Connections between Concepts Revealed by the Electronic Structure of Carbon Monoxide

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ABSTRACT: Different models for the electronic structure of carbon monoxide are suggested in influential textbooks. Therefore, this electronic structure offers an interesting subject in teaching because it can be used as an example to relate seemingly conflicting concepts. Understanding the connections between ostensibly different methods and between different concepts, related or conflicting, is important in academic studies. The related reactivities of CO, O_2, and N_2 and the notations of molecular orbitals are topics of interest and are discussed in detail.
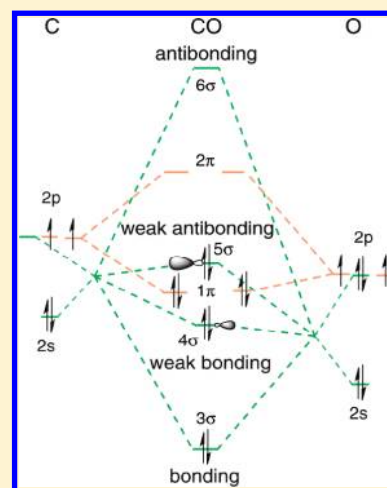
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Carbon monoxide offers an interesting subject for teaching electronic structure of molecules, particularly as different descriptions of its electronic structure are given in influential textbooks.[1−3] A comparison of the electronic structures of CO, N_2, and O_2 provide important insights for students. Different theoretical approaches, such as molecular orbital (MO) theory, self-consistent field (SCF) calculations, valence bond theory (VB), and experimental techniques such as photoelectron spectra, with bond strength indicators from bond lengths and vibration frequencies, can be introduced with emphasis on their inter-relationships. The material presented in this article can be included in course lectures or presented as extracurricular materials.

■ MOLECULAR ORBITAL DESCRIPTION

The molecular orbital diagram for CO is shown in Figure 1A. CO is isoelectronic with N_2. The principles[4−7] for the formation of the homonuclear N_2 molecular orbitals from its constituent atomic orbitals, as shown in Figure 1B, can be usefully applied to CO[8] despite it being heteronuclear. The molecular orbitals of CO formed from their constituent atomic orbitals can be obtained from two methods that are equivalent mathematically as shown below.

The first method, following the conventional SCF approach, involves mixing the 2s and 2p orbitals of carbon and oxygen atoms together. This approach gives the correct order of energy levels[9] for orbitals 1π and 5σ as shown in Figure 1A. The

second method involves two steps, first mixing carbon 2s with oxygen 2s, and carbon 2p with oxygen 2p, to give $\sigma(2s)$, $\sigma^*(2s)$ and $\sigma(2p)$, $\sigma^*(2p)$ molecular orbitals, which are bonding, antibonding and bonding, antibonding, respectively, as the precursors of 3σ, 4σ and 5σ, 6σ for CO in a manner equivalent to that established for O_2 (Figure 1C). Subsequently in the second step, the orbitals $\sigma(2s)$ and $\sigma(2p)$ with bonding symmetry as shown in Figure 1C can be mixed to give the refined 3σ and 5σ orbitals shown in Figure 1A. The mixing of $\sigma^*(2s)$ and $\sigma^*(2p)$ gives the final 4σ and 6σ. The mixing can occur because the energy difference between 2s and 2p orbitals for carbon is small. The mixing of 2s and 2p orbitals for oxygen is less than that of carbon, as indicated by the O_2 molecule, so that the second step of orbital mixing is not needed. In principle, mixing orthogonal orbitals in a molecule would not result in more effective new orbitals.[10] However, the mixing in step 2 can reduce the molecular energy further because step 1 is a first approximate.

