

Theoretical analysis of the bonding of oxygen to Cu(100)

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The chemisorption of O/Cu(100) has been modeled by a Cu_5O cluster; *ab initio* self-consistent-field electronic wave functions have been obtained for this cluster. The bonding has been analyzed using several new theoretical methods: (1) the variation of the Cu_5O dipole moment with the distance of O from the surface; (2) the projection of the O orbitals from Cu_5O ; and (3) the constrained space orbital variation (CSOV) method for the development of the bond. It is concluded that the bond is dominantly ionic but with a significant covalent contribution. Our results indicate that the excess charge on O is ~ 1.5 electrons. We have computed the CSOV analysis for Cu_5O and for Cu_5 with point charges. The comparison of these two clusters has allowed us to have a definitive measure of the contribution of the Cu *d* electrons to the covalent bond. The total contribution of the *d* electrons to the bond is rather large (1.2 eV). Once the different contributions are separated, it is shown that purely electrical polarization effects account for ~ 0.5 eV, while the direct participation of the *d* electrons in the covalent bond is ~ 0.7 eV.

I. INTRODUCTION

The molecular-orbital (MO) cluster-model approach to surface chemistry and surface phenomena provides a way to study complicated surface processes and the chemisorption bond.¹ The value of this approach relies on the fact that many properties of the adsorbate-substrate system are rather local in nature and thus reasonably well reproduced by cluster-model wave functions. We note that the specific values of features of the interaction, for example, the binding energy of the adsorbate, depend on the cluster size. However, the general character of the adsorbate-substrate bond can be described even with rather small clusters; see Ref. 1, and references therein for an extended discussion of this point. The cluster model has been used by Madhavan and Newton² to study O/Cu(100). They used clusters containing as many as 25 Cu atoms; with cluster wave functions that included electron correlation effects, they were able to obtain good agreement with experiment for the heat of adsorption. The present work focuses on the nature of the O-Cu interaction and determines the degree of ionicity of the chemical bond. The bond obtained with the cluster wave functions is analyzed using new techniques recently developed for the characterization of the chemisorption bond.³⁻⁵ In particular, one of these techniques allows us to decompose the total interaction into the contributions from different terms. With this technique, the involvement of the *d* electrons in the bond has been determined; the contributions from pure polarization and from direct covalent effects have been separated. This point is of physical importance because it indicates the extent of the participation of the *d* electrons in the adsorbate-substrate covalent bond. This participation cannot, as we have shown in an earlier paper,⁶ be represented with a treatment in which the *d* electrons are included in a pseudopo-

tential.⁷

The chemisorption of atomic oxygen on the Cu(100) surface has been studied with a cluster model, which contains the metal atoms in the first and second layers, which are nearest to the adsorbed O atom. Oxygen was placed in a fourfold site which is the experimentally known site. The resulting model for O/Cu(100) is Cu_5O , see Fig. 1. The point group of Cu_5 and Cu_5O is C_{4v} . The metal-metal distances have been kept at the bulk values,⁸ but the oxygen distance to the surface has been varied. *Ab initio*, all-electron self-consistent-field (SCF) wave functions for Cu_5O were determined using a reasonable size basis set to describe the molecular orbitals.⁹ The properties of the potential curve for Cu_5O as a function of the distance of atomic O to the surface plane have been reported in a previous paper.⁶ The purpose of this paper is to analyze the nature of the Cu—O bond. Much of the analysis will be carried out with the O placed at 1.9 bohrs

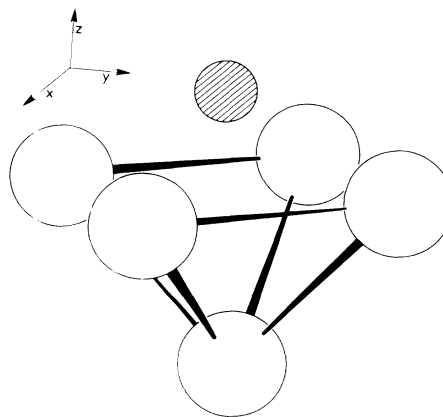


FIG. 1. Representation of the Cu_5O cluster model for O/Cu(100); the O atom is shaded.

above the surface plane; this distance is reasonably close to the equilibrium SCF distance of O above Cu_5 , $z_e = 1.78$ bohrs. The analyses are carried out for the 2E electronic state of Cu_5O , which has a singly occupied e shell and for the ground state of the Cu_5^+ cluster, which has a 3A_2 ground state with an e^2 open shell; see Ref. 6, and references therein for further details.

