Dissociations of O_2 molecules on ultrathin Pb(111) films: first-principles plane wave calculations*

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(Received 2 June 2011; revised manuscript received 11 August 2011)

Using first-principles calculations, we systematically study the dissociations of O_2 molecules on different ultrathin Pb(111) films. According to our previous work revealing the molecular adsorption precursor states for O_2, we further explore why there are two nearly degenerate adsorption states on Pb(111) ultrathin films, but no precursor adsorption states existing at all on Mg(0001) and Al(111) surfaces. The reason is concluded to be the different surface electronic structures. For the O_2 dissociation, we consider both the reaction channels from gas-like and molecularly adsorbed O_2 molecules. We find that the energy barrier for O_2 dissociation from the molecular adsorption precursor states is always smaller than that from O_2 gas. The most energetically favorable dissociation process is found to be the same on different Pb(111) films, and the energy barriers are found to be influenced by the quantum size effects of Pb(111) films.

Keywords: first-principles calculation, dissociation, Pb(111), quantum size effects

PACS: 68.43.Bc, 68.43.Fg, 73.20.Hb **DOI:** 10.1088/1674-1056/21/1/016801

1. Introduction

The adsorptions and dissociations of O_2 molecules on metal surfaces are of great importance to the subsequent oxidation reactions and also to the formation of metal oxides.[1,2] This is especially true for the formation of thin oxide films, which have been widely used as catalysts, sensors, dielectrics, and corrosion inhibitors.[3,4] Thus, extensive studies have been carried out on the O_2 adsorptions and dissociations on metal surfaces. During these studies, the theoretical *ab initio* modeling based on the adiabatic approximation has been proved successful over a wide range for studying the adsorptions and the dissociations of O_2 on transition metal surfaces. By calculating the adiabatic potential energy surface (PES), it has been found that O_2 molecules will spontaneously dissociate while being adsorbed at reactive transition metal surfaces such as on iron (Fe).[5] For noble transition metals such as gold (Au),[6] silver (Ag),[7] copper (Cu),[8] platinum (Pt)[6,9] and nickel (Ni),[9] the adsorption of O_2 turns out to be dependent on the ambient temperature, and both atomic and molecular adsorptions have been observed. Remarkably, in all of the above transition metal systems, the concept of adiabatic calculation works very well in explaining and predicting a large number of physical/chemical phenomena in the dissociation process of O_2. When attention is focused on nontransition metals with only *sp* valence electrons, an uncomfortable gap opens between *ab initio* predictions and experimental observations. Of particular note is the long-term enigma of the low initial sticking probability of thermal O_2 molecules at Al(111), which has been measured by many independent experiments[10,11] but cannot be reproduced by adiabatic state-of-the-art density functional theory (DFT) calculations.[2,12−14] The central problem is that the adiabatic DFT calculations were unable to find any sizeable barriers on the calculated PES, which has led to speculation that the nonadiabatic effect may play an important role in the oxygen dissociation process at the Al(111) surface.[13,15−22] Recently, we presented a comparative study on the electronic structure of an O_2 molecule which is respec-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 90921003, 10904004 and 60776063) and the Fundamental Research Funds for the Central Universities, China (Grant No. JD1109).

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tively close to the Be(0001), Mg(0001) and Al(111) surfaces, and find that the triplet state of O_2 is influenced by the Mg(0001) and Al(111) surfaces, but not by the Be(0001) surface.[23] Thus, we prove that the adiabatic DFT calculations are still reliable to study the O_2/Be(0001) system, and find sizable dissociation energy barriers for O_2 molecules on the Be(0001) surface.[23] However, in contrast to the systematical results on the O_2 dissociation on transition metal surfaces, there is still no criterion to judge whether an energy barrier is needed or whether a precursor molecular-adsorption state exists for the O_2 dissociation on sp metal surfaces. Motivated by these backgrounds, in this paper we investigate the dissociations of O_2 molecules on another sp metal surface, lead (Pb). We find that the adiabatic DFT calculation also leads to reliable results for the O_2/Pb(111) system.

During the past decades, atomically uniform Pb films with thickness ranging from several to tens of monolayers (MLs) have been successfully fabricated on both metal and semiconductor substrates,[24−26] which can serve as an ideal prototype for experimental researchers to investigate the surface oxidation of Pb.[27] However, it is believed that for very thin metal films, the adsorption and the dissociation of O_2 molecules become more complex because of the two boundaries. According to the "particle-in-a-box" model, electrons confined in a uniform film are quantized into discrete energy levels along the film-normal direction, forming the so-called quantum well states. Because the electron Fermi wavelength of Pb is nearly 4 times the lattice spacing along the [111] direction,[28] many properties such as thermal stability, surface energy, and work function of the Pb films oscillate with thickness with a quasibilayer period.[29−31] Recently, a unique two-step method has been devised in order to efficiently oxidize the the Pb(111) surface.[32,33] In this special oxidation process, O_2 molecules are firstly introduced at a low temperature and adsorbed in a precursor state, then the Pb(111) surface is oxidized by subsequently annealing to room temperature.[33] Most interestingly, both the oxygen coverage at low temperature and oxide coverage after annealing are found to be modulated by the quantum size effect (QSE) of ultrathin Pb(111) films.[32] These studies together with other investigations[34] clearly prove the modulation of surface oxidation by QSE. To understand the complicated experimental observations, systematic investigations on the adsorptions and the dissociations of O_2 molecules on ultrathin Pb(111) films are needed.

