

Chemisorption of OCN on Cu (100) surface: a density functional study

Jian Ming Hu,^{a,b} Yi Li,^a Jun Qian Li,^{a,*} Yong Fan Zhang,^a Wei Lin,^a and Gui Xiao Jia^a

^aDepartment of Chemistry, State Key Laboratory of Structural Chemistry, College of Chemistry and Chemical Engineering, Fuzhou University, 350002 Fuzhou, Fujian, China

^bScientific and Technical Section, Command Academy of Fuzhou, The Chinese People's Police Army, 350002 Fuzhou, China

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Abstract

The chemisorption of cyanato radical (OCN) on Cu (100) surface is studied by using density functional theory (DFT) and the cluster model method. Cu₁₄ cluster is used to simulate the surface. Vertical bonding geometries with the nitrogen or oxygen atom down, and a parallel bonding geometry are considered, respectively. The present calculations show that cyanato-N species adsorbed on the surface is more favorable than the other configurations. It indicates that OCN species is linearly bonded to the Cu (100) surface via the nitrogen atom, and is in good agreement with the experimental result. The cyanato-N species at the bridge site is most stable. For cyanato-N, the calculated symmetric and asymmetric OCN stretch frequencies are all blue-shifted compared with the calculated gaseous values, which is consistent with the experiment result. The charge transfer from the surface to OCN causes a work function increase on the surface. Bonding of OCN to the metal surface is largely ionic.

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1. Introduction

The determination of the structure of adsorbed cyanato radical (OCN) on metal surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena [1]. OCN has been detected as an adsorbed product of the dissociate adsorption of hydrogen isocyanate (HNCO), and from the reaction of cyanogen (C₂N₂) and oxygen on Cu (100) [2], Cu (111) [3–5], and on Cu (110) [6] surfaces. In addition, adsorbed OCN has been observed in the reaction of CO and NO over supported transition metal catalysts [7–9]. Cyanato has been studied on Cu (100) [2] by reflection adsorption infrared spectroscopy (RAIRS). The OCN species are predicted to be linearly adsorbed via the nitrogen atom. A very similar RAIRS study has also identified surface OCN species on Ru (100) [7,8].

The understanding of the chemisorption bonds of the OCN radical with metal surfaces is important

both from theoretical and practical points of view. While OCN presents one electron fewer than CO₂, the molecular orbitals of both species are very similar and both the ground states are linear. The adsorption of the CO₂ molecule has been extensively studied experimentally and theoretically. It is also interesting to compare the chemisorption bond of OCN with that of CO₂ in order to see how much of our knowledge of CO₂ chemisorption can be directly applied in the study of OCN chemisorption.

The objective of the present work is to study theoretically the interaction of OCN with different adsorption sites on Cu (100) surface and to establish in this way a deeper understanding of the chemisorption bond of OCN on metal surfaces. To our knowledge, only one other quantum chemical study of the interaction of neutral OCN with metal Ni (100) surface has appeared [1]. Yang and Whitten [1] studied the chemisorption of OCN on Ni (100) by using ab initio configuration interaction theory and cluster model method.

*Corresponding author.

E-mail address: quant@fzu.edu.cn (J.Q. Li).

2. Calculated models and details

There is not yet any direct information about the exact adsorption geometry of OCN on Cu surface. The cyanato can act as a terminal ligand, a bridging ligand and a side-on ligand (Scheme 1 (I)), respectively [10]. We will study adsorption model of end-on and side-on bonded OCN on Cu (100) surface in present paper.

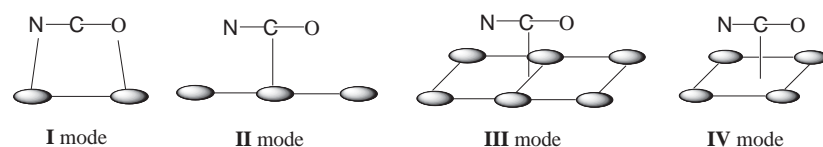
For the end-on model, the OCN can be attached to the surface by its N end (cyanato-N model) or O end (cyanato-O model). For the side-on model, we consider four possible adsorption types (see scheme 1). In scheme 1, **I** and **II** modes denote that C atom is adsorbed above the bridge and top sites, and the O and N atoms are nearly directly above the adjacent top and bridge sites, respectively. **III** mode denotes that C atom is adsorbed above the bridge site and the O and N atoms are nearly directly above the adjacent hollow sites. **IV** mode denotes that C atom is adsorbed above the hollow site and the O and N atoms are nearly directly above the adjacent bridge sites.