Three techniques have been used for the analysis of the bond. The first is based on the projection of O orbitals from the Cu_5O wave function and it is described in Sec. II. This technique provides information about the extent to which the O orbitals are occupied for chemisorbed O/Cu(100), and gives information about its effective ionicity. We shall show that the projections are consistent with O anionic by ~ 1.5 electrons. The second technique used to study the bond character is the nature of the dipole-moment curve $\mu(z)$ for motion of O normal to the surface; in particular, we will examine the slope and curvature of $\mu(z)$. This method is described in Sec. III, where we analyze $\mu(z)$ for Cu_5 interacting with a point charge (PC) as well as with O. The analysis of the Cu_5O and Cu_5 plus PC $\mu(z)$ curves also indicate an O anionicity of ~ 1.5 electrons. Finally in Sec. IV we examine the participation of the Cu $3d$ electrons in the Cu—O bond. This is done by performing constrained variations where the ability of the $3d$ orbitals to participate in the bond is successively increased. We find that while the largest part of the interaction energy between Cu and O is obtained from the $4sp$ electrons, the Cu d electrons make a significant contribution to the bond. Here also, we compare Cu_5O and Cu_5 plus PC's in order to determine the nature of the d electron involvement in the bond; in particular, its participation in covalent bonds.

We believe that the conclusions from our analysis for SCF wave functions are qualitatively correct even though we have not considered electron correlation effects. Concern about the SCF description of the metal—O bond has been expressed^{7,10} because only a small part of the interaction energies for cluster models of O/Ni(100), O/Cu(100), and O/Ag(100) is obtained with SCF wave functions. However, for the work in Refs. 7 and 10, the interaction energy was calculated for dissociation into neutral metal cluster and O units. It is well known¹¹ that this procedure does indeed yield poor SCF interaction energies for ionic systems. This is because the SCF ionization potentials (IP's), and, in particular, electron affinities (EA's) for the separated units are much smaller than the experimental values. Thus, the error of the SCF Cu—O interaction energy for Cu_5O does not arise because the SCF description of the bond is incorrect. It arises because of the poor SCF description on the IP of Cu_5 and the EA of O. A good description of the interaction energy is given by computing the SCF binding energy of Cu_5O with respect to Cu_5^+ and O^- units and correcting this value with the experimental EA for oxygen and the experimental IP for Cu_5 (or the work function for a Cu surface). For Cu_5O , we obtain a SCF binding energy of 6.4 eV with respect to the energies of Cu_5^+ and O^- . When this is corrected with the work function of Cu(100), 4.6 eV,¹² and the EA of oxygen, 1.5 eV,¹³ we obtain a binding ener-

gy, or D_e , of 3.2 eV = [6.4 - (4.6 - 1.5)]. This is smaller than the binding of 5–6 eV estimated from experiment.² This small value of D_e is not surprising because the precise value of D_e is difficult to determine with the cluster model.¹⁴ However, the SCF $D_e = 3.2$ eV is $\geq 75\%$ of the value, $D_e = \sim 4$ eV, which is obtained with correlated wave functions for Cu_5O .^{2,7,10} This $\lesssim 25\%$ SCF error arises because, as we shall show, the Cu—O bond has some covalent character. This approach may have been neglected in earlier work^{7,10} because the ionic character of the bond has not been established until the present work.

There are strong reasons to accept the SCF description of the Cu—O bond, in particular, and the metal—O bond, in general, as qualitatively correct. Given that this is the case, we proceed with our discussion of the three techniques for the analysis of the Cu—O bond.