In our previous work, we have already studied the adsorption properties for both molecular O_2 and atomic O on different Pb(111) films.[35,36] It is found that O_2 molecules will not spontaneously dissociate on Pb(111) films and a precursor molecular adsorption state exists.[35] In this work, we further analyse the electronic interactions for the adsorption of O_2, investigate the dissociation process for O_2, and study the QSE on the dissociation energy barriers. The rest of the present paper is organized as follows. In Section 2, we detail the first-principles total energy calculations. Then, in Section 3, we present our analysis for the adsorption state of O_2 on the Pb(111) surface. In Section 4, we study the O_2 dissociation on Pb(111) films and discuss the QSE on the corresponding energy barrier. Finally, in Section 5, we draw some conclusions from the present study.

2. Computational method

The DFT total energy calculation is carried out by using the Vienna *ab initio* simulation package.[37] The generalized gradient approximation (GGA) of Perdew *et al.*[38] and the projector-augmented-wave (PAW) potentials[39] are employed to describe the exchange-correlation energy and the electron–ion interaction, respectively. The so-called "repeated slab" geometries are employed to model the clean Pb(111) films ranging from 4 to 8 MLs. A vacuum layer of 20 Å is adopted to separate the Pb(111) slabs in two adjacent cells, which is found to be sufficiently convergent from our test calculations. A 2×2 supercell, in which each monolayer contains four Pb atoms, is adopted in the study of the O_2 adsorption since our test calculations have shown that it is large enough to avoid the interaction between adjacent O_2 molecules.[35] The O_2 was placed on one side of the slab, namely on the top surface, whereas the bottom layer was fixed. All other Pb layers as well as the oxygen atoms are free to relax until the forces on them are less than 0.02 eV/Å. The plane-wave energy cutoff is set to be 400 eV. A Fermi broadening[40] of 0.1 eV is chosen to smear the occupation of the bands around E_F by a finite-T Fermi function and extrapolating it to $T = 0$ K. Integration over the Brillouin zone is performed using the Monkhorst–Pack scheme[41] with $13 \times 13 \times 1$ grid points. The calculated lattice constants of bulk Pb and bond-length of an isolated O_2 molecule are 5.03 Å and 1.235 Å respectively, which are in good agreement with the experimental values of 4.95 Å[42] and 1.21 Å.[43] The calculated binding energy of an isolated O_2 molecule is 5.78 eV, which accords well with previous theoretical

calculations.[23,44,45] Compared with the experimental value of 5.12 eV,[43] the usual DFT–GGA calculation introduces an overestimation, which reflects the theoretical deficiency for describing the local orbitals of the oxygen.

To determine the one-dimensional (1D) potential energy profile for the dissociation of an incoming O_2 molecule, we first put the O_2 molecule at different heights from the Pb surface, then let the two oxygen atoms freely relax to the local minimum energy point. The dissociation energy barrier for an adsorbed O_2 was determined by calculating the two-dimensional (2D) PES for O_2. The calculation of the 2D PES was interpolated to over 6 thousand points with different O–O bond lengths and heights of O_2 from the Pb surface.

3. Adsorption properties of O_2 on the Pb(111) surface

The geometries of ultrathin Pb(111) films are first relaxed before study of the adsorption and dissociation of O_2 molecules. It is found that atoms at the outmost layer tend to relax inward, while atoms at the second layer tend to relax outward.[34]

The main reason for the wrong conclusions drawn from adiabatic first-principles calculations on the adsorption of O_2 on sp-metals lies in the fact that the lowest unoccupied molecular orbital (LUMO) state of O_2 is always aligned with the Fermi level at any distance between the molecule and metal surfaces such as Al(111), allowing the partial filling of the empty molecular orbital.[46] Due to this unphysical (metal-molecule or intramolecule) charge transfer, the adsorption of O_2 on the Al(111) surface is calculated to be dissociative without any energy barrier, which contradicts the experimental observations of low initial sticking probability at low temperatures.[10,11] In our previous work,[23] we have shown that the unphysical partial filling of the LUMO did not occur during the adsorption of O_2 on the Be(0001) surface, and thus we obtained sizeable energy barriers for the dissociation of O_2. Here, for the O_2/Pb(111) system, molecular adsorption precursor states exist, so we cannot judge the reliability of our calculations by whether a sizable energy barrier exists. We calculate and show in Fig. 1(a) the electronic density of states (DOS) of an O_2 molecule which is 7 Å away from the 5 ML Pb(111) film. In comparison with the DOSs of O_2 which are respectively 7 Å away from the Mg(0001) and Al(111) surfaces (respectively shown in Figs. 1(b) and 1(c)), we find that the triplet ground state of the O_2 molecule is not influenced at all by the Pb(111) film, but totally disturbed by the Mg(0001) and Al(111) surfaces due to the unphysical charge transfers. Therefore, we are sure that the adiabatic DFT calculations will not lead to unphysical conclusions for the O_2/Pb(111) system, and for the O_2/Be(0001) system either.