In step 2, the energy of the 3σ orbital is lowered enhancing its bonding nature, and some antibonding nature is added to the 5σ orbital making it either weakly bonding or weakly antibonding. Mixing the two antibonding $\sigma^*(2s)$ and $\sigma^*(2p)$ orbitals in a similar fashion gives the final orbitals 4σ and 6σ. Both steps result in 6σ being an antibonding orbital and 3σ being a bonding orbital,
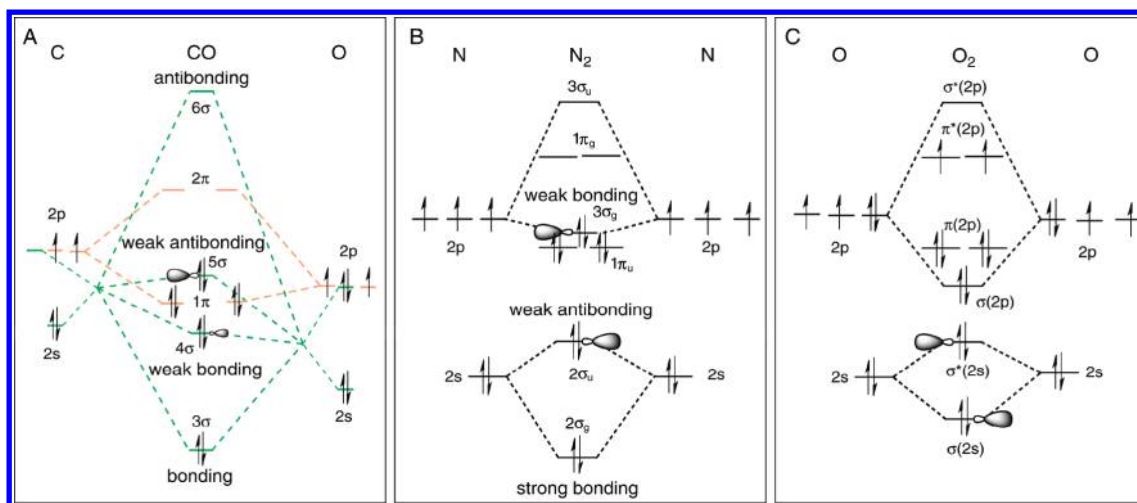
355

Figure 1. Effect of s−p mixing on relative energies of the molecular orbitals: (A) CO, (B) N_2, and (C) O_2. The levels of the atomic orbitals of the constituent atoms are shown on the left and right in each figure with molecular orbitals in the center.

although the latter might not be strongly bonding because it originates from the weakly bonding $\sigma(2s)$ in the first step.

Because the bonding and antibonding effects of the two steps on 4σ and 5σ are opposed, further information is needed to establish whether 4σ and 5σ orbitals are weakly antibonding or weakly bonding, though they behave similarly to nonbonding orbitals. Photoelectron spectra can be used to determine the nature of 4σ or 5σ orbital in N_2 and CO.[11,12]

By the Franck−Condon principle and by comparing the data of bond lengths and vibration frequencies of the relevant bonds when an electron is lost from different orbitals, it can be shown that in N_2 the $2\sigma_u$ or 4σ orbital is weakly antibonding and that the $3\sigma_g$ or 5σ orbital is weakly bonding. For N_2 $[(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2]$, the fundamental frequency $\bar{\nu}$ is 2330 cm^{-1}, the bond length is 109.78 pm, and the bond energy is 941.69 kJ/mol. The greater the bond stretch frequency, the stronger the bonding. When an antibonding electron is removed from $2\sigma_u$ to give N_2^+ $[(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^4(3\sigma_g)^2]$, $\bar{\nu}$ becomes 2373 cm^{-1}, and the bond length becomes 107.5 pm.[5−7] When a bonding electron is removed from $3\sigma_g$ or $1\pi_u$ to give N_2^+ $[(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^1$ or $(2\sigma_g)^2$-$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2]$, $\bar{\nu}$ becomes 2175 or 1873 cm^{-1}, and the bond length becomes 111.6 or 117.6 pm, and the bond energy for the former ion is 842.16 kJ/mol.

Even though CO is isoelectronic with N_2, the following data show that the 4σ orbital of CO is weakly bonding and that the 5σ orbital is weakly antibonding, thus showing a significantly different assignment from that in N_2. For CO $[(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2]$, the fundamental frequency $\bar{\nu}$ is 2159 cm^{-1}. When a weekly antibonding electron is removed from 5σ to give CO$^+$ $[(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^1]$, $\bar{\nu}$ remains unchanged at 2160 cm^{-1}. When a bonding electron is removed from 4σ or 1π to give CO$^+$ $[(3\sigma)^2(4\sigma)^1(1\pi)^4(5\sigma)^2$ or $(3\sigma)^2(4\sigma)^2(1\pi)^3(5\sigma)^2]$, $\bar{\nu}$ becomes 1690 or 1610 cm^{-1}.[12,13] Usually, σ bonding is stronger than π bonding. Note that the frequency data show that the 4σ orbital is weaker than the 1π orbital, which is evidence that the 4σ orbital is weakly bonding. Other evidence about the bonding, nonbonding, or antibonding nature of the orbitals comes from the peak patterns of the photoelectron spectrum correlated with the vibration wave function and Franck−Condon principle.

