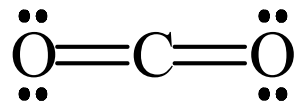# MX$_n$ Molecules with Pi-Bonding

✔ BeH$_2$ and CH$_4$ do not have pi bonding, because the $2p$ orbitals on hydrogen lie too high in energy for effective overlap with central atom AOs.

✔ Pi bonding *may* be possible with pendant atoms from the second and higher periods.
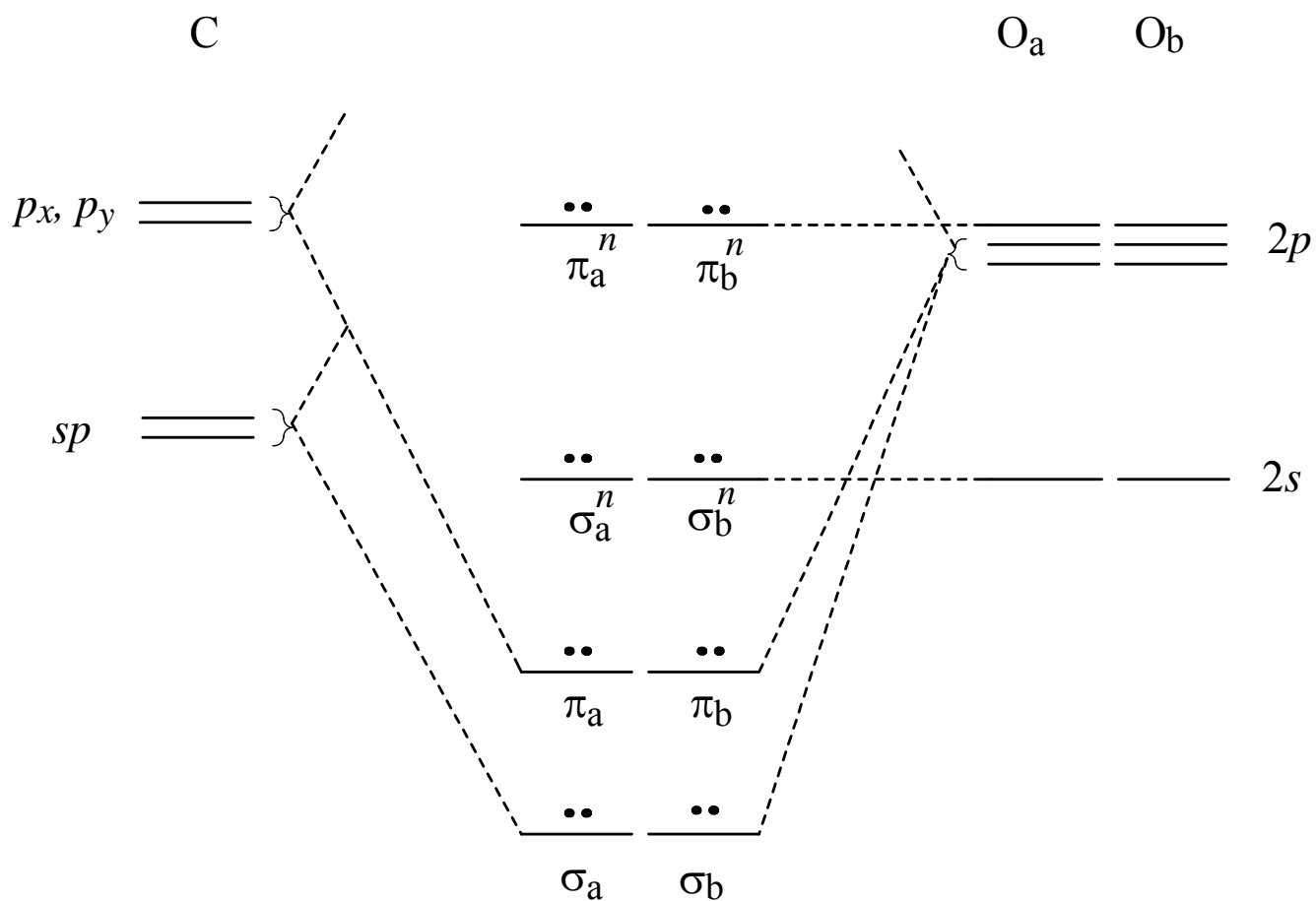
☞ Consider pi bonding in CO$_2$.

$$\ddot{\text{O}}{=}\text{C}{=}\ddot{\text{O}}$$

Simple VB Model of 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 2p_z orbitals.

