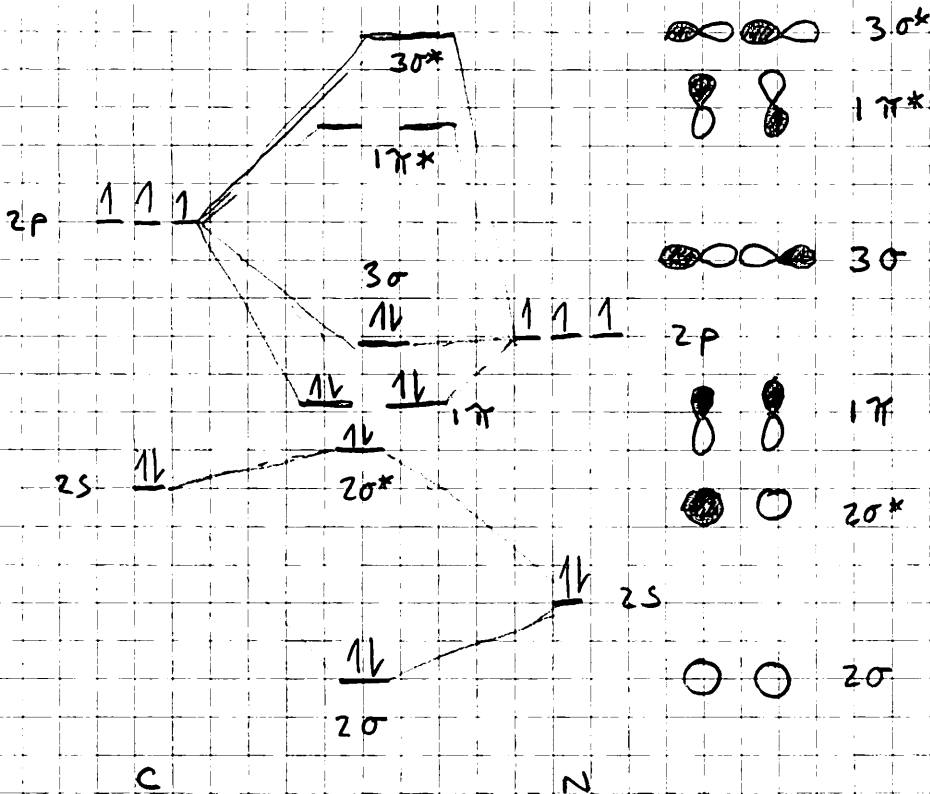


Problem Set 3

1) $:\text{C}\equiv\text{N}:$ 10 valence e^-



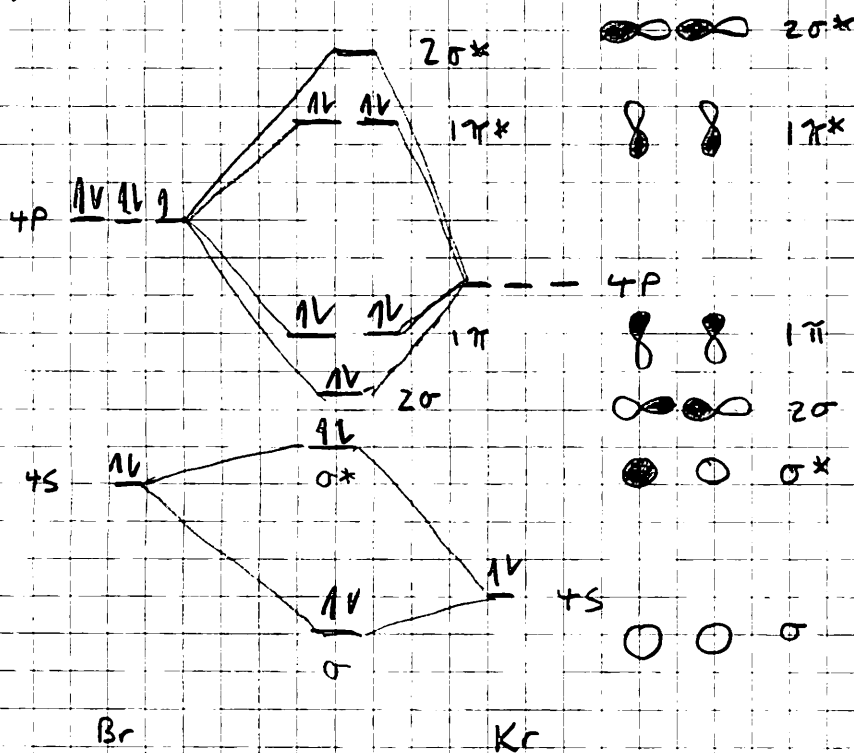
a) No unpaired spins
 \therefore Multiplicity = Singlet

$$\text{Bond Order} = \frac{1}{2}(8-2) = \frac{6}{2} = 3$$

b) The 3σ (HOMO) of CN^- would interact most w/ the LUMO of a H^+ 1s orbital, which has an energy of -13.6 eV

