Hybrid AO's and polyatomic MO's

CH101 Fall 2012

Boston University

BOSTON UNIVERSITY

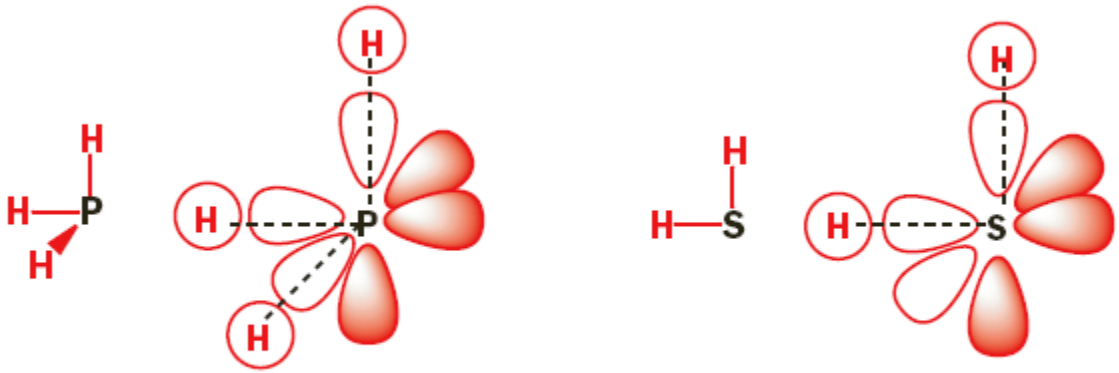
Figures on slides 4-9 are used with permission from Clayden et al., Organic Chemistry (Oxford University Press, 2000), © 2007 Oxford University Press.

Figures on slides 23, 25 and 39 are used with permission from Mahaffy et al., Chemistry: Human Activity, Chemical Reactivity (Nelson, 2011), © 2011 Nelson Education Ltd.

Hybridized AO's
account for central atom
electron-pair geometry

Central atom AO mixing: Hybrid AO's

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

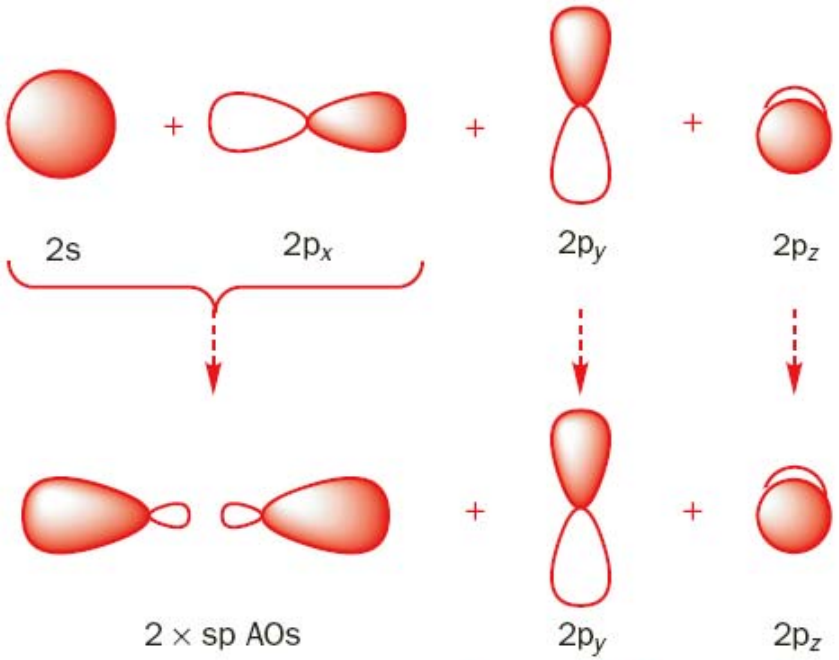


the 90° angles in PH_3 and H_2S come from the overlap of the hydrogen 1s AO with the p AO of the phosphorus or sulfur

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

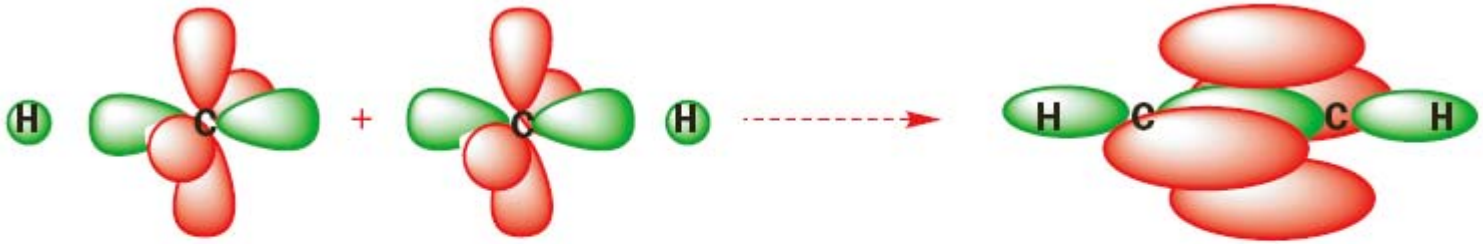


BOSTON UNIVERSITY

sp hybrids account for **linear geometry**

180^{o} angle, for SN = 2

Two p's are unchanged on each atom



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

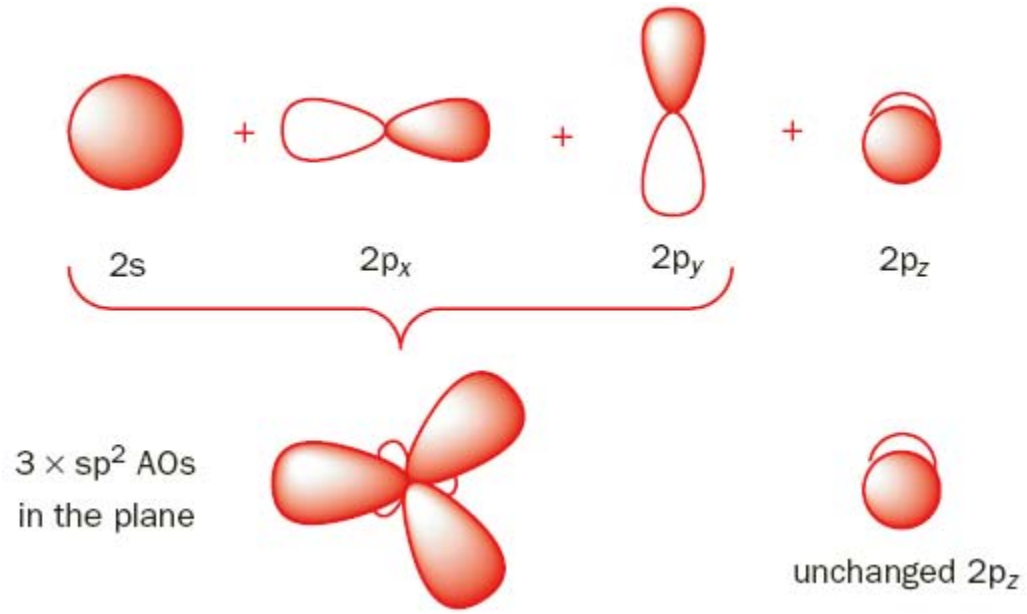
linear σ bonds form skeleton
two perpendicular π bonds