The electron pairs in the weakly bonding 4σ and 5σ orbitals for CO can also be described as lone pairs,[14] just as the $\sigma(2s)$

and $\sigma^*(2s)$ orbitals behave as lone pairs. Some authors have described the orbitals in CO differently, namely, assigned the bonding 3σ orbital as a lone electron pair,[15−17] and the weakly bonding 4σ as a bonding orbital.[15,16] But this assignment is incorrect. The erroneous assignment of 3σ as a lone electron pair may arise partly from the notation of the orbitals, because the notation of $\sigma(2s)$, $\sigma^*(2s)$, $\sigma(2p)$, and $\sigma^*(2p)$ adopted for O_2 is not suitable for N_2 where a more general notation with σ_g and σ_u is adopted to account for the mixing of 2s and 2p. The most general notation with 3σ, 4σ, and 5σ is adopted for CO. Wrong use of these notations can readily cause inaccurate assignments.

The 5σ lone pair in CO is conventionally indicated by $3\sigma_g$ in N_2, which can be confused with the 3σ in CO although the latter is a very different orbital. The other possible reason for the assignment of 3σ as a lone electron pair probably arises from the electronic structure of O_2. In the two-step method mentioned above, the 3σ and 4σ orbitals in CO obtained in the first step correspond to the two lone electron pairs $\sigma(2s)$ and $\sigma^*(2s)$ in O_2. The overall effect of $\sigma(2s)$ and $\sigma^*(2s)$ in O_2 is nonbonding, so the 3σ in CO was assigned as a nonbonded lone electron pair because 3σ in CO corresponds to $\sigma(2s)$ in O_2.

Indeed, some authors[18−20] assigned the triple bond of CO (or N_2) to the 5σ (or $3\sigma_g$) and two 1π orbitals on that the bonding 3σ (or $2\sigma_g$), was balanced by the "antibonding " 4σ (or $2\sigma_u$) by comparing with $\sigma(2s)$ and $\sigma^*(2s)$ in O_2.

It really looks like a quadruple bond in CO as shown in Figure 1A. Indeed, s and p orbital mixing reorganized the orbitals to make the 3σ, 4σ, and two 1π orbitals as all bonding while the 5σ orbital is nonbonding. But 3σ, and 4σ are weakly bonding orbitals and the total effect is that the molecule CO still has a triple bonding nature equivalent to that found in N_2.

Assigning the 3σ orbital as a lone electron pair might be reasonable because it comes from the weakly bonding $\sigma(2s)$ orbital in the first step before s and p mixing. The orbital shapes are not as easily predicted[8] and the 3σ orbital has also been assigned as an unbound 2s orbital[8,21] taking into consideration the fact that the 2s and 2p orbitals in oxygen do not mix very much. However, the peak for the 3σ orbital in the photoelectron spectrum of CO is quite broad,[11] which indicates its bonding nature from the Franck−Condon principle, whereas the peaks for the 4σ orbital are restricted in a narrow region, an indicator of weak bonding. The effect of more bonding in the

3σ orbital, and more antibonding in the 4σ orbital resulting in a weaker 4σ bond ensures that the total bond order does not change. The weakly bonding 4σ and 5σ orbitals are assigned as lone electron pairs, an assignment that is based on the consideration that the lower-energy atomic orbitals from oxygen contribute more to the bonding 3σ and weakly bonding 4σ orbitals, whereas the higher-energy atomic orbitals from carbon contribute more to antibonding 5σ and 6σ orbitals. This assignment has some merit in that it conforms to that obtained from VB theory as shown in Figure 3 of the next section. The above argument is even more relevant in the case of isoelectronic CN⁻, where the 3σ orbital becomes more bonding and the 4σ orbital becomes more nonbonding because the energy gap between 2s and 2p is smaller for N than for O. Thus, both atoms can donate electrons. In KFe[Fe(CN)$_6$], CN⁻ ions bridge ions to form Fe^{2+}−CN−Fe^{3+} moieties in a net structure. Similarly, there are SCN⁻ anions bonded through S or N with nonbonding orbitals located on N or S, respectively.

The mixing of 2s and 2p in N$_2$ and CO can be used in later courses to show the necessity of including polarization functions in basis sets used in SCF calculations to give a more accurate account of the bonding nature of a molecule. This mixing can be also considered as molecular orbital hybridization equivalent with the concept of atomic orbital hybridization.

Reactivity can also be covered at this stage. CO is more reactive than N$_2$ because the 5σ orbital in CO is a weakly antibonding orbital with higher energy whereas 3σ$_g$ in N$_2$ is a weakly bonding orbital. The highest-occupied molecular orbital (HOMO) of a molecule is usually used as a donating orbital in chemical reactions. A bonding orbital usually has a lower energy than an antibonding orbital and the electron pair in a lower-energy orbital is less likely to be donating. Thus, compared with the weak antibonding 5σ orbital in CO, the HOMO of the weakly bonding 3σ$_g$ in N$_2$ would be less likely to donate its electrons, though cautions must be taken in considering different molecules as detailed in ref 22.

