

**Density functional theory study of the interaction of monomeric water with the Ag{111} surface**V. A. Ranea,<sup>1,2</sup> A. Michaelides,<sup>3</sup> R. Ramírez,<sup>1</sup> J. A. Vergés,<sup>1</sup> P. L. de Andres,<sup>1</sup> and D. A. King<sup>3</sup><sup>1</sup>*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain*<sup>2</sup>*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas CONICET, UNLP, CICPBA, Suc. 4,**Casilla de Correo 16 (1900) La Plata, Argentina*<sup>3</sup>*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

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*Ab initio* density-functional theory has been used to investigate the adsorption of a single H<sub>2</sub>O molecule on the Ag{111} surface. A series of geometry optimizations on a slab model has allowed us to identify a preferred energy minimum and several stationary points in the potential-energy surface of this system. The most stable adsorption position for water corresponds to the *atop* site, with the dipole moment of the molecule oriented nearly parallel to the surface. The electronic structure of several H<sub>2</sub>O-Ag clusters has been compared to results obtained by the extended slab calculations. The agreement found for several properties (binding energy, tilt angle of the dipole moment of water, and interatomic distances) provides evidence for the local nature of the water-metal atop interaction. The covalent contribution to the weak H<sub>2</sub>O-Ag bond is found to be an important one.

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**I. INTRODUCTION**

Adsorption of water on metal surfaces plays a vital role in a number of important processes such as corrosion, catalytic reactions, electrochemical processes in aqueous solutions, hydrogen production, etc. The structure and properties of water adsorbed on well-defined metal surfaces has been the subject of numerous experimental and theoretical investigations.<sup>1,2</sup> Adsorbed H<sub>2</sub>O shares with other small molecules such as NH<sub>3</sub>, CH<sub>3</sub>OH, or H<sub>2</sub>S the feature that attractive lateral interactions (hydrogen bonds) are comparable in strength to the adsorbate-substrate interactions. Furthermore, the strength of interactions between molecules and with the substrate can be tuned by moving the substrate by just one step on the same row of the periodic table so to have the balance displaced towards the lateral or to the metal interaction at will.<sup>3</sup> This is a consequence of the capability of the oxygen atom to interact through its lone pairs with both the metal substrate and the neighboring water molecules. Another salient feature of H<sub>2</sub>O is its dipole moment, quite large relative to that of other small molecules commonly studied as adsorbates on metal surfaces, such as CO and NO.

Generally speaking, monomeric water, clusters of water molecules, and ice adsorbed on metals share a few general properties.<sup>1,2</sup>

(i) The binding energy of water varies in a relatively narrow interval ( $\approx 0.2$ – $0.5$  eV). This results comparable to the hydrogen bond energy between H<sub>2</sub>O molecules ( $\approx 0.22$  eV).<sup>4</sup>

(ii) H<sub>2</sub>O bonds through the oxygen atom to the surface and occupies mainly *atop* adsorption sites. Similarly, bonds between H<sub>2</sub>O and metal atoms in complexes and clusters are formed via the oxygen atom. Binding through the hydrogen atoms is less common, but it can also happen under some circumstances.<sup>5</sup>

(iii) For transition metals, the bonding is generally due to the interaction of the *d* atomic orbitals (AO's) of the metal and the oxygen lone pairs. This is usually accompanied by a

net charge donation from the oxygen lone pair orbitals to unoccupied electronic states of the metal.

(iv) The bond angle and bond lengths of the water molecule are only slightly perturbed from the gas phase values by the interaction with the surface.

(v) Formation of hydrogen-bonded clusters is common, even at low coverages, because diffusion barriers for water are low, and hydrogen bonding is energetically competitive with the H<sub>2</sub>O-metal substrate bond.

A sensible goal to better understand more complicated systems is to study first the interaction of a single molecule with the metal surface. Because of its relatively high diffusion and the tendency to form hydrogen bonds, H<sub>2</sub>O monomers are difficult to detect on a metal surface, even at low temperature. However, many experimental studies have reported evidence for isolated H<sub>2</sub>O monomers and H<sub>2</sub>O dimers on metals.<sup>6–15</sup> H<sub>2</sub>O monomers have been shown to exist on Ni and Cu films at low temperatures ( $\sim 160$  K), although the same authors report that diffusion is rapid enough to allow clustering even at 7 K.<sup>16</sup> Andersson *et al.* have shown that at 10 K H<sub>2</sub>O monomers are adsorbed on Cu and Pd crystals through the oxygen atom, with the dipole moment of H<sub>2</sub>O tilted with respect to the surface normal by an angle  $\alpha$  of 57° and 58° for Cu and Pd, respectively.<sup>17</sup> Nakamura and Ito have analyzed H<sub>2</sub>O clusters adsorbed on a Ru{0001} surface by infrared reflection adsorption spectroscopy, to find that monomeric H<sub>2</sub>O (0.06 monolayers) shows a small dipole moment component along the surface normal, supporting a model for tilted molecules. Based on the surface selection rule (a vibrational mode in which the dipole moment oscillates parallel to the surface cannot be observed), this means that the dipole moment of monomeric H<sub>2</sub>O lies nearly parallel to the surface.<sup>18</sup>

The interaction of water with the Ag{111} surface has been the subject of experimental investigations since long ago.<sup>19–21</sup> An electron stimulated desorption ion angular distribution study of a H<sub>2</sub>O monolayer on the Ag{111} surface revealed that H<sub>2</sub>O exhibits little or no azimuthal and polar

orientations. This fact is usually attributed to the weakness of the adsorption bond. This weakness is also supported by the available thermal-desorption spectra (TDS) of H<sub>2</sub>O on a clean Ag surface, from which the strength of the H<sub>2</sub>O-metal bond can be estimated. The TDS do not show any state distinguishable from the ice sublimation state (the ice sublimation energy is ( $\approx 0.5$  eV)). This suggests that H<sub>2</sub>O-Ag interaction is indeed extremely weak such that it cannot be resolved from the background of hydrogen bonded H<sub>2</sub>O molecules in the overlayer.<sup>20</sup>

In recent years, calculations based on state-of-the-art *ab initio* approaches have helped to bring theory to a state of reliability similar to that of experiments, providing accurate microscopic insight into the adsorption of water on metal surfaces.<sup>22–30</sup> A common binding mechanism for water monomer adsorption on close-packed transition and noble-metal surfaces has been identified by *ab initio* density-functional theory (DFT),<sup>3</sup> showing that H<sub>2</sub>O binds at atop adsorption sites with the molecular dipole nearly parallel to the surface. The same computational approach will be employed in this work to study the adsorption of monomeric water on the Ag{111} surface.

