

## Oxygen Molecule Dissociation on the Al(111) Surface

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The dissociative adsorption of the O<sub>2</sub> on the Al(111) surface is studied using *ab initio* calculations based on density-functional theory. In the sticking probability experiments an activation barrier for the O<sub>2</sub> dissociation exists, but our calculations predict a barrier only for one trajectory. Also our results do not support the model of charge transfer from the surface to the molecule as a bond breaking mechanism. Instead, the increasing hybridization between O<sub>2</sub> orbitals and Al states, when the adsorbate approaches the slab, is significant for the dissociation.

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In the molecular level the mechanisms of oxygen molecule chemisorption and dissociation on aluminum surfaces have not been resolved in detail although these reactions have been studied using a large variety of experimental and theoretical techniques [1–3]. From the technological point of view the oxygen molecule chemisorption and dissociation are very interesting because they are the fundamental steps for the oxidation of aluminum which is an important process anywhere Al is used. To our knowledge there are only a few models for the oxidation of the aluminum surface [2,3] and qualitative information is sparse. Experiments show that the interaction between an oxygen and an aluminum surface differs remarkably from that between an oxygen and a transition metal surface but they reveal very little of the origin of this difference. In general, an oxygen molecule has a stable chemisorbed state on a transition metal surface with a relatively high barrier for dissociation. In the case of an aluminum surface the chemisorption is always dissociative without any precursor state. Recent experiments and theoretical calculations support chemisorption only on the fcc sites of the first layer of Al(111) [2,3], and oxygen does not penetrate into subsurface sites [4]. Two possible dissociation mechanisms for an oxygen molecule on an aluminum surface have been proposed. The scanning tunneling microscopy (STM) experiments by Brune *et al.* [2] show that during the dissociation oxygen atoms move at least 80 Å away from each other on the surface before they slowly lose their kinetic energy and become immobile. According to their interpretation both the oxygen atoms behave similarly. In the article of Österlund *et al.* [1], the dissociation results from the charge transfer from the Fermi level of the surface to the antibonding, lowest unoccupied molecular orbital which creates an intermediate asymmetric repulsive ion state O-O<sup>-</sup>. This causes the nuclei to separate and enables further electron transfer from the surface to the “molecule.” Because of the asymmetric charge distribution the trajectories of the atoms of a molecule are very different. While the first oxygen ends up directly into the fcc site after dissociation and immobilizes near the point of impact, the other oxygen moves around above the surface before it also ends up into the fcc site.

Calculations for the adsorption process of O<sub>2</sub> on the Al(111) surface have not been done so far, even though the oxygen molecule dissociation paths on Pt(111) [5] and Ag(110) surfaces [6] have been examined. In this paper we study the chemisorption and dissociation of O<sub>2</sub> on Al(111). This is an excellent model system for these two processes because of its apparent simplicity compared to transition metal systems. This study also gives information of the dissociation of O<sub>2</sub> on non-*d*-electron metal surfaces and thus completes the few existing studies on Pt and Ag surfaces.

We employ density-functional theory and solve the Kohn-Sham equations self-consistently. For Al atoms, we use a norm-conserving Bachelet-Hamann-Schlüter pseudopotential [7] where the *d* component is local. O atoms are treated with Vanderbilt ultrasoft pseudopotential [8] which enables us to use the cutoff energy of 23 Ry. The electron exchange-correlation energy is described using local-spin-density approximation [9] together with generalized gradient approximation (GGA) by Becke and Perdew (BP86) [10,11] and also with the new revised Perdew-Burke-Ernzerhof (RPBE) gradient correction [12].

For the Al(111) surface a 2D grid of 16 *k*-points is used. To improve *k*-space integration we smear out the Fermi surface by using a Fermi distribution with the effective temperature  $kT_e = 0.2$  eV. All our calculations are carried out employing the parallel pseudopotential plane wave code called FINGER (Finnish general electron relaxator).

The theoretical lattice constant for equilibrium bulk Al is found to be 3.97 Å which is used in all present calculations. The Al(111) surface is modeled by a five layer thick slab with a 2 × 2 surface cell. The vacuum between slabs is 8 Å. We neglect surface relaxations because according to our calculations they seem to be small for the present system. Calculations for the O<sub>2</sub> molecule in vacuum give a binding energy 5.3 eV and a bond length 1.24 Å (BP86). Corresponding experimental values are 5.2 eV and 1.21 Å [13]. To test our system we calculate equilibrium heights of oxygen atoms above the surface. For the energetically more favorable fcc site the equilibrium height is found to be 0.91 Å, which is higher than the experimental value 0.7 ± 0.1 Å [14] and that in Ref. [15]. The energy difference between fcc and hcp sites is 0.38 eV, which is in

accordance with the value 0.37 eV reported by Jacobsen *et al.* [15].

