

# The Adsorption and Dissociation of O<sub>2</sub> on Cu Low-Index Surfaces

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The extended LEPS of O<sub>2</sub>–Cu single crystal plane systems is constructed by means of 5-MP (the 5-parameter Morse potential). Both the adsorption and dissociation of O<sub>2</sub> on Cu low-index surfaces are investigated with extended LEPS in detail. All critical characteristics of the system that we obtain, such as adsorption geometry, binding energy, eigenvalues for vibration, etc., are in good agreement with the experimental results. Our calculated results suggest there are many differences between O<sub>2</sub>–Cu (110) and O<sub>2</sub>–Pd (110) systems. On a Cu (110) surface, O<sub>2</sub> adsorbs in a tilted configuration and there are two lowest energy dissociation channels along the [001] and [110] directions, respectively. We speculate that the adsorption geometry of O<sub>2</sub> on the metal surfaces relates to the lattice constant of metal. Meanwhile, We use the concepts of the molecular dissociation limit and the surface dissociation distance to analyze again the dissociation mechanism of the O<sub>2</sub> on the low-index surfaces.

## 1. Introduction

Oxygen adsorption and dissociation on transition metal surfaces is always an interesting topic both because many important industrial oxidation processes are heterogeneously catalyzed by transition metals and feature O<sub>2</sub> as the oxidizing agent and because O<sub>2</sub> dissociation is the first step toward the corrosion of various metals.<sup>1</sup> Again, the copper single crystal is an important catalyst for industrial process, such as the catalytic oxidation of carbon monoxide to carbon dioxide, the oxidative dehydrogenation of methanol to formaldehyde, and ammonia oxidation.<sup>2</sup> So, the oxygen adsorption and dissociation on Cu surfaces is of considerable research and practical interest.<sup>1–17</sup>

At low coverage, O<sub>2</sub> dissociates directly upon adsorption on Cu (100), but with increasing coverage, molecular adsorption becomes stable.<sup>3,4</sup> In the temperature range of 0–100 K, in the thermal desorption spectroscopy (TDS)<sup>3</sup> corresponding to high coverage, three distinct peaks could be seen: oxygen multilayer, physisorbed oxygen, and chemisorbed oxygen respectively, while in the spectra of the low coverage only one desorption peak was found. For the chemisorbed state, the O–O bond is 1.52 Å, but in the physisorbed state, the O–O bond is 1.21 Å, nearly gas-phase-like. At low coverage, Daelen et al.<sup>4</sup> also found oxygen dissociated directly over a hollow site from the gas phase before a weakly adsorbed state where O<sub>2</sub> was lying parallel to the surface. Yata et al.<sup>5</sup> investigated the adsorption and dissociation of O<sub>2</sub> on the Cu (001)-(2√2 × √2)-O surface using supersonic molecular beam techniques. They thought the dissociation mechanism of O<sub>2</sub> on the Cu (100) surface was precursor-mediated dissociation at high coverage, and the activation barrier for dissociation was 0.33 eV. Fischer and Whitten's<sup>6</sup> theoretical results showed chemisorbed oxygen with one O atom atop Cu and the O–O axis paralleled to the surface.

About the Cu (110) surface, there were still questions concerning primarily the existence of molecular oxygen on the surface and the detailed mechanisms for the dissociative process.<sup>7</sup> Experimental studies had established that molecular

oxygen absorbed dissociatively on the Cu (110) surface at room temperature.<sup>8–12</sup> At low temperature, Prabhakaran and Rao<sup>9</sup> reported that they found a loss peak at 656 cm<sup>-1</sup> in their electron energy loss spectroscopy (EELS) studies, which they explained by the existence of molecular chemisorbed oxygen, and this loss peak was assigned to the frequency of the O–O stretching mode, whereas Mundemar et al.<sup>13</sup> could observe only atomic-like features in their study. The latter authors concluded that the loss peak at 656 cm<sup>-1</sup> that Prabhakaran et al. found might be either due to CO<sup>13</sup> or H<sub>2</sub>O<sup>10</sup> contamination. Recent theory studies by Liem et al.<sup>7,14</sup> supported Prabhakaran and Rao's<sup>9</sup> viewpoint, and also thought there was oxygen adsorbed molecularly.

The studies of O<sub>2</sub>–Cu (111) showed that the adsorption molecular oxygen could exist stably.<sup>15–18</sup> Prabhakaran et al. reported two possible species of molecularly adsorbed O<sub>2</sub> on polycrystalline Cu at 80 K in their EELS study, and the O–O stretching frequencies were 610 cm<sup>-1</sup> and 880 cm<sup>-1</sup> respectively. Both species disappeared upon annealing to 160 K. Using UV photospectroscopy (UPS) Spitzer et al. found a chemisorbed molecular O<sub>2</sub> species that disappeared at 160 K.<sup>16</sup> Recently, Iwasawa and co-worker<sup>17</sup> investigated the adsorption states of oxygen on Cu(111) by means of HREELS. At 100 K, the 370 cm<sup>-1</sup>, 610 cm<sup>-1</sup>, and 820–870 cm<sup>-1</sup> peaks were detected. The 370 cm<sup>-1</sup> peak was assigned to  $\nu(\text{Cu}-\text{O})$  of the atomic species. The 610 cm<sup>-1</sup> and 820–870 cm<sup>-1</sup> peaks were assigned to  $\nu(\text{O}-\text{O})$  of the peroxo-I-like state (O<sub>2</sub> adsorbed in a bridged sites) and peroxo-II-like state (O<sub>2</sub> bound on atop sites), respectively. The O–O bonds of the two peroxo species lied parallel to the surface. Xu<sup>18</sup> studied the adsorption and dissociation of O<sub>2</sub> on the Cu(111) surface using the density functional theory (DFT) method. Two types of chemisorbed molecular precursors are identified: a nonmagnetic peroxo-like state located at bridge-fcc (hcp)-bridge (BH(H')B) and a paramagnetic superoxo-like state at top-bridge-top (TBT), which respectively had the vibration frequencies of 729 cm<sup>-1</sup> and 954 cm<sup>-1</sup>.

