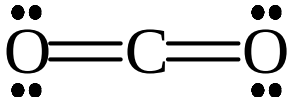
MX_n Molecules with Pi-Bonding

✔ BeH_2 and CH_4 do not have pi bonding, because the 2*p* orbitals on hydrogen lie too high in energy for effective overlap with central atom AOs.

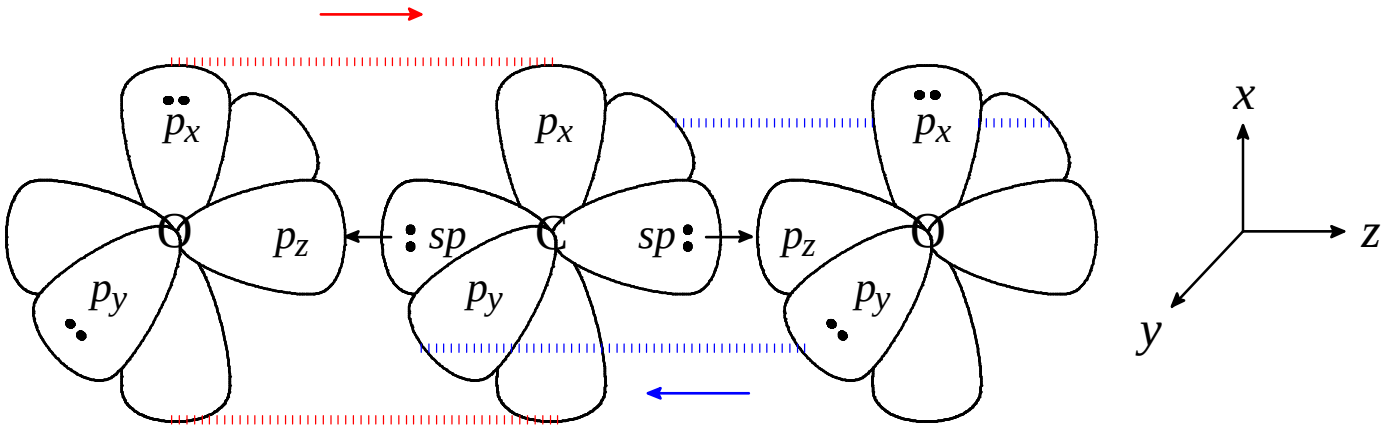
✔ Pi bonding *may* be possible with pendant atoms from the second and higher periods.

☞ Consider pi bonding in CO_2.