H—C≡C—H

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

120° angle, for SN = 3

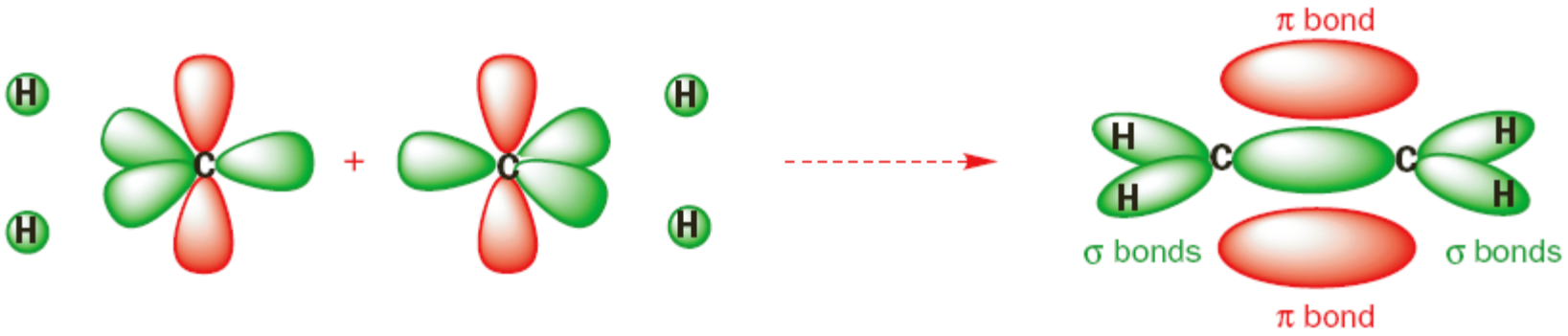
One p is unchanged on each atom



sp^2 hybrids account for **trigonal planar geometry**

120^o angle, for SN = 3

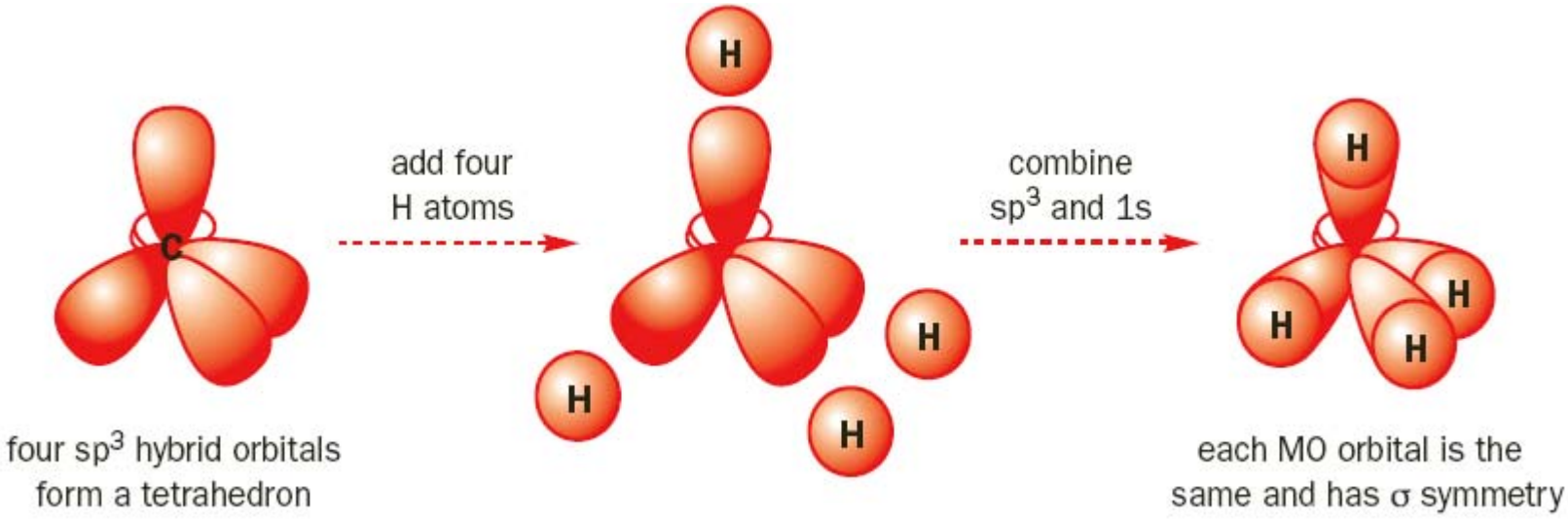
One p is unchanged on each atom



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

109^o angle, for SN = 4

sp^3 hybrids account for **tetrahedral geometry**



Which hybridization to use?

steric number → **electron-pair geometry** → hybridization

steric number = **attached atoms** + **lone pairs**

	steric number	electron-pair geometry	hybridization	molecular geometry
H_2O	4	tetrahedral	sp^3	bent at 109˚
NH_3	4	tetrahedral	sp^3	trigonal pyramidal
CH_4	4	tetrahedral	sp^3	tetrahedral
SO_2	3	trigonal planar	sp^2	bent at 120˚
BH_3	3	trigonal planar	sp^2	trigonal planar
CO_2	2	linear	sp	linear at 180˚

BOSTON UNIVERSITY

Examples

CO_2, carbon dioxide

H_2CO, formaldehyde

HCO_2^-, formate

SO_2, sulfur dioxide

Polyatomic MO recipe

Overview

- **σ framework** of **single bonds and lone pairs**
- **π framework** of **additional bond pairs**
- **π framework** can be **delocalized** (spread) over more than two atoms.

