

Now, the one half-filled sp_x -hybridized orbital of carbon atom overlap with half-filled sp_x -hybridized orbital of the oxygen atom to form a σ bond, while sp_x -hybridized lone pairs on both atoms remain non-bonding in nature. Moreover, two π bonds are formed as a result of the sidewise overlap; one between half-filled $2p_y$ orbitals, and the second one as a dative or coordinative interaction of fully filled $2p_z$ orbital of oxygen with empty $2p_z$ orbital of carbon.

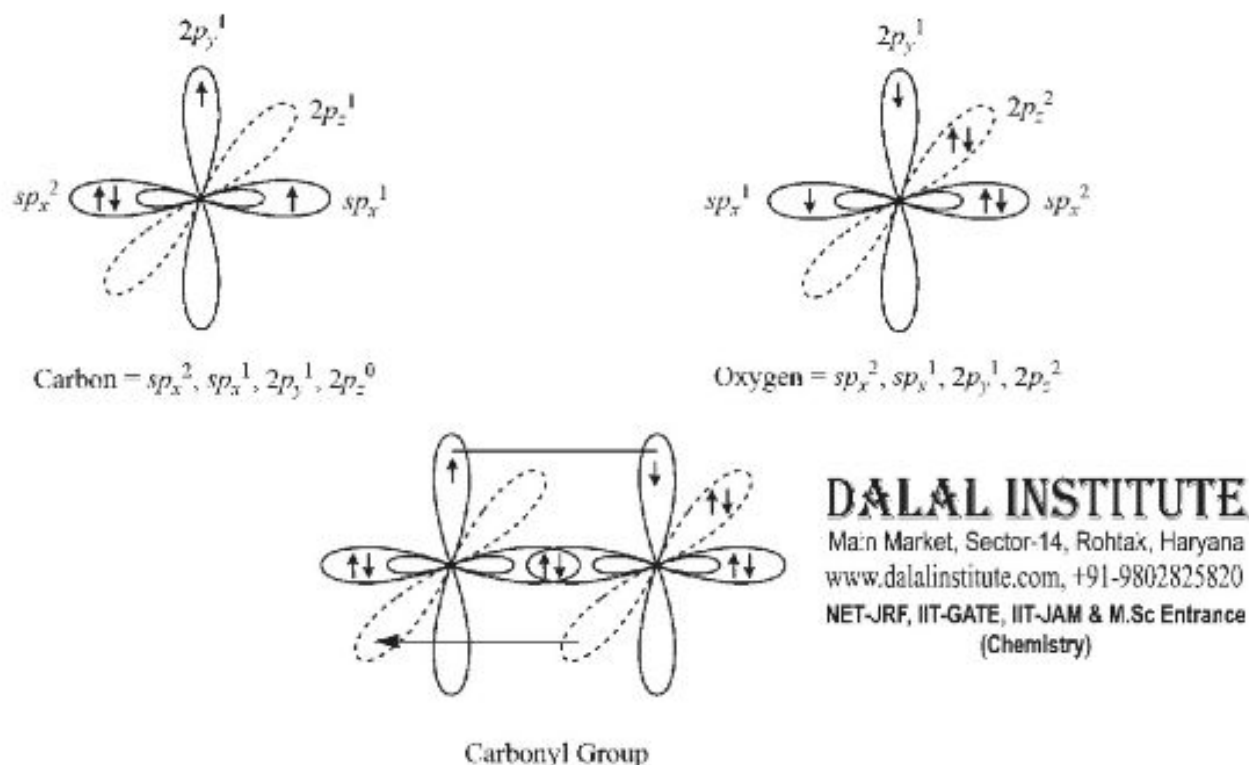


Figure 4. Bonding behaviour in CO ligand according to valence bond method.

