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Nonadiabaticity in the initial oxidation of Mg(0001): First-principles density-functional calculations

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The initial stage of magnesium oxidation, i.e., the dissociation of oxygen molecules, is investigated using first-principles density-functional calculations. Here, the lack of a barrier in all of the calculated two-dimensional cuts of the adiabatic potential energy surface is in strong disagreement with experimental evidence of a low sticking probability for thermal oxygen molecules. In light of recent developments for the related system $O_2/Al(111)$, we suggest that this discrepancy is due to nonadiabaticity in the initial oxidation. Based on a nonadiabatic charge-transfer model we provide an explanation for a recently measured thickness dependence in the oxidation rate of Mg(0001). Further, we suggest a similar behavior for the $O_2/Al(111)$ system.

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Almost all clean metal surfaces oxidize when in contact with an oxygen-rich atmosphere. Although this might sometimes be an unwanted process as is seen in car corrosion; under controlled conditions it has an enormous practical importance in both scientific and technological applications. For instance, thin oxide films are widely used as catalysts, sensors, dielectrics, and corrosion inhibitors. Hence, a general understanding of the oxidation process is one of the main goals in surface science.

The oxidation process of magnesium consists of a few elementary reaction steps, such as (i) the dissociative adsorption of the O_2 molecule, (ii) the migration of the O atom into the bulk, and (iii) the formation of the stoichiometric magnesium oxide (MgO). There is convincing experimental and theoretical evidence that the oxidation process begins with the dissociation of an oxygen molecule, which directly goes below the top Mg layer, followed by the formation of a subsurface two-dimensional (2D)-oxide layer.[1] Finally, when the oxide reaches a certain thickness it is transformed into the rock-salt structure of MgO. So far focus has been on either stage (ii) and (iii) whereas much less attention has been given to stage (i) dissociation of O_2 on the Mg(0001) surface.

According to indirect experimental studies[2,3] the initial sticking probability is low, $s_0 \approx 0.1$ for thermal oxygen molecules. The most obvious explanation is the existence of a barrier in the potential energy surface (PES) for dissociation. Using 15 trajectories based on first-principles molecular dynamics Bungaro *et al.*[4] found that all trajectories resulted in adsorbed atoms in subsurface sites. Due to the limited number of trajectories the contradiction between theory and experiment was not emphasized enough. As we will see later, there is no evidence of a barrier in any of the calculated 2D cuts of the adiabatic PES independently of the choice of exchange-correlation (xc) functional. This result suggests a unity in the sticking probability for thermal O_2 molecules on the Mg(0001), hence, a clear contradiction to experimental evidence.

The same contradicting feature is true for the closely related system $O_2/Al(111)$. Here, the most puzzling observation concerns the initial sticking probability. Molecular beam experiments find a strong translational energy dependence, going from $\sim 10^{-2}$ for thermal molecules to unity for molecules with a translational energy around 0.6 eV,[5] whereas extensive DFT calculations[6–8] reveal no evidence of a necessary barrier in the PES to explain the sticking behavior. Hence, any molecular dynamics simulation of the sticking probability based on the adiabatic PES would end up with a qualitatively wrong behavior compared with experiment, as was recently addressed and concluded[9] using first-principles molecular dynamics.

The lack of a barrier has led to the notion that one has to incorporate nonadiabatic effects into the dissociation process. In the literature a few different approaches have been suggested which are able to quantitatively reproduce the measured sticking behavior. The first approach is based on a discrete number of diabatic PESs.[10] The second approach focuses on the PES describing the triplet state of the O_2 molecule at the surface.[11] Finally, a third approach[12,13] involves charge transfer, a continuum of diabatic PESs, and an electronic dissipation channel via excitation of electron-hole (*e*-*h*) pairs[14,15] in the substrate. From the last model we were able to quantify a key parameter, electronegativity, that indicated if one needs to care about the nonadiabatic effect in the initial sticking process. Electronegativity measures the surface effected vertical affinity associated with the adsorbate. In the case of Al(111) both O_2 and NO falls into this category.[13] Due to the similarities with Mg(0001) we anticipated and here confirm that the same nonadiabaticity holds for the magnesium substrate. Hence, the concept of electronegativity can be applied to the ensemble of free-electron-like surfaces, to give us an indication of when to expect nonadiabaticity in the initial sticking process. Implications for the transition metals needs further study.

