

The Adsorption of O Atom on Cu (100), (110), and (111) Low-Index and Step Defect Surfaces

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The five-parameter Morse potential (5-MP for short) of interaction between adatom and metal cluster was constructed, and the adsorption of an O atom on Cu (100), Cu (110), Cu (111), Cu (211), and Cu (410) surfaces was studied by means of 5-MP. The data of the adsorption sites, adsorption geometry, binding energy, and eigenvibration, etc., for an O atom on the above surfaces are gained, and agree well with the experimental results. The diffusion of an O atom on plane surfaces is also dealt with. With regard to the adsorption of an O atom on the Cu (111) surface, calculation results suggest that the abnormally low experimental vibration of 29.4 meV of EELS (Dubois, L. H. *Surf. Sci.* **1982**, 119, 399) arises from the effect of the sparse steps to the nearest neighbor 3-fold hollow site on the (111) terrace.

1. Introduction

The interaction of oxygen with metal surfaces is the basis for a number of important technological processes such as bulk oxidation, corrosion, and heterogeneous catalysis and has been studied in great detail, both from a macroscopic and a microscopic point of view.^{1–34} The chemisorption of O on fcc metals had been studied by a number of different techniques such as electron energy loss spectroscopy (EELS),^{7–9} low-energy electron diffraction (LEED),¹⁵ surface-extended X-ray absorption fine-structure spectroscopy (SEXAFS),^{18,21} and so on. But there are still some disagreements for the O–Cu single-crystal surface systems. In this paper we have analyzed and discussed the controversies in detail.

For the O–Cu (100) system, at very low coverage, O atoms are favored to adsorb on the 4-fold hollow site of generally what has the highest symmetry. Characters of the adsorbed O atom (the binding energy, the vibrational frequency, and the bond length, etc.) vary with the kind of metal, the coverage, and other factors. At room temperature and above, oxygen chemisorbs dissociatively on the Cu (100) surface, and it has been suggested in the past that two superstructures exist: for low O coverage, a $(\sqrt{2} \times \sqrt{2})R45^\circ$ or, equivalently, a $c(2 \times 2)$ structure was reported which developed into a $(2\sqrt{2} \times \sqrt{2})R45^\circ$ structure at higher O exposures or at elevated temperature. However, the information gained by different techniques is often conflicting. Various inconsistent models were proposed with an O atom adsorbed on 2-fold bridge sites^{1,2} or 4-fold hollow sites either at nearly 1 Å above the surface^{3–5} or in a coplanar⁶ site. From an HREELS⁷ study, only a single adsorption site is occupied, with three different vibrational frequencies, one perpendicular 36 meV and two parallel 55.2 and 84.9 meV, resulting a nearly coplanar 4-fold hollow site. While two adsorption sites has ever been mentioned before,¹ the adsorption of an O atom on Cu (100) has already investigated by Sexton⁸ and Mohamed and Kesmodel⁹ with EELS. Sexton gained a Cu–O stretching frequency of 41 meV (331 cm^{-1}) at low coverage, which shifts to 36 meV (291 cm^{-1}) as the exposure is increased. The trend of a decrease of the frequency of O atom perpendicular vibration following the increase of O coverage is found by both of them.

Concerning the adsorption geometry, considerable debate has been carried out in recent years. Obtaining a quantitative understanding of the adsorption geometry of chemisorbed atomic oxygen on Cu (100) has proved to be surprisingly elusive. In the past most attention has been given to the $c(2 \times 2)$ structure. A previous O1s scanned energy mode photoelectron diffraction (PHD) measurement⁵ was interpreted as consistent with hollow site adsorption at an O–Cu top layer spacing of 0.8 Å. And an previous O K-edge X-ray absorption fine-structure spectroscopy in near-edge region (O K-edge NEXAFS)⁴ has reported from the $c(2 \times 2)$ phase as being consistent with hollow site adsorption at essential the same O–Cu top layer spacing of 0.7 Å with a deduced value of O–Cu nearest neighbor distance of 1.94 Å. They are all involved with the $c(2 \times 2)$ phase. However, two measurements performed later by Meyer et al.¹⁰ and Wuttig et al.¹¹ claimed that the $c(2 \times 2)$ phase which is most investigated on Ni (100) may not exist on Cu (100). Instead, the stable surface structure formed by 0.5 ML of adsorbed O atom on Cu (100) was the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ phase.

Asensio et al.¹² have studied the structure of the Cu (100) surface in the presence of adsorbed oxygen on the basis of new scanned energy O1s PHD measurements in conjunction with qualitative LEED and O K-edge NEXAFS. They believe that there are considerable differences between Ni (100) and Cu (100) in their interaction with oxygen. With respect to the $c(2 \times 2)$ phase, they agreed with Meyer et al.¹⁰ and Wuttig et al.¹¹ and believe that a different phase at lower coverages exists as what is characterized by a “four-spot” pattern. A subsequent SEXAFS study¹³ concluded that O atoms occupy 4-fold hollow sites 0.8 Å above with a Cu–O distance of 1.88 Å at low coverage, which is consistent with the estimated 1.91 Å of LEED.¹⁴ On the other hand, a scanning tunneling microscope (STM)¹⁵ reported the formation of nanometer size $c(2 \times 2)$ domains of adsorbed oxygen on the Cu (100) surface. More recently, Kittel et al.¹⁶ studied the structure of the O atom adsorbed on Cu (100) using O1s scanned energy mode PHD at low and high coverages. They reported that at much lower coverage, the O atoms adopt unreconstructed hollow sites at a significantly larger O–Cu layer spacing of about 0.6 Å. They also believe the existence of $c(2 \times 2)$ domains. We hope our

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job will provide some useful information to the experimental work, although our calculation cannot give out the surface phase directly.

As for Cu (110), a zigzag surface, the status for O atom adsorption is a little more complicated. This system is extensively studied by a number of different experimental techniques including SEXAFS,^{17,20} neon ion scattering (NIS),¹⁸ photoelectron diffraction (PHD),¹⁹ LEED,²⁴ HREELS,^{21,23,26} ICISS,¹⁸ and XPD.¹⁹ There is general agreement that the O atom is located in long bridge site along the [001] row. There is, however, still conflicting evidence concerning whether the O atom is above the copper surface, as proposed from SEXAFS,¹⁷ or located between the first and second layers of copper atoms, as proposed on the basis of NIS.¹⁸ Robinson et al.¹⁹ have studied the adsorption of atomic oxygen on Cu (110) using scanned energy mode PHD. They found that the O atom is adsorbed in the long bridge site at a distance of 1.98 Å from copper atoms in the second layer. This is consistent with the O atom lying 0.23 Å above the surface with a Cu–O bond length of 1.82 Å from SEXAFS.¹⁷ Döbler et al.²⁰ from the same group have gained that atomic oxygen on the overlayer on Cu (110) was adsorbed in the long bridge site with the O atom about 0.3 above the surface using SEXAFS. By assuming that the substrate is rigid, Wendelken²¹ gained a 49 meV vibrational energy for the O atom on the Cu (110) surface and concluded that the O atom is located in or beneath the surface, in support of the result of an earlier ion scattering study.²² Highly resolved EELS and angle-resolved UPS²³ have been used. Their EELS data for the P (2 × 1) O overlayer support previous reports of a single long-bridge adsorption site, while indicating that two sites are populated in the C (6 × 2) O overlayer: a long-bridge site and a four-coordinated hollow site. The long-bridge site is populated at all coverages, while the four-coordinated hollow site occupied only after high exposures ($\geq 2 \times 10^4$ L) at room temperature, or after exposures > 2 L at low temperature (100 K). Correspondingly, an O–Cu vibration of 48.5 meV is observed at all coverages, and three vibration of 41, 48.5, 62 meV can be gained only after high exposure.

