

CO to form CO^+ is still a mystery because the electron is lost from a highest occupied molecular orbital (HOMO) of nonbonding bonding nature, and the bond order should have been decreased.

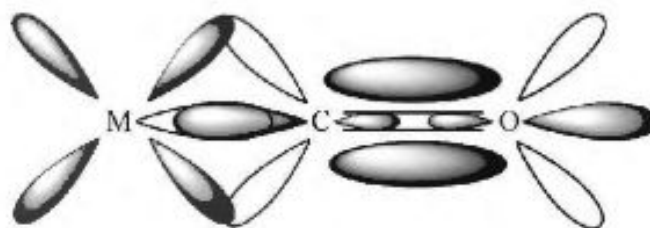


Figure 10. The nature of σ and π overlap in metal carbonyls.

iii) This molecular orbital diagram of carbon monoxide is most widely accepted to rationalize its σ -donor and π -acceptor strength. 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. A total of four singly degenerate σ -molecular orbitals and two doubly degenerate sets of π -molecular orbitals are formed. One doubly degenerate set of π -molecular orbitals will be bonding while the other one will be antibonding in nature. The nature of σ -molecular orbitals is more complex as three out of four are of bonding character. Initially, the σ_5 was thought to be of antibonding to justify the higher bond order of CO^+ . However, the σ_5 is slightly bonding in nature because there is some mixing with the p atomic orbitals of the right symmetry. Out of four σ -molecular orbitals, only σ_6 possesses the antibonding character, while σ_5 goes with expected bonding characteristics. The σ_5 is essentially non-bonding and almost centred on the oxygen atom. 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. The π -bonding molecular orbitals set will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, will be rich in atomic orbitals of carbon atom.

However, the problem that why does the bond order increase when an electron is removed from CO still persists. Because we are removing the electron from a bonding molecular orbital, its bond order must be decreased. The possible explanation for the shortening of bond after ionization is that the ionization induces a shift of the electron-polarization in CO ligand. In other words, the ionization occurs as the loss of an electron from a σ -HOMO orbital which is mostly carbon-centred; and since the HOMO- σ orbital is only slightly bonding in nature, the loss of bonding character is quite small and could easily be compensated by the advantage in covalent character; i.e. the formation of a positive partial charge on the carbon atom increases the strength of the covalence of the bond and thus decreases the bond length. This enhanced covalent character can also be visualized in terms of better interaction of two atomic orbitals if their energies are comparable. In carbon monoxide molecule the atomic orbitals of oxygen lie energetically a lot below than the atomic orbitals of carbon; But when the CO is oxidized to CO^+ , the partial positive charge on carbon shifts the atomic orbitals of carbon down in energy, and thereby makes the energies closer to the related atomic orbitals of oxygen, which leads to a stronger interaction when bonds are made.