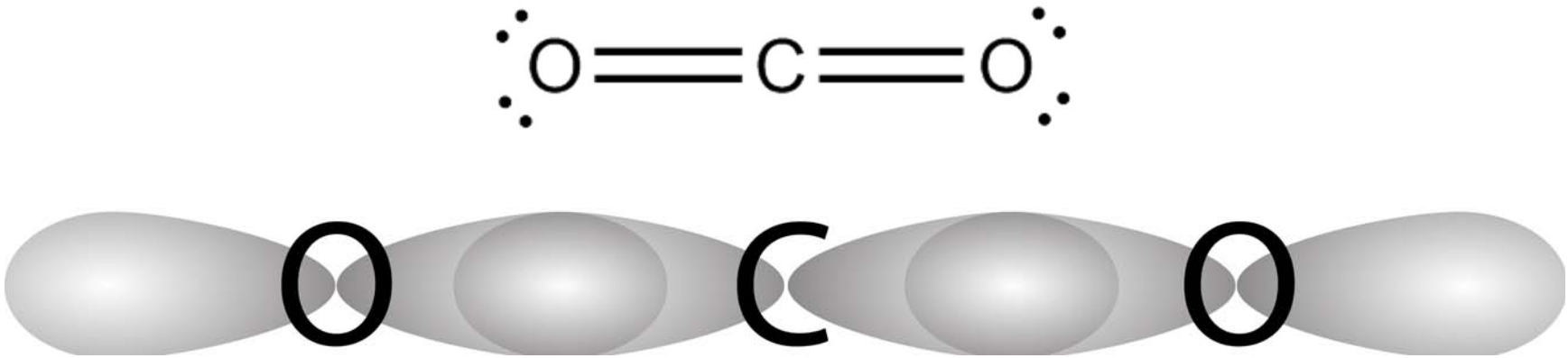
Polyatomic MO recipe

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 recipe

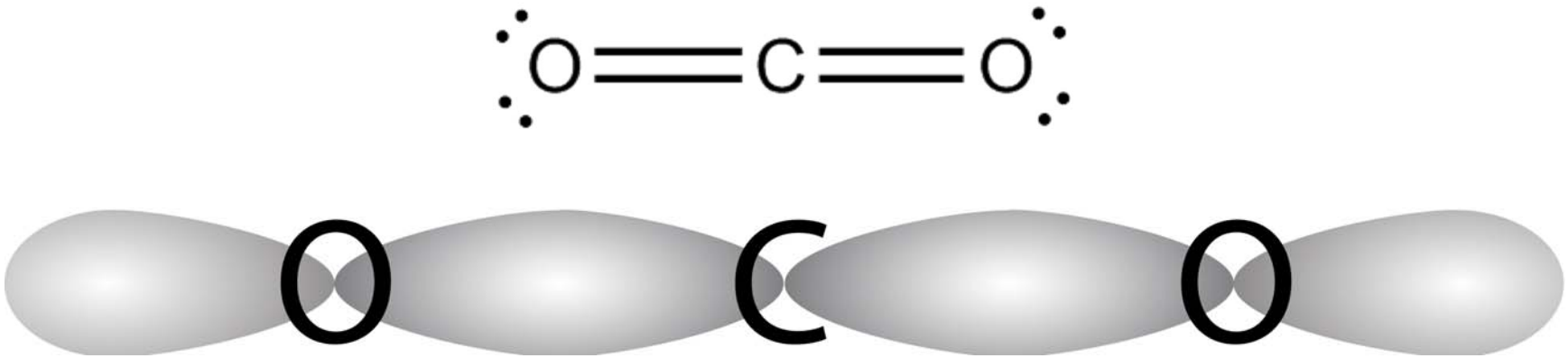
- Hybridization of **terminal atoms** the **same as their central atom**
- Terminal H **never hybridized**
- One pair in each hybrid AO **σ bonding MO**
- One pair in each **non-bonded hybrid AO**

CO_2 sp σ framework



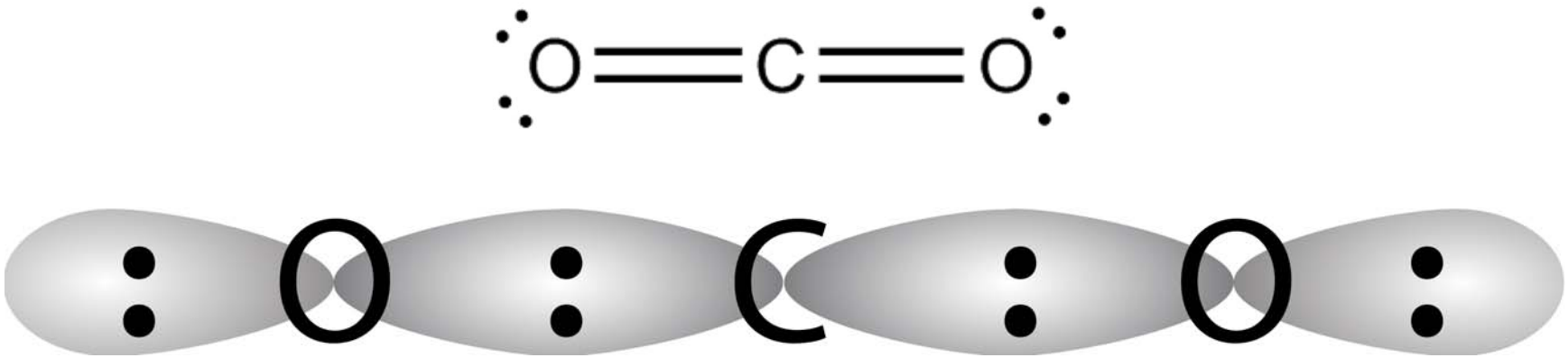
sp hybrids overlap to make
two sp σ bonding MO's,
leaving **two sp nonbonding AO's**.
These can hold …

