VIVEKANANDA COLLEGE
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NAACC ACCREDITED ‘A’ GRADE

Topic: MO Theory

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Name of the Department: Chemistry

MO diagram of CO

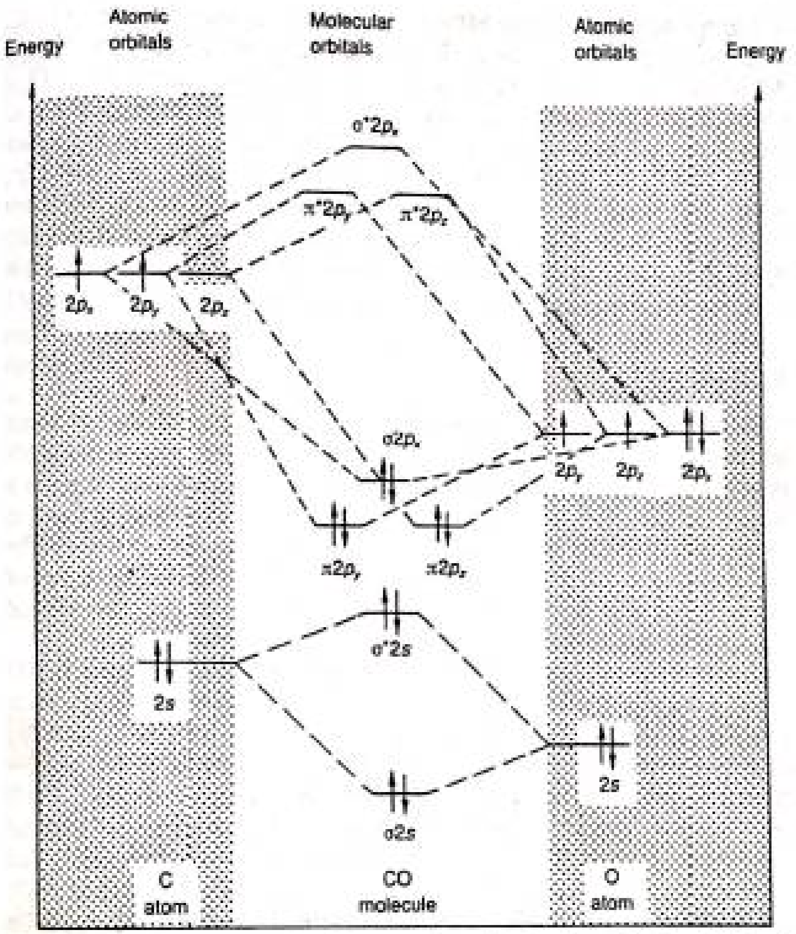

Figure 4.32 Electronic configuration, atomic orbitals and molecular orbitals for carbon monoxide. (The $\sigma 1s$ and $\sigma^* 1s$ MOs are omitted for simplicity.)

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2,\ \left\{\begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix}\right. \sigma 2p_x^2$$

This is shown in Figure 4.32.

The inner shell is non-bonding, and the bonding and antibonding $2s$ orbitals cancel, leaving one σ and two π bonds – and thus a bond order of 3. Alternatively the bond order may be calculated using the formula (bonding − antibonding)/2, that is $(10 - 4)/2 = 3$. This simple picture is not adequate, since if CO is ionized to give CO^+ by removal of one electron from the $\sigma 2p_x$ orbital then the bond order should be reduced to 2½ and the bond length increased. In fact the bond length in CO is 1.128 Å and in CO^+ it is 1.115 Å. Thus the bond length decreases when we expected it to increase, and it indicates that the electron must have been removed from an antibonding orbital. The problem remains if we assume the order of energy for the MOs is the same as for atoms heavier than C, since this only reverses the position of the $\sigma 2p_x$ and the ($\pi 2p_y$ and $\pi 2p_z$) MOs. The most likely explanation of the bond shortening when CO is changed to CO^+ is that the $\sigma 2s$ and $\sigma^* 2s$ molecular orbitals differ in energy more than is shown in the figure. This means that they are wider apart, and the $\sigma^* 2s$ MO is higher in energy than the $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ MOs. This illustrates very plainly that the order of MO energy levels for simple homonuclear diatomic molecules used above is not automatically applicable when two different types of atoms are bonded together, and it is certainly incorrect in this particular heteronuclear case.

HCl molecule

With heteronuclear atoms it is not obvious which AOs should be combined by the LCAO method to form MOs. In addition because the energy levels of the AOs on the two atoms are not identical, some MOs will contain a bigger contribution from one AO than the other. This is equivalent to saying that the MO 'bulges' more towards one atom, or the electrons in the MO spend more time round one atom than the other. Thus some degree of charge separation $\delta+$ and $\delta-$ occurs, resulting in a dipole. Thus partial ionic contributions may play a significant part in the bonding.

Consider the HCl molecule. Combination between the hydrogen $1s$ AO and the chlorine $1s$, $2s$, $2p$ and $3s$ orbitals can be ruled out because their energies are too low. If overlap occurred between the chlorine $3p_y$ and $3p_z$ orbitals it would be non-bonding (see Figure 4.22) because the positive lobe of hydrogen will overlap equally with the positive and negative lobes of the chlorine orbitals. Thus the only effective overlap is with the chlorine $3p_x$ orbital. The combination of H $1s^1$ and Cl $3p_x^1$ gives both bonding and antibonding orbitals, and the two electrons occupy the bonding MO, leaving the antibonding MO empty. It is assumed that all the chlorine AOs except $3p_x$ are localized on the chlorine atom and retain their original AO status, and the $3s$, $3p_y$ and $3p_z$ orbitals are regarded as non-bonding lone pairs.

This over-simplification ignores any ionic contribution such as can be shown with the valence bond resonance structures

$$H^+Cl^- \text{ and } H^-Cl^+$$

The former would be expected to contribute significantly, resulting in a stronger bond.