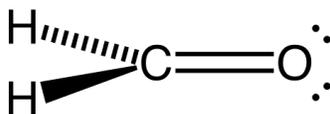


## 2.7: The Carbonyl Group

[http://mutuslab.cs.uwindsor.ca/Wang/...1/341\\_109c.pdf](http://mutuslab.cs.uwindsor.ca/Wang/...1/341_109c.pdf)

Let's look at the electron transitions of  $\text{H}_2\text{CO}$ , formaldehyde, for a typical description of the MO of an organic molecule.

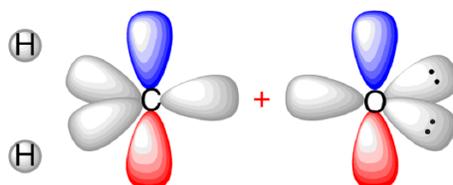


### Pretty valence-bond theory

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

#### View 1: Before (but after hybridization)

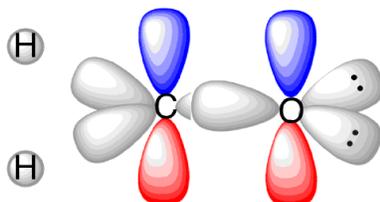
Carbon and the oxygen are both  $sp^2$  hybridized.



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

#### View 2: Moved together to demonstrate overlap

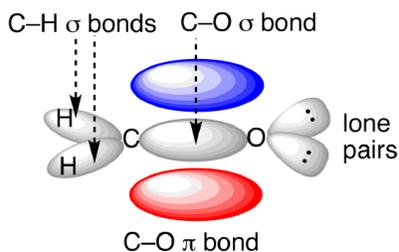
When moved together, there is overlap of the  $\pi$  and  $sp^2$  orbitals.



(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  $\pi$  bond from the two non-hybridized  $p$  orbitals on C and O.



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

$\text{H}_2\text{CO}$  is a planar molecule with  $C_{2v}$  symmetry. We ignore the  $n(1s)$  core electrons on C and O as well as the  $\sigma$  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>