Furthermore, the valence bond theory treats the bonding mode of carbonyl with metal centre in terms of hybridization and the resonance phenomena. The central metal atom or ion provides the required number of empty hybrid orbitals with proper orientation to accept the electron pair from surrounding ligands. For instance, in $\text{Cr}(\text{CO})_6$ the chromium atom undergoes a dsp^2 hybridization to generate six empty hybrid orbital equivalent shape and same energy. When one of the carbonyl ligand approaches this metal ion with its internuclear axis along x -axis, the filled hybrid lone pair of electron on carbon atom overlap with one of the two empty hybrid orbital orientated oppositely in x -direction. The metal-carbon multiple bond is explained in terms of various resonating structures which consequently reduces the bond strength of carbon-oxygen bond. It should also be noted that, though there are two hybrid lone pairs (one on carbon and the other on the oxygen); the bonding of carbonyl group with metal takes place via donation though carbon end always. This can be explained in terms of higher energy of hybrid lone pair carbon than oxygen.

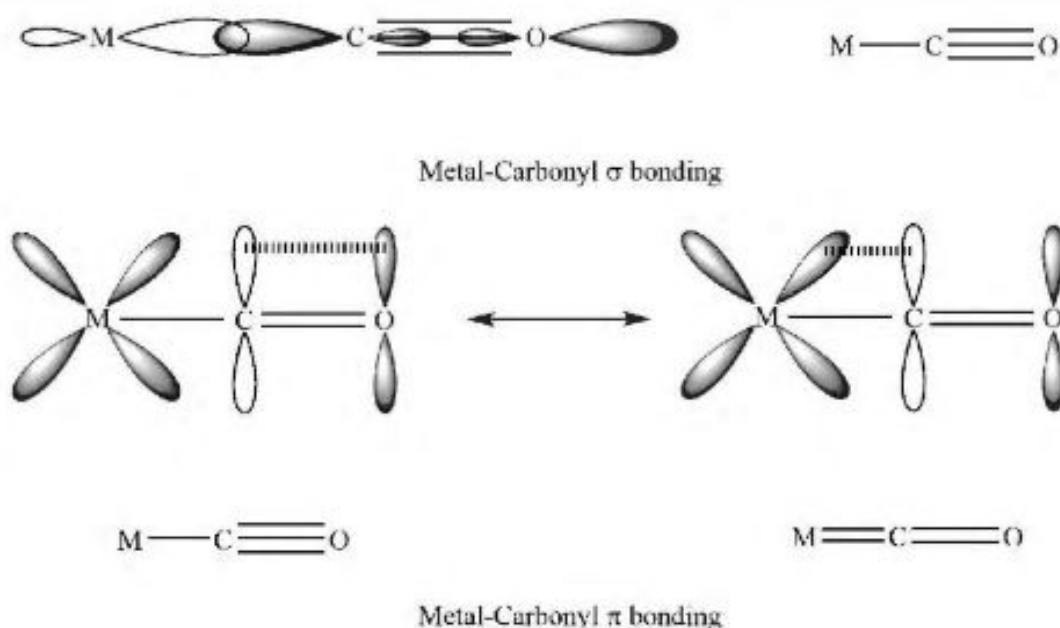
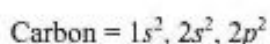


Figure 5. The valence bond nature of σ and π overlap in metal carbonyls.

2. Molecular orbital theory: This is the best model to explain the bonding within the CO ligand as well as in metal carbonyl complexes. There are total three molecular diagram for carbonyl ligand which were proposed from time to time. Though, all the three molecular orbital (MO) diagrams are able to explain the nature of metal-carbonyl π -bonding; the initial treatment was not so effective to explain the σ donation, the second one does also suffer from some minor anomalies. The third molecular orbital diagram is most widely accepted in the scientific community as it gives logical explanation to what had been a mystery in metal carbonyl chemistry. We will study these MO diagrams in the order they were proposed.

i) The first molecular orbital diagram of carbon monoxide assume that the atomic orbitals of carbon and oxygen interact with each other to create molecular orbitals. The electronic configurations of C and O are:



