MX\textsubscript{n} Molecules with Pi-Bonding

✓ BeH\textsubscript{2} and CH\textsubscript{4} do not have pi bonding, because the 2\textit{p} orbitals on hydrogen lie too high in energy for effective overlap with central atom AOs.

✓ Pi bonding \textit{may} be possible with pendant atoms from the second and higher periods.

☞ Consider pi bonding in CO\textsubscript{2}.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]
Simple VB Model of $\text{CO}_2$

- Carbon 1s is assumed not to be involved in bonding (i.e., core electrons).
- Carbon is assumed to be $sp$ hybridized, using 2s and 2$p_z$ orbitals.
- Pendant oxygen 2s orbitals are assumed to be nonbonding.
- Sigma-bonding interactions are between oxygen 2$p_z$ orbitals and carbon $sp$ hybrids.
- Pi-bonding interactions are between oxygen 2$p_x$ or 2$p_y$ orbitals with “empty” 2$p$ orbitals of the same kinds on the central carbon.
Implied Localized MO Model

\[ \left[ (\sigma_a)^2 (\sigma_b)^2 \right] \left[ (\pi_a)^2 (\pi_b)^2 \right] \left[ (\sigma_a^n)^2 (\sigma_b^n)^2 \right] \left[ (\pi_a^n)^2 (\pi_b^n)^2 \right] \]
CO$_2$ General MO Model

Starting Assumptions

1. Only 2s and 2p orbitals on C are used in bonding. The 1s orbital will be a "core" non-bonding level in the MO scheme.

2. Only the 2p orbitals on the two O atoms are used in bonding. The two 2s orbitals are assumed to form a pair of nonbonding MOs:

\[
\sigma^n_g = \frac{1}{\sqrt{2}} (2s_a + 2s_b)
\]

\[
\sigma^n_u = \frac{1}{\sqrt{2}} (2s_a - 2s_b)
\]

These assumptions will need to be examined in light of experimental data, once the MO scheme has been constructed.
Vector Basis for a Representation of Oxygen SALCs
To avoid the problems of reducing a representation in the infinite-order group $D_{\infty h}$, we will construct the reducible representation for the oxygen SALCs in the finite-order subgroup $D_{2h}$.

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>$E$</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>$i$</th>
<th>$\sigma(xy)$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
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</thead>
<tbody>
<tr>
<td>$\Gamma_{SALC}$</td>
<td>6</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>$A_g$</td>
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<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
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<tr>
<td>$B_{1g}$</td>
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<td>0</td>
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<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>$B_{2g}$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>$B_{3g}$</td>
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<td>0</td>
<td>-2</td>
<td>2</td>
</tr>
<tr>
<td>$A_u$</td>
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<td>0</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>$B_{1u}$</td>
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<td>-2</td>
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<td>0</td>
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<td>0</td>
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<tr>
<td>$B_{2u}$</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>-2</td>
<td>2</td>
</tr>
<tr>
<td>$B_{3u}$</td>
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<td>2</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>-2</td>
</tr>
</tbody>
</table>

$\Gamma_{SALC} = A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ in $D_{2h}$

$\Gamma_{SALC} = \Sigma_g^+ + \Pi_g + \Sigma_u^+ + \Pi_u$ in $D_{\infty h}$

AOs on carbon:

$\Sigma_g^+ = 2s$ \hspace{1cm} $\Sigma_u^+ = 2p_z$ \hspace{1cm} $\Pi_u = (2p_x, 2p_y)$
CO$_2$ General MO Model

Sigma MOs

$\Sigma_{g^+}$: \[ \sigma_g(s) = c_1 2s + c_2 \left\{ \frac{1}{\sqrt{2}} \left[ 2p_z(a) + 2p_z(b) \right] \right\} \]

$\Sigma_{g^+}$: \[ \sigma_g^*(s) = c_3 2s - c_4 \left\{ \frac{1}{\sqrt{2}} \left[ 2p_z(a) + 2p_z(b) \right] \right\} \]

$\Sigma_{u^+}$: \[ \sigma_u(z) = c_5 2p_z + c_6 \left\{ \frac{1}{\sqrt{2}} \left[ 2p_z(a) - 2p_z(b) \right] \right\} \]

$\Sigma_{u^+}$: \[ \sigma_u^*(z) = c_7 2p_z - c_8 \left\{ \frac{1}{\sqrt{2}} \left[ 2p_z(a) - 2p_z(b) \right] \right\} \]
CO$_2$ General MO Model
Pi MOs

\[ \Pi_u: \quad \pi_u(x) = c_9 2p_x + c_{10} \left\{ \frac{1}{\sqrt{2}} \left[ 2p_x(a) + 2p_x(b) \right] \right\} \]

\[ \Pi_u: \quad \pi_u(y) = c_{11} 2p_y + c_{12} \left\{ \frac{1}{\sqrt{2}} \left[ 2p_y(a) + 2p_y(b) \right] \right\} \]

\[ \Pi_u: \quad \pi_u^*(x) = c_{13} 2p_x - c_{14} \left\{ \frac{1}{\sqrt{2}} \left[ 2p_x(a) + 2p_x(b) \right] \right\} \]

\[ \Pi_u: \quad \pi_u^*(y) = c_{15} 2p_y - c_{16} \left\{ \frac{1}{\sqrt{2}} \left[ 2p_y(a) + 2p_y(b) \right] \right\} \]
CO$_2$ General MO Model
Nonbonding Pi MOs

