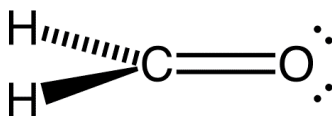


2.7: The Carbonyl Group

http://mutuslab.cs.uwindsor.ca/Wang/...1/341_109c.pdf

Let's look at the electron transitions of H_2CO , formaldehyde, for a typical description of the MO of an organic molecule.

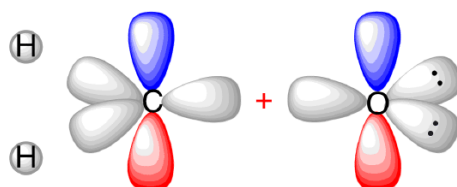


Pretty valence-bond theory

(first year description of formaldehyde): <https://www.chemtube3d.com/orbitalsformaldehyde>

View 1: Before (but after hybridization)

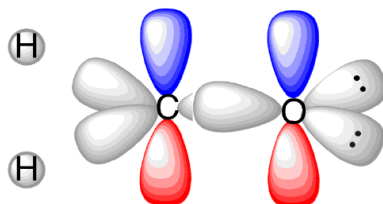
Carbon and the oxygen are both sp^2 hybridized.



(CC BY-SA-NC; Nick Graves via [ChemTube3D](https://www.chemtube3d.com))

View 2: Moved together to demonstrate overlap

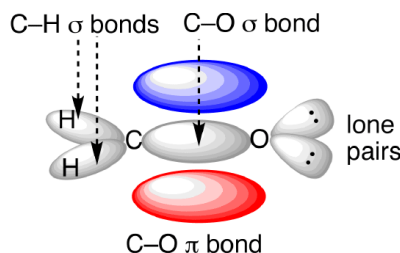
When moved together, there is overlap of the π and sp^2 orbitals.



(CC BY-SA-NC; Nick Graves via [ChemTube3D](https://www.chemtube3d.com))

View 3: Generation of new bonds to make the carbonyl bond

Formation of bonding interactions to form the sigma bond (from the sp^2 orbitals on C and O AND an π bond from the two non-hybridized p orbitals on C and O.



(CC BY-SA-NC; Nick Graves via [ChemTube3D](https://www.chemtube3d.com))

H_2CO is a planar molecule with C_{2v} symmetry. We ignore the $n(1s)$ core electrons on C and O as well as the σ electrons in the C-H bonds. Very low energy excitations will not be involved in the UV-VIS region. The ground state valence electronic configuration of

interest is:

$$n_a^2 \sigma^2 \pi^2 n_b^2 (\pi^*)^0 (\sigma^*)^0$$

This is the lowest energy MO's that originate from the **valence atomic orbitals** of the C and O.

What do they look like? <http://pubs.acs.org/doi/pdf/10.1021/ed050p400>

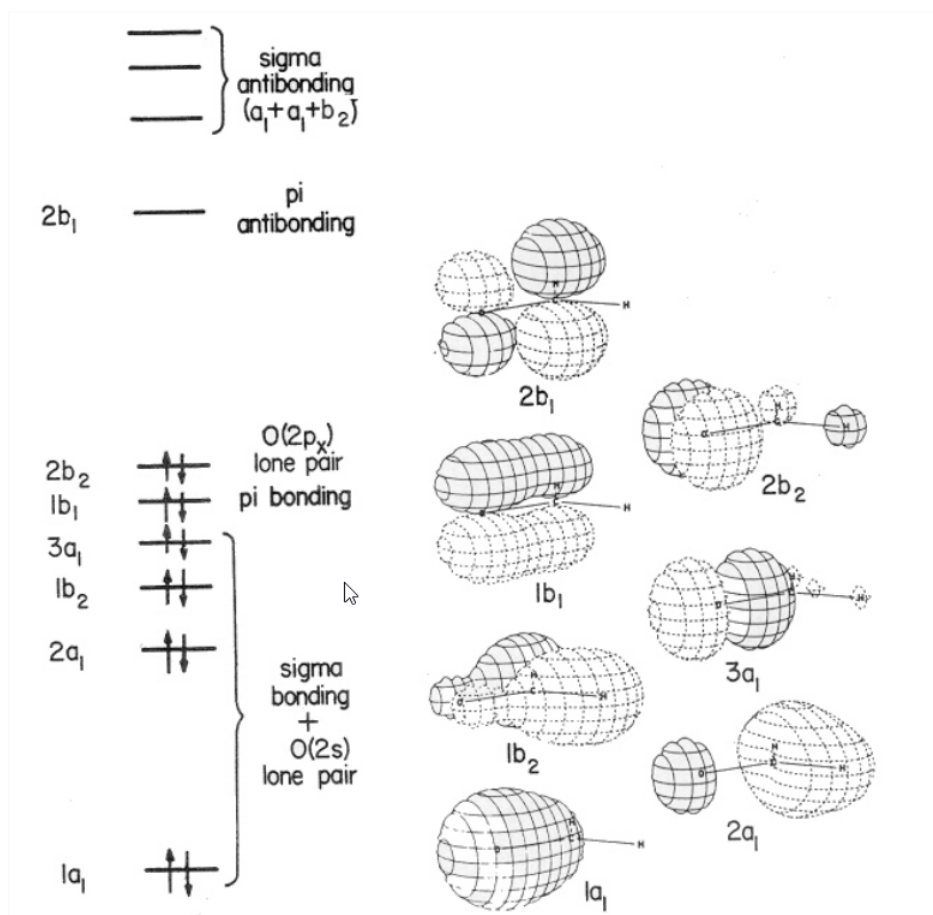


Figure XX: <http://pubs.acs.org/doi/pdf/10.1021/ed050p400>. All Rights Reserved ACS