These frontier orbitals are well matched in symmetry + energy

2) $[\text{Kr}-\text{Br}]^+$ 14 valence $e^- \Rightarrow$ Same as dihalide (i.e. Br_2)

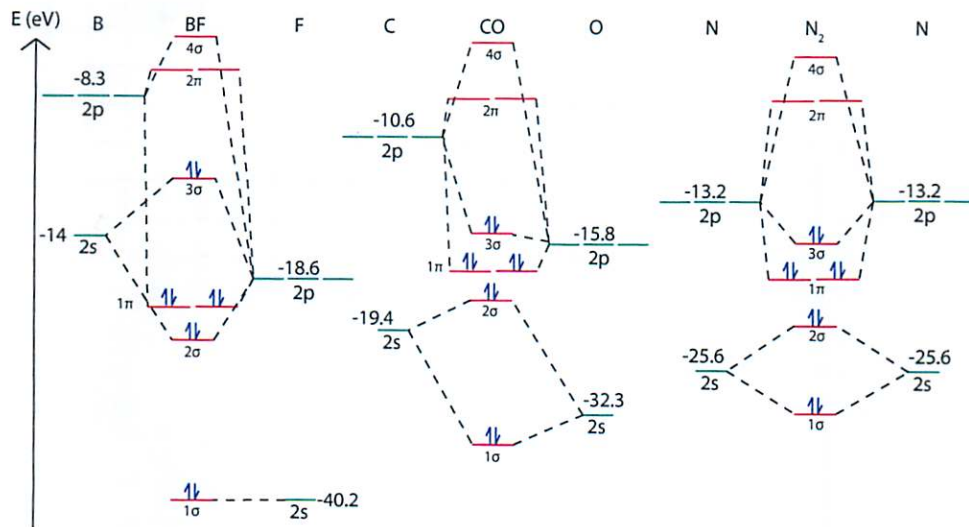


a) The HOMO is $1\pi^*$. Since this MO is closer in energy to the $p_x + p_y$ orbitals of Br than those on Kr, the HOMO will be polarized toward Br.

$$\text{Bond Order} = \frac{1}{2}(8-6) = \frac{2}{2} = 1$$

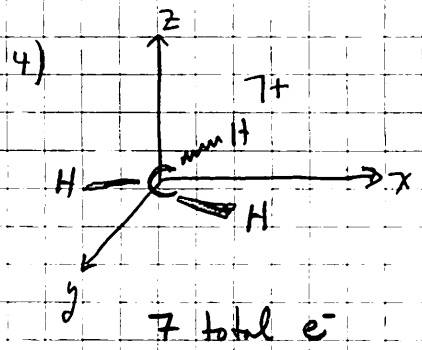
3)

The first ionization energies of BF, CO, and N₂ are 11.06 eV, 14.01 eV, and 15.57 eV, respectively. Explain the increase in ionization energy for this isoelectronic series on the basis of atomic-orbital composition of the highest occupied molecular orbital.



Note: Not showing s-p mixing for all 3 molecules.

We can answer this question simply by inspecting the HOMO levels of each molecule because the HOMO level is a minimum value for ionization energy (IE). The HOMO level of BF is the highest since it is higher than -14.0 eV. The HOMO level of CO is slightly higher than the O 2p orbital (-15.8 eV) from s-p mixing; therefore, its HOMO level is lower than the HOMO level of BF, so its IE is larger. The HOMO level of N₂ is the lowest because its 3σ bond is strongly bonding despite weak s-p mixing. Therefore, diatomic nitrogen has the largest IE.



