

BONDING IN METALLIC CARBONYLS

Carbon monoxide:

In order to understand the bonding in metal carbonyls, let us first see the MO diagram of carbon monoxide.

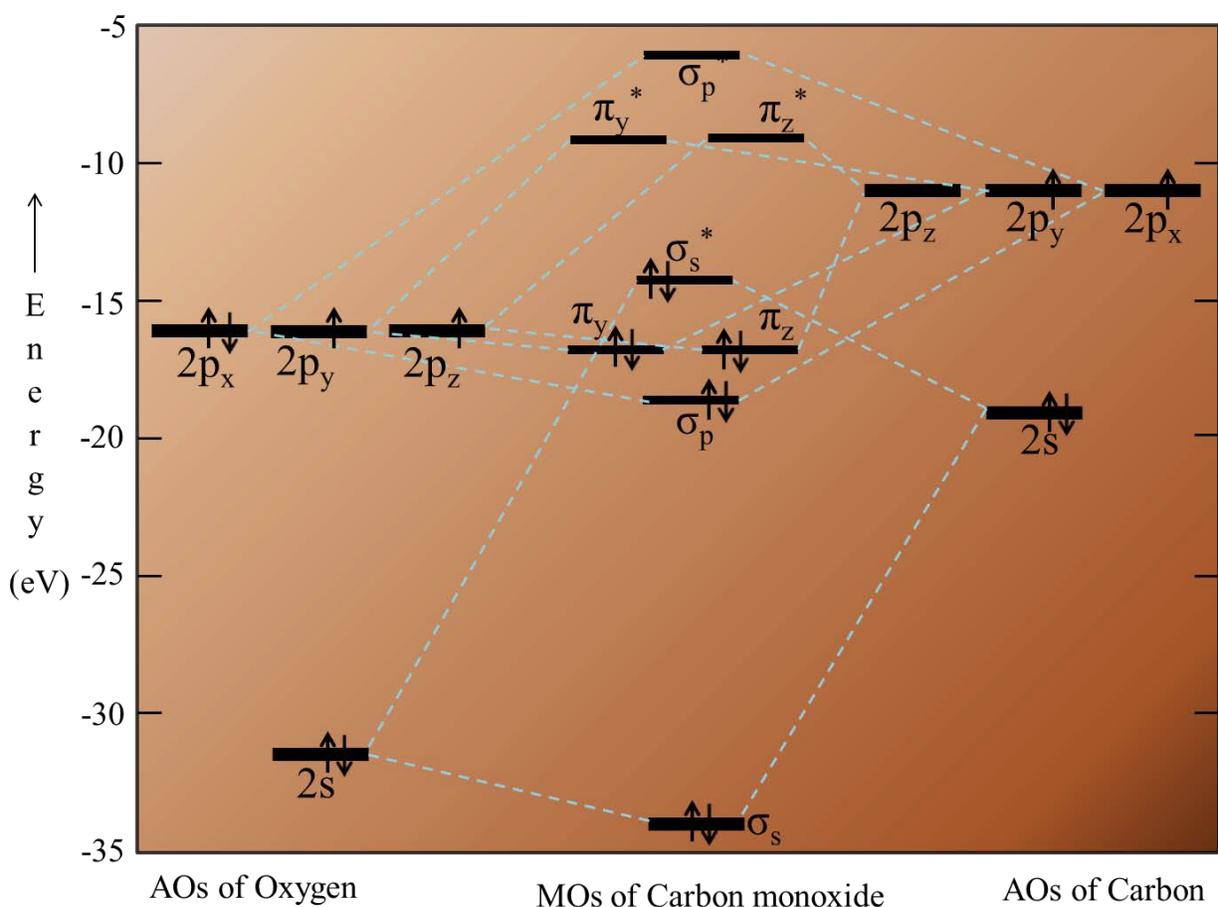


Figure: Molecular Orbital Energy Level Diagram of Carbon Monoxide

The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as:

$$(\sigma_s^b)^2 (\sigma_p^b)^2 (\pi_y^b = \pi_z^b)^4 (\sigma_s^*)^2 (\pi_y^* = \pi_z^*)^0 (\sigma_p^*)^0$$

(σ_s^*) is the highest occupied molecular orbital (HOMO) which can donate the lone pair of electrons for the formation of a $OC \rightarrow M$ σ bond.

