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Molecular-orbital self-consistent-field cluster model of H_2O adsorption on copper

M. W. Ribarsky, W. D. Luedtke, and Uzi Landman
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
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The interaction of H_2O with a Cu(100) surface is modeled via cluster calculations using the self-consistent-field–linear-combination-of-atomic-orbitals–$X\alpha$ method. In the equilibrium on-top configuration bonding is through the oxygen with the molecular plane tilted from the normal by 70°. Bonding involves the H_2O lone-pair orbitals and a charge donation to the metal. The calculated normal mode vibrational and low-frequency hindered molecular rotational frequencies agree with recent data.

Understanding of the bonding and structural characteristics of water interacting with metal surfaces is of importance due to the abundance of water in our surroundings and the physical and chemical processes of fundamental and technological interest which occur in such systems, such as corrosion, catalytic reactions in which H_2O is one of the reactants, electrochemical processes in aqueous solutions, and the mechanisms of adsorption and nucleation of ice on solid substrates. Recent experimental studies of water adsorption at low temperatures on single-crystal surfaces[1,2] show that for most metals H_2O monomers adsorb molecularly and tend to form hydrogen-bonded clusters, thus prohibiting studies of the fundamental interaction of H_2O monomers with the surface.

The impetus for our investigations is provided by the electron-energy-loss spectroscopy (EELS) experiments of Andersson, Nyberg, and Tengstal[2] of water adsorption on Cu(100) at low temperatures ($T \sim 10$ K) and low coverages in which evidence for H_2O monomer molecular adsorption has been found. Assignment of vibrational modes and analysis of spectral intensities allowed them to conclude that the water molecule is bonded to the metal via the oxygen with the molecular H_2O axis tilted approximately 60° away from the surface normal. Previous detailed theoretical studies of the molecular electronic structure of neutral aquametallic complexes are limited to simple metal atoms[3] (e.g., Li, Al) and most earlier studies[4] of H_2O interacting with noble and transition-metal clusters are semiempirical or qualitative in nature and do not contain optimized structural information. In this paper we investigate the electronic structure of the H_2O interaction with a Cu atom and a Cu_5 atomic cluster [designed to model localized adsorption on a Cu(100) surface] and provide new structural and dynamical information as well as an elucidation of the bonding mechanisms in these systems. In our calculations we use an extended basis set spin-unrestricted self-consistent-field–linear-combination-of-atomic-orbitals (SCF–LCAO) method with local $X\alpha$ exchange, and perform systematic optimizations with regard to the molecular internal coordinates in addition to its location and orientation with respect to the metallic cluster. The binding energies of the complexes (relative to the separated H_2O and metal) in the calculated optimized configurations are 0.76 and 0.38 eV for H_2O–Cu and H_2O–Cu_5, respectively, in accord with experimental estimates of molecular H_2O adsorption energies on metals.[1,2] Bonding occurs via coupling of the H_2O lone-pair orbitals to the metal states with an associated charge transfer to the metal of $\sim 0.15e$. As a consequence of the bonding mechanism, in the equilibrium geometry the oxygen end of the molecule points toward the metal cluster situated at a distance of 2.2 Å (2.0 Å for H_2O–Cu) with the H_2O molecular axis tilted with respect to the Cu–O bond by angles of 67° and 70° for the single Cu and Cu_5 clusters, respectively. (The molecular internal coordinates change only slightly upon adsorption.)

In the SCF-LCAO-$X\alpha$ method[5] non-muffin-tin $X\alpha$ one-electron equations are solved self-consistently using a Gaussian-type orbitals (GTO) LCAO approach. In our calculations the charge density and the exchange ($X\alpha$) potential are fitted using GTO expansions, thus circumventing four-center integrals and allowing calculations for large systems using extended basis sets.[5] We have used Wachter's[6] $(14s,9p,5d)$ GTO orbital basis set for $Cu(^2S)$, augmented with diffuse p, d, and f Gaussians (exponents $=0.1$, 0.1, and 1.0 a_0^{-2}, respectively). Extensive studies by Dunlap and co-workers[7] concerning basis set dependence for transition-metal clusters have shown that exponents in this range yield adequate basis set flexibility. In the case of calculations involving the Cu_5 cluster, the Wachter's basis set is contracted[6] to $(8s,5p,3d)$ for the four Cu atoms farthest from the H_2O molecule. Van Duijnevelt's[8] GTO basis was used for oxygen ($9s,6p$ augmented with diffuse p and d Gaussians) and hydrogen ($4s$ with diffuse p). The above molecular basis sets are used to derive the basis sets for the charge density and exchange fits following a procedure developed by Dunlap, Connolly, and Sabin.[5] We note that the calculations presented in this paper involve the largest basis sets ever used for a system of this size, thus providing a benchmark for future calculations.

