Hybrid AOs and polyatomic MOs

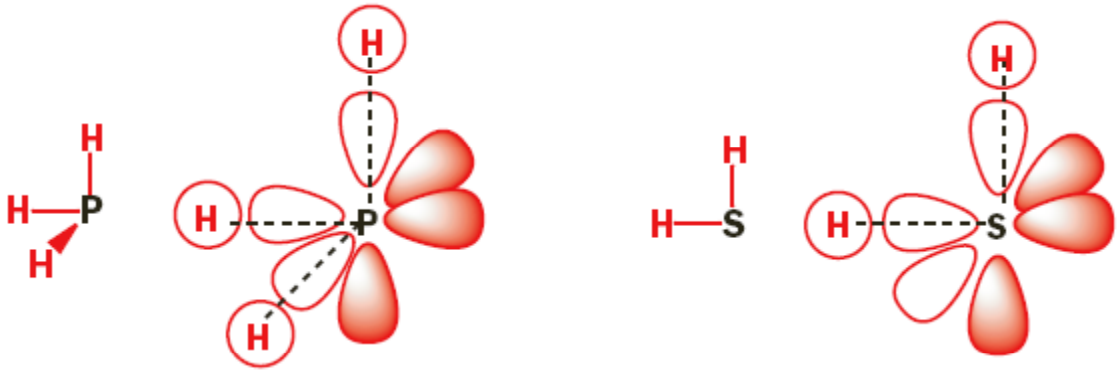
CH101 Fall 2009

Boston University

Hybridized AO’s account for central atom shape

Central atom AO mixing: Hybrid AO's

Unmixed AO's have the *wrong* central atom *geometry*

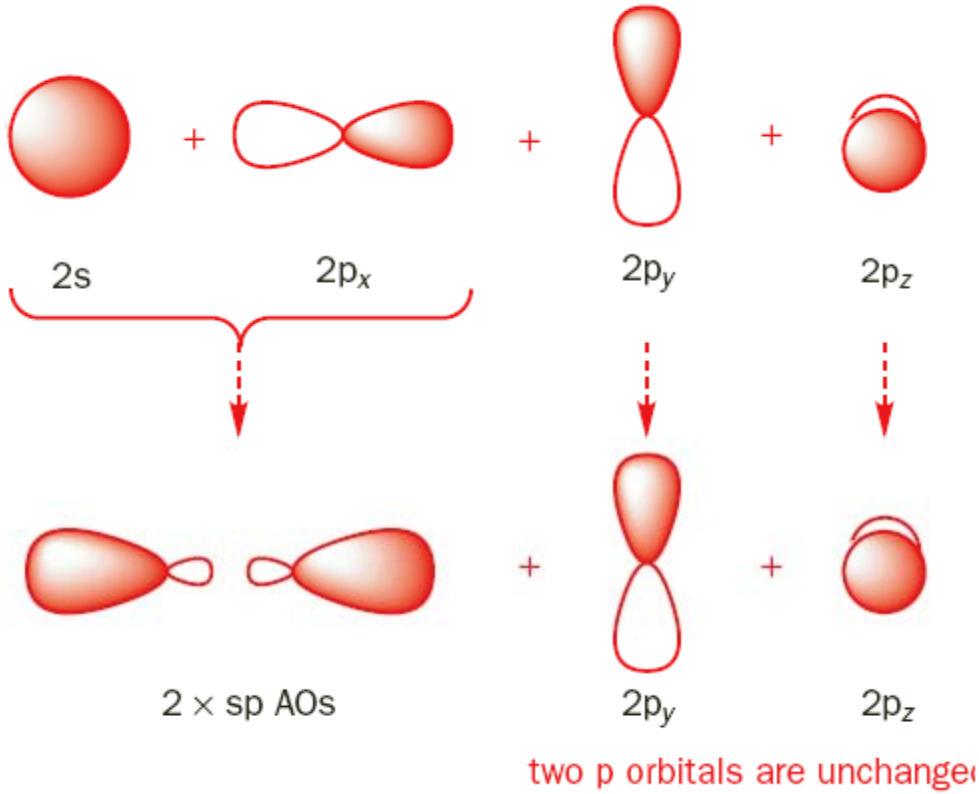


the 90° angles in PH_3 and H_2S come from the overlap of the hydrogen 1s AO with the p AO of the phosphorus or sulfur