D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₆	3σ _v
Γ_{H}	3	0	1	3	0	1
Γ_{C}	3	0	1	3	0	1
Γ_{H}	3	0	-1	3	0	-1
Γ_{H}	3	0	0	6	0	0
Γ_{H}	3	0	-1	-3	0	-1
Γ_{H}	3	0	-1	-3	0	1
Γ_{H}	6	0	0	-6	0	0

Reduce

Σ	Σ/h
12	1
0	0
12	1
0	0
0	0
0	0

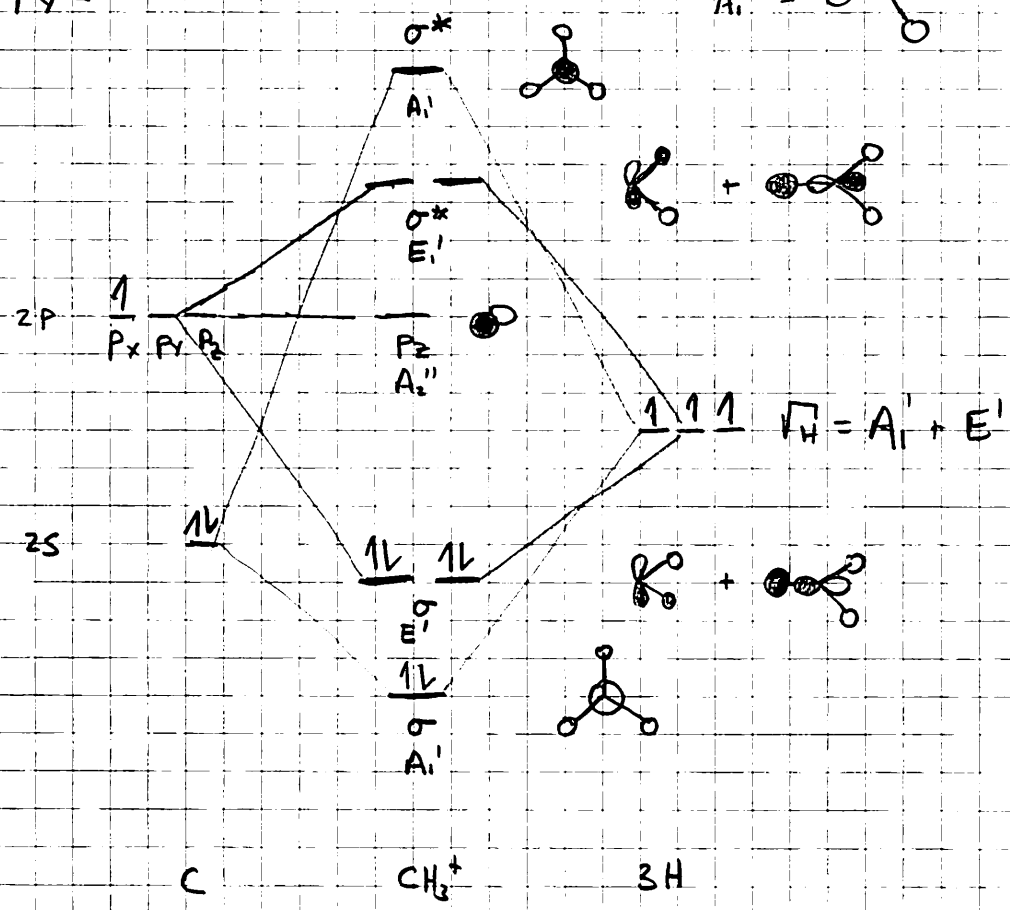
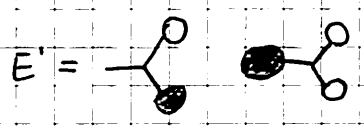
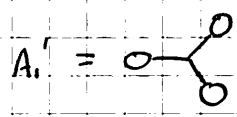
For Carbon atom in D_{3h}

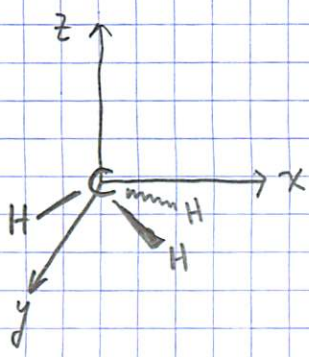
s → A₁'

p_z → A₂'