In this paper we examine the initial step in the oxidation of Mg(0001) by first principles. First, to get some idea about the dissociation process, large pieces of the multidimensional PES of O_2 on Mg(0001) are calculated by using density-functional theory (DFT) (Refs. 16 and 17) in the plane-wave pseudopotential code DACAPO.[18] The lack of a barrier prevents us from providing an explanation for the low thermal sticking probability of O_2 molecules on the Mg(0001) surface in an adiabatic picture. Instead we introduce nonadiabaticity by applying concepts as diabatic PESs, charge-transfer, and competing time scales which has been successfully applied to the $O_2/Al(111)$ system. As a result we can explain recent experiments that measured a thickness-dependent reactivity in the oxidation of Mg(0001).[3]

The Kohn-Sham wave function is expanded using plane waves with an energy cutoff of 25 Ry, whereas a 45 Ry cutoff is used for the charge density grid. Ultrasoft pseudopotentials[19] are used to describe the ionic cores; the k point sampling of the first Brillouin zone is preformed with a (4,4,1) Monkhorst-Pack grid,[20] and the xc functional is RPBE.[21] The magnesium surface is represented by a (2×2) surface with five layers in the supercell with an additional 18 Å of vacuum. The three top layers are allowed to relax, minimizing the Hellmann-Feynman force to less than 0.05 eV/Å. The found surface structure is later kept in frozen positions as we introduce the O_2 molecule.

The 2D cuts of the six-dimensional PES over high-symmetry sites shown in Fig. 1, are obtained by calculating total energies for different intramolecular (d_{O-O}) and center of mass (CM) distances (Z) from the Mg surface, with a stepsize of 0.1 and 0.5 Å, respectively. Note that both angular coordinates θ and ϕ are kept fixed. For a smoother PES a bicubic interpolation algorithm is used, taking into account the forces on the oxygen molecule and energies at each point.

In all of the 2D cuts, the lack of a barrier is evident. Instead there is an attraction of at least 0.1 eV stretching as far out as 3.5 Å. Farther out the attractive van der Waals forces should take over as the prominent effect. Hence, the low sticking probability of O_2 on Mg(0001) cannot be explained using the adiabatic PES, all in line with similar discussions on the oxidation of Al(111).

It has been reported[21] that some physical quantities, e.g., the chemisorption energy, depend rather strongly on the choice of the xc functional, especially when the density variations are substantial. To examine this effect we use two additional generalized-gradient approximations (GGA) along two reaction paths, the most attractive PES (perpendicular orientation over the fcc site) and the least attractive PES (parallel orientation of the atop site). The two GGA's are the Perdew-Wang 91 (PW91),[22] and the Perdew-Burke-Erzenhof (PBE) (Ref. 23) functional, both frequently used in the literature.

In Figs. 2(a) and 2(b), the effect of the xc along the reaction path is shown. Note that, here, the ϕ coordinate is allowed to relax. Although there are some changes in the strength of the attraction there is no sign that the present state-of-the-art xc functional would give rise to a barrier in the adiabatic PES. Of course this does not completely rule out the possibility that there is something missing in the approximative xc functionals. However it is beyond the scope of this study to investigate this further.