An s and a p AO make two sp hybrid AO's

180° angle, for SN = 2

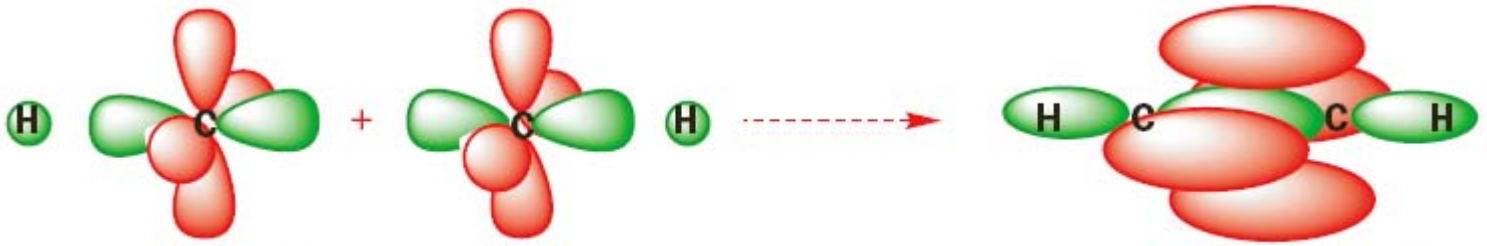
Two p's are unchanged on each atom



sp hybrids account for *linear geometry*

180° angle, for SN = 2

Two p's are unchanged on each atom



2sp hybridized carbon atoms
$2p_y$ and $2p_z$ orbitals remain

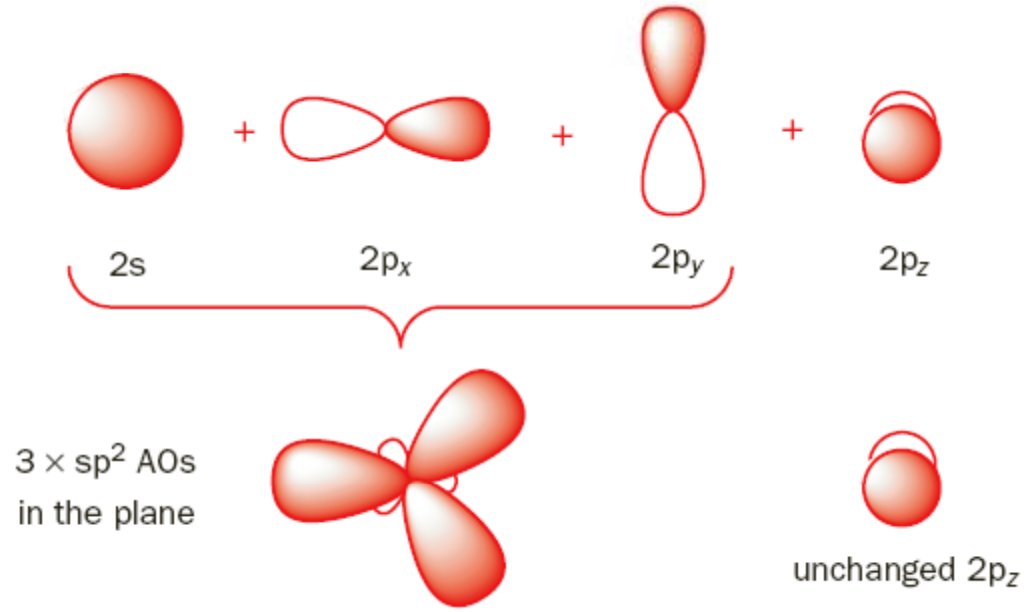
linear σ bonds form skeleton
two perpendicular π bonds

