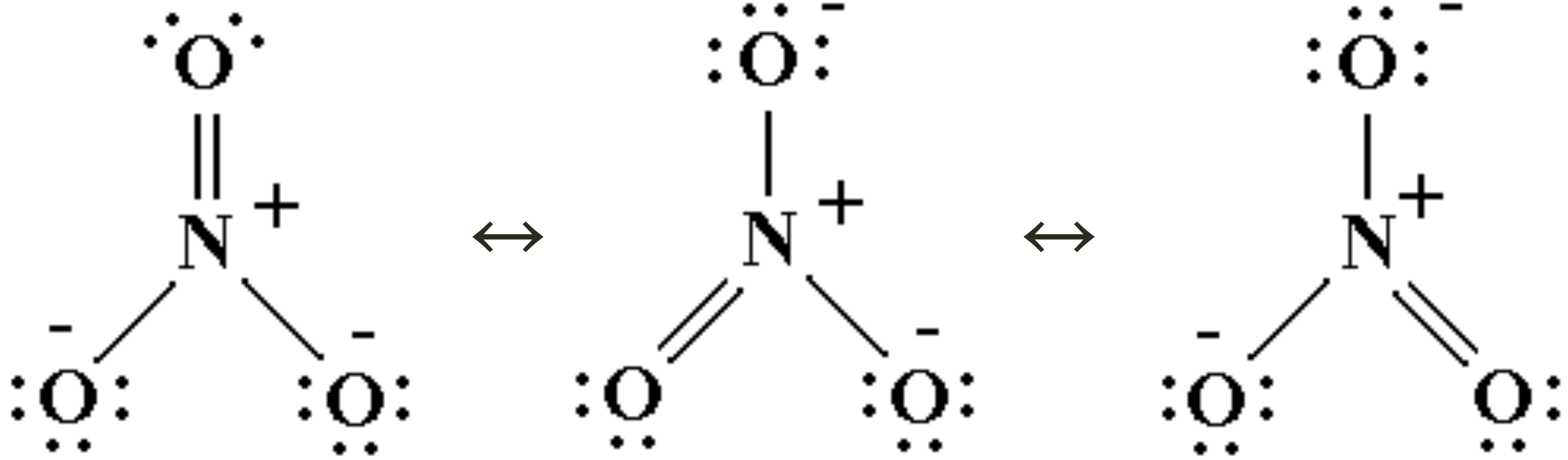
- We know covalent bonding as electrons being shared in a fixed position
- Sometimes, electrons have more freedom and are less restricted than this
- the tendency is to be shared between more than one bonding position - this is called delocalization
- the delocalized electrons spread themselves out and are more stable