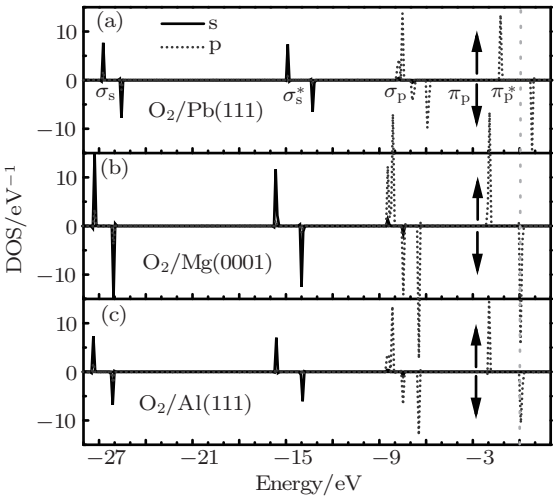


Fig. 1. The electronic densities of states for an O_2 molecule which is respectively 7 Å away from the 5 ML Pb(111) film (a), the Mg(0001) surface (b), and the Al(111) surface (c). The Fermi energies are all set to be 0.

To facilitate our discussion, we first give some notations. Formally, there are four high-symmetry sites on the Pb(111) surface, i.e., top (T), bridge (B), hcp (HH), and fcc (FH) hollow sites. Our previous study has already shown that the high-symmetry sites play crucial roles in the adsorption of O_2 molecules on Pb(111) films.[35] Therefore, we no longer consider other surface sites. At each surface site, an O_2 molecule has three different high-symmetry orientations along the x (i.e., $[0\bar{1}1]$), y (i.e., $[\bar{2}11]$), and z (i.e., [111]) directions. Therefore, we will use T-x, y, z, B-x, y, z, HH-x, y, z, and FH-x, y, z to respectively represent the 12 high symmetry adsorption channels for O_2.

After geometric optimizations by initially setting the O_2 molecule at 4.0 Å along each adsorption channel, we have obtained 6 molecular adsorption states for O_2.[35] By using numbers 1, 2, and 3 to represent the O_2 orientation along the x, y, and z directions, we name the six adsorption states respectively as HH-x, HH-y, HH-z, FH-x, FH-y, and FH-z. The atomic geometries for the HH-x, HH-y, and HH-z states are presented in Figs. 2(b), 2(c), and 2(d), respectively. The

geometries for the FH-x, FH-y, and FH-z states are very similar to the HH-x, HH-y, and HH-z states, with the adsorbed oxygen atoms at fcc hollow sites instead of hcp hollow sites. Among the six precursor states, HH-x and HH-y are the most stable and two nearly degenerate states. The adsorption energies per oxygen atom in the HH-x, HH-y, FH-x, and FH-y adsorption states are 0.55, 0.57, 0.54, ad 0.56 eV, respectively. In our previous work, we have already discussed in detail the interactions between oxygen and Pb for the HH-x state.[35] Here, we further analyse the electronic interactions for the HH-y state to discuss why the two adsorption states with different O_2 orientations (i.e. HH-x and HH-y states) are almost degenerate.

