# Adsorption of O, H, OH, and H₂O on Ag(100)

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The adsorption of $H_2O$ and its dissociation products, O, H, and OH, on Ag(100) has been studied using an ab initio embedding method. Results at different sites (atop, bridge, and hollow) are presented. The four-fold hollow site is found to be the most stable adsorption site for O, H, and OH, and the calculated adsorption energies are 87.1, 42.7, and 76.2 kcal mol$^{-1}$, respectively. The adsorption energy of water at the atop and bridge sites is almost identical with values of 11.1 and 12.0 kcal mol$^{-1}$, respectively. The formation of adsorbed OH species by adsorption of water on oxygen-precovered Ag(100) is predicted to be exothermic by 36 kcal mol$^{-1}$.

## 1. Introduction

The interaction of water and its dissociation fragments, O, H, and OH, with metal surfaces is of fundamental interest due to the role of these species in electrochemistry, catalysis, and corrosion. Many experimental studies have been performed using different techniques, and their results are well-reviewed by Thiel[1] and Henderson.[2] Silver is an important partial oxidation catalyst, and the adsorption and dissociation of water on its surface could modify its catalytic behavior. For example, water has been studied as a catalytic promoter for partial oxidation of propylene.[3,4] Understanding such processes requires a clear description of the adsorption of water and its dissociation products on silver surfaces.

For silver surfaces and thin films of silver deposited on oxide surfaces, the catalytic activity is primarily associated with s- and p-electrons. This is in contrast to transition metal catalysis where d-electrons play an important role in modulating bonding at the surface. To delineate effects due to supporting oxides or to subsurface dopants, it is important to have accurate values for adsorption energies on pure silver. Surprisingly, values reported in the literature show large variations for several of the aforementioned adsorbates. In recent density functional theory (DFT) calculations of O adsorption on Ag(110)[5] or Ag-(100),[6] values ranging from 72 to 100 kcal mol$^{-1}$ are reported. For $H_2O$ on silver, a recent DFT calculation of the adsorption energy gave only 4 kcal mol$^{-1}$,[7] a value low enough to imply that dipole interactions and hydrogen bonding of coadsorbed species will determine the surface structure. The objective of the present work is to obtain accurate adsorption energies and geometries for H, O, OH, and $H_2O$ adsorbed on Ag(100) at very low coverage. These results will provide reference points for a subsequent study of adsorption on two-layer Ag overlayers on MgO.

For the O/Ag(100) system, two phases have been reported,[8,9] a $c(2 \times 2)$ structure at low temperature and a $p(1 \times 1)$ structure at high temperature. Two energy-loss peaks, 37 and 30 meV, are assigned to two oxygen−surface stretching modes, respectively. A reversible transition between the corresponding surface species can be brought about by changing the temperature. It is

noticeable that the $p(1 \times 1)$ structure only corresponds to a low coverage and 1 monolayer oxygen coverage is not attainable. DFT calculations by Wang et al.[6] show the 4-fold hollow site as the favorable site for the oxygen atom. Adsorption energies are calculated to be 100, 78, and 53 kcal mol$^{-1}$ for the 4-fold hollow, 2-fold bridge, and 1-fold atop sites. Coverage effects on the adsorption energy and O−Ag distance for different adsorption structures are also investigated using DFT generalized gradient approximation (GGA) methods.[10,11] It is found that both the adsorption energy and the O−Ag distance decrease with oxygen coverage due to the high electrostatic repulsion between the adsorbed, negatively charged oxygen atoms. The calculated adsorption energy is about 91 kcal mol$^{-1}$ for a $p(2 \times 2)$ structure at a coverage of $\theta = 0.25$.

Experimental studies on atomic hydrogen on Ag(100) are not available, but DFT calculations show binding at the 4-fold hollow and bridge sites to be comparable.[12] The adsorption energy at the 4-fold site is 45 kcal mol$^{-1}$, which is only 1 kcal mol$^{-1}$ higher than that of the 2-fold bridge site and 16 kcal mol$^{-1}$ higher than that of the 1-fold atop site. The theoretical potential energy surface (PES) for dissociative adsorption of $H_2$ on Ag(100) is also described with DFT methods.[13] The adsorption is found to have a 30 kcal mol$^{-1}$ barrier, but that of the desorption is only 13 kcal mol$^{-1}$. The process is endothermic and thermodynamically unfavorable.

