

First-principles study of H₂O diffusion on a metal surface: H₂O on Al{100}A. Michaelides,¹ V. A. Ranea,^{2,3} P. L. de Andres,² and D. A. King¹¹*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*²*Instituto de Ciencia de Materiales (CSIC), Cantoblanco, E-28049 Madrid, Spain*³*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (CONICET, UNLP, CICPBA)**Sucursal 4, Casilla de Correo 16 (1900) La Plata, Argentina*

(Received 23 August 2003; published 18 February 2004)

Density functional theory has been used to investigate the adsorption and diffusion of H₂O on Al{100}. The favored adsorption site for H₂O is the atop site with a binding energy of ~ 350 meV. H₂O binds only very weakly at bridge sites and does not adsorb at fourfold hollow sites. The activation energies for H₂O diffusion depend on the specific orientation of the H₂O molecule on the surface and range from 307–327 meV. We show that the barriers for H₂O diffusion are consistently larger than the difference in adsorption energies between H₂O at the most stable (atop) and next most stable (bridge) adsorption sites.

DOI: 10.1103/PhysRevB.69.075409

PACS number(s): 68.43.Bc, 82.65.+r, 68.43.Fg

The nature of the H₂O-metal interaction is of obvious importance to any number of scientific disciplines. As a result many investigators have devoted considerable time and effort towards understanding these systems.^{1,2} One need only look at the impressive list of references in Henderson's review article for evidence.² Of the many publications in this area several recent scanning tunneling microscopy (STM) experiments on single crystal metal surfaces stand out.^{3–6} These studies have shed light on important aspects of the clustering and diffusion of H₂O molecules on Ag{111}, Cu{111}, and Pd{111}. On Pd{111}, for example, the diffusion parameters of isolated H₂O monomers and H₂O clusters were measured.⁵ Unfortunately, however, the internal structure of the adsorbed H₂O molecules was not resolved in any of these studies and thus an atomic level description of the H₂O diffusion mechanisms has not yet been arrived at. It is not known, for example, what the orientation(s) of the H₂O molecules are as they navigate their way across a metal surface.

Many studies have now demonstrated that density functional theory (DFT) can accurately predict the adsorption and diffusion properties of atoms and molecules on metal surfaces.^{7–10} Further it has been shown that excellent agreement between DFT and experimentally determined diffusion barriers can be obtained.^{11–13} Despite numerous theoretical investigations of H₂O on model metal surfaces, however, none has explicitly examined the diffusional potential energy surface (PES) of H₂O on a metal surface.^{14–28} Thus activation energies for H₂O diffusion on metal surfaces have not been calculated. Rather it is often assumed that the barrier to diffusion can be obtained by comparing adsorption energies at different high symmetry sites. Here we perform the first DFT investigation of the diffusional potential energy surface of H₂O on a metal surface. We find that on Al{100} H₂O monomers diffuse between favored atop adsorption sites over twofold bridge sites. We show that the barriers determined are consistently larger than the difference in H₂O adsorption energies at atop and bridge sites.

All calculations presented here were performed within the DFT framework as implemented in the CASTEP code.²⁹ Electron-ion interactions were included through the use of

ultrasoft pseudopotentials,³⁰ which were expanded within a plane wave basis with a cutoff energy of 340 eV. Electron exchange and correlation effects were described by the Perdew Wang (PW91) generalized gradient approximation.³¹ The Al{100} surface was modeled by a periodic array of six layer-slabs separated by a vacuum region equivalent to a further six layers. A $p(2 \times 2)$ surface unit cell was employed and a single H₂O molecule was placed on one side of the slab, corresponding to a coverage of 0.25 monolayers. A Monkhorst-Pack³² mesh with $6 \times 6 \times 1$ **k**-point sampling within the surface Brillouin zone was used. Structure optimizations for H₂O adsorption were performed with the Al atoms fixed at their bulk-truncated positions and also with the top layer of Al atoms allowed to relax. For the calculations on H₂O diffusion, however, only results with all the Al atoms held fixed are presented. Initial calculations revealed that it was necessary to fix the surface in order to prevent the top Al layer from slipping *en masse* to follow H₂O during diffusion.

