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ABSTRACT

Theoretical electronic structure calculations are reported for the photoinduced dissociation of water adsorbed on a 31-atom silver cluster, Ag₃₁ to produce H₂ and adsorbed O. Both ground and excited electronic state processes are considered. The excited electronic state of interest is formed by photoemission of an electron from the Ag cluster and transient attachment of the electron to the adsorbed water molecule. A very large energy barrier for H₂ formation (3.51 eV) is found for the ground state process while the barrier in the excited state is much smaller (0.47 eV). In the excited state, partial occupancy of an OH antibonding orbital facilitates OH stretch and the electron hole in the metal cluster stabilizes OH and O adsorbates. The excited state pathway for dissociation of water begins with the formation of an excited electronic state at 3.49 eV. Stretch of the OH bond up to 3.44 a.u. (1.82 Å) occurs with little change in energy. In this region of OH stretch the molecule must return to the ground state potential energy surface to dissociate fully and to form H₂. Geometry optimizations are carried out using a simplex algorithm which allows the total energy to be calculated using configuration interaction theory.

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1. Introduction

The production of H₂ from water is being pursued on many fronts with the ultimate goal of producing a versatile and nearly unlimited fuel. Among these investigations are heterogenic processes on catalytic surfaces, homogenous reactions involving transition metal complexes and the design of biologically inspired catalytic systems. Since the overall reaction $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2$ is endothermic, an energy source is required, and, for this purpose, sunlight would be very attractive if reasonable efficiencies could be attained.

In heterogeneous reactions involving the dissociation of gas phase water on catalytically active transition metal surfaces, one can envision processes that successively remove hydrogen atoms to produce adsorbed H and OH or processes that form H₂ directly by inter- or intra-molecular processes. None of these processes will be successful, however, unless hydrogen and oxygen can be removed from the surface. Thus, the driving force for the reaction cannot be strong bonding with the surface, but rather from another energy source such as radiation.

In recent work, we have examined the photoinduced dissociation of water adsorbed on a small cluster of Ag atoms and transport of the H atom released to a nearby Ag cluster [1]. We now pursue a different direction and explore the direct formation of H₂ by photoinduced electron transfer to a water molecule adsorbed on a sin-

gle Ag cluster (31 atoms). The dissociation pathway involves both ground and excited electronic states, and, in order to assess the feasibility of the process, we need to know accurate values for critical geometries and energy barriers. This requires calculations on both ground and excited electronic states using a high level theory in which electron correlation is properly included. For this purpose, we use the full many-electron Hamiltonian for the electronic structure problem, introduce core electron pseudopotentials for silver and construct wavefunctions by configuration interaction, i.e., a many-electron *ab initio* approach as opposed to density functional theory (DFT). Since the cross-section for photon absorption is larger for the metal cluster than for the adsorbed water molecule, we consider the formation of the excited state to be equivalent to an electron attachment reaction in which a photoemitted electron of silver transiently attaches to an adsorbed water molecule. The electronic state that results can be viewed as an electron transfer excited state of the H₂O-metal cluster system. This photoinduced excited state can evolve on the excited state potential energy surface or return at some point to the ground state surface and undergo further reaction because of excess vibrational energy. Energy barriers will determine whether a viable process exists in which H₂ can be formed directly leaving O adsorbed on the surface.

2. Silver surface and nanoparticle

A cluster of 31 Ag atoms in a fcc structure is chosen to represent the nanoparticle; there are 7 Ag atoms in the (111) first layer and 12 Ag atoms in both the second and third layers. A schematic rep-

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representation of the geometry of a H₂O molecule adsorbed at a fcc (hollow) adsorption site on the first layer of the cluster is depicted in Fig. 1. The Ag–Ag distance is set at the experimental bulk value, 5.46 a.u. (2.89 Å). The three Ag atoms in the first layer (labeled 1, 2, 3 in Fig. 1) which directly bond to H₂O are described by a 28-electron core potential with 4s, 4p, 4d and 5s electrons outside the core [2]. The latter, valence electrons are described by 4s, 4p, 4d', 4d'', 5s', 5s'' and 5p basis functions. All other silver atoms have a 46-electron core and 5s', 5s'' basis functions [1]. The hydrogen atoms are described by 1s', 1s'' and p functions, and oxygen has five s-type functions, two p-type functions plus a set of d-polarization functions [3,4]. An additional diffuse Gaussian s function with exponent 0.08 is added to oxygen to describe the charge transfer excited state; O d-polarization functions have an exponent of 0.8. The basis is large enough to ensure near Hartree–Fock quality atomic solutions. The additional basis functions allow orbitals to polarize in a molecular environment and permit correlation excitations to the next atomic shell.