The number of outer electrons in carbon and oxygen are four and six, respectively. Thus, a total of 10 electrons are to be filled in the molecular orbitals of carbon monoxide molecule. The higher energy of corresponding atomic orbitals of carbon is due to its lower electronegativity, which makes the bonding and antibonding molecular orbitals to receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals will have more characteristics of atomic orbitals of Oxygen and antibonding Molecular orbitals would have more

characteristics of carbon. The electronic configuration of CO molecule will be $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2$ which gives a bond order three i.e. triple bond between carbon and oxygen. The molecular orbital diagram and expected bonding mode of the carbonyl ligand are given below.

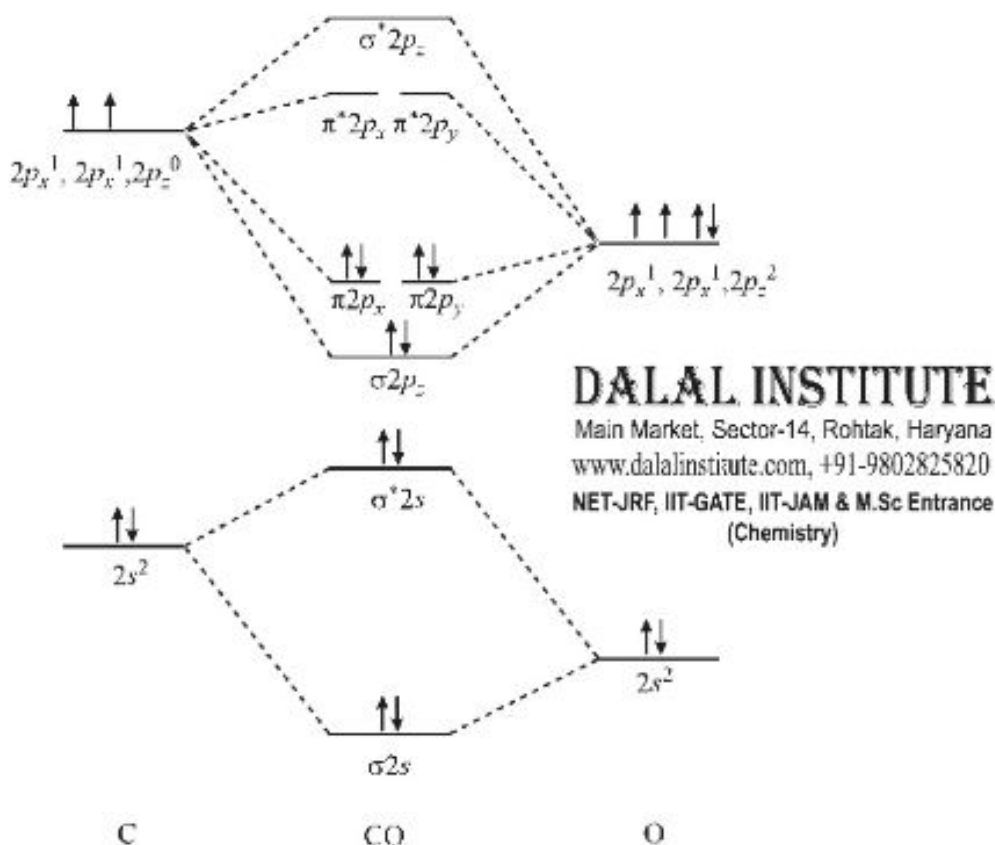


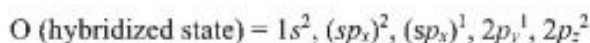
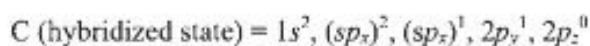
Figure 6. The first generation molecular orbital diagram of carbonyl ligand.