Adsorption of $H_2O$ on oxygen-precovered Ag(100) to form surface hydroxyl groups was first reported by Klaua and Madey.[14]

$$H_2O_{ads} + O_{ads} \leftrightarrow 2OH_{ads} \qquad (1)$$

The authors found that OH species form an ordered $c(2 \times 2)$ structure with the OH axis perpendicular to the surface. The surface OH species can then recombine to give desorbed $H_2O$ after heating to a higher temperature than 300 K. Later high-resolution electron energy-loss spectroscopy (HREELS) studies by Ding et al.[15] failed to detect this phenomenon due to the low instrumental resolution, but a strong enhancement of the water sticking coefficient by preadsorbed atomic oxygen was observed. A recent theoretical study by Hu et al.[16] on the OH/Ag(100) system with the DAM-MP2 method shows the same adsorption site preference as OH/Ni(100), i.e., hollow > bridge > atop. At the 4-fold hollow site, the calculated adsorption

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energy is 109 kcal mol$^{-1}$ with a 1.46 Å oxygen–surface distance; the adsorption energy at the 2-fold bridge and 1-fold atop sites is found to be lower by 6 and 11 kcal mol$^{-1}$, respectively.

The adsorption of water on clean Ag(100) is weak and reversible, with the desorption occurring at T ≈ 170 K.[14] It is generally thought that water binds to the metal surface through its oxygen lone pair orbitals as an electron donor. For the H₂O/Ag(100) system, theoretical studies show two conformations to prevail, bridge-perpendicular and top-tilted at approximately a 60° tilt angle from the surface normal. Calculated DFT adsorption energies from calculations on small clusters are 6.4 and 6.2 kcal mol$^{-1}$, respectively.[17] A recent DFT study of a single H₂O molecule on Ag(111), treated periodically, by Ranea et al.[7] found the atop site to be the most stable adsorption, with an adsorption energy of only 4.2 kcal mol$^{-1}$. The H₂O molecule is found to be tilted by 81° to the surface normal, and the change of the H₂O molecular structure due to the adsorption is reported as negligible. It is unclear whether the difference in equilibrium geometry found in these two theoretical studies is due to differences in cluster and periodic models or to details of the functionals used.

## 2. Theory and Method

The adsorbate/Ag(100) system is described in the present work using an embedded cluster method that is designed to give an accurate description of adsorbate–surface interactions. All calculations are performed at the configuration interaction (CI) level. The details of the theory and method are extensively discussed in refs 18–21, and only a brief summary of this approach is given below.

There are two distinct components of the embedded cluster method described in the references cited above, boundary conditions on the cluster itself that appropriately couple the cluster to the bulk system and the localization transformation that defines the electronic subspace treated by configuration interaction. In the present work, since we are ultimately interested in islands containing one to three layers of silver deposited on oxide surfaces, no cluster boundary conditions are employed. The terminology "embedding" refers only to the creation of a subspace that is treated by configuration interaction. Calculations are performed by first solving the total electronic Hamiltonian of the adsorbate/surface system using self-consistent field (SCF) methods. The occupied and unoccupied SCF orbitals are then localized separately to maximize their interaction with the adsorbate and the metal atoms of the binding sites. Highly localized orbitals are used to define the CI active space. Finally, the CI wave function, $\Psi$, is generated from the dominant SCF configuration, $\Psi_0$, plus other important configurations by single and double excitations

$$\Psi = \Psi_0 + \sum_k C_k \Psi_k \qquad (2)$$

All configurations, $\Psi_k$, are retained if an interaction threshold

$$|\langle \Psi_k | H | \Psi_0 \rangle|^2 / (E_k - E_0) > 1 \times 10^{-6} \text{ au} \qquad (3)$$

is satisfied. Contributions of excluded configurations are estimated using second-order perturbation theory.