The objective of the present work is to consider photoinduced dissociation of water to form H₂ in free space and leave O adsorbed on the cluster surface; both ground and electronically excited states are calculated in order to determine the energy barrier for each potential energy surface. The same silver clusters are used in all calculations and no attempt has been made to vary cluster size or the surface face for water adsorption.

3. Theory and method

The water–silver cluster system is described in the present work by an embedding method that is designed to give an accurate many-electron description of the adsorbate–surface region. Many applications of the method to ground and excited states of adsorbates on metals have been reported previously and details of the method can be found in Refs. [5–7]. There are two distinct components of the method described in the references cited above, boundary conditions on the cluster itself that appropriately couple the cluster to a larger bulk system and the localization transformation that defines the electronic subspace treated by configuration interaction. In the present work, since we are interested in a small, 31-atom, silver cluster, no cluster boundary conditions are employed, and the terminology “embedding” refers only to the creation of a subspace that is treated by configuration interaction. A brief summary of the main elements of the approach is given below.

Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron potentials), and wavefunctions are constructed by self-consistent-field (SCF) and multi-reference configuration interaction (CI) expansions [5–7],

$$\Psi = \sum_k c_k \det (\chi_1^k \chi_2^k, \dots, \chi_n^k)$$

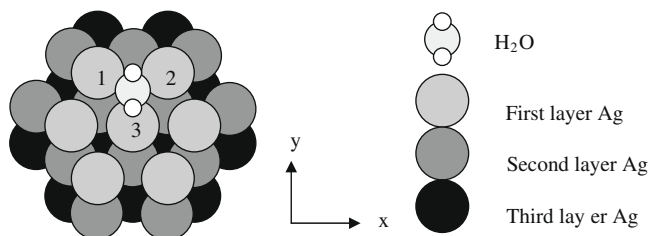


Fig. 1. Top view of the fcc site for H₂O adsorption/dissociation on the Ag(111) surface of the Ag-31 cluster. Radii of the silver atoms are shown at reduced size for clarity of visualization. Silver atoms defining the adsorption region are labeled 1, 2 and 3.

The Hamiltonian, including atomic core potentials, V^{core} , is of the form,

$$H = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 + \sum_k^Q \frac{-Z_k}{r_{ik}} \right) + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_i^N V_i^{core}$$

where

$$\langle a(i) | V_i^{core} | b(i) \rangle = \langle a(i)b(i) | 1/r_{ij} | \rho(j) \rangle - \langle a(j)b(i) | 1/r_{ij} | \gamma(i,j) \rangle + \sum_m \lambda_m \langle a(i) | Q_m(i) \rangle \langle Q_m(i) | b(i) \rangle$$

and ρ , γ and Q_m denote atomic densities, exchange functions and core atomic orbitals, respectively. This type of effective core potential and basis construction, discussed in Refs. [2] and [5], maintains rigorous orthogonality of valence and core basis functions on the same nucleus.

Initial variational energy minimization calculations are carried out at the single-determinant, self-consistent field (SCF) level. The occupied and unoccupied SCF orbitals are then localized separately to maximize their interaction with the adsorbate and the metal atoms of the adsorption sites. Highly localized orbitals are used to define the CI active space. CI wavefunctions for ground and excited electronic states are expanded as linear combinations of determinantal wavefunctions

$$\Psi = \sum_k \lambda_k \det (\chi_1^k \chi_2^k \dots \chi_n^k) = \sum_k \lambda_k \Phi_k$$

For both ground and excited states there are three stages in the process: (1) An SCF calculation to determine the main configuration for the ground state and for the excited state; (2) Generation of small CI expansions for both ground and excited states to identify the most important contributions; (3) Generation of a second, large CI expansion for each state.