H₂O adsorption at all three high symmetry adsorption sites on Al{100} (atop; twofold bridge and fourfold hollow sites) was considered. During these structure optimizations O was (laterally) constrained to remain precisely above each adsorption site. We find that H₂O binds most strongly to the atop site with a calculated adsorption energy of 348 meV (242 meV when the surface is relaxed). The O-Al distance is 2.00 Å and the molecule deforms only moderately from its gas phase equilibrium structure: the O-H bonds are elongated to 0.98 Å from a calculated gas phase value of 0.97 Å; and the HOH internal angle is expanded by 4° from a calculated gas phase value of 104°. At this site H₂O lies fairly flat on the surface with the molecular plane tilted by $\sim 70^\circ$ from the surface normal. Adsorption at the bridge site is considerably less stable, with a binding energy of only 60 meV at this site. When the surface is allowed to relax the adsorption energy is 58 meV. Despite considering five different initial orientations for H₂O at the fourfold hollow site our calculations indicate that H₂O does not bind to the surface at this site. The atop binding site identified here on Al{100} agrees with two previous cluster studies for H₂O adsorption on Al surfaces.^{20,25} Moreover, in broader terms, it is consistent with a general model for monomeric H₂O adsorption on transition and

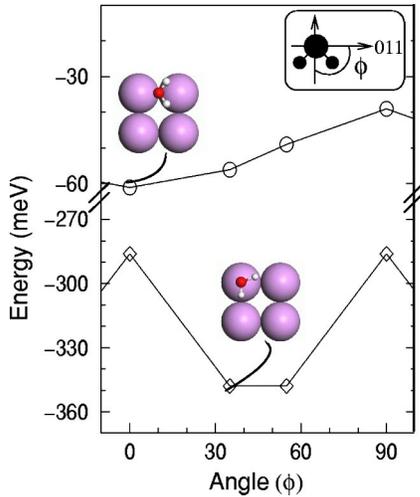


FIG. 1. Total variation in H₂O adsorption energy with azimuthal orientation (Φ) for H₂O adsorbed at the atop and bridge sites. The angle Φ , described by the inset, is defined as the angle between the H₂O dipole plane and the $\langle 011 \rangle$ surface plane. The structure of the most stable orientations at each site are also shown. Note the different scales for the upper and lower parts of the graph.

noble metal surfaces recently proposed by Michaelides *et al.*³³

Next the azimuthal orientation of adsorbed H₂O, i.e., rotation about the O-Al bond, was investigated. The total energy variation in the H₂O adsorption energy with respect to the azimuthal orientation for H₂O at the atop and bridge sites is shown in Fig. 1. We define the azimuthal angle, Φ , as the angle between the H₂O dipole plane and the $\langle 011 \rangle$ surface plane, as shown by the inset in Fig. 1. The structures of the preferred orientation at each site are also shown in Fig. 1. It can be seen that the favored orientations for H₂O at the atop site are those that have an OH bond directed towards a neighboring atop site. At the bridge site, H₂O prefers to have the molecular dipole plane aligned along the $\langle 011 \rangle$ surface plane. It is apparent, however, from Fig. 1 that at both sites azimuthal rotation is facile and that a strong preference for a particular orientation does not exist. The various orientations considered do not differ by more than 60 and 20 meV at the atop and bridge sites, respectively.

Given a H₂O monomer at an atop site we then sought to investigate how it would negotiate its way across the Al{100} surface. Since we find that H₂O does not adsorb at fourfold hollow sites, only diffusion mechanisms between bridge and atop sites were examined. For H₂O at a given atop site, arbitrarily labeled T_0 in Fig. 2, we obviously have four nearest atop sites (labeled T_{1-4}) to which it can diffuse. For any given H₂O orientation, however, a complete atop to atop diffusion step between T_0 and T_1 is equivalent to diffusion between T_0 and T_3 . Likewise diffusion between T_0 and T_2 is equivalent to diffusion between T_0 and T_4 . Thus the number of distinct candidates for diffusion mechanisms is reduced to two: for example, $T_0 \leftrightarrow T_1$ and $T_0 \leftrightarrow T_2$. Given that the azimuthal rotation (Φ) of H₂O at both the atop and bridge sites is facile, routes to T_1 and T_2 have been considered with H₂O in two distinct orientations. In one we use the favored