Three recent first-principle calculations of water over the Ag{111} surface have given some results on the adsorption of a single molecule.<sup>30–32</sup> The focus of these investigations was the study of the molecular reorientation of water on charged Ag{111} surfaces,<sup>30</sup> the molecular dynamics of the water-metal interface at room temperature,<sup>31</sup> and the adsorption of hydronium ions on Ag{111}.<sup>32</sup> The discrepancies reported for the adsorption geometry and the binding energy of a single molecule call for further clarification. In particular, the tilt angle of the water dipole moment was predicted to be  $\alpha = 61^\circ$  in Ref. 31, but  $\alpha = 107^\circ$  in Ref. 30. Moreover, the binding energy of a single water molecule is reported in a range from 0.53 eV (Ref. 31) to 0.2 eV (Ref. 30). The present investigation aims to characterize the adsorption sites and binding energies of a single H<sub>2</sub>O molecule on a Ag{111} surface by state-of-the-art *ab initio* DFT calculations. We will identify both the absolute minimum-energy configuration and other stationary points in the potential-energy surface (PES) of the adsorbed molecule. The preferred tilt angle of water in atop sites will be rationalized on the basis of the local interaction of the H<sub>2</sub>O molecule with its nearest silver atom.

The manuscript is organized as follows. In Sec. II the employed computational methods, used to study both periodically extended slabs and cluster models, are described. The geometry and binding energies of several adsorption sites of a H<sub>2</sub>O molecule on the Ag{111} surface are presented in Sec. III. A cluster model comprising one H<sub>2</sub>O molecule and one Ag atom is studied in detail in Sec. IV to help understand the nature of the local H<sub>2</sub>O-Ag interaction. And, in particular, to understand the preferred tilt angle of the H<sub>2</sub>O molecule, equilibrium distances and binding energy. The conclusions are given in Sec. V.

## II. COMPUTATIONAL APPROACH

The interaction of a single H<sub>2</sub>O molecule with the Ag{111} surface has been investigated by an *ab initio* DFT

approach using the computer code CASTEP.<sup>33</sup> DFT takes advantage of the Hohenberg and Kohn theorem<sup>34</sup> to reduce the electronic many-body problem to the task of minimizing an energy functional of the density (itself depending on only three independent coordinates at each spatial position). The expansion of the Kohn and Sham<sup>35</sup> wave functions in a plane-wave basis has been performed by introducing a cutoff in the kinetic energy of 340 eV. The convergence of the binding energy of water with the employed cutoff has been checked by test calculations using a larger cutoff of 380 eV. The resulting change in the binding energy was lower than 0.001 eV. Vanderbilt ultrasoft pseudopotentials have been used to represent the core electrons of the Ag and O atoms.<sup>36</sup> The exchange and correlation functionals have been included through the generalized gradient approximation (GGA) in the Perdew-Wang form.<sup>37</sup> For comparison, we have performed test calculations within the simple local-density approximation (LDA). We find that LDA provides a poor description of the water-metal interaction as the binding energy of water is overestimated by a factor of 2 with respect to the GGA result.

In the perpendicular direction, the slabs are separated by a distance of 16.53 Å (equivalent to a six-layer thickness). For silver, it is known that surface states decay slowly into the bulk, and the interaction between the two surfaces of a slab may not be negligible. Previous studies conclude that for a nine-layer slab the splitting of the surface state is  $\approx 0.3$  eV,<sup>38</sup> low enough to expect no significant effect on either the adsorption geometry or the binding energy of the H<sub>2</sub>O molecule. We confirmed this by a test calculation of the final optimized geometry of water by comparing results for six and nine layers of silver. For nine layers, we find a negligible difference in the adsorption geometry and energy with respect to the six-layer calculation.

In the surface plane, our model is defined by a  $2 \times 2$  overlayer, which contains one water molecule, resulting in a coverage  $\theta = 0.25$ . The employed supercell is large enough to avoid interactions between H<sub>2</sub>O molecules, as previously demonstrated by considering a  $3 \times 3$  overlayer.<sup>3</sup> The distance  $d(\text{OO})$  between the oxygen atoms of nearest-neighbor H<sub>2</sub>O molecules amounts to 5.78 Å. For comparison, the value  $d(\text{OO})$  in the most common crystalline forms of ice (*Ih* and *Ic*) is 2.76 Å, at 273 K and atmospheric pressure,<sup>1</sup> while in the water dimer is 2.98 Å.<sup>39</sup> The H<sub>2</sub>O molecule has been adsorbed on one side of the slab. Both the H<sub>2</sub>O molecule and the two top surface layers were allowed to relax freely, according to the Hellmann-Feynman forces. A run was considered converged when the root-mean-square force on the atomic nuclei was less than 0.05 eV/Å, the root-mean-square displacement of the nuclei was less than 0.001 Å, and the energy change per atom was less than  $2 \times 10^{-5}$  eV. The sampling of the Brillouin zone was performed by a  $4 \times 4 \times 1$  Monkhorst-Pack mesh,<sup>40</sup> resulting in a set of ten  $k$  points. This set of special points, corresponding to a oblique two-dimensional Bravais lattice, can be alternatively derived by the geometrical method of Ref. 41.