The lack of a barrier in the adiabatic PES raises the question of how well the initial oxidation of magnesium is described using the Born-Oppenheimer approximation. In the literature there are several studies providing experimental evidence of nonadiabatic effects associated with the oxidation process of magnesium, such as, photoemission and exoelectrons,[24] chemicurrent[25] and, as we will see below, thickness-dependent reactivity.[3]

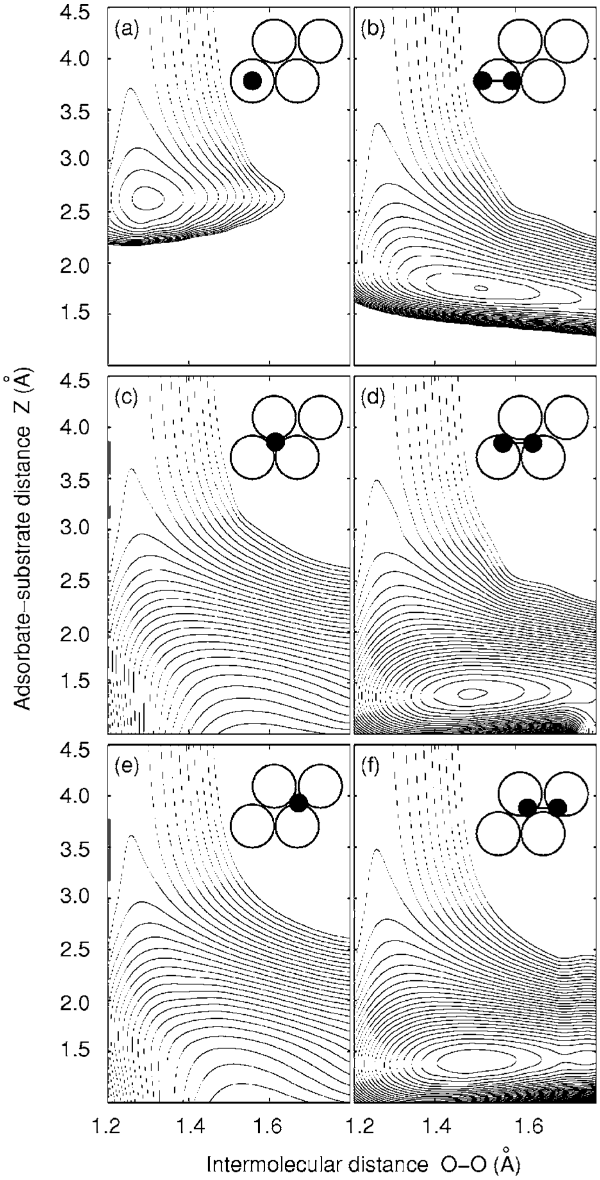

FIG. 1. Cuts through the six-dimensional PES of O_2 with bond length d_{O-O}, a distance Z above the Mg(0001) surface on all high-symmetry sites. Oxygen molecules are perpendicular over the (a) atop site, (c) fcc site, (e) hcp site, and parallel over (b) atop site, (d) fcc site, (f) hcp site. The equipotential contours are separated by 0.1 eV.

These nonadiabatic effects are a result of the dynamic conditions taking place during the dissociation process. As the O_2 molecule approaches the surface its lowest unoccupied molecule orbital (LUMO) $2\pi^*$ starts to interact with the substrate electrons, i.e., the LUMO broadens and its energy becomes lower until it is finally pushed below the Fermi energy, at which point a charge transfer (CT) from the substrate to the adsorbate takes place. The CT rate depends exponentially on the distance to the surface, and there exist a narrow region where a competition between the CT process