The model for the Ag(100) surface expressed as a 41-atom cluster is shown in Figure 1; it consists of a 16-atom surface layer, a 9-atom second layer, and a 16-atom third layer. The Ag–Ag distance is fixed at the experimental bulk value, 2.89 Å, and the relaxation of the Ag surface is not considered. The
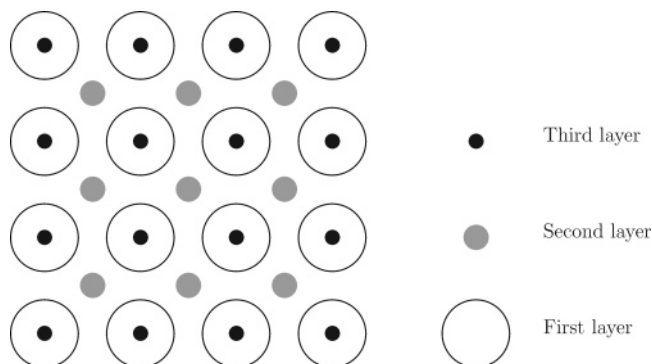


**Figure 1.** Three-layer, 41-atom cluster model for Ag(100).

four central silver atoms in the first layer are selected to define possible adsorption sites; these atoms are described by an effective [1s–3d] core potential plus valence 4s, 4p, 4d, 5s, and 5p orbitals. Other silver atoms in the surface layer and all silver atoms in the second layer are described with a [1s–4d] core and only 5s orbitals. The silver atoms in the third layer are represented as a polarizable boundary core potential with no electrons explicitly included. Relativistic core potential functions[22] are placed on all silver atoms.[23] For the present Ag-(100) system, relativistic and nonrelativistic calculations give essentially the same adsorption energy. The Ag basis is obtained by expansion and slight truncation of orbitals from four-component relativistic atomic calculations of Okada and Matsuoka.[22] The basis contains diffuse s- and p-type components that permit a good description of the polarization of the electron density into the vacuum and the onset of long-range interaction with an adsorbate. For hydrogen, the same basis functions as described in refs 24 and 25 are adopted. For oxygen, the basis set includes the double-$\zeta$ s- and p-functions taken from ref 26 and a set of d-polarization functions with an exponent of 0.8.

The present theoretical method allows us to calculate accurately the adsorption energies and to optimize the geometrical parameters. For each adsorbate, three binding sites are considered: a 1-fold atop site, a 2-fold bridge site, and a 4-fold hollow site. The computation of vibrational frequencies is based on a one-dimensional harmonic oscillator model. The basis set superposition error (BSSE) is also checked to be less than 0.5 kcal mol$^{-1}$.

## 3. Results and Discussion

Calculated results (geometrical parameters, energetics, and electronic properties) obtained for the different adsorbate/surface systems are presented in separate subsections.

**3.1. Oxygen Adsorption on Ag(100).** Calculated adsorption energies, equilibrium distances, and vibrational frequencies for the adsorption of atomic oxygen on Ag(100) are listed in Table 1.

At the 4-fold hollow site, the adsorption energy is calculated to be 87.1 kcal mol$^{-1}$, considerably larger than values found for the 2-fold bridge and 1-fold atop sites. The present calculations show the same site preference, hollow > bridge > atop, as reported in DFT-GGA calculations for O/Ag(100),[6,10,11] but the calculated adsorption energy for the hollow site is 12.5 kcal mol$^{-1}$ smaller than the DFT value.[6] Our value of 87.1 kcal mol$^{-1}$ is more consistent with the 83 kcal mol$^{-1}$ reported by Li et al.[27] for periodic DFT-GGA calculations on O/Ag(111) at 0.11 monolayer coverage. DFT calculations on O/Ag(110)[5] gave only 72.4 and 71.7 kcal mol$^{-1}$ for 4-fold hollow and long bridge site adsorption energies, respectively. The oxygen–surface equilibrium distance for the hollow site is found to be 0.85 Å

**TABLE 1: Adsorption Energies, Equilibrium Distances and Vibrational Frequencies for Oxygen Adsorption on Ag(100) Calculated at the CI Level**

| site | $E_{ads}$ (kcal mol$^{-1}$) | $R_{O-surface}$ (Å) | $R_{O-Ag}$ (Å) | O charge (e) | O-surface stretch (cm$^{-1}$) |
|---|---|---|---|---|---|
| atop | 40.7 | 2.12 | 2.12 | −0.71 | 494 |
| bridge | 49.4[a] | 1.59 | 2.15 | −1.05 | 456 |
| hollow | 87.1 | 0.85 | 2.21 | −1.30 | 270 |
| hollow (expt) | | 0.6[b] | | | 242[c], 298[d] |