In the O–Cu (110) system, the detailed surface structure and adsorption mechanism have been debated intensively in the past. Different techniques have been providing very different conclusions regarding both the nature of the reconstruction of the copper structure and the height that the O atoms are held above (or below) the topmost Cu layer. A multiple-scattering analysis of LEED intensities²⁴ made for the Cu (110) 2 × 1–O surface structure confirms the missing-row model for this surface. And they find that the O atoms are held around 0.04 Å above the Cu atoms. Two structural models have been discussed intensively; a missing-row and a buckled-row until an added-row structure was proposed recently. Katagiri et al.²⁵ have studied the structural and vibrational properties of added-row reconstructions of O–Cu and O–Ag systems using a first-principle method. They gained the distances of 1.83 and 2.04 Å between the oxygen atom and the first and second nearest copper atom by calculation using a first-principle method and vibration of 44.1 meV for O–Cu (4 × 1) structure at 0.25 ML and 45.2 meV for O–Cu (2 × 1) structure at 0.5 ML. Pantförder et al.²⁶ have gained an experimental result of 47.5 meV for O–Cu (4 × 1) structure at 0.25 M and 48.9 meV for O–Cu (2 × 1) structure at 0.5 ML. Toyoshima and Somorjai²⁷ gained an O–Cu (110) binding energy of 109 kcal/mol (4.73 eV) by experiment, in good agreement with a subsequent calculation result²⁸ of O–Cu (110) binding energy at zero coverage, 109 kcal/mol (4.73 eV).

For the O–Cu (111) system, HREELS²⁹ found a fairly low perpendicular vibrational frequency of 29.4 meV for O atom adsorption, from which it concluded that the O atom adsorbed in 3-fold hollow sites in or below the outermost plane of Cu atoms. A SEXAFS study³⁰ also found that O atoms are adsorbed in 3-fold hollow sites with Cu–O bond lengths of 1.83 ± 0.02 and 0.2 ± 0.2 Å above the surface. At low temperature a mixture of chemisorbed molecular oxygen and atomic oxygen species is found on the surface. The molecular species are not detectable at temperatures above 170 K. The estimated saturation coverage of atomic oxygen differs from 0.3³¹ to 0.5 ML³⁰ at the room temperature. Ye Xu and Manos Mavrikakis,³² using periodic self-consistent density functional calculations, have studied the adsorption and dissociation of dioxygen on the Cu (111) surface. At a coverage of $\frac{1}{4}$ ML, they calculated the properties of adsorbed atomic oxygen. Atomic oxygen is found to clearly prefer 3-fold hollow to top and bridge sites, with a binding energy of 4.3 eV with respect to a gas-phase O atom. And fcc hollow is slightly favored to hcp hollow site. Surface Cu atoms show appreciable relaxation upon adsorption of atomic O. The diffusion of an O atom on the Cu (111) surface is studied also. They reported that the diffusion most likely starts from one 3-fold hollow site and proceeds over a bridge site to an adjacent 3-fold hollow site. At room and moderately higher temperature, no ordered oxygen overlayer is observed in most LEED experiments.^{29–30,33} From above we can see that there is a good agreement on the adsorption site both from experiments and theoretical calculations. But discrepancy still exists on the adsorption geometry. In particular, the data about the vibrational frequency are lacking, and the unique accessible value of 29.4 meV is quite doubtful only from the magnitude. Dubois,²⁹ who obtained the abnormally low vibration of 29.4 meV for the O atom adsorbed on Cu (111) surface before, also deliberated over assigning the vibration to the stretching-vibration frequency of O atom adsorption and gave out an expected value of 45.9 meV in references behind on the basis of the force constants and bond lengths from adsorption of O on Cu (100) face. To find out the nature of O–Cu (111) system, we make a further investigation to the characteristics of O atom adsorbed on the step defective surfaces of Cu (211). We have use the same method to investigate the O–Ag (111) system, in which the perpendicular vibrational frequency is also abnormally low, and we have gained an agreeable result, which is gathered in another paper.³⁵

Cu (n11) step surfaces have been the study aim for a long time,^{36–40} but the study to O–Cu (211) system has not made much progress these years. Thompson and Fadley³⁹ presented X-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) study on the O–Cu (211) system. They demonstrated that on the reconstructed surface the O atom occupies 4-fold hollow sites at the bottom of the step, which gained support from Witte et al.⁴⁰ in a subsequent study. And the adsorption behavior of the O atom has not gained comprehensive description to date. Our effort to the O–Cu (211) system will help to shed light on the nature of the adsorbed O atom and Cu (211) step surface.

Unlike Cu (n11) surfaces, Cu (410) is a (100) vicinal surface with (110) type steps, i.e., 4(100) × (110) in compact step notation. The first four rows of atoms are all exposed to the surface; the steps are not close packed, resulting in a surface which is not expected to be thermodynamically stable. Upon exposure to oxygen, however, this surface is known to become extremely stable.

Due to the [110] orientation of the steps of the (410) surface, the lateral separation of Cu step atoms along the step direction

is 3.61 Å. This exposes gaps along the step edges which provide an ideal adsorption site for the O atom since 1.85 Å (≈ 3.61 Å/2) is the Cu–O bond length in Cu₂O and in several O-induced Cu reconstructions.⁴¹

Despite O–Cu (410) system having been investigated a lot, a full structural determination has not been performed, studies on the adsorption site are inconsistent today, and adsorption characteristics such as adsorption geometry, adsorption energy, vibration frequency, etc., to date remain ambiguous.