To obtain a qualitative of different bonding possibilities, the ideal Cu (100) has been studied using small cluster models that are able to describe the local features of OCN at different possible adsorption sites, while still keeping a reasonable computational cost. The surface cluster model contains three layers having nine, four and one atoms, respectively (Fig. 1). The sites considered for OCN adsorption on Cu (100) are follow a top site, a bridge site, a hollow 4-fold site with second layer Cu atom underneath (hollow extension for the lattice), and denoted by T, B and H, respectively (Fig. 1). For this Cu₁₄ cluster model, the positions of the atoms have been fixed at the bulk metal, with a lattice

parameter of 3.615 Å [11]. A number of the theoretical reports [12–14] have showed that a simple cluster-model calculation using the Cu₁₄ cluster model can describe essentially the interaction between adsorbate and Cu (100) surface.

The equilibrium geometry and vibrational frequency of chemisorbed OCN have been studied for various adsorption sites using a given cluster model (cf. Fig. 1). The use of the same cluster model to study different sites permits us to directly compare the calculated properties without considering the possible changes due to different cluster models.

The equilibrium geometry of the OCN molecule and the corresponding stretching frequency are obtained from the density functional calculations. In particular, calculations have been performed using the hybrid density functional method including Becke's 3-parameter nonlocal-exchange functional [15] with the correlation functional of Lee et al. [16] (B3LYP) as in the Gaussian 03 suite of programs [17]. The 3s²3p⁶3d¹⁰4s¹ electrons for copper were explicitly considered within the LANL2DZ basis set and pseudopotentials from Hay and Wadt [18]. For OCN, all electrons were explicitly considered within the 6–31+G(2d) basis set including diffuse functions and the polarization d-function. Adsorption energies were calculated as the different between the total energy for supersystem cluster-OCN, and the total energies of the cluster model and the isolated OCN molecule in the geometric structure optimization. All calculated adsorption energies (E_{ads}) of OCN on Cu (100) surface were corrected with the basis set superposition error (BSSE), which was calculated with the counterpoise method proposed by Boys and Bernardi [19].



Scheme 1.

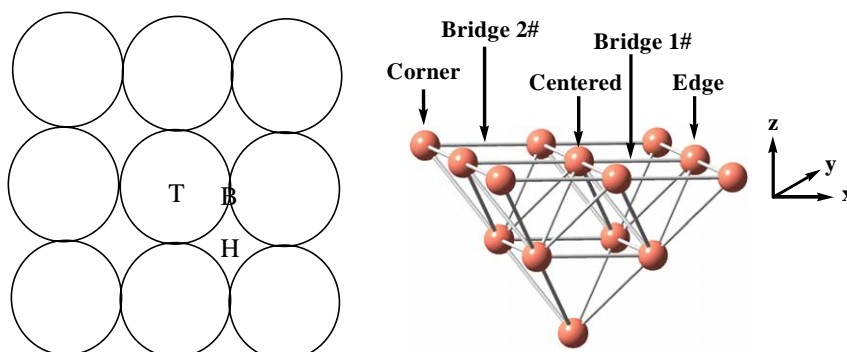


Fig. 1. The structure and adsorption site of cluster Cu₁₄; the notations T, B, and H refer to top, bridge and hollow sites, respectively.

We should point out that because we did not make periodic calculations, we can observe three different copper atoms and two different Cu–Cu bonds (bridge site) in the cluster model: these three different copper atoms are labelled as center, corner and edge, and these two different bridge sites are labelled as bridge 1# and bridge 2# (Fig. 1). The different environments may lead to different values for equilibrium geometry of adsorbed OCN or for OCN stretching frequencies. To determine the extent to which these properties may vary, we calculated the equilibrium geometry sites and cyanato-N stretching frequencies in the five cases: on the center, corner, edge, bridge 1# and bridge 2#, respectively (Table 1). The cyanato-N geometry was fully optimized, remaining vertical at on-top and bridge sites. When cyanato-N bonded on the different top sites, only slight differences in the Cu–N distance appeared, and the differences in the OCN distances and OCN stretching frequencies are insignificant. For cyanato-N on the different top sites, the variation of E_{ads} only is from 57.7 to 59.7 kcal mol⁻¹. Similar results are obtained for cyanato-N on the different bridge sites. So, we believe that our cluster model can be used to study the adsorption of OCN on Cu (100) surface. For adsorbate on the metal surfaces, the others theoretical work [20] also showed that cluster edge effects are small.