[a] Improved by using a larger cluster model (no changes for the atop and hollow sites). [b] Measured by X-ray photoelectron diffraction for the $p(1 \times 1)$ low-energy electron diffraction structure.[9] [c] Obtained from HREELS spectra for $p(1 \times 1)$ structure.[8,9] [d] Obtained from HREELS spectra for $c(2 \times 2)$ structure.[8,9]

**TABLE 2: Adsorption Energies, Equilibrium Distances, and Vibrational Frequencies for Hydrogen Adsorption on Ag(100) Calculated at the CI Level**

| surface site | $E_{ads}$ (kcal mol$^{-1}$) | $R_{H-surface}$ (Å) | $R_{H-Ag}$ (Å) | H charge (e) | H-surface stretch (cm$^{-1}$) |
|---|---|---|---|---|---|
| atop | 35.3 | 1.95 | 1.95 | −0.19 | 1306 |
| bridge | 37.4 | 1.50 | 2.08 | −0.29 | 860 |
| hollow | 42.7 | 0.75 | 2.18 | −0.56 | 576 |

in the present work, 0.74 Å from DFT-GGA calculations,[6] 0.80 Å from DFT-GGA calculations using a different functional,[10] and 0.6 Å experimentally for a $p(1 \times 1)$ structure. Coverage effects noted in ref 10 and 11 suggest that the oxygen−surface distance would decrease at higher coverage on Ag(100). If this were the case, then the present calculated result would lie in the correct relationship to the experimental value for a $p(1 \times 1)$ structure. As we seek a physical basis for the variation in calculated theoretical values, a note of caution is appropriate since even in good GGA calculations, as pointed out in the work by Li et al.[27] and others, the adsorption energy is often overestimated. Likewise, in ab initio theory it is a challenge to treat the change in correlation energy between the $^3P$ state of a desorbed oxygen atom and spin-paired oxygen adsorbed on the surface. In the present work, we have checked that the adsorption energies are consistent when different dissociation limits O $^1D$ and O $^3P$ are used. The calculated stretching frequency of adsorbed atomic oxygen against the surface is found to be 270 cm$^{-1}$ at the hollow site. The HREELS value is 298 cm$^{-1}$ for a $c(2 \times 2)$ structure and 242 cm$^{-1}$ for a $p(1 \times 1)$ structure, first reported by Fang[8] and recently confirmed by Rocca et al.[9] Such a difference is within theoretical uncertainties and HREELS resolution. Mulliken charges of adsorbed oxygen atom at the atop, bridge and hollow sites are calculated to be −0.71e, −1.05e, and −1.30e, respectively, indicative of the strong ionic character of the O−Ag bonds.

**3.2. Hydrogen Adsorption on Ag(100).** Table 2 shows the calculated adsorption energies, equilibrium distances, and vibrational frequencies for the adsorption of atomic hydrogen on Ag(100). Hydrogen adsorption at the 4-fold hollow site is found to be the most stable. The calculated adsorption energy is 42.7 kcal mol$^{-1}$ with a 0.75 Å hydrogen−surface perpendicular distance. Adsorption at the atop and bridge sites is calculated to be less stable by 5.3 and 7.4 kcal mol$^{-1}$, respectively. Relative stabilities are the same as those computed with DFT methods,[12] but the difference in adsorption energies between sites is found to be smaller in the present work. Our calculated adsorption energies at the hollow and bridge sites are 2.4 and 6.9 kcal mol$^{-1}$ smaller than the DFT values, respectively, but 6.1 kcal mol$^{-1}$ larger at the atop site. The