First, we present our results pertinent to the separated species. The ground-state electronic configuration for the single-Cu atom is (Ar core, $3d^{10}4s^1$). The Cu_5 cluster is arranged with the atoms located at the vertices of a square base pyramid (see Fig. 1) with an edge length of 2.54 Å (the Cu lattice nearest-neighbor distance). The ground-state molecular-orbital configuration for the cluster was found to be $17a_1^2 11b_1^2 18e^3 5b_2^2 4a_2^2$, in agreement with previous calculations.[9] Throughout our calculation a value of 0.708 96 was used for α in the local exchange potential. While different α values would yield different total energies, extensive studies have shown[5] that structural, binding, and spectroscopic properties are essentially insensitive to moderate variations in α.

In the equilibrium configuration of H_2O, the O-H bond length is 0.968 Å [the experimental value (Ref. 10) is 0.957 Å] and the H-O-H angle is 105.3° [the experimental value

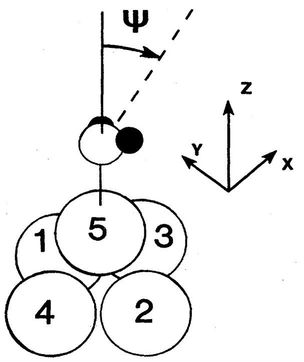

FIG. 1. Schematic picture of the H_2O–Cu_5 equilibrium configuration. Numbered open circles denote Cu atoms. The oxygen atom is represented by an open circle and the hydrogens by solid ones. The molecular H_2O plane is tilted from the Cu(5)–O axis by the angle $\psi = 70°$. The binding energy of H_2O to the Cu_5 cluster is insensitive to rotations of the molecule about the Cu(5)–O axis. In the configuration shown Cu(1) and Cu(2) are equivalent (see also Table I).

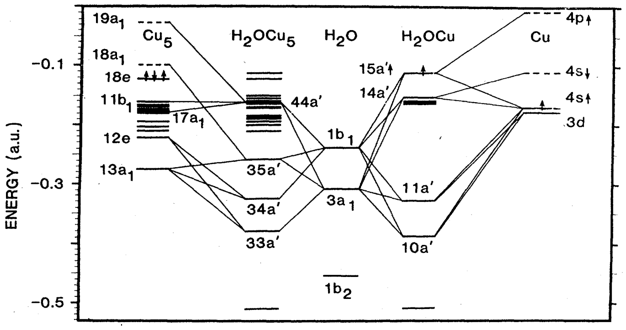

FIG. 2. Orbital-energy correlation diagrams for the equilibrium configurations of H_2O–Cu and H_2O–Cu_5 obtained via spin-unrestricted SCF-LCAO with local $X\alpha$ exchange calculations. Occupied and partially occupied levels are denoted by solid lines; broken lines denote unoccupied levels. The higher-lying states of Cu_5 are predominantly of d character (and s,p character for the top states) and are not all depicted separately.

(Ref. 10) is 104.52°] with a dipole moment of $2.02D$ [the experimental value (Ref. 10) is $1.88D$]. The vibrational frequencies calculated from a 14-point fit to the potential surface in the vicinity of the equilibrium configuration including quadratic, cubic, and angle-bending bond-stretch cross terms are 228, 463, and 470 meV for the H-O-H bending, O-H symmetric and antisymmetric stretches, respectively, in close agreement with measured values[10] (198, 453, 466 meV, respectively).