$(\pi_y^* = \pi_z^*)$ are the lowest unoccupied molecular orbitals (LUMO) which can accept the electron density from an appropriately oriented filled metal orbital resulting into formation of a $M \rightarrow CO$ π bond.

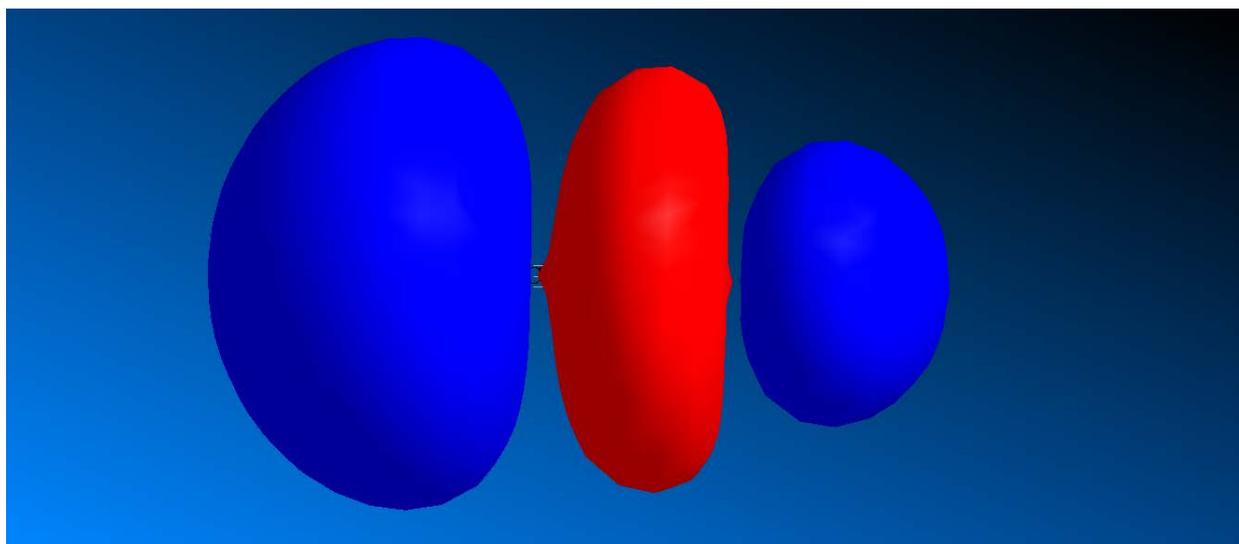


Figure: Highest occupied molecular orbital (HOMO) of carbon monoxide

(N.B: Red colour is for positive sign of the wave function while the blue colour indicates negative sign of the wave function)

