PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Electronic structure of CO adsorbed on a Cu(111) surface analyzed with molecular cluster models

J. Paul and A. Rosén

Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

(Received 20 October 1981; revised manuscript received 7 June 1982)

Using the self-consistent Hartree-Fock-Slater model we have calculated the electronic structure for various $Cu_x(CO)_y$ clusters symbolizing not only CO bound to "on-top" and "bridge" sites but also some lateral CO-CO interaction on a Cu(111) surface. By comparison with experimental photoemission data we are able to reproduce the observed energies of the occupied CO 4σ, 1π, and 5σ orbitals as well as the partly occupied 2π orbital. In our model we assume CO to be adsorbed on "top" sites for coverages less than $\Theta = 0.33$ $[(\sqrt{3}\times\sqrt{3})R\,30°]$ and on both top and bridge sites for $\Theta > 0.33$. The experimentally observed peak of intensity at the Fermi edge which increases with coverage above 0.33 is in our model explained by the occupation of CO orbitals of the b_1 and b_2 symmetry types, i.e., "π" orbitals, degenerate for top positions (C_{3v}), split by the change to bridge positions (C_{2v}). Our results further indicate that the broadened 5σ-1π intensity peak at high coverages is a result of CO bound to top and bridge sites.

I. INTRODUCTION

The adsorption of CO on transition-metal surfaces has been extensively studied experimentally as well as theoretically during the last few years. One of the most characteristic features of these adsorbate systems is the energetic overlapping of the levels originating from the 1π and 5σ orbitals of the adsorbed CO molecules. A lot of work has been focused on the identification of these levels by the use of angle resolved photoemission spectroscopy.[1] Another feature is the assumed broad 2π resonance at the Fermi level. The adsorption of CO at different sites as well as the CO-CO interaction would appear as a shift of the CO molecular levels and moreover lead to a shift of the CO-stretch vibrational frequencies. The latter could be interpreted by different occupation numbers of the 2π orbital.

One of the metal-CO systems which has been studied by various techniques including ultraviolet photoelection spectroscopy (UPS) (Refs. 2–6), infrared spectroscopy[7] (IRS), and low-energy electron diffraction (LEED) (Ref. 8) is the adsorption of CO on Cu single-crystal surfaces. A Cu substrate has the advantage of a filled $3d$ band and thus a low density of states at the Fermi level. This behavior makes it easier to observe the increase of electrons in occupied states caused by the partly filled 2π resonance.

The main purpose of this paper is to show that accurate cluster calculations can distinguish between different adsorption sites when comparing partial density of states and ionization energies to photoemission data. We have modeled not only the interaction between CO and a Cu(111) surface for different CO positions but also the CO-CO interaction which was not considered in recent cluster calculations.[9,10]

II. CALCULATIONS

Our calculations have been done within the Hartree-Fock-Slater (HFS) model with a statistical-exchange potential of the following form[11]:

$$V_x(r) = -3\alpha[(\tfrac{3}{8}\pi)\rho(\underline{r})]^{1/3} ,$$

where $\rho(\underline{r})$ is the electron density at position r. α is the exchange parameter, which has been chosen as 0.70 in these calculations. A variational method is used to find the molecular wave functions which are approximated by a linear combination of symmetry orbitals built up of numerical atomic basis functions. The matrix elements in the secular equation are evaluated by a numerical integration procedure known as the discrete variational method.[12] The molecular potential is determined in the successive iterations from Mulliken gross orbital occupation numbers of atomic basis functions which are generated in numerical form by an atomic HFS program. Self-consistency is obtained when the input and output occupation numbers are equal. This method is known as the self-consistent-charge procedure.[13] We have in this model increased the number of integration points until no relevant changes (<0.1 eV) could be seen in the eigenvalues of the studied orbitals for a chosen geometry of the cluster.

