



RAJDHANI COLLEGE

UNIVERSITY OF DELHI



Topic: Bonding in metallic carbonyls

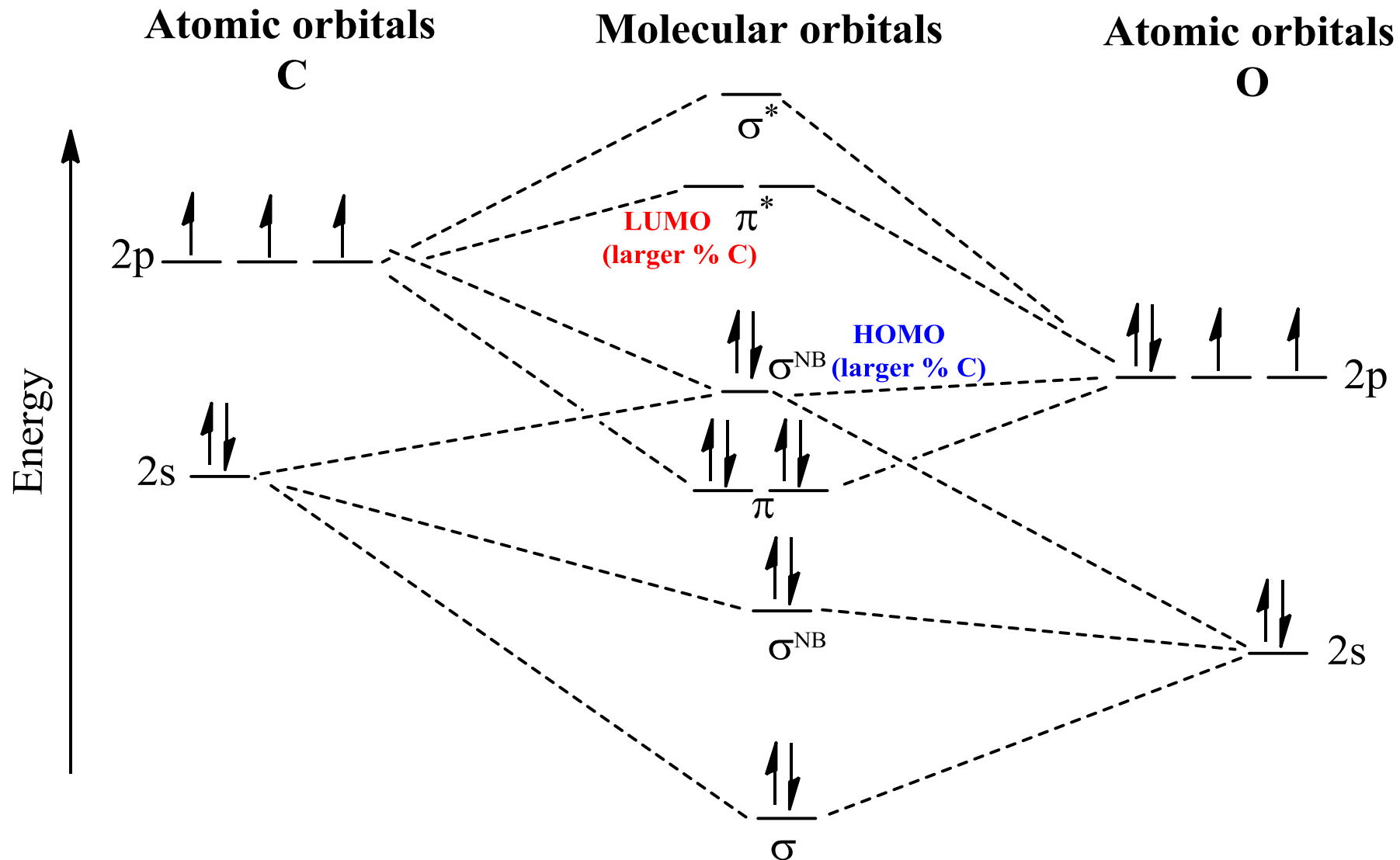
**For
B.Sc. APS
Semester VI**

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Molecular orbital diagram for CO



✓ For the carbon monoxide molecule, the highest energy occupied molecular orbital (HOMO) is a σ_{2p} orbital essentially derived from the high energy 2p carbon and oxygen atomic orbitals. We assume this orbital resembles a lone pair on the carbon atom.