The initial representation of the excited state, Φ_r , is obtained from the following sequence of calculations:

- SCF calculation of the ionized system.
- Localization of the virtual SCF orbitals (using exchange maximization) about H₂O and surface Ag atoms; removal of transformed virtual orbitals that do not contain appreciable H₂O character.
- SCF calculation of the electron attached excited state corresponding to electron excitation from the metal cluster to H₂O. The resulting single configuration representation of the state which corresponds physically to a transfer of an electron from the metal to a OH antibonding orbital with diffuse O character is defined as Φ_r .

Double excitations from this single-determinant wavefunction, Φ_r , are then considered to create the small CI expansion, Ψ'_r ,

$$\Psi'_r = \Phi_r + \sum_{ijkl} \lambda_{ijkl} \Gamma_{ij-kl} \Phi_r = \sum_m \lambda_m \Phi_m$$

Configurations, Φ_k , are retained if the interaction with Φ_r satisfies a relatively large threshold condition

$$|\langle \Phi_k | H | \Phi_r \rangle|^2 / (E_k - E_r) > 10^{-4} \text{ a.u.}$$

Since Φ_r is an SCF wavefunction, it is not necessary to consider single excitation configurations at this stage since these do not contribute because of Brillouin's theorem.

In stage (3), we refine the description of the excited state by generating a large CI expansion, Ψ_r , by single and double excitations from all important members of Ψ'_r , (those with coefficient >0.06), to obtain

$$\Psi_r = \Psi'_r + \sum_m \left[\sum_{ik} \lambda_{ikm} \Gamma_{i-k} \Phi_m + \sum_{ijkl} \lambda_{ijklm} \Gamma_{ij-kl} \Phi_m \right]$$

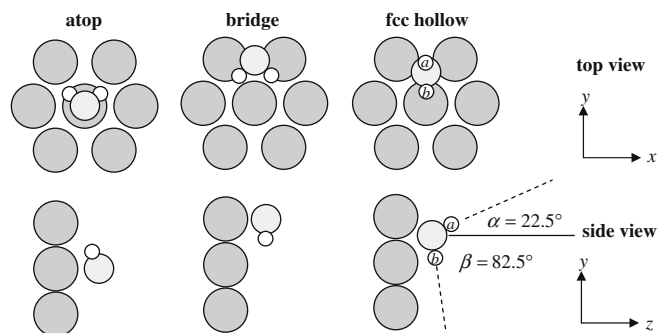


Fig. 2. The optimized geometry of H₂O at atop, bridge and fcc hollow adsorption sites on the (111) face of Ag₃₁. Only the top layer of Ag atoms is shown. The H, O, and Ag atoms are depicted as in Fig. 1. Two H atoms at the fcc hollow site have been labeled as a and b. Parameters α and β are defined as the angles between O–Ha, O–Hb axis and surface normal z-axis, respectively.

where Φ_m is an important member of Ψ_r' . The additional configurations are generated by identifying and retaining all configurations, Φ_k , that interact with Ψ_r' such that

$$|\langle \Phi_k | H | \Psi_r' \rangle|^2 / |E_k - E_r| > 10^{-7} \text{ a.u.}$$

For this lower threshold, typically 5×10^4 configurations occur in the final CI expansion, and, in principle, the expansion can contain single through quadruple excitations from an initial representation of the state Φ_r .

The procedure assures that the representation of the excited state, Ψ_r , is orthogonal to and non-interacting with intervening excited states, at least within the configuration space considered.

Since

$$\langle \Psi_k | H | \Psi_r \rangle = 0$$

and

$$\langle \Psi_k | \Psi_r \rangle = 0$$

for all lower energy states, Ψ_k , it follows that the calculated energy of Ψ_r is an upper bound to the exact energy. Separate CI calculations are carried out on the ground state to assure an accurate description of the bonding and equilibrium distance from the surface. All calculations are carried out for the full electrostatic Hamiltonian of the system except for core electron potentials. Details of the procedure and references to previous applications to excited states are reported in earlier work [5–7].