H—C≡C—H

An s and two p AO's make three sp^2 hybrid AO's

120° angle, for SN = 3

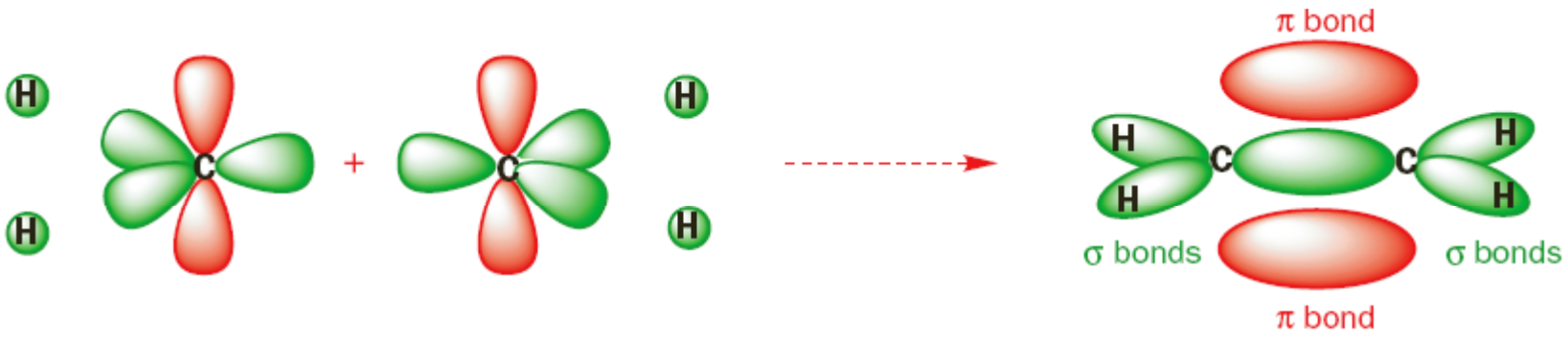
One p is unchanged on each atom



sp^2 hybrids account for *trigonal planar geometry*

120° angle, for SN = 3

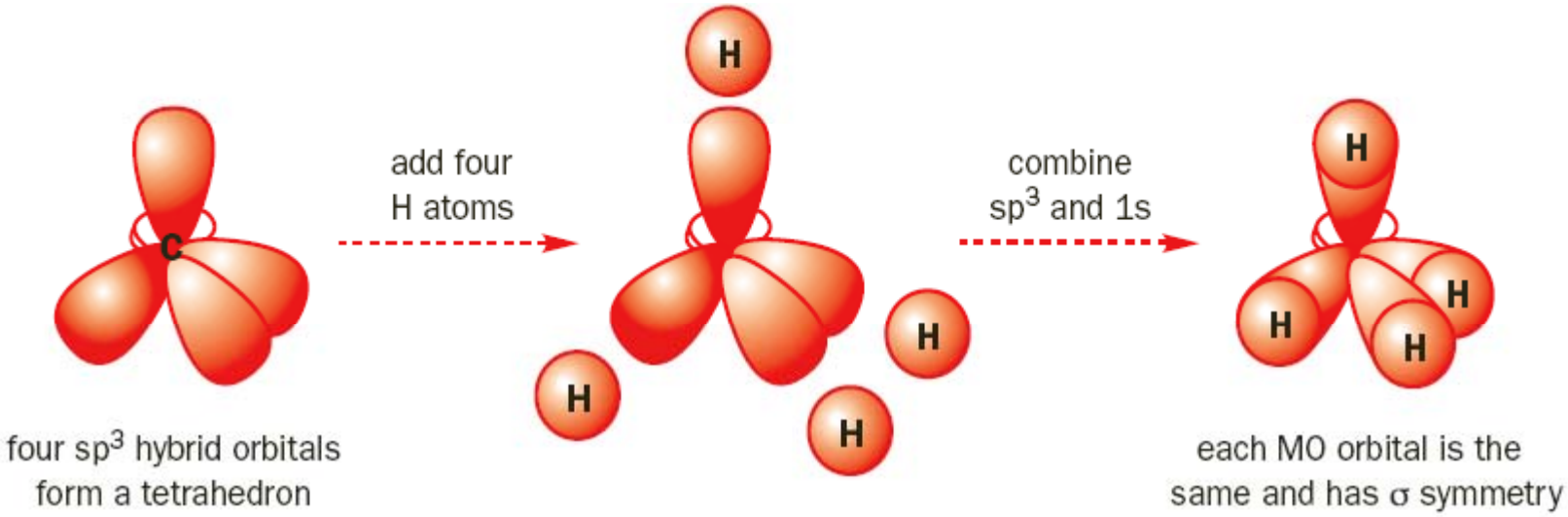
One p is unchanged on each atom



An s and three p AO's make four sp^3 hybrid AO's

109° angle, for SN = 4

sp^3 hybrids account for *tetrahedral geometry*



Examples

CO_2, carbon dioxide

H_2CO, formaldehyde

HCO_2^-, formate

SO_2, sulfur dioxide

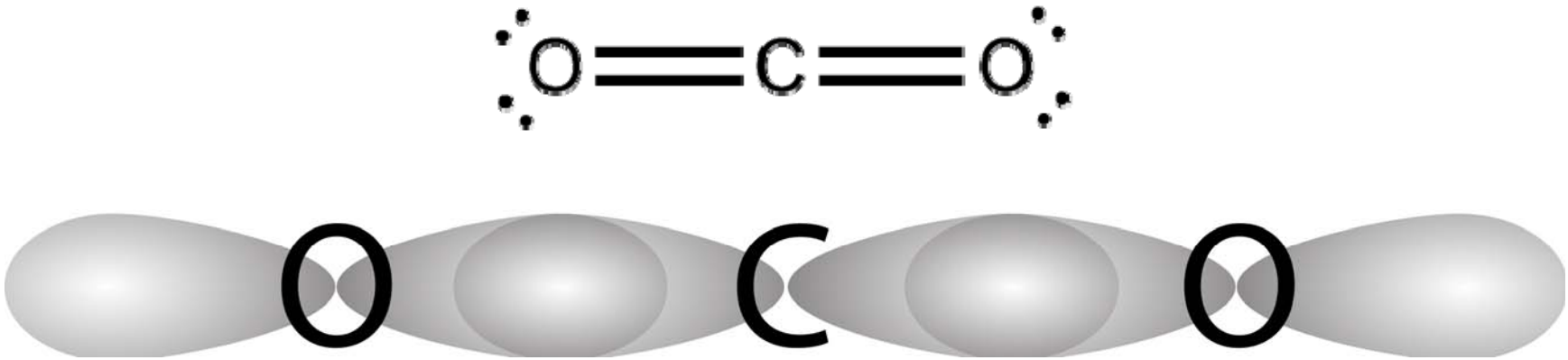
Polyatomic MO recipe

1. Use the Lewis structure to get
   - the *number of electron pairs*
   - make *hybrid AO's* on each atom (except H)
2. Sketch the *σ framework* and *place pairs*
   - in each *bonding σ MO*
   - in each *nonbonding hybrid AO*
3. Sketch the *π framework MO's*,
   - mark as *bonding, nonbonding, antibonding*
   - place *remaining pairs* (Auf Bau)
   - get the *π bond order*

