Influence of Pb adatom on adsorption of oxygen molecules on Pb(111) surface: a first-principles study*

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(Received 2 February 2010; revised manuscript received 9 June 2010)

Using first-principles calculations, we systematically study the influence of Pb adatom on the adsorption and the dissociation of oxygen molecules on Pb(111) surface, to explore the effect of a point defect on the oxidation of the Pb(111) surface. We find that when an oxygen molecule is adsorbed near an adatom on the Pb surface, the molecule will be dissociated without any obvious barriers, and the dissociated O atoms bond with both the adatom and the surface Pb atoms. The adsorption energy in this situation is much larger than that on a clean Pb surface. Besides, for an adsorbed oxygen molecule on a clean Pb surface, a diffusing Pb adatom can also change its adsorption state and enlarge the adsorption energy for O, but it does not make the oxygen molecule dissociated. And in this situation, there is a molecule-like PbO_2 cluster formed on the Pb surface.

Keywords: Pb adatom, oxygen, adsorption, first-principles

PACC: 8200, 8265N

1. Introduction

It is of fundamental importance to understand the adsorption, the dissociation, and their corresponding kinetic processes of diatomic molecules on materials surfaces.[1,2] As a prototypical example, the adsorption and the dissociation of O_2 on metal surfaces have attracted considerable attention because the resulting metal oxides have been widely used as catalysts, sensors, dielectrics, and corrosion inhibitors.[3−5] Of all the substrates, lead (Pb) (111) surface is a good model system, because atomically-flat Pb(111) terraces have been fabricated on both metal and semiconductor substrates such as Ru(0001)[6] and Si(111).[7,8] Many experimental and theoretical publications are now available for such surfaces.[9−12] Experiments reveal that in a high vacuum environment, a clean Pb(111) surface is very resistant to the adsorption and the dissociation of O_2 molecules.[13,14] If an impurity exists, then O_2 molecules will be easily dissociated around the impurity and around the subsequently formed oxides. The Pb(111) surface can thus be oxidized from the impurity in an autocatalytic way.[13] However, to determine the atomic composition of the impurity is somehow very difficult. And what kind of impurities or defects can activate the oxidation of the Pb(111) surface remains unclear.

During the epitaxy process of a Pb(111) terrace, the deposited Pb adatoms are very easy to move and incorporate into vacancies or step kinks,[15,16] so the top surface of the deposited Pb terrace is always believed to be without concave defects.[15] However, also because of their fast-movements, the existence of Pb adatoms is very hard to detect, and so they cannot be easily excluded from epitaxial Pb(111) surfaces. Consider that the unknown impurity can greatly enhance the oxidation of the Pb(111) surface, it will be very interesting and meaningful to study the adsorption and the dissociation of an O_2 molecule on the Pb(111) surface with a Pb adatom around.

At another point, the preparation and the characterization of different kinds of metal oxide clusters are also fascinating fields both experimentally and theoretically.[17−19] Self-assembly as a bottom-up approach is a promising method to form large arrays of nanostructures, especially for metal oxide clusters.[20−22] Some special impurities such as dislocation lines, reactive assistant layers or sputtered metal atoms are employed on the surface to obtain special metal–oxide clusters.[20,23,24] The chemical components of the assembled clusters are often recognized from their geometry and stoichiometry.[21,22,24] However, the electronic structures for these clusters have seldom been discussed theoretically while the

*Project supported by the National Natural Science Foundation of China (Grant No. 10904004).

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special properties such as the catalytic activity of the metal–oxide clusters are based on their electronic structures. In our present work, we reveal that separated Pb adatoms may help to form PbO_2 clusters on the Pb(111) surface, and the electronic structures of the formed cluster keep most of the orbital characters of a PbO_2 molecule.

The rest of this paper is organized as follows: In Section 2, we describe our first-principles calculation method. In Section 3, our calculational results for the adsorption of an O_2 molecule directly around a Pb adatom are presented and the structural model, the adsorption states, and the corresponding electronic structures are discussed in detail. In Section 4, we present our calculational results for the interaction between an adsorbed O_2 molecule and a diffusing Pb adatom, similar to what we do in Section 3. And finally in Section 5, we draw some conclusions from the present study.