CO_2 sp σ framework



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

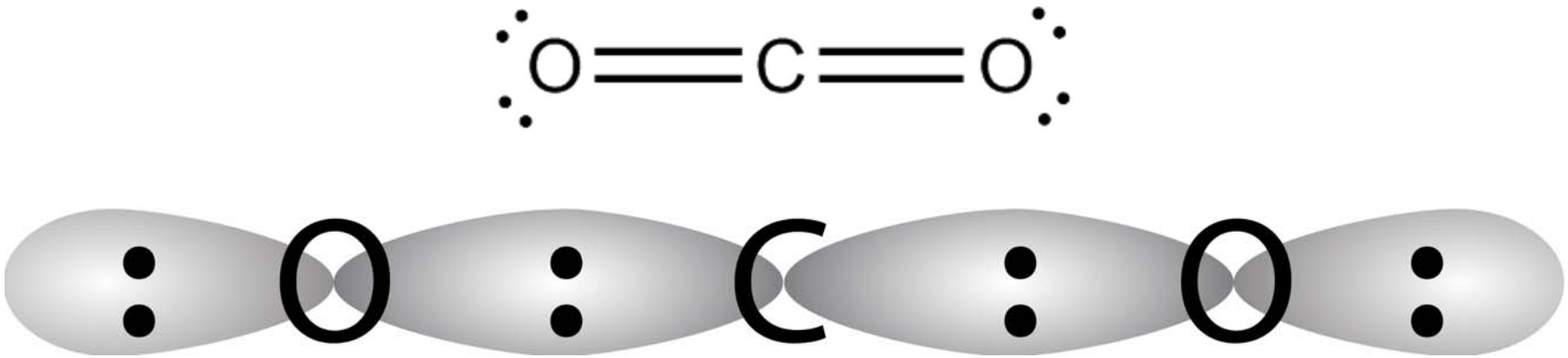
CO_2 sp σ framework



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

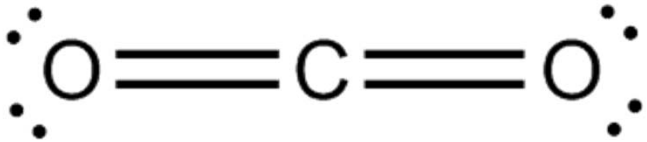
BOSTON UNIVERSITY

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 …

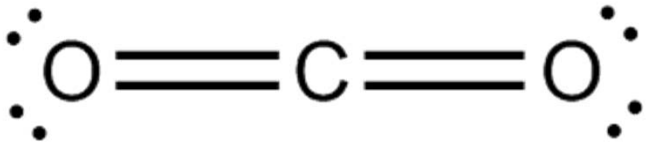
CO_2 π framework



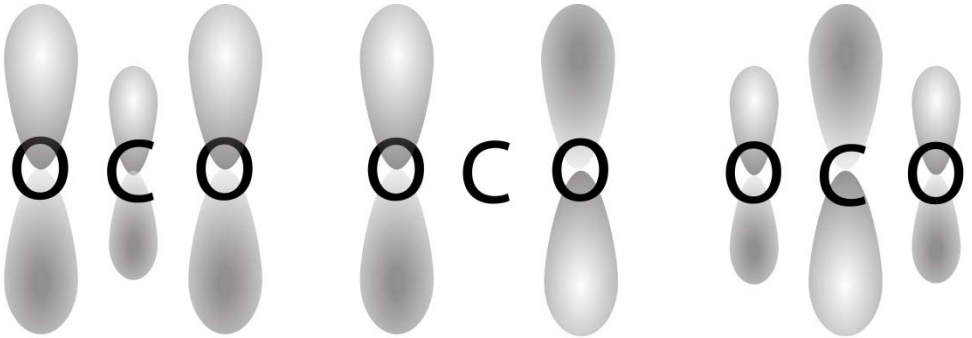
π framework recipe

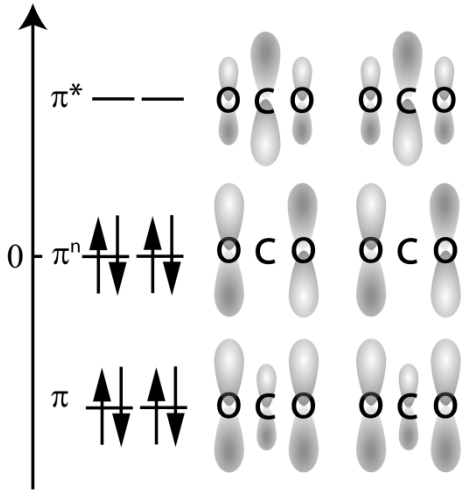
- Unused p AO's form **same number** of **π MO's**
- **Number of loops** and **AO overlap** determine whether π MO is …
  - **bonding (π)**
  - **nonbonding (π^n)**
  - **antibonding (π*)**

CO_2 π framework



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



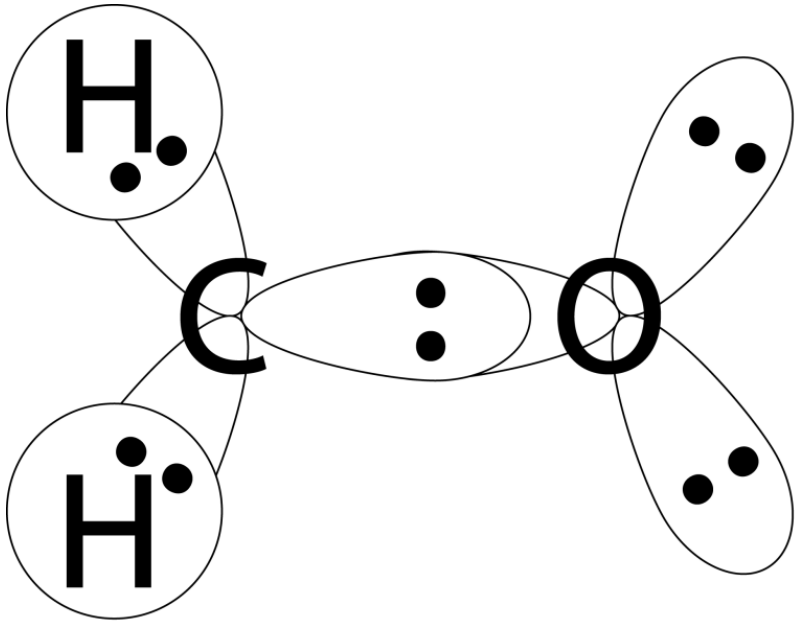


2 pairs in π (bonding) and 2 pairs in π^n (nonbonding);