Algra, Suurmeijer and Boers,⁴² using low-energy ion scattering, found only one type of O adsorption site in Cu (410) for low O exposures, concluding that oxygen adsorbs dissociatively into the hollow sites of the steps. A photoelectron diffraction study by Thompson and Fadley³⁹ confirmed that the O atom is found to lie predominantly on the steps for low exposures. The O atom resides at the 2-fold step sites at the top of the step which appeared to be the only site, but at higher coverage, a second adsorption geometry on the (100) terrace was determined. In this case, the O atom occupies both the 2-fold top step-edge site and the 4-fold hollow site in the middle of the (100) terrace, as proposed by Perdereau and Rhead.⁴⁴ They reported that O atom adsorption is some 0.5⁴² or 0.4 Å^{39,44} above the nearby Cu atoms on the 4-fold hollow sites. Robinson, Vlieg, and Ferrer⁴⁵ hypothesized that the O atom would sit in the hollow sites in the first and third Cu rows, and the fourth Cu row would be missing. More recently, Walko and Robinson⁴⁶ studied Cu (410) and (311) facets transforms from (511) using surface X-ray diffraction. They concluded that the hollow sites in the first and third rows are inequivalent. The O atom in the third row (terrace site) is 4-fold coordinated with bonds ~ 1.84 Å to the Cu atoms in the second, third, and fourth rows; this is almost a coplanar structure, quite unlike the O coordination on the ($2\sqrt{2} \times \sqrt{2}$) structure or in bulk Cu₂O. The O atom in the first row (step-edge site) is only 2-fold coordinated; it is located 1.85 Å from the adjoining Cu step atoms, but then > 2.4 Å from the next nearest Cu atoms. The expectation for O atom adsorption at the mid-terrace site of Cu (410) is that the four main bonds should average out at close to 1.90 Å.⁴¹ The Cu (410)–O surface, involving a 0.5 monolayer (ML) coverage of oxygen, is known to be extremely stable and a range of Cu (100) vicinal surfaces facet to (410) in the presence of adsorbed oxygen. A new surface X-ray diffraction investigation⁴⁷ of this surface has been conducted to determine its structure, and the detailed structural parameter values obtained are compared with the results of a density functional theory (DFT) calculation. The results show that the metal structure is unreconstructed, with the oxygen forming an overlayer with 0.25 ML O atoms at near-collinear step-edge sites with the topmost Cu atoms at 1.88 Å on average and 0.25 ML O atoms at mid-terrace hollow sites, approximately 0.6 Å above the terraces with an average O–Cu bond length being close to 1.87 Å. We perform calculation on this system with our theory of 5-MP so as to shed light on the nature of the O atom adsorbed on the Cu (410) surface and, meanwhile, validate the scientific characteristic of our theory.

To make a comprehensive understanding of the mechanism for atoms or molecules adsorption on metal surfaces, it's necessary to get the specific characteristic of all the critical points. Generally, the systems were simulated with numerical codes on the basis of ab initio or semiempirical theory, reproducing the experimental results. The five-parameter Morse potential of mutual interaction between the adatom and metal surface has been performed on O–Ag,³⁵ H–Ni,⁴⁸ C–Ni,⁴⁹ and O–Ni⁵⁰ surface systems recently. In this paper we make a further study of O–Cu surface system using the five-parameter

Morse potential. The advantage of this method lies in the independence between the parameters and the metal surface structure. That is to say, we can deal with different metal surfaces with the same set of parameters, including metal surfaces with defect sites. So we examined the influences of defects on Cu surfaces for O adsorption using the same theory. All the work is preparation for a further study of hydrocarbons or other polyatomic molecular adsorptions on metal surfaces. In section 2, we will give out theoretical method and calculate model, and our calculation results are gathered and discussed in section 3, which contains the O atom adsorption on Cu three low index planes and two step defective surfaces.

2. Theoretical Calculate Method and Surface Cluster Models

2.1. Theoretical Calculate Method—5-MP. First, we made an assumption that the metal cluster is frozen, namely, the metal atoms of the surface layer are fixed, and the approximation is adopted for the whole surface cluster. So the interaction energy $U_i(\vec{R})$ between an atom, which coordinate is specified by \vec{R} , and the i th atom in the metal surface cluster can be written in the form of Morse potential:

$$U_i(\vec{R}) = D_i \{ \exp[-2\beta(R_i - R_0)] - 2 \exp[-\beta(R_i - R_0)] \} \quad (1)$$

In eq 1, R_i is the distance between adsorbed atom and the i th surface atom (denoted as \vec{r}_i), namely, $R_i = |\vec{R} - \vec{r}_i|$. β and R_0 are the parameters for vibration and equilibrium distance, respectively. D_i is binding energy and can be described as

$$D_i = D \left(\frac{h_i + Q_1}{R_i + Q_2} \right) \quad (2)$$

Where D is a simulating energy parameter, h_i is the vertical distance between the adatom and the surface where the i th metal atom is in, and Q_1 and Q_2 are two simulating parameters. We employ such a method to deal with the adsorption system in order to take account of the orientation affect of transition metal d electrons. We distinguish different adsorbed atom using the atomic weight M and distinguish different metallic system using lattice constant a_0 .

The total potential energy $V(\vec{R})$ for the adatom and the whole surface cluster constructed by n metal atoms can be expressed as the sum of pair-potential $U_i(\vec{R})$ as the following:

$$V(\vec{R}) = \sum_{i=1}^n U_i(\vec{R}) \quad (3)$$

The potential function $V(\vec{R})$ we have constructed consists of only five parameters: D , β , R_0 , Q_1 , and Q_2 . Apparently, $V(\vec{R})$ is relation to the surface structure embodying by R .

Oxygen atoms possess three degrees of freedom when it moves on the cluster surface. In eq 3, the potential function $V(\vec{R})$ gives out a potential hypersurface of four-dimensionality. The second derivative of $V(\vec{R})$ with respect to \vec{R} in the critical point composes a Hessian matrix of 3×3 dimensionality. Then there are four kinds of critical points for the potential hypersurface. We apply the number of negative eigenvalues from Hessian matrix which is denoted as λ to characterize the nature of critical points. The critical point of $\lambda = 0$ is the minimum point which corresponds to atomic surface adsorption state. The one of $\lambda = 1$ is the saddle point which corresponds to surface diffusion transitional state. The one of $\lambda = 2$ and $\lambda = 3$ is the maximum point, and the one of $\lambda = 2$ corresponds to surface

diffusion maximum point (the case of $\lambda = 3$ does not exist on the cluster surface). That is to say, our calculation can directly give out the adsorption state, transitional state, etc., for the adatom on the cluster surface by λ of critical points. Moreover, eigenvalues from Hessian matrix are relevant to the frequency of vibration for the adatom on the cluster surface. And the adsorption geometry is also determined by the information of adsorption state; we generally prescribe the height of the surface as the zero point. In our calculation, different parameters can derive different results. If a set of parameters can gain the result that is consistent with the information from experiments, we then believe they are the optimum one. The characteristic that experimental scientists have not provide because of the limit of experiment or the time or any other inexplicable reasons can be given by our calculation. On this point, we can see that our calculation can provide helpful information for experiment in reverse.

Therefore, in the whole work of the calculation, the key step is how to adjust the parameters. We employed the experimental data of three low index copper surfaces (100), (111), and (110) to adjust the five parameters at the same time. And the kinetic characteristics of adsorption such as the adsorption sites, adsorption geometry, binding energy, and eigenvalue for vibration, etc., for the adatom on a metal surface can be gained through our theoretical method; in this way, the potential function $V(\vec{R})$ constructed by the optimum seeking parameters is applicable to deal with the atom adsorption system on low index copper surfaces (100), (111), and (110) synchronously. And without doubt $V(\vec{R})$ is also applicable to the adsorption system on the stepped surfaces that are constructed of low index surfaces mentioned above. That is to say, $V(\vec{R})$ is independent of the surface structure now after the five parameters are fitted and fixed.