Based on the former experiments and theoretical researches, we find that the dissociation of O<sub>2</sub> on the compact Cu (111) surface is more difficult than on the Cu(100) and Cu(110)

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surfaces. It is similar to the adsorption and dissociation of O<sub>2</sub> on Pd surfaces.<sup>19</sup> In the investigation of the O<sub>2</sub>-Pd system, we brought forward first the conceptions of the molecular dissociation limit and the surface dissociation distance, which offer the answer to the question why O<sub>2</sub> dissociates with more difficulty on the (111) surface than on the (100) and (110) surfaces.<sup>19</sup> For the surface molecular dissociation, the molecule does not dissociate into atomic states until the length between two atoms (the molecular bond) stretches enough to conquer the atomic side interaction. Then, there is a threshold of the length of molecular dissociation bond, which is called the molecular dissociation limit. That is to say, only the length of the molecular bond exceeds the molecular dissociation limit and the molecule can dissociate.<sup>19</sup> On the other hand, any positions on the catalytic metal surface may form the dissociation and adsorption channel of the incidence molecule, while the dissociated atoms cannot adsorb in any positions on the surface because the atomic adsorption is decided by the adsorption geometry. The dissociated atoms often adsorb in the high symmetrical sites. It is easy to assume that only the neighboring vacant adsorption sites (or the surface vacant twain sites) exist on the surfaces, and the diatomic molecule can dissociate. Evidently, the distance of the neighboring adsorption sites (the distance of the surface vacant sites) is the shortest distance of the molecular dissociation, which is called as the surface dissociation distance for the diatom molecule.<sup>19</sup> The magnitude of the surface dissociation distance is relative to metal's lattice constant and surfaces. Only the surface dissociation distance over the molecular dissociation limit, the molecule can dissociate easily, otherwise the molecular dissociation is difficult.<sup>19</sup> According to the experience, the oxygen molecular dissociation limit is estimated about double the gaseous O-O bond length, approximately 2–2.3 Å and the surface dissociation distance can be obtained in quantification.<sup>19</sup>

Both Cu and Pd belong to FCC lattice metals, but copper's lattice constant is smaller. Then, what is the same and what is different when O<sub>2</sub> adsorbs and dissociates on the two metals? We have studied the system of O<sub>2</sub>-Pd in detail.<sup>19</sup> Here, based on the study of oxygen atom adsorbing and diffusing on Cu low-index and stepped surfaces,<sup>20</sup> we make a further study of the adsorption and dissociation of O<sub>2</sub> on Cu low-index surfaces with the extended LEPS. Using the five-parameter Morse potential (5-MP) of interaction between an adatom and metal surface cluster, we have already dealt with O-Cu,<sup>20</sup> O-Ni,<sup>21</sup> O-Pd<sup>22</sup> low index surfaces and O-Cu(211)(410),<sup>20</sup> O-Ni(510)(115),<sup>21</sup> O-Pd(311)<sup>22</sup> stepped surface systems, and obtained the good results that agree well with the experimental data. The extended LEPS constructed by 5-MP has been successfully used in the investigations of O<sub>2</sub>-Pd,<sup>19</sup> CO-Ni<sup>21</sup>, and H<sub>2</sub>-Ni<sup>23</sup> systems.

## 2. Extended LEPS Constructed by 5-MP and Cluster Models

McCreedy and Wolken<sup>24,25</sup> first put the extended LEPS method forward, which is the technique frequently used in investigating the interaction of the diatomic molecule and metal surface cluster. However, to date this method has become a built-up potency. Analyzed from the mathematical physics, the extended LEPS potential deduced by valence bond theory is constructed by three pair-potential functions: one for a gaseous diatom, the other two for a single atom and a surface cluster, respectively. Moreover, three Sato parameters ( $\Delta$ ) are also needed. The pair-potential functions for a gaseous diatom can be obtained from spectroscopic data, while the other two should be constructed by other means. Therefore, the latter is the brilliant part of the

**TABLE 1: Five Parameters for the O-Cu System**

system	$D/\text{eV}$	$\beta/\text{\AA}^{-1}$	$R_0/\text{\AA}$	$Q_1/\text{\AA}$	$Q_2/\text{\AA}$
O-Cu <sup>[20]</sup>	0.98	2.17	2.02	1.45	0.18

extended LEPS method. In this paper, we construct the extended LEPS by three pair-potential functions as such: one is a Morse function employed for the gaseous diatom and the 5-MP is used for the other two.

As for the O<sub>2</sub>-Cu surface system, the LEPS includes O<sub>2</sub> molecular potential and O-Cu surface potential. Whether the LEPS is good or not will depend on whether the three pair potentials are good or not. Commonly, the pair-potential function for diatomic molecule can be obtained from spectroscopic data. So it is pivotal whether the two pair-potential functions between single gaseous atoms and surface clusters are excellent and reliable, which is the most important part of the extended LEPS method. In this paper, we present the excellent O-Cu pair-potential by the 5-MP method and have successfully dealt with the O-Cu system using this method (see ref 20). Therefore, we can obtain a good O<sub>2</sub>-Cu pair-potential function. Moreover, once the parameters are ascertained, the O<sub>2</sub>-Cu surface interaction potential is independent of surface cluster structure. That is to say, the extended LEPS can dispose the O<sub>2</sub>-Cu (100), O<sub>2</sub>-Cu (110), and O<sub>2</sub>-Cu (111) at the same time.

