

# Investigation of chemisorbed molecular states for oxygen on rhodium (111)

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(Received 10 March 2000; accepted 5 June 2000)

Using density-functional theory, we provide the first conclusive evidence of the existence of a molecularly chemisorbed state for oxygen on the Rh (111) surface. Four species are identified: a paramagnetic state above the bridge site with a binding energy of 1.95 eV, a more weakly bound paramagnetic state above the top site with a binding energy of 0.95 eV, and two nonmagnetic states above the face-centered-cubic (fcc) and hexagonal-close-packed (hcp) hollow sites each with a binding energy of 1.98 eV. We compare these results with our calculations of the binding energy for atomic oxygen on the fcc and hcp hollow sites and an upper bound on the dissociation barrier to understand major portions of the dissociation reaction coordinate. Combining our data with the experimental and theoretical results for oxygen dissociation on many other fcc (111) metal surfaces, we conclude that all these metal surfaces possess similar minima corresponding to physisorption, molecular chemisorption, and dissociative chemisorption. Despite these similarities, the differing binding energies and barrier heights account for the varying mechanisms of oxygen dissociation on different fcc (111) surfaces. © 2000 American Institute of Physics. [S0021-9606(00)70633-7]

## I. INTRODUCTION

A fundamental step in heterogeneous catalytic oxidation is the initial adsorption of oxygen onto metal surfaces. Much attention has been directed towards understanding the potential energy surfaces (PES) involved in this process. Detailed knowledge of the species involved in the PES can allow for a greater understanding of ways to improve the catalytic properties or impede oxidation and corrosion of metal surfaces.

On most fcc (111) metal surfaces, evidence of three general types of adsorption (physisorption, molecular chemisorption, and dissociative chemisorption) have been shown experimentally and/or theoretically. In many cases adsorption is seen to go sequentially through these three steps with the physisorbed state leading first to molecular chemisorption and then proceeding to dissociation. Pt, Ni, Pd, Cu, Ag, Ir, and even the simple metal Al are examples of fcc metals for which there is evidence for a molecularly chemisorbed state.<sup>1-7</sup> However, there is no direct evidence for such a state on Rh (111). There have been two recent<sup>8,9</sup> experimental investigations of the adsorption of oxygen on Rh (111). The first study directly probed the low-temperature adsorption of oxygen and found no evidence of a stable chemisorbed precursor. The second investigation detailed the adsorption kinetics for oxygen on Rh (111). In this second paper, dissociation kinetics suggested the existence of a transient

molecularly chemisorbed species, but no direct evidence was shown. Because the apparent lack of stable molecularly chemisorbed states sets the behavior of oxygen on Rh (111) apart from other metals, it is important to investigate the nature of molecular oxygen on this surface. In this paper, we present calculations using density functional theory (DFT)<sup>10,11</sup> showing the first conclusive evidence of the existence of a molecularly chemisorbed oxygen species on the Rh (111) surface.

## II. METHOD

In this investigation, all calculations were performed using the plane-wave pseudopotential method.<sup>12-14</sup> Unless otherwise specified, all calculations used the generalized gradient approximation<sup>15</sup> self-consistently as well as spin-polarization. Oxygen was modeled using the optimized pseudopotential method<sup>16</sup> while rhodium was modeled with a designed nonlocal pseudopotential<sup>17</sup> to achieve higher accuracy. Before calculations with oxygen on the rhodium surface were performed, we first investigated bulk rhodium and the bare (111) surface. Using 60 irreducible *k*-points in the primitive fcc unit cell we obtained an equilibrium lattice constant of 3.81 Å and a bulk modulus of 2.82 Mbar. This lattice constant was used in all subsequent calculations. These values are in excellent agreement with the experimental values of 3.803 Å and 2.69 Mbar.<sup>18</sup> For the bare (111) surface, a relaxation of -1.7% for the first layer spacing and -1.0% for the second are in excellent agreement with experimental

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low-energy electron diffraction (LEED) studies<sup>19</sup> which show  $(-1.4 \pm 0.9)\%$  and  $(-1.4 \pm 1.8)\%$  for the first and second layer spacing, respectively.

