Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (First year)

Subject: Chemistry

Paper Code: CHC-101

Paper Title: Inorganic Chemistry and Organic Chemistry (Section A)

Unit: Chemical Bonding and Molecular Structure

Module Name: MO treatment of heteronuclear diatomic molecules,
Comparison of VB and MO approaches.

Module No: 27

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Notes

Molecular orbital energy level diagram for CO molecule

Fig. 1 depicts the molecular energy level diagram for CO molecule. From this figure, we can see that the atomic orbitals of oxygen have lower energy compared to the atomic orbitals of Carbon. This is because, the oxygen is more electronegative as compared to C.

Carbon monoxide possesses 10 valence electrons and therefore have the following configuration.

$$\mathrm{KK}(\sigma_{2s}^{b})^2\ (\sigma_{2s}^{*})^2\ (\pi_{2px}^{b}\cdot\pi_{2py}^{b})^4(\sigma_{2pz}^{b})^2$$

The bond order for the CO molecule can be calculated using the following formula :

Bond order = ½ (number of electrons in bonding MO’s – number of electrons in antibonding MO’s)

Since there are 8 electrons in the bonding orbitals and two electrons in antibonding orbital , the bond order in case of CO will be

Bond order = ½(8-2)

Bond order = 3

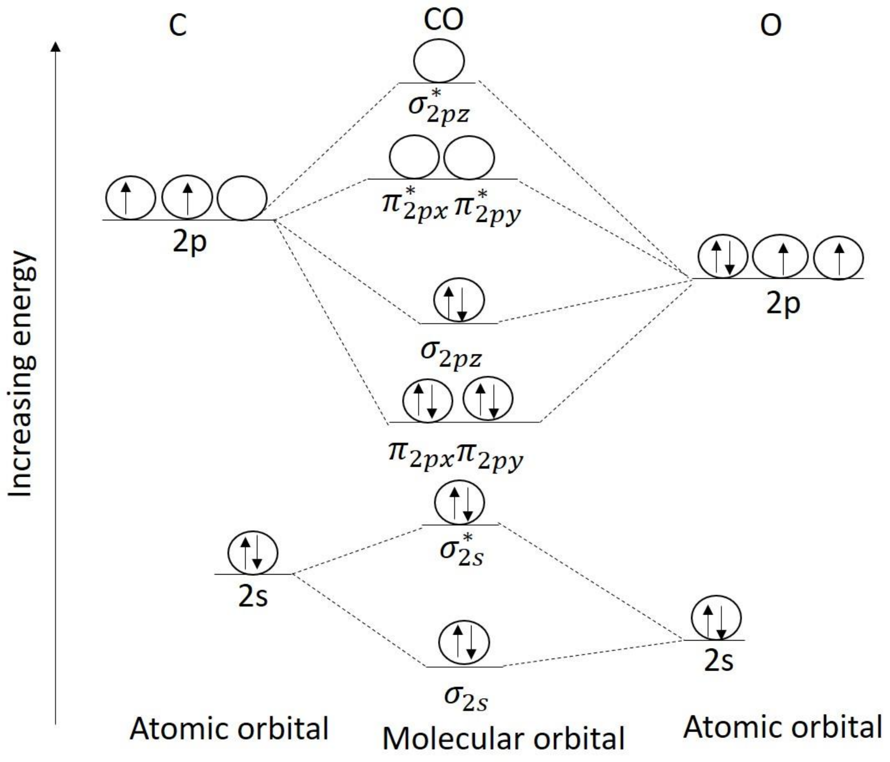

Fig. 1 : MO diagram for CO molecule

Since there are no unpaired electrons, CO is a diamagnetic molecule and it has net three bonding pairs (C≡ O)

MO energy level diagram for NO molecule

The MO energy level diagram for NO molecule is shown in Fig. 2. From this figure, we can see that the bonding M.O. are close to oxygen atom whereas the antibonding M.O. are closer to N atom.