**2.1. 5-MP Function.** The 5-MP (5-parameter Morse potential function) has been described in the literature,<sup>20–22</sup> here, stated briefly, as follows: on the assumption that the metal cluster is frozen, the approximation is adopted for the whole surface cluster. So the interaction energy  $U(\vec{R})$  as the 5-MP between an atom, which coordinate is specified by  $\vec{R}$ , and the whole metal surface cluster can be written in the form of a Morse potential:

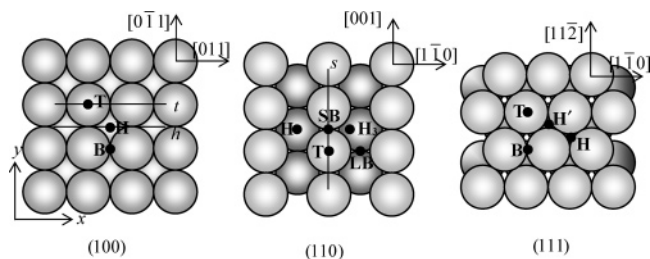
$$U(\vec{R}) = D \sum_{i=1}^{\text{cluster}} \left( \frac{h_i + Q_1}{R_i + Q_2} \right) \{ \exp[-2\beta(R_i - R_0)] - 2 \exp[-\beta(R_i - R_0)] \} \quad (1)$$

In eq 1,  $R_i$  is the distance between the adatom and the  $i$ th metal surface atom and denoted as  $R_i = |\vec{R} - \vec{r}_i|$ ;  $r_i$  specifies the coordinate of adsorbed atom and the  $i$ th metal surface atom respectively;  $h_i$  is the vertical distance between the adatom and the  $i$ th metal surface atom;  $D$  is a simulating energy parameter and  $Q_1$  and  $Q_2$  are two simulating parameters;  $\beta$  and  $R_0$  are the parameters for vibration and equilibrium distance, respectively. The five adjustable parameters of the O-Cu obtained from the literature<sup>20</sup> are listed in Table 1. The main characteristic of 5-MP is that the parameters are independent of structure for the surface clusters, so we use the same set of optimized of the parameters. The adsorption systems of an adatom on a low-index surface are easy to deal with at one time, and the adsorption systems on the stepped surface constituted by the low-index surfaces are also easy to carry out.

**2.2. Extended LEPS Constructed by 5-MP.** The 5-MP (eq 1) is regarded as the bonded interaction potential. According to the extended LEPS method, the antibonded interaction potential between the adatom and the metal surface cluster can be expressed as

$$U^+(\vec{R}) = D^+ \sum_{i=1}^{\text{cluster}} \left( \frac{h_i + Q_1}{R_i + Q_2} \right) \{ \exp[-2\beta(R_i - R_0)] + 2 \exp[-\beta(R_i - R_0)] \} \quad (2)$$

where  $D^+ = 0.5D(1 - \Delta)/(1 + \Delta)$  and  $\Delta$  is the so-called Sato



**Figure 1.** Cluster models and adsorption sites for low-index surfaces.

parameter. Thus, the Coulomb integral  $J(J = U + U^+/2)$  and the exchange integral  $K(K = U - U^+/2)$  for a special point can be obtained from eqs 1 and 2. Finally, the extended LEPS potential energy surface of diatomic molecule (AB) and metal (M) surface can be expressed as

$$E = J_{AB} + J_{AM} + J_{BM} + [K_{AB}^2 + (K_{AM} + K_{BM})^2 - K_{AB}(K_{AM} + K_{BM})]^{1/2} \quad (3)$$

In eq 3,  $J_{AB}$  and  $K_{AB}$  are Coulomb integral and exchange integral for the diatom AB while  $J_{iM}$  and  $K_{iM}$  are Coulomb integral and exchange integral for atom and the metal cluster ( $i = A, B$ ). For the interaction of O<sub>2</sub> and Cu surfaces ( $O=A=B$ ), the potential function includes two adjustable Sato parameters ( $\Delta_{O-O}$  and  $\Delta_{O-Cu}$ ). Just like the five parameters mentioned above in the 5-MP, we also adjust them simultaneously according to the experimental data of three low-index (100), (110), and (111) surfaces. Therefore, our extended LEPS is also independent of the structure of the surface clusters. Obviously, the same set of optimum Sato parameters can be used both in the adsorption of diatomic molecules on the metal low-index surfaces and the stepped defect metal surfaces.

### 2.3. Construction of Cluster Models for Copper Surfaces.

Metal copper belongs to FCC lattice with the lattice constant  $a_0 = 0.3615$  nm. Considering the local geometrical symmetry in a point group and the lattice displacement symmetry for the crystal cell as well as the boundary effect of adatoms, we simulate the Cu surface cluster with at least five (high) layers of cell atoms, and every layer contains at least  $10(\text{length}) \times 10(\text{wide})$  atoms, which contains about 400–500 copper atoms. The size of the cluster is defined by the principle that there is no boundary effect in our calculation, which means: “The cluster simulated must have certain size. For the same adsorption site, the critical characteristics of adsorption atom at the boundary are different slightly from that of in the interior of the cluster surface, which is the so-called boundary effect. To ignore the boundary effect, the range of the surface cluster is simulated at least two unit cells from the center to boundary.”

