Interaction of the atoms (H, S, O, C) with the Cu(111) surface

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Abstract

A density functional approach has been applied to study the interaction of the atoms (i.e. H, S, O, and C atoms) with two different cluster models of the Cu(111) surface, and either considering or neglecting the reconstruction of the surface. It is found that H atom forms essentially a covalent bond with the surface, while S, O, and C atoms form largely an ionic bond. Optimized results indicate that H, S, O, and C adsorbates prefer the high-coordination three-fold hollow site, the hcp site, at the Cu(111) surface. The adsorption energies of these adatoms on the Cu(111) surface are in the order of C > O > S > H. We also attempt to discuss the correlation between the properties of the adatoms and their adsorption characteristics on the Cu(111) surface. It can be concluded that the atomic valence and the electronegativity may better be used together to elucidate the difference in the adsorption energy between different adatoms for a given metal surface, and the atomic valence plays a more important role in such correlation. Our first-principle calculations agree well with the experimental reports. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Cu(111) surface; Density functional calculations

1. Introduction

The location of the adatoms at a crystal surface is a fundamental quantity in the description of surface processes. In particular, the geometry is clearly basic to understand bonding. It can also be very useful knowledge in analyzing the results of various experimental techniques that investigate bonding of surface processes, including, for example, electron spectroscopic techniques. Furthermore, the interaction of the atoms with metal surfaces plays a key role in many electrochemically and heterogeneously catalyzed reactions [1–8]. For instance, the adsorption of atomic oxygen on metal surfaces is of considerable interest in connection with a number of important technological processes such as bulk oxidation, corrosion, and heterogeneous catalysis [2]. Therefore, there stands a requirement that these fundamental issues should be rigorously and energetically described and predicated from first-principle theoretical methods. Fortunately, recent advances in both quantum-chemical methods and computational resources are driving this goal closer to reality.

Adsorption sites on metal surfaces differ mainly in the number of nearest metal neighbors (the coordination number) and the two-dimensional symmetry [1–4]. Since the interaction of the adatom with the

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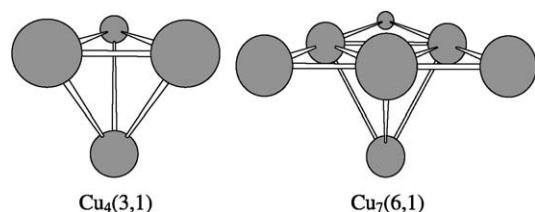
Fig. 1. Cu$_4$(3,1) and Cu$_7$(6,1) represent the Cu(111) surface with different cluster size.

metal is an attractive one, one might expect that the adatom will interact with more metals to get the largest binding energy, thus the hollow site may be the most stable adsorption site. Experimentally, on flat low-index surface, the site of adatom adsorption is indeed almost always the hollow site. Experiments such as LEED, HREELS, and EXAFS have demonstrated this point in a variety of adatoms including H, O, N, C, S, and halogens. Sometimes, the bridge coordination site involving two metals is favored (e.g. the divalent oxygen chooses the two-fold coordinated short-bridge site on Ni(110) and Ir(110), while on Ag(110) the long-bridge site with an uncertain coordination number may be chosen, and the systems of H/bccW(100) and O/fccCu(100) have the similar situations), but the on-top coordination never occurred. In addition, the bridge coordination site may be related to the surface reconstruction and/or coverage effects. With the bond order conservation (BOC) model [7,8] it is possible to explain why practically all known atomic adsorbates prefer to chemisorb at hollow sites, and this model also gives reasonable diffusion barriers for motion of the atoms on the surface. Density functional theory (DFT) has been used in the past to compute the adsorption energy of O and S atoms on various Pt surfaces, and concluded that the most stable site is the hollow site [9–12]. We feel that model calculations of atom–surface interactions can sometimes be as accurate as experiment, or at least complement them, and supply more accurate input data for the BOC model method.

As we know, many reactions are catalyzed by copper, such as Water Gas Shift reaction, methanol synthesis, and HCOOH decomposition, and the studies of the interaction of some species (i.e. H, O, S, C atoms) with the surface are important. A property of general interest is the difference in adsorption energy for different adatoms on a single crystal surface. However, no systematic work on the analysis of the binding characteristics of the non-metal atom adsorbates in their most stable adsorption site can be found in the literature to our knowledge. Theoretical treatments of atom–surface interactions remain open to some extent. In addition, to understand the chemical origin of the binding, quantum-chemical calculations are needed. Although the studies of C, H and O atoms on the Cu(111) surface have been done by Au et al. [13], the differences between the calculated adsorption energy and the experimental values are large. In the present work, we will employ density functional techniques to study the equilibrium geometry and the binding characteristics of the atoms (i.e. H, O, S, and C atoms) at the Cu(111) surface with two different cluster sizes. We also try to probe into the correlation between the properties of the atoms and their adsorption characteristics on the Cu(111) surface. In addition, the results have been compared with the experimental values in order to validate present calculations.