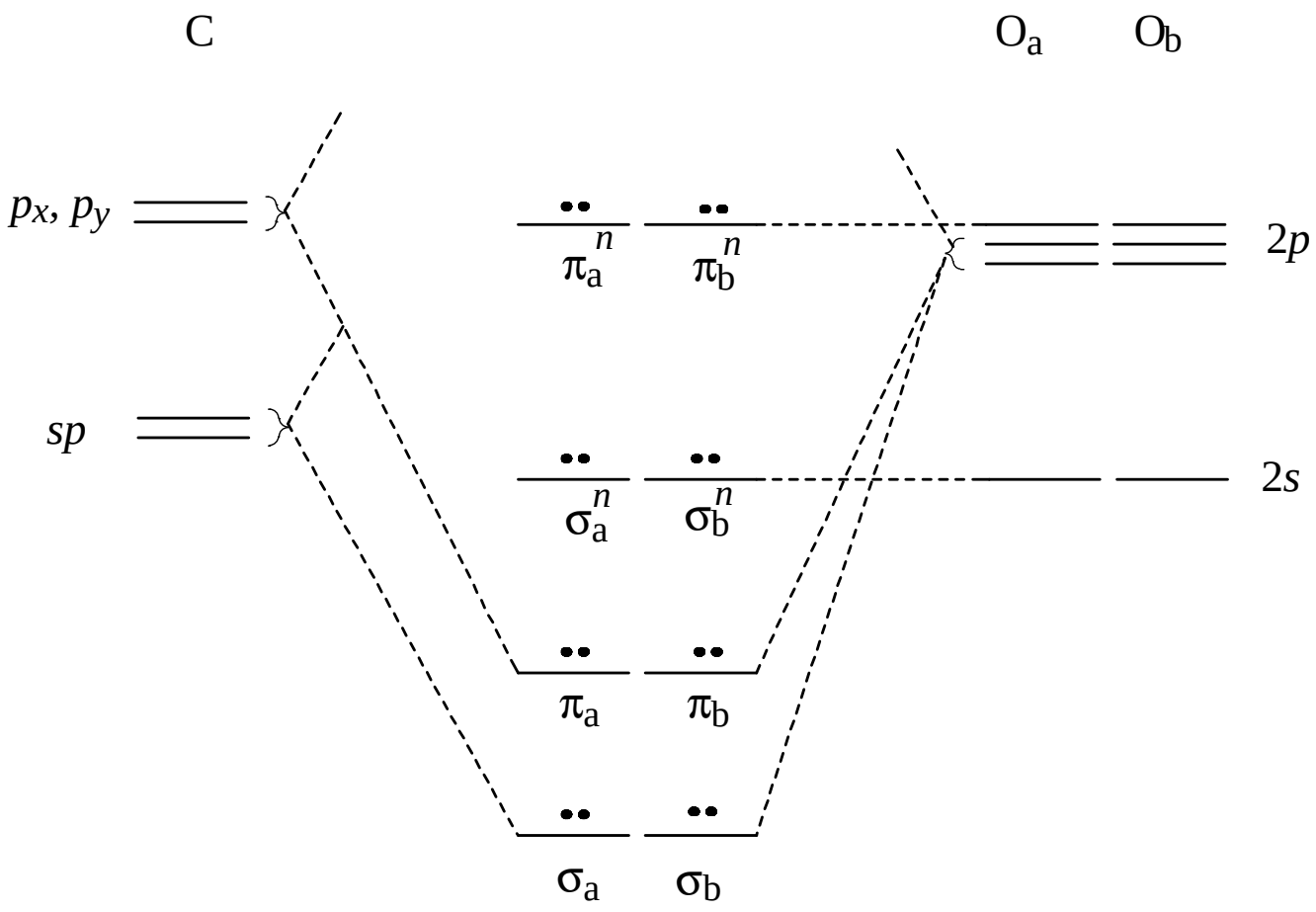
Simple VB Model of CO_2

- ✔ Carbon 1*s* is assumed not to be involved in bonding (i.e., core electrons).
- ✔ Carbon is assumed to be *sp* hybridized, using 2*s* and $2p_z$ orbitals.
- ✔ Pendant oxygen 2*s* 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" 2*p* orbitals of the same kinds on the central carbon.



Implied Localized MO Model

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



CO_2 General MO Model
Starting Assumptions

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

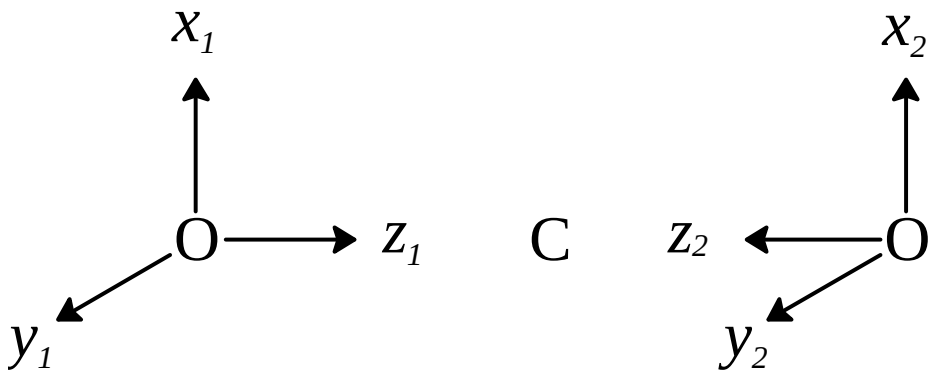
2. Only the 2*p* orbitals on the two O atoms are used in bonding. The two 2*s* orbitals are assumed to form a pair of nonbonding MOs:

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

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

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



CO_2 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	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
Γ_{SALC}	6	-2	0	0	0	0	2	2	Σ	$\Sigma/8$
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

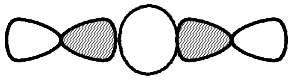
Σ_g^+: $$\sigma_g(s) = c_1 2s + c_2\left\{\frac{1}{\sqrt{2}}\left[2p_z(a) + 2p_z(b)\right]\right\}$$

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

$\sigma_g(s)$ 

$\sigma_g^*(s)$ 

$\sigma_u(z)$ 

$\sigma_u^*(z)$ 

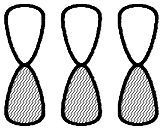
CO_2 General MO Model
Pi MOs

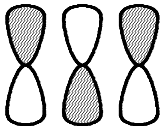
Π_u: $$\pi_u(x) = c_9 2p_x + c_{10}\left\{\frac{1}{\sqrt{2}}\left[2p_x(a) + 2p_x(b)\right]\right\}$$

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

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

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

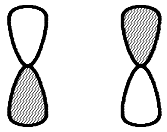
$\pi_u(x)$ or $\pi_u(y)$ 

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

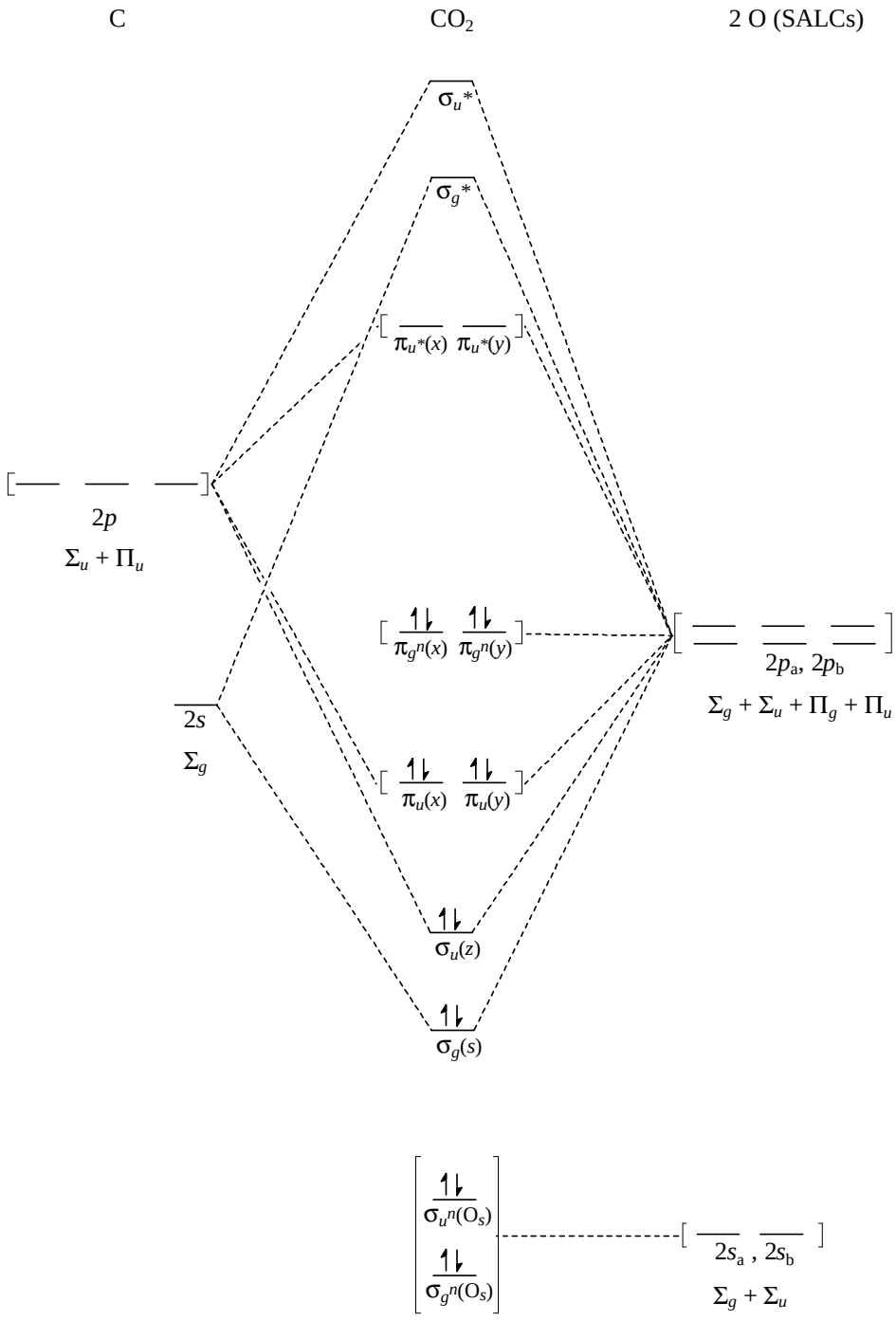
CO_2 General MO Model
Nonbonding Pi MOs

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



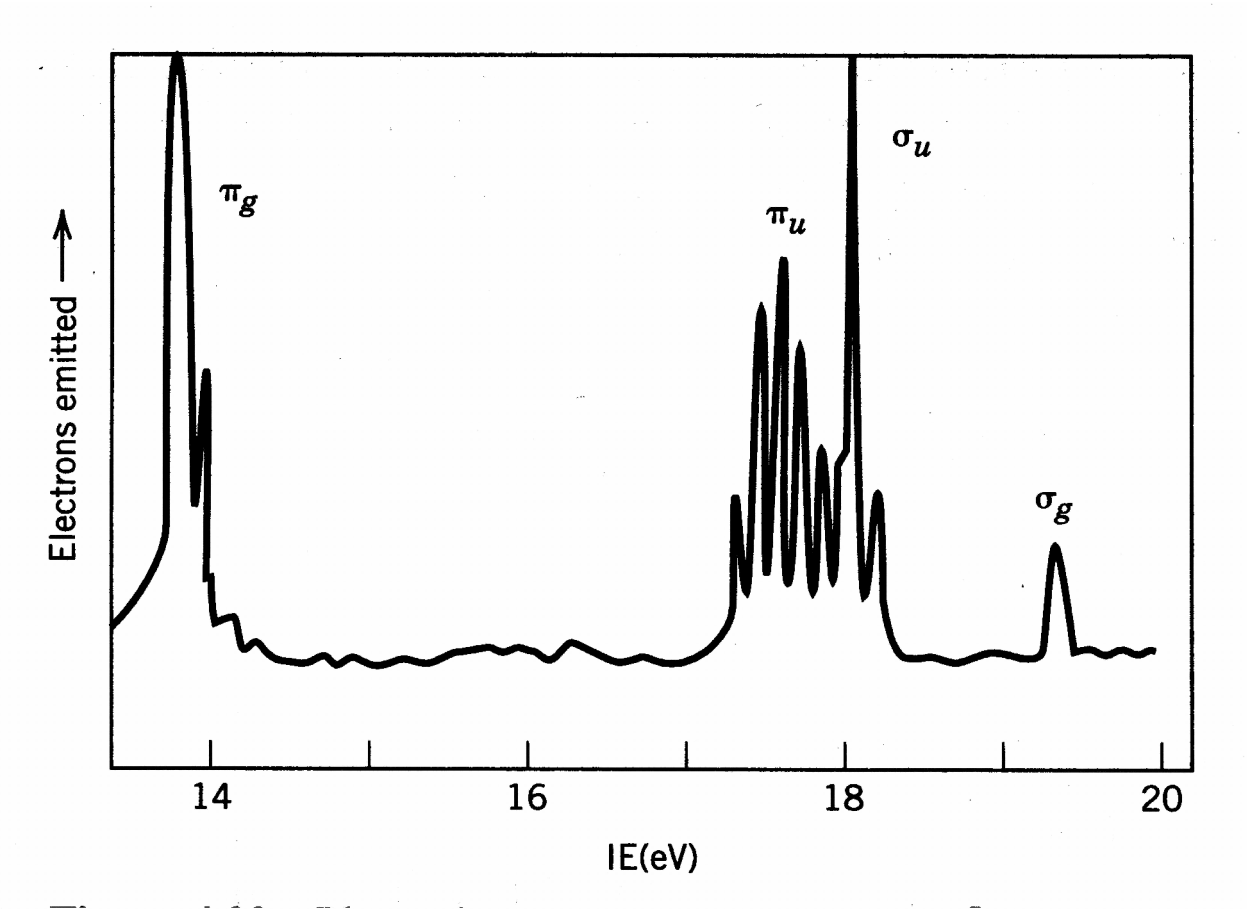
CO_2 General MO Model
Predicted Electronic Configuration