In addition to the calculations of the extended model, the local interaction of a H<sub>2</sub>O molecule with a single Ag atom was studied within the DFT formalism by using the GAUSS-

IAN 98 program package.<sup>42</sup> The employed basis sets were cc-PVTZ (Ref. 43) for both hydrogen and oxygen atoms and SDD (Ref. 44) for the silver atom. Core electrons of the Ag center are described by an effective core potential, and the Perdew-Wang (PW91) form was used for both exchange and correlation functionals.<sup>37</sup> Both the convergence of the electronic structure and the geometry optimization of the cluster was achieved by using the default thresholds of the GAUSSIAN program.

### III. STATIONARY CONFIGURATIONS FOR H<sub>2</sub>O ADSORBED ON Ag{111}

Before presenting our results for the adsorbed system, we comment on some results obtained for the separate components. The geometry optimization of the Ag{111} substrate (without adsorbed water) shows that the distance between the first two layers increases by +0.4%, while the second interlayer spacing does not display any significant relaxation from the ideal bulk distance. This result should be compared with the experimental work by Soares *et al.*,<sup>45</sup> where a negligible relaxation was found using an accurate low-energy electron diffraction structural determination.

The optimized geometry for the H<sub>2</sub>O molecule, using the same supercell as the one employed for the H<sub>2</sub>O/Ag{111} system, yields the following results for the molecular structure:  $d(\text{OH})=0.97 \text{ \AA}$  and  $\angle(\text{HOH})=105^\circ$ . These values have to be compared with the experimentally reported values of  $0.96 \text{ \AA}$  and  $105^\circ$ , respectively.<sup>1</sup> The discrepancy in the calculated  $d(\text{OH})$  bond length is very small and might be related to physical effects not included in the theory, e.g., the effect of the anharmonicity of the interatomic potential on the molecular zero-point vibrations.

We turn now to present the results obtained for the slab model of monomeric water adsorption on the Ag{111} surface. The potential-energy surface of the system has been explored by looking for the absolute energy minimum and additional stationary points of the system. To achieve this goal, a set of geometry optimizations have been performed by locating the water molecule at one of the high-symmetry adsorption sites of the surface, i.e., the *bridge*, the *fcc hollow*, the *hcp hollow*, and the *atop* sites. Although the starting point is a high-symmetry one, we allow the molecule to access nonsymmetric positions, to make our search for a global minimum as complete as possible. Furthermore, different initial orientations and distances of the water molecule with respect to the surface have been explored in the calculations to avoid being trapped by possible small activation barriers as much as possible. For each site, the water molecule and the first two substrate layers were allowed to relax to a stationary position (while we consider the substrate relaxations significant, if the substrate atoms are kept fixed in their ideal positions we find the same conclusions, and the adsorption energy changes only by 0.02 eV).

We have found several adsorption configurations that represent stationary points in the PES of water on Ag{111}. A schematic representation of the geometry of these adsorption sites is displayed in Fig. 1. All adsorption sites, except the *bridge*, are characterized by having several metastable con-

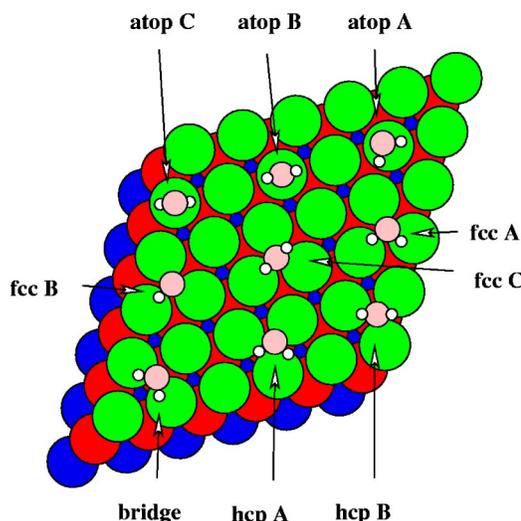


FIG. 1. (Color online) Schematic top view of the adsorption sites studied for H<sub>2</sub>O on the Ag{111} surface. White small circles represent H atoms and gray circles represent O atoms. The larger light gray, dark gray, and black circles represent Ag atoms of the first, second, and third layers, respectively. For the atop, fcc hollow, and hcp hollow sites different configurations of the water molecule are found. Each configuration is characterized by its tilt angle with respect to the surface normal. The label employed for the different water configurations is given.

figurations of the water molecule, labeled by a letter following a sequence of decreasing binding energy (e.g., atop A, atop B, and atop C). A side view of some configurations is displayed in Fig. 2. In Table I, we summarize the binding energy of the different configurations as well as the tilt angle of the dipole moment of H<sub>2</sub>O. For all studied configurations, the bond lengths  $d(\text{OH})$  and bond angles  $\angle(\text{HOH})$  of water are not (or only slightly) perturbed by the presence of the substrate.

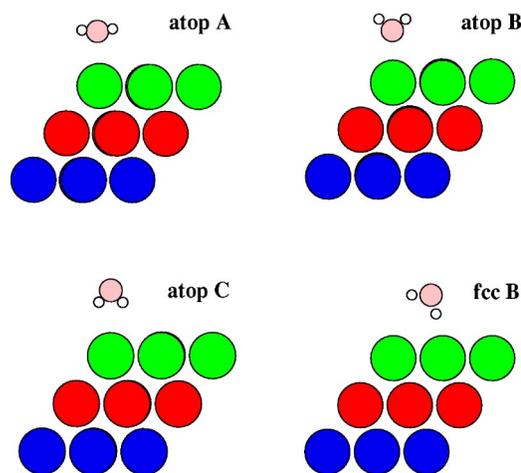


FIG. 2. (Color online) Schematic side view of several adsorption configurations for the H<sub>2</sub>O molecule on Ag{111}. The tilt angle associated with the atop A, atop B, and atop C configurations is  $81^\circ$ ,  $0^\circ$ , and  $180^\circ$ , respectively. H, O, and Ag atoms are displayed as in Fig. 1.