Figure 1 shows cluster models and adsorption sites for the three low-index surfaces of Cu(111), Cu(100), and Cu(110). They are the top site (T), the hollow site (H), bridge site (B) for the surfaces; fcc hollow site (H) and hcp hollow site (H') for Cu (111) surface; the long-bridge site (LB), short-bridge site (SB), and the pseudo-3-fold hollow site (H<sub>3</sub>) for Cu (110) surface, respectively.

Commonly, the coordinate of the zero point is oriented on the top atom, the  $x$  axis and  $y$  axis respectively corresponding with the crystal axis as shown in Figure 1, the  $z$  axis pointing to vacuum, and the distance of the nearest two lines (or two rows) is regarded as the unit length of  $x$  and  $y$  axis, which is so-called the lattice coordinate. There are six degrees of freedom in the movement of the diatomic molecule, and there are several definitions about the coordinate. We adopt the lattice coordinates

for the centroid of the diatomic molecule to denote the orientation of molecule on the cluster surface, and adopt the polar coordinates for the diatomic molecule itself. Here,  $\theta$  shows the angle between O–O bond and surface normal ( $z$ -axis), while  $\varphi$  is the angle between the projection of O–O bond and  $x$ -axis. The systemic potential function  $-E(x, y, z, r, \theta, \varphi)$  includes six variables that constitute seven-dimension energy hypersurface. The critical point is the one for which the first derivative is zero on the hypersurface, and the second derivatives of the critical points form the Hessian matrix. The number (denoted as  $\lambda$ ) of negative eigenvalues of Hessian matrix characterizes the nature of critical points. The critical point of  $\lambda = 0$  corresponds to the stable state of the system and the one with  $\lambda = 1$  corresponds to the trans state. They are what we pay more attention to. There are two stable states with  $\lambda = 0$ . One is the adsorption state of dissociated atoms on the surface, and the other is the adsorption state of diatomic molecule on the surface. The former has been studied systematically,<sup>20</sup> and the latter is mainly the concern in this paper. Regarding the diatomic molecular adsorption system, there are also two trans states with  $\lambda = 1$ : the diffusion trans state forms with the negative eigenvalue of Hessian matrix appearing in the critical point of lattice coordinates ( $x, y, z$ ), and the construction trans state forms with the negative eigenvalue of Hessian matrix appearing in the critical point of polar coordinates ( $\theta, \varphi$ ). It is dissociation trans-state only when the negative eigenvalue of Hessian matrix appears in the critical point of bond length ( $r$ ) in the polar coordinates. In this paper we report the study of the adsorption and dissociation of O<sub>2</sub> molecule on the low-index surfaces of Cu, so we just pay attention to the critical points with  $\lambda = 0$  or  $\lambda = 1$ .

## 3. Result and Discussion

According to the experimental data, we get the optimization of the Sato parameters  $O-Cu = -0.153$  and  $O-O = 0.312$  by calculating and adjusting. From the spectrum data, the O–O bond length of  $1.21 \text{ \AA}$  and the vibration frequency of  $1555 \text{ cm}^{-1}$  for gas molecule have been given.<sup>26</sup> Our calculated results are listed in Table 2. Where,  $E_b$  represents the binding energy;  $f_{O-O}$  represents the intermolecular O–O stretching vibration frequency;  $Z_{O1-Cu}$ ,  $Z_{O2-Cu}$  represent the heights of the close O atom and the far O atom to the surface, respectively;  $R_{O-O}$  is the O–O bond length, and  $R_{O2-Cu}$  is the distance of the center of mass of O<sub>2</sub> above the surface. The meanings of  $\lambda$ ,  $\theta$ , and  $\varphi$  are same as mentioned in the former. The comparison between our results and the data from literature are listed in Table 3.

**3.1. O<sub>2</sub> Dissociation and Adsorption on Cu(111).** In the low-index surfaces of the face-centered cubic (FCC) metal, the (111) surface is the most compact one, and the adsorption and dissociation of O<sub>2</sub> on this surface is complex comparatively, so the interaction of O<sub>2</sub> and Cu(111) is always investigated by all kinds of experimental and theoretical methods that have offered a great deal of information about the molecular adsorption state. In this paper we calculate all critical characteristics of the O<sub>2</sub>–Cu (111) surface and list a part of the results in Table 2.

Our calculated results suggest that there is only one molecular adsorption state ( $\lambda = 0$ ) with the centroid of O<sub>2</sub> projecting over bridge site (B), the two atoms locating at the nearest three-fold hollow sites and O–O bond paralleling to the surface. Here, we name it H–B–H. The O–O stretching frequency is  $597 \text{ cm}^{-1}$  and O–O bond length is  $1.57 \text{ \AA}$ . In the instance, the molecular side interaction still remains between the two atoms and the molecule does not dissociate. Over the H (fcc) and H' (hcp) sites, we find two construction trans states ( $\lambda = 1$ , the negative eigenvalue in  $\theta$ ) named H and H' state. Over the two



**TABLE 2: Critical Characteristics of O<sub>2</sub>–Cu Surface System**

system	site	$\lambda$	$E_b$ (eV)	$f_{O-O}$ (cm <sup>-1</sup> )	$Z_{O1-Cu}$ (Å)	$Z_{O2-Cu}$ (Å)	$R_{O-O}$ (Å)	$R_{O2-Cu}$ (Å)	$\theta$ (°)	$\varphi$ (°)
O <sub>2</sub> –Cu(100)	H1	1	2.67	1109	0.1	1.45	1.35	0.78	0	-4
	H2	1	2.16	536	1.4	1.4	1.45	1.4	90	0
	BHB	2	1.63		1.51	1.51	2.6	1.51	90	0
	S	2	2.21		0.82	1.95	2.2			
O <sub>2</sub> –Cu(110)	H <sub>3</sub> –H–H <sub>3</sub>	0	2.85	649	0.669	1.23	1.47	0.95	67	0
	LB	1	1.56	979	0.2	1.56	1.36	0.88	0	-17
	H <sub>3</sub>	1	0.81	1029	0.65	1.98	1.34	1.31	5	0
	H <sub>3</sub> –SB	1	2.63		0.679	1.51	2.32			
	H <sub>3</sub> –LB	1	2.70		0.378	1.52	2.53			
O <sub>2</sub> –Cu(111)	H	1	0.14	832	1.34	2.68	1.35	2.01	0	-72
	H'	1	0.15	833	1.33	2.68	1.35	2.01	0	21
	H–B–H	0	3.58	597	1.36	1.36	1.57	1.36	90	90
	H–BB–H	1	3.11		1.35	1.49	1.97			