Potential energy surfaces were computed by freezing the N- or O-surface distances at various values and then optimizing the O–C and C–N distances. Points on the curves were computed with step length 0.05 Å from 1.10 to 2.10 Å as well as 2.40 and 2.60 Å.

Table 2 lists the present calculated molecular properties for gaseous OCN, as well as the results of the early MP2 calculations by Bradforth and coworkers [21] and experimental values [22,23]. For the gaseous OCN radical, the lengths of O–C bond predicted by B3LYP/6–31+ $G(2d)$, MP2/6–31+ G^* and B3LYP/6–311+ $G(3df)$ method are smaller than the experimental value of 1.206 Å [22], and the corresponding C–N bond is longer than the experimental value of 1.200 Å [22]. In fact, it appears that all levels of ab initio theory do not accurately describe the relative bond lengths ($R_{\text{O–C}}$ and $R_{\text{C–N}}$) in either anion or neutral [21]. It was well known that multiply bonded systems are difficult to describe. However, the data in Table 1 suggest that change in equilibrium structure involves very little variation in the overall end-to-end length ($R_{\text{O–(C)–N}}$). And the calculated vibrational frequencies are in good agreement with experimental values. Thus, the B3LYP/6–31+ $G(2d)$ level is able to reasonably describe the properties of OCN molecule.

3. Results and discussion

3.1. Adsorption geometries and adsorption energies

The calculated values of adsorption energies (E_{ads}), equilibrium distances ($R_{\text{ads-surface}}$), and bond length of O–C, C–N and O–(C)–N for OCN adsorbed on Cu (100) are listed in Table 3. For cyanato-N and cyanato-O end-on bonded on the bridge site of the Cu (100) surface, the potential energy surfaces obtained by

Table 1
Equilibrium geometry, adsorption energy and stretching frequency for cyanato-N on a center, corner and edge atom, respectively

Adsorption sites	E_{ads} (kcal mol ⁻¹)	$R_{\text{Cu–N}}$ (Å)	$R_{\text{O–C}}$ (Å)	$R_{\text{C–N}}$ (Å)	$\nu_{\text{O–C–N}}$ (cm ⁻¹) (sym. stretch)	$\nu_{\text{O–C–N}}$ (cm ⁻¹) (asym. stretch)
Center	57.7	1.9247	1.1934	1.1971	1373.6	2279.0
Corner	59.7	1.8776	1.1922	1.1976	1383.4	2286.2
Edge	57.8	1.9075	1.1925	1.1984	1376.2	2274.7
Bridge 1#	60.2	2.0922	1.1864	1.2074	1351.6	2243.2
Bridge 2#	64.6	2.0448	1.1833	1.2094	1358.2	2251.7

Table 2
Molecular properties for gaseous OCN

	$R_{\text{O–C}}$ (Å)	$R_{\text{C–N}}$ (Å)	$R_{\text{O–(C)–N}}$ (Å)	$\nu_{\text{O–C–N}}$ (cm ⁻¹) (sym. stretch)	$\nu_{\text{O–C–N}}$ (cm ⁻¹) (asym. stretch)
B3LYP/6-31+ $G(2d)^a$	1.1798	1.2269	2.4067	1293.6	1977.8
B3LYP/6-311+ $G(3df)^a$	1.1745	1.2216	2.3961	1298.6	1993.3
MP2/6-31+ $G(d)^b$	1.166	1.254	2.410		
Exp.	1.206 ^c	1.200 ^c	2.406 ^c	1266.6 ^d	1921.3 ^d

^aThis work.

^bListed in Ref. [21].

^cRef. [22].

^dRef. [23].

Table 3
OCN adsorption geometries and adsorption energies

Model	Site	E_{ads} (kcal mol ⁻¹)	$R_{\text{ads-surf}}$ (Å)	$R_{\text{O-C}}$ (Å)	$R_{\text{C-N}}$ (Å)	$R_{\text{O-(C)-N}}$ (Å)
Cyanato-N	T	57.7	1.9247	1.1934	1.1971	2.3905
	B	60.2	1.6564	1.1864	1.2074	2.3938
	H	56.2	1.5145	1.1813	1.2191	2.4004
Cyanato-O	T	37.0	1.9777	1.2455	1.1770	2.4225
	B	39.5	1.7263	1.2573	1.1736	2.4309
	H	37.6	1.6106	1.2665	1.1723	2.4389
Side-on bonded OCN	I	52.2	2.1909	1.1961	1.2226	2.4187
	II	43.5	2.2764	1.1996	1.2252	2.4248
	III	40.9	2.2628	1.2001	1.2224	2.4225
	IV	52.1	2.0574	1.1958	1.2233	2.4191