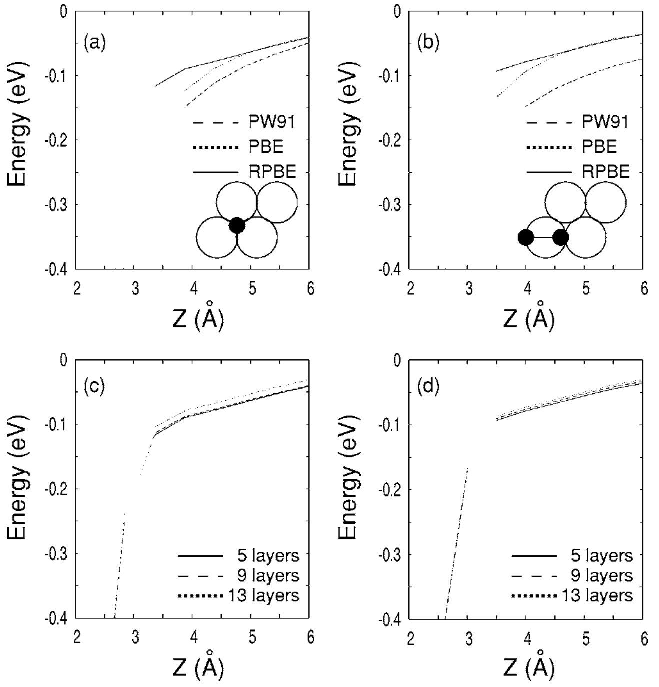

FIG. 2. The reaction path for an O_2 molecule in (a) perpendicular orientation over the fcc site (most attractive) and (b) parallel orientation over the atop site (least attractive) depending on the flavor of the xc functional. However, none of the used xc functionals show any sign of a barrier. In addition, we show the reaction path as a function of layers Mg(0001) for the (c) fcc site and (d) atop site. It is clear that the reaction path is not sensitive to the number of layers.

and the motion of the nuclei determines the occupancy of the $2\pi^*$ resonance. Incoming molecules with low initial translation energy might reach their classical turning point, i.e. the initial kinetic energy equals the obtained potential energy, before this region and bounce back into the gas phase. Molecules with high translation energies reach their classical turning point closer to the surface, hence, these molecules are inside this region and are more apt for CT, i.e., much more likely to dissociate. This is especially important for the simple metals where the wide *sp* band makes the CT rate small compared to the transition metals with their *d* states close to the Fermi energy.

Here we use the CT model,[12,13] even if the other two models[10,11] might be equally suited for the problem at hand, to provide an explanation for the low initial thermal dissociative sticking probability of O_2 on Mg(0001). The first pillar of the CT model is a diabatic picture in which there is a competition between the CT process and the motion of the adsorbate. The time development of the electronic population, $n_{O_2^-}$, of the approaching O_2 molecule is described by

$$\frac{d}{dt}n_{X_2^-}(t) = \tau_{res}^{-1} f(E^A[z(t)])[1 - n_{X_2^-}(t)], \qquad (1)$$

where τ_{res}^{-1} is the resonance filling rate, $f(E)$ the Fermi-distribution function, and $E^A[z(t)]$ the surface-affected vertical affinity. The resonance-filling rate is approximated as $\hbar\tau_{res}^{-1}=2\Delta\exp(-\alpha z)$,[26,27] where Δ and α describe the resonance width as a function of CM distance. It should be noted that Δ is linearly proportional to the density of states at the Fermi level $[\mathrm{DOS}(E_F)]$.[26,27] The second pillar of the CT model is the diabatic PESs on which the O_2 molecule approaches the surface. Here, the most important PESs are the O_2/Mg(0001)-PES and the O_2^-/Mg$^+$(0001)-PES, as the initial oxidation is initiated by a CT effectively bringing the system from the former PES to the latter one. As the *e-h* pair associated with the CT is a very efficient dissipation channel, we will assume that the hopping between the PESs is irreversible. In the case of O_2/Al(111) two different methods were used to calculate the diabatic PESs. The first is based on the Thomas-Fermi (TF) theory and the other is a DFT-based delta self-consistent-field (SCF) method[28] that we have developed to calculate diabatic PESs in different gas-surface systems. Due to computational reasons, we restrict ourselves to the TF method.

Except for surface properties specific to the Mg(0001) system, such as the diabatic PESs, we use the same parameters in Eq. (1) as in the O_2/Al(111) system.[13] From the CT model the initial thermal sticking probability s_0 is calculated to be ≈ 0.27, which is within a factor of 3 from experiment.[2,3] Hence, a nonadiabatic approach can explain the low initial sticking, even in the absence of an adiabatic barrier.