2. Cluster models and computational details

The development of modern surface science provided the opportunity to investigate the interaction between catalysts and molecules or atoms on the atomic scale. However, computations of molecules containing transition metal atoms have proven to be more difficult than those for first- and second-row atoms [5,6]. Recent advances in methodology based on the technologies of pseudo-potential and plane-wave basis sets and high-speed computers have now made it possible to obtain quantitative information on the surface phenomena. In this work, cluster models of the surface have been employed to simulate atoms (i.e. H, O, S, C atoms) adsorption on the Cu(111) surface.

To observe the effect of the adsorbates on the structural relaxation or reconstruction of the surface, calculations with small clusters are practical, and similar studies can be found in the literature [6]. The Cu$_4$(3,1) and Cu$_7$(6,1) cluster models, shown in Fig. 1 have been chosen to represent the Cu(111) surfaces. Cluster Cu$_4$(3,1) contains two layers with three Cu atoms in the first layer and one Cu atom in the second layer, and cluster Cu$_7$(6,1) contains six Cu atoms in

Table 1
Results of calculation of Cu$_4$X (X = H, S, O, C) complexes

Atom	Neglecting the relaxation of the surface		Considering the relaxation of the surface		E_{ads} (eV)	
	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Exp.	Ref.
H	1.20	2.12	− 0.01	2.70	2.43	[18]
S	1.89	3.40	− 0.08	4.11	(3.80)	[8]
O	1.24	4.34	− 0.65	4.97	4.46	[19]
C	1.16	5.15	− 0.64	5.46	(5.20)	[8]

Z_{eq}, the distance from the first metal plane, a negative sign meaning that the adatom resides below the surface; E_{ads}, the adsorption energy of the neutral adsorbate, and values in parentheses are estimated or deduced from molecular energies of adsorption described in Ref. [8].

the first layer and one Cu atom in the second layer. In the following, we will use two sets of calculation schemes. In the first set of calculations, only the distance of the adatom above the surface is optimized with the fixed Cu$_4$(3,1) and Cu$_7$(6,1) geometries where the Cu–Cu distances are set equal to the bulk distance (2.556 Å). In the second set of calculations, the Cu$_4$(3,1) and Cu$_7$(6,1) cluster models are allowed to relax. The atoms (i.e. H, O, S, C atoms) were freely located above these surfaces, then the systems containing atoms and cluster models are optimized based on above-described specification without symmetry restriction. Strictly speaking, to investigate the effect of the relaxation or reconstruction of the

Table 2
Results of calculation of Cu$_7$X (X = H, S, O, C) complexes

Atom	Neglecting the relaxation of the surface		Considering the relaxation of the surface		E_{ads} (eV)	
	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Exp.	Ref.
H	1.18	1.80	− 0.37	2.56	2.43	[18]
S	2.52	3.18	− 0.06	3.59	(3.80)	[8]
O	1.40	3.92	− 0.26	4.46	4.46	[19]
C	1.44	4.62	− 0.43	5.31	(5.20)	[8]

The notes of Z_{eq} and E_{ads} are the same as the footnotes of Table 1.

surface, one could better choose the cluster model with more layers and more metal atoms.

The interaction of the atoms (i.e. H, O, S, C atoms) with the different cluster models of Cu(111) surface has been studied by first-principle density functional calculations that use the hybrid B3LYP exchange-correction functional [14,15] as implemented in GAUSSIAN94 program package [16]. For Cu atoms, the relativistic effective core potentials (RECP) reported by Hay and Wadt [17] have been used to describe the 1s–2p core while the electrons arising for the 3s, 3p, 3d, 4s, 4p shells are treated explicitly. It is customary to refer to these ECPs as LANL2. The standard double-ζ basis set also reported by Hay and Wadt [17], and denoted as usual as LANL2DZ, is used to describe the electron density of the valence electrons of Cu. For H, O, S, C atoms, the standard 6-31G basis set is used. The initially geometric parameters of the cluster, the basis set and the computational method are kept the same in our calculations.