The electronic configuration of N and O are

$$N : 1s^2\ 2s^2\ 2p^3$$

$$O : 1s^2\ 2s^2\ 2p^4$$

In total, there are five valence electrons in N whereas oxygen has 6 valence electrons. Thus the electronic configuration of NO will be

$$\mathrm{KK}(\sigma^b_{2s})^2(\sigma^*_{2s})^2(\sigma^b_{2pz})^2(\pi^b_{2px}\cdot\pi^b_{2py})^4\ (\pi^*_{2px})^1$$

The bond order in NO = ½ (8-3) = 2.5

It is paramagnetic with a single unpaired electron and can be readily oxidized to NO^+ by loss of π* electron.

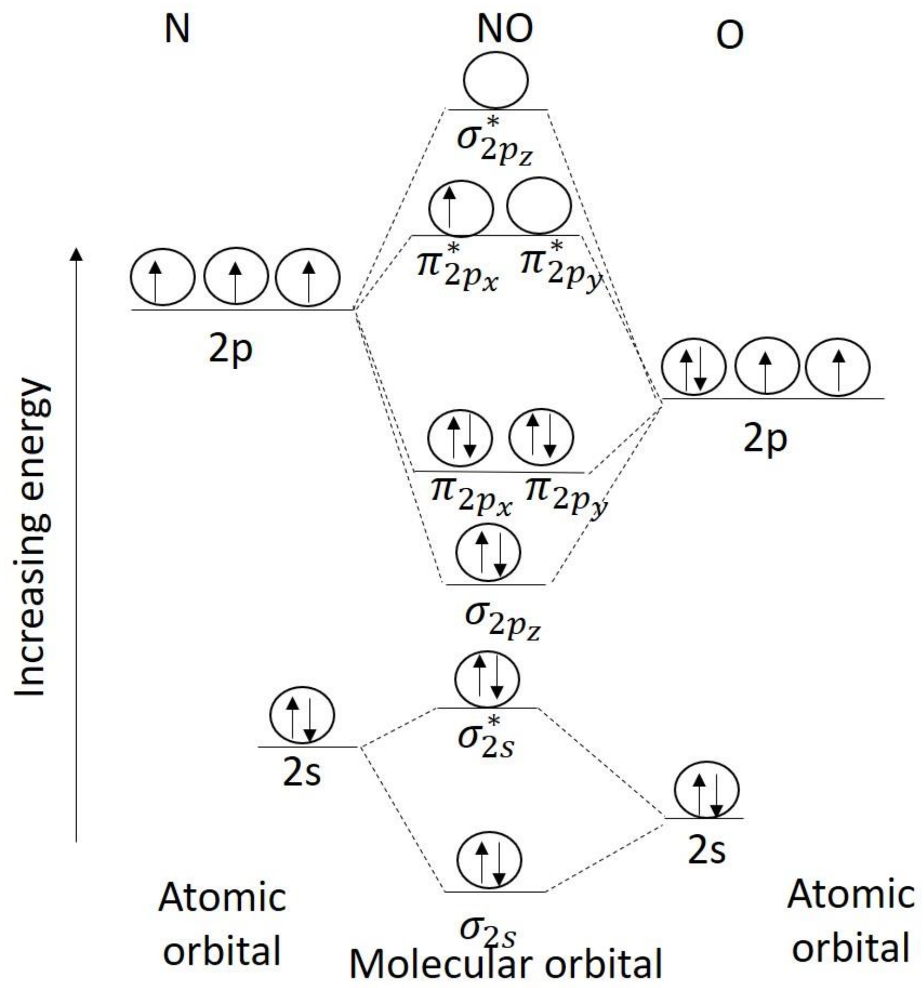

Fig. 2 : MO diagram for NO molecule

MO energy level diagram for NO^+ molecule

Fig. 3 depicts the MO energy level diagram for NO^+ molecule. The Nitrosyl ion, NO^+ can be formed by removal of one electron from the nitric oxide molecule.

$$NO \rightarrow NO^+ + e^-$$

Electronic configuration of NO^+ :

$$KK(\sigma^b_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma^b_{2pz})^2(\pi^b_{2px})^2(\pi^b_{2py})^2$$

Bond order in NO = ½ (8-2) = 3

Bond order in NO^+ is 3 represents one σ and two π- bonds.