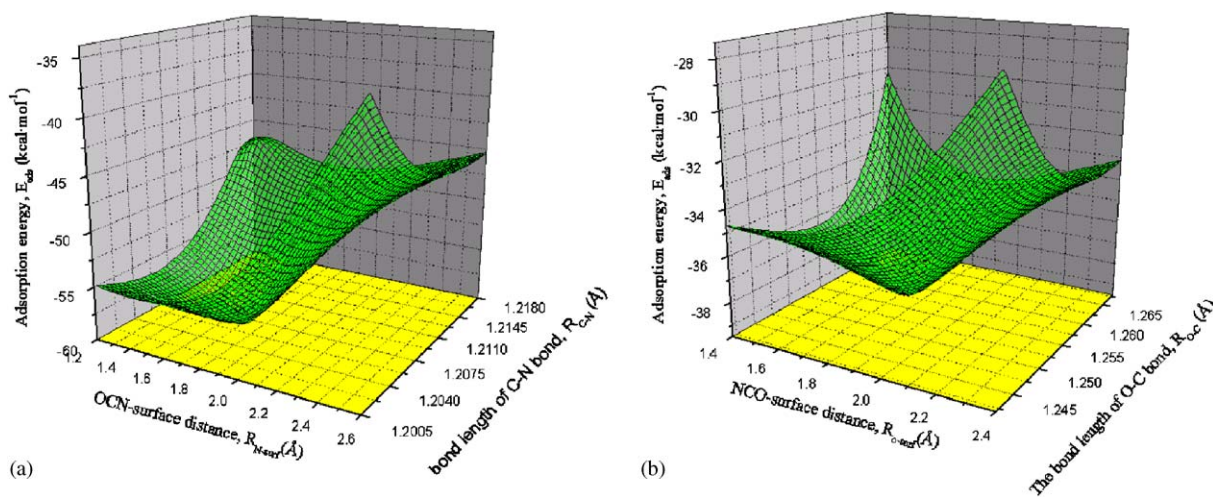


Fig. 2. (a) Adsorption energy of end-on bond cyanato-N on the bridge site of Cu (100) surface versus the OCN-surface distance and the bond length of C–N bond. (b) Adsorption energy of end-on bond cyanato-O on the bridge site of Cu (100) surface versus the NCO-surface distance and the bond length of O–C bond.

varying the N-surface distance and the O-surface distance are presented in Fig. 2. The E_{ads} for cyanato-N is 57.7, 60.2 and 56.2 kcal mol⁻¹ at the top, bridge and hollow sites, respectively. It indicates that cyanato-N is able to adsorb on all sites of Cu surface with very small differences in total energy (≤ 4 kcal mol⁻¹), and the bridge site is more favorable than other adsorption sites.

For cyanato-O, the bridge site also is more favorable, however, the calculated E_{ads} is smaller than that of corresponding cyanato-N model.

For side-on bonded OCN, the I and IV modes are more favorable than the other adsorption sites. However, the E_{ads} of I and IV modes are smaller than that of cyanato-N models. Therefore, the OCN is preferred to be adsorbed on the end-on bridge site or end-to-end bridge site, and the bridge site for cyanato-N adsorbed on Cu surface is the most stable at all adsorption modes.

For cyanato-N adsorbed on the different sites of Cu (100), the data in Tables 1 and 2 suggest that the values of adsorbed $R_{\text{O-(C)-N}}$ are shorter than that of free

$R_{\text{O-(C)-N}}$. And for other adsorption models, the values of adsorbed $R_{\text{O-(C)-N}}$ are longer than that of free OCN.

In cyanato-bridged polynuclear copper compounds the end-on coordination mode is usually found [10]. In the context of this paper, we suggest that it is linearly bonded to the bridge site through the nitrogen atom for OCN adsorbed on Cu (100) surface. Our result is in good agreement with the experimental report of Celio et al. [2], and that of OCN adsorbed on Ru (100) surface [7,8], respectively. However, this result is different from the CO₂ adsorbed on Cu (100) surface [12]. Au and Chen [12] results showed that the side-on adsorption mode with near linear CO₂ lying at the short bridge site had the larger adsorption energy of 5.6 kcal mol⁻¹ for CO₂ adsorbed on Cu (100) surface.