**TABLE 3: Adsorption Energies, Equilibrium Distances, and Vibrational Frequencies for OH Adsorption on Ag(100) Calculated at the CI level**

| surface site | $E_{ads}$ (kcal mol$^{-1}$) | $R_{O-surface}$ (Å) | $R_{O-Ag}$ (Å) | OH charge (e) | Ag−OH stretch (cm$^{-1}$) |
|---|---|---|---|---|---|
| atop | 58.6 | 2.12 | 2.12 | −0.60 | 345 |
| bridge | 64.5 | 1.85 | 2.34 | −0.60 | 326 |
| hollow | 76.2 | 1.32 | 2.43 | −0.61 | 288 |

calculated 35.3 kcal mol$^{-1}$ for the atop site is in good agreement with the 34.9 kcal mol$^{-1}$ calculated with the complete active space configuration interaction (CASCI) methods.[28] The hydrogen−surface stretching frequencies are calculated to be 1306, 860, and 576 cm$^{-1}$ for the atop, bridge, and hollow sites, respectively. The charges of hydrogen atom at the atop, bridge, and hollow sites are −0.19e, −0.29e, and −0.56 e, respectively, indicative of electron transfer from the surface to the adsorbed hydrogen atom. If we assume two adsorbed hydrogen atoms are widely separated such that the H−H interactions are negligible, then the enthalpy for dissociative adsorption of H$_2$ on Ag(100) can be computed by

$$\Delta H_{H_2 \rightarrow 2H_{ads}} = -2E_{ads} - \Delta H_{fH_2} \qquad (4)$$

where $\Delta H_{fH_2}$ is −104.0 kcal mol$^{-1}$. The calculated enthalpy is 18.6 kcal mol$^{-1}$, and the process is endothermic and thermodynamically unfavorable as predicted by Eichler et al.[13]

**3.3. OH Adsorption on Ag(100).** Calculated adsorption energies, equilibrium distances, and vibrational frequencies for the adsorption of OH on Ag(100) are listed in Table 3.

Values in the table are for the O−H axis perpendicular to the surface and for an O−H bond distance of 0.979 Å. The present calculations show that the 4-fold hollow site is the most stable site for OH adsorption on Ag(100). The calculated adsorption energy is 76.2 kcal mol$^{-1}$ for an oxygen−surface perpendicular distance of 1.32 Å (the corresponding distance from O to the nearest Ag is 2.43 Å). Adsorption energies at atop and bridge sites are calculated to be 58.6 and 64.5 kcal mol$^{-1}$, respectively. Even if the O−H axis is tilted from the normal to the surface (a change of 2.0−3.1 kcal mol$^{-1}$ reported by Hu et al.[16]), these sites will remain less favorable than the hollow site. The calculated HO−surface stretching frequencies are 345, 326, and 288 cm$^{-1}$ for the atop, bridge, and hollow sites, respectively, at the optimized oxygen−surface distances. The value at the hollow site is consistent with the HREELS value on Ag(110) of 280 cm$^{-1}$.[29]

As would be expected, the strong interaction of OH with Ag-(100) involves electron transfer from the surface to OH. For OH adsorbed at the 4-fold hollow site, the net charge transfer from the surface to OH is calculated to be 0.61e. Since the 4d orbitals of silver are fully occupied, these transferred electrons are mainly from the silver 5s orbitals. Assuming the perpendicular O−H axis as the z axis, the occupation numbers of oxygen 2p$_x$ and 2p$_y$ are both 1.87, while the corresponding gas-phase values are 2.00 and 1.00, respectively. The electronic population of H is increased from 0.36e to 0.55e, consistent with the relative electronegativity of Ag and H atoms. In the gas phase, the O−H bond has more oxygen 2p$_z$ character than when OH bonds to the silver surface, an observation similar to that reported for SH adsorption on Ag(100).[30]

The adsorption energy of OH at the hexagonal close-packed hollow site on Ag(111) is reported to be 58.8 kcal mol$^{-1}$ from DFT-GGA calculations.[31] Normally, one would expect the adsorption energy of OH at the 4-fold hollow site on Ag(100)

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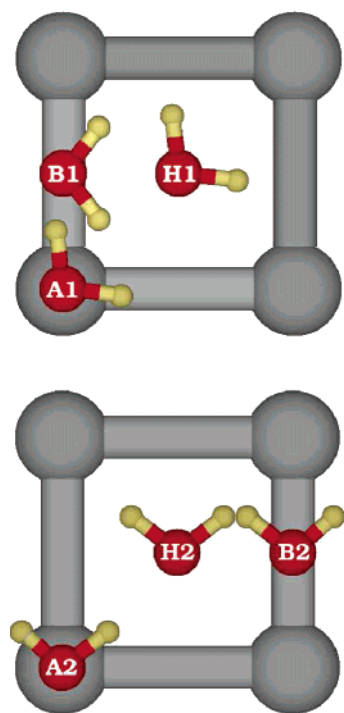*J. Phys. Chem. B, Vol. 109, No. 18, 2005* **8855**