$\begin{matrix} p_x \\ p_y \end{matrix} \rightarrow E'$

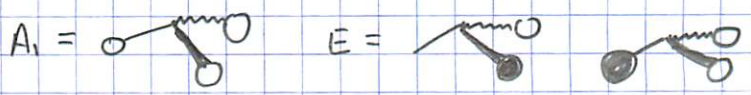
∴ $\Gamma_{\text{H}} = A_1' + E'$





C_{3v}	E	$2C_3$	$3C_2$
Γ_H	3	0	1

By simple inspection, $\Gamma_H = A_1 + E$

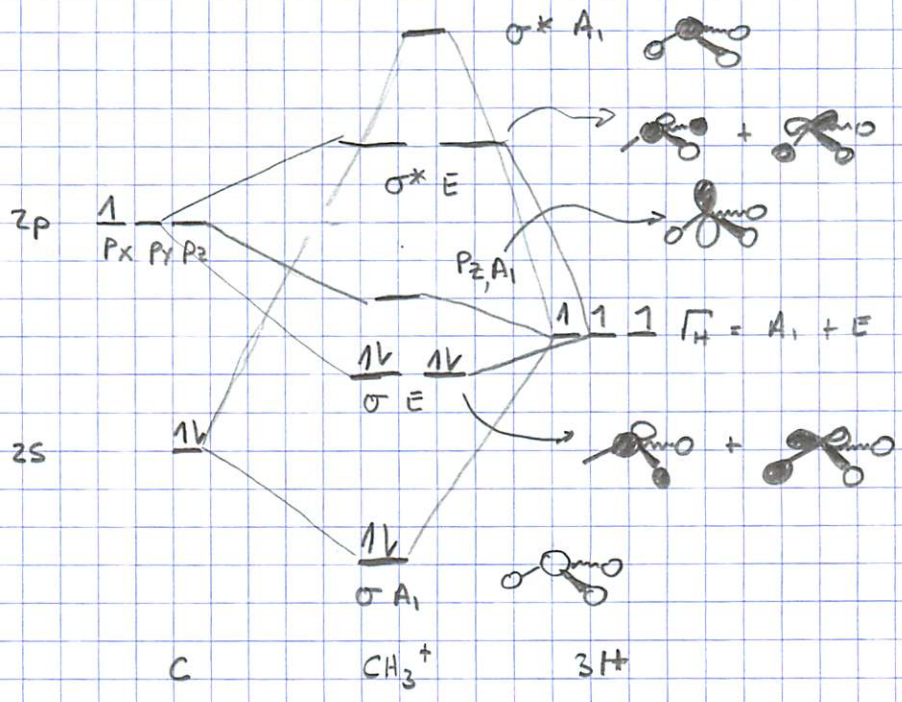


For Carbon atom in C_{3v}

$s \rightarrow A_1$

$p_z \rightarrow A_1$

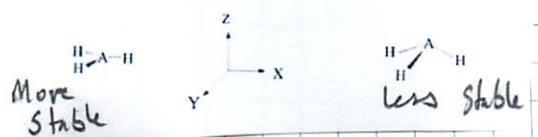
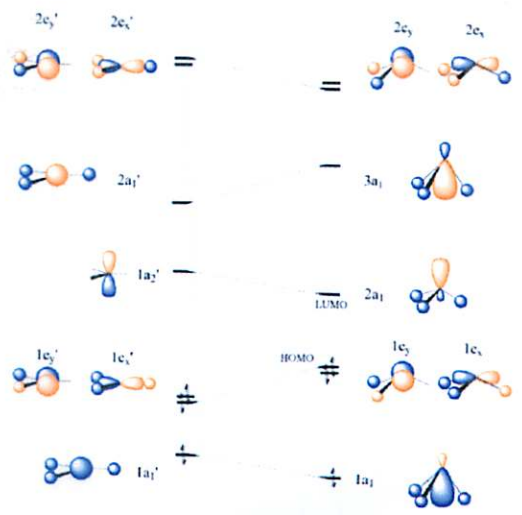
$p_x, p_y \rightarrow E$

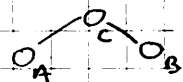
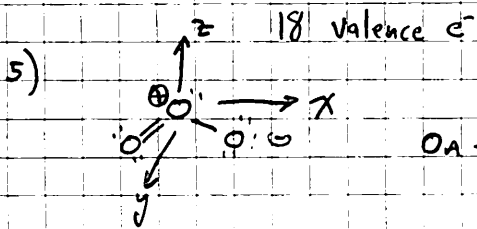


Based on the two MOs, we expect D_{3h} (planar) geometry to be preferred for CH_3^+

Upon pyramidalization the E symmetry HOMO is raised in energy + the non-bonding LUMO drops. Since CH_3^+ has a larger HOMO-LUMO gap in D_{3h} , this geometry will be more stable.