**TABLE 3: Comparison between Our Results and Literature**

	system	experiment	theoretical calculated	this work
$f_{O-O}$ (cm <sup>-1</sup> )	O <sub>2</sub> –Cu(110)	656[9]		649
	O <sub>2</sub> –Cu(111)	610(peroxo-I)[15,17]	729(peroxo)[18]	597
		810–870(peroxo-II)[17]	789(H') [18]	832(H), 833(H')
		880(peroxo-II) [15]	954(superoxo)[18]	
$R_{O2-Cu}$ (Å)	O <sub>2</sub> –Cu(110)		1.04(H)[14]	0.95(H)
$R_{O-O}$ (Å)	O <sub>2</sub> –Cu(111)	1.65(peroxo-I)[16]	1.32(B)[18]	1.57(H–B–H)
		1.48(peroxo-II)[16]	1.47(H), 1.48(H')[18]	1.35(H, H')
			1.54(H)[14]	1.47(H <sub>3</sub> –H–H <sub>3</sub> )
	O <sub>2</sub> –Cu(110)		1.41(LB)[14]	1.36(LB)

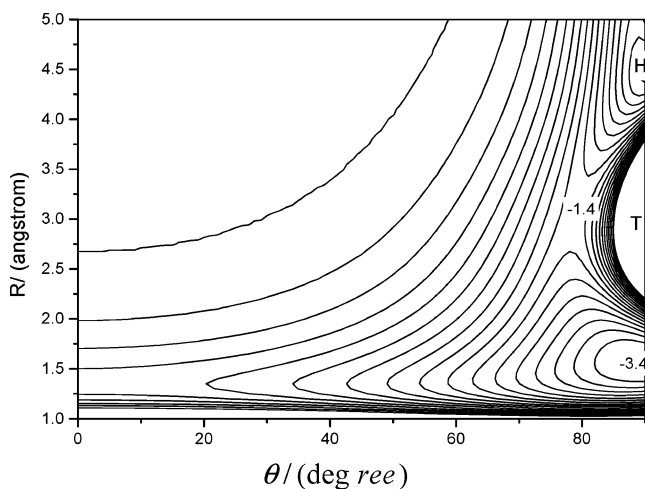
sites, O<sub>2</sub> adsorbs in an upright orientation. From the Table 2, we can see the characteristics of the two states are almost the same: the distances of the O<sub>2</sub> centroid above the surface are 2.01 Å; O–O bond lengths are 1.35 Å; the stretching frequencies of O–O are 832 cm<sup>-1</sup> and 833 cm<sup>-1</sup>, and binding energies are 0.14 eV and 0.15 eV, respectively. It is difficult to distinguish them by means of experimental methods only from the frequency, bond length, etc., so they can be seen as identical states.

In the experimental and theoretical studies, scientists had found evidence for the existence of two molecular O<sub>2</sub> adsorption species on Cu(111).<sup>15–18</sup> The peroxo-I-like state with O–O stretching frequency of 610 cm<sup>-1</sup>, O<sub>2</sub> centroid over bridge site (B), O–O bond parallel to the surface, was found in HREELS.<sup>17</sup> The H–B–H molecular state (O–O stretching frequency of 597 cm<sup>-1</sup>) we obtain is similar to it. With the coverage increasing, the construction trans states with  $\lambda = 1$  are transformed into stable molecular adsorption states. The O–O stretching frequencies of 832 cm<sup>-1</sup> and 833 cm<sup>-1</sup> are in good agreement with those of the experimental peroxo-II-like state (880 cm<sup>-1</sup>(ref 15), 820–870 cm<sup>-1</sup> (ref 17)). From these experimental results we can see there are a lot of O<sub>2</sub> molecular states on the Cu(111) surface in the different coverages, and these indicate that molecular O<sub>2</sub> is difficult to dissociate on Cu(111).

Differing from the system of O<sub>2</sub>–Pd,<sup>19</sup> we do not find the diffusing trans state adsorbing perpendicularly over the B site, and the possible reason is the smaller lattice constant of Cu, in contrast to Pd.

In the system of O<sub>2</sub>–Pd,<sup>19</sup> we have shown that only when the length of molecular bond exceeds the molecular dissociation limit will the molecule dissociate. Surface dissociation distance ( $\sqrt{6}/6a_0$ ) of (111) surface is far shorter than the molecular dissociation limit, so the molecular state (H–B–H) exists naturally at the low coverage. At low coverage, for the molecular trans states (H and H'), they are unstable originally but will exist as the form of molecular adsorption state (H–B–H) ultimately, whether the molecules drop down directly or

diffusely. With the coverage increasing, they will become stable due to the interaction between the adsorption molecules, and in the experiments, the O–O stretching frequencies can be detected (880 cm<sup>-1</sup>(ref 15) and 820–870 cm<sup>-1</sup> (ref 17)). So only the H–B–H state with  $\lambda = 0$  is the dissociative precursor state. The dissociation of the H–B–H state is similar to O<sub>2</sub> on Pd(111).<sup>19</sup> The dissociation along the molecular axis needs to span the top site, and it will encounter the high potential barrier from the strong repulsion potential. To more distinctly depict the process, we scan the sketch map of the potential energy surface (PES). We fix one O atom closing to the surface at the three-fold site (H), and then change the angle of  $\theta$  from 0 to 90 degrees and the length of O–O bond from 1.0 to 5.0 Å. In this way, we can gain the PES along the molecular axis (see Figure 2) with the counter of 0.2 eV. From the PES, we can see the potential barrier is up to 2.0 eV, so along this direction, the diffusion of O atom is almost impossible. It needs one atom of the diatom molecule to diffuse in the proper direction and dissociate through the lower potential. The H–BB–H state