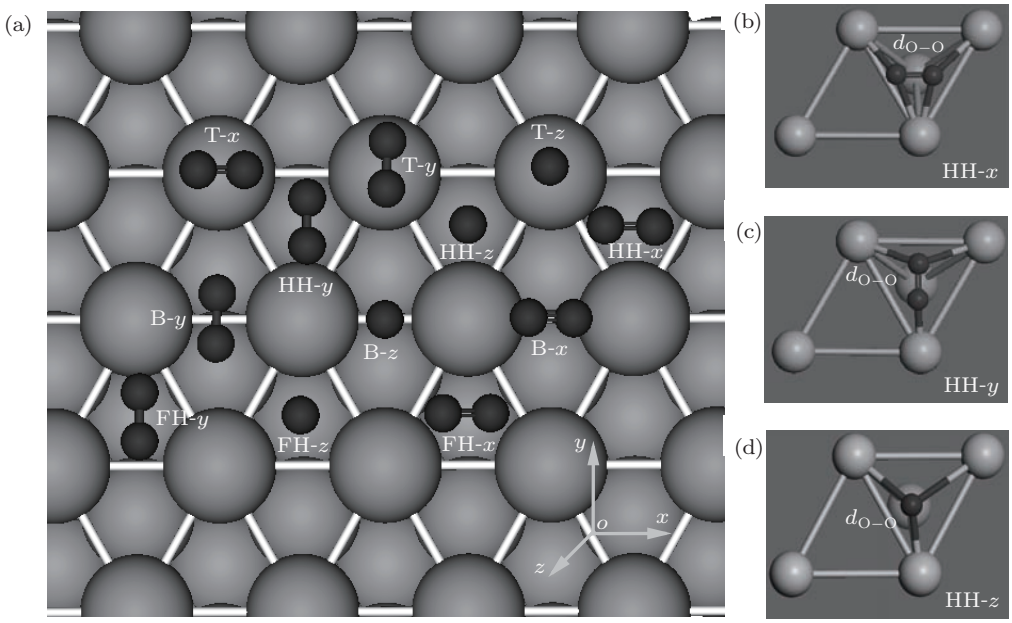


Fig. 2. (a) The considered twelve high-symmetry adsorption channels for O_2 on the Pb(111) surface. (b), (c) and (d) The three molecular adsorption states for O_2 at the surface hcp hollow site. Dark and gray balls represent O and Pb atoms. There is a Pb atom in the second layer below the HH site to make it distinct from the FH site.

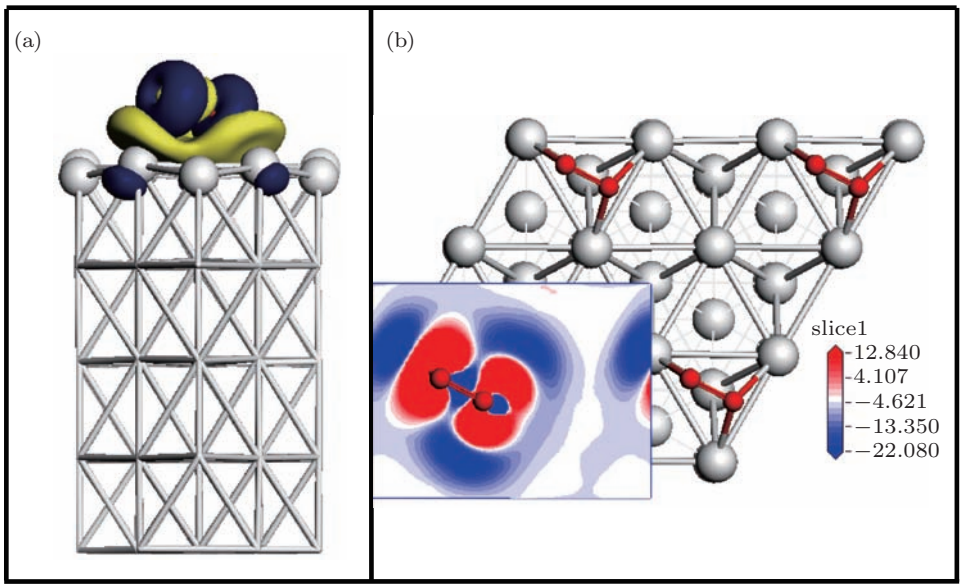


Fig. 3. (colour online) (a) Difference charge density for the HH-y adsorption state of O_2 on the 5 ML Pb film. Dark and gray atoms represent O and surface Pb. Regions of electron accumulation/depletion are displayed in dark/gray, respectively, and the isosurface value is $\pm 0.02\ e/\text{Å}^{-3}$, where e is the charge of one electron. (b) Contour plots of the difference charge density in the plane that contains the two oxygen atoms and is parallel to the Pb(111) surface.

Figure 3 shows the calculated difference charge density $\Delta\rho(r)$ for the HH-y state on the 5 ML Pb(111) film, which is obtained by subtracting the electron densities of noninteracting component systems, $\rho_{\mathrm{Pb(111)}}(r) + \rho_{\mathrm{O_2}}(r)$, from the density $\Delta\rho(r)$ of the HH2 state, while retaining the atomic positions of the component systems at the same location as that in HH2. A positive $\Delta\rho(r)$ here represents charge accumulation, whereas a negative $\Delta\rho(r)$ represents charge depletion. Figure 3(a) clearly shows a charge transfer from Pb to O_2, which is consistent with the electronegativity difference between O and Pb atoms, and the same as what we found for the HH-x state.[35] The contour plot for $\Delta\rho(r)$ in the plane containing the two O atoms and being parallel to the Pb surface is shown in Fig. 3(b), and we can see that there is an electron depletion area in the middle of the two oxygen atoms, indicating the donation of electrons from bonding orbitals of O_2 to Pb. We can also see two electron accumulation areas around the two oxygen atoms, indicating the back donation of electrons from Pb to the π_p^* antibonding orbital of O_2. This interaction mechanism of O_2-to-surface donation and surface-to-$O_2\pi_p^*$ back donation is the same as that in the HH-x state.[35] Therefore, it is no wonder that the two adsorption states are nearly degenerate and have similar adsorption energies.