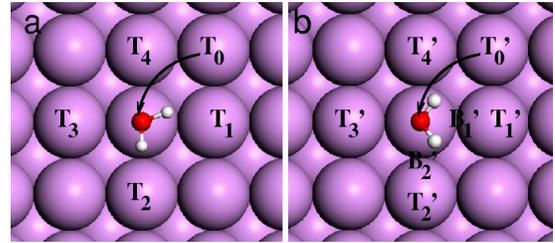


FIG. 2. Top views of the two H₂O orientations used to investigate H₂O diffusion on Al{100}. The labels assigned to various high symmetry sites are also shown.

orientation of H₂O at the atop site, i.e., with an OH bond pointing toward an adjacent atop site, as shown in Fig. 2(a). Diffusion processes with this orientation are labeled $T_0 \leftrightarrow T_1$ and $T_0 \leftrightarrow T_2$. The second orientation is the preferred orientation for H₂O at the bridge site, i.e., with the molecular dipole plane aligned to the $\langle 011 \rangle$ plane [Fig. 2(b)]. Diffusion processes with this orientation are labeled $T'_0 \leftrightarrow T'_1$ and $T'_0 \leftrightarrow T'_2$. Thus four microscopic diffusion processes were mapped out in detail. Each route was investigated by moving H₂O from its initial to its final atop site subject to a single (Cartesian) constraint on the oxygen.

Table I lists the activation energies (E_a) determined for the four diffusion mechanisms investigated. The E_a for a given route is the energy difference between the highest and lowest energy points along that route. The activation energies determined for the four routes range from 307–327 meV. It is clear, therefore, that all diffusion mechanisms have reasonably similar activation energies. This implies that given a H₂O at an atop site on Al{100} it does not have a strong preference for a particular direction in which to diffuse. An examination of Fig. 3, however, which displays the energy profiles for each route, reveals that each route exhibits some interesting characteristics. The most striking features of the calculated energy profiles are the minima at 0.05–0.10 Å from the precise atop sites. This is most apparent for routes $T'_0 \leftrightarrow T'_1$ and $T'_0 \leftrightarrow T'_2$ where ~ 60 meV minima are located on either side of the precise atop site. These minima demonstrate that H₂O prefers to be displaced slightly from the precise atop sites. Indeed structure optimizations with H₂O allowed to fully relax, i.e., with no constraints on the O position, confirm this. In practice, therefore, when H₂O ad-

TABLE I. Activation energies (E_a) for H₂O diffusion along the four pathways investigated, as shown in Fig. 3. E_a is the energy difference between the highest and lowest energy points along each route. The energy differences between H₂O at the atop and bridge sites ($\Delta_{\text{top-bridge}}$) along each route are also shown.

Route	E_a (meV)	$\Delta_{\text{top-bridge}}$ (meV)
$T_0 - T_1$	307	292
$T_0 - T_2$	309	299
$T'_0 - T'_1$	327	225
$T'_0 - T'_2$	309 (294) ^a	247 (244) ^a

^aThe values in parentheses have been calculated with a $12 \times 12 \times 1$ \mathbf{k} -point mesh and a plane wave cut-off energy of 440 eV.