In addition to the adsorption of OCN, we also studied the adsorption of another isomer, the fulminate (CNO) on the Cu (100) surface. In CNO, the N atom is bonded to both O and C atom. The calculated result shows that the CNO prefers to be adsorbed on the bridge site of Cu

(100) surface by the C atom, and the corresponding adsorption energy is only $0.3 \text{ kcal mol}^{-1}$ compared to the case of OCN, the adsorption of CNO is not favorable. This conclusion can help us understand the reaction between CN molecule and O atom on the Cu (100) surface, which can produce two possible products, the OCN or CNO. The above results indicate that the formation of OCN species is more favorable than that of CNO species. Yang and Whitten's [24] results also showed that the interaction between the adsorbed O atom and the C of adsorbed CN, leading to the formation of C–O bond, is the important factor in forming surface OCN species for the reaction $\text{CN(ads)} + \text{O(ads)} = \text{OCN(ads)}$ on Ni (100).

The calculated adsorption energies are dependent on the size of clusters. However, a number of theoretical reports [25,26] showed that the adsorbate structures and equilibrium distances of the adsorbed bond only have slight differences for the different cluster, and the relative order of the calculated adsorption energies do not vary.

3.2. Vibrational frequencies

For the adsorbed OCN, the calculated symmetric and asymmetric stretch frequencies are in the range 1150–1380 and 2120–2280 cm^{-1} , respectively. Relative to the free OCN, the C–N bond of the adsorbed OCN still remains its triplet bonding characteristic [1,13] and the C–O bond corresponds to singlet bonding [1].

According to data of Tables 2 and 4, it can be seen clearly that the asymmetric stretch frequencies of adsorbed OCN are blue-shifted compared to the free OCN, while the red-shifted variations are observed for

the symmetric stretch frequencies, except the cyanato-N adsorption model.

Celio et al. have studied the oxidation of HNCO and C_2N_2 molecules on Cu (100) surface by using RAIRS experiment [2]. All of these molecules are decomposed into OCN and then are adsorbed on the surface. Three frequencies are observed at 2201 cm^{-1} (very strong), 1321 cm^{-1} (very weak), and 3448 cm^{-1} (very weak), respectively. The peaks at 1321 and 2201 cm^{-1} are attributed to the symmetric stretch and asymmetric stretch mode, respectively, and the combination of these two modes leads to the peak at 3448 cm^{-1} . After adsorption on the surface, the asymmetric and symmetric stretch modes of OCN are blue-shifted about 279.7 and 54.4 cm^{-1} , respectively, compared to the free OCN which the peaks are located at about 1266.6 and 1921.3 cm^{-1} [23].

Based upon the data of Table 4, we can see that the symmetric and asymmetric OCN stretch frequencies of cyanato-N adsorbed on Cu (100) surface are all blue-shifted. Only asymmetric OCN stretch frequencies for other adsorption models are blue-shifted. This is also demonstrated that our previous viewpoint is logical, which the OCN molecule is linearly bonded to the Cu (100) surface through the nitrogen atom.

For cyanato-N end-on bonded on Cu (100) surface, the asymmetric stretch frequencies are blue-shifted about 301.2, 265.4 and 222.2 cm^{-1} for the adsorption at top, bridge and hollow sites, respectively, compared to the value of free OCN. Similar results are also observed for the symmetric stretch mode. It is interesting to note that, only when the OCN is adsorbed at the bridge site of the surface via the N atom, the calculated frequencies of asymmetric and symmetric modes are in good agreement with the experimental result [2].

Table 4
The calculated vibrational frequencies (cm^{-1}) of adsorbed OCN on Cu (100) surface

Model	Site	$\nu_{\text{O-C-N}}$ (sym. stretch)/ $\Delta\nu$	$\nu_{\text{O-C-N}}$ (asym. stretch)/ $\Delta\nu$
Cyanato-N	T	1373.6 (vw)/80.0	2279.0 (vs)/301.2
	B	1351.6 (vw)/58.0	2243.2 (vs)/265.4
	H	1318.3 (vw)/51.7	2200.0 (vs)/222.2
Cyanato-O	T	1255.7 (s)/–65.3	2274.3 (vs)/296.5
	B	1201.4 (s)/–92.2	2276.5 (vs)/298.7
	H	1153.7 (s)/–139.9	2266.0 (vs)/288.2
Side-on bonded OCN	I	1250.0 (vw)/–43.6	2160.3 (m)/182.5
	II	1240.2 (vw)/–53.4	2124.2 (m)/164.4
	III	1246.9 (vw)/–46.7	2120.3 (m)/142.5
	IV	1248.3 (vw)/–45.3	2155.7 (m)/177.9
Exp.	Ads. [2]	1321 (vw)/54.4	2201 (vs)/279.7
	Free [23]	1266.6	1921.3
Cal.	Free	1293.6	1977.8

The symbol in parenthesis is defined as follows: vw—very weak; w—weak; s—strong; vs—very strong; m—medium.

