

# Theoretical Study of Linear NiCO and CuCO and its Implication to Adsorption

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Z. Naturforsch. **34a**, 114–116 (1979); received October 16, 1978

*Ab initio* RHF-MO calculations are made for the linear NiCO and CuCO clusters. The ground states of them involve Ni  $3d^9 4s^1$  and Cu  $3d^{10} 4s^1$  electron configurations, respectively. The orbital energies of the CO like levels in both clusters are closely similar to each other. The CO  $5\sigma$ -like level shifts toward the CO  $1\pi$ -like level due to the bonding interaction of the  $5\sigma$  with the metal  $4s$  and  $3d_{z^2}$ . The results are discussed in relation to the difference of the  $3d$ -level positions and the similarity of  $4s$  levels of Ni and Cu. For NiCO both the  $4s$  and  $3d$  orbitals contribute to the metal-CO binding while for CuCO only the  $4s$  orbital contributes to it. The present results are in agreement with the UPS experiments on adsorption.

## 1. Introduction

Extensive experimental studies have been done on carbon monoxide (CO) adsorption on Ni- and Cu-metal surfaces [1]. Recent experiments [2–3] revealed close similarities to the corresponding transition metal carbonyl compounds. A recent interesting finding of *ab initio* molecular orbital calculations is that a single Ni atom has a  $3d^9 4s^1$  electron configuration in complexes such as NiH, NiCO, NiC<sub>2</sub>H<sub>2</sub>, etc. [4–7]. The ground state,  $^3F$ , of a free Ni atom arises from the  $3d^8 4s^2$  electron configuration. The excited state  $^3D$  arising from the  $3d^9 4s^1$  configuration is only 0.025 eV higher than  $^3F$  ( $d^8 s^2$ ). The Hartree-Fock calculation of Clementi and Roetti [8] showed that the  $3d$  orbital energy of Ni $^3D$  ( $d^9 s^1$ ) (–12.4 eV) is much higher than that of Ni $^3F$  ( $d^8 s^2$ ) (–19.2 eV) and is also higher than that of Cu $^2S$  ( $d^{10} s^1$ ) (–13.4 eV). The  $4s$  orbital energies for the Ni $^3D$  ( $d^9 s^1$ ) and Cu $^2S$  ( $d^{10} s^1$ ) states have a very similar value of ca. –6.4 eV. The UPS experiments on Ni and Cu metals [9] showed that the Ni  $3d$  band lies ca. 2 eV higher than the Cu  $3d$  band. The  $4s 4p$  conduction bands of these metals are considered to be closely similar. Recently extended Hückel (EH) calculations of CO adsorption on small Ni and Cu clusters with use of parameters consistent with the UPS experiments were reported [10].

The purpose of the present paper is to apply an *ab initio* MO theory to linear NiCO and CuCO clusters to examine qualitatively by the bonding properties of the adsorption systems and the metal

carbonyl compounds in order to understand the recent experiments [11–12].

## 2. Method and Model

*Ab initio* RHF-MO calculations have been carried out using the program system GVBONE [13]. Gaussian basis sets contracted to a minimal basis set for the C and O atoms are used [14]. Effective potentials to replace the Ar cores of Ni and Cu are employed [15–16]. Then, only the  $3d$ ,  $4s$  and  $4p$  valence orbitals for the metal atoms are taken into account. The  $3d$  functions are taken from Ref. [17] and are incremented with one  $s$  function of exponent 0.20, one  $p$  function of exponent 0.25 and one  $d$  function of exponent 0.20 as suggested by Veillard et al. [18]. Then, a minimal basis set is used except for the metal  $3d$  functions, which are split.

The CO bond distance is taken as 1.15 Å, which is the experimental CO bond distance in Ni(CO)<sub>4</sub>.