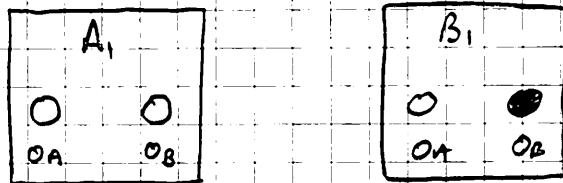
D_{3h} (planar) geometry to be preferred





C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
$O_A + O_B \sqrt{2s}$	2	0	2	0		
\Downarrow Reduce						
$\sqrt{2s} \cdot A_1$	2	0	2	0	<u>Σ</u>	<u>Σ/4</u>
$\sqrt{2s} \cdot A_2$	2	0	-2	0	0	0
$\sqrt{2s} \cdot B_1$	2	0	2	0	4	1
$\sqrt{2s} \cdot B_2$	2	0	-2	0	0	0

$\therefore \sqrt{2s} = A_1 + B_1$



For Central Oxygen (O_C)

$2s \rightarrow A_1$

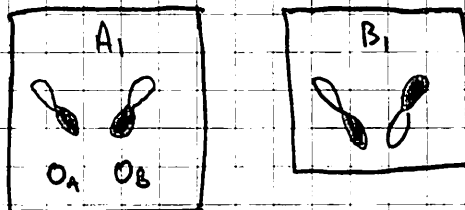
$2p_z \rightarrow A_1$

$2p_x \rightarrow B_1$

$2p_y \rightarrow B_2$

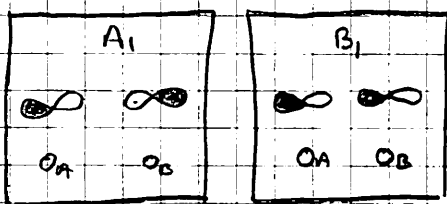
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
$O_A + O_B \sqrt{p_z}$	2	0	2	0

$\therefore \sqrt{p_z} = A_1 + B_1$ (See Reduction above)



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
$O_A + O_B \sqrt{p_x}$	2	0	2	0

$\therefore \sqrt{p_x} = A_1 + B_1$

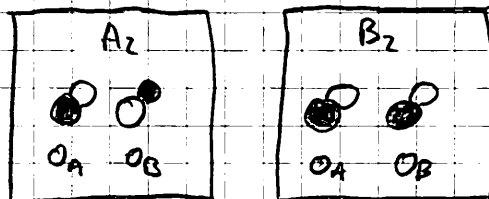


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
$O_A + O_B \sqrt{p_y}$	2	0	-2	0

\Downarrow Reduce

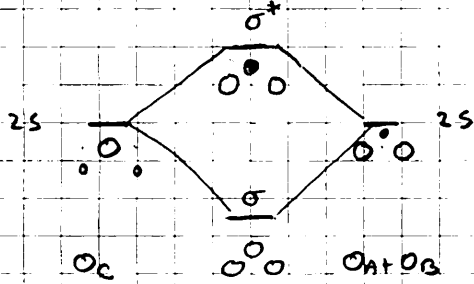
$\sqrt{p_y} \cdot A_1$	2	0	-2	0	0	0
$\sqrt{p_y} \cdot A_2$	2	0	2	0	4	1
$\sqrt{p_y} \cdot B_1$	2	0	-2	0	0	0
$\sqrt{p_y} \cdot B_2$	2	0	2	0	4	1

$\therefore \sqrt{p_y} = A_2 + B_2$

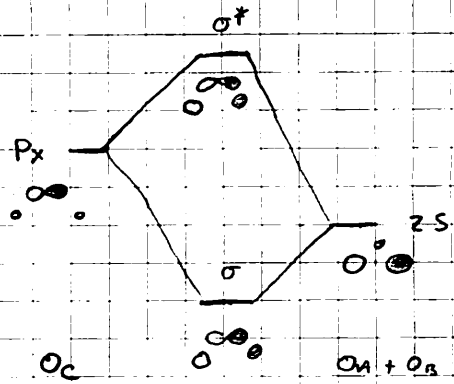


2S group orbitals

(A₁)