bond order 2

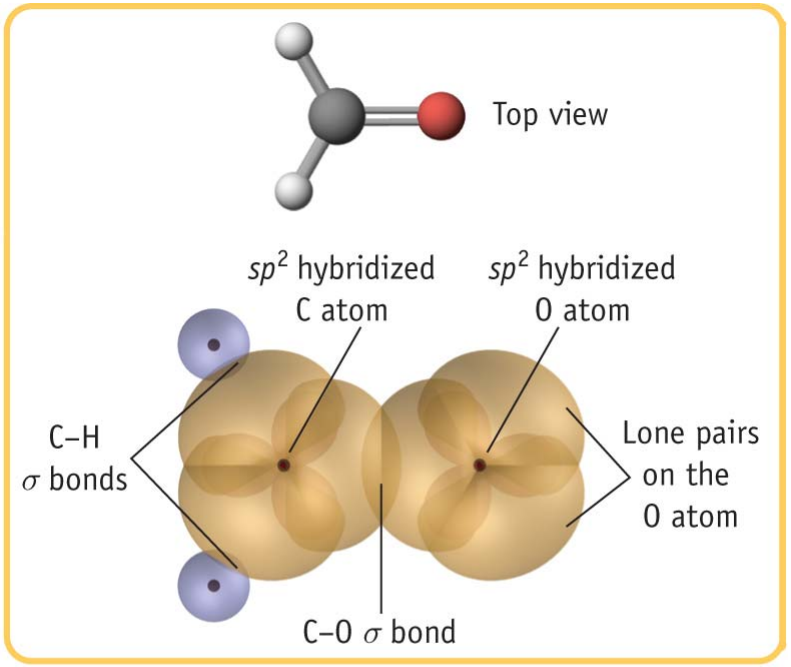
H_2CO sp^2 σ framework

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



H_2CO sp^2 σ framework

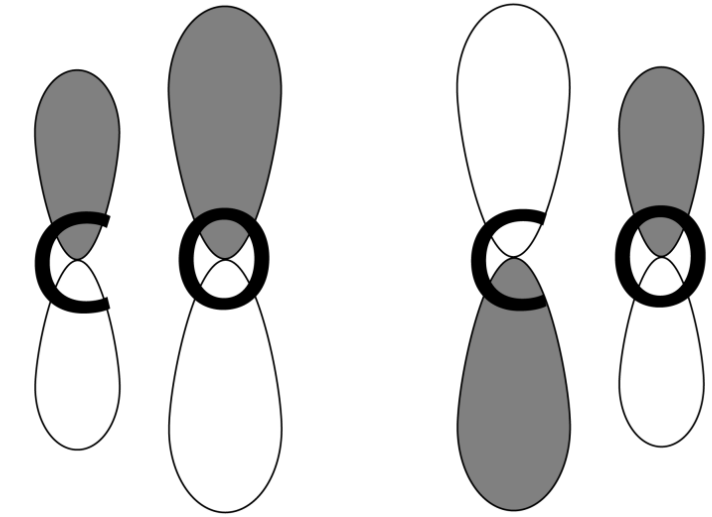
6 pairs in Lewis structure, 5 pairs in σ framework, and so 1 pair in (**localized**) π framework.



(b) The C–H σ bonds are formed by overlap of C atom sp^2 hybrid orbitals with H atom 1*s* orbitals. The σ bond between C and O atoms arises from overlap of sp^2 orbitals.

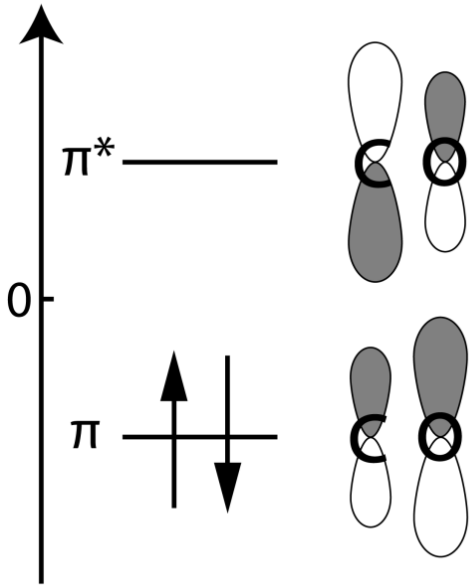
H_2CO π framework

1 pair in (**localized**) π framework



π (bonding)
one loop
mostly O

π* (antibonding)
two loops
mostly C

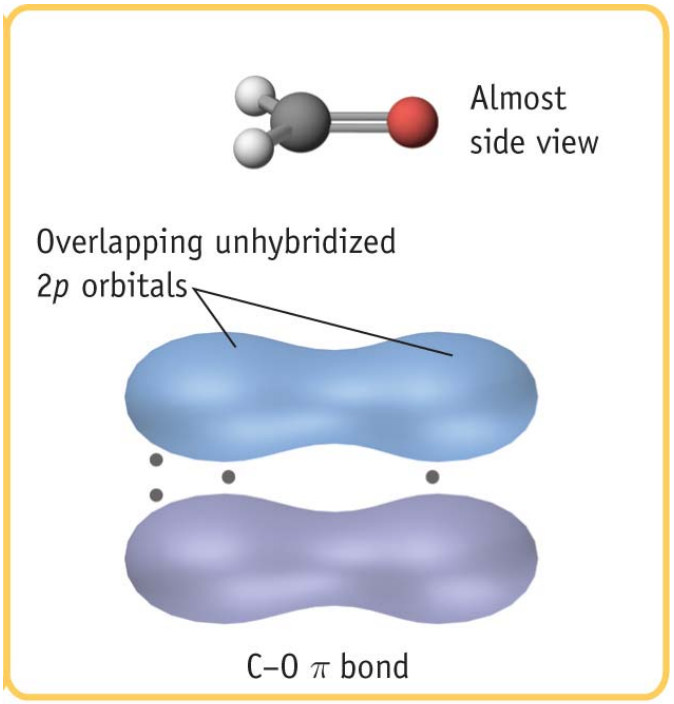


1 pair in π (bonding); **bond order 1**

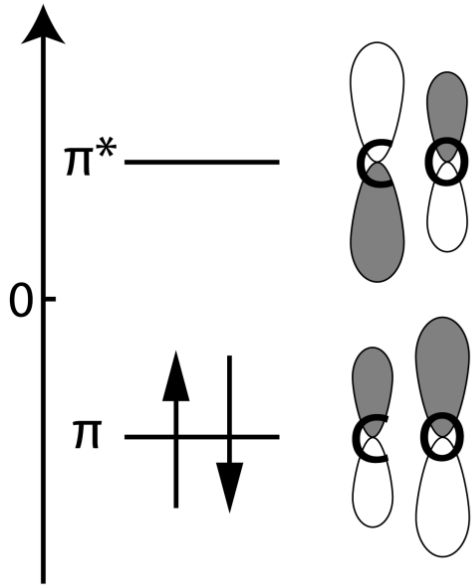
BOSTON UNIVERSITY

H_2CO π framework

1 pair in (**localized**) π framework

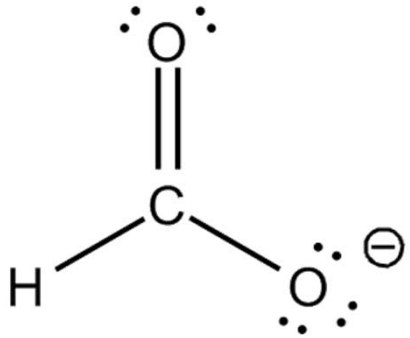


(c) The C–O π bond comes from the sideways overlap of *p* orbitals on the two atoms.