So we call $V(\vec{R})$ the five-parameter Morse potential (5-MP for short) between an adatom and the metal surface cluster, and D, β, R_0, Q_1, Q_2 are adjustable parameters. Essentially, the 5-MP is the pair potential for an atom adsorption on surface cluster. The main characteristic of 5-MP is that the parameters are independent of structure for the surface clusters. We have accomplished using the same set of optimized parameters to fit the experimental data of the three surfaces in several different systems. Then the adsorption systems of an adatom on three low-index surfaces are easy to deal with at one time. And the adsorption systems on the stepped surface that consists of the three low-index surfaces of (100), (110), and (111) are easy to carry out also. This method has been performed on O–Ag,³⁵ H–Ni,⁴⁸ C–Ni,⁴⁹ and O–Ni⁵⁰ surface cluster systems in previous studies, and all the results indicate that our method approaches the intrinsic nature of interaction of the atom-metal surface system very well.

2.2. Construction and Adsorption Site of the Cu Surface Cluster. Metal copper belongs to fcc lattice with the lattice constant $a_0 = 0.3615$ nm. Considering both the local geometrical symmetry in a point group for crystal cell and the whole surface lattice displacement symmetry, we simulate the Cu plane by a copper cluster with at least five layers of cell atoms, and every layer contains at least 6(length) \times 6(wide) atoms, which contains about 300 copper atoms. The size of the cluster is defined by the principle that there is no boundary effect in our calculation.

The adsorption sites of O on Cu plane are defined as in Figure 1. They are the hollow site (H), bridge site (B), and top site (T) for Cu (100) surface; the fcc hollow site (H) and hcp hollow site (H') for Cu (111) plane; and the pseudo-3-fold hollow site (H₃), long-bridge (LB) site, and short-bridge (SB) site and the

TABLE 1: The Morse Potential Parameter for O–Cu System

system	D/eV	$\beta/\text{\AA}^{-1}$	$R_0/\text{\AA}$	$Q_1/\text{\AA}$	$Q_2/\text{\AA}$
O–Cu	0.98	2.17	2.02	1.45	0.18

transitional state (S) between LB and H₃ of Cu (110) plane, respectively.

Figure 2 shows schematic diagram of the cluster model and adsorption sites for Cu (211) step surface what attribute to the $\{n(111) \times (100)\}$ type of step surface. And we use H₁–H₄ to denote the 3-fold hollow sites on (111) terrace and H₅ to denote the 4-fold hollow site on (100) facet. Figure 3 shows the cluster model and adsorption sites for Cu (410) step surface. Because the surface density of the crystal atom (the number of metal atoms on unit area) on the step defective surface is small and the space between metal atom layers is little, we simulate step surfaces with at least 10 layers of cell atoms, and generally every layer contains at least 10(length) \times 10(wide) atoms. Then the metal cluster for step surfaces mentioned above contains 500 atoms at least.

3. Results

We have examined the O–Cu surface systems by the 5-MP method, and in Table 1 we list the five simulating parameters for O–Cu system. The results of our calculation on O–Cu (100), (110), and (111) are gathered in Table 2; in Table 3, we make a comparison between our results and the results from literatures on O–Cu (100), (110), and (111) systems. Table 4 gives out the calculation results in the O–Cu (211) and (410) stepped surface systems. For the O–Cu surface system, we have gained binding energies (E_b), bond length between O adatom and its nearest neighbor Cu atoms ($R_{\text{O–Cu}}$), the vibrational frequencies (f), and the distance of the O atom above the surface ($Z_{\text{O–Cu}}$) for O adsorption on all the sites of Cu plane mentioned above. Moreover, the influences of stepped defect on Cu (111) and (100) surfaces on O adsorption are examined. And we use N denote the number of nearest neighbor Cu atoms around the adsorbed O atom. All the symbols mentioned above denote the same in all tables.

There's still one issue to be clarified: we define $R_{\text{O–Cu}}$ (distance between the adatom and its nearest neighbor coordination) in the range of less than 2.20 Å.

3.1. Adsorption, Vibration, and Diffusion of O–Cu (100), (110), and (111) Plane Surface Systems. The interaction of oxygen with copper surfaces has been extensively studied. In this paper, we report our calculation results in Table 2 and comparisons with the experimental and theoretical data in Table 3 for O–Cu surface system.

First, we will discuss the cases for the O–Cu (100) surface system. As shown in Figure 1, three nonequivalent critical points exist on this surface. The surface-stable adsorption state lies on the H site, which has a C_{4v} local geometrical symmetry, the same as that of the crystal cell; the surface diffusion transitional point lies on the B site, and the T site is the surface diffusion maximum point. Our calculation results definitely support experimental results^{3–5} that O atoms adsorbed on 4-fold hollow site exclude the possibility of O atoms adsorbed on 2-fold bridge site.^{1–2} From our calculation, we gained $\lambda = 0$ for the H site and $\lambda = 1$ and $\lambda = 2$ for the B and T sites. This evidently shows that only the H site is absorption site, while the B and T sites are the surface diffusion transitional point and the surface diffusion maximum point, respectively.

We have determined the eigenvalue for vibration parallel to the surface for an O adatom of $f_{\parallel} = 73.66$ meV corresponding

TABLE 2: Critical Characteristics of O–Cu (100), (110), and (111) Plane Surface Systems^a

system	site	N	λ	E_b (eV)	f (meV)		R_{O-Cu} (Å)	Z_{O-Cu} (Å)
						⊥		
O–Cu (100)	H	4	0	5.13	73.66×2	39.21	1.98×4	0.81
	B	2	1	3.42	59.02	69.08	1.98×2	1.51
	T	1	2	2.26		74.63	1.96	1.96
O–Cu (111)	H	3	0	4.39	51.63×2	68.59	2.00×3	1.35
	H'	3	0	4.40	51.93×2	68.58	2.00×3	1.35
	B	2	1	3.82	64.05	73.35	1.97×2	1.50
	T	1	2	2.41		77.77	1.95	1.95
O–Cu (110)	H	1	2	4.65		78.73	1.96	0.68
	H3	3	0	4.67	25.58, 21.74	75.36	$2.12 \times 2, 1.97$	0.68
	LB	4	0	4.76	113.11, 23.24	46.90	$1.85 \times 2, 2.09 \times 2$	0.38
	S	2	1	4.66	23.32	77.20	1.97, 2.12	0.68
	SB	2	1	3.14	58.21	67.63	1.99×2	1.52
	T	1	2	2.02		71.92	1.97	1.97

^a Note: The multiplier of the R_{O-Cu} row denotes the number of nearest-neighbor coordination atoms to the adatom.