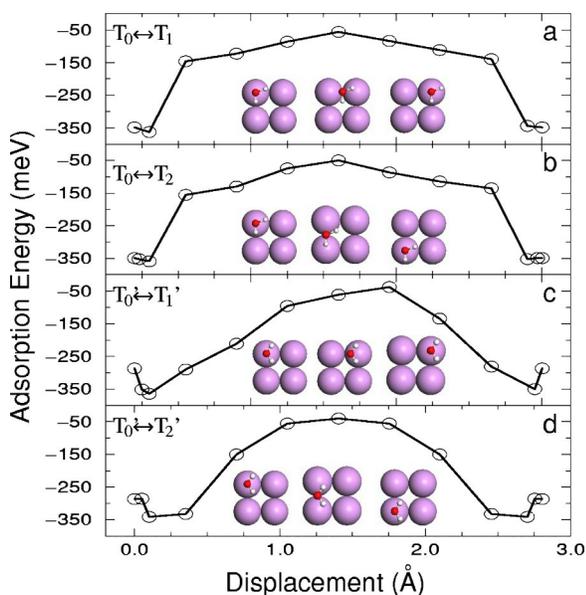


FIG. 3. Variations in H₂O adsorption energy as a function of the lateral displacement of O from its original atop site for the four H₂O diffusion routes investigated on Al{100}. The structure of the initial, transition and final states of each pathway are also shown. The solid lines connecting the data points are guides to the eye. Note that route $T_0' \leftrightarrow T_2'$ (d) is entirely symmetric about the transition state at the bridge site.

sorbs on Al{100} it will be displaced slightly from the precise atop site. In fact our calculations indicate that the precise atop is not an energy minimum on the multidimensional PES. An implication for diffusion is that there tends to be a small energy barrier, the magnitude of which depends on the orientation of H₂O, for H₂O to move from one side of the precise atop site to another. The second thing we note from Fig. 3 is that the energy profiles are reasonably symmetric about the highest energy points, which tend to be located at bridge sites. For route $T_0' \leftrightarrow T_2'$ this is trivial since the bridge site is a mirror plane along this route. $T_0 \leftrightarrow T_1$ and $T_0 \leftrightarrow T_2$ exhibit a small asymmetry in energy on either side of the bridge site, on the order of 50 meV. Route $T_0' \leftrightarrow T_1'$, however, stands out as it clearly exhibits the greatest asymmetry. Indeed in this case the barrier for diffusion is not even located over a bridge, rather it is displaced towards the atop site T_1' . Thus for H₂O diffusion in this orientation there is a small barrier (25 meV) between the bridge site B_1' and the atop site T_1' (Fig. 2). It is obvious from the energy profiles displayed in Figs. 3(a)–3(d) that the bridge site is not an energy minimum. Rather it tends to be an energy maximum. Given that the fourfold hollow sites and the *precise* atop sites

are also not minima, then none of the high symmetry sites are minima on the PES. However, as can be inferred from Fig. 3 and as stated above, minima are located very close to the atop sites.

It is almost universally assumed that the diffusion barrier for an adsorbate can be simply predicted from the difference in adsorption energies at the most stable and the next most stable high symmetry adsorption sites. An important consequence of the complexities in the diffusional potential energy surfaces shown in Fig. 3, however, is that this is clearly not the case for H₂O diffusion on Al{100}. The barriers obtained for each route are always larger than the binding energy difference for H₂O at the atop and bridge sites. These comparisons are made in Table I where it can be seen that the differences in binding energies between bridge and atop sites range from 225–299 meV (depending on the orientation of H₂O) whereas the diffusion barriers are between 307 and 327 meV. Also shown, in parenthesis, for route $T_0' \leftrightarrow T_2'$, are the results obtained with a more accurate computational setup (12×12×1 **k**-point mesh and a plane wave cutoff energy of 440 eV). These results differ from the standard calculations by ≤15 meV, which gives an indication of the numerical accuracy of our calculations.

The results presented here clearly reveal that in order to accurately determine the activation energy for the diffusion of H₂O monomers on Al{100} it is necessary to explicitly calculate points on the PES between the atop and bridge sites. Ge and King recently came to a similar conclusion for CO diffusion on metal surfaces,^{8,9} where it was shown that for CO diffusion along $\langle 1\bar{1}0 \rangle$ plane of Pt{110} and Cu{110} there exists energy barriers of ~150 meV between atop and bridge sites. Finally, we note that the results presented here relate to the diffusion of H₂O monomers at low coverage across the Al surface. The diffusion of H bonded H₂O clusters (dimers, trimers, etc.) across metal surfaces can be more complex, as recently discussed elsewhere.^{5,34}

To conclude, the adsorption and diffusion of H₂O on Al{100} has been examined within the plane-wave pseudo-potential formalism of DFT. We have found that H₂O adsorbs preferentially at atop sites and the activation energies for H₂O diffusion over bridge sites are >300 meV. There is a small orientational dependence on the magnitude of these diffusion barriers and in every case the barriers are larger than those that would be predicted based on a comparison of H₂O binding energies at atop and bridge sites.

