# A Comparative Study of the Bonding of $N_2$ and CO to Ru(001) and the Role of 5σ Orbital in Their Molecular Vibrational Frequency Changes

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The adsorption of $N_2$ and CO on transition metal surfaces has been the subject of many experimental and theoretical studies over the past few decades.[1~10] Their interactions with surfaces have been used to present prototypical systems of molecular chemisorption for many years. The great activity in this area arose mainly because of the importance of these systems to the understanding of catalytic surface processes such as the ammonia synthesis and the so-called Fischer-Tropsch process. Particular attention has been given to the chemisorptive behavior of $N_2$ and CO, two isoelectronic molecules, on transition metal surfaces. It has been suggested that the bonding of the two molecules to transition metal surfaces should be fundamentally different.[11] We investigate the differences in the surface-adsorbate bonding of these two molecules and the effect of 5σ donation on their molecular bond weakening upon adsorption on Ru(001). Concerning the latter, in particular, it appears that a decrease in the stretching frequencies for $N_2$ and CO upon adsorption is mainly attributable to the degree of π back-donation, but there is also some effect due to donation. We find that the character of the 5σ HOMO shifts toward the antibonding nature as one goes from $N_2$ to CO. Thus, the 5σ depletion due to charge donation accounts for the change in $N_2$ and CO bond strength.

The simplest standard picture used to describe $N_2$ chemisorption is an extension of the basic Blyholder model[12] for CO-transition metal bonding, which involves σ electron donation from CO into metal orbitals and π back-donation from metal orbitals into 2π orbitals of CO. Our results indicate that the surface chemical bonding is not qualitatively different between the two molecules. The main difference is that the interaction of the antibonding 2π orbitals with the metal d states is considerably weaker for $N_2$ than for CO. The analysis was carried out using the tight-binding calculations of the extended Hückel type[13~18] with the atomic parameters in Table 1. We used two conceptual tools,[19] density of states (DOS) and crystal orbital overlap population (COOP), to identify the most important adsorbate-surface interactions.

Experimentally, a $(\sqrt{3}\times\sqrt{3})R30^{o}$ overlayer structure at a coverage of one-third was found to be formed in which both $N_2$ and CO molecules were located at the on-top site on the Ru(001) surface.[20~22] We used this unit cell model of the unreconstructed Ru(001) surface to calculate the adsorption energy and selected bonding information shown in Table 2. The Ru substrate is modeled by a three-layer slab with the adsorbate molecules on one side of the two-dimensional slabs. The molecules are adsorbed with their molecular axes normal to the surface. CO is upright on the surface with the C end down. The molecular bond lengths for $N_2$ and CO are set to 1.11 Å and 1.15 Å, respectively. The Ru-N and Ru-C distances are derived from the density functional theory calculations (Ru-N 2.00 Å and Ru-C 1.92 Å).[23] For the average property calculations a mesh of 66 k points was chosen in the irreducible part of the Brillouin zone, according to the Ramirez and Böhm method.[24] Concerning the bonding of the neutral isoelectronic molecules $N_2$ and CO to the Ru(001) surface, the four frontier orbitals (4σ, 5σ and 2π pair) of the adsorbate molecules are important in the mole-

**Table 1**. Extended Hückel parameters

| orbital | $H_{ii}$, eV | $\zeta_1$ | orbital | $H_{ii}$, eV | $\zeta_1$ |
|---|---|---|---|---|---|
| Ru[b] 5s | -7.78 | 2.08 | C[d] 2s | -18.20 | 1.63 |
| 5p | -2.72 | 2.04 | 2p | -9.50 | 1.63 |
| 4d[a] | -9.57 | 5.38 | O[d] 2s | -29.60 | 2.27 |
| N[c] 2s | -23.95 | 1.95 | 2p | -13.60 | 2.27 |
| 2p | -10.95 | 1.95 | | | |

[a] $\zeta_2$=2.30; $C_1$=0.5573, $C_2$=0.6642. C=contraction coefficients used in double-ζ expansion. [b] From ref 26. [c] From ref 27. [d] From ref 10.

