Acetylene adsorption on Cu(111) and stepped Cu(111): theoretical study

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Abstract. ASED MO and DV-X_α methods have been employed to describe the adsorption of C_2H_2 on the Cu(111) and stepped Cu(111) surface. Our results show that all adsorbed C_2H_2 molecules are distorted because both the acetylene π donation to the surface and substrate back-donation to the acetylene π^* orbital result in the equilibrium bonding geometry. On the Cu(111) surface, two stable configurations are found. One is on the bridge site with the C–C axis parallel to the surface; the other is two C atoms on the two symmetrically distinct threefold-coordinated hollow sites on the surface. The influence and mechanism of a monatomic step with (110) geometry on the binding energy and the structure of the adsorbate substrate complex have been investigated. The results show that two new types of chemisorption complex can be formed; the binding energies are largely increased.

1. Introduction

The adsorption structure and configuration of small unsaturated hydrocarbons (typically C_2H_2, C_2H_4, etc) on metal and semiconductor surfaces is an important factor in providing a key to understanding surface reactivity and the detailed mechanisms of heterogeneous catalysis [1–8]. A variety of surface techniques, such as electron energy loss spectroscopy, ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, photoelectron diffraction and semi-empirical quantum theories have been applied to these systems, including C_2H_2–Cu(111) [1–3], C_2H_2–Ni(100) [3], C_2H_2–Si(100) [4–6].

Vibrational spectroscopy has indicated that substantial rehybridization occurs when acetylene is adsorbed at a low temperature onto some transition-metal surfaces [2]. The substantial rehybridization on Cu(111) has been proposed to be related to coordination of the acetylene molecule [2, 3]. However, a recent near-edge x-ray absorption fine structure (NEXAFS) study of acetylene on Pd(111) shows rather a different vibrational spectrum, which suggested that a different adsorption geometry is found on this surface [3]. Therefore, the further geometry of acetylene adsorption has been studied by some groups in order to understand the possible structural role in the changing bonding and vibrational spectrum. It is urged that theoretical studies should be done on this.

In addition, as we know, surface defects extensively exist on many metal and semiconductor surfaces. As a rule, the study of surface defects is experimentally and theoretically difficult; so the influence of surface defects is far from well understood. We have tried to make clear the function of the surface step in the adsorption system.

In this paper, we offer much information about the configuration and mechanisms of C_2H_2 on Cu(111) and stepped Cu(111). As the *ab-initio* methods are difficult for

systems containing too many electrons, we use a simple molecular orbital theory to decide the structure and then use the first-principles discrete variational method to calculate the electronic properties of these systems, with modest demands on computer resources.

2. Models and methods

In this paper, two model clusters Cu_{24}–C_2H_2 and Cu_{33}–C_2H_2 are adopted to simulate the C_2H_2 adsorption on Cu(111) (figure 1(*a*)) and stepped Cu(111) (figure 1(*b*)), respectively.
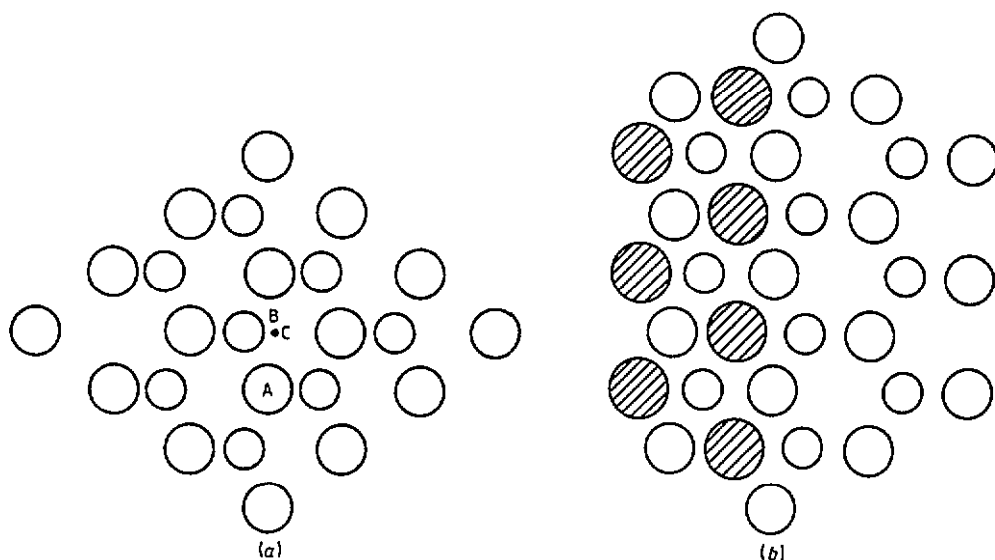