A.M. gratefully acknowledges Gonville and Caius College for support. V.A.R. acknowledges support from CONICET (Argentina). The Cambridge High Performance Computing Facility is thanked for computing time.

¹P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987).

²M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002), and references therein.

³M. Morgenstern, T. Michely, and G. Comsa, Phys. Rev. Lett. **77**, 703 (1996).

⁴K. Morgenstern and J. Nieminen, Phys. Rev. Lett. **88**, 066102 (2002).

⁵T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, Science **297**, 1850 (2002).

⁶K. Morgenstern and K.-H. Rieder, J. Chem. Phys. **116**, 5746

- (2002).
- ⁷J. Greeley, J. K. Nørskov, and M. Mavrikakis, *Annu. Rev. Phys. Chem.* **53**, 319 (2002).
- ⁸Q. Ge and D. A. King, *J. Chem. Phys.* **111**, 9461 (1999).
- ⁹Q. Ge and D. A. King, *J. Chem. Phys.* **114**, 1053 (2001).
- ¹⁰S. Yamagishi, S. J. Jenkins, and D. A. King, *Chem. Phys. Lett.* **367**, 1343 (1999).
- ¹¹J. Kua, L. J. Lauhon, W. Ho, and W. A. Goddard III, *J. Chem. Phys.* **115**, 5620 (2001).
- ¹²X. W. Sha and B. Jackson, *Chem. Phys. Lett.* **357**, 389 (2002).
- ¹³A. Michaelides, P. Hu, and A. Alavi, *J. Chem. Phys.* **111**, 1343 (1999).
- ¹⁴A. Michaelides and P. Hu, *J. Chem. Phys.* **114**, 513 (2001).
- ¹⁵A. Michaelides and P. Hu, *J. Am. Chem. Soc.* **128**, 4235 (2001).
- ¹⁶A. Michaelides, A. Alavi, and D. A. King, *J. Am. Chem. Soc.* **125**, 2746 (2003).
- ¹⁷P. J. Feibelman, *Science* **295**, 99 (2002).
- ¹⁸P. J. Feibelman, *Phys. Rev. Lett.* **90**, 186103 (2003).
- ¹⁹S. Meng, L. F. Xu, E. G. Wang, and S. Gao, *Phys. Rev. Lett.* **89**, 176104 (2002).
- ²⁰J. E. Muller and J. Harris, *Phys. Rev. Lett.* **53**, 2493 (1984).
- ²¹S. Seong and A. B. Anderson, *J. Phys. Chem.* **100**, 11 744 (1996).
- ²²E. Sophr and K. Heinzinger, *Chem. Phys. Lett.* **123**, 218 (1986).
- ²³A. B. Anderson, *Surf. Sci.* **105**, 159 (1981).
- ²⁴S. K. Saha and N. C. Debnath, *Chem. Phys. Lett.* **121**, 490 (1985).
- ²⁵S. Jin and J. D. Head, *Surf. Sci.* **318**, 204 (1994).
- ²⁶H. Yang and J. L. Whitten, *Surf. Sci.* **223**, 3131 (1989).
- ²⁷C. Bauschlicher, Jr., *J. Chem. Phys.* **83**, 3129 (1985).
- ²⁸S.-B. Zhu and M. R. Philpott, *J. Chem. Phys.* **100**, 6961 (1994).
- ²⁹M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- ³⁰D. Vanderbilt, *Phys. Rev. B* **41**, R7892 (1990).
- ³¹J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ³²H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ³³A. Michaelides, V. A. Ranea, P. L. de Andres, and D. A. King, *Phys. Rev. Lett.* **90**, 216102 (2003).
- ³⁴V. A. Ranea, A. Michaelides, R. Ramirez, P. L. de Andres, J. A. Verges, and D. A. King (unpublished).