2. Calculation method

Our calculations are performed using the spin-polarized version of the Vienna *ab-initio* simulation package.[25] The PW91[26] generalized gradient approximation and the projector-augmented wave potential[27] are employed to describe the exchange–correlation energy and the electron–ion interaction, respectively. The cutoff energy for the plane wave expansion is set to be 400 eV. The Pb(111) surface is modeled by a slab with 4 atomic layers and a vacuum layer of 15 Å (1 Å = 0.1 nm) in thickness. A 2×2 supercell, in which each monolayer contains 4 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. The integration over the Brillouin zone is done using the Monkhorst–Pack scheme[28] with $7 \times 7 \times 1$ grid points. The lattice constant of bulk Pb and the bondlength of isolated O_2 are calculated to be 5.03 Å and 1.24 Å, respectively, which are in good agreement with the experimental values of 4.95 Å[29] and 1.21 Å.[30] The O_2 is placed on one side of the slab, namely on the top surface, whereas the bottom layer is fixed. All other Pb layers as well as the oxygen atoms are free to relax until the forces on them are less than 0.01 eV/Å. We have made sure that asymmetric arrangements of the O_2 adsorbates would make no quantitative difference.

3. Adsorption of an O_2 molecule around a Pb adatom

First we carry out the geometry optimization for the clean Pb(111) surface, and study the adsorption of a Pb adatom on it. We find that after surface relaxations, the first interlayer spacing of the Pb(111) surface is compressed by 2.3%, while the second interplay spacing is expanded by 4.4%.[31] For the adsorption of a Pb adatom, we find that there are three different adsorption states, separately at the surface bridge, hcp and fcc hollow sites. The energy differences between these three states are below 60 meV. These results accord well with previous studies,[16] and thus prove the correctness of our method.

Since the energy differences between the three adsorption states are very small, a Pb adatom has similar possibilities to stay at the three surface sites, and so we should consider the adsorption of an O_2 molecule around three different Pb adatoms. However, our calculations reveal that for a structure with the adsorbed atoms near the surface fcc hollow site and a corresponding structure near the surface hcp hollow site, there is only a small energy difference within 20 meV. So we will not distinguish the hcp hollow site from the fcc hollow site any more. Our model to study the adsorption of an O_2 molecule directly around a Pb adatom is depicted in Fig. 1. Figure 1(a) is a top view showing the A1–A3 and B1–B3 sites for the adsorption of an O_2 molecule, while figure 1(b) is a side view indicating the initial height of the O_2 molecule, which is 4 Å from the Pb adatom. An O_2 molecule at each surface site has three high-symmetry orientations, respectively along x (i.e., $[0\bar{1}1]$), y (i.e., $[\bar{2}11]$), and z (i.e., [111]) directions. For the adsorption of an O_2 molecule outside the two triangles in Fig. 1(a), we assume that its adsorption is not influenced by the Pb adatom. It is noted that if the O_2 molecule is oriented along the z direction, then the B1 and B3 sites are just the same. So, we consider a total of 17 different initial configurations here.

After geometry optimizations, we find that the different initial configurations lead to four final adsorption states. The relaxation results are summarized in Table 1, and the atomic structures for the four adsorption states are shown in Fig. 2, together with their electron localization function (ELF) graphs.[32,33] For the structure shown in Fig. 2(a), one Pb adatom and two O atoms form a tilted triangle (TT) on the surface, and so the structure is called the

TT structure. For the structure shown in Fig. 2(b), one Pb adatom and two O atoms form an untilted triangle on the surface, and because another structure we will talk about in the following section has a similar character, we will call the two structures respectively as T1 structure and T2 structure. For the structures shown in Figs. 2(c) and 2(d), one Pb adatom and two O atoms both form a square with a surface Pb atom, so these two structures are respectively called as S1 structure and S2 structure.

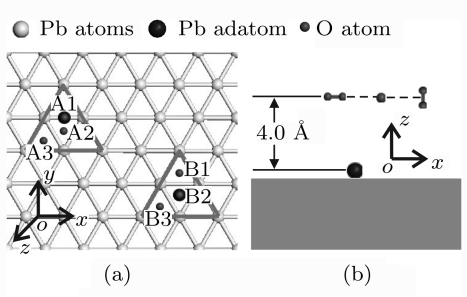


Fig. 1. Initial configurations for studying the direct adsorption of an O_2 molecule around a Pb adatom. Surface Pb atoms, Pb adatoms and O atoms are represented respectively by white, large black and small black balls. Panel (a) is top view depicting all the considered sites for the adsorption of an O_2 molecule. The sites A1, A2 and A3 are around a Pb adatom at the bridge site, and the sites B1, B2 and B3 are around a Pb adatom at the hollow site. Panel (b) is side view depicting that the O_2 molecule can be oriented along x (i.e., $[0\bar{1}1]$), y (i.e., $[\bar{2}11]$), and z (i.e., [111]) directions. In all the initial configurations, the centre of mass of the O_2 molecule is set to be 4 Å away from the surface sites.