II. ORBITAL PROJECTIONS

For the analysis of the ionicity of the Cu—O bond for O/Cu(100), we use the projection of the O atomic orbitals, ϕ_i , $i = 1s, 2s, 2p_\sigma, 2p_\pi$, from the Cu_5O wave function. The expectation value P_ϕ of the projection operator for $\phi, \phi\phi^\dagger$, is taken with the Cu_5O SCF wave function Ψ ;

$$P_\phi = \langle \Psi | \phi\phi^\dagger | \Psi \rangle . \quad (1)$$

The value of P_ϕ indicates the extent to which the orbital ϕ is occupied in the total Cu_5O wave function Ψ , see Ref. 15. Three different cases may be considered for P_ϕ . If $P_\phi \approx 2$, then ϕ is fully occupied in Ψ . If $P_\phi \approx 0$, then ϕ is not occupied. The intermediate case $0 < P_\phi < 2$ indicates that ϕ may be involved in a covalent bond with Cu. In this case, it is necessary to consider that there is an overlap between ϕ and the orbitals of the bare Cu_5 cluster.¹⁵ It is possible to estimate the partial occupation of ϕ in $\Psi(\text{Cu}_5\text{O})$, N_ϕ , by taking this overlap into account by

$$N_\phi = \langle \Psi(\text{Cu}_5\text{O}) | \phi\phi^\dagger | \Psi(\text{Cu}_5\text{O}) \rangle - \langle \Psi(\text{Cu}_5) | \phi\phi^\dagger | \Psi(\text{Cu}_5) \rangle . \quad (2)$$

For the Cu_5O cluster with O at $1.9a_0$ above the surface, the projection of O orbitals from the Cu_5O wave function was performed. This distance is close to the equilibrium distance of O above Cu_5 ; the projections do not depend strongly on the O distance from the Cu surface and similar values are obtained for distances within $\sim 0.25a_0$ of the equilibrium. The SCF orbitals for neutral O and anionic O^- have both been used for the projection to test if the choice of the O orbitals is important. We find that the use of either set of orbitals, O or O^- , gives similar information about the character of the Cu—O bond. This insensitivity to the choice of adsorbate orbitals to be used for the projection is consistent with earlier studies.¹⁵ The values of these projections are given in Table I, where we also give the projections of the O orbitals on the bare Cu_5 cluster.

We consider first the projections of the neutral O orbitals. The projections of the $1s$ and $2s$ are 2.00 and 1.99;

TABLE I. Projection of the O and O⁻ atomic orbitals on Cu₅O and on Cu₅.

	O/Cu ₅ O	O ⁻ /Cu ₅ O	O/Cu ₅	O ⁻ /Cu ₅
1s	2.00	2.00	0.00	0.00
2s	1.99	1.99	0.25	0.27
2p _σ	1.91	1.96	0.09	0.16
2p _π	3.64	3.87	0.22	0.42
Total	9.55	9.83		

these orbitals are fully occupied. The projection of the 2p_σ atomic orbital is 1.915 with only a 4% reduction from complete occupation. This small reduction arises in part from a change in the shape of the 2p_σ orbital due to the oxygen ionicity in Cu₅O. When we project the O⁻ 2p_σ orbital on Cu₅O, the projection is 1.964 or only 2% less than fully occupied. While the 2p_σ orbital may be involved, to a small degree, in a covalent bond, it is essentially fully occupied. The projection of O(2p_σ) on the bare Cu₅ cluster is not negligible; ~0.25 for either O or O⁻ orbitals. However, this arises simply because the orbitals of interacting units overlap. Since the occupation of the 2p_σ is so close to 2, it is not appropriate to use the correction of Eq. (2). On the other hand, the projection of the O 2p_π orbital is 3.64 or 9% smaller than the complete occupation. In this case, the correction of Eq. (2) is appropriate to identify the polarity, or ionic contribution, to the Cu—O covalent π bond. The projection of O(2p_π) on Cu₅ is 0.22, leading to an estimate of the O(2p_π) of 3.43. It is, of course, impossible to completely separate ionic and covalent components of a bond when the orbitals on different subunits have a significant overlap. Thus, it is better to view the values using Eqs. (1) and (2) as providing bounds on the ionicity. Summing the O σ projections from Cu₅O, Eq. (1), and the π projections using both Eqs. (1) and (2), we obtain bounds on the O anionicity, -q, of 1.33 < q < 1.55. Similar results are obtained from the projection of the O⁻ orbitals.