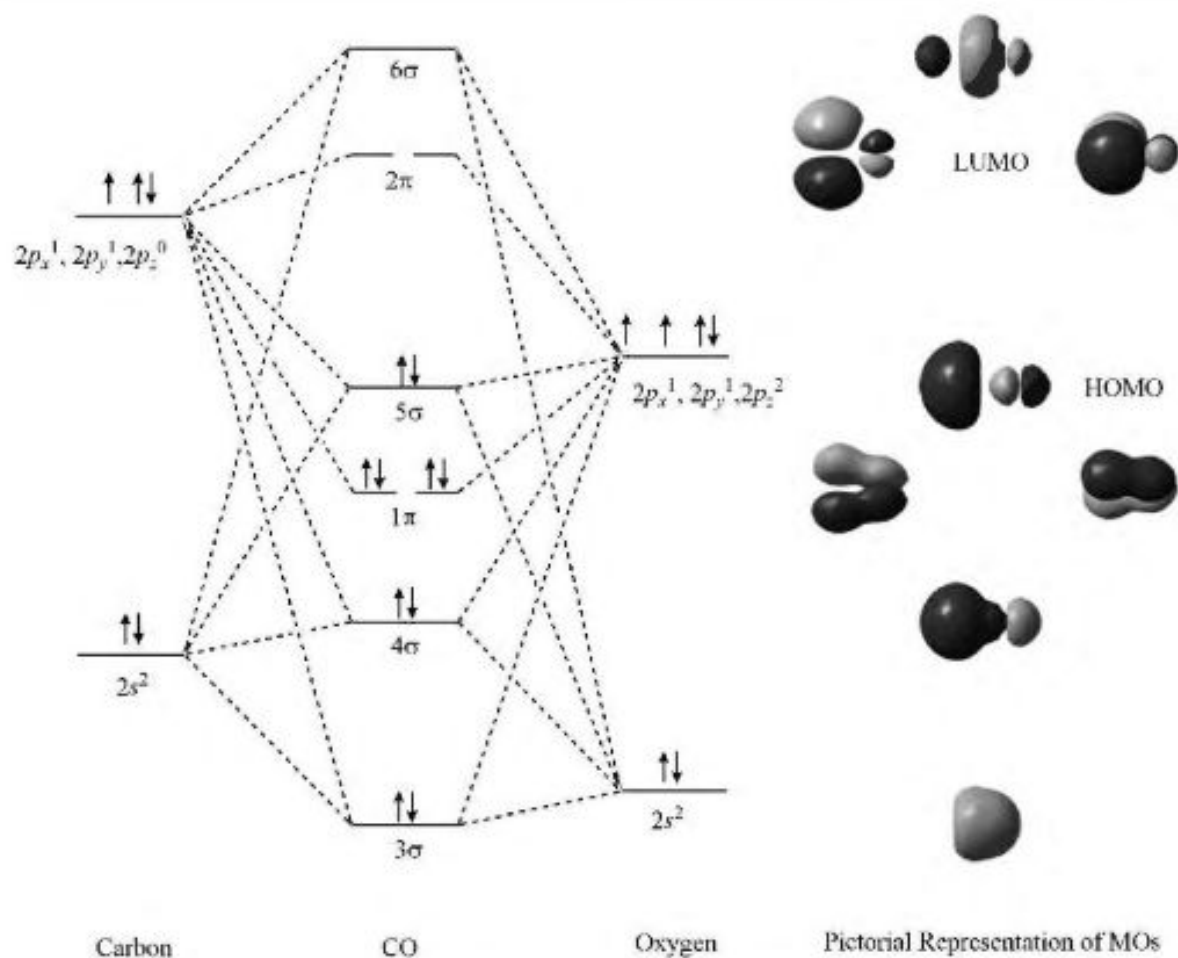


Figure 11. Third molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between metal centre and carbonyl ligand. The carbonyl ligand uses its HOMO for sigma donation while simultaneously accepts electron density from filled metal d-orbital to its π^* LUMO.

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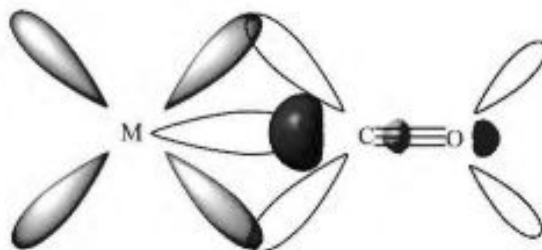


Figure 12. The second molecular orbital diagram of carbonyl ligand.

❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation

Vibrational spectroscopy is one of the most important method used for the characterization of metal carbonyls. This technique provides very useful information not only about the structural prototype of different metal carbonyl compositions, but also rationalizes the nature of bonding in them. Now, it is quite a well-known fact that the C–O vibration for free carbonyl group (CO gas) is typically denoted as ν_{CO} , and absorbs at 2143 cm^{-1} . However, this C–O absorption shifts downward (sometimes upward) to cover a very wide range of wavenumber as the carbonyl ligand gets attached to a metal centre. This is obviously due to the fact that the energies of the ν_{CO} band for the metal carbonyls directly correlate with the strength of the carbon-oxygen bond, and are inversely correlated with the strength of the π -backbonding between the metal and the carbon. In other words, the molecular orbital diagram of carbonyl group suggests that the highest occupied molecular orbital, used for σ -donation is weakly bonding; but the lowest unoccupied molecular orbital, used for accepting d -electron density from metal centre is strongly antibonding; therefore, the σ -donation does not affect the CO bond order very much but the acceptance of electron density in π^* orbital decreases the bond order and consequently the bond strength in significant way. This effect reduces the force constant of C–O bond, while the magnitude of force constant for M–C will be increased by this backbonding. As a result, the enhancement of backbonding shifts the metal-carbon and carbon-oxygen stretching to higher and lower values, respectively. The main features about the bonding and structure of metal carbonyls which can be obtained from the vibrational spectra of metal carbonyls are discussed below:

➤ 1. π -Basicity of the Metal Centre

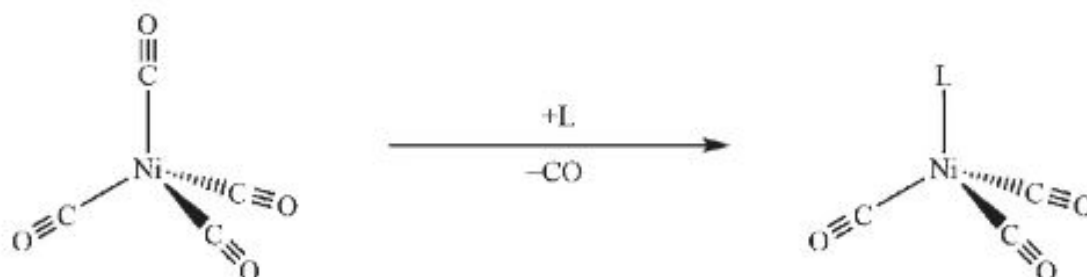
The π -basicity of the metal centre (and thus the C–O stretching frequency) depends upon a lot of factors like the nature and magnitude of the charge on metal centre, and the π -accepting tendency of ligands attached other than the carbonyl. A negative charge on the metal centre, or ligands with greater σ -donation and weaker π -accepter strength, are expected to decrease the CO stretching frequency; while an accumulation of positive charge on metal centre, or ligands with weaker σ -donation stronger π -accepter strength are bound to increase the CO stretching frequency. For example, in the isoelectronic series of $\text{Ti} \rightarrow \text{Fe}$, the hexacarbonyls show decreasing π -backbonding as one increases (makes more positive) the charge on the metal.

Compound	$[\text{Ti}(\text{CO})_6]^{2-}$	$[\text{V}(\text{CO})_6]^{1-}$	$[\text{Cr}(\text{CO})_6]$	$[\text{Mn}(\text{CO})_6]^{1+}$	$[\text{Fe}(\text{CO})_6]^{2+}$
$\nu_{\text{CO}} (\text{cm}^{-1})$	1748	1859	2000	2095	2204
Compound	$[\text{Hf}(\text{CO})_6]^{2-}$	$[\text{Ta}(\text{CO})_6]^{1-}$	$[\text{W}(\text{CO})_6]$	$[\text{Re}(\text{CO})_6]^{1+}$	$[\text{Os}(\text{CO})_6]^{2+}$
$\nu_{\text{CO}} (\text{cm}^{-1})$	1757	1850	1977	2085	2190

Hence, π -basic ligands increase π -electron density at the metal, and improved backbonding reduces ν_{CO} .