The copper surface was represented by a 10-atom cluster with somewhat different geometry for the bridge and top bonding of CO as can be seen from the left-hand side of Fig. 1. A crucial question in this approximation is how well the electronic structure of the surface is represented by such a limited number of atoms. We have compared our calculated density of states (DOS) with the DOS for the first layer of a five-layer Cu(111) slab calculation.[14] Owing to the close agreement between these two DOS we believe the cluster to be sufficient for an analysis of the CO—Cu bond although we have not applied any embedding solid-state boundary conditions. We have hence compared the DOS as a function of energy $N(E)$ and found the width of the $3d$ band and the width of the conduction band, i.e., the Fermi-energy ϵ_F to agree well with what is known from experiments and slab calculations. Moreover, the energy separation between the upper edge of the $3d$ band and the Fermi edge is approximately 2 eV. This separation is important, since the location of the d electrons with respect to the unoccupied states determines many properties of adsorption (cf. Cu and Ni). In contrast to the localized $3d$ orbitals the s-p electrons are free-electron-like and expected to be more sensitive to the cluster size. However, it is found[10] that ionization energies and occupation numbers are less sensitive than vibrational frequencies and adsorption energies to the number of metal atoms (5 to 70) for CO adsorbed on Li clusters. The coordinates for the copper atoms were given by a lattice parameter of 6.82 a.u. The copper-carbon distance (h_T) for the "on-top" position was fixed at 3.50 a.u. which agrees well with 3.59 a.u. as given by LEED data for CO on Cu(100) (Ref. 8) and also with the energy minimum at 3.57 a.u. for CO above a hexagonal Cu_7 cluster.[10] In the bridge position we have varied the carbon coordinate normal to the surface (h_B) between 2.50 and 3.00 a.u. A value of 2.50 a.u. leaves the Cu-C distance unchanged at 3.50 a.u. whereas 3.00 a.u. increases it by 10% which represents an average value for transition-metal carbonyl complexes.[15] The internal CO coordinate (R_{CO}) was fixed at the value 2.13 a.u. observed for free CO as well as for CO adsorbed on Cu(100).[8] We have not varied the polar angle of the CO symmetry axis. Although there may be some discussion about the small variations of the h_T, h_B, and R_{CO} values our basic conclusions about the difference between top and bridge sites remain unchanged.

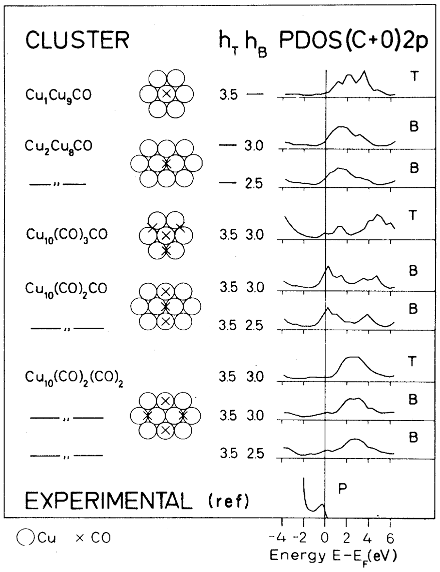

FIG. 1. Partial density of states per CO molecule for (C + O)$2p$ is given at the right for different clusters (left). The position of the analyzed molecule is indicated by a B for bridge or a T for top. The figures at each atom type indicate the number of atoms given the same potential. For the Cu_1Cu_9CO and $Cu_{10}(CO)_3CO$ clusters there are also three copper atoms in a second layer not shown in the drawings. h_T and h_B stand for the distance (given in atomic units) between the carbon atom in top or bridge position and the first Cu layer. The C—O bond length (R_{CO}) is frozen to the value, 2.13 a.u., for the free molecule.

The cluster geometry chosen for the calculations was further justified by the LEED pattern similarities between the well-known Pt(111) + CO system[16,17] and the Cu(111) + CO system.[18] The first-ordered structure to appear for both systems is thus $[(\sqrt{3}\times\sqrt{3})R30°]$ which is followed with further adsorption by a $c(4\times2)$ and finally a compressed structure. For the $[(\sqrt{3}\times\sqrt{3})R30°]$ structure and less dense overlayers all CO molecules could be adsorbed on equivalent sites. The Cu_1Cu_9CO and Cu_2Cu_8CO clusters (Fig. 1) are thus assumed to describe adsorption on top and bridge sites below this coverage ($\Theta=0.33$). In addition to these two clusters the $Cu_{10}(CO)_3CO$ and $Cu_{10}(CO)_2CO$ ones were chosen to give some indication of the perturbing effect of CO-CO interaction on the molecule in the center position. It is thus not advisable to look upon the surrounding molecules as an adequate description of CO in bridge and top positions, respectively, but merely as a cause of a small perturbation on the molecule in the middle. Finally the denser $c(4\times2)$ structure is consistent with the positions given for the CO molecule in the $Cu_{10}(CO)_2(CO)_2$ cluster (bottom of Fig. 1) transferred from the Pt(111) + CO system.[16] The superimposed partial density of states (PDOS) for the C 2*p* and O 2*p* orbitals given at the right of Fig. 1 and its connection with the observed photoemission spectrum are discussed below.