In comparison with the Be(0001), Mg(0001) and Al(111) surfaces, Pb(111) is unique in that an O_2 molecule is adsorbed only on it. This is because of the different surface electronic structures. As shown in Fig. 4, the p electronic states around the Fermi energy strongly hybridize with s states for both the Mg and Al surfaces (also for the Be(0001) surface[23]), but does not hybridize at all for the Pb(111) surface. As we have seen,[35] the interaction between O_2 and the Pb(111) surface contributes mainly to the electronic hybridizations between the frontier molecular orbitals (the orbitals nearest to the Fermi energy) of O_2 and electronic states of Pb. According to the frontier orbital theory, the interactions between O_2 and other metals have a similar mechanism. However, the frontier orbitals of O_2 (i.e. σ_{p}, π_{p}, and π_{p}^*) are composed of the p electrons of oxygen, thus they are more compatible with p electronic states than sp hybridized electronic states. This compatibility between frontier orbitals of O_2 and p states of Pb finally leads to the molecular adsorption precursor state.

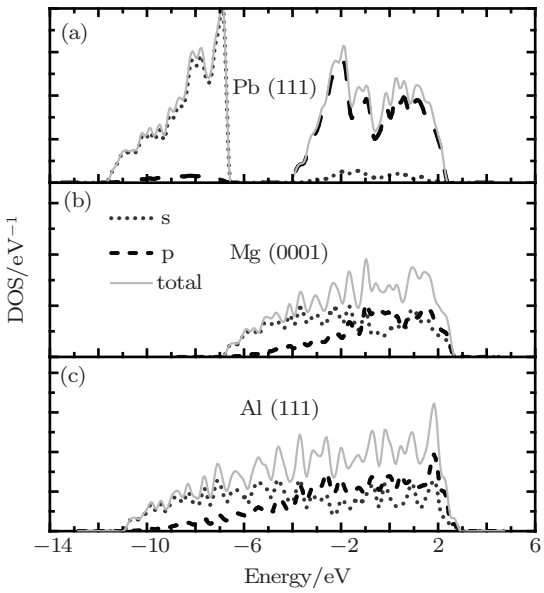


Fig. 4. The projected density of states for the 5 ML Pb(111) film (a), Mg(0001) (b) and Al(111) (c) surfaces. The Fermi energies are all set to be 0.

4. Dissociation of O_2 molecules

After studying and discussing the adsorptions on different Pb(111) films, we now investigate the O_2 dissociation. Because of the existence of precursor states, there are two different kinds of dissociation processes for O_2, respectively from O_2 gases and from the molecular adsorption states. We will calculate the 1D and the 2D PES cuts to evaluate the dissociation energy barriers for O_2 molecules. The 1D PES cuts for an O_2 molecule along the T-x, y and B-x, y channels are shown in Fig. 5, together with the O–O bond length, each as a function of O_2 height h from the 5 ML Pb(111) film surface. The O_2 gas adsorbed along the FH- and HH-x, y channels will evolve into the molecular adsorption precursor. Clearly, the dissociative adsorptions of O_2 along the T-x, y and B-y channels are direct and activated, but no dissociative adsorption is found for an O_2 molecules along the B-x channel. It is apparent that the B-x channel results in a molecular adsorption state with a binding energy of 0.8 eV. This is different from the O_2/Be(0001) system, where the O_2 dissociation along B-x channel also occurs.[23] Among the calculated channels, the lowest dissociation energy barrier is found to be 0.36 eV along the B-y channel, with the O–O bond length and O_2 height at the highest energy point being 1.33 and 2.20 Å. The energy barriers for O_2 dissociation along the T-x, y channels are, respectively, 0.68 and 0.59 eV.