**Figure 2.** Dissociation PES of the O<sub>2</sub> on Cu (111) surface along the molecular axis ( $R - \theta$ )( $\varphi = 90^\circ$ ).

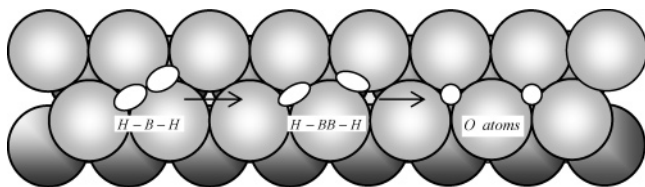


Figure 3. Sketch map of the O<sub>2</sub> dissociation on Cu(111).

( $\lambda = 1$ ) is the dissociation trans state (the negative eigenvalue in  $r$ ) (see Table 2). The geometry of this state is one atom adsorbing in the three-fold hollow site and the other one diffusing to sub-neighbor bridge site (see Figure 3). For molecular state transformation into the dissociation trans state through one atom diffusing, 0.47 eV potential is needed. From Figure 3, we can see the dissociated atoms adsorb in the three-fold site of the interphase crystal cell finally. Thus it can be seen that the main channel of O<sub>2</sub> dissociation on Cu(111) should be precursor dissociation, but the dissociation potential of this channel is high. So the H-B-H state is a longevity precursor state.

**3.2. O<sub>2</sub> Dissociation and Adsorption on Cu(110).** The Cu(110) surface is a zigzag surface constituted by two (111) facets colliding with each other top to top, and has symmetrical zigzag along the  $[1\bar{1}0]$  direction, so it is the most rough one among the low-index surfaces. There are double adsorption sites, a long-bridge site (LB) and a pseudo-three-fold site (H<sub>3</sub>) (see Figure 1). In this paper we research the critical characteristics of the molecular state with  $\lambda < 2$  (see Table 2). Only one molecular adsorption state named H<sub>3</sub>-H-H<sub>3</sub> is found with  $\lambda = 0$ . The adsorption geometry of the state is that O<sub>2</sub> tipsily adsorbs on the surface with tilt angle ( $\theta$ ) of 67° along the  $[1\bar{1}0]$  direction and the midpoint of the O<sub>2</sub> molecular is located at the hollow site, with the two atoms adsorbing above the nearest pseudo-three-fold sites. The stretching frequency of O-O is 649 cm<sup>-1</sup>, which is in agreement with the experiment data (656 cm<sup>-1</sup>) obtained by Prabhakaran and Rao in their EELS.<sup>9</sup> Otherwise, we also find two molecular construction trans states with  $\lambda = 1$  (the negative eigenvalue in  $\theta$ ): One is named LB state with O<sub>2</sub> molecular located perpendicularly at the long-bridge site; the other is named the H<sub>3</sub> state in which the oxygen molecule tilts ( $\theta = 5^\circ$ ,  $\varphi = 0^\circ$ ) in the pseudo-three-fold site. Other critical characteristics are listed in Table 2.

On the Cu(110) surface, there are many kinds of surface vacant twain sites because of the existence of surface double adsorption sites. By analyzing the surface geometrical structure, it is easy to see that the distances of surface vacant twain sites from the neighboring unit cells (the surface dissociation distance)

are longer than the molecular dissociation limit; only the distance of the H<sub>3</sub>-H<sub>3</sub> vacant twain sites from the same unit cell is shorter than the molecular dissociation limit. Therefore, the H<sub>3</sub>-H-H<sub>3</sub> molecular adsorption state forms on the (110) surface.

In the system of O<sub>2</sub>-Pd(110), molecular oxygen lied flat on the surface and there was only one lowest potential channel along the  $[001]$  direction when the molecular state dissociated.<sup>19</sup> But for the O<sub>2</sub>-Cu (110) system, from the calculated results we can see there are two lowest potential channels along the  $[001]$  and  $[1\bar{1}0]$  direction, respectively. The H<sub>3</sub>-LB and H<sub>3</sub>-SB states listed in Table 2 are the dissociation trans states (the negative eigenvalue in  $r$ ) with  $\lambda = 1$  we have searched for. From the characteristics, we can see that one oxygen atom locates in the H<sub>3</sub> site and the other one passes the near LB site along the  $[001]$  direction. Finally, the molecule exists in the form of molecular dissociation states (H<sub>3</sub>-LB) with the length of the O-O bond stretching to 2.53 Å. When the other atom passes the near the SB site along the  $[1\bar{1}0]$  direction and the O-O bond length reaches 2.32 Å, the dissociation trans state (H<sub>3</sub>-SB) comes into being. When the molecule state transforms into molecular dissociation states (H<sub>3</sub>-LB, H<sub>3</sub>-SB), potential barriers of 0.15 and 0.22 eV are needed respectively, which is in good agreement with the present theoretical study (0.11 eV).<sup>27</sup> Obviously, the molecular adsorption state (H<sub>3</sub>-H-H<sub>3</sub>) is a sub-stable molecular dissociation precursor state, and it exists only in the low temperature. It will dissociate easily with rising temperature. This is in accord with experimental studies.<sup>8-9</sup>