The formation of molecular orbitals given above is actually an oversimplification of a ticklish problem. This statement is made on the basis of two facts. The first one is that when one electron removed from CO to form CO⁺, the bond order actually increases, which is actually opposite of what is expected if electron is lost from a highest occupied molecular orbital (HOMO) of bonding nature. Its bond order should be decreased from the removal of electron from $\pi 2p_x^2$ or $\pi 2p_y^2$, which suggest that the HOMO of carbon monoxide should be of antibonding nature rather bonding. The second anomaly also arises from the MO diagram of CO ligand which clearly shows that in order to donate electron density from π -bonding molecular orbital, the carbonyl ligand must approach the metal centre with its carbon-oxygen internuclear axis perpendicular to x , y or z -axis assigned to central atom. This explains how the empty $\pi^* 2p_x$ and $\pi^* 2p_y$ could be used to accept electron density from filled d -orbitals of central metal atom or ion. However, in actual practice, the carbonyl ligand binds to metal centre in linear fashion via carbon end only.

Metal-Carbonyl σ donation and π acceptance

Figure 7. The expected nature of σ and π overlap in metal carbonyls from first MO of CO.

ii) The second molecular orbital diagram of carbon monoxide was suggested by Coulson which assumes that the first molecular orbital diagram of CO is not correct. According to Coulson, $2s$ and $2p_x$ atomic orbitals of both carbon and oxygen undergo hybridization before they create molecular orbitals. The carbon and oxygen atom in carbon monoxide are sp -hybridized with following electronic configurations.



The total number of valence electrons in carbon and oxygen are four and six, respectively; and thus, ten electrons are to be filled in the molecular orbitals of CO molecule. The half-filled sp_x hybrid orbitals of carbon and oxygen interact to form σ and σ^* molecular orbitals; while the fully-filled sp_x hybrid lone pair orbitals of carbon and oxygen remains non-bonding. Moreover, doubly degenerate sets of π -bonding and π -antibonding molecular orbitals are also formed due to the sidewise overlap of $2p_y$ orbitals and $2p_z$ orbitals.