σ framework

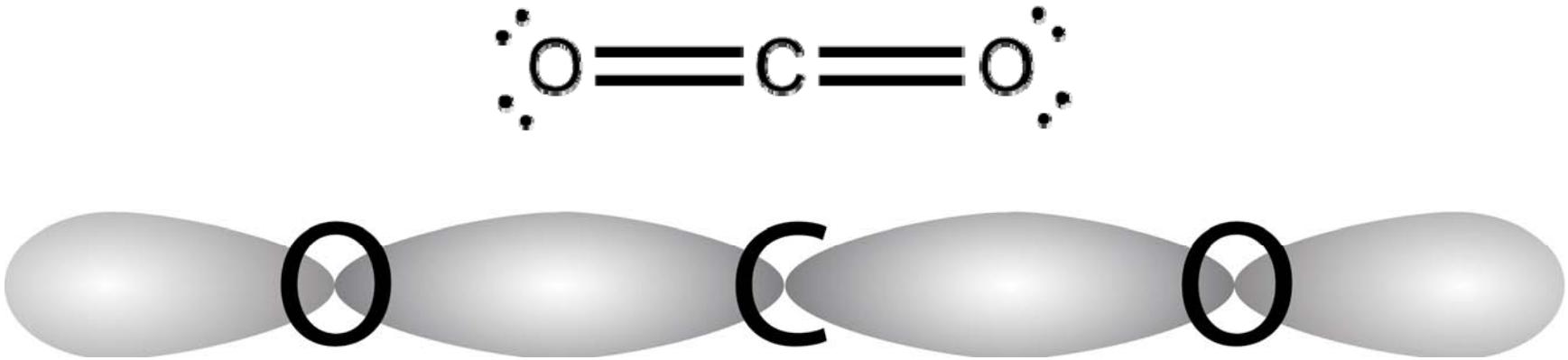
- Hybridization of *terminal atoms* the *same as their central atom*
- Terminal H *never hybridized*
- One pair in each hybrid AO *σ bonding MO*
- One pair in each *non-bonded hybrid AO*

CO_2 sp σ framework



sp hybrids overlap to make
two sp σ bonding MO's,
leaving *two sp nonbonding AO's*.
These can hold …

CO_2 sp σ framework



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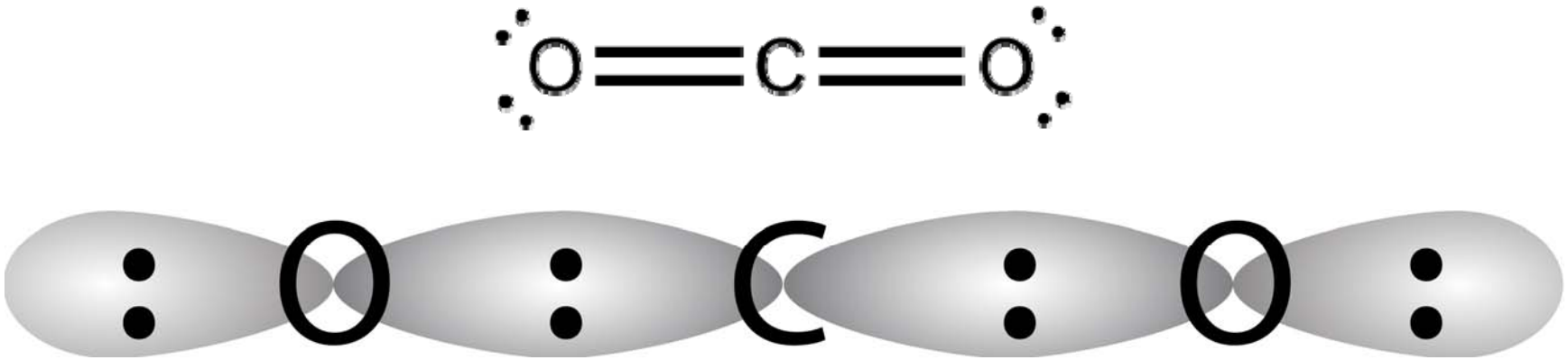
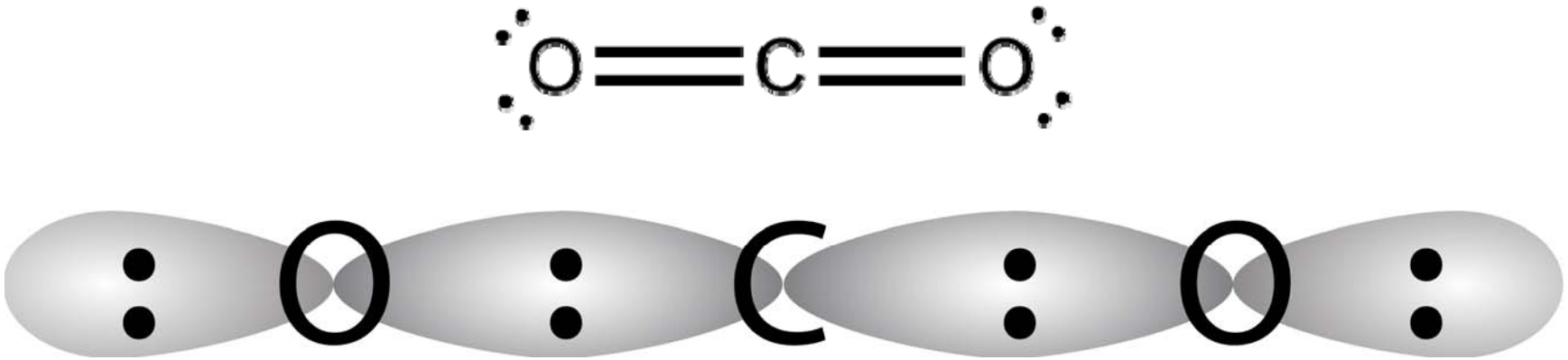


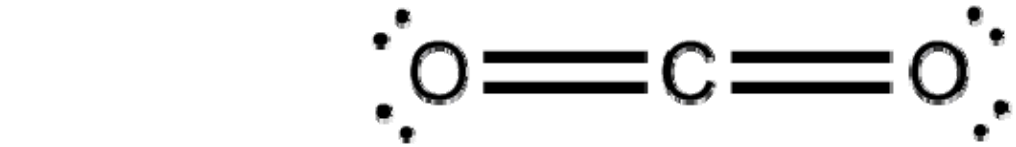
sp hybrids overlap to make
two sp σ bonding MO's,
leaving *two sp nonbonding AO's*.
These can hold *4 pairs of electrons*.