Because of the small bond length in gas phase  $O_2$ , a small core radius must be used when computing an atomization energy with pseudopotentials. Because of this, we have followed a procedure for adjusting the zero of energy of the oxygen pseudopotential to match a smaller core calculation as given in Ref. 20. For the small core data, we have chosen the highly accurate calculation given by Porezag *et al.*<sup>21</sup>

All calculations of molecular chemisorption energies were performed in a  $2 \times \sqrt{3}$  surface unit cell with a  $(2 \times 2 \times 1)$   $k$ -point set<sup>22</sup> and a temperature broadening of 0.3 eV. The Brillouin zone sampling was checked by comparing it to calculations using a  $(6 \times 6 \times 1)$   $k$ -point set which is converged to within 5 meV/unit cell. Our testing shows that although the  $(2 \times 2 \times 1)$   $k$ -point set yields errors of 150 meV/unit cell, energy differences are converged to 30 meV. In all molecular chemisorption calculations the oxygen coverage was one molecule for every four rhodium surface sites (1/4 coverage). Because of the complexities involved in searching the six-dimensional coordinate space associated with chemisorption of molecular oxygen, a preliminary search of the coordinate space was first performed by using a number of less well-converged (and therefore, less expensive) calculations to locate the preferred oxygen orientations. A first series of calculations used a three layer rhodium slab with four layers (8.73 Å) of vacuum. Also, this first set of calculations was performed with the non-spin-polarized local density approximation<sup>23</sup> for the exchange and correlation energies. Using these preliminary results as a guide, a second set of calculations was performed to determine the binding energies of the molecules accurately. This second phase used a five layer rhodium slab with seven layers of vacuum (15.28 Å). Also, the generalized gradient approximation (GGA) and spin-polarization were used in this final phase.

### III. RESULTS

During our comprehensive search for minima, oxygen was placed on one side of the rhodium slab and the top layer of rhodium and the perpendicular coordinates were relaxed (in-plane oxygen coordinates were fixed throughout the relaxation). This process was repeated for many different center-of-mass (COM) positions and rotation angles ( $\theta$ ) about the COM parallel to the surface. In all calculations, the initial tilt angle ( $\phi$ ) was selected to be 0 and allowed to relax. Seven COM locations were examined, distributed about the irreducible wedge of the (111) surface, as shown in Fig. 1. For each COM position, from 1 to 6 lateral rotation angles were chosen as starting positions for the molecule. The binding energies and lateral forces obtained are reported in Table I. Restricting the relaxation to the perpendicular coordinates allowed for a systematic study of the effects that the rotation angle and COM position have on the binding energy of the molecule. For example, the low binding energy of ls2 compared to all its neighbors (ls1, ls3, top, and bridge) mark it as a local maximum. The lateral forces on the molecule give additional information concerning the preference

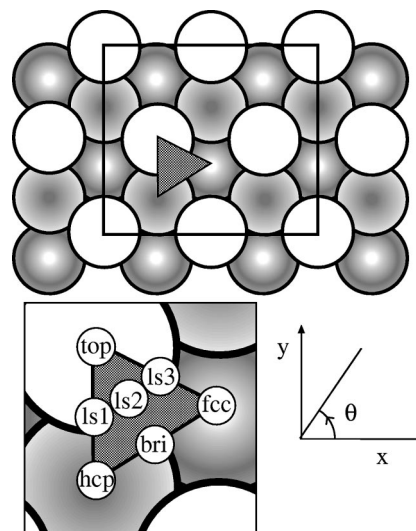


FIG. 1. Illustration of the Rh (111) surface. Outlined in black is the  $2 \times \sqrt{3}$  unit cell used in the calculations. The shaded triangle is the irreducible wedge of the surface. The top, bridge, fcc, and hcp hollow sites are marked in the enlarged frame. Also marked are the three low-symmetry sites (ls1, ls2, and ls3) that were investigated.

of a COM or orientation. Sites ls1 and ls3 show a clear COM force toward more stable bridge and hollow sites. Also, the bridge site shows rotational forces towards its preferred  $110^\circ$  orientation. This comprehensive search identifies the top, fcc and hcp sites with  $30^\circ$  rotations and the bridge site with  $110^\circ$  rotation as the most probable candidate structures for bound molecular states based on binding energies. These four candidates were also the only structures to have nearly equal and opposite forces on the oxygen atoms directed along the molecular bond axis, indicating a preference for the selected rotation.

To complete the identification of the candidate sites and orientations of the molecule, a relaxation of the in-plane degrees of freedom of the molecule and the top layer of the

TABLE I. Local density approximation (LDA) binding energies and oxygen atom forces for candidate geometries for molecular chemisorption of oxygen on rhodium (111). In this table,  $\theta$  is the in-plane rotation angle in degrees. The oxygen atoms are designated "left" or "right" relative to the COM in the plane of Fig. 1.  $F_{\text{mag}}^L$  is the magnitude of the force on the left oxygen atom in eV/Å and  $F_\theta^L$  is the angle (in degrees) that the force on this atom makes with Cartesian  $x$  axis shown in Fig. 1.