TABLE I. Binding energy and structural parameters of a H<sub>2</sub>O molecule adsorbed on different sites of the Ag{111} surface as obtained with CASTEP. For the atop, hcp hollow, and fcc hollow sites several water configurations are possible with different binding energies and tilt angles. Listed are: the binding energy per H<sub>2</sub>O molecule  $E_b$ , the tilt angle of the H<sub>2</sub>O dipole moment with respect to the external surface normal  $\alpha$ , the bond angle  $\angle(\text{HOH})$  and the bond length  $d(\text{OH})$  of water, the shortest OAg distances,  $d(\text{OAg})$ , and the vertical relaxations of the surface atoms closest to the oxygen center with respect to the clean surface coordinate,  $\Delta z$ .

Site	$E_b$ (eV)	$\alpha$ (deg)	$\angle(\text{HOH})$ (deg)	$d(\text{OH})$ (Å)	$d(\text{OAg})$ (Å)	$\Delta z$ (Å)
Atop A	0.18	81	105	0.97	2.78	0.04
Atop B	0.07	0	107	0.97	2.64	0
Atop C	0.05	180	105	0.97	3.20	-0.01
Hcp A	0.14	105	104	0.98	3.28, 3.43, 3.57	0.04, -0.01, 0
Hcp B	0.04	1	107	0.97	3.24, 3.25, 3.29	0.01, 0.01, 0
Fcc A	0.13	104	104	0.98	3.31, 3.43, 3.54	0, 0.02, 0
Fcc B	0.08	142	105	0.98	3.56, 3.56, 3.72	0.01, 0.01, 0.01
Fcc C	0.04	3	107	0.97	2.96, 2.96, 3.06	0, 0, -0.04
Bridge	0.13	103	104	0.97	3.50, 3.50	0, 0

### A. Atop site

For the atop position, we find three different configurations of the water molecule. The atop A configuration is the global energy minimum. The calculated binding energy of 0.18 eV shows a close agreement to the value of 0.2 eV calculated by Sánchez<sup>30</sup> (calculations keeping the substrate atoms frozen in ideal positions show that the difference in energy due to the 26° difference in the tilt angle is small, less than 0.01 eV. This can also be inferred from Fig. 2 in Ref. 3, where it can be seen that the energy changes slowly around  $\alpha=0^\circ$ ). The binding energy of 0.53 eV reported by Izvekov and Voth is too large, possibly, as authors point out, due to the low kinetic energy cutoff employed to speed up the *ab initio* Car-Parrinello molecular dynamics simulation.<sup>31</sup> The binding energy derived by an *ab initio* Möller-Plesset (MP) second-order method using a 28 atom silver cluster was 0.34 eV.<sup>32</sup> The adsorbate geometries were optimized at the Hartree-Fock level, while the adsorbate-surface distance was further optimized at the MP2 level of theory. The metal atoms were kept fixed in this calculation.

The tilt angle of the water molecule in the minimum-energy configuration (atop A) is  $\alpha=81^\circ$ . This angle implies that the water molecule lies nearly parallel the surface, with the hydrogen atoms pointing slightly up from the surface. It has recently been shown that this adsorption geometry is a common property for many close-packed transition and noble-metal surfaces.<sup>3</sup> The calculation of Izvekov and Voth gives a value of 60° for the tilt angle of water,<sup>31</sup> while the result reported by Sánchez<sup>30</sup> is 107°, implying in the latter case that the hydrogen atoms are tilted towards the surface.

For the near atop A configuration, we find that the oxygen atom center is shifted away from the exact atop position by 0.29 Å towards the nearest bridge site. However, the binding energy difference between the exact atop site and the atop A position is very small ( $\leq 0.01$  eV). Moreover, the binding energy changes by less than 0.01 eV upon rotation of the water molecule around the oxygen-silver axis, showing that the azimuthal orientation of the H<sub>2</sub>O molecule must be

nearly random at most usual temperatures, and, indeed, that one rotational degree of freedom is maintained in the adsorbed state. Binding energies associated with the atop B and atop C configurations are lower than for the parallel orientation of water. The microscopic mechanism responsible for this behavior will be studied in Sec. IV.

### B. Hcp hollow sites

We find two metastable adsorption configurations of the H<sub>2</sub>O molecule for the hcp hollow site of the Ag{111} surface. The hcp A site is preferred energetically with a tilt angle of 105°. The O atom is shifted towards a nearest atop site by 0.27 Å (see Fig. 1). In the hcp B site, the H<sub>2</sub>O molecule is oriented perpendicular to the surface (tilt angle  $\alpha=1^\circ$ ), with the O atom closer than the H atoms to the silver surface.

### C. Fcc hollow site

For the fcc hollow site, three different water configurations are found. Again, we find that the energetically preferred orientation (fcc A) corresponds to the H<sub>2</sub>O molecule nearly parallel to the surface; the tilt angle is 104°. The O atom is shifted from the exact fcc hollow site by 0.23 Å. The fcc B site is characterized by having one of the OH bonds pointing towards the surface, while the other OH bond is almost parallel to the substrate (see Fig. 2). In the fcc C site the plane of the H<sub>2</sub>O molecule is perpendicular to the surface, with the O atom closer to the surface than the hydrogen atoms.

### D. Bridge site

In the bridge site, the plane of the H<sub>2</sub>O molecule is almost parallel to the Ag{111} surface. The tilt angle of water is 103°. The H<sub>2</sub>O molecule is shifted from the exact bridge site by 0.38 Å towards a nearest hcp hollow site.