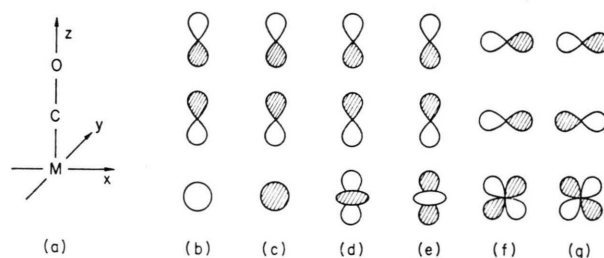


Fig. 1. Interactions between the CO orbitals and the metal orbitals. Atomic orbitals shown in (b)–(g) are arranged as in (a). (b) and (c) are bonding and antibonding between CO  $5\sigma$  and M  $4s$ , respectively. (d) and (e) are bonding and antibonding between CO  $5\sigma$  and M  $3d_{z^2}$ , respectively. (f) is bonding between CO  $1\pi$  and M  $d\pi$ . (g) is bonding between CO  $2\pi^*$  and M  $d\pi$ . The  $2s$  orbitals of the C and O atoms in the CO  $5\sigma$  orbital are omitted for simplicity.

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The metal M—C distance is taken as 1.84 Å, as in Ni(CO)<sub>4</sub>. The molecular axis is taken as the z-direction as shown in Figure 1a.

### 3. Results and Discussion

At first the orbital energies are reported. The calculations showed that the ground state of NiCO is <sup>3</sup>Σ with a single d hole at a d<sub>z</sub><sup>2</sup> orbital arising from the Ni d<sup>9</sup>s<sup>1</sup> electron configuration while that of CuCO is <sup>2</sup>Σ arising from Cu d<sup>10</sup>s<sup>1</sup>. Walch and Goddard [5] and Bagus [6], using much larger basis sets than ours, concluded that the ground state of NiCO is <sup>3</sup>Δ, which differs from our result. Since the purpose of the present paper is not to predict the molecular properties of NiCO accurately but to explain the difference of the molecular properties of NiCO and CuCO qualitatively, it was deemed sufficient to use the present basis set.

In the ground states of the MCO clusters the CO-like orbitals retain very much of their molecular character. Calculated orbital energies of the CO-like orbitals of a free CO, NiCO and CuCO are shown in Table 1. From this table it is seen that the CO-like levels shift from their free CO ones due to the interaction of CO with the metal atom. The orbital energies of each level for both NiCO and CuCO are closely similar. It should be noted that large bonding and antibonding interactions between two orbitals occur when the energy difference is small and the overlap of the two orbitals is large. The magnitudes of the 5σ like level shifts, which are 2.5 eV for Ni and 3.1 eV for Cu, are much larger than those of the other level shifts because the shift of the 5σ like level arises from the bonding interaction of the CO 5σ mainly with the expanded metal 4s and slightly with the localized 3d<sub>z</sub><sup>2</sup> as shown in Fig. 1b and d, respectively. In the 5σ like level of CuCO there exists also a considerable amount of bonding interaction between CO 5σ and

Cu 3d<sub>z</sub><sup>2</sup> because the Cu 3d level lies nearer to CO 5σ in energy than Ni 3d does, although 3d is localized. As a result of this, the magnitude of the 5σ level shift for CuCO is larger by ca. 0.6 eV than for NiCO. The 4s- and 3d<sub>z</sub><sup>2</sup>-like levels are antibonding with respect to the C atom and the metal atom as shown in Fig. 1c and e, respectively.

The CO 1π like orbital arises from the bonding interaction between the CO 1π and the metal dπ orbitals as shown in Figure 1f. The 1π level shift is much smaller than the 5σ shift because of the localized character of the 3d orbital and the large energy separation between the 1π and 3d levels. On the other hand, the metal dπ like orbitals arise from the weak bonding interaction of the dπ orbital with the antibonding CO π\* orbital as shown in Figure 1g.

The magnitudes of the CO 5σ level shifts towards to the CO 1π level, which are larger than those given by the previous EH calculation, are in agreement with the UPS experiments [19–27]. Recently Shirley et al. [28] have shown, using angle-resolved photoemission spectroscopy, that on the Pt surface the order of the CO 5σ- and 1π-like levels is reversed compared to free CO, i.e. the 5σ like level is deeper in energy than the 1π like level. This may be understood to arise from a stronger bonding interaction of the 5σ with the Pt 6s and 5d orbitals because they are more expanded than the Ni 4s and 3d, respectively, and because the Pt 5d level is nearer the CO 5σ in energy than the Ni 3d level [29].