4. Results and discussion

4.1. H₂O adsorption

The equilibrium geometry of H₂O adsorbed on the Ag(111) surface is determined by an optimization program based on the Nelder–Mead simplex method [8,9]. This is an effective minimization method for the present investigation since the potential energy surface is determined directly at the CI level. Six variables are chosen for optimization: the O–Ag surface distance,

OH bond length, and four angles (two angles for each OH in spherical coordinates). All structures have a plane of symmetry as indicated in Fig. 2. Three high-symmetry adsorption sites (atop, bridge and fcc hollow) are considered, and the energy minimum determined for each site. The optimized geometries corresponding to the energy minima are depicted in Fig. 2. In Table 1, adsorption energies and the geometrical parameters of H₂O are tabulated.

As indicated in Table 1, comparing the three adsorption sites, water adsorbed at the fcc hollow site is found to be the energy minimum, and the calculated adsorption energy of 0.24 eV is indicative of a rather weak interaction between water and silver. We refer to this site as the global energy minimum. The H₂O molecular plane is perpendicular to the (111) surface with the two OH axes forming angles of 22.5° and 82.5° with respect to the surface normal, as shown in Fig. 2. The adsorption energies for the atop and bridge sites are 0.14 and 0.19 eV, respectively, only slightly less than at the fcc hollow site. In these two cases, the H₂O molecular plane is more nearly parallel to the Ag surface, especially at the bridge site. In all three cases, as shown in Table 1, the optimized OH bond length $d(\text{OH})$ and bond angle $\angle(\text{HOH})$ are found to be close to the experimental gas phase molecular geometry of 0.96 Å and 105.2° [10]. The calculated optimum geometry of the free water molecule has bond lengths and angles of 0.977 Å and 104.1°, respectively. The perpendicular orientation of the H₂O molecular plane relative to the Ag surface differs from the optimum geometry found in a high quality periodic DFT calculation of water on Ag(111) where the molecular plane for water at an fcc hollow site was found to be tilted 104° with respect to the surface normal [11]. Since water is very weakly adsorbed on the Ag surface and the change of adsorption energy in the DFT calculation is only 0.09 eV in going from perpendicular to a 104° tilt, the difference could be attributable to differences in theoretical method. One would not normally expect DFT to account for van der Waals interactions while these weak interactions are described by CI. In view of the small change in total energy in both calculations, we agree with one of the main conclusions of the DFT work that the orientation of coadsorbed water molecules would be determined by dipolar interactions and the opportunity of lone pair oxygen orbitals to hydrogen bond with a neighboring water molecule. At higher coverage, both of these effects should favor a structure with the H₂O plane more nearly parallel to the surface.

In order to determine the sensitivity of the total energy to the tilt angle of a water molecule constrained to be in a plane perpendicular to the Ag surface (the yz plane in Fig. 2), we varied the orientation of the O–Ha axis keeping the HOH angle fixed. The results, plotted in Fig. 3 for H₂O at the fcc hollow site, show that the change in energy is very small (<0.01 eV) in going from 22.5° (the minimum) to 0°, while in the opposite direction the adsorption energy increases more rapidly; the tilt directions are not equivalent by symmetry, but the asymmetry near the minimum is not large.

4.2. Dissociation of H₂O

The task of finding critical energy barriers for the dissociation of adsorbed H₂O to form H₂ and adsorbed O, could, in principle, require extensive geometry searches. For example, in the previous

Table 1
Adsorption energy and structural parameters of H₂O adsorbed at different sites on the (111) face of a Ag₃₁ cluster. Results are from CI calculations. Tabulated are the adsorption energy, E_{ads} , the tilt angle of the H₂O molecular plane with respect to the Ag surface normal, θ , the bond angle $\angle(\text{HOH})$, the OH bond length, $d(\text{OH})$, and the distance between the O and Ag surface, $d(\text{O–Ag surface})$.