CO_2 sp σ framework



sp hybrids overlap to make
two sp σ bonding MO's,
leaving *two sp nonbonding AO's*.
These can hold *4 pairs of electrons*.
The remaining *4 pairs are* in the …

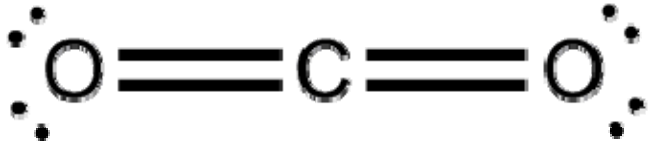
CO_2 π framework



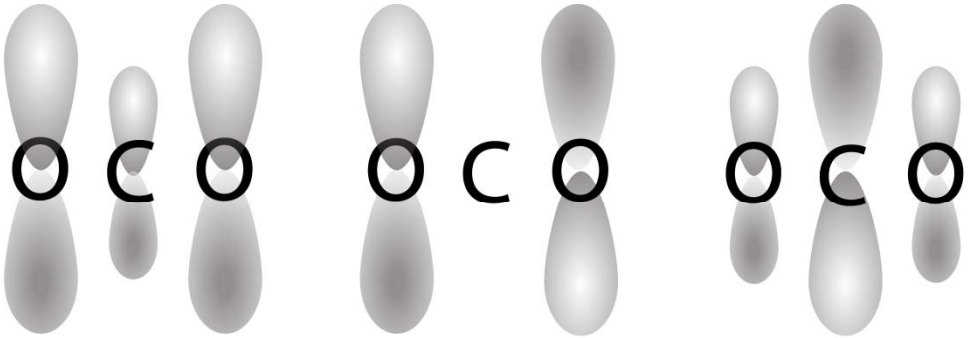
π framework

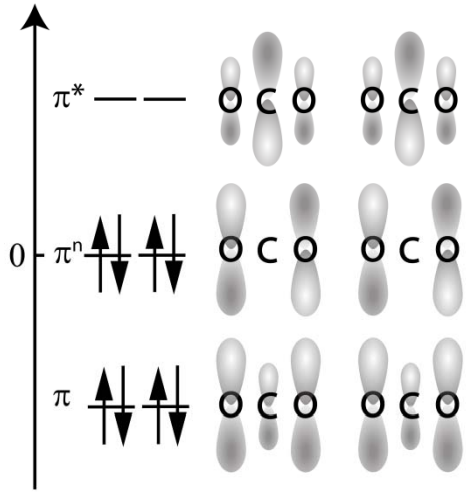
- Unused p AO's form *same number* of π *MO's*
- *Number of loops* and *AO overlap* determine whether π MO is …
  - *bonding* (π)
  - *nonbonding* (π^n)
  - *antibonding* (π*)

CO_2 π framework



4 pairs are in the (*delocalized*) π framework



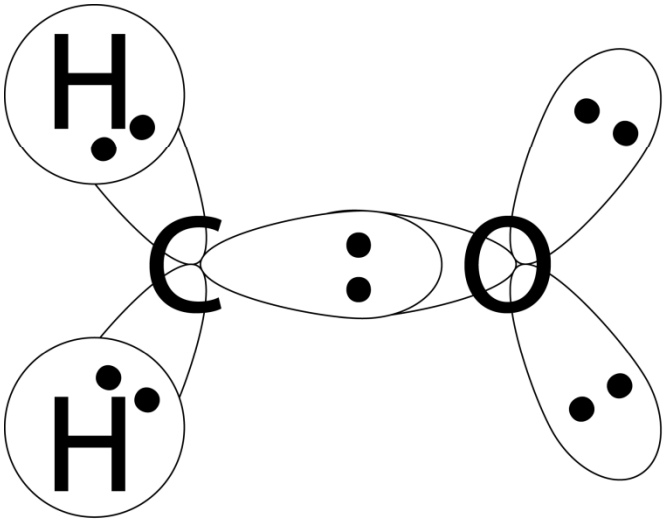


2 pairs in π (bonding) and 2 pairs in π^n (nonbonding);