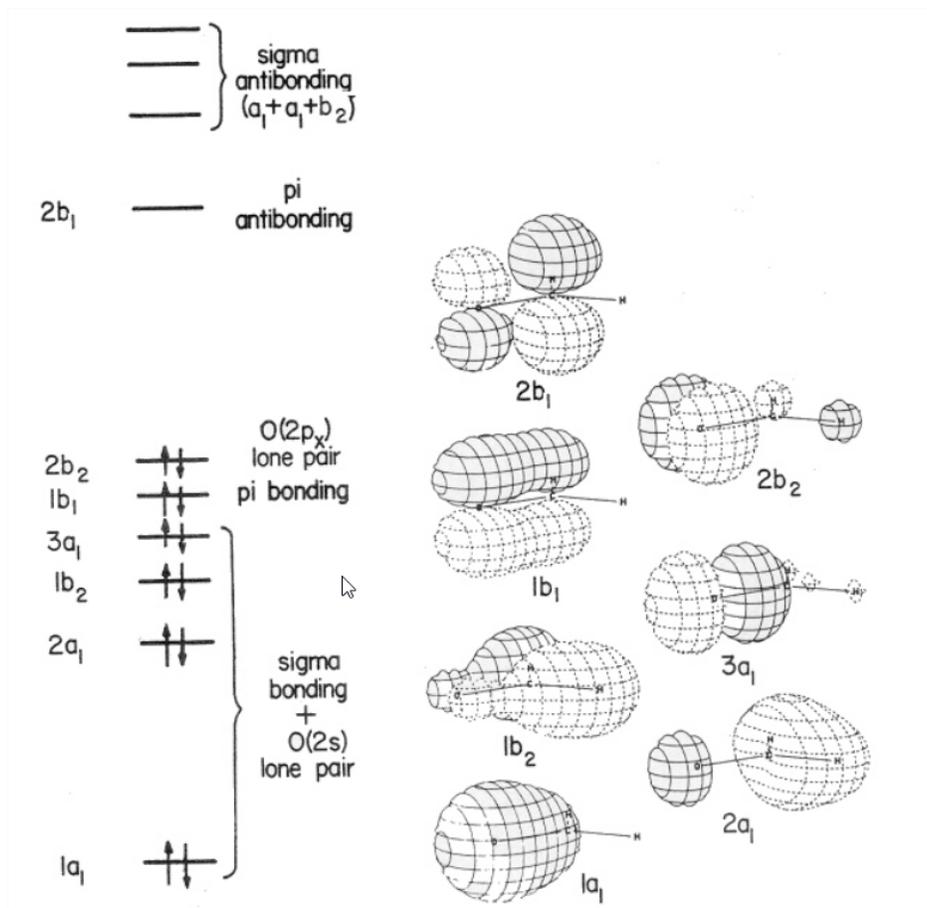


Figure XX: <http://pubs.acs.org/doi/pdf/10.1021/ed050p400>. All Rights Reserved ACS

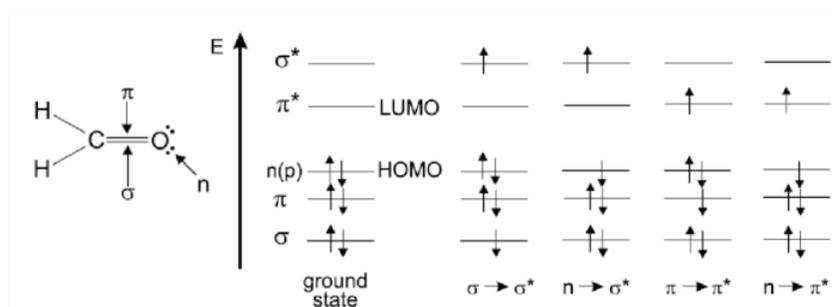
The MO energies are

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

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.

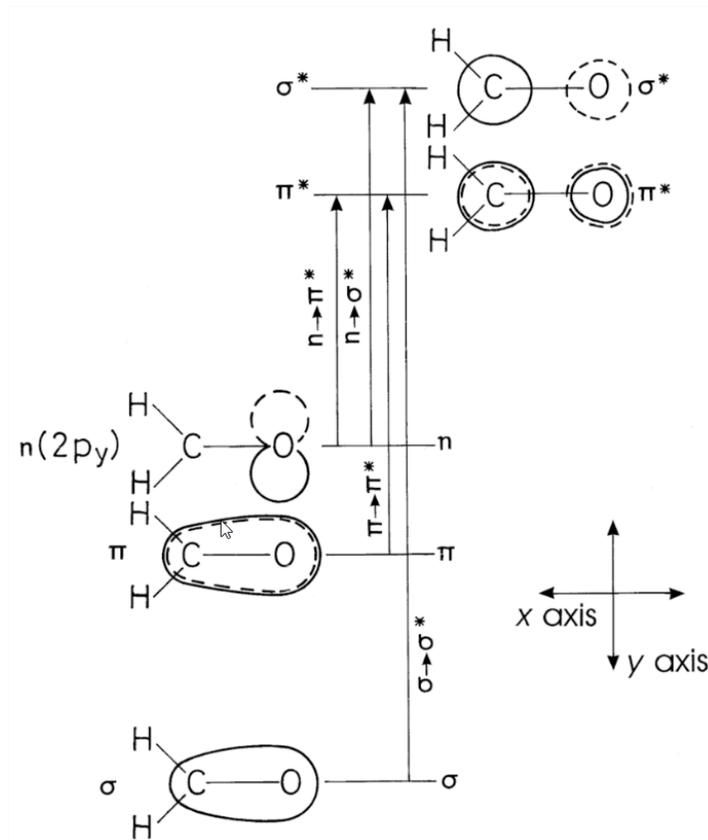
### Possible Electronic Transitions

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  $\Delta E$  and shorter  $\lambda$ .



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.

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