Table 1. The adsorption states for an O_2 molecule around a Pb adatom on Pb(111) surface.

site of Pb adatom	site of O_2	O_2 orientation	evolved state
bridge	A1	x	TT
		y	S2
		z	TT
	A2	x	TT
		y	T1
		z	S2
	A3	x	TT
		y	TT
		z	S1
hollow	B1	x	TT
		y	TT
		z	S2
	B2	x	TT
		y	TT
		z	T1
	B3	x	TT
		y	TT

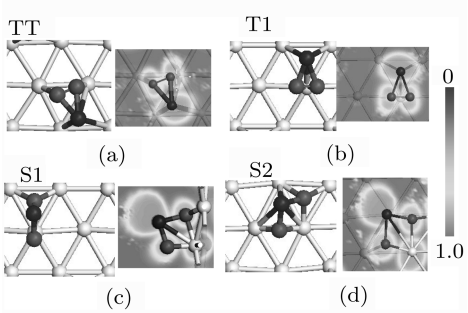


Fig. 2. Atomic structures (left) and ELF graphs (right) for the TT (a), T1 (b), S1 (c), and S2 (d) states. Surface Pb atoms, Pb adatom and O atoms are respectively represented by white, large black and small black balls. The ELF graphs are shown in the plane that contains the Pb adatom and the two O atoms.

From the ELF graphs in Figs. 2(a) and 2(b), we can see that there are still nonpolar covalent bondings between the two O atoms in TT and T1 structures, which means that the O_2 molecule is not dissociated in them. It can also be seen that there is a polar bonding between O atom and the Pb adatom. In the TT structure, the O–O bond length is 1.50 Å, and the distances between the O atoms and the Pb adatom are both 2.27 Å. The heights from the Pb surface of the two O atoms and the Pb adatom are respectively 2.32 Å, 2.35 Å and 2.67 Å. In the T1 structure, the lines crossing the two O atoms are parallel to the Pb surface with the height of 2.60 Å, while the height of the Pb adatom is 2.72 Å. The O–O bond length is also 1.50 Å, the same as that in the TT structure. And the distances between the two O atoms and the Pb adatom are both 2.29 Å. For S1 and S2 structures, we can see from their ELF graphs in Figs. 2(c) and 2(d) that there are no covalent bondings between the two O atoms, proving the dissociation of the O_2 molecules. Each of the dissociated O atoms bonds both with the Pb adatom and some surface Pb atoms in polar ways. In the S1 structure, one O atom is at the top site bonding with one surface Pb atom and the adatom, while the other O atom is at the hollow site bonding with three surface Pb atoms and the adatom. The distances between the Pb adatom and the O atoms are 2.23 Å and 2.09 Å respectively. The O–Pb–O bond angle is 85°. In the S2 structure, one O atom is at the bridge site bonding with two surface Pb atoms and the adatom, and the other O atom is at the hollow site bonding with three surface Pb atoms and the adatom. The distances between the Pb adatom and the two O atoms are 2.25 Å and 2.18 Å respectively. The O–Pb–O bond angle is 83°.

The adsorption energy per O atom is defined as

$$E_{\rm ad} = (E_{\rm O_2} + E_{\rm surface+adatom} - E_{\rm final\ structure})/2,$$

where $E_{\rm O_2}$, $E_{\rm surface+adatom}$ and $E_{\rm final\ structure}$ are respectively the total free energies of an O_2 molecule, the surface with an adatom and the final structure. The former two terms, $E_{\rm O_2}$ and $E_{\rm surface+adatom}$ are chosen to be the energies in their lowest energy states. For the O_2 molecule, it is the triplet state. For the surface with an adatom adsorbed, it is the adsorption state with the Pb adatom adsorbed at the bridge site, and the free energy in our calculations is −59.30 eV. Our calculated $E_{\rm ad}$ for all the four evolved structures are summarized in Table 2, together with the adsorption energy on a clean Pb(111) surface.[31]