Figure 1. (*a*) Model clusters Cu_{24} applied to simulate the Cu(111) surface: O, first-layer Cu atom; o, second-layer Cu atom. (*b*) Model clusters Cu_{33} applied to simulate the stepped Cu(111) surface: O, first-layer Cu atom; o, second-layer Cu atom; , the step layer Cu atom.

The atom superposition and electron delocalization (ASED) molecular orbital (MO) theory is used in our total-energy (TE) calculation, which has been applied to many systems [9–12]. This fast method seems appropriate especially for calculating bond geometries and force constants of complex systems. The atomic parameters used in calculations are listed in table 1 [13, 14]. Using these parameters, the C–H and C–C bond lengths of the free C_2H_2 molecule are overestimated by 0.11 Å and 0.09 Å while the C–H stretch and C–C stretch frequencies are 3299 cm^{-1} and 1945 cm^{-1}, respectively, in good agreement with the experimental results 3374 cm^{-1} and 1974 cm^{-1} (relative errors are only 2.22% and 1.47%, respectively).

The discrete variational X_α (DV-X_α) method is employed to develop a deeper insight into the bonding mechanism and electronic properties. The molecular wavefunctions and eigenvalues were determined using the self-consistent charge (SCC) approximation to the potential. In the present procedure, the C 1s and the Cu 1s-3p core orbitals have not been varied, that is to say the 'frozen-core' approximation has been used. More details about this method have been given in [16].

Table 1. Atomic parameters employed in the calculations: n, the principal quantum number; I_p, the ionization potential; ζ, the Slater orbital exponent.

Atom	n	s orbital I_p (eV)	ζ (au)	n	p orbital I_p (eV)	ζ (au)	n	d orbital I_p (eV)	ζ_1 (au)	ζ_2 (au)	c_1	c_2
H	1	12.30	1.20									
C	2	15.29	1.658	2	9.96	1.618						
Cu	4	7.73	1.85	4	3.94	1.55	3	9.65	2.10	5.95	0.611 96	0.581 86

3. Results and discussion

3.1. C_2H_2 adsorption on Cu(111)

As a first step, we studied the chemisorption of C_2H_2 using the ASED MO method. Three possible adsorption sites are considered in our calculations, including atop A, bridge B and long bridge C as shown in figure 1. For each adsorption site, we calculated the TE in order to determine the stable structure. For convenience, we started with two simple cases: one is linear C_2H_2 adsorption (just free molecules) and the other is distorted C_2H_2 (represented by $C_2H_2^*$ in the following) adsorption with the H–C–C angle set at 120°.

It is found that not only linear C_2H_2 but also $C_2H_2^*$ are both energetically unfavourable on all possible adsorption sites when the C–C bond length is 1.29 Å. However, when we varied the length of the C–C bond, the linear C_2H_2 cannot adsorb onto all three possible adsorption sites in any case, while the distorted $C_2H_2^*$ structure is able to adsorb onto the short-bridge and the long-bridge sites with C–C bond lengths of 1.50 Å and 1.58 Å, respectively. In order to understand the adsorption structure better, we have proceeded to make further calculations. On the bridge site, when we varied the C–C bond length l_{C-C}, the C–H bond length l_{C-H}, the C–C–H angle θ and the adsorption height h we found that the stable local complex is distorted $C_2H_2^*$ on the short-bridge site with $l_{C-C} = 1.50$ Å, $l_{C-H} = 1.17$ Å, $\theta = 55°$, $h = 1.90$ Å and a binding energy of 0.504 eV (see figure 2(a); only part of the cluster is drawn). On the long-bridge site, we have obtained the other stable complex in which C atoms occupy the two symmetrically distinct threefold-coordinated hollow sites on the surface with a binding energy of 0.703 eV (figure 2(b); only part of the cluster is drawn). This complex is the favourable structure, in agreement with the result of a photoelectron diffraction experiment [1]. The C–C bond lengths mainly stretch to 0.21 Å and 0.29 Å respectively, i.e. to a value between those of the double and single bonds, indicating a drastic weakening of the C–C triple bond. Furthermore, we calculated the vibrational frequencies of C–C bonds to compare with the high-resolution electron energy loss spectroscopy (HREELS) study. We use a Morse-type expression to simulate the TE curve versus the adsorption height or bond length near the equilibrium position [12]:

$$E(x) = E_0 + [a + b(x - x_0) + c(x - x_0)^2]\{1 - \exp[-\alpha(x - x_0)]\}^2$$

where $E(x)$ is the TE at position x, x is the adsorption height or bond length, and x_0, E_0, a, b, c, and α are the parameters to be found. Using the least-squares method on the data of our calculated TEs near the equilibrium position x_0, we can obtain the equilibrium position x_0, minimum TE E_0 and force constants $k = (d^2E/dx^2)|_{x=x_0} = 2a\alpha^2$.

We obtained the C–C bond-stretching modes of 1229 cm^{-1} and 1145 cm^{-1}, respectively. The large decrease in the C–C bond-stretching vibrational frequencies to values between the double-bond value (1600 cm^{-1}) and the single-bond value (1000 cm^{-1}) [15] also indicates
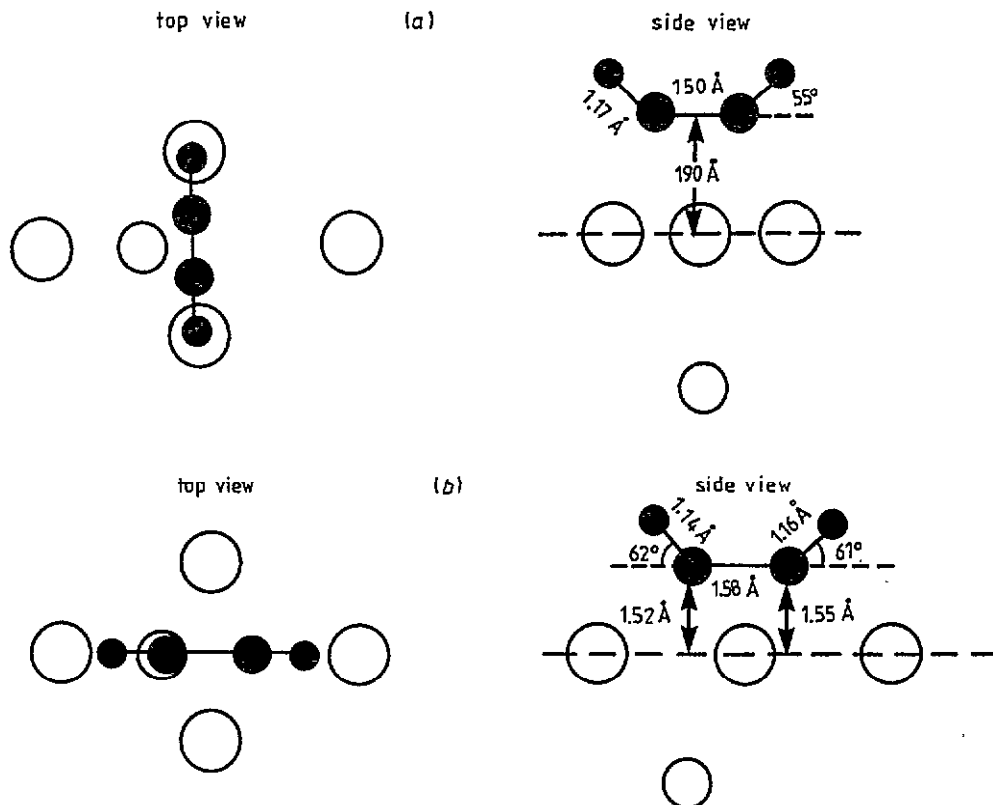
top view   (a)   side view

top view   (b)   side view

Figure 2. (*a*) Schematic adsorption geometry for C_2H_2 on the short bridge of ideal Cu(111). (*b*) Schematic adsorption geometry for C_2H_2 on the long bridge of ideal Cu(111).

significant lowering of the C–C bond order, in agreement with the results of photoelectron diffraction [1] and the HREELS study [3]. In order to study the strengths of the C–C and C–H bonds in C_2H_2, the bond orders have been calculated. The results are shown in table 2. The C–C bond order is decreased to 1.10 and 0.87 for C_2H_2 adsorbed on short-bridge and long-bridge sites, respectively, and the C–H bond order hardly varies.