When there are ionic and covalent contributions to a bond, it is not possible to assign the bonding electrons uniquely to one subunit or another. However, the projections clearly indicate that O/Cu(100) is strongly ionic and there is also a significant covalent contribution, in particular, for the π bond. It also suggests that -1.5 is a reasonable estimate of the ionicity; other measures discussed in the following sections support this estimate.

III. DIPOLE MOMENT CURVES

As discussed elsewhere,¹⁵ the slope of the curve of the dipole moment versus the distance, in the region near the equilibrium bond distance, is an excellent indication of the ionicity of a bond. For an ideal ionic molecule denoted A⁺B⁻ the slope of that curve is |-1|. Of course, this is an oversimplified model which does not include the effects of the polarization of A⁺ by B⁻ and of B⁻ by A⁺. In this section, we shall present an analysis of the dipole moment curve of Cu₅O, which takes this polariza-

tion into account.

We consider the dipole-moment curves, μ(z) [here, μ is the z component of the dipole moment, the only nonzero component for the O/Cu(100) cluster model], for the motion of O normal to the surface. The curve is expanded in a Taylor series about z_e = 1.78a₀ which is the O equilibrium distance,

$$\mu = M_0 + M_1(z - z_e) + M_2(z - z_e)^2 + \dots \quad (3)$$

The Taylor expansions made using quartic polynomial fits to five points about z_e are given in Table II. We consider first the value of the dipole moment for Cu₅O at z_e, M₀ = +0.24 a.u. A simple formula is often used to relate the ionicity of an adsorbate to the difference between the surface dipole, or work function, for the bare and adsorbate covered surface. With this formula, the ionicity q is given by q = [μ(ads) - μ(bare)]/z. The dipole moment of the bare Cu₅ cluster is +0.004 a.u. and using the simple formula above O is positively charged by ~0.1 electrons. This is completely inconsistent with the ionicity estimated above from the projection operator. However, this simple formula neglects the polarization of the O and Cu₅ units; Pettersson and Bagus¹⁶ have shown that the change of the work function cannot be used as a guide to the ionicity of the adsorbate precisely because of these polarizations. Following the work of Nelin *et al.*,¹⁵ we shall show that the slope of the dipole-moment curve provides a useful indication of the adsorbate ionicity; one that is consistent with the results obtained by projecting the O character. We note, see Table II, that the dipole-moment curve is reasonably linear; the curvature M₂ is less than 1/3 of the slope M₁. This is a strong indication of an ionic bond. If the interactions were entirely ionic and if the polarization scaled linearly with adsorbate distance near the z_e, then the curvature M₂ would be zero. The fact that M₂ is not insignificant is consistent with an ionic bond which has some covalent character. The value of the slope should indicate extent of the ionicity but there is an uncertainty related to the polarization of Cu₅^{q+} and O^{q-}. This can be seen by considering the dipole-moment curve for the motion of a test charge q normal to a metal surface. If the surface is not allowed to polarize in response to the test charge, then the slope of the dipole-moment curve is q. If, on the other hand, the surface is assumed to polarize and to form an image charge, the slope of the dipole-moment curve is 2q. The actual response of the Cu₅ cluster and the response of the oxygen anion put wide limits on our ability to relate M₁ = -1.2 to the O anionicity; we can only say that O

TABLE II. Coefficients of the Taylor series expansions of the dipole-moment curves for the Cu₅O, Cu₅-PC1, and Cu₅-PC2 clusters; see Eq. (3). For Cu₅-PC1 and Cu₅-PC2, point charges of -1 or -2, respectively, interact with the Cu₅⁺ cluster.

	Cu ₅ O	Cu ₅ -PC1	Cu ₅ -PC2
M ₀	0.24	0.21	
M ₁	-1.17	-0.70	-1.52
M ₂	-0.36	-0.27	-0.47

has considerable anionicity. It is worth noting that the infrared adsorption-reflection intensity I for the vibration of O normal to the Cu surface is related to the slope of the dipole-moment curve by¹⁷ $I \propto M_1$.² It is possible, in principle, to determine M_1 from measurements of I and this could provide experimental confirmation of our prediction of a large ionicity for O/Cu(100). Unfortunately, we are not aware of such measurements for O/Cu.