$\Pi_g$: 
$$\pi^n_g(x) = \frac{1}{\sqrt{2}}[2p_x(a) \ - \ 2p_x(b)]$$

$\Pi_g$: 
$$\pi^n_g(y) = \frac{1}{\sqrt{2}}[2p_y(a) \ - \ 2p_y(b)]$$
Qualitative Delocalized MO Scheme for CO$_2$

\[ \begin{align*}
\sigma_u^* \quad & \quad \sigma_g^* \\
\pi_u(x) \quad & \quad \pi_u(y) \\
\pi_u^*(x) \quad & \quad \pi_u^*(y) \\
\sigma_d(z) \quad & \quad \sigma_d(s) \\
\pi_d(x) \quad & \quad \pi_d(y) \\
\Sigma_u + \Pi_u \quad & \quad \Sigma_g + \Sigma_u + \Pi_g + \Pi_u \\
\Sigma_g + \Sigma_u + \Pi_g + \Pi_u \quad & \quad 2\Sigma_u + 2\Sigma_g + 2\Pi_u + 2\Pi_g \\
\Sigma_g + \Sigma_u \quad & \quad 2\Sigma_u + 2\Sigma_g
\end{align*} \]
CO$_2$ General MO Model
Predicted Electronic Configuration

\[
[\sigma_g^n]^2[\sigma_u^n]^2[\sigma_g(s)]^2[\sigma_u(z)]^2\{[\pi_u(x)]^2[\pi_u(y)]^2\} \{[\pi_g^n(x)][\pi_g^n(y)]^2\}
\]

In simplified notation:

\[
(\sigma_g^n)^2(\sigma_u^n)^2[\sigma_g(s)]^2[\sigma_u(z)]^2[\pi_u(x,y)]^4[\pi_g^n(x,y)]^4
\]
Four observed bands consistent with the electronic configuration from the MO scheme \((\sigma_g^n)^2(\sigma_u^n)^2[\sigma_g(s)]^2[\sigma_u(z)]^2[\pi_u(x,y)]^4[\pi_g^u(x,y)]^4\). (Core \((\sigma_g^n)^2(\sigma_u^n)^2\) configuration requires too high an ionization energy to be seen with u.v. P.E.S.)

- Lack of fine structure on first band is consistent with the nonbonding character of the configuration \([\pi_g^u(x,y)]^4\).
- Only the second band, due to \([\pi_u(x,y)]^4\), shows pronounced fine structure consistent with ejection of electrons from bonding MOs.
**s-p Mixing in CO₂**

✓ Lack of fine structure on bands due to ionizations from the lowest lying MOs with the configuration \( [\sigma_g(s)]^2[\sigma_u(z)]^2 \) suggests that they are virtually nonbonding.

✓ Nonbonding character of these MOs results from s-p mixing.
  - The SALCs formed by 2s orbitals on oxygen atoms, which we have assumed to be nonbonding core electrons, have the same symmetries as the SALCs formed from 2pz orbitals on the oxygen atoms; i.e., \( \Sigma_g^+, \Sigma_u^+ \).

  ![Diagram showing \( \Sigma_g^+ \) and \( \Sigma_u^+ \) SALCs]

  - On the basis of symmetry, these SALCs are as capable of forming MOs with like-symmetry AOs on carbon as the 2pz SALCs we used in our model.
  - The s- and p_z-SALCs mix, making the formerly nonbonding \( \sigma_g(O_{2s}) \) and \( \sigma_u(O_{2s}) \) SALCs lower in energy and more bonding in nature through overlap with carbon 2s and 2pz orbitals, respectively. These are now designated \([1\sigma_g]^2[1\sigma_u]^2\).
  - The formerly bonding MOs \( \sigma_g(s) \) and \( \sigma_u(z) \) move up in energy, becoming less bonding in character (more antibonding), and their configuration should be re-designated \([2\sigma_g^\pi]^2[2\sigma_u^\pi]^2\).

☞ Energy levels with the same symmetry in a molecular system repel one another, such that one level becomes lower energy (is stabilized) and the other level becomes higher energy (is destabilized).
Effect of $s$-$p$ Mixing on CO$_2$ MO Levels

$s$-$p$ mixing on the oxygen atoms causes these orbitals to become mainly nonbonding.

No $s$-$p$ mixing  With $s$-$p$ mixing
CO$_2$ General MO Model  
Corrected Electronic Configuration  
Based on P.E.S. Data

$[1\sigma_g]^2[1\sigma_u]^2[2\sigma_g^n]^2[2\sigma_u^n]^2\{[1\pi_u(x)]^2[1\pi_u(y)]^2\}[1\pi_u^n(x)][1\pi_u^n(y)]^2}$

In simplified notation:

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g^n)^2(2\sigma_u^n)^2(1\pi_u)^4(1\pi_g^n)^4$

There are still four pairs in bonding MOs over two C–O bonds, so the bond order of each is still 2.