3. Results and discussion

The results of calculations with two cluster models (as shown in Fig. 1) are reported in Tables 1 and 2 and compared with available experimental data. In these tables, the atomic adsorption energy (E_{ads}) is calculated according to the formula:

$$E_{ads} = E_b(Cu_n) + E_b(A) − E_b(Cu_nA)$$

where A denotes the atom (i.e. H, O, S, and C atoms), and $E_b(Cu_n)$, $E_b(A)$, $E_b(Cu_nA)$ is the calculated energy of a cluster without an adatom, the free atom, and a cluster with an adatom, respectively.

3.1. Adsorption geometry of the atom

In general, there are four different adsorption sites on the Cu(111) crystal surface: the atop site which resides above a surface atom, two three-fold hollow sites which correspond to the 'fcc site' and the 'hcp site' (the hcp site resides above a subsurface atom in the second substrate layer; the fcc site does not), and the 'bridge' site which lies half-way between the fcc and hcp sites. In present calculations, the initial location of the adatom is not on a fixed site. The
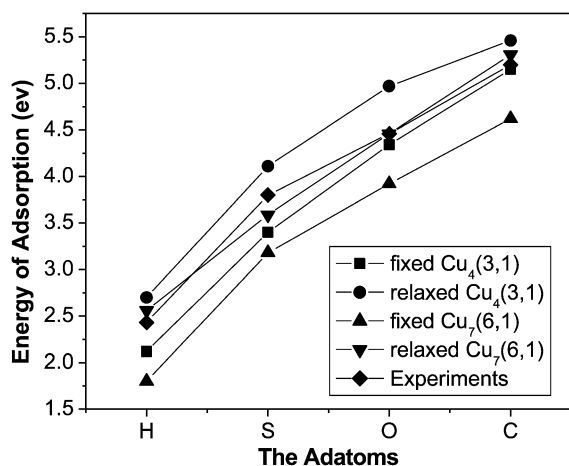
Fig. 2. The adsorption energies of the adatoms on the Cu(111) surface.

optimized results show that the adatoms are always in the hcp site in the final structure of adsorbate–surface systems according to both cluster models. Therefore, it can be observed that all adatoms prefer the high-coordination sites. This kind of adsorption geometries of the adatoms on the Cu(111) surface is in good agreement with experimental reports [20,21].

Rhodin and Estl reported [1] that adsorption sites with many nearest neighbors are usually also sites of high symmetry. Therefore, the adatoms appear to favor sites of high symmetry. Koper and van Santen [22] have also found that O and OH prefer the three-fold hollow sites to the on-top site on some fcc(111) surfaces, however, no uniquely preferred adsorption site is found for H. Several LEED studies [23,24] have favored the four-fold site with surface–adatom distance (Z_{eq}) of 1.2–1.4 Å for the Cu(001)-(2 × 2) structure. Though there are discrepancies between our methods and others by the fact that the present calculations address the adsorption of an isolated atom on the surface, the very high stability of the hcp site strongly suggests that the choice of hcp site is prior to other sites for atoms adsorption on the Cu(111) surface. It is consistent with the general features of atomic chemisorption which have been elegantly described using the BOC model [7]. These findings are also supported by a SEXAFE study [25] which found that the O atom chemisorbs in three-fold hollow sites.

From Tables 1 and 2, the computed results show

that if the cluster is not allowed to change geometry, all adatoms prefer to stay outside the surface, while these adatoms penetrate into the surface in the case of considering the relaxation of the surface. On the fcc(111) surface, the three-fold hollow sites are so tightly packed and the metal interlayer spacing is so small that the adatoms usually do not penetrate deeply enough to form a direct bond with a metal in the second metal layer [8]. Nevertheless, the drive to occupy higher coordination sites may be strong enough to cause proper reconstruction of the fcc(111) surfaces. For example, S and C atoms on Ni(111) induce a pseudo-fcc(100)-(2 × 2) overlayer structure on top of an fcc(111) substrate [26,27]. There also exist findings that C and N atoms cause reconstruction and even move into the plane of the surface [28,29]. Thus, the above-mentioned adsorption phenomena of the adatoms (i.e. H, O, S, and C atoms) on the close-packed Cu(111) surface may be explained by the strong inclination of the atom to occupy a higher coordination site. Moreover, the free atom tends to bond with more metal atoms. Therefore, the adatoms prefer to lie below the first layer of surface as considering the relaxation of the surface.