III. RESULTS AND DISCUSSION

A. Ionization energies

In Fig. 2 we compare experimental data with ionization energies evaluated with the transition-state procedure for top and bridge CO, in the latter site for two different values of the copper-carbon distance h_B. The transition-state concept of Slater[19] gives a good approximation of the energy value for a photoemitted electron leaving a redistributed electron structure and is understood to be a valid approximation when compared to experimental UPS data. It should be noted that neither the transition-state nor the ground-state one-electron energies shown in Figs. 2 and 3 give any indication about the total energy for different symmetries. Nevertheless we find that the calculated values for the $11e$ (1π), $10a_1$ (5σ), and $8a_1$ (4σ) orbitals agree well with the experimental peaks denoted as A_1-B_1 and A_3-B_3, respectively. Spectrum A was measured by Conrad *et al.*[2] for a Cu(111) surface with a coverage less than $\Theta=0.33$ while B (Ref. 4) represents a saturation value of Θ greater than 0.33. For comparison the results for a Cu(100) surface[6] are given to the right in Fig. 2. We interpret the observed broadened peak B_{1-2} which is deconvoluted by the spectroscopists into two levels, as being the result of an increased population of bridge sites. This is consistent with the observation by Jugnet and Tran Minh Duc (B) who observed that the peak B_1 is gradually broadened to a B_{1-2} peak when CO is adsorbed beyond the $[(\sqrt{3}\times\sqrt{3})R30°]$ ordered structure. As can be seen in Fig. 2 the wide peak in our model is not only a result of the separation of the 5σ and the 1π levels but also of the symmetry splitting of the 1π orbital into the $8b_1$ and $9b_2$ levels. This latter splitting (broadening) ought to be more clearly seen on a Ni(111) surface where the CO molecules are believed to adsorb predominantly on bridge sites.[20,21] The fourth peak (A_4-B_4) could not

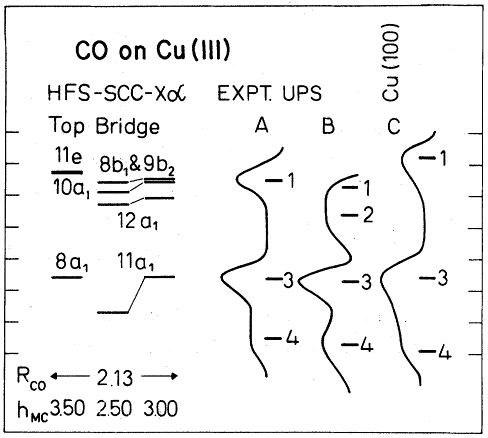

FIG. 2. Calculated ionization energies (left) compared with experimental UPS data for CO on Cu(111) (A-B) and Cu(100) (C). The peak positions as given in Refs. 2, 4, and 6 are indicated in the figure. The clusters modeling the top and bridge positions are Cu_1Cu_9CO and Cu_2Cu_8CO (Fig. 1). R_{CO} is the bond length of the CO molecule and h_{MC} is the distance between the first plane of Cu atoms and the carbon atom. The CO symmetry axis is normal to the surface. Expt. A is Ref. 2 ($\Theta_{CO}<0.33$), expt. B is Ref. 4 ($\Theta_{CO}>0.33$), expt. C is Ref. 6 [CO on Cu(100)]. The following relations hold for the notation of the molecular orbitals: $1\pi \leftrightarrow 11e$ (T) and $8b_1/9b_2$ (B); $5\sigma \leftrightarrow 10a_1$ (T) and $12a_1$ (B); $4\sigma \leftrightarrow 8a_1$ (T) and $11a_1$ (B).