✔ Pendant oxygen 2s orbitals are assumed to be nonbonding.

✔ Sigma-bonding interactions are between oxygen 2p_z orbitals and carbon sp hybrids.

✔ Pi-bonding interactions are between oxygen 2p_x or 2p_y orbitals with "empty" 2p orbitals of the same kinds on the central carbon.
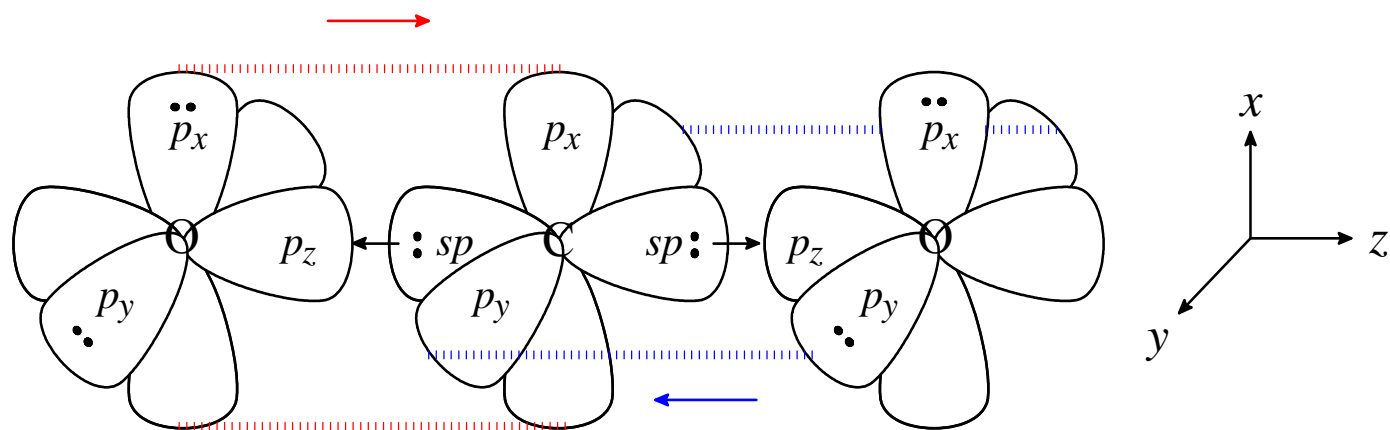
Implied Localized MO Model

$$[(\sigma_a)^2(\sigma_b)^2][(\pi_a)^2(\pi_b)^2][(\sigma_a^{\,n})^2(\sigma_b^{\,n})^2][(\pi_a^{\,n})^2(\pi_b^{\,n})^2]$$

C O_a O_b

p_x, p_y

sp

$\pi_a^{\,n}$ $\pi_b^{\,n}$

                                         $2p$

$\sigma_a^{\,n}$ $\sigma_b^{\,n}$

                                         $2s$

π_a π_b

σ_a σ_b

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:

$$\sigma_g^n = \frac{1}{\sqrt{2}}(2s_a + 2s_b)$$

$$\sigma_u^n = \frac{1}{\sqrt{2}}(2s_a - 2s_b)$$

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

x_1

y_1 O $\longrightarrow$ z_1

C

z_2 $\longleftarrow$ O

x_2

y_2
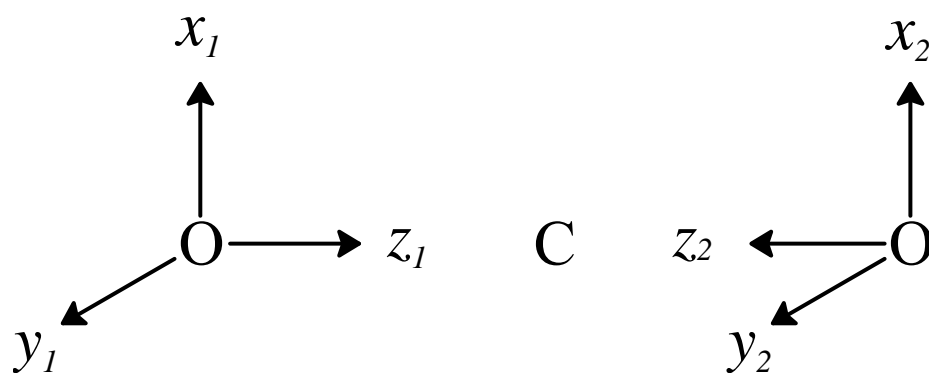
CO₂ General MO Model
Using D_{2h} as a Working Group for the Representation