Further, the same CT model also provides an explanation for recent measurements on the Mg(0001) surface's reactivity.[3] Here, Aballe *et al.* measured oscillation in the oxidation rate depending on the thickness of the Mg(0001) film. The reason was suggested to be an oscillation in the height of a proposed barrier along the PES for O_2 dissociation. However, as seen in Figs. 2(c) and 2(d) it is clear that such oscillations in the PES do not have any theoretical support. There are only negligible changes in the reaction path as the number of layers change from five to fifteen. Specifically, no barrier appears that could motivate the measured oscillations in the oxidation rate. Within the CT model these oscillations appear neutral as there is a linear dependence, see Eq. (1), between $\mathrm{DOS}(E_F)$, and the CT rate.[26,27] Hence, the CT rate oscillates with respect to the number of Mg layers, which was also measured by Aballe *et al.*

To quantify this property we calculate the projected $\mathrm{DOS}(E_F)$, averaged over the slab, using a different number of atomic layers (1×1 supercell, $40\times 40\times 1$ *k*-point mesh). As expected, the electronic confinement associated with a finite slab,[29] gives rise to a periodic oscillation in $\mathrm{DOS}(E_F)$. In Fig. 3(a) the periodicity of the oscillations is seven layers long, which is also found by experiment.[3,30] However, the calculated amplitude in the $\mathrm{DOS}(E_F)$ is considerably smaller, and the position of the maxima and/or minima is shifted by two layers, compared to experiment. This might be an effect from the additional interface associated with experiment, as the Mg film is grown on a W(110)[3] or Si(111)[30] surface. Here, we settle this by verifying that in the nonadiabatic CT model an oscillating behavior in the initial oxidation rate occurs naturally.

As a further test of the CT model we calculate $\mathrm{DOS}(E_F)$ for the related Al(111) system, see Fig. 3(b). Here, our results

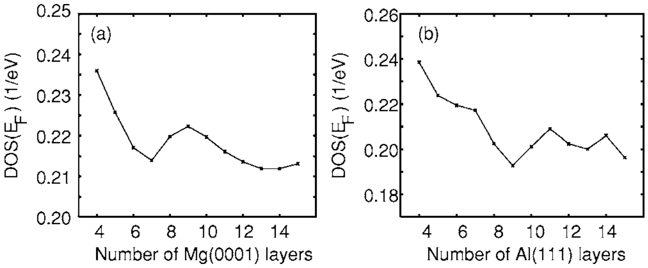

FIG. 3. (a) The DOS(E_F) as the number of Mg(0001) layers change. Due to the linear dependence between DOS(E_F) and the CT rate the same oscillating behavior is found in the initial oxidation rate. (b) The DOS(E_F) calculated for the Al(111) surface, indicating that the initial oxidation rate for Al(111) should have a similar oscillating behavior.

are in good agreement with other recent theoretical studies.[31] Given the results in Fig. 3(b) we propose that a similar thickness dependence in the initial sticking probability should be found even for the Al(111) system, although with a different amplitude and phase compared to the Mg(0001) system, see Fig. 3(a). Hopefully this prediction put forth by the CT model will challenge other coexisting nonadiabatic models[10,11] and/or provide the experimentalists with an opportunity to cast final judgment.

To elucidate the fundamental processes governing the initial stage of magnesium oxidation a comprehensive DFT study of the multidimensional adiabatic PES has been carried out. It is found that there exists no energy barrier for O_2 dissociation, hence it offers no explanation for the low thermal sticking probability of O_2 on magnesium. However, within a nonadiabatic framework, not only can the low thermal sticking probability be understood but it also provides an explanation for the thickness dependence in the oxidation rate found by experiment. This has further consequences for the O_2/Al(111) system as theory suggests a similar thickness dependence should also be found for this system.

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