➤ 2. Tolman Electronic Parameter

The electron donating or withdrawing ability of a ligand is calculated in terms of Tolman electronic parameter (TEP), named after the inventor, Chadwick A. Tolman. It is determined by measuring the frequency of the A_1 vibrational mode of carbonyl group in complex, $Ni(CO)_5L$ by infrared spectroscopy, where L is the ligand being studied. $Ni(CO)_5L$ was chosen as the model compound because such complexes can easily be synthesized from $Ni(CO)_4$.



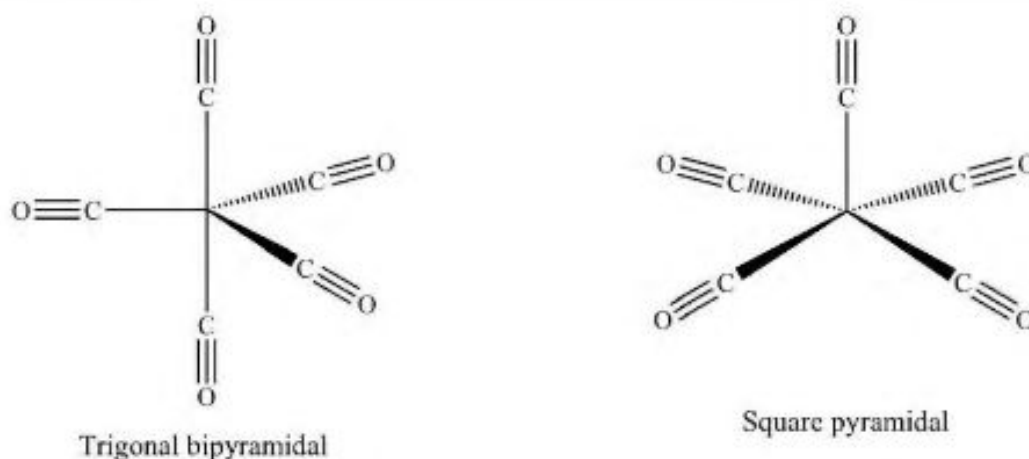
The CO band is pretty much unique, and is rarely affected by other bands in the analyte's IR spectra. Moreover, owing to the small size of carbonyl ligand, steric factors do not muddle the analysis. The coordination of CO to a metal, typically decreases ν_{CO} value from 2143 cm^{-1} (free CO). This can be rationalized by π -backbonding, resulting from the sidewise overlap of metal orbitals of π -symmetry with the empty anti-bonding π^* orbitals on CO ligand. This increases the strength of metal-carbon bond, but also weakens the C–O bond. If some other ligand enhances the π -electrons-density on the metal, the CO bond strength decreases and so the ν_{CO} value. On the other hand, if other ligands present compete with CO for π -backbonding, ν_{CO} increases. TEP for selected phosphines are given below.

L	P(t-bu) ₃	P(Me) ₃	P(Ph) ₃	P(OEt) ₃	PCl ₃	PF ₃
ν_{CO} (cm ⁻¹)	2056.1	2064.1	2068.9	2076.3	2097.0	2110.8

The Tolman electronic parameter has been widely used to characterize the electronic properties of phosphine based ligands.

➤ 3. Structural Prototype of Metal Carbonyls

The symmetry behaviour of different metal carbonyls can be used to determine the number of infrared active vibrational modes, which in turn enable us to comment on structural prototypes. In other words, it is well known from the group theory that only those vibrational modes will be observed which transform as the electric-dipole moment operator; therefore, the number of observable infrared transitions for a particular geometry can be predicted theoretically. These predictions are then matched with the experimentally observed infrared spectra to shortlist the various possible structural prototypes. For instance, consider the case of five-coordinated homoleptic metal carbonyl complexes. The two possible geometries are square-pyramidal and trigonal bipyramidal.

Figure 13. Two possible geometries of Iron pentacarbonyl i.e. $\text{Fe}(\text{CO})_5$ complex.