Site	E_{ads} (eV)	θ	$\angle(\text{HOH})$	$d(\text{OH})$ (a.u.)	$d(\text{O–Ag surface})$ (a.u.)
atop	0.14	124°	102°	1.86 (0.98 Å)	6.56 (3.47 Å)
bridge	0.19	85°	100°	1.85 (0.98 Å)	5.70 (3.02 Å)
fcc hollow	0.24	0°	105°	1.84 (0.97 Å)	5.54 (2.93 Å)

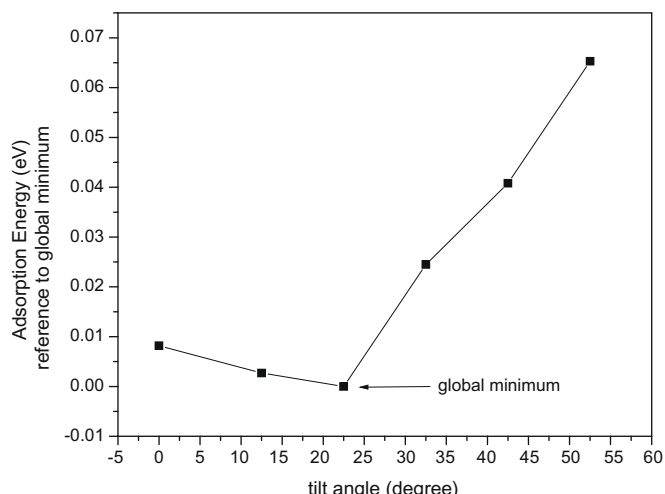


Fig. 3. Adsorption energy of H₂O versus tilt angle of the O–Ha axis (defined as the angle α at the fcc hollow site in Fig. 2). The $\angle(\text{HOH})$ is fixed at 105°.

section, six parameters are varied to find the optimum geometry of H₂O adsorbed on the Ag surface. However, at the global minimum for water on silver (the fcc hollow site in Fig. 2), we note that the molecular plane of water (*yz* plane) is perpendicular to the Ag surface. Therefore, two of the angular variables can be fixed under the reasonable assumption that the dissociation of water can be considered as taking place in the *yz* plane. Also, as shown in Fig. 3, the energy varies by less than 0.01 eV, when the (O–Ha) axis is changed from an angle of 22.5° to 0°. It follows that we can safely set the starting point of the optimization to correspond to an O–Ha axis perpendicular to the Ag surface and allow Ha to move away from O in the *z* direction. Fig. 4 depicts the allowed motions of the constituent atoms of water. As Ha is moved in steps toward free space along the direction of the surface normal, three independent variables (the O–Ag surface distance, $d(\text{O–Ag surface})$; the O–Hb distance, $d(\text{O–Hb})$; and the angle between O–Ha and O–Hb, $\angle(\text{HOH})$) are optimized by the simplex method to give the optimum structure for each O–Ha distance.

The calculated ground state energy versus O–Ha distance is shown in Fig. 5 and the optimized geometrical parameters of

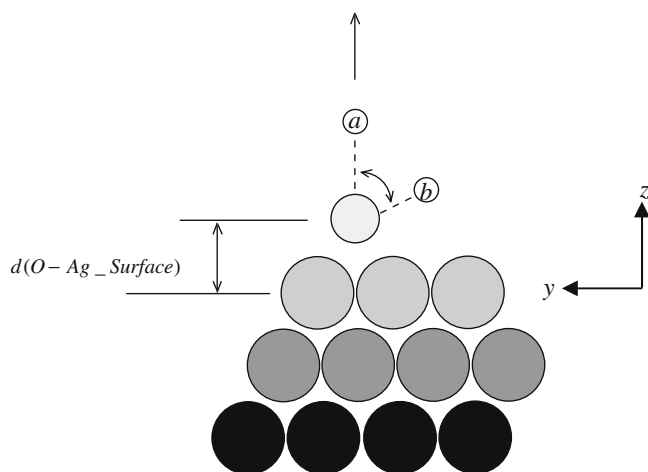


Fig. 4. Schematic view of the allowed motions of Ha, Hb, and O atoms in the calculation of water dissociation to produce H₂ in the gas phase and adsorbed O on the (111) face of the Ag₃₁ cluster. Parameters are: the O–Ag surface distance, $d(\text{O–Ag surface})$; the O–Ha distance, $d(\text{O–Ha})$; the O–Hb distance, $d(\text{O–Hb})$; and the angle between O–Ha and O–Hb, $\angle(\text{HOH})$.