COM	$\theta$	$E_b$	$F_{\text{mag}}^L$	$F_\theta^L$	$F_{\text{mag}}^R$	$F_\theta^R$
fcc	0	2.20	1.0	338	1.4	165
fcc	30	2.65	0.2	208	0.9	33
hcp	30	2.77	1.0	210	0.5	29
bri	0	2.08	2.2	150	1.9	328
bri	30	1.50	0.3	197	1.1	215
bri	90	2.60	1.1	350	1.1	78
bri	100	2.63	0.8	100	0.8	294
bri	110	2.65	0.6	118	0.6	293
bri	120	2.58	0.6	113	0.5	289
top	0	1.37	0.4	182	0.4	358
top	30	1.43	0.5	206	0.5	26
ls1	30	1.64	1.2	221	0.5	186
ls2	30	1.33	1.2	201	1.1	30
ls3	30	1.53	0.4	7	1.1	13

TABLE II. Binding energies and geometries for molecular chemisorption of oxygen on rhodium (111). In the table,  $R$  is the oxygen–oxygen bond length,  $z$  is the distance between the COM of the molecule and the surface,  $\theta$  is the rotation angle and  $\phi$  is the tilt angle.

Site	$E_b$	$R$	$z$	$\theta$	$\phi$
fcc	1.98	1.37	1.75	30	11
hcp	1.98	1.37	1.76	30	10
bri	1.95	1.32	1.93	116	0
top	0.95	1.32	1.94	27	0

surface was performed. After achieving the optimized structure, a perturbation of the rotation angle and bond length of the molecule was performed. Then, a final relaxation was performed to ensure that the same minimum structure was obtained.

After identifying the sites for molecular chemisorption, a full relaxation of each candidate geometry was performed using a 5 layer slab with 7 layers of vacuum. This final set of molecular calculations was performed using GGA and spin-polarization in order to determine the binding energies accurately. These results are shown in Table II. For these calculations, oxygen was placed on both sides of the surface to remove any dipole effects. The data show that the fcc and hcp states are the lowest energy configurations, with a binding energy of 1.98 eV for both and no magnetic moment. The bridge site is slightly less stable with a binding energy of 1.95 eV. One more weakly bound state is identified at the top site with a binding energy of 0.95 eV. Both the bridge and the top site have a magnetic moment of about  $1 \mu_B$ .

#### IV. DISCUSSION

The existence of molecular chemisorption on Rh (111) is not surprising when one considers that all other fcc (111) transition metals (excluding gold which does not adsorb oxygen at low temperatures) have been shown to exhibit a molecularly chemisorbed precursor state. For example, a peroxo state ( $O_2^-$ ) at the bridge site and the top site have been identified on Cu (111) using high-resolution electron energy-loss spectra (HREELS).<sup>4</sup> Similarly, a peroxo and superoxo ( $O_2^-$ ) state have been found on Ir (111) using EELS measurements,<sup>6</sup> although the states were not seen until a partial coverage of atomic oxygen was formed. Recent molecular beam experiments have shown evidence suggesting that molecularly chemisorbed states form on Ni (111).<sup>24</sup> This was verified by first-principles calculations of molecular precursor states on Ni (111).<sup>2</sup> Molecular beam experiments have also shown evidence for molecular precursors on Ag (111).<sup>5</sup>

Platinum is perhaps the most widely studied example of oxygen chemisorption on an fcc (111) surface. Experiments have conclusively shown that the bridge, fcc and hcp hollow sites are locations for stable molecular chemisorption.<sup>27</sup> A recent *ab initio* study of the molecular states on Pt (111) found non-magnetic peroxo states at the fcc and hcp hollow sites.<sup>1</sup> Both states were found to be tilted downward towards the bridge site ( $10.4^\circ$  for the fcc and  $8.4^\circ$  for the hcp bound state). On Rh (111) we find a non-magnetic peroxo state with a  $10^\circ$  tilt at the fcc site and one with almost the same tilt

TABLE III. Binding energies (in eV/atom) of atomic oxygen on selected fcc (111) surfaces.

Metal	Coverage	$E_b^{\text{fcc}}$	$E_b^{\text{hcp}}$
Rh	0.5	2.20	2.11
Rh	1.0	1.67	1.55
Ni <sup>a</sup>	0.25	2.3	2.2
Ni <sup>a</sup>	0.5	1.9	1.8
Pt <sup>b</sup>	0.25	1.23	0.78

<sup>a</sup>From Ref. 2.