Table 5
The results of NPA (e) for OCN adsorbed on the surface

Model site		q_{OCN}	$q_{\text{O}} (\Delta q_{\text{O}})$	$q_{\text{C}} (\Delta q_{\text{C}})$	$q_{\text{N}} (\Delta q_{\text{N}})$
<i>Before adsorption</i>		0.0	−0.368	0.643	−0.275
<i>After adsorption</i>					
Cyanato-N	T	−0.969	−0.617 (−0.249)	0.764 (0.121)	−1.116 (−0.841)
	B	−0.949	−0.584 (−0.216)	0.791 (0.148)	−1.156 (−0.881)
	H	−0.956	−0.558 (−0.190)	0.796 (0.153)	−1.194 (−0.919)
Cyanato-O	T	−1.003	−0.991 (−0.623)	0.601 (−0.042)	−0.613 (−0.338)
	B	−0.962	−0.978 (−0.610)	0.593 (−0.050)	−0.577 (−0.302)
	H	−0.951	−0.973 (−0.605)	0.578 (−0.065)	−0.556 (−0.281)
Side-on bonded OCN	I	−0.935	−0.729 (−0.361)	0.611 (−0.032)	−0.817 (−0.542)
	II	−0.967	−0.732 (−0.364)	0.533 (−0.110)	−0.768 (−0.493)
	III	−0.936	−0.720 (−0.352)	0.547 (−0.096)	−0.763 (−0.488)
	IV	−0.911	−0.730 (−0.362)	0.614 (−0.029)	−0.795 (−0.520)

The value in parenthesis is defined as follows: the difference charge between the charge of before adsorption OCN and the charge of after adsorption OCN.

3.3. Charge transfer and work function

Chemisorption leads to partial electron transfer between the copper cluster and the OCN molecule. This can be seen in the calculated charge distribution by natural population analysis (NPA [27]), which shows a negative charge (see Table 5) located on OCN and leaves a positive charge on the copper cluster. This charge transfer and the geometric changes in OCN upon adsorption are clear evidence of the chemical nature of the interaction.

The charge transfer from the copper cluster to OCN can be understood on the basis of the chemical potentials of the two compounds. While the two compounds come into interaction, their electronic chemical potentials tend to equalize; this determines the direction of electron transfer [28], which is from the species with higher chemical potential toward that with lower chemical potential. The electronic chemical potential μ can be estimated from its vertical ionization potential (IP) and electron affinity (EA) values [29]:

$$\mu = -\frac{\text{IP} + \text{EA}}{2},$$

where $\text{IP} = E^+ - E^0$, $\text{EA} = E^- - E^0$, which E^+ , E^0 , E^- are the total energies of the cationic, neutral, and anionic species in the equilibrium geometry of the neutral species. For OCN, we obtain $\text{IP} = 13.53$ eV and $\text{EA} = 3.52$ eV (the EA experimental value is 3.61 eV [21]), thus $\mu_{\text{OCN}} = -8.54$ eV. The electronic chemical potential μ of the copper cluster is -3.82 eV by using the same method. Therefore, electronic charge transfer is expected to occur from the copper cluster or the actual copper surface (the Lewis base) toward OCN (the Lewis acid); the same situation is found for acrylonitrile [25]

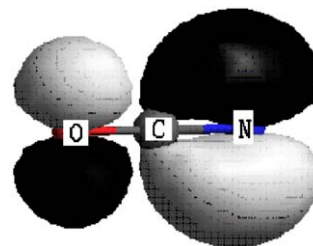


Fig. 3. The HOMO of OCN molecular.

absorbed on Cu (100) surface, and cyanide adsorbed on Cu (100) [14] and Pt (100) [26] surfaces.