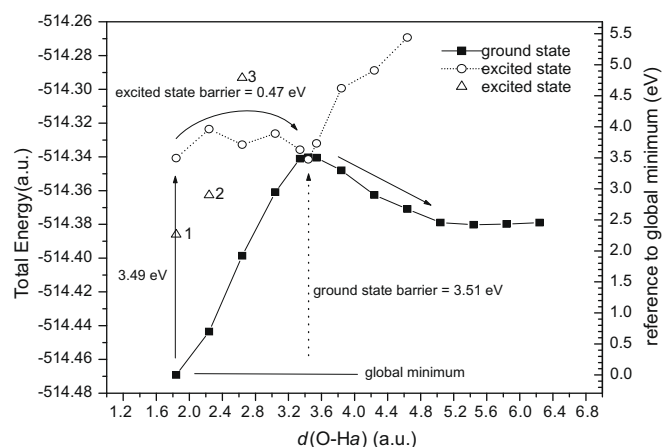


Fig. 5. Total energy of ground (solid square symbols) and excited (open circles and triangles) electronic states for H₂O dissociation to form H₂ and O adsorbed on Ag.

H₂O for each choice of O–Ha distance are tabulated in Table 2. In Fig. 6, the geometries at the three most important steps are depicted.

We find a very large increase in energy of the ground state when $d(\text{O–Ha})$ increases from 1.84 a.u. in the initial state to 3.44 a.u. in the transition state, resulting in an energy barrier of 3.51 eV to release H₂ as shown in Fig. 5. From Table 2 and Fig. 6 we note that in going from the initial state to the transition state, the O–Hb bond rotates upward from 105° to 69.4° toward the surface normal, however, the O–Hb bond length shows almost no change which means Hb is still tightly bound to O during this part

Table 2

Structural parameters of H₂O during dissociation and formation of H₂. Tabulated are the O–Ha distance, $d(\text{O–Ha})$; the O–Hb distance, $d(\text{O–Hb})$; the bond angle, $\angle(\text{HOH})$; the Ha–Hb distance, $d(\text{H–H})$; and the distance between O and the Ag surface, $d(\text{O–Ag surface})$. Results are shown in atomic units and Å.

$d(\text{O–Ha})$	$d(\text{O–Hb})$	$\angle(\text{HOH})$	$d(\text{H–H})$	$d(\text{O–Ag surface})$
1.84 (0.97 Å)	1.84 (0.97 Å)	105.0°	2.92 (1.55 Å)	5.50 (2.91 Å)
2.24 (1.19 Å)	1.86 (0.98 Å)	99.5°	3.14 (1.66 Å)	5.43 (2.87 Å)
2.64 (1.40 Å)	1.86 (0.98 Å)	94.7°	3.35 (1.77 Å)	5.13 (2.71 Å)
3.04 (1.61 Å)	1.86 (0.98 Å)	89.4°	3.55 (1.88 Å)	4.73 (2.50 Å)
3.34 (1.77 Å)	1.85 (0.98 Å)	78.6°	3.48 (1.84 Å)	4.06 (2.15 Å)
3.44 (1.82 Å)	1.85 (0.98 Å)	69.4°	3.28 (1.74 Å)	3.66 (1.94 Å)
3.54 (1.87 Å)	1.90 (1.01 Å)	30.3°	2.13 (1.13 Å)	3.15 (1.67 Å)
3.84 (2.03 Å)	2.29 (1.21 Å)	0.2°	1.55 (0.82 Å)	2.80 (1.48 Å)
4.24 (2.24 Å)	2.74 (1.45 Å)	0.4°	1.50 (0.79 Å)	2.76 (1.46 Å)
4.64 (2.46 Å)	3.15 (1.67 Å)	0.1°	1.49 (0.79 Å)	2.75 (1.46 Å)
5.04 (2.67 Å)	3.56 (1.88 Å)	0.2°	1.48 (0.78 Å)	2.72 (1.44 Å)
5.44 (2.88 Å)	3.96 (2.10 Å)	0.8°	1.48 (0.78 Å)	2.71 (1.43 Å)
5.84 (3.09 Å)	4.36 (2.31 Å)	0.6°	1.48 (0.78 Å)	2.73 (1.44 Å)
6.24 (3.30 Å)	4.77 (2.52 Å)	0.5°	1.47 (0.78 Å)	2.74 (1.45 Å)