**Table 2**. Calculated Results for $(\sqrt{3}\times\sqrt{3})R30^{o}$ overlayer structure of $N_2$ and CO adsorbed on Ru(001)

| | $N_2$/Ru(001) | CO/Ru(001) |
|---|---|---|
| | Overlap Populations | |
| Ru-C | - | 0.78 |
| Ru-N | 0.49 | - |
| C-O | - | 1.09 (1.21 in free CO) |
| N-N | 1.64 (1.70 in free $N_2$) | - |
| | Electron Densities | |
| 4σ | 1.91 | 1.89 |
| 1π | 3.99 | 4.00 |
| 5σ | 1.62 | 1.63 |
| 2π | 0.26 | 0.60 |
| | Binding Energies (eV)[a] | |
| | 2.01 | 2.61 |
| | Vibrational Frequencies ($cm^{-1}$)[b] | |
| | 2195 (2359)[c] | 2015 (2170)[c] |

[a] E (Ru slab and separated molecule) - E (Ru slab and adsorbed molecule) for one unit cell. [b] The experimental data are taken from ref 11 and the values in parentheses are for the gas-phase molecules. [c] From ref 25.

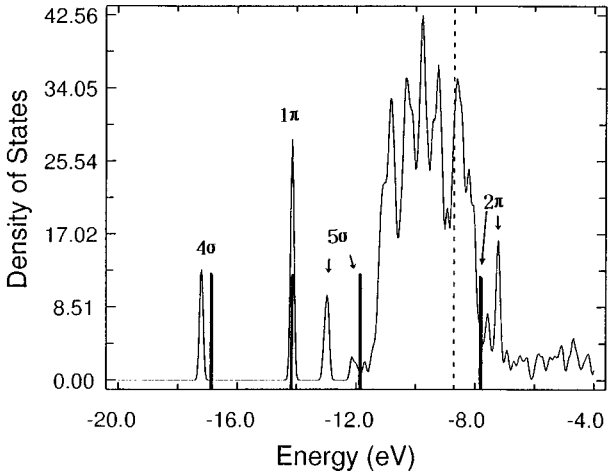


**Figure 1**. Total DOS for on-top CO/Ru(001). Major peaks are labeled. The corresponding molecular orbital energies of free CO are indicated by vertical bars. The dashed line refers to the Fermi level.

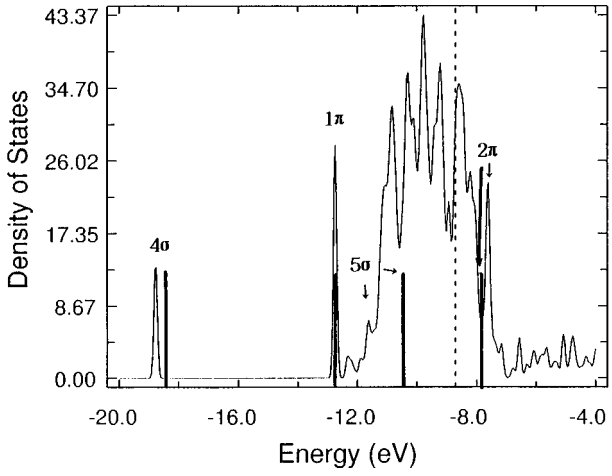


**Figure 2**. Total DOS for on-top $N_2$/Ru(001). Major peaks are labeled. The corresponding molecular orbital energies of free $N_2$ are indicated by vertical bars. The dashed line refers to the Fermi level.

cules' interactions with the metal surface. For simplicity, we refer to $2\sigma_u$, $\pi_u$, $3\sigma_g$, and $\pi_g$ of $N_2$ as $4\sigma$, $1\pi$, $5\sigma$, and $2\pi$, respectively, according to the CO orbital labeling scheme. The $5\sigma$ orbital of $N_2$ lies slightly higher in energy than $1\pi$ as a result of substantial mixing of $3\sigma_g$ with $2\sigma_g$ and represents the HOMO, as in CO.