✓ The lowest-energy unoccupied molecular orbitals (LUMOs) are the π^*_{2p} antibonding orbitals. Again, the predominant contribution comes from the 2p atomic orbitals of carbon, so they too, are focused around the carbon rather than around the oxygen atom.

✓ The HOMO of the CO is a σ orbital having a higher amplitude on the carbon atom than the oxygen atom and is therefore considered as a carbon based orbital which is also slightly antibonding in nature with respect to oxygen atomic orbitals. The π^* antibonding orbitals which are the LUMOs are closer in energy to the carbon atomic orbitals and thus have a greater amplitude on carbon.

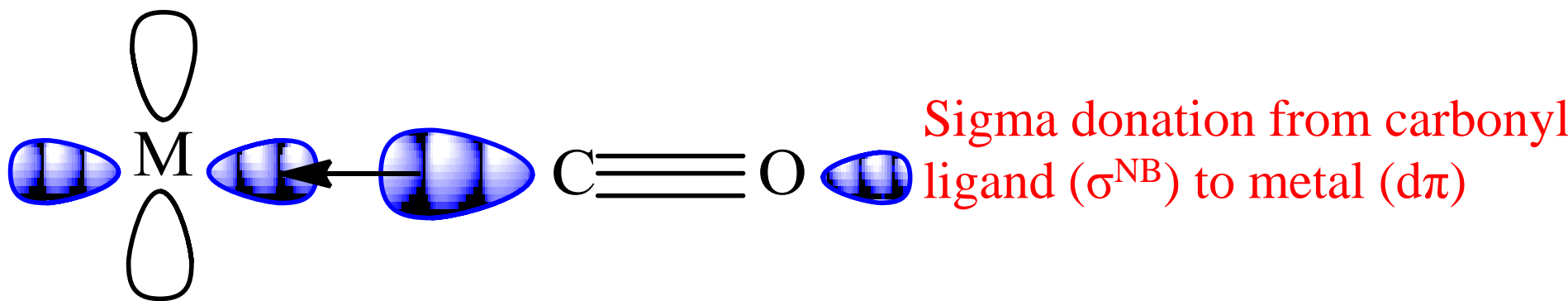
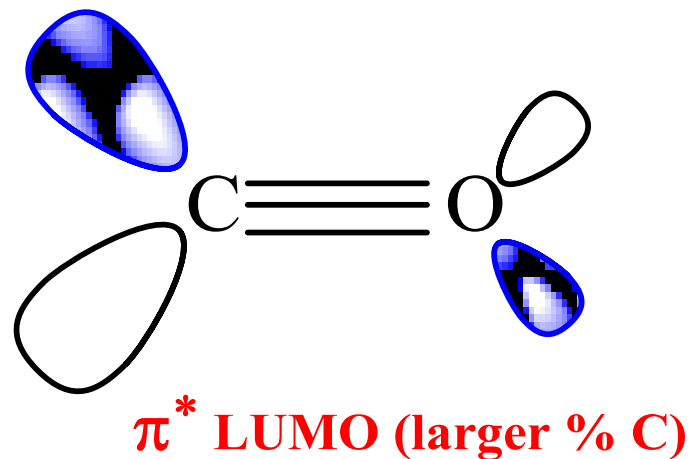
✓ This explains why CO binds through the carbon atom and also why it is good σ -donor and a good π -acceptor. There exist a strong back bonding or π overlap of metal electrons to the π^* antibonding orbitals of CO.

✓ Most of the metal carbonyls obey the 18 electron rule and in cases where it is not obeyed, the carbonyl will be comparatively more reactive and will undergo reactions such as dimerisation or electron abstraction to gain eighteen electrons.

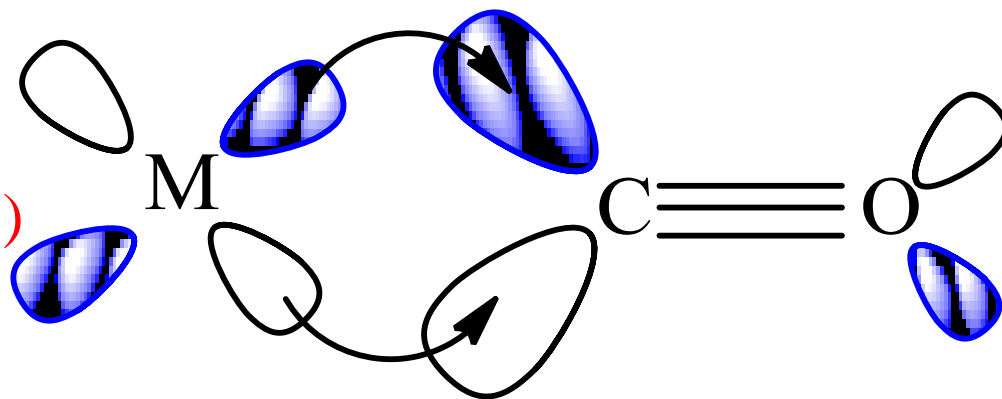
✓ Dimerisation is also dependent upon the size of the metal and the number of ligands it can accommodate without steric repulsion.