The trajectory of O<sub>2</sub> on the Al(111) surface is explored by calculating the total energy as a function of the height of the molecule from the surface, and the O-O bond length is optimized at each height. We have four starting geometries with BP86: top-top, hcp-top, and for hcp-fcc, both the parallel and tilted configurations (see the inset in Fig. 1). By tilted configuration we mean that the angle between the normal of the surface and the molecular axis is fixed but not equal to 90°. The potential energy decreases monotonically along the reaction coordinate for the dissociation paths. Our calculations support the direct dissociation channel for all the studied trajectories, in agreement with the experiments [1]. With the new RPBE gradient correction we explore six starting geometries: top-top, hcp-top, top-bridge-top, fcc-fcc, hcp-hcp, and hcp-fcc (see Fig. 1). We found three distinct type trajectories. The hcp-fcc trajectory has a 0.14 eV barrier about 2.5 Å from the surface. The adsorption paths 4, 5, and 6 are flat whereas 1 and 2 are more attractive. In Fig. 1 we compare the potential energy along three adsorption trajectories calculated with both the gradient corrections. Generally, the shapes of the curves are very similar but the small barrier observed with RPBE along the fcc-hcp trajectory is clearly visible. The three uppermost curves belong to RPBE calculations while the curves below these are obtained with BP86.

When the height of the molecule from the surface decreases, the O-O bond length increases and the spin polarization of O<sub>2</sub> decreases as shown in Table I for the hcp-fcc configuration.

Similar O-O bond stretching and spin lowering have been reported for the oxygen molecule dissociation on the

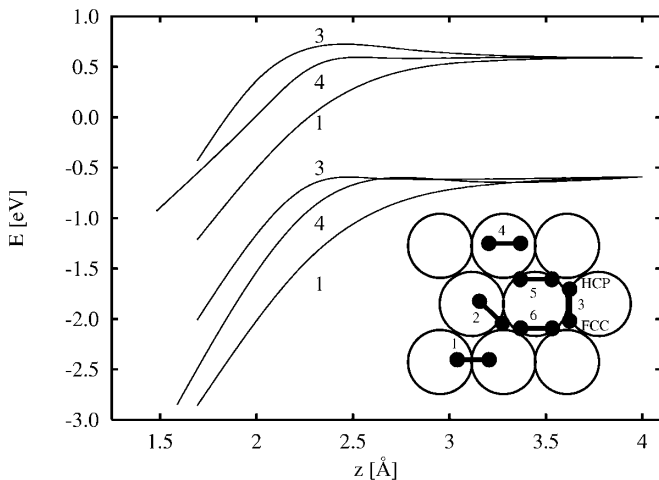


FIG. 1. The potential energy along the adsorption trajectories. The upper curves are calculated with RPBE and the lower curves with BP86. The zero energy level is the average of the potentials at 4 Å. The curves are labeled according to the numbering in the inset. The starting geometries: (1) top-bridge-top, (2) hcp-top, (3) hcp-fcc, (4) top-top, (5) hcp-hcp, and (6) fcc-fcc are indicated in the inset.

Ag(110) surface [6]. The molecular bond stretching has also been seen for the O<sub>2</sub>/Pt(111) system [5]. These quantities together with calculated vibrational frequencies have been interpreted to be the result of the charge transfer from the *d* orbitals of the surface atoms to the antibonding orbital of the oxygen molecule. The oxygen molecule first becomes superoxolike O<sub>2</sub><sup>-</sup> and then peroxolike O<sub>2</sub><sup>2-</sup> molecule. This finally leads to two separate oxygen atoms. The dissociation may take place directly or through molecular precursor states.