1 2 3 4 5

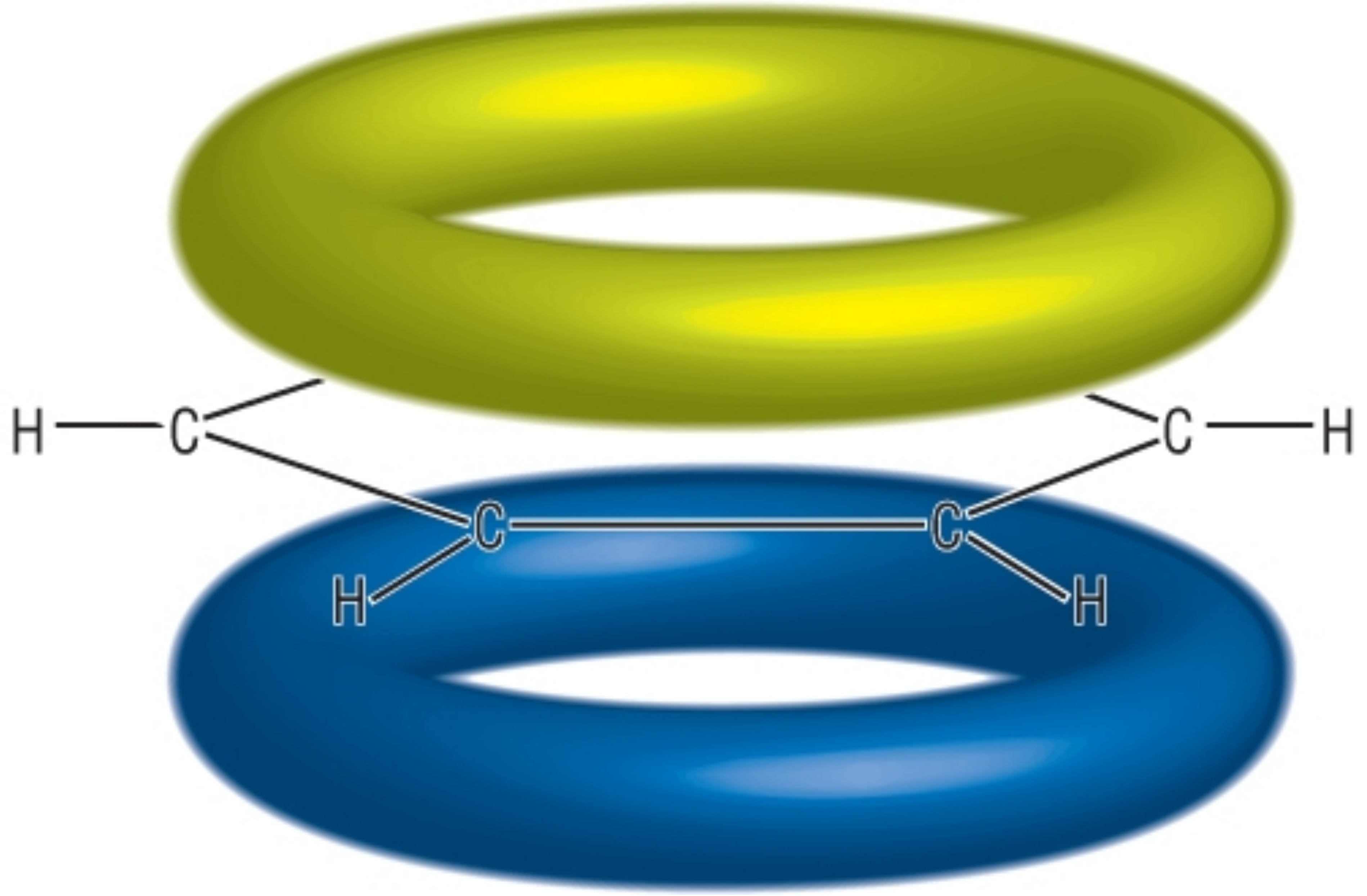
What happens?

- As discussed before...nitrate will undergo resonance
- more specifically, the electrons are delocalized and are shared among the three positions