To summarize, we find the preferred adsorption site is located near, but not exactly above, the atop site, with a

binding energy of 0.18 eV, quite comparable to the gas phase value for the binding of the water dimer. The distance from oxygen to the atop silver atom is 2.78 Å, and the molecule is lying almost parallel to the surface. In general, in this adsorption system we find: (i) weak bonding, (ii) weakly corrugated energy hypersurface with many similar energy minima, and (iii) a general preference of the molecule to keep its dipole oriented nearly parallel to the surface. We also note that in the atop site the molecule may retain one degree of rotational freedom.

#### IV. LOCAL H<sub>2</sub>O-Ag INTERACTION

In the preceding section, it has been shown that the most favorable tilt angle of the H<sub>2</sub>O molecule corresponds to a nearly parallel orientation with respect to the metal surface. Furthermore, this was the most stable configuration at all the adsorption sites examined and seems to be a general property of the H<sub>2</sub>O-metal interaction. Since, at these distances, the interaction of the water dipole with the image one on the metal will favor a perpendicular orientation of the molecule,<sup>46</sup> we look at the formation of a weak chemical bond, which might well be determined by local interactions. To assess this we have studied the simplest model for an atop bonded water, i.e., H<sub>2</sub>O bonded to a single Ag atom. As pointed out in Sec. II the H<sub>2</sub>O-Ag atom calculations were carried out with the GAUSSIAN 98 program package.

We summarize first the results of the geometry optimization of an isolated H<sub>2</sub>O molecule under the employed computational conditions (see Sec. II). The bond length results  $d(\text{OH})=0.97$  Å and the interatomic angle is  $\angle(\text{HOH})=104^\circ$ . The Mulliken population analysis of the density matrix predicts that the O atom has a negative net charge of  $0.41e$ . The dipole moment computed from the electronic density amounts to 1.89 D, which is close enough to the experimental value of 1.83 D.

##### A. Cluster structure

The interaction of a H<sub>2</sub>O molecule with a single silver atom was studied by performing a series of geometry optimizations where the water molecule was initially located at various OAg distances and with different tilt angles with respect to the OAg direction. As a result, we found three different structures for the H<sub>2</sub>O-Ag complex, labeled as atop A', atop B', and atop C', respectively, which represent stationary points in the PES (see Fig. 3). These clusters resemble the local structure found for the atop A, atop B, and atop C configurations in the Ag{111} surface (see Fig. 2). We will show that the cluster calculations reproduce the general features that describe the interaction of water with the Ag surface: water bonds through the oxygen atom to the metal, bonding is accompanied by a net charge transfer to the metal, and the internal structure of water is only slightly perturbed from the gas phase values.

These features are clearly reflected by the data summarized in Table II, which include binding energies, structural parameters, and net charges of the H<sub>2</sub>O-Ag complex. In the most stable clusters (atop A' and atop B'), water is coordi-

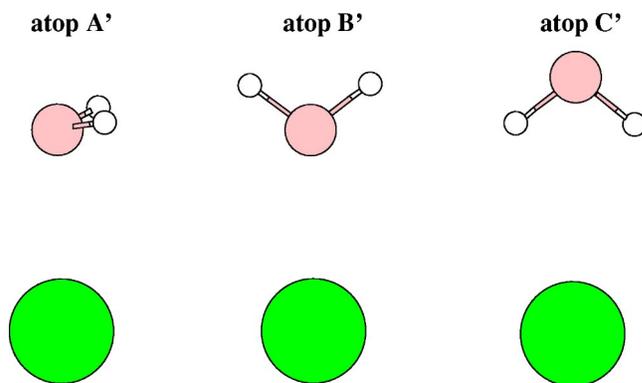


FIG. 3. (Color online) Schematic side view of the stationary cluster structures found for the Ag-H<sub>2</sub>O complex. The tilt angle associated with the atop A', atop B', and atop C' clusters is 73°, 0°, and 180°, respectively. H, O, and Ag atoms are displayed as in Fig. 1.

nated through the oxygen atom to the silver atom. The coordination through hydrogen (atop C' cluster) has a binding energy that is nearly one half of the value corresponding to the most stable atop A' cluster. The Mulliken population analysis of the density matrix shows a net charge transfer from water to the silver atom. The largest charge transfer amounts to  $0.13e$  for the atop A' cluster. We note that the larger the magnitude of charge transfer the larger the stability of the cluster. The internal structure of water does not change, except for the slight increase of 2° in the  $\angle(\text{HOH})$  angle found for the atop B' cluster.

By comparing Tables I and II we see that the bonding of H<sub>2</sub>O to atop sites on the extended metal surface is remarkably well described by the bonding of H<sub>2</sub>O to a single silver atom. The existence and relative stabilities of three different configurations with tilt angles at 0°, 81°, and 180°, respectively, is correctly predicted by the cluster calculations, although the absolute values are different. The binding energy of the atop A' cluster is somewhat larger than the value derived for the atop A configuration in the extended system (see Tables I and II). This comparison, however, needs to take into account corrections inherent to the different methods employed. In particular, the cluster calculations may be corrected for the so-called basis set superposition error, reducing the 0.26 eV value to 0.16 eV for one Ag atom cluster (in particular, for a seven Ag atom cluster calculation, as reported in Ref. 32, the value would be reduced from 0.30 eV to 0.13 eV, which is close enough to be considered inside our estimated error bar). The tilt of 73° in the H<sub>2</sub>O dipole moment for the atop A' cluster is close to the value of 81° found for the the atop A configuration in the extended system, while the tilt angles of the atop B' and atop C' clusters are identical to those corresponding to the extended atop B and atop C configurations, respectively. We observe also that the interatomic distances  $d(\text{OAg})$  predicted by the cluster calculations are in reasonable agreement with the results of the extended calculation. In particular, we notice that the distance  $d(\text{OAg})$  in the atop B' cluster is shorter than in the more stable cluster, atop A'. Identical behavior was found in the extended system between the atop B and atop A configurations (see Table I). Also the small increase in the

TABLE II. Binding energy and structural parameters of the three cluster arrangements found for the Ag-H<sub>2</sub>O complex. Listed are: the binding energy  $E_b$ , the tilt angle of the H<sub>2</sub>O dipole moment with respect to the OAg axis  $\alpha$ , the bond angle  $\angle(\text{HOH})$ , the bond length  $d(\text{OH})$ , the distance  $d(\text{OAg})$ , the distance  $d(\text{HAg})$ , and the net charge transferred from the water molecule to the Ag atom.