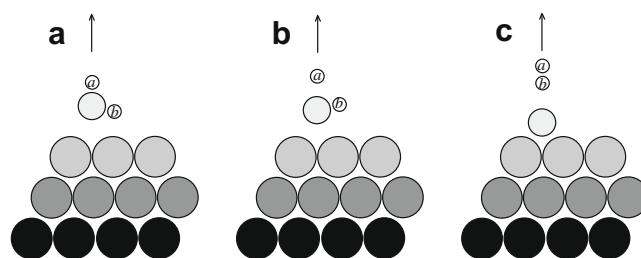


Fig. 6. Three stages of water dissociation and H₂ formation: (a) initial state, $d(\text{O–Ha}) = 1.84$ a.u.; (b) transition state, $d(\text{O–Ha}) = 3.44$ a.u.; and (c) final state, $d(\text{O–Ha}) \geq 5.04$ a.u. Other geometrical parameters are given in Table 2.

of the process in which the O–Ha bond is broken. The distance from O to the Ag surface in the transition state is 3.66 a.u., a value not far from the equilibrium distance, 3.1 a.u., for an OH adsorbate at the fcc hollow site on the Ag(111) surface [1]. The ground state energy decreases as $d(\text{O–Ha})$ is further increased from 3.44 a.u. to 5.04 a.u., while the O–Hb bond continues to rotate upward until it becomes perpendicular to the surface and the distance between O and Hb increases as H_2 is formed and moves into free space.

In the final state depicted, the optimized H–H bond length is 1.48 a.u. (0.78 Å), which is close to the experimental value of 1.40 a.u. (0.74 Å) [12]. The O to Ag surface distance of 2.72 a.u. (1.44 Å) is similar to the value of 2.9 a.u. reported by Kokh et al. [13] for O adsorption on an extended silver surface where an adsorption energy of 3.2 eV was calculated. The dissociation process can be qualitatively understood by comparing calculated adsorption energies and experimental gas phase bond dissociation energies. In earlier work [1], we found the adsorption energy of OH at the fcc hollow site on the (111) face of a Ag cluster surface to be 2.5 eV for an optimum orientation of the OH bond perpendicular to the surface. Once the O, Hb, and Ha atoms are in alignment along the surface normal, taking the dissociation energies of H_2 and OH as 4.7 and 4.6 eV [10,12], respectively, we estimate the energy for the reaction $\text{OH}_{\text{ads}} + \text{H} \rightarrow \text{H}_2 + \text{O}_{\text{ads}}$ to be -0.8 eV indicating that H_2 and O_{ads} products are slightly preferred.