bond order 2

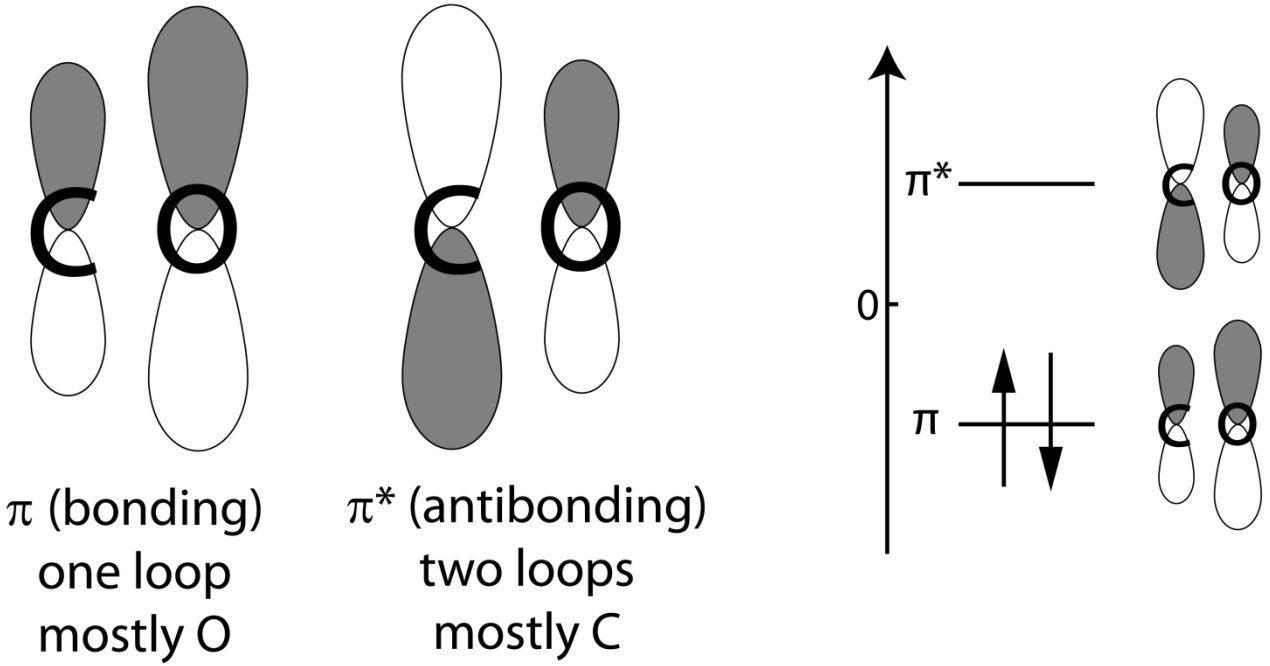
H_2CO sp^2 σ framework

6 pairs in Lewis structure, 5 pairs in σ framework, and so 1 pair in (*localized*) π framework.



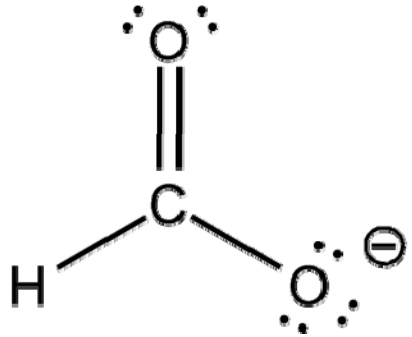
H_2CO π framework

1 pair in (*localized*) π framework

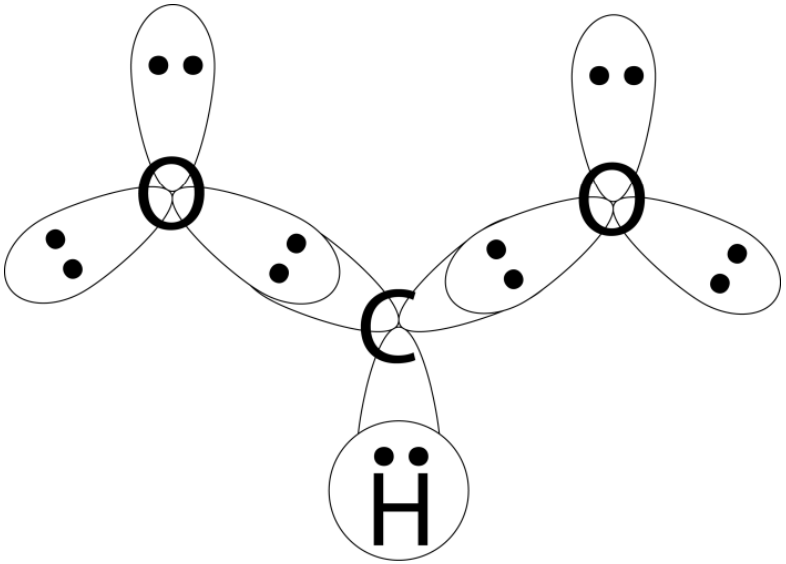


1 pair in π (bonding); *bond order 1*

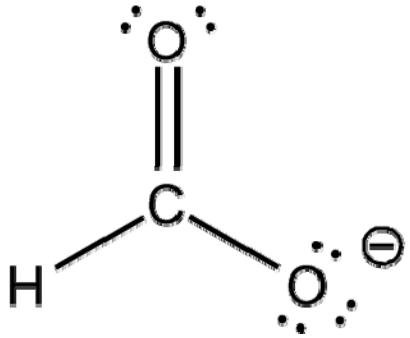
$HCOO^-$ sp^2 σ framework



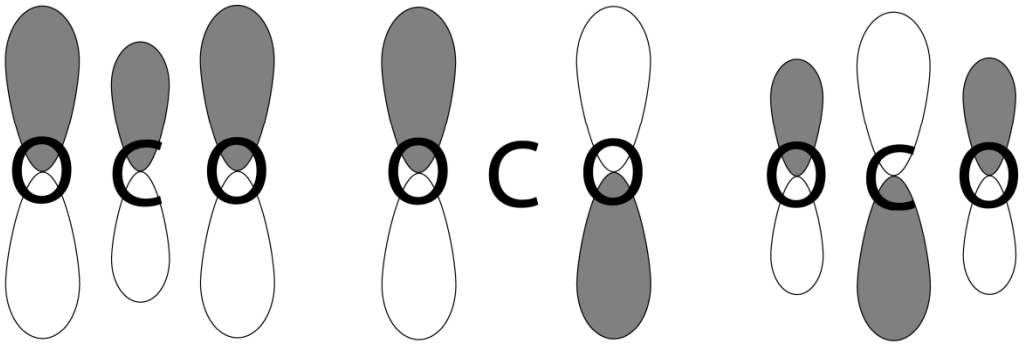
9 pairs in Lewis structure, 7 pairs in σ framework, and so 2 pairs in (*delocalized*) π framework.