For trigonal bipyramidal geometry, reducible representation based on five C–O bonds is:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_4$	$3\sigma_d$	Irreducible components
Γ_π	5	2	1	3	0	3	$2A_1' + A_2'' + E'$

Out of four irreducible representations, A_2'' transforms as z-component while E' transforms with x- and y-components of the dipole moment. Now, owing to two doubly degenerate vibrational modes (E'), only two peaks are expected in the experimental infrared spectrum. However, in the Raman infrared spectrum, three peaks are expected as only $2A_1'$ and E' irreducible components transform alongside the polarizability tensors.

For square pyramidal geometry, reducible representation based on five C–O bonds is:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Irreducible components
Γ_π	5	2	1	3	3	$2A_1 + B_1 + E$

Out of four irreducible representations, $2A_1$ transforms as z-component while E transforms with x- and y-components of the dipole moment. Now, owing to two doubly degenerate vibrational modes (E), only three peaks are expected in the experimental infrared spectrum. However, in the Raman infrared spectrum, four peaks are expected as all of the irreducible components transform alongside the polarizability tensors.

Similarly, the CO ligands of octahedral complexes, e.g. $\text{Cr}(\text{CO})_6$, transform as A_{1g} , E_g , and T_{1u} , but only the T_{1u} mode (anti-symmetric stretch of the apical carbonyl ligands) is infrared-active; and therefore, only a single carbonyl stretching is observed in the IR-spectra of the octahedral metal hexacarbonyls. Spectra for complexes of lower symmetry are more complex. For example, the IR spectrum of $\text{Fe}_2(\text{CO})_9$ displays CO bands at 2082, 2019, 1829 cm^{-1} . The number of observable infrared-active vibrational modes for some metal carbonyls are listed in the following below.

Table 1. The number of IR-active vibrational modes of several prototypical metal carbonyl complexes.


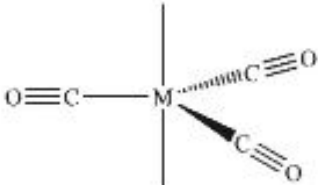
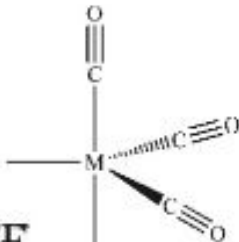
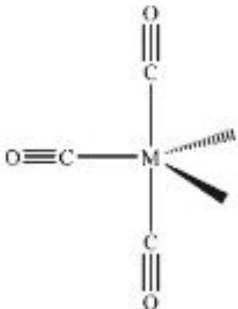
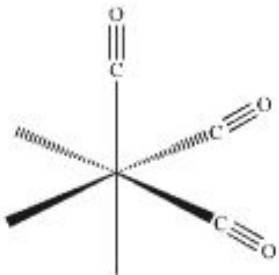
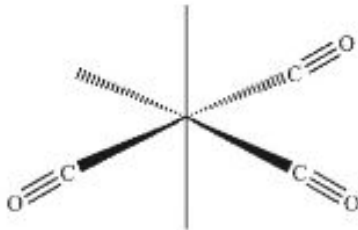
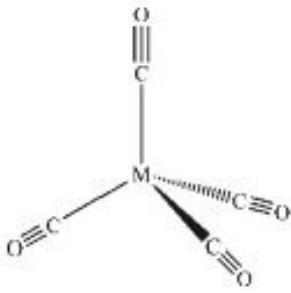
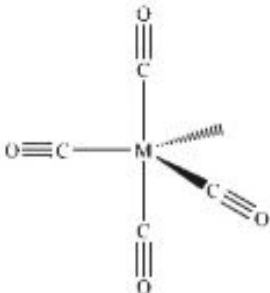
No. of carbonyls	Structural prototype (No. of IR-peaks)	Structural prototype (No. of IR-peaks)
Three		
	(2)	(1)
		
	(3)	(3)
		
	(2)	(3)
Four		
	(1)	(4)

Table 1. continued on next page...