System	$E_b$ (eV)	$\alpha$ (deg)	$\angle(\text{HOH})$ (deg)	$d(\text{OH})$ (Å)	$d(\text{OAg})$ (Å)	$d(\text{HAg})$ (Å)	$q(e)$
Atop A'	0.26	73	104	0.97	2.61	2.94	0.13
Atop B'	0.21	0	106	0.97	2.58	3.26	0.10
Atop C'	0.14	180	104	0.97	3.30	2.80	0.06
H <sub>2</sub> O			104	0.97			

$\angle(\text{HOH})$  angle found for the atop B' cluster agrees well with the slab result for the atop B configuration.

### B. Chemical bond

The reasonable agreement found between extended and cluster calculations suggests that the atop interaction between water and the silver surface is mainly of local character. Therefore, the analysis of the bond in the H<sub>2</sub>O-Ag complex should provide at least qualitative insight into the bonding interaction of water on atop sites of silver surfaces. In Fig. 4, we display the molecular orbital (MO) diagram corresponding to the three studied H<sub>2</sub>O-Ag clusters for an energy window between 0 and -14 eV. In this energy window there appear three occupied MO's of water: the  $1b_1$ ,  $3a_1$ , and  $1b_2$  orbitals. The highest occupied MO (HOMO),  $1b_1$ , has oxygen lone pair character. The  $3a_1$  MO represents an oxygen lone pair with a small admixture of a bonding OH interaction, while the  $1b_2$  has the character of a bonding OH interaction.<sup>1</sup> The lowest unoccupied state of water (LUMO) is the  $4a_1$  MO. As the binding energy between water and the silver atom is relatively low, the MO's of the H<sub>2</sub>O-Ag clusters have been identified in Fig. 4 as mainly of silver AO character or of water MO character. The percentage contribution of these orbitals to the one-electron states has been summarized in Table III.

The MO diagram reveals large differences when the water coordination to the metal is through the oxygen atom (atop A' and atop B' clusters), or through the hydrogen atoms (atop C' cluster). In the former case, the proximity of the oxygen lone pairs to the metal produces a ligand field that is reflected by a destabilization of the  $4d$  and  $5s$  AO's of silver. We define this ligand field effect  $\Delta_{Ag}^{LF}$  as the difference in the average energy of the  $4d$  and  $5s$  silver AO's in the complex and in a free Ag atom,

$$\Delta_{Ag}^{LF} = \bar{E}_{complex}(4d,5s) - \bar{E}_{Ag,free}(4d,5s). \quad (1)$$

The value of  $\Delta_{Ag}^{LF}$  is 0.6, 0.8, and -0.3 eV for the atop A', atop B', and atop C' clusters, respectively. Note the opposite sign of this electrostatic effect when the water coordination is through the hydrogen atoms. For water, we define the corresponding ligand field effect by the energy shift encountered in the  $1b_2$  state with respect to the free water molecule,

$$\Delta_{H_2O}^{LF} = E_{complex}(1b_2) - E_{H_2O,free}(1b_2). \quad (2)$$

The reason to choose the  $1b_2$  MO in this definition is that this state, having character of an OH bonding interaction, is less affected than the  $1b_1$  and  $3a_1$  lone pairs by possible overlaps with the silver AO's. The parameter  $\Delta_{H_2O}^{LF}$  takes the values of -1.1, -1.1, and -0.2 eV for the atop A', atop B', and atop C' clusters, respectively. An alternative definition of  $\Delta_{H_2O}^{LF}$  by using the  $2a_1$  water MO as reference (it lies

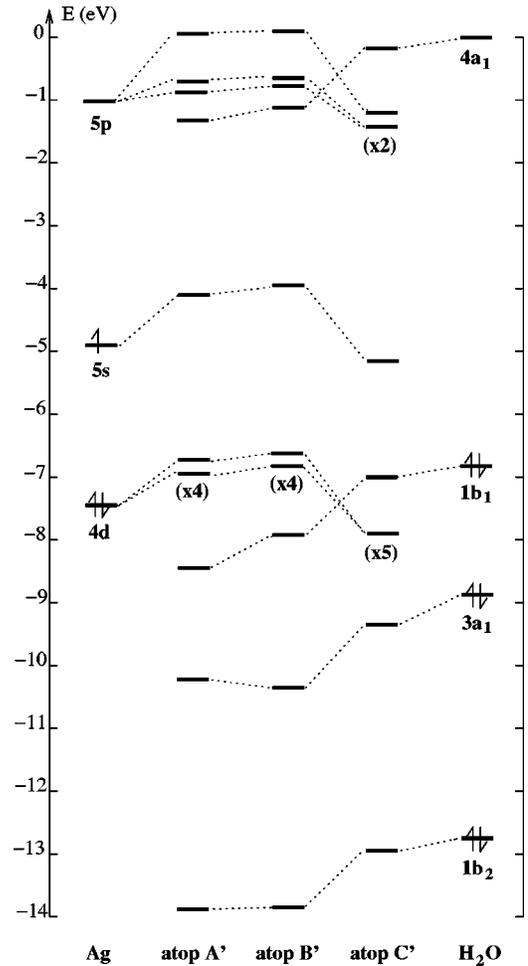


FIG. 4. DFT MO-like diagram of the interaction between a silver atom and a water molecule for the three studied clusters. The dotted lines connect orbitals with similar character. The number of  $4d$  orbitals that appear as approximately degenerate is given. The displayed MO's correspond to one-electron states associated with the  $\alpha$  spin.