✔ 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}.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Σ	$\Sigma/8$
Γ_{SALC}	6	-2	0	0	0	0	2	2		
A_g	6	-2	0	0	0	0	2	2	8	1
B_{1g}	6	-2	0	0	0	0	-2	-2	0	0
B_{2g}	6	2	0	0	0	0	2	-2	8	1
B_{3g}	6	2	0	0	0	0	-2	2	8	1
A_u	6	-2	0	0	0	0	-2	-2	0	0
B_{1u}	6	-2	0	0	0	0	2	2	8	1
B_{2u}	6	2	0	0	0	0	-2	2	8	1
B_{3u}	6	2	0	0	0	0	2	-2	8	1

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

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

AOs on carbon:

$$\Sigma_g^+ = 2s \quad \Sigma_u^+ = 2p_z \quad \Pi_u = (2p_x, 2p_y)$$

CO$_2$ General MO Model
Sigma MOs

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

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

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

Σ_u^+:
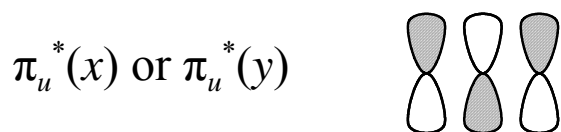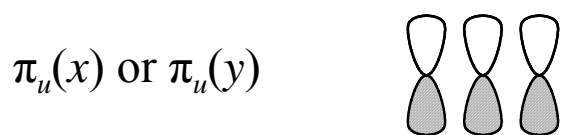$$\sigma_u^*(z) = c_7 2p_z - c_8 \left\{ \frac{1}{\sqrt{2}} \left[2p_z(a) - 2p_z(b) \right] \right\}$$

$\sigma_g(s)$

$\sigma_g^*(s)$

$\sigma_u(z)$

$\sigma_u^*(z)$

CO$_2$ General MO Model
Pi MOs

Π_u: $\qquad \pi_u(x) = c_9 2p_x + c_{10}\left\{\dfrac{1}{\sqrt{2}}\left[2p_x(a) + 2p_x(b)\right]\right\}$

Π_u: $\qquad \pi_u(y) = c_{11} 2p_y + c_{12}\left\{\dfrac{1}{\sqrt{2}}\left[2p_y(a) + 2p_y(b)\right]\right\}$

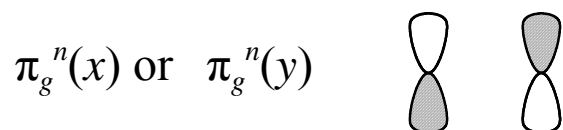Π_u: $\qquad \pi_u^*(x) = c_{13} 2p_x - c_{14}\left\{\dfrac{1}{\sqrt{2}}\left[2p_x(a) + 2p_x(b)\right]\right\}$

Π_u: $\qquad \pi_u^*(y) = c_{15} 2p_y - c_{16}\left\{\dfrac{1}{\sqrt{2}}\left[2p_y(a) + 2p_y(b)\right]\right\}$

$\pi_u(x)$ or $\pi_u(y)$

$\pi_u^*(x)$ or $\pi_u^*(y)$

CO$_2$ General MO Model
Nonbonding Pi MOs

Π_g:
$$\pi_g^n(x) = \frac{1}{\sqrt{2}}\left[2p_x(a) - 2p_x(b)\right]$$

Π_g:
$$\pi_g^n(y) = \frac{1}{\sqrt{2}}\left[2p_y(a) - 2p_y(b)\right]$$

$\pi_g^n(x)$ or $\pi_g^n(y)$

Qualitative Delocalized MO Scheme for CO$_2$

C   CO$_2$ 2 O (SALCs)

$\sigma_u{}^*$

$\sigma_g{}^*$

$[\ \overline{\pi_u{}^*(x)}\ \ \overline{\pi_u{}^*(y)}\ ]$

$[\ \underline{\quad}\ \ \underline{\quad}\ \ \underline{\quad}\ ]$
2p
$\Sigma_u + \Pi_u$