3.2. Adsorption energies of the atoms

The adsorption energy can be acted as a kind of quantitative criterion to appraise which cluster model is more fit for the system studied here. From Tables 1 and 2 it is easy to find that the adsorption energy of the atom calculated from the relaxed cluster model is higher than that from the fixed cluster model for a given Cu_nX ($n = 4, 7$) complex. The calculated results are in good agreement with the experiments. Especially, according to the relaxed $Cu_7(6,1)$ model, the adsorption energy of the atomic oxygen is the same as the experimental value (4.46 eV). The adsorption energies of these adatoms are comparatively shown in Fig. 2. It can also be concluded from Tables 1 and 2 and Fig. 2 that the adsorption energies of the atoms on the Cu(111) surface are in the order of C > O > S > H, either neglecting or considering the relaxation of the surface.

From Tables 1 and 2, one can see that the atomic adsorption energies calculated from the relaxed $Cu_4(3,1)$ are conspicuously higher than the experimental values. The reason for this may be that this

Table 3
Results of Mulliken population analysis and natural bond orbital analysis of Cu_4X complexes for considering of the relaxation of the surface

Atom	Mulliken charge	Natural charge	Natural population analysis				X_{atom}	ΔX
			Core	Valence	Rydberg	Total		
H	− 0.35	− 0.36	0.00000	1.35658	0.00101	1.35759	2.20	0.30
S	− 0.75	− 0.98	9.99999	6.95888	0.01740	16.97627	2.58	0.68
O	− 0.80	− 1.02	2.00000	7.00976	0.01492	9.02468	3.44	1.54
C	− 1.01	− 1.31	2.00000	5.29942	0.01029	7.30971	2.55	0.65

X, the electronegativity of the atom taken from Ref. [34]; ΔX, the electronegativity difference between the adatom and the Cu atom ($X_{Cu} = 1.90$).

type of cluster model ($Cu_4(3,1)$) is rather simplistic, and the geometry relaxation gives a quite exaggerated picture of the distortions in contrast to what actually occurs in a real surface. For example, according to the adsorption of C atom on the relaxed $Cu_4(3,1)$ model, the Cu–Cu distance in the first-layer plane sharply increases from the bulk bond length 2.556 to 3.051 Å (these data are not listed in tables). As it can also be seen from Tables 1–2 that the adsorption energies of the adatoms are closer to the experiments with the increase in the cluster size because of the fact that the atomic adsorption energies calculated from the relaxed $Cu_7(6,1)$ model are closer to the experimental reports than those from the relaxed $Cu_4(3,1)$ model. However, the employment of bigger cluster model is limited because of the expensive computer time. Fortunately, this kind of restriction would be compensated by using the precise basis set and taking into account the relaxation effect.
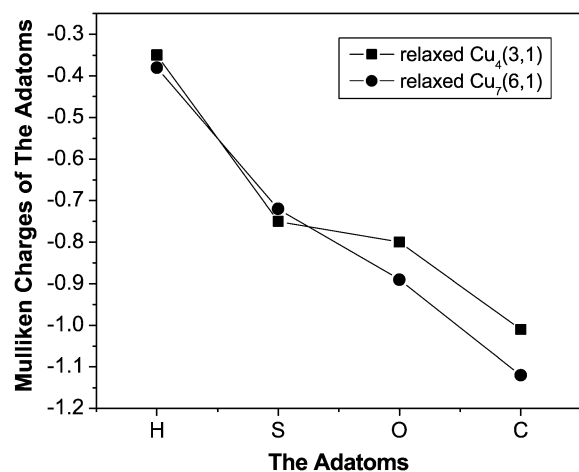

Fig. 3. The Mulliken charges of the adatoms on the Cu(111) surface.

This indicates that, in the systems studied here, the relaxation or reconstruction of the surface has a knowable effect on the energy of adsorption. The differences in the perpendicular distances of the adatoms to the first-layer plane found before and after the cluster is allowed to relax are quite illustrative of forces present. For instance, the surface–oxygen distance (Z_{eq}) decreases from 1.04 to − 0.26 Å after the $Cu_7(6,1)$ model is relaxed. The gain in adsorption energy for oxygen is 0.54 eV resulting from penetration into the surface. Similarly, the large attraction towards the Ni(100) surface for C, N, and O atoms is also clearly seen from the studies by Panas et al. [30]. They also found that the adsorption energies increase if the cluster is allowed to relax.