TABLE III. Character of the MO's found in an energy range up to  $-4$  eV for the three cluster arrangements of the Ag-H<sub>2</sub>O complex. The metal and water contribution to the MO's has been estimated from the expansion coefficients by treating the basis functions as if they were an orthogonal set. The results correspond to one-electron states associated with the  $\alpha$  spin.

MO	Atop A'				Atop B'				Atop C'			
	Ag <i>s</i> (%)	Ag <i>p</i> (%)	Ag <i>d</i> (%)	H <sub>2</sub> O (%)	Ag <i>s</i> (%)	Ag <i>p</i> (%)	Ag <i>d</i> (%)	H <sub>2</sub> O (%)	Ag <i>s</i> (%)	Ag <i>p</i> (%)	Ag <i>d</i> (%)	H <sub>2</sub> O (%)
$2a_1$	0	0	0	100	0	0	0	100	0	0	0	100
$1b_2$	0	0	0	100	0	0	0	100	0	0	0	100
$3a_1$	1	1	2	96	3	1	4	92	3	2	5	90
$1b_1$	5	1	15	79	0	0	8	92	0	0	4	96
	0	0	100	0	0	0	100	0	0	0	100	0
	0	0	100	0	0	0	100	0	0	0	99	1
$4d$	0	0	100	0	0	0	100	0	0	0	100	0
	0	0	99	1	0	0	97	3	0	0	100	0
	3	0	91	6	1	0	96	3	0	0	98	2
$5s$	90	1	1	8	90	2	1	7	98	0	0	2

at about  $-29.4$  eV in free water) gives a result of  $-1.2$ ,  $-1$ , and  $-0.2$  eV for the atop A', atop B', and atop C' clusters, respectively.

An interesting bonding property is revealed by the distinct stabilization of the MO's of water depending upon the tilt angle of the water molecule. When the H<sub>2</sub>O molecule is coordinated nearly perpendicular to the OAg axis (atop A' cluster), the HOMO of water ( $1b_1$ ) has the appropriate symmetry for a  $\sigma$  overlap with the  $4d_{z^2}$  AO of the metal. A display of this orbital for the atop A' cluster is given in Fig. 5. The bonding interaction with the  $4d_{z^2}$  AO of silver is clearly seen in the figure. The  $1b_1$  state for the atop A' cluster lies  $-1.7$  eV below the corresponding state of the free water molecule (see Fig. 4). As the ligand field stabilization,  $\Delta_{H_2O}^{LF}$ , was estimated to be  $-1.1$  eV, the additional stabilization of about  $-0.6$  eV can be considered as a covalent effect due to the overlap of the fragment orbitals.

When the tilt angle of water is  $0^\circ$ , as in the atop B' cluster, the HOMO ( $1b_1$ ) of water does not have the appro-

appropriate symmetry for  $\sigma$  overlap with any of the  $4d$  AO's of the metal. In fact, we find the stabilization of this orbital with respect to the free water state amounts to  $-1.1$  eV, i.e., it is nearly equal to the ligand field effect,  $\Delta_{H_2O}^{LF}$ , derived for the atop B' cluster. However, the  $3a_1$  MO of water is oriented in this cluster along the OAg bond and therefore it displays a  $\sigma$  overlap with the  $4d_{z^2}$  AO of silver. A plot of this MO is presented in Fig. 6. This state lies  $-1.5$  eV below the corresponding MO of the free water molecule. Considering that the ligand field stabilization was  $-1.1$  eV, we find that the additional stabilization due to covalent effects amounts to  $-0.4$  eV.

An interesting consequence of the previous analysis of the one-electron energy shifts is that the difference between the  $1b_1$  and  $3a_1$  MO's is obtained as  $1.7$  eV for the atop A' cluster, but as  $2.5$  eV for the atop B' cluster. This raises the possibility of distinguishing by valence-band photoemission between different tilt angles of water coordinated to metal surfaces. For a free water molecule the  $1b_1$ - $3a_1$  difference

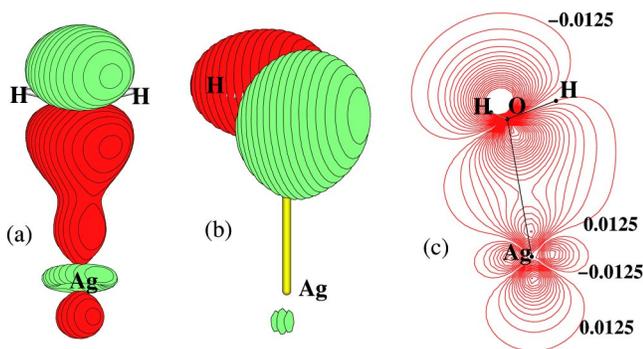


FIG. 5. (Color online) (a)  $1b_1$ - and (b)  $3a_1$ -like MO's on the atop A' cluster. (a) corresponds to an in-phase combination of the  $1b_1$  HOMO of water and the  $4d_{z^2}$  AO of silver, while it is observed that (b) does not make a significant water-Ag bond. The surface plotted corresponds to an absolute value of the wave function of  $0.08 \text{ \AA}^{-3/2}$ . Dark and light gray surfaces differentiate regions where the wave function changes its sign. The bonding formed in (a) is quantitatively shown as contour plot lines in (c). The interval between contiguous lines amounts to  $0.0125 \text{ \AA}^{-3/2}$ .