In order to understand the polarizability of the Cu_5 cluster, we have obtained the dipole-moment curve for two clusters, where the O atom is replaced by a point charge. In the first case, $\text{Cu}_5\text{-PC1}$, we place a point charge (PC) of -1 above the Cu_5^+ ; the total cluster is neutral. In the second case, $\text{Cu}_5\text{-PC2}$, we place a point charge (PC) of -2 above Cu_5^+ . The total cluster has charge -1 because we do not wish to remove a second of the polarizable "conduction-band" Cu electrons. Our choice of total cluster charges will make the polarizability of the Cu substrate similar for $\text{Cu}_5\text{-PC1}$, $\text{Cu}_5\text{-PC2}$, and Cu_5O .

The general shape of the $\mu(z)$ curve for $\text{Cu}_5\text{-PC1}$ is similar to that of Cu_5O except that the slope and curvature, M_1 and M_2 , are reduced by 30–40%. This suggests that a point charge with larger magnitude than -1 is needed to represent the effective charge of O in Cu_5O . When the charge is increased to -2 in $\text{Cu}_5\text{-PC2}$, M_1 and M_2 are 30–40% larger than for Cu_5O . A simple linear interpolation of the Cu_5O values for M_1 and M_2 between $\text{Cu}_5\text{-PC1}$ and $\text{Cu}_5\text{-PC2}$ gives an effective ionicity for O of ~ -1.5 electrons in agreement with the estimate obtained from the projection. These two tests give clear evidence for an O anionicity of 1.5. We turn now to an analysis of the contributions to the Cu—O bonding; in particular, the contribution of the d electrons.

IV. PARTICIPATION OF THE d ELECTRONS IN THE Cu-O INTERACTION

The constrained space orbital variation (CSOV) method provides a unique capability to separate the contributions to a chemical bond, including those arising from intraunit polarization and from interunit charge transfer or covalent bonding.^{3,18} Our major concern for the CSOV analysis of the Cu—O bond is to quantify the importance of the $3d$ shell participation in the bond. As in the previous section, we compare the behavior of Cu_5 interacting with O and with a point charge $q = -1$, to represent the O. The CSOV analysis applied to the Cu_5O and $\text{Cu}_5\text{-PC1}$ clusters enables us to divide the d electron involvement in the bond into polarization in response to the charge on the O ion and into direct participation in the covalent chemical bond.

For the analysis of the Cu_5O and $\text{Cu}_5\text{-PC1}$ clusters, the O or the PC is placed at $1.9a_0$ above the Cu surface. The contributions to the bond are measured by the interaction energy E_{INT} taken with respect to the ionic limits. For Cu_5O the limits are Cu_5^+ and O^- and E_{INT} is defined as

$$E_{\text{INT}} = E(\text{Cu}_5\text{O}; {}^2E) - E(\text{Cu}_5^+; {}^3A_2) - E(\text{O}^-; {}^2P) \quad (3)$$

and for $\text{Cu}_5\text{-PC1}$ as

$$E_{\text{INT}} = E(\text{Cu}_5\text{-PC1}; {}^3A_2) - E(\text{Cu}_5^+; {}^3A_2); \quad (4)$$

all the energies are computed at the SCF level. This choice of dissociation limits allows us to directly compare the Cu_5O and the $\text{Cu}_5\text{-PC1}$ results. It also avoids errors which arise from the limitations of the SCF description of the O electron affinity and the cluster ionization potential,^{6,11} and focuses on the chemical interaction between the ions. The results for the CSOV analysis for E_{int} are given in Table III.