Thus, the effects of the relaxation of the surface and the cluster size act on the adsorption energy simultaneously. Therefore, it is reasonable to conclude that the results calculated from the relaxed $Cu_7(6,1)$ are more reliable than those from other cases. Of course, the adsorption energies of these adsorbates on the Cu(111) surface are in the order of $C > O > S > H$, either neglecting or considering the relaxation of the surface. This conclusion is in good agreement with the previous reports [1,8]. The further discussion to this conclusion will be presented in Section 3.4.

3.3. Analysis of the bonding model of the adatom with the surface

In this part, we will discuss the binding characteristics of H, O, S, and C adatoms in their most stable adsorption site, the hcp site, at the Cu(111) surface. For the relaxed $Cu_4(3,1)$ and $Cu_7(6,1)$, the Mulliken Population Analysis and the Natural Bond Orbital

Table 4
Results of Mulliken population analysis and natural bond orbital analysis of Cu_7X complexes for considering of the relaxation of the surface

Atom	Mulliken charge	Natural charge	Natural population analysis				X_{atom}	ΔX
			Core	Valence	Rydberg	Total		
H	− 0.38	− 0.43	0.00000	1.43038	0.00191	1.43228	2.20	0.30
S	− 0.72	− 1.09	9.99999	7.06280	0.02665	17.08944	2.58	0.68
O	− 0.89	− 1.16	2.00000	7.14674	0.00950	9.15624	3.44	1.54
C	− 1.12	− 1.46	2.00000	5.44105	0.02031	7.46136	2.55	0.65

X, the electronegativity of the atom taken from Ref. [34]; ΔX, the electronegativity difference between the adatom and the Cu atom ($X_{Cu} = 1.90$).

Analysis have been done under the optimized geometries. Analytical results of the adsorbate–surface systems are listed in Tables 3 and 4 and also shown in Figs. 3 and 4.

The Mulliken charges and natural charges of the adatoms can be used to establish the dominant bonding mode, either covalent or ionic, for these adsorbates [31]. From Tables 3 and 4, one may observe that all adatoms carry some amounts of negative charge. Obviously, it can be seen from Fig. 3 that the variation trend of Mulliken charges of the adatoms in the relaxed $Cu_4(3,1)$ model is the same as that in the relaxed $Cu_7(6,1)$ model. Commonly, the amount of negative charges of the adatoms on the Cu(111) surface are in the order of C > O > S > H. It can also be found from the natural charges in both cluster models. The Mulliken and natural charges found considering the relaxation of the surface reveal that the bonding mode of H atom with the Cu(111)

surface may essentially be a covalent bond, while S, O, C atoms carry a relatively high negative charge and hence form an ionic bond. In the case of atomic H and O adsorption, Koper and van Santen [22] have studied the binding characteristics on the Ag(111) surface and found that the H atom essentially forms a covalent bond with the surface, whereas the O atom forms largely an ionic bond. Similarly, Bagus et al. [32] reported that the Ag–halogen (F, Cl, Br) bond is essentially ionic. The binding of chlorine to a copper surface is completely ionic with hardly any trace of covalency as demonstrated by Pettersson and Bagus [33]. Considering the relationship between the amount of negative charge and the strength of ionic bond, it may be rational to conclude that the strengths of ionic bond for the adatoms on the Cu(111) surface are in the order of C > O > S as considering the relaxation of surface. The further explanation to these conclusions will be given below.

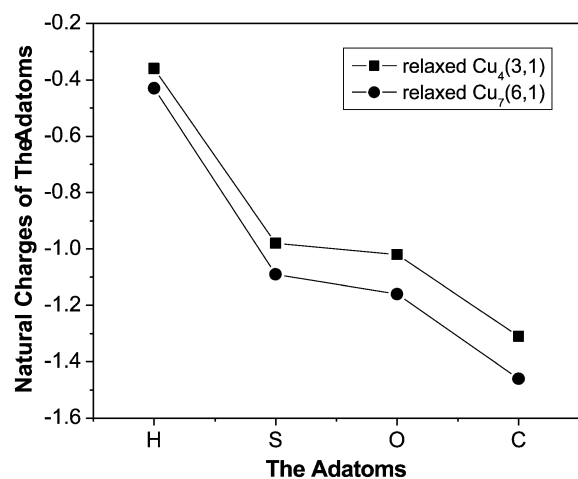### 3.4. The correlation between the properties of the atoms and their adsorption characteristics