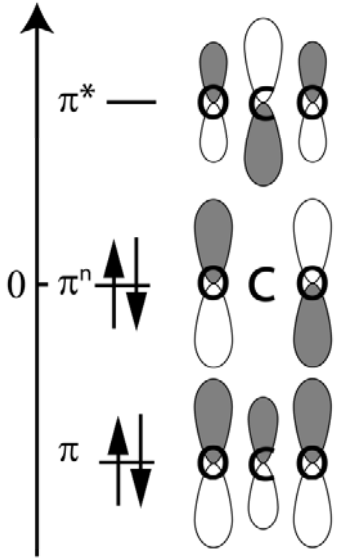


$HCOO^-$ π framework



2 pairs in (*delocalized*) π framework



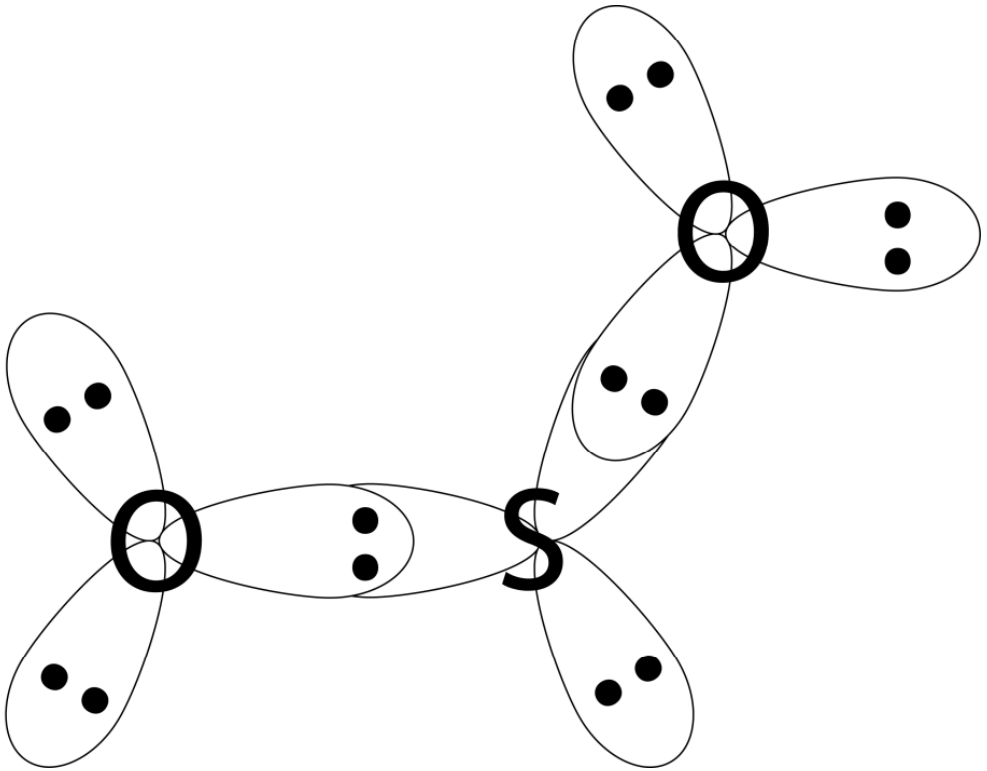


1 pair in π (bonding) and 1 pair in π^n (nonbonding);