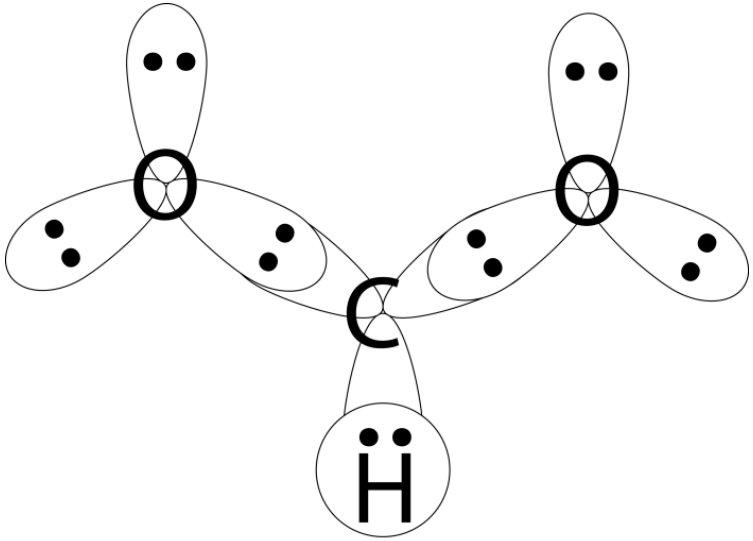


1 pair in π (bonding); **bond order 1**

$HCOO^-$ sp^2 σ framework

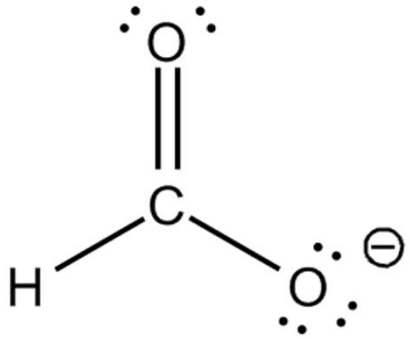


9 pairs in Lewis structure, 7 pairs in σ framework, and so 2 pairs in (**delocalized**) π framework.

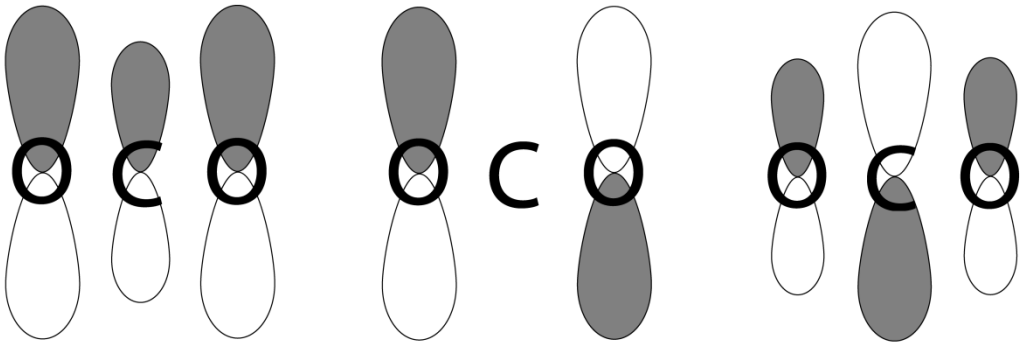


BOSTON UNIVERSITY

$HCOO^-$ π framework



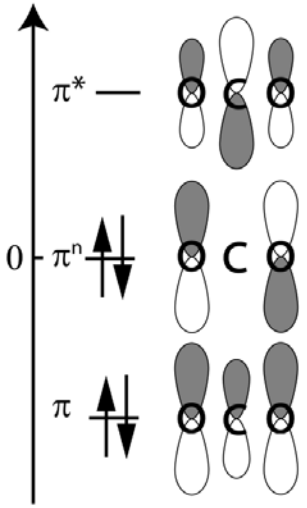
2 pairs in (**delocalized**) π framework



π (bonding)
one loop
mostly O

π^n (nonbonding)
two loops

π* (antibonding)
three loops
mostly C

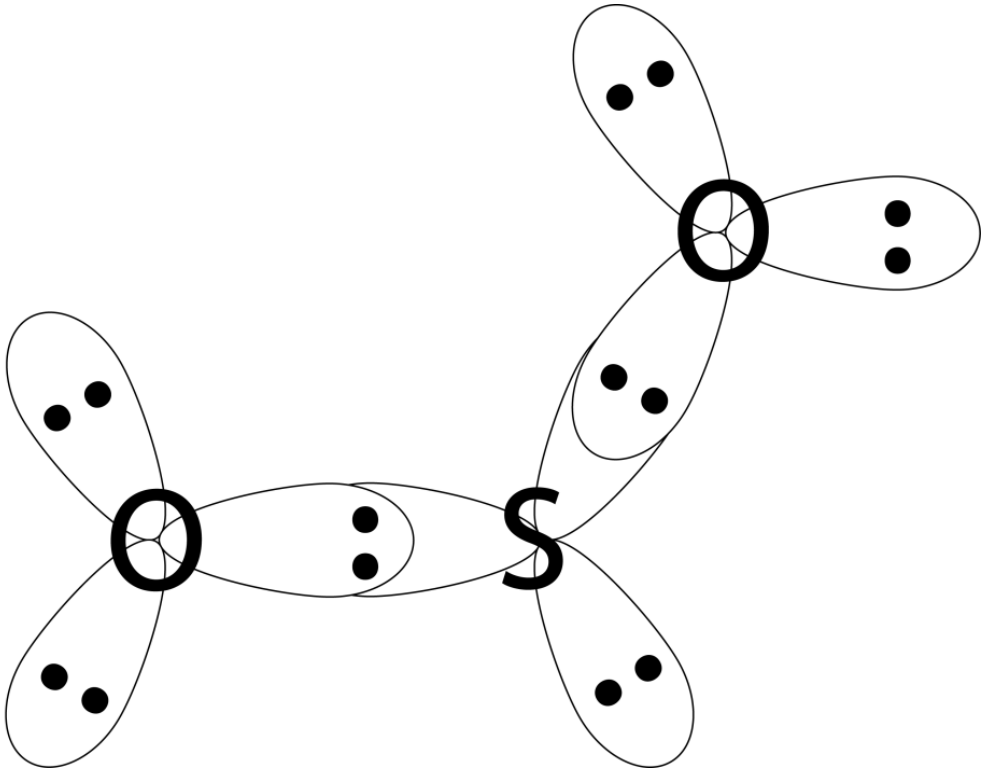


1 pair in π (bonding) and 1 pair in π^n (nonbonding);