Table 2. Values of adsorption energy ($E_{\rm ad}$) per oxygen atom for the TT, T1, S1 and S2 states, and the molecular adsorption state on the clean Pb(111) surface.

substrate	evolved state	$E_{\rm ad}$/eV
Pb(111)	molecular adsorption state	0.47[31]
adatom+Pb(111)	T1	0.70
	TT	0.75
	S1	1.83
	S2	1.95

From Table 2, we can see that the adsorption energies for all the four evolved structures are larger than the adsorption energy on a clean Pb(111) surface. And the S2 structure is the most stable structure for the adsorption of an O_2 molecule around a surface Pb adatom. We can also see from Table 2 that S1 and S2 structures where the O_2 molecules are dissociated have much larger adsorption energies. So it is energetically favourable for the O_2 molecule to be dissociated around the Pb adatom. Moreover, we observe no energy barriers in the adsorption process of an O_2 molecule into the S1 and S2 structures. Therefore, the dissociation of a gaseous O_2 molecule around a surface Pb adatom is spontaneous without any barriers. This discovery indicates that Pb adatoms, as well as surface impurities, can help O_2 molecules to be dissociated in the initial stage of the oxidation of the Pb(111) surface.

We then analyse the electronic structures for the S2 state, to explore the interaction details between O and Pb atoms. Figure 3(a) shows the local densities of states (LDOSs) for the Pb adatom, an oxygen atom, and a surface Pb atom separately. We can see that the main hybridization area ranges from −5.5 eV to the Fermi energy. Detailed wavefunction analysis reveals that the hybridization in this energy range is between 2p electrons of O and 6p electrons of Pb. We can also see from Fig. 3(a) that the hybridization between electronic states of O and the Pb adatom is much stronger than that between electronic states of O and surface Pb atoms. Comparatively, figure 3(b) shows the LDOSs of the Pb adatom and a surface Pb atom in the adsorption state of the Pb adatom. We can see that in the adsorption state, the adatom has more electronic states distributed below the Fermi energy. So the Pb adatom is chemically more active than surface Pb atoms. And as shown in Fig. 3(a), the interactions between O atoms and the Pb adatom are stronger than between O atoms and surface Pb atoms.

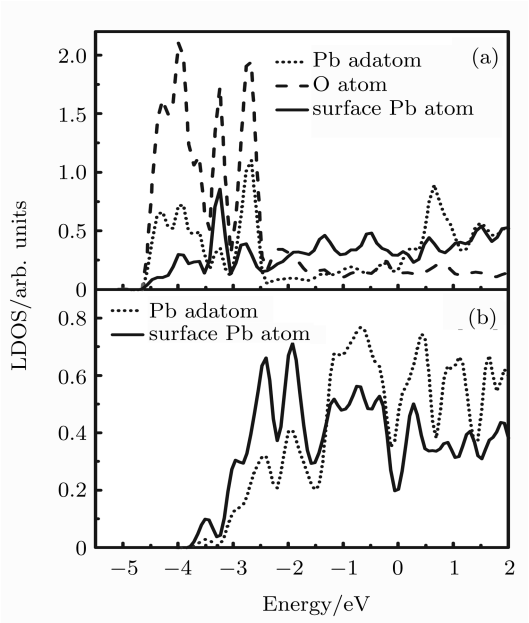


Fig. 3. (a) Local densities of states (LDOSs) of an O atom (dash line), the Pb adatom (dot line) and a surface Pb atom (solid line) for the S2 structure. (b) The LDOSs of the Pb adatom (dot line) and a surface Pb atom (solid line) for the adatom adsorbed Pb surface.

4. Interaction between an adsorbed O_2 molecule and a diffusing Pb adatom

After systematic studies on the adsorption of an O_2 molecule directly around a Pb adatom, we now turn to the study of another possible situation in experiment, i.e., the interactions between an adsorbed O_2 molecule and a diffusing Pb adatom. From earlier studies, we know that the Pb adatoms diffuse easily on the Pb surface, with a very low diffusion barrier of 20∼60 meV.[16] So what will happen when a

Pb adatom diffuses near an adsorbed O_2 molecule on the Pb surface? Will the adsorption states of the O_2 molecule change? From our previous results,[31] we know that an adsorbed O_2 molecule stays at the hollow sites of the Pb(111) surface. And for different orientations, two nearly degenerate adsorption states exist.[31] Here, we define the interaction area as the two pink triangles around the differently adsorbed O_2 molecules as shown in Fig. 4. For a diffusing Pb adatom to interact with the adsorbed O_2 molecule, it must diffuse first into the interaction area. Therefore, we initially put the adatom at the C1–C3 and D1–D3 sites, and construct 6 initial configurations.