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

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 2*s* 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^+.

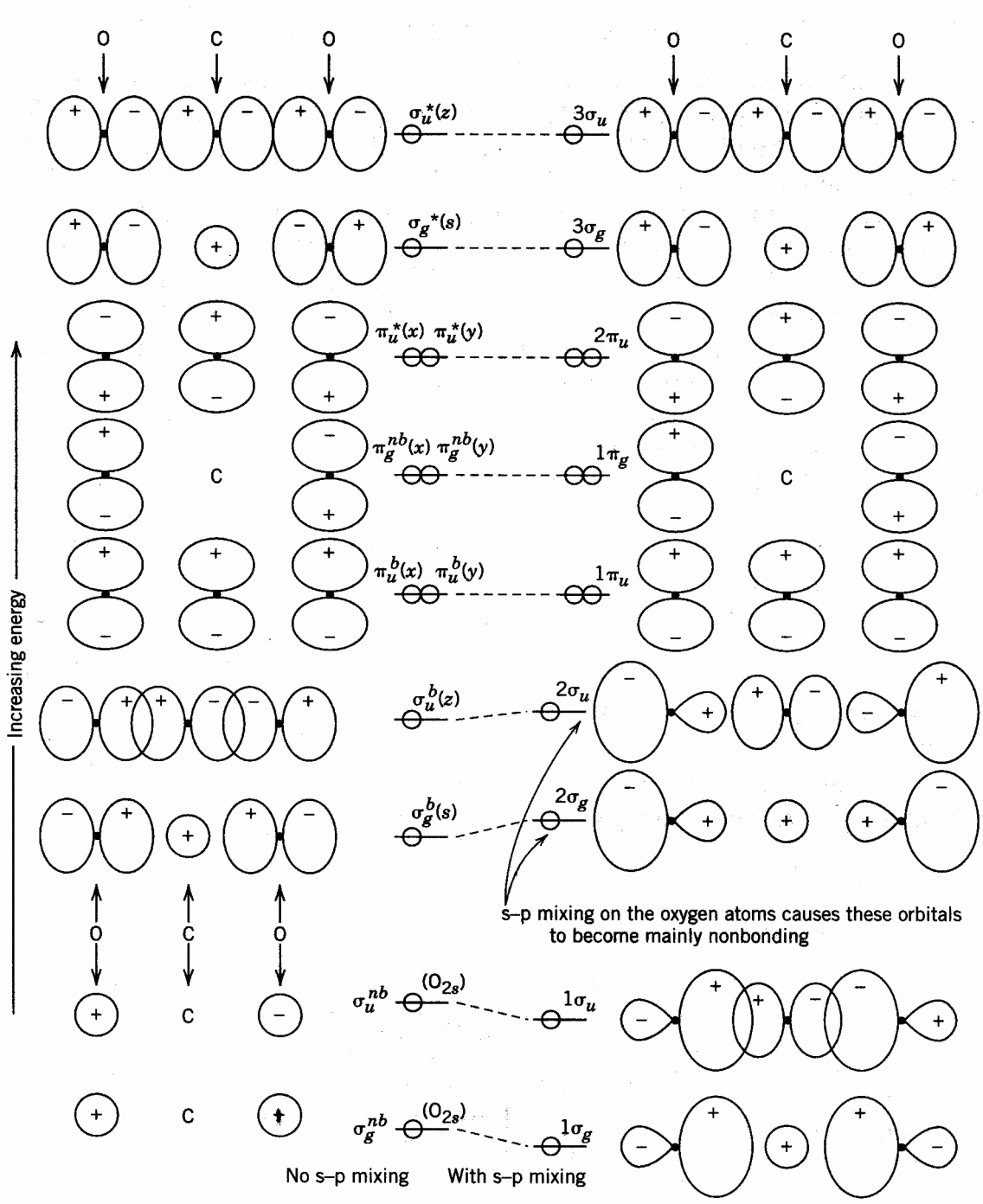
- On the basis of symmetry, these SALCs are as capable of forming MOs with like-symmetry AOs on carbon as the $2p_z$ SALCs we used in our model.