The data of Table 5 shows that the O, C and N atom of adsorbed OCN are obtained electrons compare to that of free OCN, except the C atom of adsorbed cyanato-N. The highest occupied molecular orbital (HOMO) of OCN is the O–C antibonding and C–N bonding in character (see Fig. 3). So for cyanato-O and OCN side-on bonded on Cu surface, it is propitious to weaken the O–C antibonding and strengthen the C–N bonding when the charges transfer from the Cu surface to the OCN. It causes that the bond length of the adsorbed O–C bond is enlarged and the C–N bond is shortened. It is consistent with the data of Tables 2 and 3.

For adsorbed cyanato-N, the O and N atom obtained charge is profitable to the antibonding and bonding, respectively. The C atom lost electrons is not profitable to bonding, but is profitable to antibonding. Because both cooperate with action, it leads that the bond length of adsorbed O–(C)–N bond are shorter than that of free O–(C)–N bond, and the symmetric and asymmetric OCN stretch frequencies of cyanato-N adsorbed on the bridge site of Cu (100) surface are all blue-shifted.

The electrons transfer from the surface to the OCN causes an increase in work function (ϕ) upon OCN. In this paper, “work function” refers to the first-ionization potential of the cluster, which calculated employing Koopmans’ theorem and the energy of the HOMO. The work function (ϕ) of the Cu_{14} cluster is 4.34 eV (the work function experimental value of the Cu (100) surface is 4.59 eV [30]), while 4.52 eV is obtained for cyanato-N at the top site. So adsorbed cyanato-N species caused a work function increase on Cu_{14} cluster yielding $\Delta\phi = 0.18$ eV at low coverage. Similarly, for cyanato-N at the bridge and hollow site, $\Delta\phi$ are 0.12 and 0.09 eV, respectively. For cyanato-O at the top, bridge and hollow site, $\Delta\phi$ are 0.41, 0.34 and 0.32 eV, respectively. There are no experimental work function measurements for OCN on Cu (100). However, the theoretic report showed that the OCN adsorbed on Ni (100) caused an increase of work function by Yang and Whitten [1].

Adsorbed OCN species has more negative charge, it also indicates that bonding of OCN to the metal surface is possibly ionic. The previous theoretical study has concluded that bonding of OCN to the metal surface is largely ionic [1]. The first derivative of the dipole moment curve, dD/dR , provides an indication of the ionic component of the bonding. If a system A–B is represented by two point charges of $\pm q$ (for instance, $A^{+q}-B^{-q}$) separated by a distance of R , then the dipole moment $D = R \cdot q$, $dD/dR = q$, and the dipole moment curve should be linear [1]. Although this point charge model is oversimplified when polarization effects are important, a large value of the slope for the dipole moment curve is an indication of a large ionic component [31].

Fig. 4 shows the calculated dipole moment along the surface normal with respect to the N- and O-surface distances for OCN adsorbed at various sites, respectively. For OCN adsorbed at all sites, the dipole moment curves are similar to each other. The calculated dD/dR , for cyanato-N at the top, bridge and hollow sites, is 1.42, 1.31 and 1.24, respectively. And for cyanato-O at the top, bridge and hollow site, the calculated dD/dR is 1.52, 1.38 and 1.35, respectively. By this measure, it would appear that both cyanato-N and cyanato-O have large ionic components at all sites. And based upon the calculated first derivative of the dipole moment and the strong bonding between the adsorbed OCN and copper surface, it is also expected that electrons are transferred from the copper surface to the OCN.

3.4. CO_2 adsorption on Cu (100) surface

Let us compare, in this section, OCN adsorption on Cu with CO_2 adsorption on Cu calculated using these same methods [12]. The HOMO of OCN is an unfilled

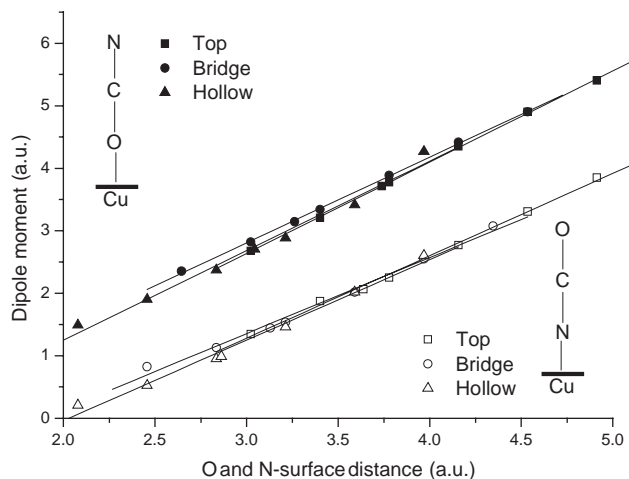


Fig. 4. Calculate dipole moment (1 a.u. = 2.54 Debye) of end-on O- and N-bond along the surface normal at various adsorption sites versus the NCO- and OCN-surface distance.