Having outlined our results for the separated species we turn now to a discussion of comparative studies of the interaction of H_2O with a single-Cu atom and a Cu_5 atomic cluster. The ground-state binding energies determined via systematic mappings of the potential-energy surfaces are $E_B(H_2O\text{–}Cu) = 0.76$ eV and $E_B(H_2O\text{–}Cu_5) = 0.38$ eV. In the equilibrium geometry of the H_2O–Cu system, bonding to the Cu is via the oxygen located at a distance $R_{\text{Cu-O}} = 2.0$ Å, with an O-H bond length $R_{\text{O-H}} = 0.98$ Å, a H-O-H angle $\gamma = 105°$ and a Cu-O-H angle $\alpha = 103.6°$ (i.e., the molecular H_2O plane is tilted by an angle $\psi = 67°$ from the Cu-O axis). The corresponding values for the equilibrium H_2O–Cu_5 system are $R_{\text{Cu-O}} = 2.2$ Å, $R_{\text{O-H}} = 0.98$ Å, $\gamma = 106°$, and $\alpha = 100.6°$ ($\psi = 70°$). Rotations about the Cu–O axis are essentially unhindered. Note that the H_2O structural parameters are close to those of the free molecule except for a slight increase of the O-H bond length which is consistent with the charge transfer, and that the structure is modified only slightly upon increasing the cluster size.

The nature of the bonding is best described using the orbital correlation diagrams (ocd) shown in Fig. 2 deduced from analysis of the orbital coefficients and the Mulliken population analysis shown in Table I. We emphasize that the Mulliken population analysis is employed as a guide in identifying orbital admixtures, and is used in conjunction with detailed analysis of orbital composition and electron-density distributions. Note also that while a small amount of charge transfer from the Cu d-atomic states is seen in the population analysis, the molecular orbitals of predominantly d character are fully occupied in all our calculations involving Cu, in agreement with experimental and theoretical findings.[11] Both our H_2O-metal clusters are of C_S symmetry leading to classification of the molecular orbitals according to their symmetry under reflection in the plane containing the Cu–O and the molecular H-O-H axes (A'-symmetric and A''-antisymmetric representations).

An explanation of the binding mechanism of H_2O to Cu systems must invoke the participation of unoccupied and/or partially occupied orbitals, since combinations of the H_2O lone-pair orbitals (LPO's), $1b_1$ (π–LPO) and $3a_1$ (σ–LPO), with the metal fully occupied orbitals form bonding and antibonding orbitals with net zero bond order (the same argument was used in a recent study of H_2O binding to an Al cluster[12]).

First, in the case of H_2O-Cu, the unoccupied Cu ($4p$) state admixes, in the presence of the H_2O molecule, with the H_2O LPO($|L\rangle$) resulting in charge donation [in the amount given by Eq. (1)] and with the Cu($3d$) orbital resulting in p-d promotion [Eq. (2)],

$$\beta[4p,L] = \langle 4p|V|L\rangle / (\epsilon_{4p} - \epsilon_L) \ , \tag{1}$$

$$\beta[4p,3d] = \langle 4p|V|3d\rangle / (\epsilon_{4p} - \epsilon_{3d}) \ . \tag{2}$$

These effects yield energy lowerings given by (i) ΔE_L

TABLE I. Mulliken atomic populations for Cu atoms in Cu_5, H_2O–Cu_5, and H_2O–Cu.

	s	p	d	f	Total
			H_2O–Cu_5		
Cu(1)	6.706	12.348	9.945	· · ·	28.999
Cu(2)	6.706	12.348	9.945	· · ·	28.999
Cu(3)	6.811	12.259	9.955	· · ·	29.025
Cu(4)	6.873	12.237	9.933	· · ·	29.043
Cu(5)	6.552	12.508	9.957	0.062	29.079
Total	33.648	61.70	49.735	0.062	145.145
			H_2O–Cu		
Cu	7.122	12.107	9.904	0.017	29.15
			Cu_5		
Cu(1–4)	6.748	12.291	9.931	· · ·	28.97
Cu(5)	6.697	12.490	9.877	0.057	29.121
Total	33.689	61.654	49.601	0.057	145.00