It is difficult to describe accurately the dissociation process of the molecular adsorption state (H<sub>3</sub>-H-H<sub>3</sub>), because six degrees of freedom change in the process. But the important mode is as follows: one oxygen atom adsorbs in the H<sub>3</sub> site while the other oxygen atom turns to the  $[1\bar{1}0]$  direction, diffuses along the groove on the surface, and passes the potential barrier of H<sub>3</sub>-SB, then adsorbs in H<sub>3</sub> of the nearest unit cell (see in Figure 4, where (a) is a side view, (b) is a top view). To more distinctly depict the process, we scan the sketch map of the potential energy surface (PES) (see Figure 5). In the PES, one oxygen atom is fixed in the H<sub>3</sub> site, the degrees of  $\theta$  (0-90°) and the length of the O-O bond are set as the  $x$ -axis and  $y$ -axis, respectively. The PES indicates that the molecular state dissociates very easily when the molecular axis rotates to parallel the surface, and for the diffusing oxygen atom the two H<sub>3</sub> sites of the neighbor unit cell are the same. Then, we scan the molecular dissociation channels according to the parallel construction and simply draw the short-bridge line named  $s$  in Figure 1. There are two molecular dissociation channels: one is near the  $s$  line with the two dissociated atoms located at the

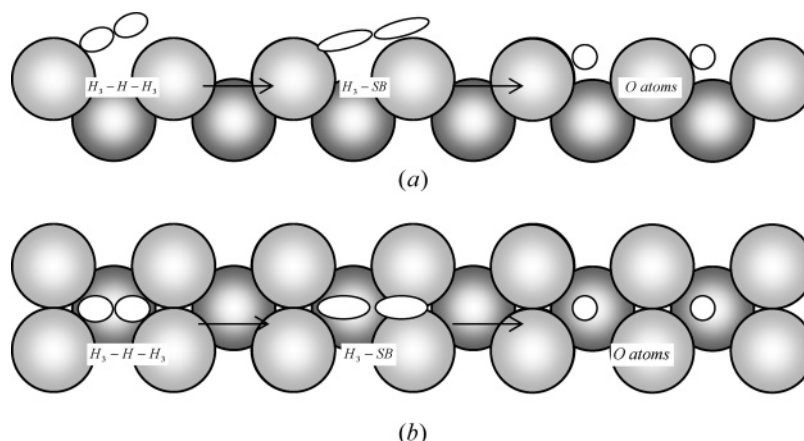
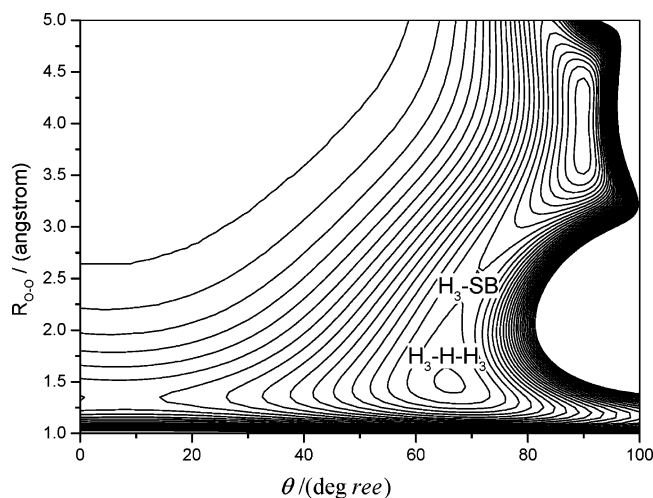


Figure 4. Sketch map of the O<sub>2</sub> dissociation on Cu(110) (a) side view (b) top view.



**Figure 5.** PES of  $O_2$  on Cu(110) ( $R - \theta$ ) ( $\varphi = 0^\circ$ ).

LB site or  $H_3$  site of the nearest unit cells and the alternation unit cells, the other is near the hollow site along the  $[001]$  direction (the direction of the  $y$ -axis in Figure 1) with the two dissociated atoms located at the nearest LB sites. The dissociation mode of the molecular construction trans states ( $H_3$  and LB) is flat. The dissociated atoms locate in the nearest  $H_3$  sites and LB sites, respectively. So the construction trans states  $H_3$  and LB only exist as twinkling life.

The former study we have made has suggested that  $O_2$  adsorbs in a parallel configuration on the Pd(110) surface.<sup>19</sup> Meanwhile, we consult a lot of the literature and found that molecular oxygen is lying parallel to the surface either on Ag (110)<sup>28–30</sup> or Pt (110)<sup>31,32</sup> surfaces. But our calculated results show that molecular  $O_2$  adsorbs not in a parallel<sup>14</sup> but in a tilted configuration on the Cu(110) surface. Why does this phenomenon appear? Analyzing the lattice constants of these metals, we can discover that the lattice constants are ordered as  $Cu < Pd < Pt < Ag$ . So we surmise that the adsorption of molecular oxygen will probably suffer the limit from the space and tend to adsorb aslant, due to the smaller lattice constant of Cu. But on the surfaces of the other metals, such as Pd, Pt, Ag,  $O_2$  prefer parallel configuration because of the bigger lattice constants.