- 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 2*s* 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



CO_2 General MO Model
Corrected Electronic Configuration
Based on P.E.S. Data

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

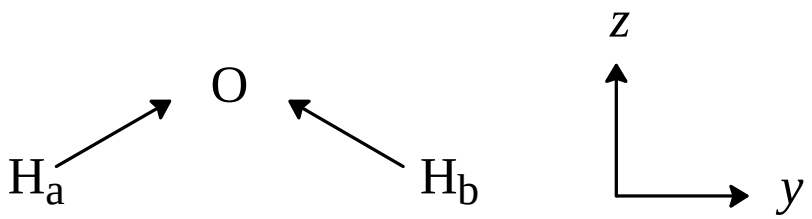
In simplified notation:

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

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

MO Scheme of H_2O
Hydrogen SALCs

- Taking the two hydrogens as a basis for the SALCs



we obtain the following reducible representation:

C_{2v}	E	C_2	σ_v	σ_v'
Γ_H	2	0	0	2

for which $\Gamma_H = A_1 + B_2$.

- The equations for the SALCs are

$$\Phi_{a_1} = \frac{1}{\sqrt{2}}(1s_{H_a} + 1s_{H_b})$$

$$\Phi_{b_2} = \frac{1}{\sqrt{2}}(1s_{H_a} - 1s_{H_b})$$

Symmetries of Oxygen AOs

- From the C_{2v} character table, oxygen AO symmetries are

$$s = A_1 \quad p_x = B_1 \quad p_y = B_2 \quad p_z = A_1$$

- The p_x AO (B_1) has no matching SALC and must be nonbonding.

- The p_y orbital can form bonding and antibonding combinations with the B_2 SALC.

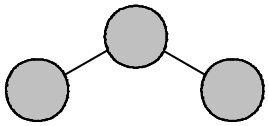
- Both *s* and p_z orbitals on oxygen match with the A_1 SALC, so *s*-*p* mixing can be expected.

☹ If we formed bonding and antibonding combinations for both of these, we would end up with more MOs in the final scheme (seven) than there are available AOs on the component atoms (six).

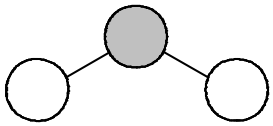
☛ To avoid this, we must make only three MOs from the A_1 AOs and SALC.

☺ For simplicity, we will assume that the *s* and p_z orbitals on oxygen both form bonding MOs, and together they form one *s*-*p* mixed antibonding orbital.