✓ This is a reason why the 17 electron species $\text{V}(\text{CO})_6$ does not undergo dimerisation while another 17 electron species $\text{Mn}(\text{CO})_5$ dimerises readily to gain 18 electrons by the formation of metal-metal bond.

Sigma donation and pi back bonding

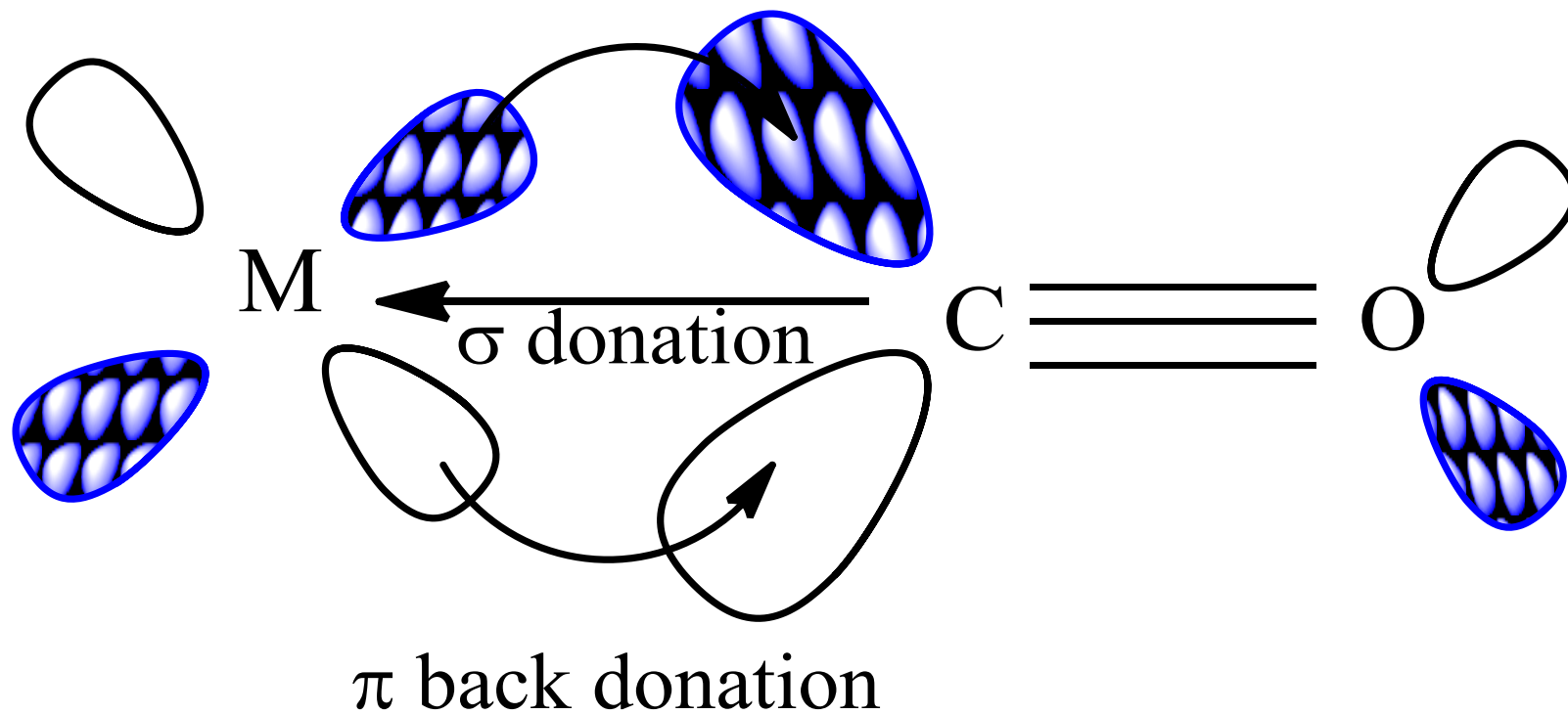


Pi back bonding from metal ($d\pi$) to carbonyl ligand (π^*)