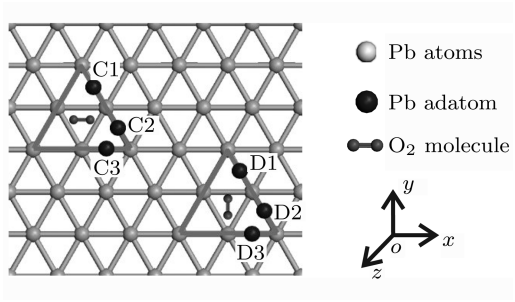


Fig. 4. Initial configuration for studying the interaction between an adsorbed O_2 molecule and a diffusing Pb adatom. Surface Pb atoms, Pb adatoms and O atoms are respectively represented by white, large black and small black balls. The C1–C3 and D1–D3 are initial sites for the Pb adatom to interact with the adsorbed O_2 molecule. The two adsorbed O_2 molecules are respectively oriented along x and y directions.

After geometry optimizations, we find three different states. The relaxation results are summarized in Table 3, and the atomic structures for two evolved states are shown in Fig. 5, together with the corresponding ELF graphs. The atomic and the electronic structures for the TT state have already been described in the previous section, and will not be discussed here any more. In the T2 and folded line (FL) structures, the Pb adatom and the two O atoms form a triangle and an FL respectively. The T2 structure is similar to the T1 structure, except that the triangles lie in different directions on the surface. In the T2 structure, the Pb adatom bonds with both of the two O atoms through polar bondings. The two O atoms are parallel to the Pb surface, with a height of 2.42 Å, while the height of the Pb adatom is 2.85 Å. The bond length of the two O atoms is 1.50 Å, and the distances from them to the Pb adatom are both 2.27 Å. In the FL structure, the Pb adatom only bonds with one O atom through polar bonding. The distance between the two O atoms is 1.47 Å, and the Pb adatom is 2.32 Å away from its nearest O atom. The heights of the two O atoms and the Pb adatom are respectively 1.79 Å, 2.03 Å and 2.43 Å.

Table 3. Final evolved states for the interaction of an adsorbed O_2 molecule with a diffusing Pb adatom, and the corresponding adsorption energies (E_{ad}).

O_2 orientation	site of Pb adatom	evolved state	E_{ad}/eV
	C1	T2	0.74
x	C2	FL	0.65
	C3	FL	
	D1	TT	0.75
y	D2	FL	
	D3	FL	

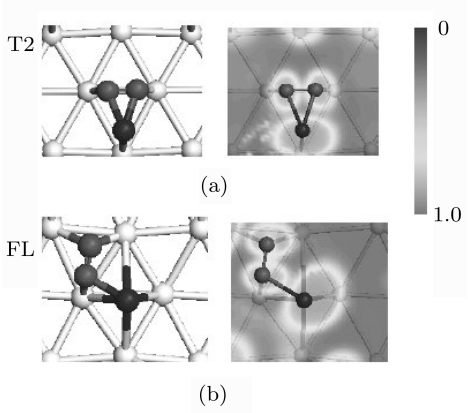


Fig. 5. Atomic structures (left) and ELF graphs (right) for T2 (a) and FL (b) states. Surface Pb atoms, Pb adatom and O atoms are represented respectively by white, large black and small black balls. The ELF graphs are shown in the planes that contains the Pb adatom and the two O atoms.

We can see from the ELF graphs in Figs. 5(a) and 5(b) that there are still covalent bondings between the two oxygen atoms after the interaction between the adsorbed O_2 molecule and the diffusing Pb adatom. So different from the direct adsorption of an O_2 molecule around a Pb adatom, the interaction between an adsorbed O_2 molecule and a diffusing Pb adatom leads to no dissociation. From Table 3, we can see that the adsorption energy for the TT structure is the largest, and so it is the most stable evolved adsorption state. We can also see from Tables 2 and 3 that the adsorption energy of oxygen is increased by 0.28 eV after the interaction with a diffusing Pb adatom, indicating an enhancement of the adsorption through the Pb adatom.