Furthermore, when the bonding σ(2p) orbital is mixed with the σ2s orbital in an antibonding way, the resulting 5σ orbital becomes more nonbonding. When a bonding orbital becomes more antibonding, the electrons are dispersed away from the area between atoms. For heteronuclear molecules, this nonbonding effect results in a lone electron pair. Thus in CO, the orbitals from carbon contribute more to the 5σ orbital making it an outward-pointing lone pair centered on C,
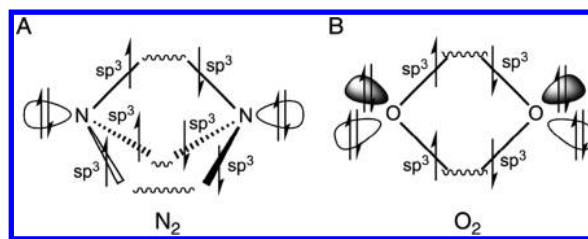

Figure 2. Bonds formed between two nitrogen or two oxygen atoms. Another way to represent the bonds in (A) N$_2$ and (B) O$_2$ as a unitary transformation of the σ and 1π orbitals represented in Figure 1 to their equivalent bending bonds.

whereas in N$_2$ orbitals on both nitrogen atoms contribute similarly to the 3σ$_g$ orbital so that they are balanced on the two nitrogen atoms. These effects make CO more reactive than N$_2$.

The bonding strength in dinitrogen is not affected significantly even when both electrons are removed from the 3σ$_g$ weak bond to form a donating complex. This gives an explanation why the bond of N$_2$ is difficult to break as the strength of bonding in N$_2$ is not affected very much by such donation. Likewise, when the 2 electrons in the 5σ orbital form a donating bond, the bond strength in CO is also only marginally affected.

At first sight it seems difficult to explain why N$_2$ is more stable than O$_2$ because the second step of mixing the σ(2s) and σ(2p) orbitals creates a 3σ$_g$ orbital in N$_2$ which is higher in energy than the 1π orbitals and because the energy of the 1π orbitals are not changed in the second step of the orbital mixing described above. Furthermore, the π bonds in ethylene are easier to break than the σ bond. So the higher-energy 3σ$_g$ bond should be easier to break. However, the 1π orbitals in N$_2$ are not so reactive, being inner orbitals. It should be remembered that both the two steps of orbital mixing that occur in dinitrogen contribute to lowering the energy. It should also be noted that N and O are different atoms. Both the 3σ$_g$ and 1π bonds in N$_2$ are stronger than those corresponding bonds in O$_2$.

The matter can also be looked from a different angle. The σ and 1π orbitals in N$_2$ and in O$_2$ can be represented differently (Figure 2) by a unitary transformation (eq 1, nonequivalent hybridization is not considered for simplicity) similar to that which transforms the s and p orbitals to 4 tetrahedral sp^3 hybrid orbitals (eq 2), where a and b in eq 1 denote different nuclei in the diatomic molecule.

$$\begin{pmatrix}\sigma_1\\\sigma_2\\\sigma_3\\\sigma_4\end{pmatrix}=\begin{pmatrix}1&1&1&1\\1&1&-1&-1\\1&-1&-1&1\\1&-1&1&-1\end{pmatrix}\begin{pmatrix}s_a+s_b\\p_{za}+p_{zb}\\p_{xa}+p_{xb}\\p_{ya}+p_{yb}\end{pmatrix}=\begin{pmatrix}1&1&1&1\\1&1&-1&-1\\1&-1&-1&1\\1&-1&1&-1\end{pmatrix}\begin{pmatrix}\sigma(2s)\\\sigma(2p)\\\pi(p_x)\\\pi(p_y)\end{pmatrix}$$

(1)

$$\begin{pmatrix}sp_1^3\\sp_2^3\\sp_3^3\\sp_4^3\end{pmatrix}=\begin{pmatrix}1&1&1&1\\1&1&-1&-1\\1&-1&-1&1\\1&-1&1&-1\end{pmatrix}\begin{pmatrix}2s\\2p_z\\2p_x\\2p_y\end{pmatrix}$$

(2)

The resulting orbital orientations in N_2 and O_2 from eq 1 are much like those in NH_3 or H_2O from eq 2. Three bonds are formed between two N atoms as shown in Figure 2A. They are equivalent mathematically to one σ and two π bonds. A bending bond in N_2 is stronger than the bending bond in O_2 because the bonding length of N_2 is shorter than that of O_2. The antibonding orbitals, which have not been considered in eq 1, should be included for a complete description.