Since the bond order of NO^+ is greater than NO, the Bond dissociation energy of NO^+ is greater than that of NO while the Bond length of NO^+ is smaller than that of NO.

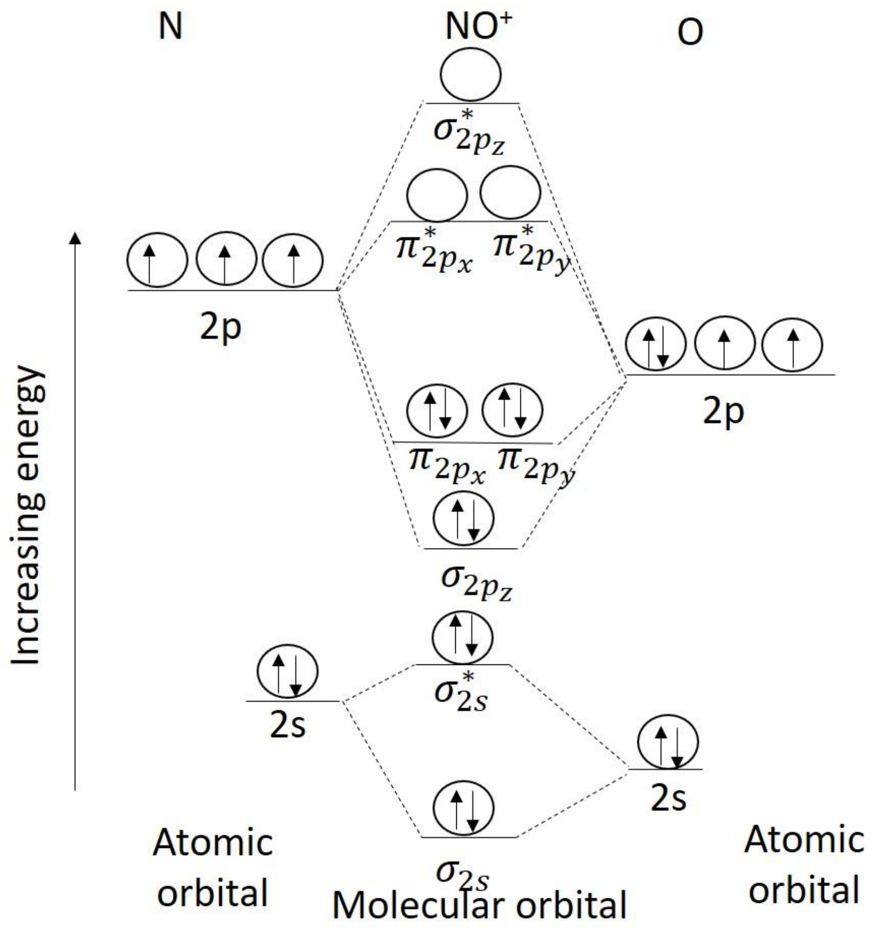

Fig. 3 : MO diagram for NO^+ molecule

Similarity between valence-bond and molecular orbital theory

- Both these theories are approximations
- Both interpret covalent bonds as orbitals embracing two atomic nuclei
- Both require that the combining atomic orbitals should be of nearly equal energy: they should be capable of overlapping and the combining orbitals must have the same symmetry.
- Both predict the concentration of electron density between the nuclei

- Both can account for directed valency
- Both predict the non-existence of helium molecule

Difference between Valence bond and Molecular orbital theory

Valence bond theory	Molecular orbital theory
Electrons in molecules are localized as if they are in isolated atoms.	It treats the nuclei of the molecule as polycentric and then constructs one electron molecular orbital
The total wave function in the valence bond treatment takes the contribution due to ionic terms.	Molecular orbital theory overlapping estimates the role of ionic terms in its total wave functions.
It could not explain the paramagnetism of O_2.	It can easily explain the paramagnetism of O_2.
Resonance is an integral part of valence bond theory.	Resonance has no role in molecular orbital theory
It is simple to apply.	It is more difficult to apply.