To start the CSOV process, we consider the interaction of the Cu $4sp$ conduction band with O. This is accomplished by fixing the 140 Cu_5 electrons corresponding to the Ar cores and the filled d shells of the Cu atoms as they are in the Cu_5^+ cluster. We note that the choice of the Cu_5^+ cluster d orbitals allows some small amount of d electron involvement in the Cu conduction band^{6,19} because of the $d \rightarrow 4sp$ hybridization. However, this creates the correct conduction-band environment for the cluster and approximates that of the metal. In this first CSOV step, we vary, for Cu_5O , 13 electrons: the five Cu_5 $4sp$ conduction-band electrons and the eight electrons arising from O. The orbital space for this variation is the occupied Cu_5^+ a_1 and e orbitals of the $4sp$ conduction band and the O occupied $1s$, $2s$ and $2p$ orbitals and the full set of virtual (or unoccupied) orbitals for both Cu_5^+ and O. For the $\text{Cu}_5\text{-PC1}$ variation, four electrons are varied in the orbital space of the Cu_5^+ a_1 and e conduction orbitals and all the virtual orbitals of Cu_5^+ . We chose this as a starting point because of the large ionic and covalent interactions of the Cu conduction band with O. In other words, we do not attempt to separate this interaction into ionic and covalent contributions. Given the large overlap of the Cu conduction band with the O orbitals, such separation may, in any case, not be possible. We rely on the evidence obtained from the dipole-moment curves and the O orbital projection to characterize the ionicity. At this step, the interaction of Cu_5O is 5.10 eV, with respect to the energies of Cu_5^+ and O^- and the interaction of $\text{Cu}_5\text{-PC1}$ is 7.99 eV with respect to the energy of Cu_5^+ ; see Table III. The Cu_5O interaction energy is smaller because there is a nonbonding Pauli repulsion (or surface wall) between the O charge distribution and the Cu conduction-band charge;^{1,3,5,15} this repulsion is absent when the O is replaced by a point charge. We will see

TABLE III. A CSOV analysis of the interaction energy E_{INT} of atomic oxygen and of a -1 point charge with a Cu_5 surface cluster model, Cu_5O or $\text{Cu}_5\text{-PC1}$; see text for the definition of the CSOV steps. The values reported correspond to the interaction with respect to the ionic limits in eV and the numbers in parentheses are the increase in E_{INT} relative to the previous step.

	Cu_5O	$\text{Cu}_5\text{-PC1}$
Step 1: Vary $4sp$ and O	5.10	7.99
Step 2: A. Core space	5.34/(0.25)	8.25/(0.26)
B. Full space	6.16/(0.81)	8.51/(0.25)
Step 3: Closed with open	6.31/(0.14)	
Step 4: Full SCF	6.35/(0.04)	8.53/(0.02)

that the 5.1-eV interaction at this starting point is the largest contribution to the Cu-O interaction, $\sim 80\%$ of the total.⁶ However, the d electrons do make a significant, ~ 1 eV or 20%, contribution to the interaction. Electron correlation effects, as obtained, for example, through configuration interaction,¹⁰ would change the precise numerical values of the conduction-band $4sp$ and $3d$ contributions to the bond from the SCF values obtained in this work. However, there is overwhelming evidence both, in general, for cluster models of the adsorbate surface interaction¹ and, in particular, for the O/Cu interaction^{1,6,10} that the SCF wave function gives a correct qualitative description of the bond.

We now turn to a variation of the 50 electrons arising from the closed Cu d shells. We fix the orbitals for the remaining 103 electrons (Cu₅O cluster) or 94 electrons (Cu₅-PC1 cluster) as they were in the CSOV step 1 wave functions. Two orbital spaces are used for the variation of the 50 Cu d electrons. In the first case, a virtual space is formed from the s , p , and d contracted basis functions for the Cu atom, which are in the region of space near the $3d$ shell. (Recall that the $\langle r \rangle$ for the $3s$, $3p$, and $3d$ orbitals of the Cu atom are $0.723a_0$, $0.757a_0$, and $0.991a_0$, respectively, as obtained from numerical Hartree-Fock wave functions. These have to be compared with $\langle r \rangle = 3.331$ for the $4s$ atomic orbital.) These virtual orbitals are added to the occupied $3d$ cluster orbitals to form the full orbital space for this variation denoted CSOV step 2A. Basically this step is performed to examine the polarization of the $3d$ electrons in the contracted or core region of space where they are distributed. For Cu₅O, this CSOV step increases the interaction energy by 0.25 eV. This increase is likely to be due to the polarization of the d shell by the electric field arising from the adsorbate oxygen anion.²⁰ We would expect that a similar change in E_{INT} would arise from replacing O by a point charge. We find that this is indeed the case for Cu₅-PC1 where at the CSOV step 2A, $\Delta E_{\text{INT}} = 0.26$ eV.