MOLECULAR ORBITAL VERSUS VALENCE BOND

First-year students are often asked to consider molecular orbital (MO) and valence bond (VB) methods as two independent theories. It is common practice to teach the two methods separately, but it is then essential to introduce the connection between the two methods. Conceptually, VB theory is a model using hybridization and resonance, whereas MO theory is a model using delocalized orbitals and configuration interaction. The MO and VB methods are equivalent from the viewpoint of mathematics at their logical extreme of configuration interaction and ionic–covalent resonance approaches.[23–25] That is to say, the resonance in VB is equivalent to adding ionic wave functions to covalent wave functions, whereas configuration interaction in MO is equivalent to adding excited states to ground-state wave functions to reduce the undue emphasis given to the ionic contribution. The resulting final effects are the same.

The CO molecule is a good example to illustrate the connection between MO and VB methods without the need of introducing complicated mathematics involving configuration interaction and resonance. If the usual sp hybrid orbitals are used for C and O in CO, the hybrid sp orbitals that are directed toward each atom combine to form the bonding 3σ and the antibonding 6σ MOs (Figure 3). Note that in the VB model, a
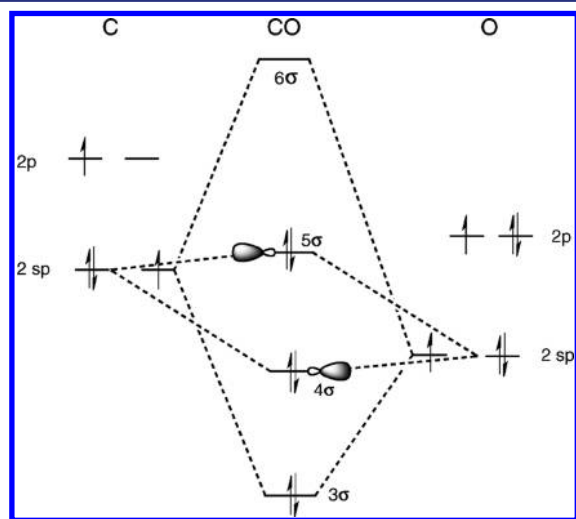

Figure 3. Sketch of the formation of σ orbitals in CO from hybrid sp orbitals, the π orbitals are omitted for clarity.

bond can only be formed when two orbitals approach each other each with an electron in an antiparallel way. The other hybrid orbitals in each atom, each containing two electrons, are directed away from the other atom and do not participate in bonding. They are equivalent to our assignment of lone-pair character to the 4σ and 5σ orbitals. So, the VB and the MO approaches give rise to approximately the same result.

CONCLUSIONS

Different models for electronic structures of carbon monoxide are suggested by emphasizing different principles. Some authors have suggested[1] that the 4σ orbital is antibonding with a greater weighting of carbon orbitals to those of oxygen. Others have suggested[2] that the energy level of the 5σ orbital is lower than that of the 1π orbital. The electronic structure of carbon monoxide invoked in this article is consistent with ref 3. It is informative to compare the electronic structures suggested in different textbooks.

To understand the connection between concepts[26–28] is a useful experience for students. However, it can introduce confusion and this is why the MO and VB methods are often taught separately. It has been shown that the two methods can be readily connected by interpreting the electronic structure of CO, N_2, and O_2. The difference between the notations of $\sigma(2s)$, $\sigma(2p)$ and σ_g, σ_u and 3σ, 4σ are emphasized. The reasons for the different reactivities of CO, N_2, and O_2 are clarified. Indeed, important principles relative to both VB and MO methods can be obtained from the electron structures of these diatomic molecules. Other correlated concepts, such as the vibration wave function and Franck–Condon principle[29–32] involved in photoelectron spectrum, can be invoked. It is also relevant to mention that the bending bonds in Figure 2 are equivalent mathematically to the conventional σ and π bonds when each of the bending bonds is decomposed onto the x, y, and z axis.[33]

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(14) Nonbonding is a term used in the molecular orbital theory and is ostensibly similar to the term "lone pair" in the valence bond model. Thus, the "nonbonding orbitals" in MO theory have been connected with "lone pairs" in the valence model because the MO and VB methods are equivalent mathematically at the logical extreme of configuration interaction and ionic−covalent resonance approaches.[10,23]

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