- ✓ The HOMO (σ) of the carbon monoxide overlap with an empty d orbital of the metal, that is the carbon monoxide is acting as a Lewis base and donating a pair of electrons to the metal that acts as a Lewis acid. This leads to high electron density on the metal.
- ✓ All CO ligands simultaneously donating electrons to a metal centre which if it is in a low oxidation state will already be electron rich.
- ✓ At the same time, there is an overlap of a full d orbital on the metal with the π^* LUMO of the carbon monoxide. These two orbitals have the correct symmetry to allow this interaction, and thus the electron density is removed from the metal center back onto the carbonyl ligand to some extent. This additional bond is π bond.
- ✓ So the carbon monoxide is said to be a σ -donor and a π -acceptor and the metal is a σ -acceptor and a π -donor.

Synergistic effect/bonding



✓ Thus, there would be a flow of electrons from the carbon monoxide to the metal through the σ -system and a flow (back bonding or synergistic bonding) through the π -system in the reverse direction.

✓ This synergistic effect leads to a strong, short, almost double covalent bond between the metal and carbon atoms. It is the removal of electron density from the metal by the carbonyl ligand that enables us to account for the stabilization of low-oxidation states of transition metals.

✓ In a low- or zero-oxidation state, the metal would have a full, or nearly full, complement of electrons even before the bonding of the carbonyl ligands. The even higher electron density that results from coordination is then effectively removed to the ligands by the synergistic effect.

✓ According to this representation of the bonding, electrons would be “pumped” into the π^* antibonding orbital of the carbon monoxide. An increased occupancy of antibonding orbitals would lead to a reduction of the bond order below its value of 3 in the free carbon monoxide.

Evidence for synergistic bonding in metal carbonyls: IR study

Transition metal carbonyl	ν_{CO} (cm ⁻¹)
Free CO	2143
[Fe(CO) ₆] ²⁺	2204
[Mn(CO) ₆] ⁺	2098
[Cr(CO) ₆]	2000
[V(CO) ₆] ⁻	1860
[Ti(CO) ₆] ²⁻	1747

Transition metal carbonyl	ν_{CO} (cm ⁻¹)
Free CO	2143
[Fe(CO) ₄] ²⁻	1790
[Co(CO) ₄] ⁻	1890
[Ni(CO) ₄]	2060
[Ni(CO) ₃ PMe ₃]	2064
[Ni(CO) ₃ PPh ₃]	2069
[Ni(CO) ₃ PF ₃]	2111

✓ Infrared spectroscopy is a useful tool for investigating the structures of carbonyl compounds. The CO triple bonds vibrates around 2143 cm^{-1} in the gaseous state.

✓ The vibration frequency in carbonyl compounds lies within the range 2150 to 1850 cm^{-1} , depending on the structure and nature of other ligands present. If the synergistic bonding model is valid, then we would expect the length and strength of the C–O bond to be affected as electrons are pushed into the π^* orbital. As the bond becomes weaker and longer, it should vibrate at a lower frequency.

✓ The fact that CO triple bonds in carbonyl compounds do vibrate at lower frequencies than gaseous carbon monoxide does, indeed, support this model.

✓ The C–O stretching frequency is very sensitive to the electronic environment around the metal. For example, a higher electron density on the metal will cause an increase in the extent of the back bonding as more electron density is removed. This leads to an increase in the electron density in the π^* orbital, a lengthening of the bond, and a decrease of the C–O stretching frequency.

✓ As the negative charge on the complex increases, the metal has a higher electron density to be dispersed and so the back bonding is increased. Consequently, the electron density in the π^* will be increased, and the bond between the carbon and oxygen will become weaker and vibrate at a lower frequency. (See the table).

✓ In substituted carbonyls, the extent of back bonding can be observed by examining CO frequencies.

✓ In $[\text{Ni}(\text{CO})_3\text{PMe}_3]$ the methyl groups on PMe_3 show an inductive effect. In this case, electron density will be pushed toward the metal. This leads to an increase in the extent of back bonding, stronger M–C bonds, and a weaker C–O interaction, shown by the lower infrared stretching frequency.

✓ By contrast in $[\text{Ni}(\text{CO})_3\text{PF}_3]$ complex, fluorine in PF_3 is electron withdrawing and will remove electron density from the metal. This leads to a reduction in the extent of back bonding required, and so the C–O bond remains stronger and shorter, indicated by the higher stretching frequency.