The electron density shift between bare Ru(001) and molecular adsorbate in the chemisorbed system is shown in Table 2. The major surface chemical bonding is described by the interactions of the $5\sigma$ and $2\pi$ molecular states with the metal d states in a donation and back-bonding picture because the $5\sigma$ and $2\pi$ levels have a good energy match with the d band of the Ru slab (see Figures 1 and 2). Since the degree of the depopulation of $4\sigma$ and $5\sigma$ and the population of $2\pi$ provides a rough measure of their interactions with the surface, we can use their electron occupancies to compare the relative strength of the bonding of these orbitals to the metal surface. We analyzed the on-top CO situation first. Both $4\sigma$ and $5\sigma$ orbitals donate 0.11 and 0.37 electrons, respectively, on interaction with the Ru slab. The $2\pi$ set receives 0.60 electrons upon chemisorption. The adsorbed CO thus fits nicely with the Blyholder picture. One consequence of the strong metal to CO back-donation is a significant weakening of the C-O bond. The overlap population is reduced from 1.21 for the free CO molecule to 1.09 for the adsorbed CO (see Table 2). These interactions form a strong Ru-C bond; the corresponding overlap population is 0.78. The on-top $N_2$ case follows closely the CO situation. The $5\sigma$ orbital of $N_2$ interacts efficiently with the d band of the Ru slab; 0.38 electrons are donated. We see in Table 2 that the $2\pi$ set is populated by 0.26 electrons. This metal to $2\pi$ back-donation is not as strong as in CO, resulting in a weaker Ru-N bond. The result is a relatively small Ru-N overlap population, 0.49. To illustrate our point, the total and projected DOS curves are depicted in Figures 1 and 2 for on-top CO and $N_2$. In both cases, the $5\sigma$ is the most important bonding orbital. Note its large downshift of ~1.2 eV in energy, which is originated from the strong mixing between $5\sigma$ and metal d orbitals. The $4\sigma$ bands are shifted down ~0.3 eV after adsorption. This indicates that the strength of the $4\sigma$-surface interaction is considerably weak compared with the $5\sigma$ case. Since there are no significant interactions between the adsorbate $1\pi$ and the metal d states, as seen in the electron density and the DOS curves of the $1\pi$ in Table 2 and Figures 1 and 2, these interactions are essentially not involved in surface-adsorbate bonding. There seems to be little doubt that the $5\sigma$ and $2\pi$ are responsible for most of the surface-adsorbate bonding. The most significant factor in the difference between the bonding of $N_2$ and CO to Ru(001) is the coupling of the metal d$\pi$ to the $2\pi$ states. Table 2 and Figures 1 and 2 show that the population of CO $2\pi$, 0.60 electrons, and also the shift of the antibonding $2\pi$ DOS peak after adsorption, ~0.5 eV, are larger than the corresponding values (0.26 electrons and ~0.2 eV) for $N_2$. This explains the stronger binding of CO to the metal surface compared with $N_2$ (2.61 eV *vs.* 2.01 eV in binding energies). The stronger $\pi$ back-bonding in CO is largely a result of the fact that the $2\pi$ orbitals have a higher amplitude on the atom closer to the surface.

We finally consider the shifts of the $N_2$ and CO vibrational frequencies upon adsorption. From the increased occupancies of the antibonding $2\pi$ molecular orbitals for both adsorbed $N_2$ and CO shown in Table 2 one would expect decreased vibrational frequencies for the $N_2$ and CO upon adsorption. The stronger coupling of the CO $2\pi$ to the Ru d$\pi$ states and the consequent increased population of the $2\pi$ states should give rise to a greater lowering of the frequency for CO than for $N_2$. From Table 2, however, a comparison of the stretching frequencies for chemisorbed CO and $N_2$ with those for the gas phase CO and $N_2$ molecules shows about the same magnitude in the ratio of frequency shifts. The reason is that there is also some effect due to donation from $5\sigma$. Exploring this, it is interesting to examine the bonding or antibonding character for the $5\sigma$ orbitals of $N_2$ and CO. The Mulliken overlap populations calculated for these molecular

orbitals in gas-phase are 0.11 ($N_2$) and -0.01 (CO). Judging from these numbers, the 5σ orbital is *slightly bonding* for $N_2$ but *slightly antibonding, close to nonbonding* for CO. The 2π orbitals of $N_2$ and CO have a pronounced antibonding character. Thus, for $N_2$ bond weakening must be considered as the result of two effects: back-donation from the metal d into the 2π orbitals and depopulation of the 5σ orbital, while for CO bond weakening is primarily a result of back-donation into the 2π orbitals. The effect of both 5σ depletion and less 2π population on the bond strength for $N_2$ seems to be comparable to that of more 2π population for CO. The electron depletion of CO 5σ orbital does not affect the bond weakening because it has a nearly nonbonding character. The effect of orbital character and occupation leads to a comparable weakening of the $N_2$ and CO bonds and the resultant decrease of the vibrational frequencies.

In summary, a molecular orbital analysis has been presented of the differences in the bonding of $N_2$ and CO to Ru(001). The adsorbate-surface bonding depends on the σ and π electron donor-acceptor capabilities of the adsorbate molecule. The interaction of the 5σ and the Ru d band seems to be the most important factor in the bonding of both $N_2$ and CO molecules to Ru(001). The Ru d bands also interact substantially with the 2π orbitals of CO, with a large amplitude on the carbon atom, but not with those of $N_2$, which is responsible for the difference in adsorption energies for the two molecules. Although the $N_2$ 2π orbitals have less mixing with the substrate states, the $N_2$ molecule shows a vibrational frequency shift comparable to that of CO due to the depopulation of the slightly bonding 5σ orbital.

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