To analyze in more detail whether a similar charge transfer from the Al(111) surface to the oxygen molecule occurs we examine four points (shown in Table I) along the fcc-hcp-configuration dissociation path. At each height we investigate the changes in the charge density. The density difference has been defined as

$$\Delta\rho = \rho(\text{Al}(111) + \text{O}_2) - \rho(\text{Al}(111)) - \rho(\text{O}_2),$$

where  $\rho(\text{Al}(111) + \text{O}_2)$  is the full charge density,  $\rho(\text{Al}(111))$  is the density of the Al slab without the O<sub>2</sub> molecule, and  $\rho(\text{O}_2)$  is the density of the molecule in vacuum. In our system the charge transfers from the surface to the partially filled antibonding  $1\pi_g$  molecular orbital. In order to estimate the total charge flow to the molecule we integrate  $\Delta\rho$  within an equal strip around the molecule for each height in Table I. At the distances from 4.0 to 3.2 Å above the surface the total charge flow is about 0.1 electrons and from 2.3 to 1.5 Å the charge flow amounts to about 0.3 electrons. When the O-O bond length is 1.82 Å and the total spin of the system is zero, the charge transfer from the surface is at most 0.3 electrons. This bond length and total spin correspond to those of O<sub>2</sub><sup>2-</sup> but our analysis indicates that the charge of O<sub>2</sub> is *neither* 2-, nor 1-. When we integrate the density differences for each Al layer separately, it shows that the charge mainly transfers from the surface layer to the molecule while layers below the topmost layer practically remain unchanged. Separate integrals for positive and negative density differences in the proximity of the molecule and the uppermost layer of the slab show that there is a charge redistribution between the oxygens.

In Fig. 2 we display the charge densities of orbitals  $3\sigma_g$ ,  $1\pi_u$ , and  $1\pi_g$  when the molecule is in the hcp-fcc configuration and 1.5 Å from the surface. The charge density of

TABLE I. O-O bond length and spin for hcp-fcc configuration of the O<sub>2</sub> molecule with four distances from the surface (calculated with BP86).

| O-Al | Distance (Å) |  | Spin |
|------|--------------|--|------|
|      | O-O          |  |      |
| 4.0  | 1.25         |  | 1.89 |
| 3.2  | 1.26         |  | 1.77 |
| 2.3  | 1.33         |  | 0.98 |
| 1.5  | 1.82         |  | 0.00 |

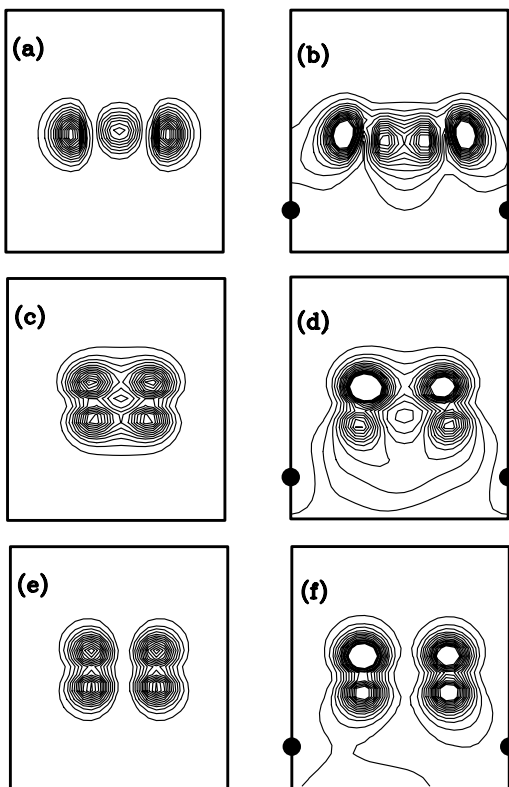


FIG. 2. The  $3\sigma_g$ ,  $1\pi_u$ , and  $1\pi_g$  orbitals for the  $O_2$  molecule are in (a), (c), and (e), respectively. The corresponding orbitals for  $O_2/Al(111)$  are in (b), (d), and (f). The black circles denote the positions of the two uppermost surface Al nuclei.

energy level is  $\rho_{ik}(\mathbf{r}) = |\psi_{ik}|^2$ , where  $i$  is the level and  $k$  is the  $k$ -point index. We concentrate here on one  $k$ -point. The molecular orbital charge densities are the sums of  $\rho_{ik}$  for the degenerate levels, and the orbitals are identified according to the shape of the electron density contours. In addition to these three orbitals we also see some slightly occupied  $3\sigma_u$  like states near the Fermi energy which are not seen when the molecule is  $2.3 \text{ \AA}$  from the surface. The number of states which density profile reminds that of the antibonding orbitals of  $1\pi_g$  and  $3\sigma_u$  increases considerably when the molecule approaches the surface, whereas the number of bonding type states decreases. As seen in Fig. 2 it is still reasonable to talk about the molecular orbitals even though the O-O bond has remarkably stretched. Figures 2b, 2d, and 2f indicate that there is some bonding interaction between the molecule and the substrate but it is difficult to estimate the strength of this interaction.