orbital. So, adsorption of OCN is dominated by substantial charge transfer from the Cu into the unfilled 2π orbital of OCN. For free CO_2 , this orbital is already filled. This result in a negative electron affinity of -1.60 eV for free CO_2 [32], compared to the sizeable positive electron affinity of 3.61 eV for free OCN [21]. This difference explains the difference in the ionicity of the chemisorption: there is negative charges transferred from Cu to CO_2 [12], but in absolute value, they are much lower than those seen on adsorbed OCN (Table 5). Given the above discussion of adsorption energies, it is then easy to understand that increased ionicity for OCN results in a much larger adsorption energy: the smallest adsorption energies of OCN on Cu (100) is $37.0 \text{ kcal mol}^{-1}$, however, the largest adsorption energies of CO_2 on Cu surface is only $5.6 \text{ kcal mol}^{-1}$ [12].

3.5. Relaxation and reconstruction of Cu (100)

At the previous section, the large adsorption energies ($> 56 \text{ kcal mol}^{-1}$) of cyanato-N end-on bonded on the Cu (100) surface indicated its chemisorption. For the strong adsorption, it possibly leads to decompose of the adsorbate; on the other hand, it is likely to cause relaxation or reconstruction of the substance surface, if the decomposition of the adsorbate is not caused. It is well known that the Cu (100) surface occurs little relaxation [33]. So, we only consider reconstruction of Cu (100) surface and cyanato-N adsorbed on the top site in this paper. Our calculation results (Table 6 and Fig. 5) show that the reconstruction of Cu (100) surface has a tendency to form ideal surface along with the converge increase after adsorbed OCN. The tendency does not influence the structures of the adsorbed OCN.

Table 6
The results of reconstruction of Cu (100) surface

	Ideal surface	Clean surface	After adsorption		
		Reconstruction	Reconstruction		
		a	b	c	d
R_1 (Å)	2.556	2.624	2.649	2.501	2.516
R_2 (Å)	2.556	2.466	2.541	2.461	2.493

R_1 is the bond length between the center Cu atom and the adjacent Cu atom of Cu14 cluster. R_2 is the bond length between the corner Cu atom and the edge Cu atom of Cu14 cluster (see Fig. 4).

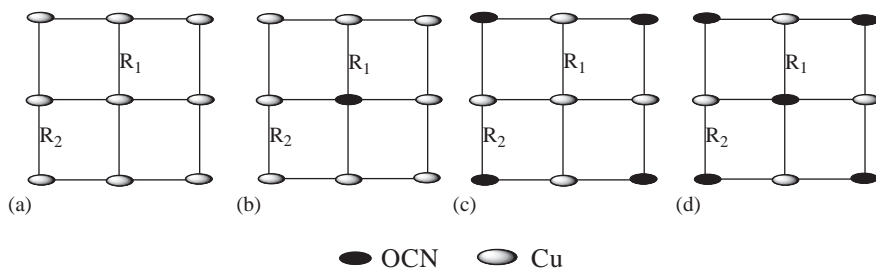


Fig. 5. (a) The cluster model of Cu (100) surface. The reconstruction of ideal Cu surface. (b) Adsorption of one OCN molecule on a reconstructive Cu surface. (c) Adsorption of four OCN molecules on a reconstructive Cu surface. (d) Adsorption of five OCN molecules on a reconstructive Cu surface.

4. Conclusions

The OCN species adsorbed on the Cu (100) surface, three adsorption models, end-on bonded cyanato-O, end-on bonded cyanato-N and side-on bonded OCN, are considered in present work. The calculated results show that the cyanato-N model is more favorable than other adsorption models, in which the OCN species is linearly bonded to the Cu (100) surface via the nitrogen atom. Our result is in good agreement with the experimental report. The cyanato-N species at the bridge site of the surface is the most stable. For cyanato-N on the Cu (100) surface, the calculated symmetric and asymmetric OCN stretch frequencies are all blue-shifted compared to the values of the free OCN species, which also agrees with the experimental study. The charge transfer from the Cu surface to the OCN species leads to an increase in work function upon the Cu (100) surface, and the interactions between OCN and metal surface is largely ionic.

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