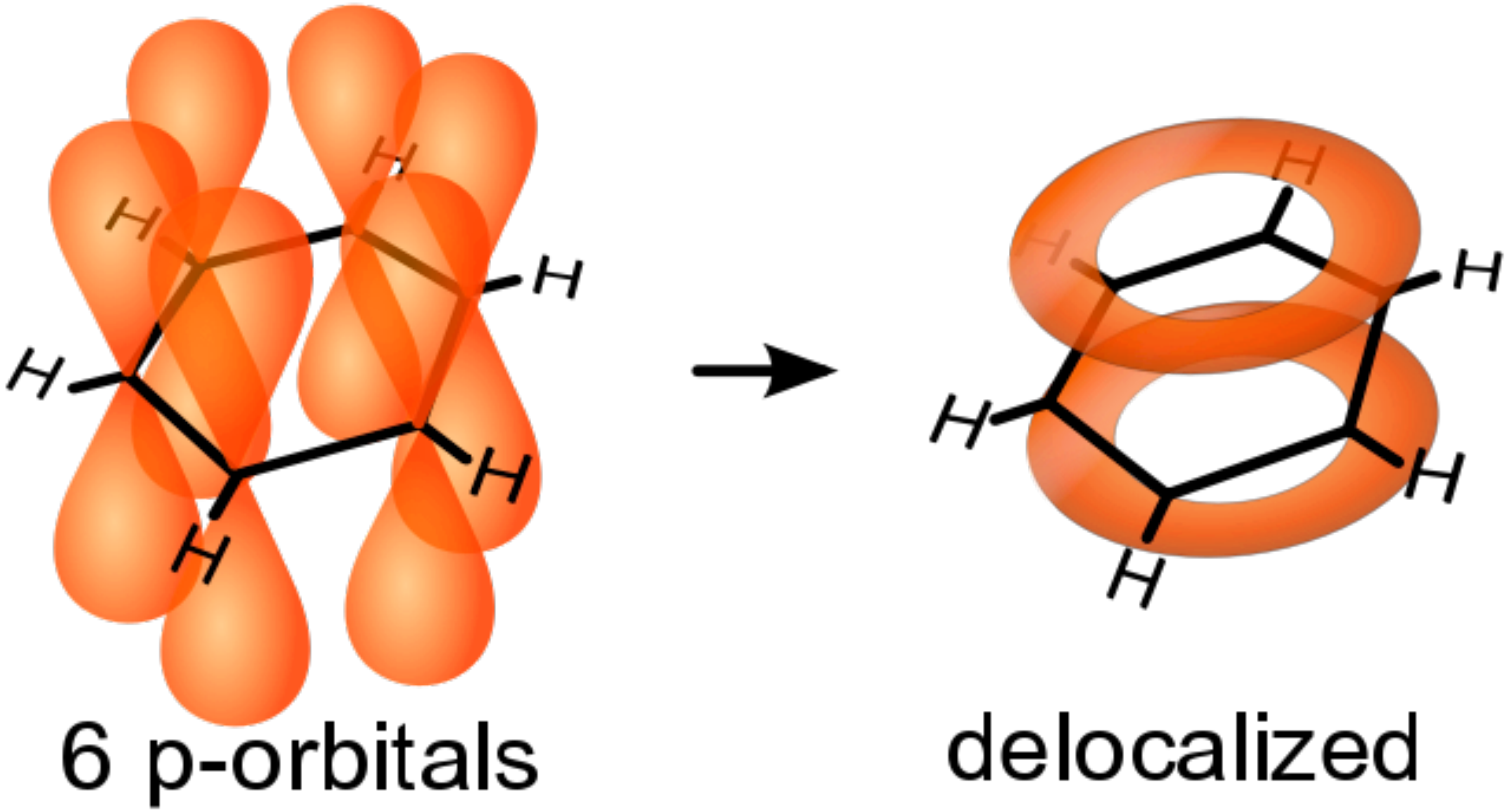
Benzene

- three slides back...
- the electron density will lie above and below the plane of the molecule
- these are the ‘pi’ bonds (the sigma bonds are in between the C atoms)



More Benzene

- gives benzene great stability and generally unreactive
- benzene is a molecule that can be inhaled through contaminated air or absorbed into your skin through contact with gasoline - found to cause leukemia



Question...

- Compare the structures of CH_3COOH and CH_3COO^- with reference to potential resonance structures

Properties of compounds with delocalized electrons

- Bond Lengths and strength
  - Bond order
    - ***# of shared pairs / # of bond positions***
    - single bond =1
    - double bond = 2
    - triple bond = 3
    - NO_3^- = 4/3 = 1.33
- Greater Stability
  - delocalization spreads the electrons as far apart as possible in order to minimize the repulsion between them
  - less chemically reactive
  - extra energy (resonance energy) must be put in to disrupt the delocalized pi bond

More on stability

- ethanol: C_2H_5OH vs. $C_2H_5O^-$

- phenol: C_6H_5OH vs. $C_6H_5O^-$

- ethanoic acid: CH_3COOH vs. CH_3COO^-

Properties of compounds with delocalized electrons

- electrical conductivity in graphite
  - due to the freedom electrons have in the delocalized bonds

Physical Properties

Physical Properties

- MP and BP
- Solubility
- Electrical Conductivity
- you are responsible for review this on your own pages 178-180 in your books
- a good way to study would be to complete the questions on pg 181
    - Review Metallic Bonding - strength (# of e-, charge, cation radius)
    - IMFs - Van der Waals