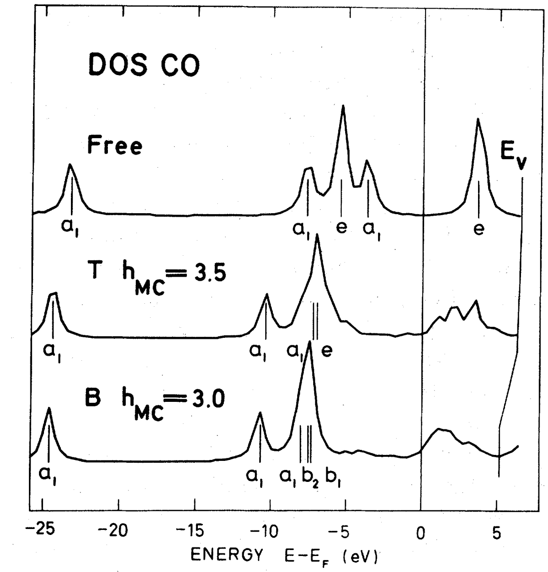

FIG. 3. Density of states (DOS) for free CO and CO adsorbed in top (T) and bridge (B) positions on a Cu(111) surface. Each discrete level is replaced by a Lorentzian curve. h_{MC} is given in a.u. Symmetry and HFS-$X\alpha$ ground-state eigenvalues for CO orbitals as well as the vacuum level are indicated in the figure. The energies are given relative to the Fermi energy which in our calculations is defined as the mean energy between the highest occupied and lowest unoccupied levels.

be fitted into any one-electron ionization energy without assuming unphysical coordinates for the adsorbate. It is in agreement with the assumption for CO on Cu(100) (C_4) recognized as a result of a shakeup.[6] We have not made any further investigation of this many-electron feature.

Based on a comparison with the observed peaks of the photoemission intensity as a function of coverage our calculations thus indicate that CO is adsorbed on top sites for $\Theta < 0.33$ and that further adsorption leads to the occupation of bridge sites. Returning to Fig. 3 we show the ground-state DOS for CO absorbed on top and bridge sites with h_{MC} as determined from transition-state energies. We have related the eigenvalues to the Fermi level (E_F) and not the vacuum level (E_V) since the calculated position of the d band is correct with respect to E_F whereas the work function is not so well described in these models. As can be seen, the main features, i.e., the 5σ bonding shift and the 2π backbonding resonance, are similar for the two sites. There are, however, minor differences in the DOS close to the Fermi level which are addressed in the next section.

B. Backbonding states

A recent observation[5] of a peak at the Fermi edge which appears for coverages beyond the $[(\sqrt{3}\times\sqrt{3})R30°]$ ordered structure and then increases with coverage has given us another possibility to test the change of bonding geometry with coverage (Fig. 1). The obvious interpretation of this peak is that it is an occupied "back-donated" tail of a broadened CO 2π level which is commonly believed to lie close to, but above, the Fermi level. To investigate this picture we have by means of a Mulliken analysis[22] calculated the partial density of states (PDOS) of the (C + O) $2p$ orbitals for various clusters (Fig. 1). The 2π level is of the e or b_1/b_2 symmetry type and is for the free molecule composed of one-third O $2p$ and two-thirds C $2p$. This justifies the superposition of the two densities. We have also calculated the π and σ symmetry parts of the PDOS for (C + O) $2p$. Integrated over the occupied states from 1 eV below the Fermi level it is found to consist of approximately 80% π symmetry or 0.15 CO π electrons for Cu_1Cu_9CO ($h_T=3.50$) vs 0.25 for Cu_2Cu_8CO ($h_B=3.00$). Since the total adsorption induced increase of (C + O) $2p$ occupation numbers are 0.18 for the top site and 0.37 for the bridge one we find that the major part of the backbonding π electrons are located in states near the Fermi level.