**Figure 2.** Molecular orientations of water on Ag(100).

to be larger than on Ag(111), which is the result found here. A value for OH/Ag(100) of 108.6 kcal mol$^{-1}$ has been reported based on DAM-MP2 calculations.[16] This value seems quite high when compared with the present calculations and published DFT calculations on Ag(111).

**3.4. H₂O Adsorption on Ag(100).** The adsorption of H₂O on Ag(100) at different sites with different orientations (Figure 2) is studied, and the calculated results are described in Figure 3 and tabulated in Table 4.

In the initial calculations, the H₂O molecule is fixed at its experimental geometry with H−O distances of 0.964 Å and an H−O−H angle of 103.8°. We discuss these results first and note at the end of the section a confirmation of the geometrical assumptions by direct optimization at the CI level using a simplex algorithm. At the atop site, if the projection of the H₂O $C_{2v}$ axis is 45° with respect to the Ag−Ag axis (A1 orientation in Figure 2), then the optimal tilt angle between the molecular plane and the surface is found to be 60°, in good agreement with previous theoretical and experimental studies.[17] However, for a projection of the H₂O $C_{2v}$ axis along the Ag−Ag axis (A2 configuration of Figure 2), the system is 0.7 kcal mol$^{-1}$ more stable when the molecular plane is perpendicular to the surface. For the bridge site, the B2 configuration with the molecular plane perpendicular to the surface forms a tetrahedral bonding configuration and gives the highest adsorption energy of 12 kcal mol$^{-1}$. This value is 2.8 kcal mol$^{-1}$ larger than that of the B1 configuration in which the molecular plane is tilted toward the surface by 80 °. Adsorption at the hollow site gives 7.9 kcal mol$^{-1}$, a value smaller than any of the previous cases. Generally, it is found that orientations with the H₂O molecular dipole moment perpendicular to the surface are the more stable. A perpendicular or nearly perpendicular orientation of the molecular plane relative to the surface differs from the conclusion of a recent periodic DFT calculation on Ag(111) where the molecular plane of water was found to be tilted 80 ° from the surface normal. In that calculation, a very small adsorption energy of 4.2 kcal mol$^{-1}$ was found.[7] While in principle the CI calculation through its inclusion of dynamic correlation effects
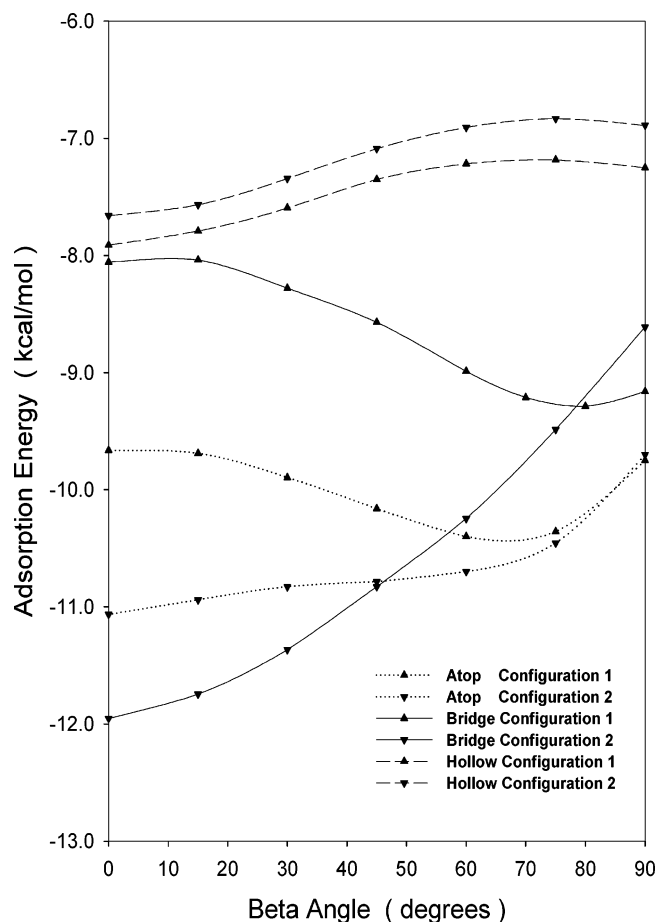