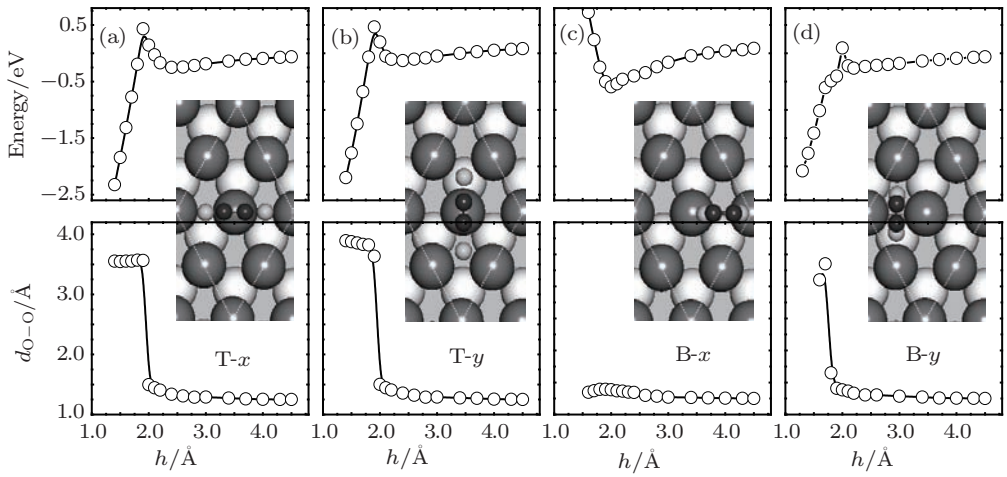


Fig. 5. One-dimensional cuts of the potential energy surfaces and the corresponding O–O bond lengths (d_{O-O}), each as a function of O_2 distance h from the 5 ML Pb(111) film for four different dissociative channels (a) T-x, (b) T-y, (c) B-x, (d) B-y. The inset in each panel indicates the initial (dark circles) and final (gray circles) atomic positions of the two oxygen atoms.

The electronic interactions are then analysed for the dissociation process from O_2 gases. Figure 6 shows the projected densities of states (PDOSs) for an O_2 molecule at the initial, the highest and final points of the dissociation path along the B-y channel, respectively. We can see that at the initial point, the O_2 molecule keeps its triplet electronic structure. As we have discussed, the LUMO of O_2 is above the Fermi energy, proving that our adiabatic DFT calculations are reliable. The highest occupied molecular orbital (HOMO) and LUMO are the spin-up and spin-down antibonding π_p^* molecular orbitals, respectively. Besides HOMO and LUMO, p electrons of O_2 make up of two bonding orbitals, σ_p, and π_p. For both spins, the σ_p orbitals are lower in energy than the π_p orbitals. When the O_2 molecule evolves into the highest energy point, electrons transfer from the σ_p and the π_p molecular orbitals to Pb through electronic hybridizations. As shown in Fig. 6(b), the σ_p and π_p peaks diminish. We can also see from Fig. 6(b) that the HOMO and LUMO of O_2 are broadened through hybridizations with electronic states of Pb. During the electronic hybridizations, the spin splittings for all the O_2 molecular orbitals are all reduced. In the final dissociated adsorption state, the total spin of the adsorption system becomes zero. We can see from Fig. 6(c) that the molecular orbitals of O_2 no longer exist after electronic hybridizations. As discussed in our previous work,[36] the interactions between O and Pb atoms display a mixed ionic/covalent character.

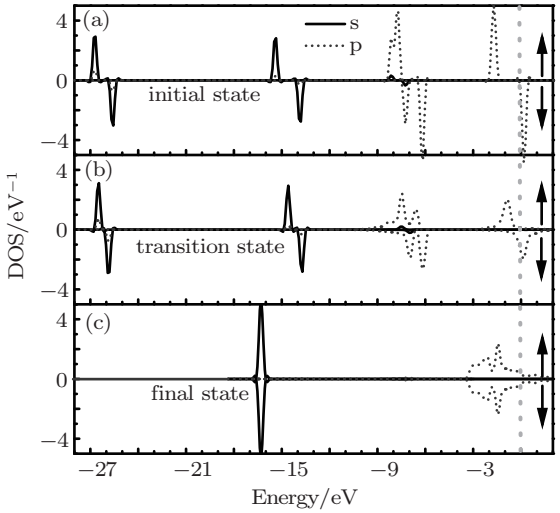


Fig. 6. The projected densities of states around the two oxygen atoms at the initial (a), the highest (b) and final points (c) along the B-y adsorption channel. The Fermi energies are set to be 0.

For the dissociation of O_2 from the molecular adsorption precursor states, the formation of different O–Pb bonds needs to be considered. Detailed information about the atomic adsorption of oxygen on the Pb(111) surface can help us to simplify the problem. In our previous study,[36] we have found that the O atoms are selectively adsorbed at hollow sites on the Pb(111) surface. Thus, we only need to consider the dissociation of an adsorbed O_2 molecule into different hollow sites.

For an O_2 molecule in the HH-x or HH-y state, there are two different dissociation paths, respectively to the atomic adsorption of oxygen at two neighbour-

ing fcc and hcp hollow sites and to the atomic adsorption of oxygen at two fcc hollow sites. The calculated 2D PES cuts for the adsorbed O_2 molecules in the HH-x and HH-y states to dissociate into two neighbouring hollow sites are shown in Figs. 7(a) and 7(b), while the calculated 2D PES cuts for O_2 to dissociate into two fcc hollow sites are also shown in Figs. 7(c) and 7(d). The calculated energy barriers for these four paths are respectively 0.22, 0.26, 0.59 and 0.37 eV. These values indicate that the most energetically favourable dissociation path for an adsorbed O_2 molecule is from the HH-x adsorption state into the atomic adsorption of oxygen at two neighbouring fcc and hcp hollow sites. The saddle point in Fig. 7(a) corresponds to the adsorption structure of two oxygen atoms near the two neighbouring bridge sites, with their horizontal distance being 1.40 Å. The smallest energy barriers for an O_2 molecule in the FH-x and FH-y states to dissociate are both found to be 0.25 eV, which are larger than the smallest energy barrier from the HH-x state, 0.22 eV. We can see that the dissociation energy is much smaller at $T = 0$ K than the molecular adsorption energy. Hence, it can be concluded that an adsorbed O_2 has a much larger probability to dissociate than to be desorbed from the Pb surface. The small dissociation energy barrier also accords well with the experimental phenomenon that the low-temperature adsorbed O_2 molecules can easily dissociate in a room-temperature annealing process.[32] As to the high resistance to oxidation of the clean Pb(111) surfaces at room temperature, it has already been explained to be due to the enlarged desorption probability after taking into consideration of the entropy of O_2 in high vacuum environments.[47]