Through careful wavefunction analysis, we find that LDOSs of the two O atoms in the TT structure have very similar distributions to that in a PbO_2 molecule. Since the fabrication of different kinds of metal–oxide clusters becomes more and more important, here we would like to answer whether the TT structure is of a PbO_2 molecule that adsorbed on the Pb(111) surface. So we here add the total LDOSs of the Pb adatom and the two O atoms together, to compare with the molecular orbitals of a PbO_2 molecule in vacuum. The bands decomposed charge densities for the molecular orbitals of PbO_2 and corresponding bands of the TT structure are comparatively shown in Fig. 6. As shown in the figure, there are 8 occupied molecular orbitals for a PbO_2 molecule in vacuum, and molecular orbitals e and f are degenerate. We can also see from Fig. 6 that only the wavefunctions of orbitals c and f have considerable distributions around the Pb adatom, the wavefunctions of other orbitals are all distributed mainly around the two O atoms. In the TT structure, there are 6 corresponding localized bands that have similar band decomposed charge densities to that of the lower 6 molecular orbitals of PbO_2 as shown in Fig. 6. According to the weak chemisorption picture from the Newns–Anderson model,[34] the TT structure is in a chemisorption state for a PbO_2 molecule on the Pb(111) surface, with the highest two molecular orbitals being broadened through electronic hybridizations.

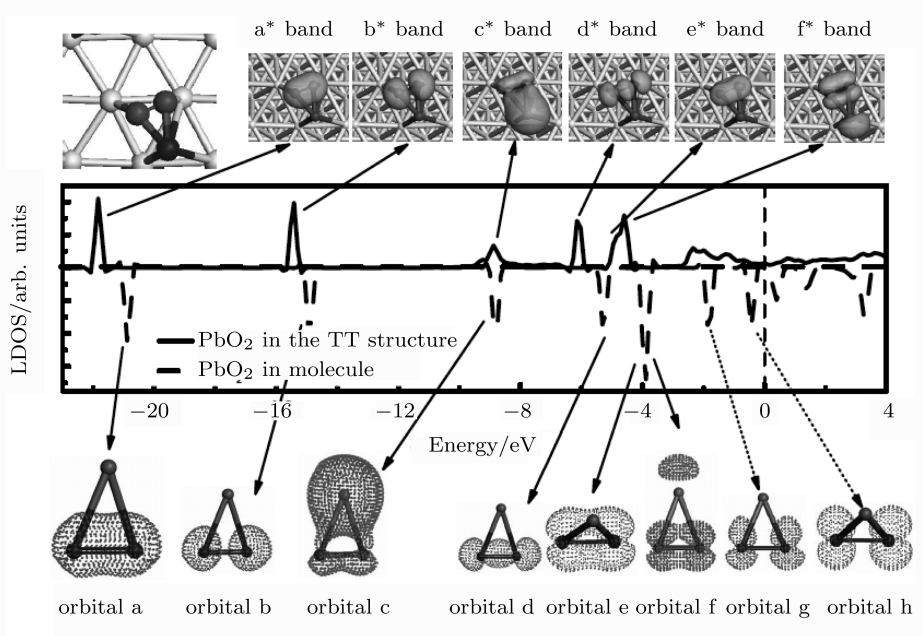


Fig. 6. The molecular orbitals for an isolated PbO_2 molecule (down) and the band decomposed charge densities for the electronic states that distribute around the two O atoms and the Pb adatom in the TT state (up).

5. Conclusion

We have systematically studied the direct adsorption of an O_2 molecule around a Pb adatom, and the interaction between an adsorbed O_2 molecule and a diffusing Pb adatom, using first-principles calculations. We find that the direct adsorption of an O_2 molecule around a Pb adatom is spontaneous without any energy barriers, and the adsorption energy after dissociation is much larger than that of the molecular adsorption state on a clean Pb(111) surface. Through electronic analysis, we find that the electronic states of O hybridize strongly with electrons of the Pb adatom, and less strongly with electrons of surface Pb atoms. For an adsorbed O_2 molecule on the clean Pb(111) surface, we find that the interaction with a diffusing Pb adatom will not make it dissociated. However, the adsorption energy of oxygen is increased after the interaction. And the evolved state is also the adsorption state of a PbO_2 molecule on the Pb(111) surface.

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