The sticking probability measurements of Österlund *et al.* [1] have indicated a small activation barrier (approximately 0.3 eV) for the oxygen molecule dissociation on the Al(111) surface. Our calculations with BP86 for the different adsorption paths do not show any activation barrier for the dissociation. The RPBE gradient correction improves the situation. One trajectory has a barrier and

three trajectories are very flat. We believe that these last-mentioned trajectories might also have a barrier but inaccuracies in the exchange-correlation interaction and the possible finite-size effects miss the barrier. Unfortunately, studying these finite-size effects is, at the moment, beyond our computational resources. Another explanation for missing the barrier could be the spin-flip effect. When the molecule is far from the surface it has a total spin 1 but closer to the surface the total spin approaches zero. In our calculations the spin can change continuously whereas in reality the spin can change only in quanta. We calculate (with BP86) four different  $O_2$  geometries with both spin states 1 (triplet) and 0 (singlet). Our calculations showed that the trajectories are always attractive and  $S = 0$  and  $S = 1$  curves cross without the barrier.

On transition metal surfaces local  $d$  orbitals, different for each adsorption site, donate charge to the molecule and the backdonation from the molecule to the substrate atoms may also take place. For CO on Pd(100) and CO on Rh(100) the back and forth charge transfer between the molecule and surface has been interpreted as a formation process of the bond [16,17]. We see some bonding between the  $O_2$  molecule and the surface atoms in the examined configuration. This is a bit of a surprise because no bonding is reported on the Ag(110) surface.

The total charge flow integrals suggest that there is only a small charge transfer from the surface to the antibonding orbital of the molecule but this transfer alone is not enough to break the oxygen-oxygen bond. When the oxygen molecule approaches the substrate the interaction between the molecule and the aluminum atoms increases which stretches the O-O bond. As a result of this the antibonding states come down in energy but are still above the bonding states. When the antibonding states are below the Fermi energy they weaken the O-O bond. The situation is rather delicate; the increase of the occupation of the antibonding orbitals will happen without significant external charge transfer. Electrons move from the bonding to the antibonding orbitals which is possible due to the hybridization of the molecular and the metallic states. In other words the weight of the bonding states *in the molecule* diminishes (note that the part of the charge of these states is in the metal) while the weight of the antibonding states in the molecule increases.

There is no indication of the asymmetrical charge transfer, so the intermediate asymmetric ion state  $O-O^-$  proposed by Österlund *et al.* seems improbable. The real dissociation events are dynamical processes and our total energy calculations are static. So it is difficult to say anything conclusive about the large distances between oxygen atoms after dissociation, seen in STM experiments of Brune *et al.* That would require a much bigger surface cell and real dynamic simulations.

In summary, we have presented *ab initio* total-energy calculations for  $O_2$  adsorptive dissociation on the Al(111)

surface. Our results support, with the RPBE gradient correction, the direct dissociation mechanism. The existence of the dissociation barrier of the  $O_2$  depends on the chosen GGA. With all the gradient corrections we found barrierless trajectories. In literature dissociation is generally thought to proceed via  $O_2^-$  and  $O_2^{2-}$  states in which the *antibonding* orbitals become occupied and thus first weakens the O-O bond and finally breaks it. This interpretation is based on the O-O bond length, spin lowering, and vibrational frequencies. In our calculations the bond lengths and spins are in a solid agreement with previous works, but our density difference analysis shows only a very small charge transfer from the surface to the molecule. In our understanding the dissociation mainly results from the redistribution of the charge inside the oxygen molecule and secondarily the charge transfer from the surface to the antibonding orbital. The amount of charge flow from the surface seems to be much less than one electron, so the dissociation via  $O_2^-$  and  $O_2^{2-}$  states does not seem probable to us.

During the preparation of this Letter two theoretical studies of  $O_2$  adsorption on the Al(111) were published [18,19]. Both works support the nonactivated dissociation process.

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