We consider a more extended variation of the Cu $3d$ orbitals in the CSOV step 2B. The orbitals, which are fixed, and the electrons, which are varied, are the same as in step 2A above. However, all of the Cu₅⁺ and O virtual orbitals are included in the variational space for Cu₅O. This step 2B allows the $3d$ electrons to hybridize with the Cu $4sp$ and O $2p$ orbitals and to form dative covalent bonds with O; this is in addition to the polarization of the $3d$ orbitals studied in the previous CSOV step 2A. For the Cu₅-PC1 cluster, dative covalent bonding of the $3d$ with O is, of course, not possible; only $3d$ to $4sp$ hybridization can be induced by the electric field of the point charge. In Cu₅O, the change in E_{INT} , ΔE_{INT} , due to the $3d$ to $4sp$ hybridization and dative covalent bonding with O, is 0.81 eV; see Table III. In Cu₅-PC1, $\Delta E_{\text{INT}} = 0.25$ eV, but, as noted above, only $3d$ to $4sp$ hybridization is possible here. In other words, at this step the d participation in the Cu—O bond contributes 0.56 eV to the interaction. As we noted above, the SCF wave function does not include correlation effects. In general, we expect that correlation effects will give an improved description of a covalent bond and will increase the d contribution to the Cu—O bond at this and future CSOV steps.

In the previous step, we have noted that we considered only d participation for dative covalent bonding with O. However, the d 's can also participate in the covalent bonds between Cu $4sp$ and O. This can be studied by allowing rotation between the closed and open shells as obtained from the step 2B CSOV calculation. (For Cu₅O, this mixing is important only for e symmetry where there is an e^1 open shell; the a_1 symmetry contains only closed shells.) This closed-open mixing for the Cu₅O CSOV step 3 contributes an additional 0.14 eV to E_{INT} due to d electron involvement in the Cu—O covalent bonding. The sum of the direct d involvement in the Cu—O bond from CSOV steps 2 and 3 is 0.70 eV = 0.56 (step 2B) + 0.14 (step 3). Finally, at step 4, we perform unconstrained full SCF calculations for Cu₅O and Cu₅-PC1; this is done to identify whether any important steps have been omitted from the CSOV sequence. We see that the improvements for E_{INT} for the full SCF over the last CSOV step are quite small, 0.04 eV for Cu₅O and 0.02 for Cu₅-PC1. Thus, the 0.7 eV given by the CSOV analysis is a correct measure of the contribution to E_{INT} due to the direct involvement of the Cu d electrons in the Cu—O bond. This is about 15% of the estimate of 5 eV for the heat of adsorption of O on Cu. We expect that the d involvement will become larger when electron correlation effects are included.²¹

This value for the d involvement is larger than the one reported in previous work by Mattsson *et al.*⁷ and Wahlgren *et al.*²² This is because those works have not made a careful enough analysis of the d involvement and neglected some essential features of the interaction. Mattsson *et al.*⁷ have fixed the Cu cores as they are in the isolated atoms and have neglected the d hybridization to the Cu sp conduction band. Wahlgren *et al.*²² have not properly taken into account the large overlap between the Cu₅ and O virtual orbitals. In effect, they have used Cu₅ orbitals to represent, albeit approximately, O atom character. We have been careful to avoid this source of error. In particular, our comparison of Cu interacting with a point charge has allowed us to clearly distinguish polarization from participation in the chemical bond. For Cu₅O, the total d participation in the bond contributes 1.24 eV to E_{INT} ; this is the difference between E_{INT} for the CSOV step 1 and the full SCF. For the Cu₅-PC1, the d contribution to E_{INT} is 0.53 eV and is due entirely to polarization of the d orbitals by the point charge representing O⁻. The difference between Cu₅O and Cu₅-PC1, 0.7 eV, is the contribution to E_{INT} due to the presence of the O atom.

V. CONCLUSIONS

The bonding of atomic oxygen to Cu(100) with a surface cluster model has been analyzed by different techniques. It has been shown that this is a rather ionic bond with a net charge on the oxygen atom of about 1.5 electrons. This is supported by both orbital projection and dipole-moment curves. It has been found that the amount of d electron participation in the Cu—O bond is

about 0.7 eV. Our analysis supports the commonly held belief that the *d* electrons participate in the bond and provide an estimate for its energetic importance. In conclusion, the bond of atomic oxygen to a Cu(100) surface is rather ionic with a considerable participation of the *d* electrons in the bond.

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