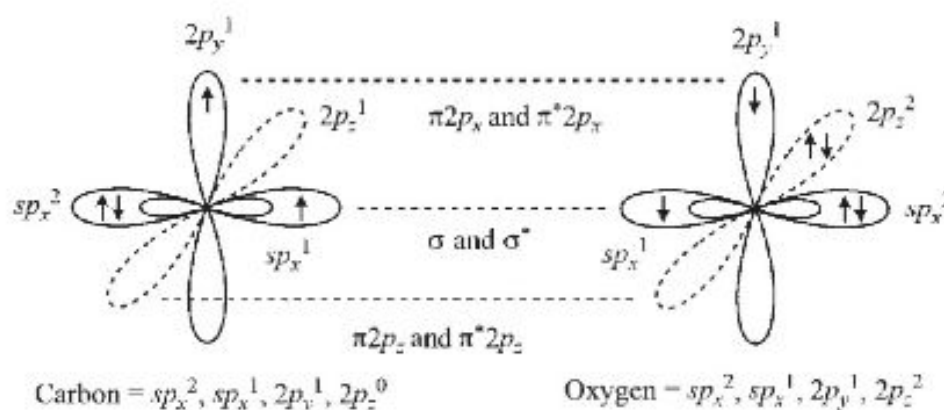
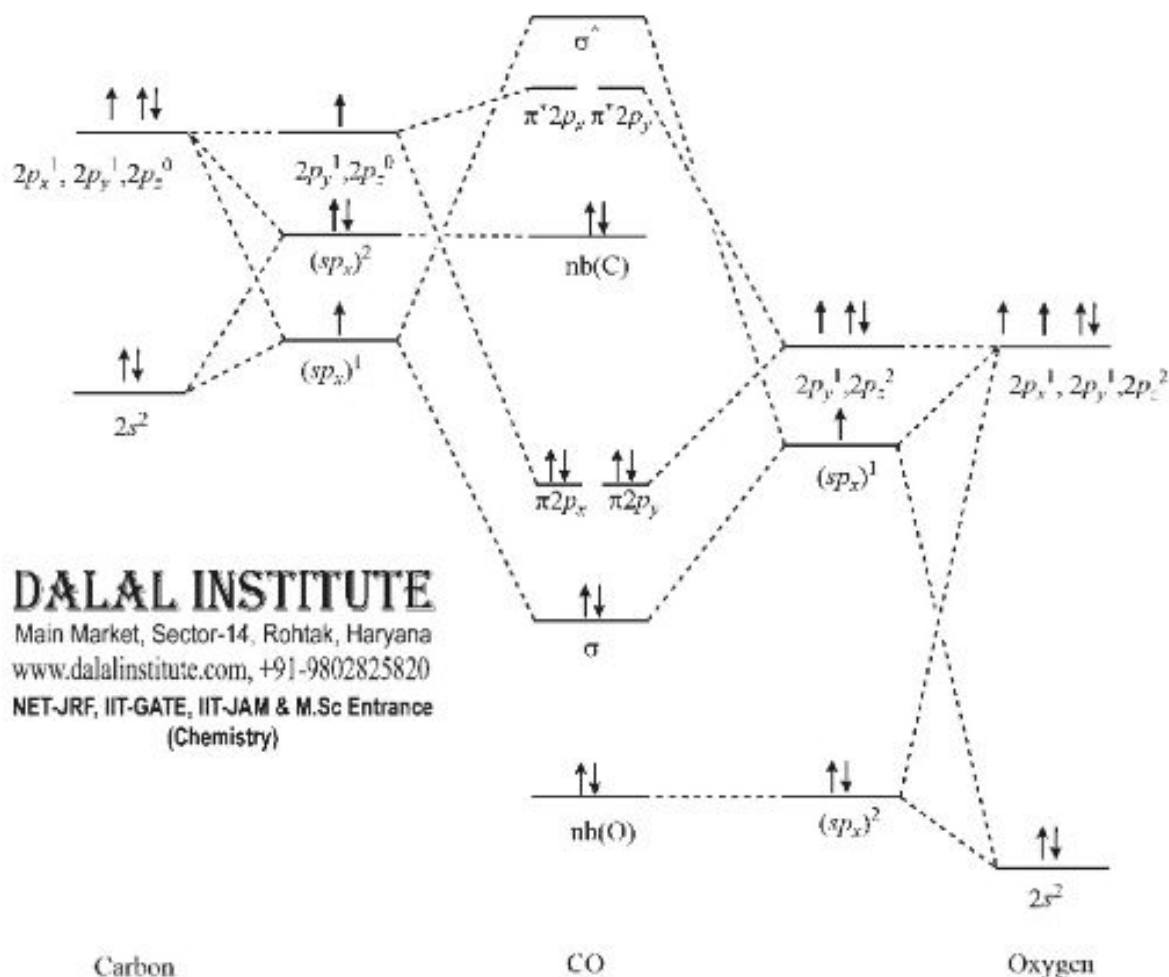


Figure 8. The nature of σ and π in carbonyl ligand.

The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals

will have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of carbon. The molecular orbital diagram carbon monoxide proposed by Coulson is given below.



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Figure 9. The second molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between metal centre and carbonyl ligand. This diagram eliminates the possibility of sigma donation through bonding molecular orbital and perpendicular orientation CO ligand as the HOMO is now non-bonding hybrid lone pair rather π -bonding. This also explains why the carbonyl group prefers to bond via carbon end in linear manner. This also explains how the lowest unoccupied molecular orbital (LUMO) $\pi^* 2p_x$ and $\pi^* 2p_y$ could be used to accept electron density from filled d -orbitals of central metal atom or ion. Moreover, the reduced CO stretching frequency of metal coordinated carbonyl can be attributed to the reduced bond order due to transfer of d -electron density from metal to π^* orbital carbonyl ligand. However, the increase in bond order when one electron is removed from