$[\ \overline{\underset{\pi_g{}^n(x)}{\uparrow\downarrow}}\ \ \overline{\underset{\pi_g{}^n(y)}{\uparrow\downarrow}}\ ]$ $[\ \overline{\underline{\quad}}\ \ \overline{\underline{\quad}}\ \ \overline{\underline{\quad}}\ ]$
2p_a, 2p_b
$\Sigma_g + \Sigma_u + \Pi_g + \Pi_u$

2s
Σ_g

$[\ \overline{\underset{\pi_u(x)}{\uparrow\downarrow}}\ \ \overline{\underset{\pi_u(y)}{\uparrow\downarrow}}\ ]$

$\overline{\underset{\sigma_u(z)}{\uparrow\downarrow}}$

$\overline{\underset{\sigma_g(s)}{\uparrow\downarrow}}$

$\begin{bmatrix} \overline{\underset{\sigma_u{}^n(O_s)}{\uparrow\downarrow}} \\ \overline{\underset{\sigma_g{}^n(O_s)}{\uparrow\downarrow}} \end{bmatrix}$ $[\ \overline{2s_a}\ ,\ \overline{2s_b}\ ]$
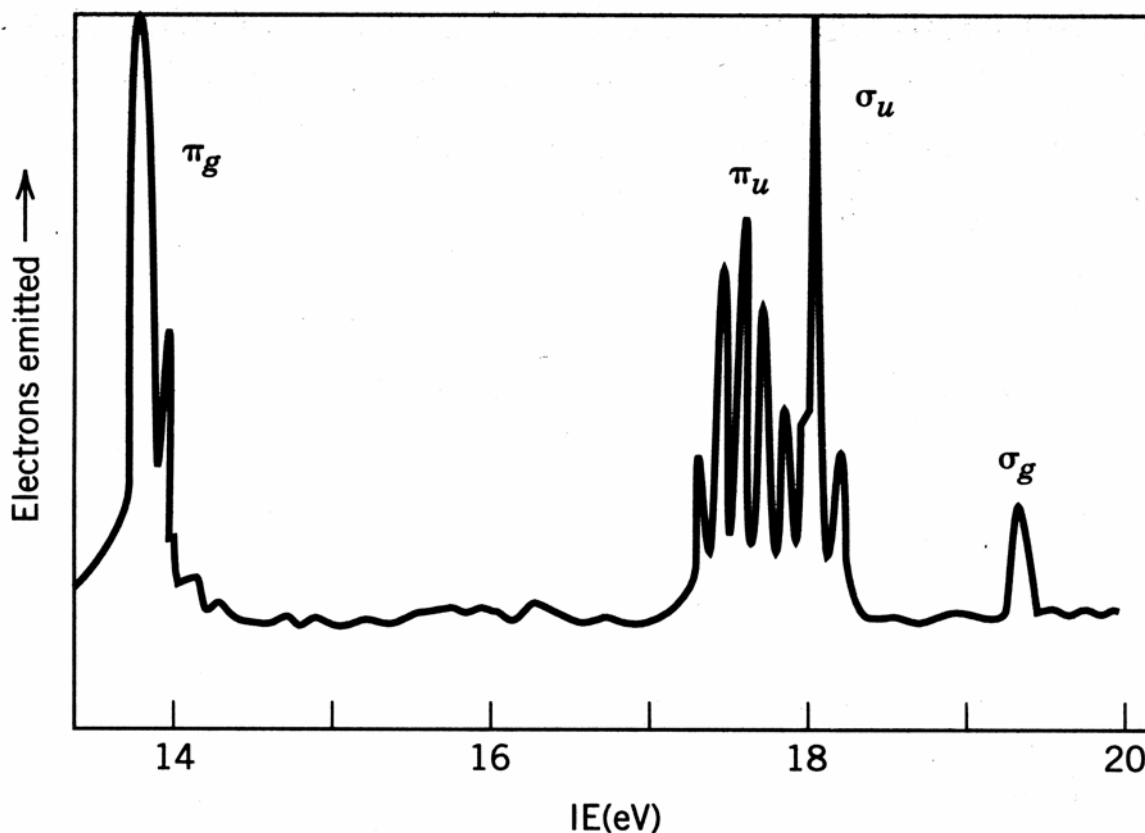$\Sigma_g + \Sigma_u$
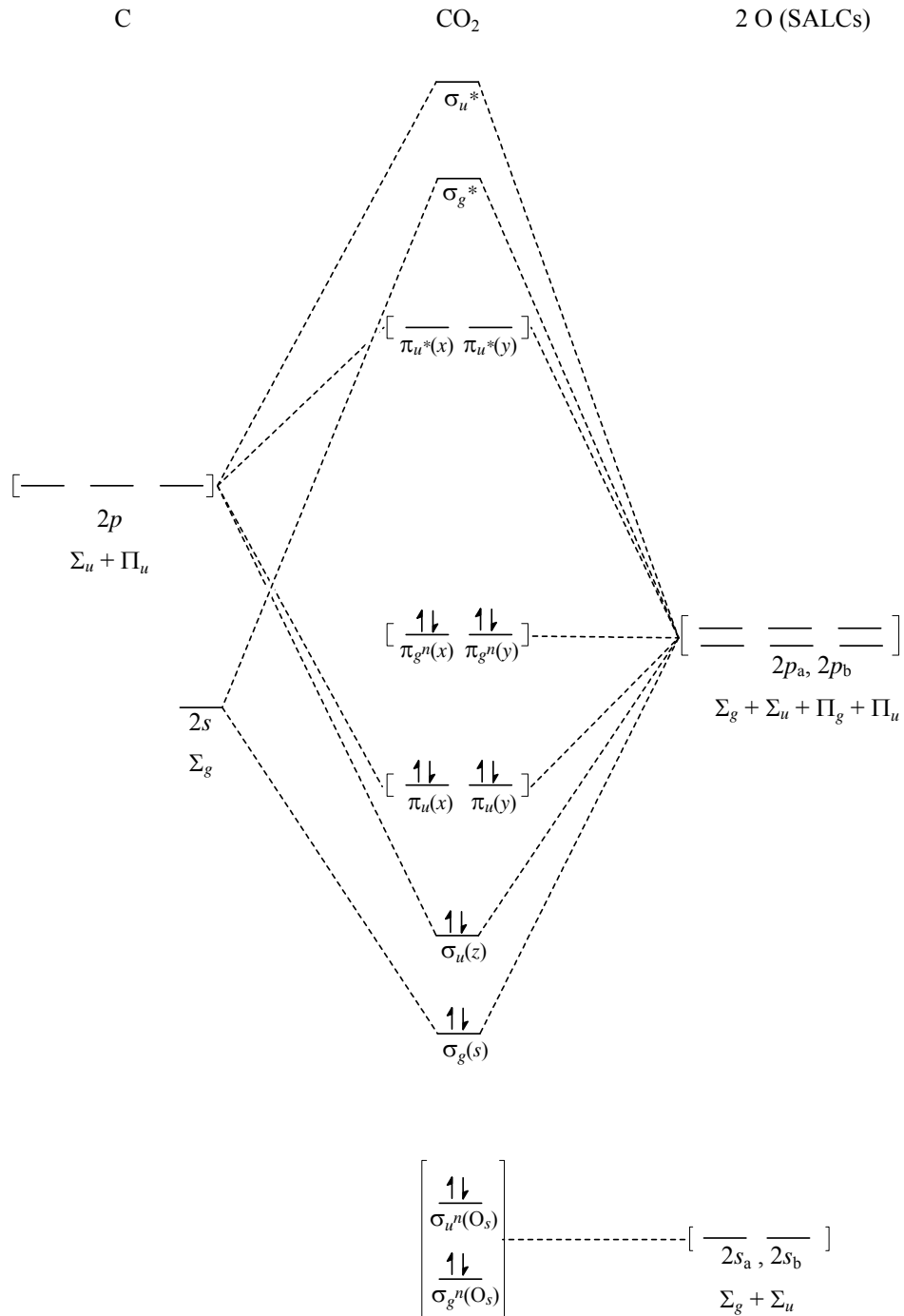
CO$_2$ General MO Model
Predicted Electronic Configuration