bond order 1

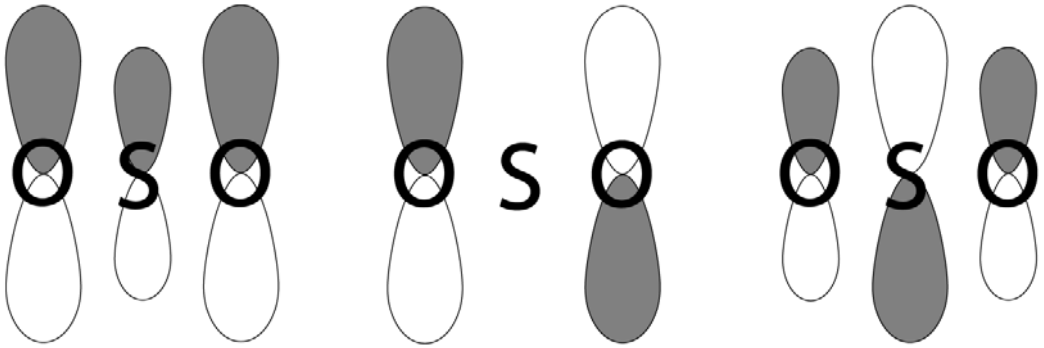
SO_2 sp^2 σ framework

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



SO_2 π framework

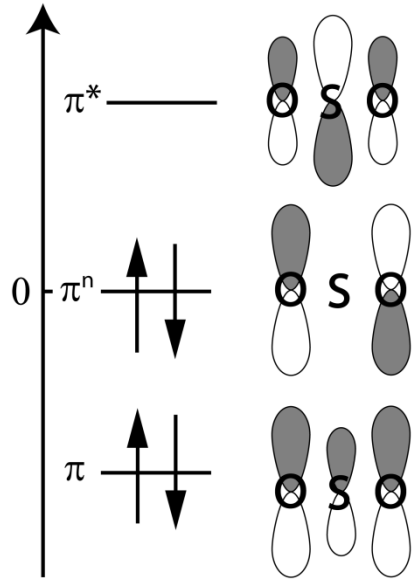
2 pairs in (**delocalized**) π framework



π (bonding)
one loop
mostly O

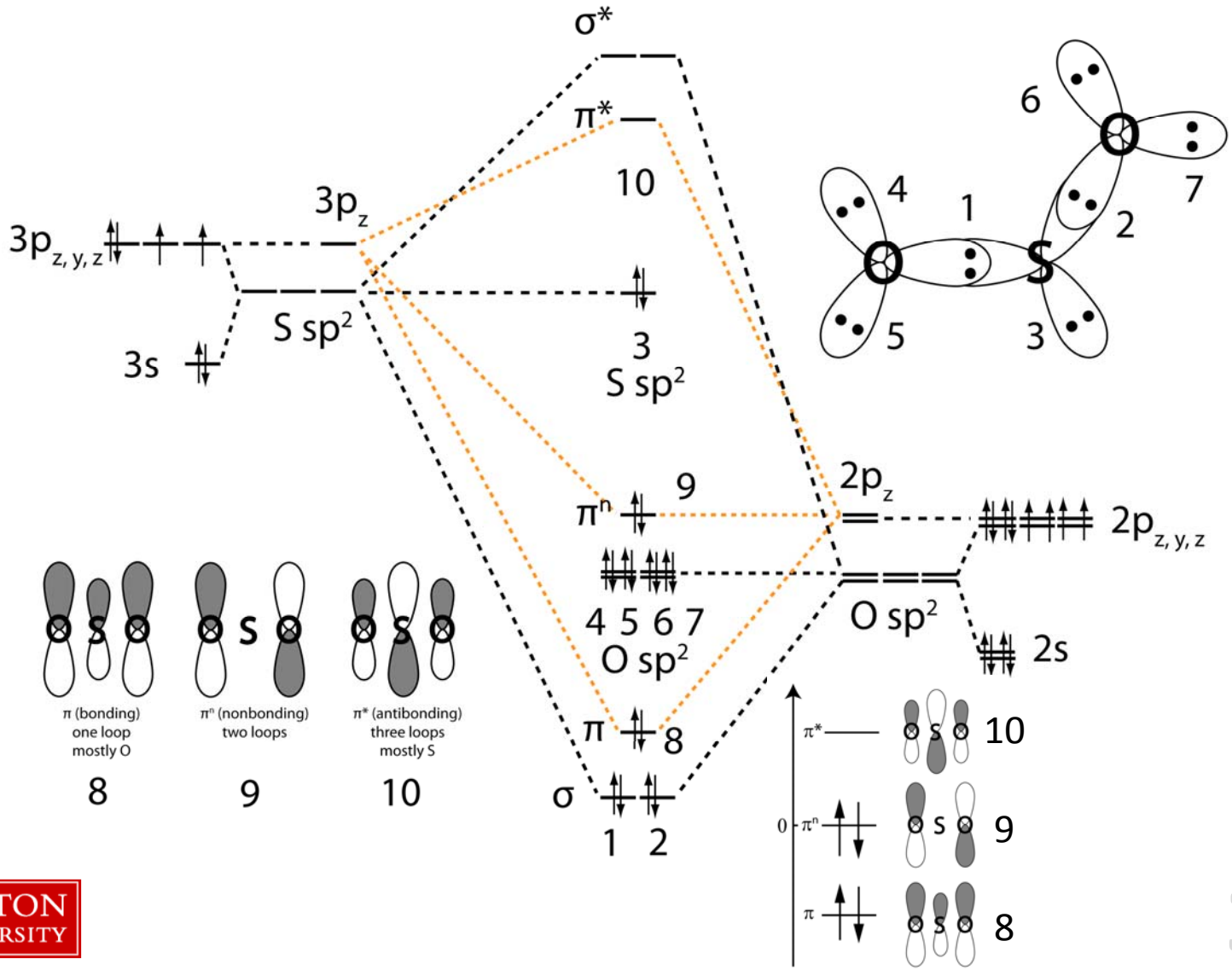
π^n (nonbonding)
two loops

π* (antibonding)
three loops
mostly S



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

allyl: $[H_2C{=}CH{-}CH_2]^-$, anion; $[H_2C{=}CH{-}CH_2]^+$, cation

$H_2C{=}C{=}CH_2$, allene

$H_2C{=}CH{-}CH{=}CH_2$, 1,3-butadiene

O_3, ozone

For each one,

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

HCOOH, formic acid

Formate, $HCOO^-$ π , is planar and has

- 9 pairs
- 7 pairs in **σ framework**
- 1 pair in a **delocalized bonding π_1** orbital
- 1 pair in a **delocalized nonbonding π_2^n** orbital