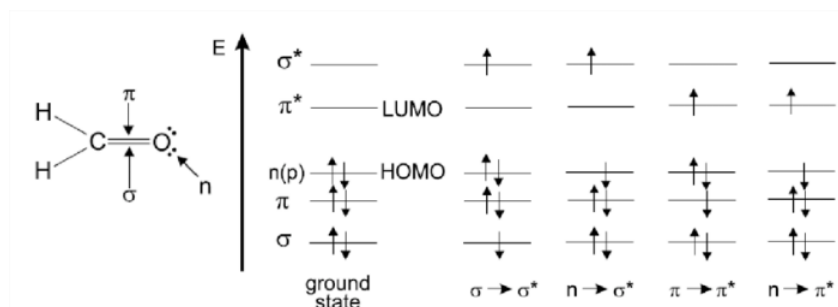
The MO energies are

$$n_a < \sigma < \pi < n_b < \pi^* < \sigma^*$$

from a simple MO calculation. $n < \sigma$ because $2s \ll 2p$. Let's ignore the lowest non-bonding state and focus on the "frontier orbitals" - the higher lying MOs.

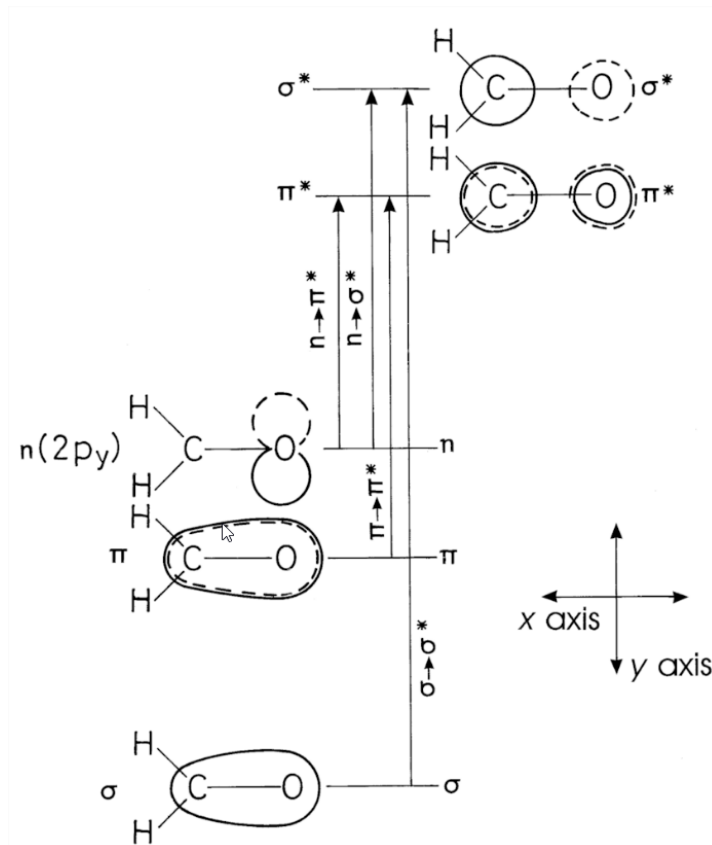
Possible Electronic Transitions

There are six outer valence e- are involved in major electronic transitions. The lowest energy transition is a $n \rightarrow \pi^*$ transition, while $\pi \rightarrow \pi^*$ and $n_a \rightarrow \sigma^*$ occur at higher ΔE and shorter λ .



Energy levels of molecular orbitals in formaldehyde.

Molecular orbitals of formaldehyde emphasizing the transitions (after Guillet [19]).



Triplet States

In addition to change in the orbital type, the excited electron may keep the same m_s , spin quantum number producing a singlet excited state. If m_s changes during the transition, the excited state had two $\uparrow\uparrow$ electrons and is a **triplet state**. For instance, the $n \rightarrow \pi^*$ transition can lead to a $^1(n_1\pi^*)$ if the m_s does **not change**, but to $^3(n_1\pi^*)$ if it **does change (flip)**. Both the singlet and triplet states have the same configuration, but lies lower in energy because $\uparrow\uparrow$ electrons are on average further apart than $\downarrow\uparrow$ electrons (reducing e-e correlation).

This MO description is oversimplified. e-e interactions are different in an excited state than in the ground state. So A single configuration description is not very good; however this descriptions can be improved by allowing configurations to exit together to minimize the energy of the excited state (e.g. CI-doubles, CI-triples). We will discuss this later.

2.7: The Carbonyl Group is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.