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 $90^\circ$ angles in PH$_3$ and H$_2$S 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
2$p_x$ and 2$p_z$ orbitals remain

linear $\sigma$ bonds form skeleton
two perpendicular $\pi$ bonds

\[ \text{H—C≡C—H} \]
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

$109^\circ$ angle, for $SN = 4$

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

four $sp^3$ hybrid orbitals form a tetrahedron

add four H atoms

combine $sp^3$ and 1s

each MO orbital is the same and has $\sigma$ symmetry
Examples

CO$_2$, carbon dioxide
H$_2$CO, 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*
$\text{CO}_2 \text{ sp sp } \sigma$ framework

sp hybrids overlap to make two $sp \sigma$ bonding MO’s,
leaving two $sp$ nonbonding AO’s.
These can hold ...
sp hybrids overlap to make *two sp σ bonding MO’s*, leaving *two sp nonbonding AO’s*. These can hold …
$\text{CO}_2 \text{ sp } \sigma \text{ framework}$

sp hybrids overlap to make

*two sp $\sigma$ bonding MO’s,*

leaving *two sp nonbonding AO’s.*

These can hold *4 pairs of electrons.*
CO$_2$ sp $\sigma$ framework

sp hybrids overlap to make 
*two sp $\sigma$ bonding MO’s*,
leaving *two sp nonbonding AO’s*. 
These can hold *4 pairs of electrons*.  
The remaining *4 pairs are in the ...*
$\text{CO}_2 \pi$ framework

\begin{center}
\begin{tikzpicture}
\draw (0,0) -- (1,0) -- (1.5,0.5) -- (1,1) -- (0,1) -- (0,0);
\end{tikzpicture}
\end{center}
\pi \text{ framework}

• Unused \(p\) AO’s form \textit{same number} of \(\pi\) MO’s

• \textit{Number of loops} and AO overlap determine whether \(\pi\) MO is ...
  – \textit{bonding} (\(\pi\))
  – \textit{nonbonding} (\(\pi^n\))
  – \textit{antibonding} (\(\pi^*\))
$\text{CO}_2 \pi$ framework

4 pairs are in the (delocalized) $\pi$ framework

2 pairs in $\pi$ (bonding) and 2 pairs in $\pi^*$ (nonbonding); bond order 2
$\text{H}_2\text{CO}$ sp$^2$ $\sigma$ framework

6 pairs in Lewis structure, 5 pairs in $\sigma$ framework, and so 1 pair in (localized) $\pi$ framework.
H₂CO 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*
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 πⁿ (nonbonding);

*bond order 1*
SO$_2$ sp$^2$ $\sigma$ framework

9 pairs in Lewis structure, 7 pairs in $\sigma$ framework, and so 2 pairs in (delocalized) $\pi$ framework.
$\text{SO}_2 \pi$ framework

2 pairs in \textit{(delocalized)} $\pi$ framework

1 pair in $\pi$ (bonding) and 1 pair in $\pi^n$ (nonbonding);
\textit{bond order 1}
SO$_2$ correlation diagram
Do these on your own

HCOOH, formic acid
H₂C=CH-CH=CH₂
NO₃⁻, 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