TABLE 3: Comparisons between Our Results and Literature

	system	theoretical values	experimental data	this work
E_b (eV)	(110) LB	4.73 ²⁸	4.73 ²⁷	4.76
	(111) H	4.3 ³²	4.47 ³⁴	4.35
R_{O-Cu} (Å)	(100) H		1.94 ⁵ , 1.97 ⁶ , 1.88 ¹³ , 1.91 ¹⁴	1.98(4)
	(110) LB	1.83, 2.04 ²⁵	$1.84 \pm 0.02, 2.00 \pm 0.05^{17}$, 1.81 ± 0.01 , $1.90 \pm 1 \times 10^{18}$, 1.98 ± 0.05^{19}	1.85(2), 2.09(2)
	(111) H		1.83 ± 0.02^{30}	2.00(3)
Z_{O-Cu} (Å)	(100) H		$1.2-1.5^3, 0.8^{4,13}, 0.7^5, 0.6^{16}$	0.81
	(110) LB		0.23 ¹⁷ , 0.3 ²⁰	0.38
	(111) H		0.2 ± 0.2^{30}	1.35
f (meV)	(100) H _⊥		36 ⁷ , 41 ⁸ , 43 ¹¹	39.21
	(100) H		55.2 ⁷ , 84.9 ⁷	73.66
	(110) LB _⊥	44.1 ²⁵	49 ²¹ , 48.5 ²³ , 47.5 ²⁶	46.96
	(111) H _⊥		29.4 ²⁹	69.68

TABLE 4: Critical Characteristics of O–Cu (211) (410) Stepped Surface Systems^a

system	sites	N	l	E_b (eV)	f (meV)		$R_{(O-Cu)}$ (Å)	h (Å)
						⊥		
O–Cu (211)	H ₁	3	0	4.19	53.69, 49.10	67.92	$1.998 \times 2, 2.005$	1.03(1.35)
	H ₂	3	0	4.24	50.60, 51.94	67.71	1.982, 2.006, 2.011	0.79(1.35)
	H ₃	3	0	4.41	50.41, 47.59	67.92	$2.005 \times 2, 2.004$	0.30(1.36)
	H ₄	—	—	—	—	—	—	—
	H ₅	4	0	5.35	100.91, 104.34	28.25	$1.875 \times 2, 1.892 \times 2$	−0.30(0.53)
O–Cu (410)	LB	4	0	5.43	68.24, 64.91	40.17	$2.031, 2.008 \times 2, 1.984$	−0.47
	H ₁	4	0	5.03	72.98, 73.32	38.98	$1.963, 1.980 \times 2, 1.997$	0.35(0.72)
	H ₂	4	0	5.05	73.83, 73.40	39.04	$1.963, 1.980 \times 2, 1.997$	−0.09(0.72)
	B	2	0	4.39	18.95, 110.84	48.15	$1.847 \times 2, (2.108, 2.074)$	0.31

^a Note: h in the last column denotes the height of the O atom from the step surface, and the data in the bracket following the h item are the height of the O atom from the corresponding facet. The values in the bracket at the bottom of the table in $R_{(O-Cu)}$ column are the next nearest Cu–O distances on B site of Cu (410) surface.

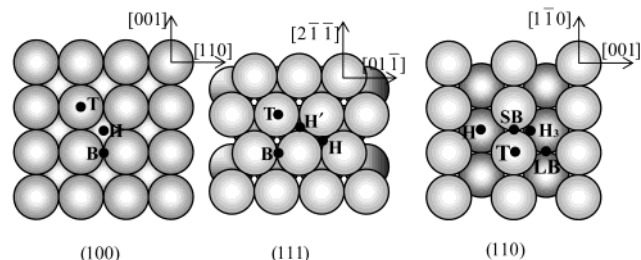


Figure 1. Surface sites are illustrated on Cu (100), (111), and (110). Shaded circle: copper atom. ●: adsorption site.

to the irreducible representation E in C_{4v} point group and the one perpendicular to the surface is 39.21 meV, which belongs to the fully symmetrical A_1 representation in C_{4v} . The perpendicular vibrational frequency agrees with the experimental studies very well.^{7–8,11} Concerning ref 7, we believe that the 36 meV mode is consistent with our calculation result of 39.21

meV; the parallel mode of 84.9 meV is also near to our calculation result of 73.66 meV. As we all know, on the (100) surface, the adsorption site H has a C_{4v} geometry, which determine the possible vibration mode on the H site of a perpendicular vibration mode corresponding to the fully symmetrical A_1 representation and two degenerate parallel vibration modes corresponding to the irreducible representation E. That is to say, the vibrational frequency for the two parallel modes are equal to each other. Even if on the reconstructed surface the E splits, the discrepancy between two parallel vibration modes is also relatively small. Evidently, more than 20 meV, the discrepancy as indicated from ref 7, is too big for the two parallel modes. So we tentatively postulate that the 55.2 meV mode is not the parallel mode for the O atom adsorbed on Cu (100) plane. Maybe, it can be describe as a loss for the O atom adsorbed on a step-defective surface. On the other hand, a quite large reconstruction may also result in the appearance of this phenomenon. Comparison between the perpendicular and

parallel vibration frequency gives us a picture that the former is far less than the latter one for an O atom adsorbed on Cu surfaces, which is the typical nature of O–Cu interaction system in our view.

Our calculations also gained very good agreements on $R_{\text{O-Cu}}$ of 1.98 Å and $Z_{\text{O-Cu}}$ of 0.81 Å with experimental results^{3–6,13–14} when O atoms adsorb on H site of Cu (100) plane. And the binding energy of 5.13 eV we gained is a little bigger than the experimental results of 4.73 eV²⁷ for Cu (110) and 4.47 eV³⁴ for Cu (111). We believe which is the gradual change trend of binding energy (the order of binding energy of an O atom adsorbed on three low index metal surfaces from bigger to smaller is (100) > (110) > (111) as we studied the O–Ag³⁵ and O–Ni⁵⁰ systems) for an O atom adsorbed on metal surfaces. With regard to the diffusion of the O atom on the Cu (100) surface, a surface diffusion potential barrier of about 1.71 eV is found on the lowest-energy diffusion channel of H–B–H, which gives us an obviously suggestion that the diffusion is quite difficult for an O atom on the Cu (100) surface.

The Cu (110) surface is a relatively more complex surface, which is a zigzag surface constituted by Cu (111) and Cu (11 $\bar{1}$) surfaces. From our calculations, there are six kinds of nonequivalent critical points on this surface. Among them, LB and H₃ are surface adsorption stable state with $\lambda = 0$; SB is the surface diffusion transitional state between two H₃ sites; H and T are surface diffusion maximum points; S is the surface diffusion transitional state between LB and H₃. Compared with the 3-fold adsorption H state on Cu (111), the geometrical symmetry of H₃ is like the slightly distorted C_{3v} point group, so we believe that the characteristics for H₃ state on Cu (110) and H state on Cu (111) surface are similar. This has been confirmed by our calculation. We find the eigenvalue for vibration perpendicular to the surface of H₃ site is 75.36 meV, which is very close to that of H site of 68.59 meV on Cu (111) surface. And the vibrations that should belong to the equivalent irreducible representation E now split into two one-dimension irreducible representations $\Gamma = 25.58$ and 21.74 meV, respectively, which should be the result of the slightly distortion of the geometrical symmetry of H₃. Moreover, it is reflected from the poorly equivalent O–Cu distances of 2.12 Å (two) and 1.97 Å (one) on the H₃ site. In addition, our results also show that the binding energy for an O atom on H₃ site is 4.67 eV, the optimal height above H₃ site is 0.68 Å.