From the intensities at the right of Fig. 1, which are all given per CO molecule, one may conclude that on top (T) adsorbed CO cannot give a peak such as the observed peak P. The opposite situation applies to bridge (B) bond CO where for all clusters the 2π PDOS at the Fermi level is higher than for the equivalent top cluster. This can readily be seen when comparing the Cu_1Cu_9CO (T) and Cu_2Cu_8CO (B) clusters. An enhanced difference is also observed when comparing the PDOS for the center CO of the $Cu_{10}(CO)_3CO$ (T) and the $Cu_{10}(CO)_2CO$ (B) clusters. As previously pointed out these two latter models have no observed physical background but have been chosen to simulate effects of lateral CO-CO interaction. We will make no further discussion about CO-CO interaction for these structures. On the other hand a $c(4\times2)$ structure has been observed, and via corresponding peaks in the PDOS for T and B molecules of the $Cu_{10}(CO)_2(CO)_2$ cluster, one may identify delocalized CO orbitals. Such mixed orbitals of π symmetry are found from above 1 eV below the Fermi level. This overlap between adjacent molecules tends to increase the backbonding charge transfer. Compared to the single adsorbate models (Cu_1Cu_9CO and Cu_2Cu_8CO) the transfer to (C + O) $2p$ orbitals has increased from +0.18 to +0.27 for T molecules and from +0.37 to +0.39 for B molecules. The existence of such coupling implies the significance of slab calculations of the $[(\sqrt{3}\times\sqrt{3})R30°]$ and $c(4\times2)$-ordered CO layers on Cu(111) since in solid-state terminology these states are electron bands. We do not know whether this coupling will completely average the two sites since this cluster $[Cu_{10}(CO)_2(CO)_2]$ does not include all nearest neighbors.[23] For comparison with experiment one should in our model take a weighted average of the PDOS for top (T) and bridge (B) located CO molecules.

IV. CONCLUSIONS

Our data for the CO electronic structure at the Fermi level as well as calculated ionization potentials give support to the idea that CO is adsorbed on top positions at low coverages on a Cu(111) surface and at both top and bridge sites at high coverages in the submonolayer range.

ACKNOWLEDGMENTS

We appreciate valuable comments by S. Andersson, J. Harris, S.-A. Lindgren, H. P. Myers, and L. Walldén.

[1] E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. 49, 533 (1982).

[2] H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, Solid State Commun. 17, 613 (1975).

[3] J. Kanski, L. Ilver, and P. O. Nilsson, Solid State Commun. 26, 339 (1978).

[4] Y. Jugnet and Tran Minh Duc, Chem. Phys. Lett. 58, 243 (1978).

[5] S. A. Lindgren, J. Paul, and L. Walldén, Chem. Phys. Lett. 84, 487 (1981).

[6] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Solid State Commun. 24, 531 (1977).

[7] P. Hollins and J. Pritchard, Surf. Sci. 89, 486 (1979).

[8] S. Andersson and J. B. Pendry, J. Phys. C 13, 3547 (1980).

[9] P. S. Bagus, and M. Seel, Phys. Rev. B 23, 2065 (1981).

[10] D. Post, Ph.D thesis, Vrije Universiteit te Amsterdam, 1981 (unpublished), and D. Post and E. J. Baerends, Surf. Sci. 109, 167 (1981).

[11] J. C. Slater, *The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974).

[12] D. E. Ellis and G. S. Painter, Phys. Rev. B 2, 2887 (1970).

[13] A. Rosén, D. E. Ellis, H. Adachi, and F. W. Averill, J. Chem. Phys. 65, 3629 (1976).

[14] J. A. Appelbaum and D. R. Hamann, Solid State Commun. 27, 881 (1978).

[15] E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B 18, 1673 (1978).

[16] A. M. Baró and H. Ibach, J. Chem, Phys. 71, 4812 (1979).

[17] H. J. Krebs and H. Lüth, Appl. Phys. 14, 337 (1977).

[18] J. Pritchard, Surf. Sci. 79, 231 (1979).

[19] J. C. Slater, *Computational Methods in Band Theory* (Plenum, New York, 1971), p. 477.

[20] P. M. Williams, P. Butcher, J. Wood, and K. Jacobi, Phys. Rev. B 14, 3215 (1976).

[21] S. D. Kevan, R. F. Davis, D. H. Rosenblatt, J. G. Tobin, M. G. Mason, D. A. Shirley, C. H. Li, and S. Y. Tong, Phys. Rev. Lett. 46, 1629 (1981).

[22] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955); 23, 1841 (1955); 23, 2338 (1955); 23, 2343 (1955).

[23] B. N. J. Persson and R. Ryberg, Phys. Rev. B 24, 6954 (1981).