$\simeq \beta^2[4p,L](\epsilon_L - \epsilon_{4p})$ and (ii) $\Delta E_{4p} \simeq \beta^2[4p,3d](\epsilon_{3d} - \epsilon_{4p})$. Similar admixtures occur for the spin-down Cu(4s) in the amounts $\beta[4s,L]$ and $\beta[4s,3d]$ and perhaps a $4s\uparrow$ to $4p\uparrow$ promotion. As seen from Table I the net effect is a transfer of $\simeq 0.15e$ from H_2O to Cu and a small amount of charge redistribution from d-type to s- and p-type Cu functions. The resulting bonding orbitals of H_2O–Cu are $10a'$ and $11a'$ (see Fig. 2) which possess large H_2O LPO components. The antibonding orbitals are $14a'$ and $15a'\uparrow$ which are of predominantly d and s character, respectively, and are anchored on the Cu atom.

The situation is more complicated, although similar in principle, in the case of H_2O–Cu_5 due to the larger number of states. The population analysis (Table I) indicates that in comparing the bare Cu_5 cluster with H_2O–Cu_5, the main changes occurring on the Cu atoms are an increase in d-type charge and a decrease in s-type charge on the fifth Cu atom [Cu(5), see Fig. 1] accompanied by an increase in s-type contributions on Cu(3) and Cu(4). This may be explained in terms of a polarization of the s-type charge on Cu(5) which results in mixing with orbitals having d character on Cu(5) and s character on Cu(3) and Cu(4). In addition in the Cu_5 cluster the d-electron population is deficient by $\sim 0.4e$ resulting in a decrease in electron-repulsion energy, thus lowering the centroid of the Cu_5 "d band" relative to the Cu $3d$ atomic level. Upon binding with H_2O the increase in d character is accompanied by an upward shift of the cluster "d band." The bonding orbitals of H_2O–Cu_5, $33a'$ and $34a'$ (Fig. 2), have predominant H_2O LPO components and involve mainly the $13a_1$ (mostly s and some p) and $12e$ (mostly d) orbitals of the Cu_5 cluster. The presence of H_2O causes charge promotion to the originally unoccupied $18a_1$ and $19a_1$ orbitals of Cu_5 from the originally fully occupied $13a_1$, $17a_1$, and $11b_1$ orbitals and a charge donation from the H_2O LPO's in the amounts $\beta[18a_1,L]$ and $\beta[19a_1,L]$. The antibonding orbital $35a'$, in which a cancellation of the large s component on Cu(5) [i.e., $s(5)$ coming from orbital $13a_1$] occurs, results from a mixture of the H_2O LPO's with the $13a_1$ and $18a_1$ orbitals of Cu_5. The increase in d character on Cu(5) is due to the admixture of the fully occupied $17a_1$ and $11b_1$ and the unoccupied $19a_1$ Cu_5 orbitals with the H_2O LPO's, yielding the antibonding orbital $44a'$. These antibonding orbitals contain predominantly Cu functions components.

Since the magnitudes of the charge transfer, proportional to β^2 [see Eqs. (1) and (2)], are similar in both H_2O–Cu and H_2O–Cu_5, the smaller binding energy found for the H_2O–Cu_5 system may be attributed to the fact that the Cu_5 unoccupied orbitals are closer in energy to the H_2O LPO's than are the single-Cu unoccupied states, thus yielding overall smaller energy lowerings [compare Eqs. (i) and (ii) in the text]. Alternatively, the electrostatic repulsion between the excess charge on Cu(5) in the Cu_5 cluster and the excess electronic charge on the oxygen will decrease the binding energy of H_2O to Cu_5.

The equilibrium orientation of the bonded H_2O molecule reflects the energy dependence on the tilt angle ψ. Variations in this angle influence the amount of admixture between the H_2O LPO's and the metal orbitals (MO). The factor $\beta[3a_1,\mathrm{MO}]$ is large at $\psi = 0°$, and decreases while $\beta[1b_1,\mathrm{MO}]$ increases as $\psi \rightarrow \pi/2$.