bond order 1

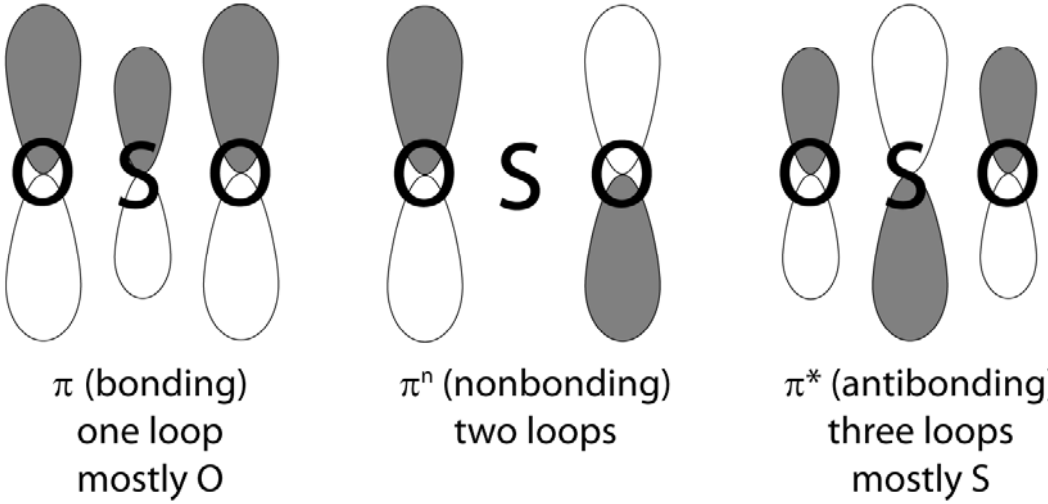
SO_2 sp^2 σ framework

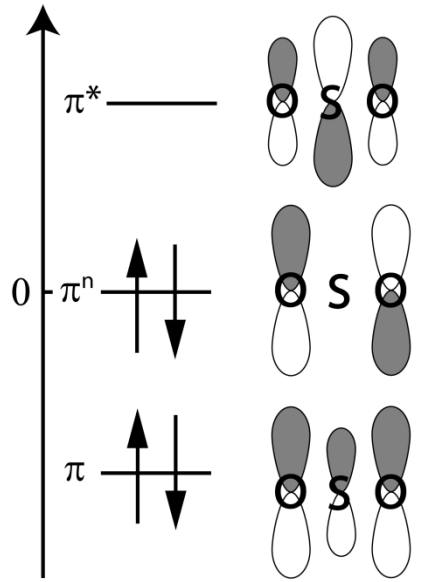
9 pairs in Lewis structure, 7 pairs in σ framework, and so 2 pairs in (*delocalized*) π framework.



SO_2 π framework

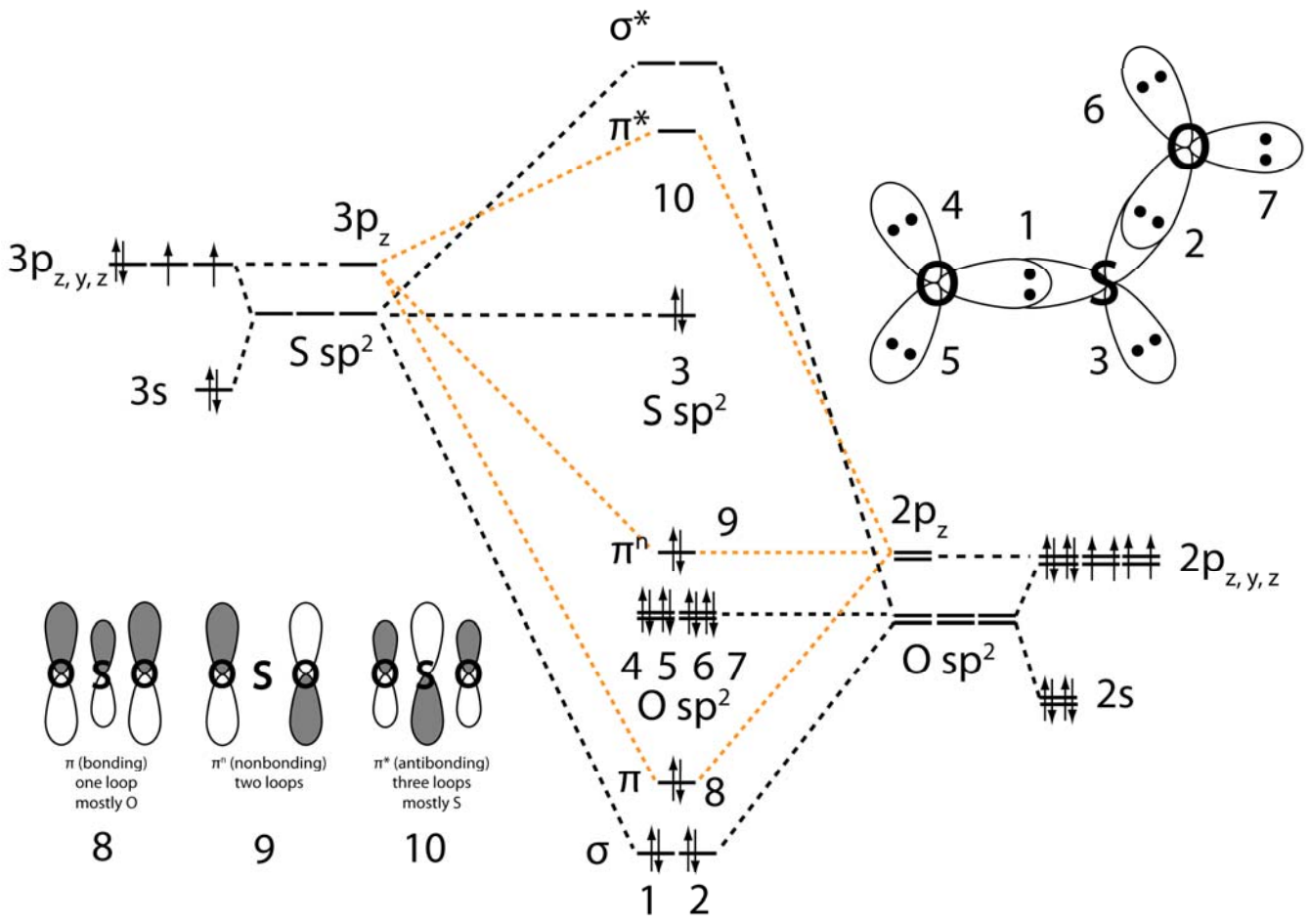
2 pairs in (*delocalized*) π framework





1 pair in π (bonding) and 1 pair in π^n (nonbonding);
bond order 1

SO_2 correlation diagram



Do these on your own

HCOOH, formic acid

$H_2C=CH-CH=CH_2$

NO_3^-, nitrate

For each one,

- Write the Lewis structure
- Sketch the σ framework and assign its pairs
- Sketch the π framework MO's, identify bonding, nonbonding, antibonding, and assign its pairs, and get the π bond order