Our calculation results show that the adsorption on LB site is the most stable adsorption state. There is a discrepancy of 0.09 eV in binding energy between the LB and H₃ sites. The binding energy of 4.76 eV we obtained enjoys good agreement with both experimental 4.73 eV²⁷ and theoretical 4.73 eV²⁸ results. The eigenvalue for vibrations of O adsorbed on LB site of $f_{\parallel} = 46.90$ meV are consistent very well with the experimental data of 49,²¹ 48.5,²³ and 47.5 meV²⁶ and theoretical result of 44.1 meV.²⁵ And we also predict two eigenvalues of 113.11 and 23.24 meV for parallel vibration, which needs further experimental confirm. The first and second layer nearest-neighbor bond distances of 1.85 and 2.09 Å we obtained by calculation are consistent with experimental results^{17–19} and first-principal method calculation results.²⁵ The result that the O atom adsorbed 0.38 Å above the Cu (110) surface from our calculation also enjoyed good agreement with SEXAFS study^{17,20} experimental results.

With regard to the diffusion of an O atom on Cu (110) surface, we analysis the lowest-energy diffusion channels of H₃–SB–H₃ and LB–S–H₃–S–LB. A potential energy barrier of 1.53 eV was found on the H₃–SB–H₃ diffusion channel,

which gives an obvious clue that the diffusion on H₃–SB–H₃ channel perpendicular to the zigzag trough on (110) surface is quite difficult to take place. Otherwise, analytical results show that on the LB–S–H₃–S–LB channel, an O atom needs to get across two potential barriers of 0.1 and 0.01 eV, respectively, which indicates that the potential barrier between H₃ and LB is considerably low and the diffusion between the two stable adsorption states is very easy. In other words, our calculation results predict a low-energy surface diffusion channel for the O atom along the zigzag trough on the Cu (110) surface. This can be embodied to some extent by the fairly low vibration of 23.24 meV parallel to the surface along the zigzag trough direction. From the analysis above, we can make a conclusion that the diffusion of an O atom on Cu (110) surface displays distinct anisotropy. Moreover, this kind of characteristic has ever been found in O–Ag (110) system in another paper of ours.³⁵ Obviously, the magnitude of parallel vibrational frequencies such as 23.24 meV for LB and 25.58 and 21.74 meV for H₃ is relatively low, so they are quite likely assigned to phonon vibration scope even if they were found in experiments. In our view more detailed experiments are in urgent in this field.

The Cu (111) surface is the most compact surface among the three single-crystal surfaces. Calculations show that there are four different nonequivalent critical points on (111) surface. H' and H 3-fold hollow sites are surface adsorption states with $\lambda = 0$ in a C_{3v} local geometrical symmetry. B is the surface diffusion transitional state. T is the diffusion peak. Considering the structure of the Cu (111) surface, although H' and H are different types of stable adsorption sites, the difference between their characteristic critical points is very little from our calculations, nearly the same $R_{\text{O-Cu}}$ and $Z_{\text{O-Cu}}$ and a considerably low discrepancy of 0.01 eV in binding energy, 0.30 meV in parallel vibrational frequencies, so they can be considered approximately equivalent. Our calculations show that the binding energy of O adsorption on a Cu (111) hollow site is 4.39 eV, in good agreement with experimental data of 4.47 eV³⁴ and calculation result of 4.3 eV.³² We support the experiment result^{29,30} that the O atom adsorbed on the 3-fold hollow site, and we definitely support the SEXAFS³⁰ result which proposed that the O atom adsorbed above the Cu (111) surface, not in or below the Cu plane of the result of HREELS.²⁹ From our calculation, the oxygen adatom has three nearest neighbor Cu atoms conjugated with $R_{\text{O-Cu}} = 2.00$ Å, which is a little longer than 1.83 ± 0.02 Å,³⁰ the SEXAFS result. But the adsorption height of 1.35 Å is much larger than the SEXAFS result of 0.2 ± 0.2 Å.³⁰ We gained that the eigenvalue for vibrations parallel to the surface of an O adatom is 51.63 meV, and it is corresponding to the irreducible representation E in the C_{3v} point group. The one perpendicular to the surface is 68.59 meV that belongs to the full-symmetrical A_1 representation in C_{3v} . Our results have not gained support from experimental data by far. We are puzzled by the EELS results in ref 29 that report the vibrational frequency of 29.4 meV. This value is shifted dramatically when compared with that of O–Cu (100) and (110) system. Moreover, a DFT study⁵¹ on the O–Ag(111) system have gained a normal vibrational frequency of 50 meV, which is near to our calculation result of 61.11 meV.³⁵ This value is a powerful support to our point that the abnormally low frequency of 29.4 meV²⁹ may not be the vibration mode for the O atom on Cu (111) plane. So further studies both experimentally and theoretically are still necessary for this system. To find out the nature of an O atom adsorbed on Cu (111) surface, we carried out another investigation to O–Cu (211) stepped surface interaction system.

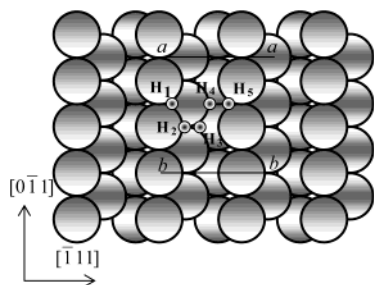


Figure 2. The structure and adsorption sites of Cu (211) stepped defective surface.

With regard to the diffusion of an O atom on the Cu (111) surface, a potential energy barrier of 0.58 eV (0.57 eV) exists on the diffusion channel $H-B-H'$, which is much smaller than that on Cu (100) surface. But it is still too high for an O atom to get across. So our calculation result on one hand is consistent with the result of Ye Xu and Manos Mavrikakis³² that the most likely diffusion channel of the O atom on Cu (111) surface is $H-B-H'$, from a 3-fold hollow to a neighboring 3-fold hollow by getting across a 2-fold bridge site; on the other hand, we consider it is very difficult for an O atom to diffuse on Cu (111) plane surface.