Electronegativity is a parameter originally introduced by Pauling to describe, on a relative basis, the tendency of an atom in molecule to attract bonding electrons. Tables 3 and 4 give the electronegativity X, on the Pauling scale, for the most common oxidation state. Since the electronegativity of the adatom (i.e. H, S, O, and C atoms) is bigger than that of Cu atom, it may be expected that these atoms will gain electron from the cluster after adsorbing on the Cu(111) surface. From the results of Mulliken population analysis and natural bond orbital analysis, it is easy to find that the electron flows from the cluster into the adatoms and the sequence of the electron transfer

Fig. 4. The natural charges of the adatoms on the Cu(111) surface.

number for these adatoms is consistent with that of the adsorption energies. That is to say, the adsorption energy of the adatom on the Cu(111) surface becomes bigger with the increase of the electron transfer number.

The electronegativity difference between the adatom and Cu atom, listed in Tables 3 and 4, suggests that the bond mode of H atom with the Cu(111) surface is essentially a covalent, whereas S, O, and C atoms form an ionic bond. It accords with the bond mode analyzed from the Mulliken population and natural bond orbital population. Though the electronegativity of O atom (3.44) is bigger than that of C atom (2.55), the Mulliken charge and the natural charge of O adatom is smaller than those of C adatom. Likewise, the adsorption energy of O atom is smaller than that of C atom on the Cu(111) surface. Therefore, it is a little difficult to find the quantitative correlation solely between the electronegativity of the adatom and its strength of ionic bond or its adsorption energy on the Cu(111) surface.

In the traditional chemical sense, the atomic valence is the number of unpaired valence electrons. For instance, the atomic valence of H, O, and C atom is monovalent, divalent, and tetravalent, respectively. A close scrutiny of the data given in Tables 1 and 2 and shown in Fig. 2 permits us to draw a conclusion that the adsorption energies for these adatoms on the Cu(111) surface increase with the increase of the atomic valence in both cluster models. It should be noticed that the metal valence of metal atom might be used to treat the bonding capacity of a metal surface. The comparison between the atomic valence of the surface metal atom and the metal valence is helpful in recognizing the difference in bonding strength between different adatoms for a given metal. For the Cu_nX ($n = 4, 7$) adsorptive system, the metal valence of Cu atom is 3.5 [35,36]. Thus, the Cu(111) surface is saturated when carbon atom is adsorbed, while it is unsaturated in the case of H, S, and O atoms. The unsaturated degrees of the Cu_nX ($n = 4, 7$) for these three adatoms are in the order of $O = S < H$. To some extent, the unsaturated degree of the Cu_nX ($n = 4, 7$) implies the intensity of the interaction of the adatom with the surface. The bigger the unsaturated degree is the smaller is the intensity of the interaction. When the unsaturated degrees of different atoms become equal, the electronegativity may be acted as a

parameter to distinguish the difference of adsorption energies of those adatoms on a special metal surface. Therefore, the adsorption energies of H, S, and O atoms on the Cu(111) surface are in the order of $O > S > H$ when considering that the electronegativity of O atom (3.44) is higher than that of S atom (2.58). In a word, the sequence of adsorption energies for these adatoms on the Cu(111) surface is in the order of $C > O > S > H$. This rationalization agrees with the calculated results quite satisfactorily, which supports our view that the atomic valence and the electronegativity may better be used together to elucidate the difference in the adsorption energy between different adatoms for a given metal surface. Furthermore, the atomic valence plays a more important role in the correlation between the properties of the atoms and their adsorption characteristics.

4. Summary

In this paper, the adsorption characteristics of some atoms (i.e. H, S, O, and C atoms) on the Cu(111) surface with two different cluster models has been studied by quantum-chemical DFT calculations. Calculated results show that all adatoms prefer the high symmetry hollow site, the hcp site, at the Cu(111) surface. It is reasonable to conclude that the adsorption energies of these atoms on the Cu(111) surface are in the order of $C > O > S > H$ either neglecting or considering the relaxation of the surface. Atomic H essentially forms a covalent bond with the surface, whereas S, O, and C atoms form largely an ionic bond. For comparison, it is more reliable to calculate the adsorption energies of these atoms on the Cu(111) surface by considering the relaxation of the surface and using appropriate cluster model. Through the discussion of the correlation between the properties of the atoms and their adsorption characteristics, it can be found that the atomic valence and the electronegativity may better be used together to elucidate the difference in the adsorption energy between different adatoms for a given metal surface, and the atomic valence plays a more important role.

Acknowledgments

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