LCAOs for H_2O

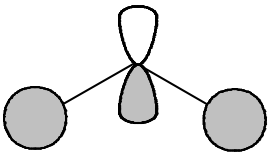


$\sigma\ (s)$ - a_1

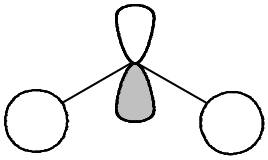


$\sigma^*\ (s)$ - a_1

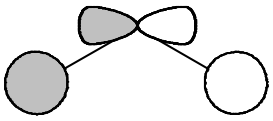
Mixed as one σ^*



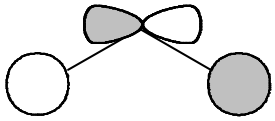
$\sigma\ (z)$ - a_1



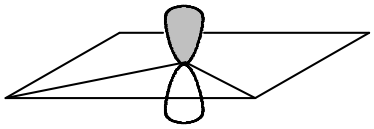
$\sigma^*\ (z)$ - a_1



$\sigma\ (y)$ - b_2

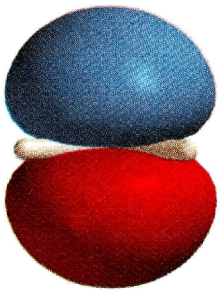


$\sigma^*\ (y)$ - b_2

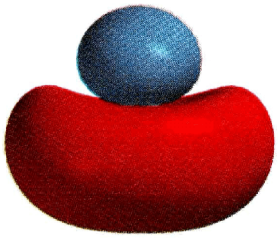


$\pi\ (x)$ - b_1

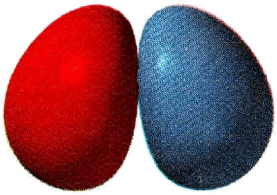
Representation of Occupied MOs of H_2O[1]