**3.3.  $O_2$  Dissociation and Adsorption on Cu(100).** Resembling the Pd(100)<sup>19</sup> surface, we cannot search for the adsorption molecular state with  $\lambda = 0$ . For the Cu(100) surface, there is only one type of atomic adsorption site and only one kind of surface vacant twain sites from the nearest unit cells. The surface dissociation distance is the  $\sqrt{2}/2 a_0$ , which is longer than the molecular dissociation limit. That is to say, it is easy to dissociate for the incidence  $O_2$ . We find two trans states in the four-fold hollow site (H), which are defined as H1 and H2 states. The H1 state is the construction trans state (the negative eigenvalue in  $\theta$ ). Its critical characteristics show oxygen molecule uprightly adsorbs in the hollow site (H) with the O–O bond length of 1.35 Å, the binding energy of 4.09 eV, and the O–O stretching frequency of 1109  $cm^{-1}$ . The H2 state is the diffusion trans state (the negative eigenvalue in  $x$ ). Its critical characteristics show that the molecular oxygen axis parallels the surface and its midpoint lies in the hollow site (H) with the binding energy of 2.16 eV; the O–O bond is stretched to 1.45 Å, and the stretching frequency of O–O falls to 536  $cm^{-1}$ . The abnormally low frequency indicates that the trans state (H2) is not stable. Our theoretical results, which are in accord with literature<sup>3,4</sup> reports, indicate that there is no adsorption molecular state on the Cu(100) surface at low coverage, and we can only find the dissociation atomic states ( $\lambda = 0$ ) with the two

dissociated atoms adsorbing in four-fold hollow sites of the nearest crystal cells.

Daelen et al.<sup>4</sup> pointed out that oxygen preferred to dissociate over a hollow site directly from the gas phase when the incidence  $O_2$  axis parallel to the surface. We scan the molecular dissociation channels and find a good many of them, but only two marked typical channels exist. And we line out the two typical molecular dissociation lines simply in Figure 1. One is named as bridge-site line (t) and the other is hollow-site line (h). After analyzing a lot of dissociation channels, we find that the direct dissociation channel appears as the  $O_2$  centroid closing to surface at the bridge-site line (t), and the precursor dissociation channel appears near the hollow-site line (h). The trans state (H1) is unstable. It drops down and dissociates easily ( $\theta = 90^\circ$ ). But in which direction does this kind of dissociation progress along? After analyzing, we can discover that the energy barrier for dissociation is virtually zero along the H–B–H direction and the dissociation process is similar to the system of  $O_2$ –Pd.<sup>19</sup> Along the H–T–H direction, the dissociation needs to pass the top site, and the energy barrier for dissociation is 0.46 eV. The S state listed in Table 2 is the dissociation trans state we search for.

Our theoretical results suggest that the incidence  $O_2$  cannot form a stable adsorption molecular state on the Cu(100) surface at low coverage. The oxygen molecules will dissociate quickly and the dissociation atoms locate in the 4-fold hollow sites either orderly or disorderly. With the coverage increasing, the interaction between the adatoms and the molecules makes the trans state (H1) change into observational adsorption state; the side interaction makes the low binding energy H2 state change into the H1 state and then becomes stable. The above-mentioned description coincides with the former studies<sup>7–9</sup> and is similar to the  $O_2$  adsorption and dissociation on Pd (100).<sup>19</sup>

#### 4. Conclusion

In this paper we investigate the mechanism of the  $O_2$  adsorption and dissociation on the Cu low-index surfaces using the extended LEPS constructed by 5-MP on the basis of the investigation of the atomic system of O–Cu.<sup>20</sup> The calculated results suggest the following conclusions.

(1) On the Cu(100) surface, the main channel of the  $O_2$  dissociative adsorption is direct dissociation, and there is no molecular adsorption state ( $\lambda = 0$ ) at low coverage. Two trans states (H1 and H2) are found above the four-fold hollow sites. At high coverage, the interaction between the adatoms and the molecular makes the H1 change into a molecular adsorption state and a precursor-mediate dissociation is dominant for the dissociative adsorption process. These characteristics are consistent with experiments<sup>3–5</sup> and similar to the system of  $O_2$ –Pd.<sup>19</sup>

(2) At low temperature and coverage, the  $O_2$  molecules are found to adsorb in a tilted configuration with the tilt angle  $\theta$  of  $67^\circ$  and  $\varphi$  of  $0^\circ$  on the Cu(110) surface, which is the only molecular adsorption state named  $H_3$ –H– $H_3$ . The vibration frequency of O–O is 649  $cm^{-1}$ , in good agreement with the experimental study.<sup>9</sup> For the dissociation of the molecular adsorption state, we find two lowest energy dissociation channels along  $[001]$  and  $[1\bar{1}0]$  directions on the surface, respectively. The energy dissociation barriers are 0.15 eV along the  $[001]$  direction and 0.22 eV for  $[1\bar{1}0]$  direction. And there are obvious differences between  $O_2$ –Cu(110) and  $O_2$ –Pd(110).<sup>19</sup>

(3) On the Cu(111) surface, the  $O_2$  will adsorb as a molecular model. At low coverage, adsorption of molecular oxygen exists as the H–B–H state, and the O–O stretching frequency is 597

cm<sup>-1</sup>. With the coverage increasing, the trans states (H and H') become stable and the O—O stretching frequencies are 832 and 833 cm<sup>-1</sup>, respectively. Our calculation results explain well the two states in the experiments.<sup>15–17</sup> and are similar to the O<sub>2</sub>—Pd(111)<sup>19</sup> system in the main.

(4) We analyze the systems of O<sub>2</sub>—Cu (100), (110) and (111) using the concepts of the molecular dissociation limit and the surface dissociation distance again. And we guess that the adsorption geometry of O<sub>2</sub> on the metal surfaces is possible to relate to the lattice constant of metals.

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