3.2. O Atom Adsorbed on Cu (211) Stepped Surface System. Now we face a problem that the only accessible experimental datum 29.4 meV²⁹ of the O atom perpendicular vibration on Cu (111) surface has a poor comparison with our result of 68.59 meV. The same situation has been encountered in the study of the O–Ag (111) adsorption system.³⁵ In view of the lower sticking coefficient (10^{-3}) of an O atom on Cu (111) plane, the accordance between nearly most of the experimental data and our calculation results as shown in Table 4, and the experimental difficulty to gain the datum, in particular, in analogue to O–Ag (111) system, we opined the assignment of the abnormally low-frequency vibration mode of 29.4 meV²⁹ from EELS study. Cu (211) is a regularly stepped vicinal copper surface that consists of Cu (100) and Cu (111) facets with Cu (100) as step and Cu (111) as the terrace, which can be regarded as a defect (111) surface. Our calculation results of the O–Cu (211) system show that there exists a low-frequency vibration of 28.25 meV perpendicular to the 4-fold hollow site H_5 at the step edge. We confer this vibration likely should be assigned to be the experimental low-frequency vibration of 29.4 meV.²⁹ The investigation to O–Ag(211) system³⁵ supports this point of view. Investigations to O–Ag (211) and O–Ag (997) interaction systems³⁵ have helped us realize that the existence of different kinds of steps: (100), (111), and (110)-type on (111) plane surface can result in the appearance of low-frequency vibration. Our calculation for O–Cu (211) has confirmed the point of view that the low-frequency vibration only exists in the area on or near the step just the same to O–Ag (111) system. On the 3-fold sites farther from the step (H_1 , H_2 , and H_3), there is no low-frequency vibration existing as shown in Table 4; these sites are more similar to 3-fold hollow H site of the Cu (111) plane in binding energy, adsorption geometry, and vibrational characteristics.

For the sake of obtaining a more straightforward figure, we scanned potential energy surface (PES) of O atom adsorption and diffusion on Cu (211) step surface along a–a and b–b sections of Figure 2 (energy interval 0.1 and 0.1 eV; lowest energy -4.40 and -5.30 eV, respectively), corresponding to Figure 3A,B. In Figure 3, the vertical coordination is the height of the adsorbed O atom from the Cu (211) surface; the abscissa shows the location of adsorption state. It is clear that H_5 is the

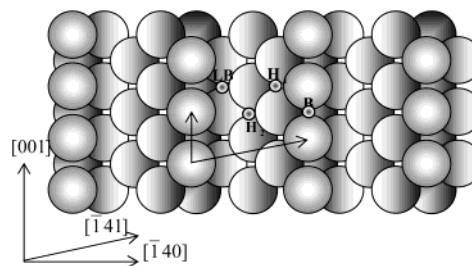


Figure 3. The model of Cu (410) surface.

most stable adsorption state, while H_4 nearest to the step among the 3-fold hollow site on Cu (211) step surface is completely annihilated; namely, there is not an adsorption state existing on the H_4 site. This is consistent with our calculation result in Table 4, which show that we have not searched out adsorption state on H_4 site.

Analysis to the binding energy also supports that 4-fold hollow adsorption state H_5 is the most stable adsorption state. We have gained that the O atom is 0.53 Å (gained by geometrical conversion) above the (100) facet on H_5 site and -0.30 Å from the Cu (211) step surface as shown in Table 4. The distance from the four nearest neighbor Cu atoms is 1.875(two) and 1.892(two) Å. Calculation results show that the O atom adsorbed on 4-fold H_5 site with a perpendicular vibration of 28.25 meV and two parallel of 100.91 and 104.34 meV.

Our calculation results also enjoyed a good agreement with experimental results.^{39–40} Thompson and Fadley³⁹ presented an X-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) study on O–Cu (211) system. They demonstrated that on the reconstructed surface the O atom occupies 4-fold hollow sites at the bottom of the step. Witte et al.⁴⁰ concluded that they supported the proposed structure model of Thompson and Fadley³⁹ that the oxygen preferentially occupies 4-fold hollow site at the step edges in a recent investigation of the chemisorption of oxygen on the vicinal Cu (211) surface and the subsequent reconstructions by means of He-atom scattering (HAS), spot profile analysis-low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and Auger-electron spectroscopy (AES). On the Cu (211) surface, the step edge locates on the outmost. When oxygen exposure is low, it will be the first place for adsorption. So we agree with the view of refs 39 and 40 that at low coverage 4-fold hollow site on the step edge is occupied, while the terraces are oxygen free. Among the 3-fold hollow site on the (111) terrace, H_4 is not an adsorption state, just as shown in Figure 4.

In the O–Cu (211) system, we have gained a low-frequency vibration of 28.25 meV perpendicular to the 4-fold hollow site H_5 . And we confer that the 29.4 meV²⁹ of O–Cu (111) is not the adsorption state on Cu (111) plane surface, but the adsorption vibration of an O atom adsorbed on sparse step defective Cu (111) surface.

Investigation to O–Cu (211) makes it clear that while no definitive conclusion could be drawn on the point of assignment, we find that low-frequency vibration of the same magnitude as the experimental data of 29.4 meV²⁹ definitely exists and only exists in the area on or near the step. So we tentatively confer that the abnormally low vibration of 29.4 meV²⁹ should be resulted by the effect of the sparse steps to the nearest neighbor 3-fold hollow site on the Cu (111) terrace.

3.3. O Atom Adsorbed on Cu (410) Stepped Surface System. From the analysis in part one we can see, there are at least two different kinds of views on the adsorption sites of O atom adsorption on the Cu (410) surface: only one type of site,