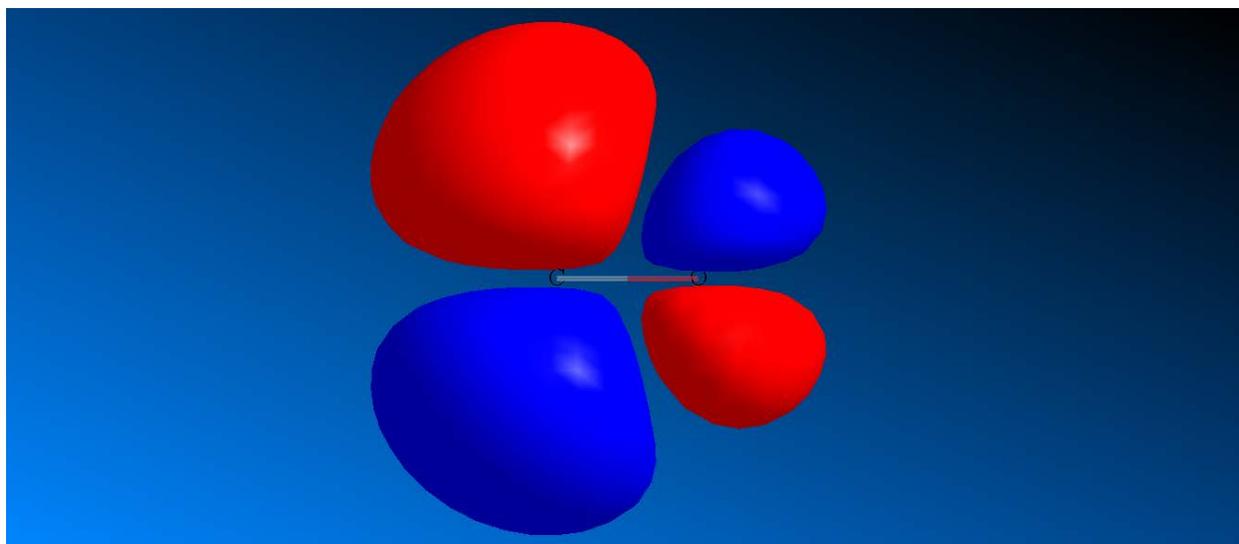


Figure: Lowest unoccupied molecular orbital (LUMO) of carbon monoxide

(N.B: Red colour is for positive sign of the wave function while the blue colour indicates negative sign of the wave function)

The nature of M-CO bonding in mononuclear carbonyls can be understood by considering the formation of a dative σ -bond and π -bond due to back donation.

Formation of dative σ -bond:

The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a $M \leftarrow CO$ σ -bond.



Figure: Formation of a $M \leftarrow CO$ σ -bond in metal carbonyls.

Formation of π -bond by back donation:

This bond is formed because of overlapping of filled $d\pi$ orbitals or hybrid $dp\pi$ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule. i.e. $M \xrightarrow{\pi} CO$

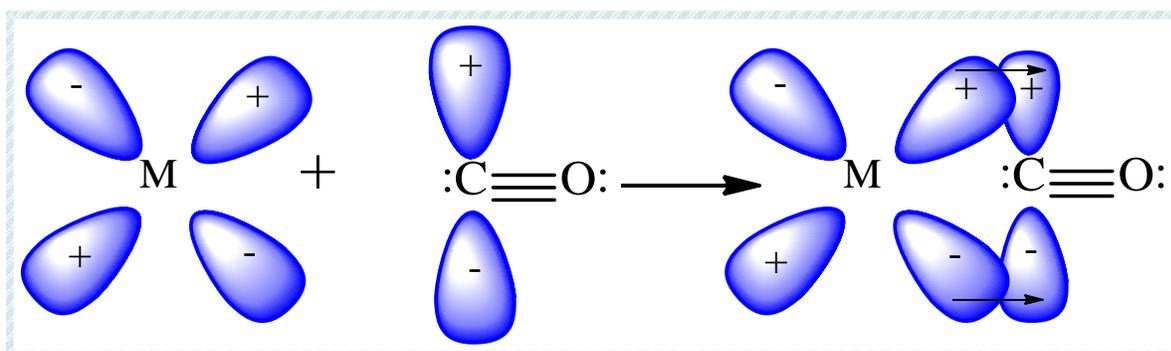


Figure: Formation of $M \xrightarrow{\pi} CO$ bond by back donation in metal carbonyls.

Bridging CO groups:

In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μ_n -CO, where n indicates the number of metals bridged. While n=2 is the most common value, it reaches to be 3 or 4 in certain less common carbonyls.

In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in μ_2 -CO group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

Source:

<http://nptel.ac.in/courses/104106064/>