In addition we have calculated the total dipole moment of the complex in terms of the electronic and nuclear-charge distributions. The charge donation to the metal is manifested via comparison of the dipole moment for the equilibrium configuration of H_2O–Cu_5 with those of Cu_5 and H_2O obtained by separating these components of the equilibrium complex to infinity: $\boldsymbol{\mu}(H_2O\text{–}Cu_5) = (1.2, 0.0, 3.2)$, $\boldsymbol{\mu}(H_2O) = (2.0, 0.0, 0.65)$, $\boldsymbol{\mu}(Cu_5) = (0.0, 0.0, 0.6)$ in Debye units. Associated with this value of $\boldsymbol{\mu}(H_2O\text{–}Cu_5)$ is a work function change $\Delta\phi \simeq -4.8$ eV, for a surface density of 10^{15} molecules per square centimeter. The only available experimental values[1] are for hydrogen-bonded water clusters and are typically $\Delta\phi \simeq -1$ eV, indicating strong cancellation and depolarization effects.

Further insight into the equilibrium bonding configuration is obtained via analysis of the dynamics of the complex. The EELS spectrum of H_2O monomers on Cu(100) exhibits[2] losses at 28.5 and 197 meV which were assigned[2] to a hindered rotation of the molecule and the H-O-H bend of H_2O, respectively. A mapping of the potential surface near equilibrium was carried out fixing the Cu_5 coordinates and varying the H_2O internal coordinates, the O-Cu stretch in the z direction, Cu-OH bend (varying the angle α), and O-Cu-Cu bend (for the last three the H_2O internal coordinates were held fixed). A normal mode analysis shows that the internal coordinates couple weakly; the calculated modes at 30, 45, and 84 meV correspond to symmetric O-Cu-Cu bend, O-Cu stretch, and symmetric O-H stretch and the modes at 194 and 423 meV correspond to H-O-H bend and symmetric O-H stretch, respectively. Only the symmetric modes will be seen for dipole excitation in EELS. Both the calculated frequencies and assignments agree with the analysis of the observed modes.[2] It should be noted, however, that not all the calculated modes have been observed experimentally,[2] due to their low intensity (small values of the dynamic dipole moments). Our calculations do not reproduce faithfully the observed relative intensities, indicating perhaps the need for larger clusters.

It is of interest to note that the mechanism of H_2O binding to Cu clusters which we described is similar to that proposed recently for H_2O binding to a simple metal (Al) cluster.[12] Moreover, the equilibrium configuration and magnitudes of the binding energy and charge transfer are found to be similar for these two systems, suggesting common trends in the weak associative binding of molecular H_2O to metals. Finally, while convergence to the semi-infinite metal case may require clusters larger than those used by us, comparison of our results for H_2O–Cu and H_2O–Cu_5 and the agreement with experimental observations lead us to conclude that calculations employing small clusters can allow elucidation of binding mechanisms and provide quantitative estimates of physical properties in weakly bonded adsorption systems.

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[1] K. Bange, D. E. Grider, J. K. Saas, and T. E. Madey, Surf. Sci. **136**, 38 (1984), and references therein.

[2] S. Andersson, C. Nyberg, and C. G. Tengstal, Chem. Phys. Lett. **104**, 306 (1984).

[3] M. Trenary, H. F. Schaefer III, and P. A. Kollman, J. Chem. Phys. **68**, 4047 (1978).

[4] S. Holloway and K. H. Bennemann, Surf. Sci. **101**, 327 (1980); A. B. Anderson, *ibid.* **105**, 159 (1981); B. C. Khanra, Chem. Phys. Lett. **84**, 107 (1981).

[5] B. J. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. **71**, 4993 (1979), and references therein.

[6] A. J. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[7] B. J. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. **71**, 3396 (1979); B. J. Dunlap and H. L. Yu, Chem. Phys. Lett. **73**, 525 (1980).

[8] F. B. Van Duijneveldt, IBM Research Report No. RJ 945, 1971.

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

[10] W. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. **24**, 1139 (1956).

[11] J. R. Smith, J. G. Gay, and F. J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980).

[12] J. E. Muller and J. Harris, Phys. Rev. Lett. **53**, 2443 (1984).