**Figure 3.** Adsorption energies versus $\beta$ angles for water on Ag(100).

**TABLE 4: Adsorption Energies, Equilibrium Distances, and Optimal Tilting Angles for H₂O Adsorption on Ag(100) Calculated at the CI level**

| surface site | | $E_{ads}$ (kcal mol$^{-1}$) | $R_{O-surface}$ (Å) | $R_{O-Ag}$ (Å) | $\beta^a$ (deg) | H₂O charge ($e$) |
|---|---|---|---|---|---|---|
| atop1 | (A1) | 10.4 | 2.91 | 2.91 | 60 | 0.22 |
| atop2 | (A2) | 11.1 | 2.91 | 2.91 | 0 | 0.25 |
| bridge1 | (B1) | 9.2 | 3.04 | 3.37 | 80 | 0.23 |
| bridge2 | (B2) | 12.0 | 2.78 | 3.13 | 0 | 0.29 |
| hollow1 | (H1) | 7.9 | 3.17 | 3.77 | 0 | 0.22 |
| hollow2 | (H2) | 7.7 | 3.31 | 3.89 | 0 | 0.22 |

$^a$ $\beta$ is defined as the angle between the H₂O molecular axis and the surface normal.

should be more accurate than the DFT method, the many differences in detail make it impossible to explain why the DFT adsorption energy is less than one-half the CI value. Since we find that the change in energy is only 2.8 kcal mol$^{-1}$ in going from perpendicular to an 80° tilt, we conclude that the orientation of coadsorbed water molecules will be determined by dipolar interactions and the opportunity of lone pair oxygen orbitals to hydrogen bond with a neighboring water molecule. These effects could favor a structure with the plane of oxygen more nearly parallel to the surface at higher coverage.

Our calculated adsorption energies at the atop and bridge sites are 5.0 and 5.8 kcal mol$^{-1}$ larger, respectively, than those from DFT calculations by Ignaczak et al.[17] and 7.8 kcal mol$^{-1}$ larger than DFT calculations at the atop site on Ag(111) by Ranea et al.,[7] but they are very close to the 12.2 kcal mol$^{-1}$ value for a Ag(111) atop site calculated by molecular dynamics (MD) DFT methods.[32] Calculated net populations of the adsorbed water molecules at different sites with different configurations are

between 0.22*e* and 0.29*e*, showing, as expected, the water molecule to be an electron donor.

Recently, a flexible optimization program has been developed in our lab, which is based on the Nelder–Mead simplex method.[33,34] We have optimized the equilibrium geometries of A1, A2, B1, and B2 configurations at the CI level, and they are all confirmed to be minima on potential energy surface. The optimized structure of the water molecule has a H–O bond length of 0.97 Å and a H–O–H bond angle of 104°. No significant change in the water molecule structure is detected, which is consistent with the result reported by Ranea et al.[7]

## 4. Conclusions

We have studied the adsorption of $H_2O$ and its dissociation products, O, H, and OH, on Ag(100) using ab initio calculations at the CI level. By comparison of the atop, bridge, and hollow sites, adsorption at the 4-fold hollow site is the most stable for O, H, and OH on Ag(100), and the calculated adsorption energies are 87.1, 42.7, and 76.2 kcal mol$^{-1}$, respectively. Water exhibits much weaker interaction with Ag(100); adsorption energies at atop and bridge sites are comparable, 11.1 and 12.0, respectively, and larger than for the hollow site. Formation of adsorbed OH species by adsorption of water on oxygen-precovered Ag(100) is calculated to be exothermic by 36 kcal mol$^{-1}$. Comparisons of the ab initio CI results with DFT-GGA calculations show in some cases very good agreement while in other cases DFT calculations of the same apparent quality show significant differences.

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