Excited electronic states that involve a change in the electronic structure in the water region of the system have been calculated as a function of geometry. These states are often referred to as electron attachment states and can be viewed as a transient attachment of a photoemitted electron to the water adsorbate. The state formed initially in such a process has the same geometry as water in its ground electronic state. There are many other electronic states at lower energy corresponding to metal–metal excitations, but these states have essentially no effect on the dissociation of water. As described in the theory section, the intervening metal–metal states are isolated from the states of interest. Excited state energies are also reported in Fig. 5. The lowest excited state, aside from the metal to metal excitations, corresponds to electron attachment to a molecular orbital on water that is a mixture of a diffuse oxygen s basis function and a Ha–OHb antibonding sigma orbital comprised of valence basis functions. This state, denoted by triangle symbols ($\Delta 1$ – $\Delta 3$) in Fig. 5, increases sharply in energy as the OH distance is increased and thus does not provide a viable route for the dissociation of H_2 . The second excited state (orthogonal to and non-interacting with other states) is also an electron attached state but higher in energy; it is denoted in Fig. 5 by open circle symbols. The state is also a mixture of O diffuse s and OH sigma antibonding basis functions, but with much less diffuse character. The energy required to produce the excited state initially is calculated to be 3.49 eV. Once formed, it is found that stretching an H–OH bond in the excited state requires only a relatively small increase in total energy as depicted in Fig. 5 by a dotted line. Thus, excitation to this state provides a viable route for dissociation to H_2 . The behavior can be understood by noting that the electron attached state corresponds to transiently occupying a Ha–OHb antibonding sigma molecular orbital which weakens the OH bond. However, the nature of the occupied “antibonding” orbital varies with OH distance and electronic state. The orbital occupied initially, before the geometry of water is allowed to change, is a mixture of diffuse O s-type basis functions on oxygen with valence basis functions corresponding to an antibonding Ha–OHb sigma orbital, i.e., the orbital has substantial Rydberg character. As the OH distance increases, the diffuse contribution decreases in the lowest excited state and the antibonding sigma orbital approaches its valence basis function description. The negatively charged water is also stabilized by

the hole in the metal which localizes near the water adsorption site. It follows that the interaction between O and Ha is much weaker than in the ground state and a much smaller change in energy occurs on Ha–OHb stretch. In Fig. 5 it is seen that elongation of the Ha–OHb bond to a distance of 3.44 a.u. occurs with an energy barrier of only 0.47 eV. Further stretch of the Ha–OHb bond is accompanied by a large increase in energy as the O–Hb bond is broken.

From these results, it is possible to identify a viable process that would lead to water dissociation and formation of H_2 and adsorbed O. Beginning with water adsorbed on a silver cluster, the key steps are as follows:

- (a) Photoexcitation to create the electron attached excited state.
- (b) Stretch of one of the O–H bonds of water on the excited state potential energy surface to a distance corresponding approximately to the location of the ground state energy barrier to dissociation, 3.44 a.u. (1.82 Å).
- (c) Decay of the excited state back to the ground state.
- (d) Continued formation of H_2 is energetically downhill, and H_2 moves into free space on the ground state potential energy surface.

Although the photoinduced reaction described above can occur at modest excitation energies, and one could envision using arrays of nanoparticles of silver, there are other questions or limitations that will determine the practical utility of the process. Among these are the relatively low cross-sections for electron attachment, the lifetime in the excited state required for sufficient H–OH stretch, and finally the removal of oxygen from the silver surface. Since relatively strong bonds are formed between oxygen and silver, one should anticipate reconstruction of the surface but we have not explored such questions.

5. Summary

Theoretical studies of H_2O adsorption and dissociation on a (111) facet of a three-layer Ag_{31} cluster are reported. Energy barriers for the formation of H_2 are calculated for both ground and photoinduced excited electronic states. Results can be summarized as follows:

- H_2O weakly adsorbs on the Ag(111) surface. At the fcc hollow site, the O–surface equilibrium distance is 5.54 a.u. (2.93 Å) and the H_2O molecular plane is perpendicular to the Ag surface. However, the energy change on tilting the molecular plane to a geometry nearly parallel to the surface is small.
- In the ground state, the energy barrier for formation of H_2 and movement into the gas phase is quite large, 3.51 eV.
- In the excited electronic state formed by photoemission from the metal and electron attachment to adsorbed water, one of the OH bonds of water is weakened and substantial elongation of the OH bond is possible. The energy increase required to reach the same OH stretch that corresponds to the ground state energy barrier is only 0.47 eV.
- Decay of the excited state with an elongated OH bond back to the ground state allows release of H_2 and movement along the ground state potential energy surface.

The present work should be viewed as illustrating the viability of a process leading to the dissociation of water and not as work to identify an optimum system. In order to design a more efficient system, surface modifiers could be used to lower the energy required to form the initial excited state and metal overlayers could be backed by oxide materials that have a higher cross-section for photon adsorption.

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