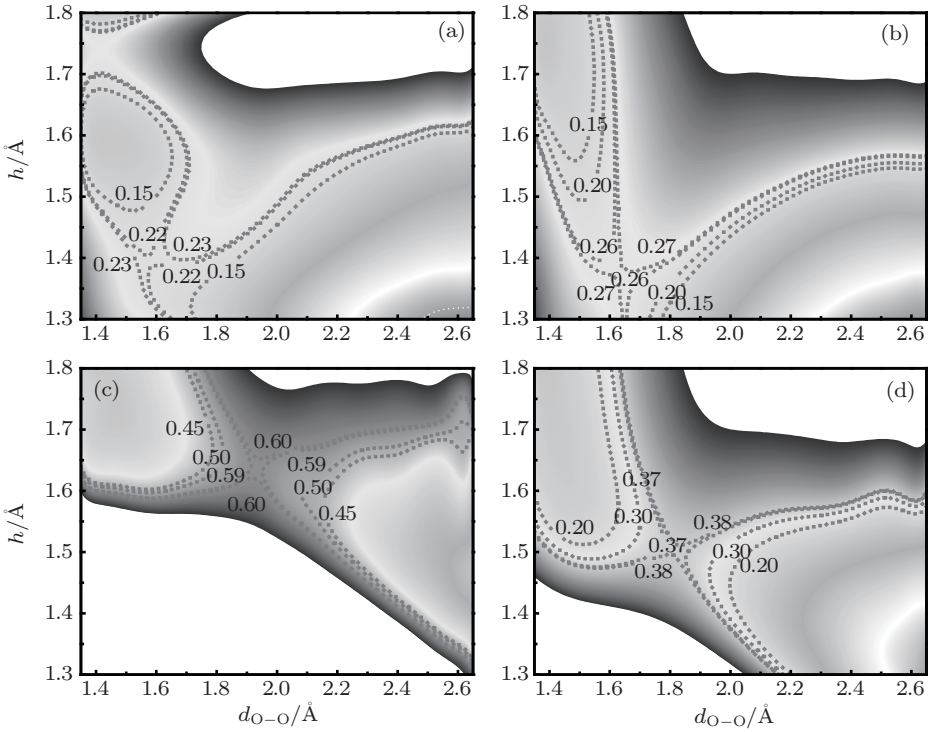


Fig. 7. Colour-filled contour plots of the potential energy surface for O_2 dissociation on the 5 ML Pb(111) film from HH-x (a) and HH-y (b) states to the atomic adsorption of two oxygen atoms at neighbouring hcp and fcc hollow sites, and from HH-x (c) and HH-y (d) states to the atomic adsorption at two fcc hollow sites, as functions of the O_2 bond length d_{O-O} and distance h (from the surface).

The electronic properties are then analysed for the dissociation path shown in Fig. 7(a), whose energy barrier is the smallest during the dissociation from molecular adsorption precursor states. The PDOSs around the two oxygen atoms are calculated for the corresponding initial, transition and final states. As shown in Fig. 8(a), the π_p^* antibonding orbitals of O_2 are broadened and shifted below the Fermi energy in the HH-x adsorption state, through hybridizations with p electronic states of Pb. At the transition state of the dissociation process, the energy interval between the σ_s and the σ_s^* orbitals is reduced from 6.58 to 6.24 eV, and the oxygen 2p states hybridize[48,49] with electronic states of Pb in a different way from that in the HH-x adsorption state. At the end of the dissociation process, the two oxygen atoms relax into

two neighbouring hollow sites, and the molecular orbitals of O_2 all disappear after electronic hybridizations.