<sup>b</sup>From Ref. 28.

angle at the hcp site, a very similar result. The Pt study also identified a magnetic superoxo state at the bridge site, with its bond axis parallel to the surface and a bond length shorter than that of the peroxo state. These structural results are in agreement with our results for the bridge site of Rh (111). The relative energetics will be discussed below.

We find one additional weakly bound state at the top site. This state appears to be similar to a state that has been seen experimentally on Pd (111) with a stretching frequency of  $1035 \text{ cm}^{-1}$ .<sup>3</sup> This high stretch frequency implies a weaker interaction with the surface compared to the normal peroxo and superoxo states seen on most fcc (111) surfaces. These results combine to demonstrate that the molecularly chemisorbed species we have found on Rh (111) are typical for oxygen interacting with a fcc (111) metal surface.

To learn more about the PES for oxygen adsorption it is instructive to compare the binding energy of the oxygen molecule to that of the atom. Rh (111) binds atomic oxygen very strongly, and, as was shown in a recent atomic beam experiment,<sup>25</sup> is limited only by the dissociation step of molecular oxygen in forming coverages beyond a half monolayer. Using a seven layer, two site unit cell (all other computational parameters equivalent to the molecular calculations), we have determined the binding energy of a half and full monolayer of oxygen adsorbed in the fcc and hcp hollow sites. These results are shown in Table III. These data are in reasonable agreement with previous *ab initio* calculations by Ganduglia-Pirovano and Scheffler.<sup>26</sup> Our results show that both atomic and molecular oxygen are strongly bound to the Rh (111) surface. The fact that experiment has not shown a molecular species with any observable lifetime may seem to contradict our findings. Examining the PES will explain how these results complement experiment.

Much can be learned by comparing our results with previous studies of oxygen adsorption on other fcc (111) surfaces. The Rh (111) surface shows behavior similar to Ni (111). For instance, on both surfaces strongly bound molecularly chemisorbed states exist above many high symmetry sites. Furthermore, the difference in the fcc and hcp adsorption energies is quite small for both atomic and molecular adsorption. On Pt (111) however, molecular and atomic oxygen (see Table III) bind much more weakly and there is a sizeable difference between binding energies at the fcc and hcp hollow sites. This points to the overall trend that the atomic and molecular chemisorption potential wells are dramatically shifted downward in energy on Rh and Ni compared to Pt.

The stability of molecular oxygen on Pt (111) compared to the more active surfaces such as Rh (111) and Ni (111) displays a significant difference in the dissociation PES. The barrier for dissociation has been estimated to be 0.75 eV for oxygen on Pt (111).<sup>1</sup> On Ni (111), a much smaller barrier of 0.2 eV was calculated for this transition. To compare with this result, we computed the total energy of molecular oxygen centered over the fcc hollow for bond lengths ranging from 1.30 Å (molecular chemisorption) to 2.30 Å (dissociated atoms). Over this entire range the binding energy stayed within 0.17 eV of the energy at 1.30 Å giving an upper limit of 0.17 eV for the dissociation barrier.

These results clarify the nature of oxygen adsorption on transition metal surfaces. Our results for oxygen on Rh (111) make clear that increased activity of a metal towards oxygen adsorption occurs because of a downward shift in energy of the entire adsorption PES (bound states as well as barriers). For instance, the atomic chemisorption potential well is much shallower for oxygen on Pt (111) compared to that of Rh (111). Furthermore, the binding energy for a molecular state is also larger on Rh (111). Most importantly, the barrier between these two states is also shifted downward resulting in a very short lived molecular species on Rh (111).

## V. CONCLUSION

We have shown the first direct evidence of the existence of a molecularly chemisorbed state of oxygen on Rh (111). We have also presented our calculations of the binding energies of atomic overlayers on Rh (111). No direct experimental evidence for molecular chemisorption of oxygen on Rh (111) has been shown to date, and our calculations provide an explanation for this result. Molecularly chemisorbed states exist and are quite stable with respect to the free molecule, but the barrier between the molecularly chemisorbed and dissociated states is found to be low enough to give the molecular state a very short lifetime.

## ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMR 97-02514 and the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant No. F49620-

00-1-0170. A.M.R. would like to thank the Alfred P. Sloan Foundation for support. Computational support was provided by the National Center for Supercomputing Applications and the San Diego Supercomputer Center. The authors would like to thank Steven J. Sibener, Cynthia M. Friend, Melvin C. Chen, and Yashar Yourdshahyan for valuable discussions.

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