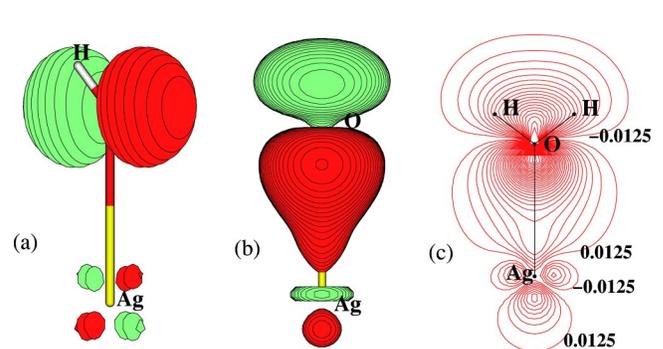


FIG. 6. (Color online) (a)  $1b_1$ - and (b)  $3a_1$ -like MO's on the atop B' cluster. (b) corresponds to an in-phase combination of the  $3a_1$  HOMO of water and the  $4d_{z^2}$  AO of silver, while it is observed that (a) does not make a significant bond. The surface plotted corresponds to an absolute value of the wave function of  $0.06 \text{ \AA}^{-3/2}$ . Dark and light gray surfaces differentiate regions where the wave function changes its sign. The bonding formed in (b) is quantitatively shown as contour plot lines in (c). The interval between contiguous lines amounts to  $0.0125 \text{ \AA}^{-3/2}$ .

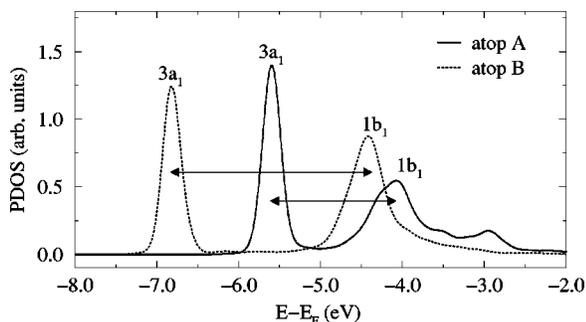


FIG. 7. Partial density of states (PDOS) projected onto the  $p$  orbitals of oxygen for  $\text{H}_2\text{O}$  adsorbed in its equilibrium position (atop A, continuous line), and an upright configuration (atop B, dashed line) on  $\text{Ag}\{111\}$ .  $E_F$  denotes the Fermi energy.

amounts to 2.2 eV in our GAUSSIAN calculation. Moreover, Fig. 7 plots the partial density of states (PDOS) projected onto the  $p$  orbitals of O for  $\text{H}_2\text{O}$  adsorbed in its equilibrium (atop A) and an upright configuration (atop B) on  $\text{Ag}\{111\}$ . These results, taken from our slab calculations for  $\text{H}_2\text{O}$  on the extended surface, confirm our findings for the  $\text{H}_2\text{O}$ -Ag complex: when the water molecule lies nearly parallel to the surface the difference between the  $1b_1$  and  $3a_1$  resonances is circa 1.5 eV, whereas when  $\text{H}_2\text{O}$  is upright on  $\text{Ag}\{111\}$  the separation between these two levels grows up to 2.5 eV. These results demonstrate that photoemission should be a good technique to probe the tilt angle of isolated  $\text{H}_2\text{O}$  monomers on metal surface.

In the case of constructive interference of orbitals, there is a displacement of the charge from the vicinity of the nucleus into the bonding region with a related decrease in the kinetic energy of the electrons, which causes bonding. When a single Ag atom and a  $\text{H}_2\text{O}$  molecule are brought together, from an infinite distance, to form any of the three studied cluster configurations, the total kinetic energy of the electrons is lowered. This lowering of energy amounts to 1.78, 1.32, and 1.03 eV, for the atop A', atop B', and atop C' configurations, respectively. Note that the trend in the kinetic energy follows the relative stability of the clusters. This fact provides further evidence of the importance of covalent interactions in the formation of the weak  $\text{H}_2\text{O}$ -Ag bond.

## V. CONCLUSIONS

We have applied an *ab initio* DFT approach using a plane-wave basis to study the adsorption of a single  $\text{H}_2\text{O}$  molecule on a  $\text{Ag}\{111\}$  surface. Our investigation of a slab model has led to the determination of the binding energies and the structural parameters of various adsorption configurations.

The most stable structure corresponds to the coordination of the oxygen atom at an atop site, with the dipole moment of water nearly parallel to the surface. The calculated binding energy amounts to 0.18 eV. Our value demonstrates that previously reported theoretical studies have overestimated this quantity by a factor of 2,<sup>31</sup> while it is in close agreement with another DFT study using atomic orbitals as basis.<sup>30</sup>

The adsorption of water on the hcp hollow, the fcc hollow, and the bridge sites leads to configurations whose binding energy appears in a range between 0.14 and 0.04 eV. Except for the bridge site, several water configurations are found for each site (including the atop position). They differ by the tilt angle of the dipole moment of water with respect to the surface normal. An interesting structural invariance is observed: in all adsorption sites, the water molecule tends to lie with its molecular plane parallel to the surface.

The microscopic origin for this structural preference has been investigated by the study of a  $\text{H}_2\text{O}$ -Ag complex, which represents the most simple model for an atop interaction between water and a metal atom. The agreement found between the cluster and slab calculations is remarkable. In particular, the existence and relative stabilities of three different atop configurations is correctly predicted by the cluster calculation. The interatomic OAg distances in the different configurations, and even the slight distortion of the water molecule when its dipole moment is oriented in the OAg direction, are also reasonably described by the cluster calculation.

Interestingly, the cluster model is consistent with the standard picture of water interacting with metal surfaces in atop positions. Water acts as an electron donor and there is  $\sigma$  overlap between one of its lone pair orbitals ( $1b_1$ ,  $3a_1$ ) and the metal  $4d_{z^2}$  AO. We find that the larger the charge transfer the larger the binding energy. Moreover, the charge transfer is maximized when the metal-water interaction is mediated by the HOMO ( $1b_1$ ) of water. The symmetry of this interaction requires that the plane of the water molecule remains nearly parallel to the OAg axis. The bond energy found between water and a silver atom corresponds to a relative weak interaction that is not purely electrostatic. The important directional character of the  $\text{H}_2\text{O}$ -Ag interaction is a strong indication that a covalent contribution, determined by the constructive interference of water MO's and silver AO's, is important in the characterization of this weak bond.

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