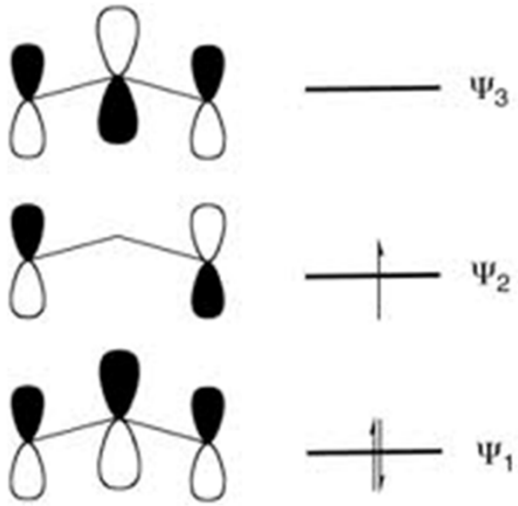
What about formic acid?

- 9 pairs
- 8 pairs in **σ framework**
- 1 pair in **localized bonding π_1** orbital

$H_2C{=}CH{-}CH_2$, allyl (radical)

What about allyl? Use $-CH_2$ sp^2, to have **increased delocalization**:

- 8 ½ pairs
- 7 pairs in **σ framework**
- 1 pair in **delocalized bonding π_1** orbital
- ½ pair (1 electron) in **delocalized nonbonding π_2^n** orbital



BOSTON UNIVERSITY

$[H_2C{=}CH{-}CH_2]^+$, allyl cation

What about allyl cation?

- 8 pairs
- 7 pairs in **σ framework**
- 1 pair in **delocalized bonding π_1** orbital

$[H_2C{=}CH{-}CH_2]^-$, allyl anion

What about allyl anion? If $-CH_2$ is sp^3, then

- 9 pairs
- 8 pairs in **σ framework**
- 1 pair in **localized bonding π_1** orbital

If $-CH_2$ is sp^2, then

- 7 pairs in **σ framework**
- 1 pair in **delocalized bonding π_1** orbital
- 1 pair in **delocalized nonbonding π_2^n** orbital

Increased delocalization makes $-CH_2$ is sp^2 more stable (extension to recipe)

$H_2C=C=CH_2$, allene

What about allene?

- 8 pairs
- 6 pairs in **σ framework**
- 2 pair in **two localized bonding π_1** orbitals

$H_2C{=}CH{-}CH{=}CH_2$, 1,3-butadiene

What about 1,3-butadiene?

- 11 pairs
- 9 pairs in **σ framework**
- 1 pair in **delocalized bonding π_1** orbital
- 1 pair in **delocalized bonding π_2** orbital

O_3, ozone

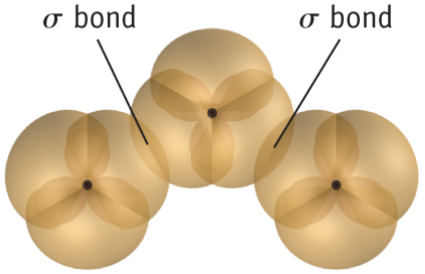
What about ozone?

- 9 pairs
- 7 pairs in **σ framework**
- 1 pair in **delocalized bonding π_1** orbital
- 1 pair in **delocalized nonbonding π_2^n** orbital

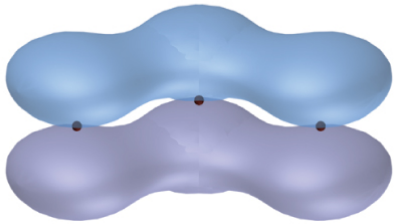
Ozone is polar. Why?

The two electrons in the nonbonding MO are **each only on the terminal O's**!

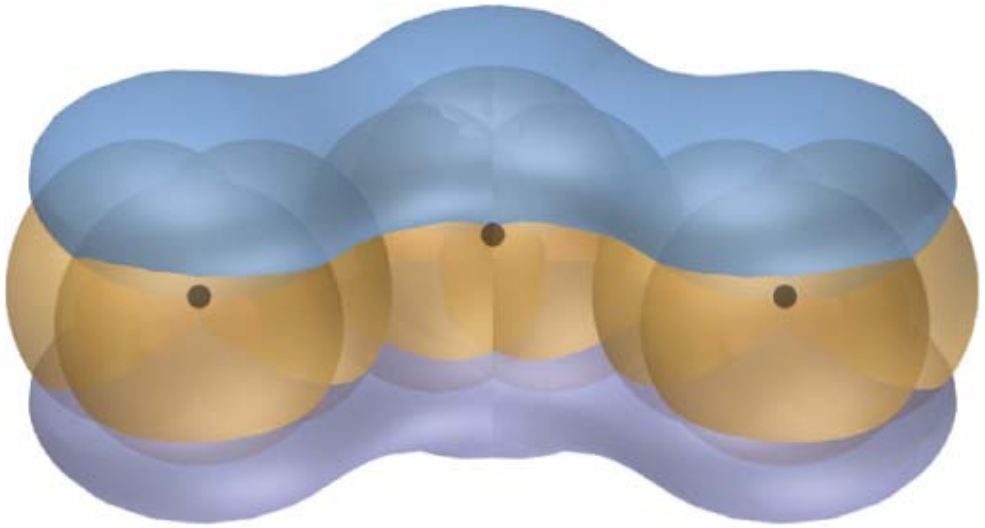
O_3 ozone σ and π frameworks



A representation of the sigma bonding framework of O_3 using sp^2 hybrid orbitals.



Bonding π orbital



σ and π bonding in ozone