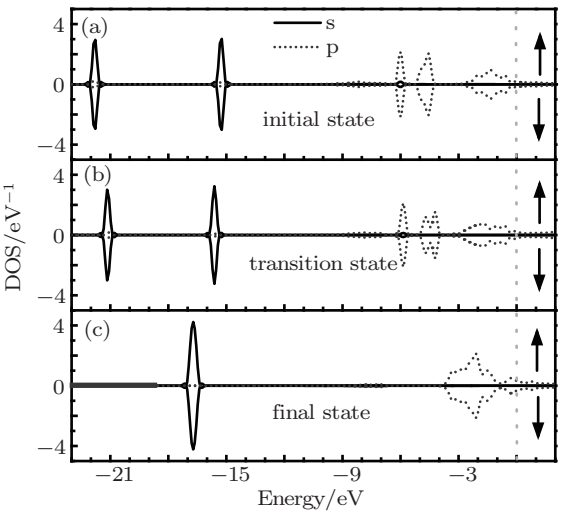


Fig. 8. The projected densities of states around the two oxygen atoms at the initial (a), saddle (b) and final points (c) of the dissociation path from the HH-x state to the atomic adsorption of two oxygen atoms at neighbouring hcp and fcc hollow sites. The Fermi energies are set to be 0.

Following the different systematic studies of the O_2 dissociation, we reveal that the most energetically favourable one enters from the HH-$x$adsorption state into two neighbouring hollow sites. It is always believed that because of the confinement of the two boundaries in the vertical direction, the quantum behaviour of electrons will cause a number of unique properties for thin metal films that could be superior to their bulk counterpart. In particular, the QSE on surface reactivity has been studied extensively for applications in catalysis, corrosion, and gas sensing. Here, we further consider the dissociation path for O_2 molecules on different Pb(111) films, including both the dissociation along the T- and B-x, y channels from O_2 gas, and the dissociation from molecular adsorption states. After systematic calculations, we find that the most energetically favourable dissociation paths are the same on different Pb(111) films, i.e. from the HH-x adsorption state to the atomic adsorption of two oxygen atoms at two neighbouring hollow sites. Figure 9 shows the 2D PES cuts for the O_2 dissociation on 4–7 monolayer Pb(111) films. For a qualitative comparison, under the same conditions, the 2D PES cuts for different Pb films are calculated, and the calculated energy barriers are 0.26, 0.22, 0.26, and 0.24 eV, as shown in Figs. 9(a)–9(d), respectively. Since many properties of Pb(111) films such as work function and surface energy show bilayer oscillation behaviours because of the QSE,[31] the even-odd oscillation of the dissociation energy barrier proves the modulation of the QSE by the O_2 dissociation on Pb(111)films. This conclusion is also consistent with our recent report that the QSE can modulate metal surface reactions.[50]

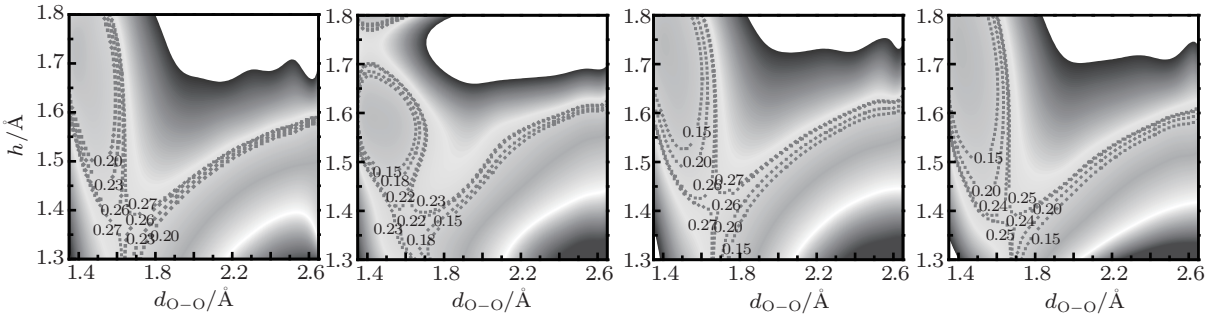


Fig. 9. Colour-filled contour plots of the potential energy surface for O_2 dissociation on (a) 4 ML, (b) 5 ML, (c) 6 ML and (d) 7 ML Pb(111) films from the HH-x state to the atomic adsorption of two oxygen atoms at neighbouring hcp and fcc hollow sites, each as a function of O_2 bond length d_{O-O} and distance h(from the surface).

5. Conclusion

We investigate the adsorptions and the dissociations of O_2 molecules on different Pb(111) films. The electronic states of an O_2 molecule which is near to the Pb film are first analyed, showing that the adiabatic calculations are reliable. For the molecular adsorption precursor states, we find that the electronic interactions are very similar in the HH-x and HH-y states, and they are thus two nearly degenerate states. We further point out that no s–p hybridization in Pb(111) film is the main reason for the existence of the molecular adsorption precursor state. According to our adiabatic PES calculations, we find that the

dissociation of O_2 from the molecular adsorption precursor state has a lower energy barrier than that from O_2 gas. The most energetically favourable dissociation paths on different Pb(111) films are found to be the same, i.e., from the HH-x adsorption state to the atomic adsorption of two oxygen atoms at two neighbouring hollow sites. The energy barriers of O_2 on different Pb(111) films are found to be modulated by the QSE of Pb(111) films, showing a bilayer oscillation behaviour. Our study further completes the theoretical picture for the adsorptions and the dissociations of O_2 molecules on different Pb(111) films.

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