Now the chemical binding between CO and the metal atoms shall be discussed. The calculated binding energies are −0.95 eV for NiCO and −1.64 eV for CuCO. The experimental CO adsorption energies are 1.3 eV on Ni and 0.7 eV on Cu [30]. The present calculation cannot explain the stability of NiCO and CuCO molecules which is observed experimentally [11–12] because this calculation does not take into account electron correlation effects [5]. However, the difference, 0.69 eV, of the calculated binding energies is in good agreement with the difference 0.6 eV of the experimental adsorption energies. The binding energy is defined as the difference between the orbital energy-sum of the combined MCO system and the sum of the separated systems, M and CO, with Coulomb and exchange energy corrections. As stated above, the energy levels of MCO are

Table 1. Calculated orbital energies, in eV, of free CO and CO like orbitals in NiCO and CuCO.

| Orbital | free CO  | NiCO     | CuCO     |
|---------|----------|----------|----------|
| 1 σ     | − 563.79 | − 564.26 | − 564.32 |
| 2 σ     | − 312.94 | − 312.58 | − 312.40 |
| 3 σ     | − 42.41  | − 42.57  | − 42.59  |
| 4 σ     | − 21.74  | − 22.23  | − 22.29  |
| 1 π     | − 18.14  | − 18.54  | − 18.53  |
| 5 σ     | − 15.12  | − 17.64  | − 18.20  |

composed of the bonding and antibonding interactions between the CO orbitals and the metal orbitals. When an electron occupies a bonding level, it contributes to a stable chemical binding. However, when it occupies an antibonding level, it destabilizes the MCO system and decreases the strength of the chemical binding because of a cancellation of bonding and antibonding contributions. For both NiCO and CuCO, the  $5\sigma$  like orbital is bonding between the  $5\sigma$  orbital and the metal  $4s$  and  $3d_{z^2}$  orbitals. The metal  $4s$ - and  $3d_{z^2}$ -like orbitals are antibonding with respect to the metal atom and the C atom. CuCO contains one more electron in the  $3d_{z^2}$  like orbital than NiCO does. This means that the  $3d_{z^2}$  contribution to the chemical binding in CuCO is completely cancelled and only the  $4s$  contribution remains. In NiCO, however, both the  $4s$  and  $3d_{z^2}$  contributions exist. The metal  $d\pi$  contribution via the interaction of the  $d\pi$  with the CO  $\pi$  is less im-

|      | C    | O    |
|------|------|------|
| Free | 5.67 | 8.33 |
| NiCO | 5.81 | 8.29 |
| CuCO | 5.81 | 8.29 |

Table 2. Calculated electron population of CO in free CO and MCO.

portant because of the localized character of the  $d\pi$  orbital.

The electron populations of the C and O atoms of free CO and MCO are shown in Table 2. The fact that the populations for both NiCO and CuCO, which are the same, are almost neutral is consistent with the observed work function changes in the CO adsorption experiments [30].

#### 4. Conclusion

The ground states of linear NiCO and CuCO involve Ni  $3d^9 4s^1$  and Cu  $3d^{10} 4s^1$  electron configurations, respectively, which are closely similar to the electron configurations of the corresponding bulk metals. Although the  $4s$  like orbital energies are closely similar to each other, the Ni  $3d$  like levels are higher in energy than the Cu  $3d$  like ones. These are also similar to the electronic structure of the bulk metals. As a result of this, it is expected that the properties of CO adsorption on these metals are closely similar to those of the corresponding carbonyl compounds as shown by the experiments.

#### Acknowledgement

This work was done with supports from the National Science Foundation Grant DMR-76-01058 and by the U.S. Air Force Office of Scientific Research Grant No. AFOSR-76-2989.

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