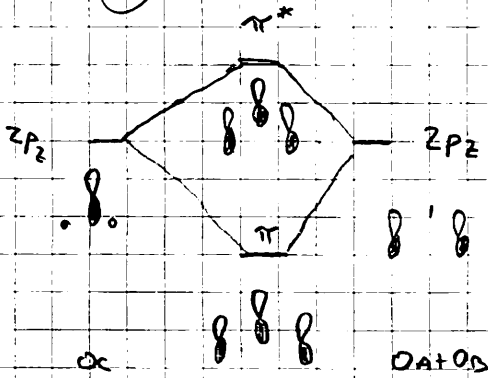


(B₁)

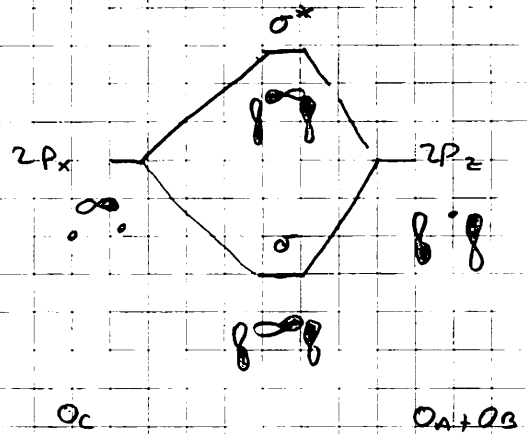


2Pz group orbitals

(A₁)

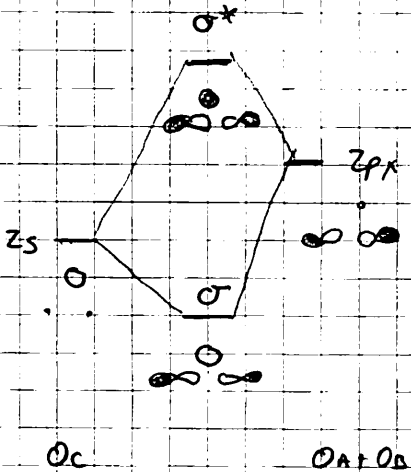


(B₁)

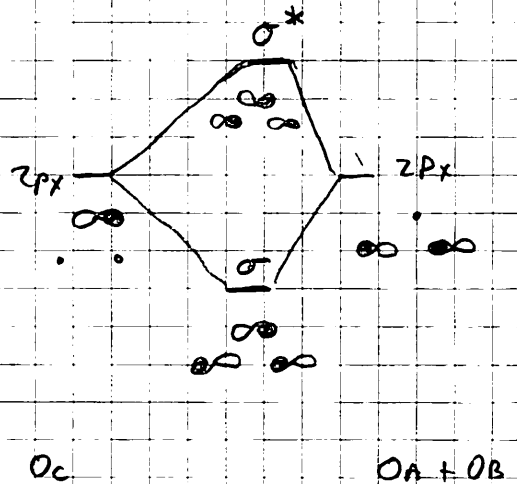


2Px group orbitals

(A₁)

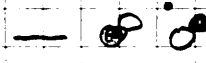


(B₁)

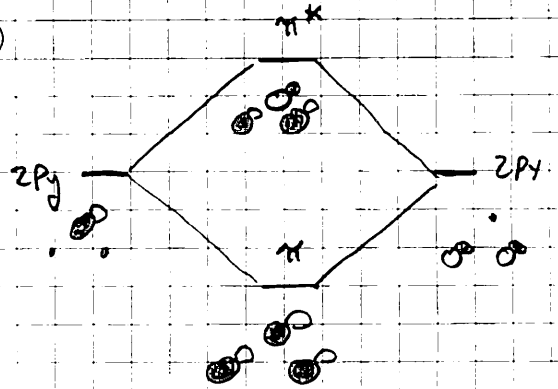


2py Group Orbitals

(A₂) No AO on central Carbon

∴ — 
 2py must be non-bonding

(B₂)



Based on this analysis we can conclude that the strongest interactions will be:

2s of O_c (A₁) can combine w/ A₁ √2s to form a σ bond

2p_z of O_c (A₁) can combine w/ A₁ √2p_z to form a π bond

2p_x of O_c (B₁) can combine w/ B₁ √2s to form a σ bond

2p_y of O_c (B₂) can combine w/ B₂ √2p_y to form a π bond