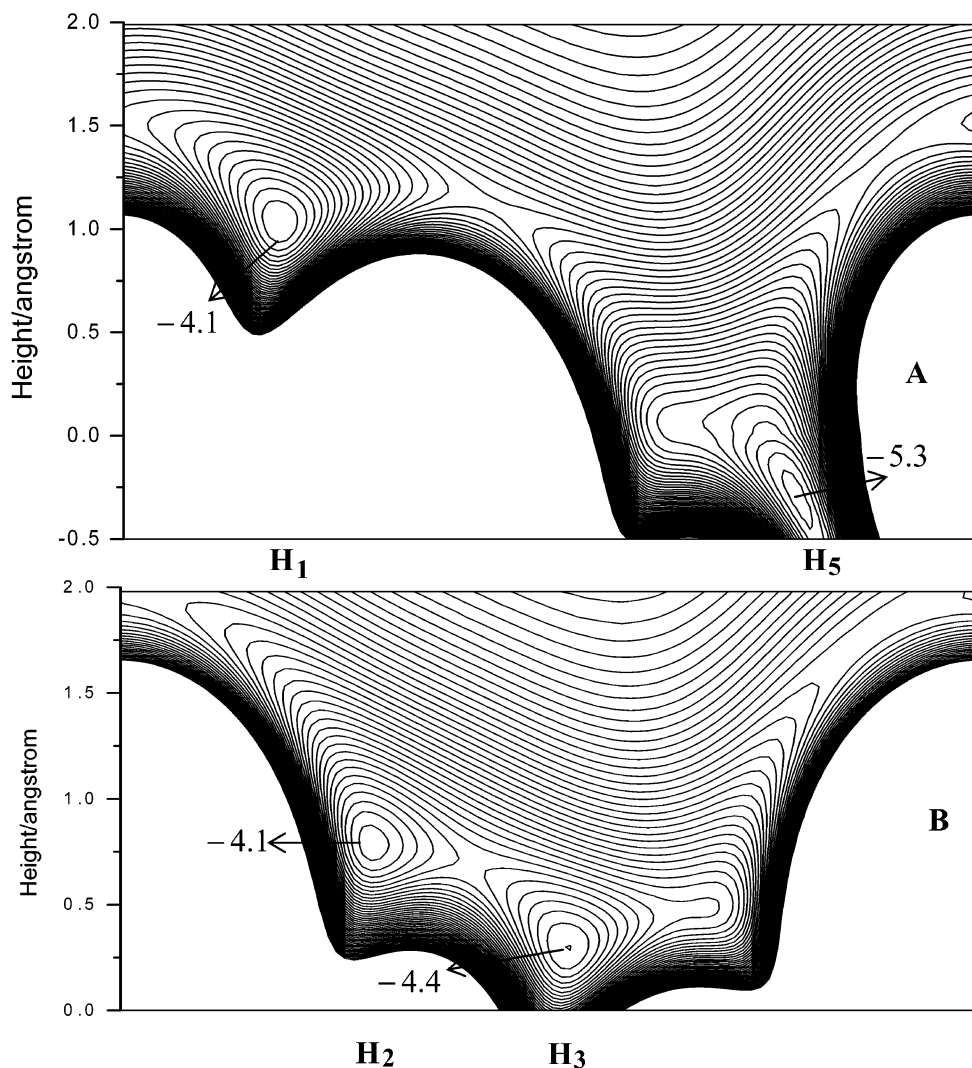


Figure 4. PESs of O atom adsorption and diffusion on Cu (211) step surface scanned along a–a and b–b sections of Figure 2 showing as A and B in Figure 3 (energy interval, 0.1 eV).

the hollow site on the step as refs 42 and 45 proposed; two type of adsorption sites, the step-edge site and the hollow site on the terrace described, as refs 39, 44, and 46–47. First, we obtained a conclusion that step edge sites are the ones first occupied by adsorbed O atoms, in support of the result of refs 39 and 44. But we gained three types of surface adsorption states with $\lambda = 0$ for the O atoms adsorption: two 4-fold hollow states H_1 and H_2 in the middle of the terrace and one 4-fold LB state located on the bottom of the terrace whose location is similar to the long-bridge site of (110) step and the 2-fold step-edge state B at the top of the step as shown in Figure 3. And our calculation results are gathered in Table 4.

On the 2-fold step-edge site, the nearest Cu–O bond length of 1.847 Å is obtained. This is in good agreement with 1.85 Å.^{41,46} We also gained that the two next nearest Cu–O bond lengths are approximately 2.10 Å. On the Cu (410) surface, the step edge locates on the outermost. When O exposure is low, it will be the first place for adsorption. So we tentatively speculate that at low O coverage, the 2-fold step-edge site is the site first occupied by an O atom. Actually, Rocca et al.⁴³ have demonstrated that open steps are active sites both for adsorption and dissociation in the study of the O₂–Ag(410) system recently.

Our calculation results also predict two 4-fold hollow adsorption sites. This gained support from refs 42 and 45–47. On these sites, the O atom resides on a slightly distorted 4-fold

hollow site with two equal bond lengths of 1.980 Å linked to the two Cu atoms on the same row and two bond lengths of 1.963 and 1.997 Å to the two Cu atoms on the upper and lower neighboring rows. These two 4-fold hollow sites are located on the second and third rows on the (100) terrace as shown in Figure 4. On this case, our calculation results have essentially differences from the view of ref 45. In the paper, they describe two hollow sites on the first and third rows, which should be the step-edge site 2-fold coordinated and one 4-fold hollow site in our view. As for ref 46, they only mentioned one hollow site on the third row, but in our calculation, the two hollow sites on second and third rows are nearly identical. They are both adsorption sites for the O atom.

On the LB site, the O atom gained the lowest binding energy of 5.43 eV. So we believe it is the most stable adsorption site for the O atom on Cu (410) surface at higher O coverages. The LB site is at the bottom of the terrace; it is not very easy for an O atom to access. So we believe higher O coverage will be helpful to the adsorption of O atoms on the LB site on the Cu (410) surface. We have gained two equal bond lengths of 2.008 Å and two unequal bond lengths of 2.031 and 1.984 Å. From the bond length of the O atom on LB site, we choose to believe that this is a pseudo-4-fold adsorption site, a distorted long-bridge site. In this view, our calculation results are more near to the point of ref 47.

As for the adsorption height, our calculation results are gained on the basis of prescribing the height of the Cu (410) surface as the zero point. After geometry conversion, we gained 0.72 Å above the (100) terrace for O atoms adsorbed on the H₁ and H₂ 4-fold hollow sites. This enjoys very good agreement with the experimental results of 0.5,⁴² 0.4,^{39,44} and 0.6 Å.⁴⁷ As for the 2-fold B site, we gained that the O atom adsorbed 0.31 Å above the Cu (410) surface. And the height on the LB sites shown in Table 4 is the distance of the O atom above the Cu (410) surface also.

Comparing the characteristics of H₁ and H₂ with the 4-fold H site on the (100) plane surface, we can clearly find that the binding energies of 5.03, 5.04, and 5.13 eV, vibration frequencies both for the perpendicular (38.98, 39.04, and 39.21 meV) and parallel modes (72.98, 73.32; 73.83, 73.40; 73.66 × 2 meV), and adsorption geometry enjoyed in good agreements, which gives us a picture that the step affects the adsorption of adsorbates evidently, but this impact will decay slowly along with elongated distance from the step.

4. Conclusion

In this paper, we have applied the 5-MP method to examine the characteristics of O—Cu (100), (110), and (111) plane surface systems and stepped defect Cu (211) and (410) surfaces. Our calculation results on one hand confirm most of the accessible experimental data and the data from other theoretical method and on the other hand provide much more information that experiments have not gained, as listed below:

- (1) In the investigation to O—Cu(111) system, we put forward different view to the assignment of the abnormally low vibration of 29.4 meV²⁹ obtained by EELS. And we proposed a new idea to try to explain the abnormally low vibration 29.4 meV²⁹ as the vibrational mode resulting by sparse steps on (111) terrace, through the investigation to the defect (111) surface system: O—Cu (211). A creditable conclusion has been made, which hopes for further support from experiments.
- (2) Moreover, the investigation to O—Cu (211) system has confirmed the experimental result on the adsorption site,^{39,40} supporting that oxygen preferentially occupies 4-fold hollow site at the step edges. And we found that there exists a competition between 4-fold and 3-fold hollow sites, and the nearest 3-fold hollow site to the 4-fold hollow site was annihilated.
- (3) In the study to O—Cu (410) system, we have discussed the existing discrepancies on the adsorption site and adsorption geometry of the O atom on Cu (410) surface. In our view, there are three types of adsorption sites on Cu (410) surface: one 2-fold bridge site on the step-edge; two 4-fold hollow sites on the (100) terrace; one long-bridge site at the bottom of the terrace.

Nevertheless, considering to the influences of interaction between the adsorbates, the surface relaxation and reconstruction or other factors may provide a more comprehensive explanation for the O atom adsorbed on a metal surface at low coverage. Further studies are necessary both theoretically and experimentally.

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