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

In simplified notation:

$$(\sigma_g{}^n)^2(\sigma_u{}^n)^2[\sigma_g(s)]^2[\sigma_u(z)]^2[\pi_u(x,y)]^4[\pi_g{}^n(x,y)]^4$$

P.E.S. Spectrum of CO_2

✔ Four observed bands consistent with the electronic configuration from the MO scheme $(\sigma_g^n)^2(\sigma_u^n)^2[\sigma_g(s)]^2[\sigma_u(z)]^2[\pi_u(x,y)]^4[\pi_g^n(x,y)]^4$. (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 $[\pi_g^n(x,y)]^4$.

✔ Only the second band, due to $[\pi_u(x,y)]^4$, shows pronounced fine structure consistent with ejection of electrons from bonding MOs.
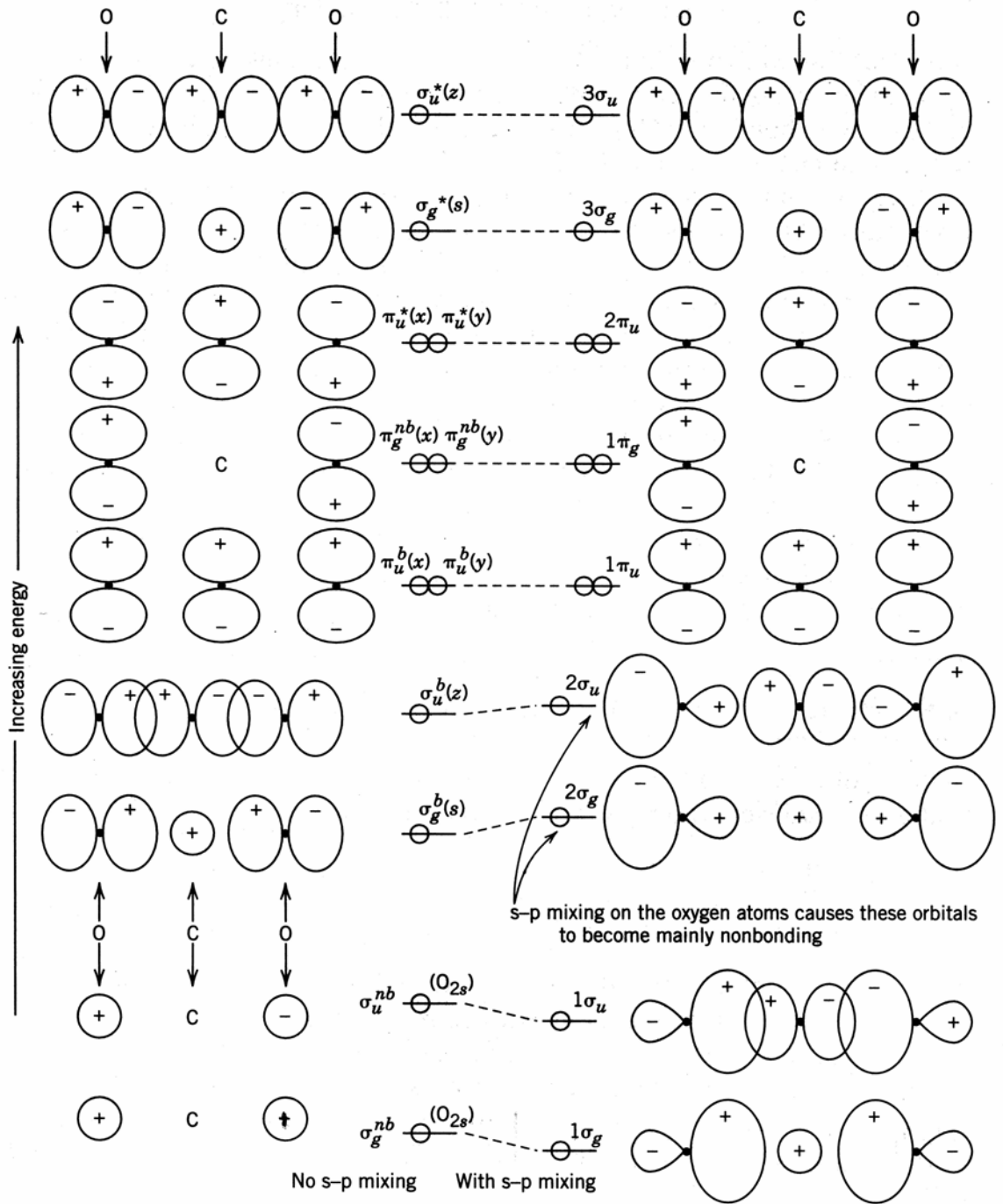
s-p Mixing in CO_2

✔ 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 $2p_z$ orbitals on the oxygen atoms; i.e., Σ_g^+, Σ_u^+.

Σ_g^+ ○ ○ Σ_u^+ ○ ⬤

- On the basis of symmetry, these SALCs are as capable of forming MOs with like-symmetry AOs on carbon as the $2p_z$ 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 $2p_z$ 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 $[2\sigma_g{}^n]^2[2\sigma_u{}^n]^2$.

☞ 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

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

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.