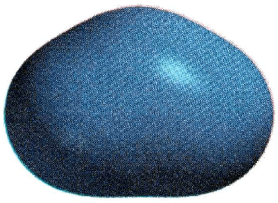
Representation of the b_1 MO



Representation of the higher energy a_1 MO



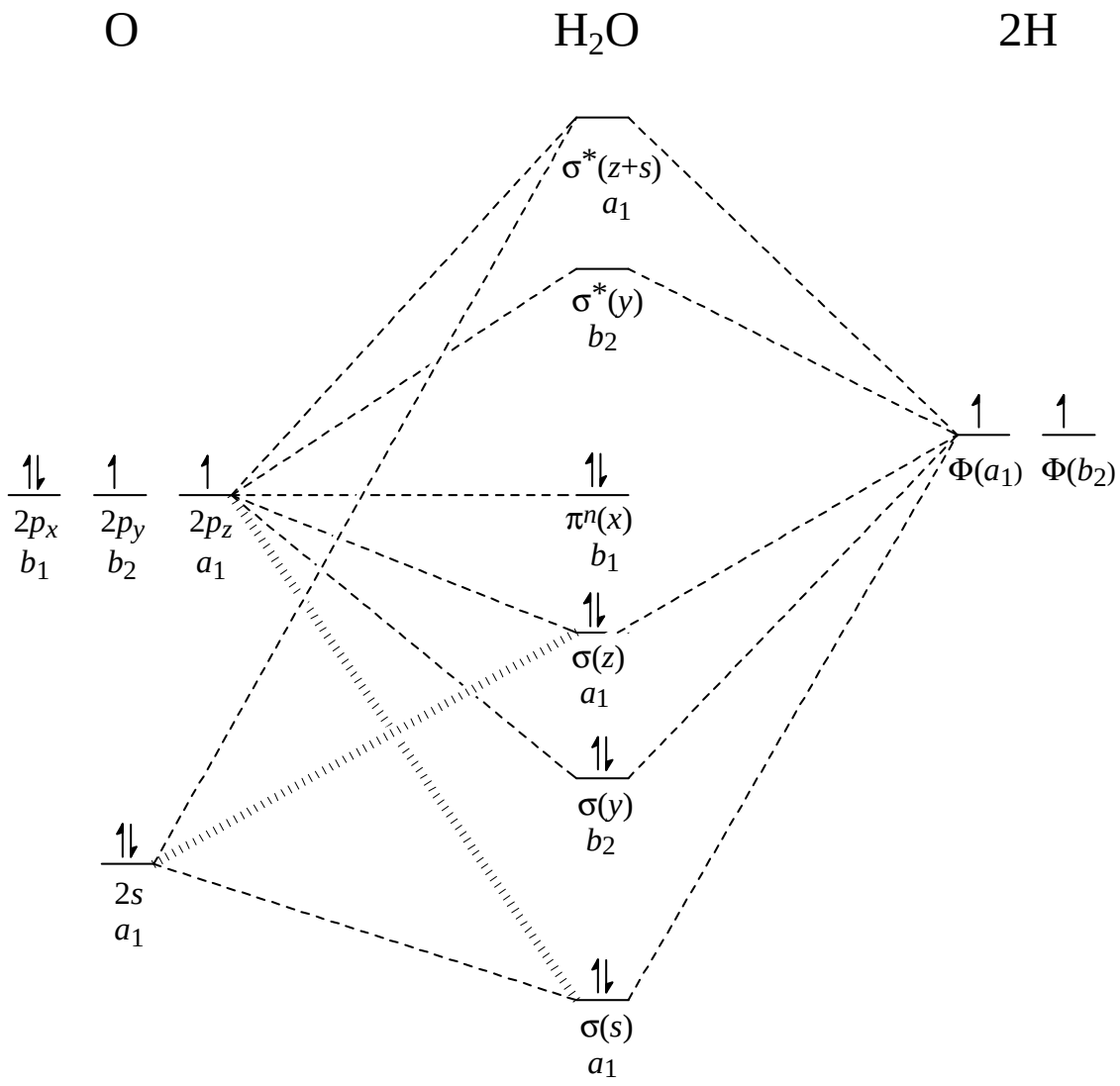
Representation of the b_2 MO



Representation of the lower energy a_1 MO

[1]Source: C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, 2nd ed., Prentice Hall, Essex, England, 2005, p. 111.

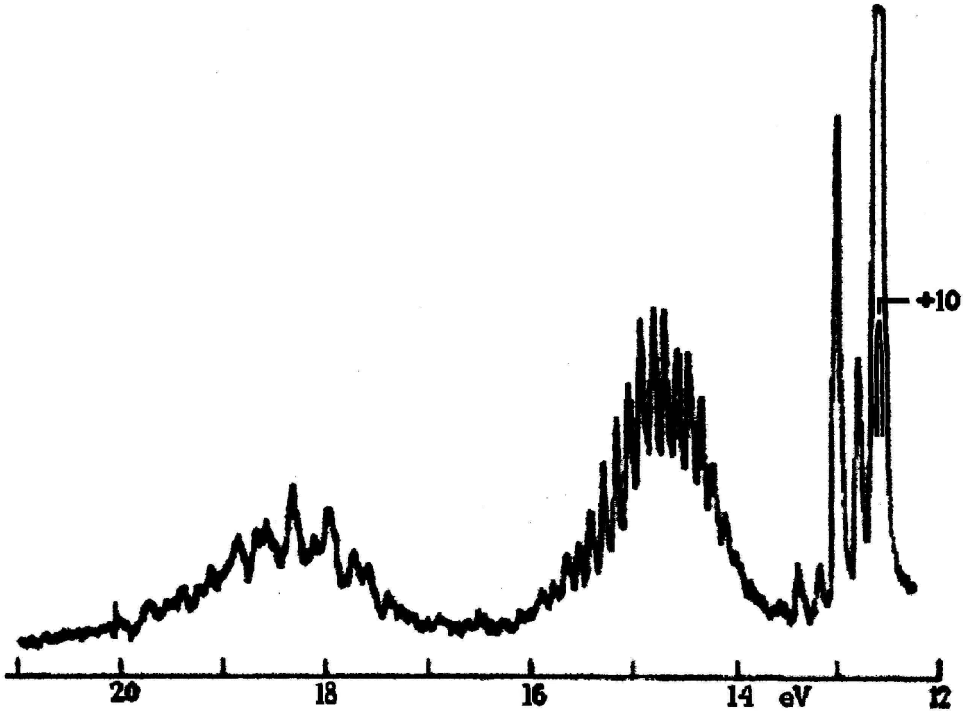
Qualitative MO Scheme for H_2O



☞ Hashed lines indicate lesser contributions arising from *s*-*p* mixing.

PES of H_2O and MO Model[2]

- Four bands:
  - Three with highest energy have fine structure.
  - Least energetic band has no fine structure, consistent with ionization from nonbonding $\pi^n(x)$.



☞ The P.E.S. results are consistent with the MO scheme.

- Rather than two lone pairs in approximately sp^3 hybrids, the MO scheme suggests a single region of electron density protruding from the back side of the molecule, created by the combination of the nonbonding $\pi^n(x)$ MO and the weakly bonding $\sigma(z)$ MO.

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[2]C. R. Brundle and D. W. Turner, *Proc. Roy. Soc., A*, **1968**, *307*, 27-36.