Table 2. The bond orders of C–H and C–C of $C_2H_2^*$ adsorbed on the ideal Cu(111) and the stepped Cu(111) surface.

		On ideal Cu(111)		On stepped Cu(111)	
	C_2H_2 (free)	Short bridge	Long bridge	First case	Second case
C–H	0.81	0.79	0.80	0.80	0.80
C–C	1.83	1.10	0.87	1.08	0.80

In order to study the dependence of the results on the size of the Cu cluster, we also have calculated the TEs of C_2H_2 adsorbed on the Cu(111) surface using the clusters Cu_{17}–C_2H_2 and Cu_{32}–C_2H_2. We found that the results of adsorption geometry and the bond orders vary little. The binding energies are listed in table 3. These results show that there is no

Table 3. The binding energies of C_2H_2 adsorbed on the ideal Cu(111) using different sizes of Cu cluster.

	Binding energy (eV)		
	Cu_{17}–C_2H_2	Cu_{24}–C_2H_2	Cu_{32}–C_2H_2
On short bridge	0.467	0.504	0.300
On long bridge	0.900	0.703	0.646

essential difference in C_2H_2 adsorption on the Cu(111) surface when the size of the cluster is varied.

Our experience shows that it is efficient using the ASED MO method to determine the geometry configuration, but it is not appropriate for calculating the ground-state levels. Therefore, we employed the DV-X_α method to describe the adsorption of C_2H_2 on Cu(111) in order to understand further the electronic properties. We adopted the coordinates of equilibrium which were determined above. For the favourable structure of $C_2H_2^*$ on Cu(111), we obtained the theoretical ground-state valence levels shown in figure 3, where the ground-state levels of free C_2H_2 and distorted $C_2H_2^*$ are given, too. From figure 3, we can explain why acetylene favours distortion on the Cu(111) surface. As we know, the free molecule unequivocally favours the linear structure. However, it is clear that, for linear C_2H_2 adsorption, acetylene only has π donation to the surface because the antibonding π^* orbitals are so high above the Cu surface orbitals that it is difficult for substrate to back-donate electrons to the empty π^* orbital. Despite the stability obtained by this π donation, it is not strong enough to cancel the repulsive interaction acting on C and H atoms to the substrate; so the linear C_2H_2 cannot absorb onto Cu(111). On the other hand, the situation for distorted $C_2H_2^*$ adsorption is very different. The distortion causes the π^* orbital to decrease to a position where it can be strongly back-donated by the Cu surface orbitals. In the meantime, the π donation is also enhanced. Therefore, for the $C_2H_2^*$ adsorption, both π donation and π^* back-donation occur; this results in the equilibrium ethylene structure with a binding energy of 0.703 eV. What is more, we calculated the electronic occupation numbers of the $C_2H_2^*$ and C_2H_2 MO in order to verify the above explanation. The results are listed in table 4. It is clear that π donations are enhanced from $0.55e$ to $1.11e$, and π^* orbitals are back-donated to more $0.87e$ when distortion occurs.

Table 4. Molecular orbital occupation numbers of C_2H_2 adsorbed on the ideal Cu(111) and the stepped Cu(111) surface.

	σ_s	σ_s^*	σ_p	π	π^*
C_2H_2 (free)	2.0	2.0	2.0	4.0	0.0
C_2H_2 (on ideal Cu)	2.0	2.0	2.0	3.45	0.27
$C_2H_2^*$ (on ideal Cu)	2.0	2.0	2.0	2.89	1.14
First case (on stepped Cu)	2.0	2.0	2.0	2.88	0.96
Second case (on stepped Cu)	2.0	2.0	2.0	2.88	1.12

The calculated total density of states (TDOS) for the clusters of the favourable structure is shown in figure 4(*a*), where the Fermi energy is considered as zero and the broken curve represents the TDOS of the clean Cu surface. Figure 4(*b*) is the differential spectrum between the cluster of $C_2H_2^*$ on the Cu(111) surface and the clean Cu surface. The peaks at 13.3 eV, 9.66 eV and 7.62 eV below the Fermi energy in the TDOS come from the σ_s, σ_s^* and σ_p C_2H_2 MOs.
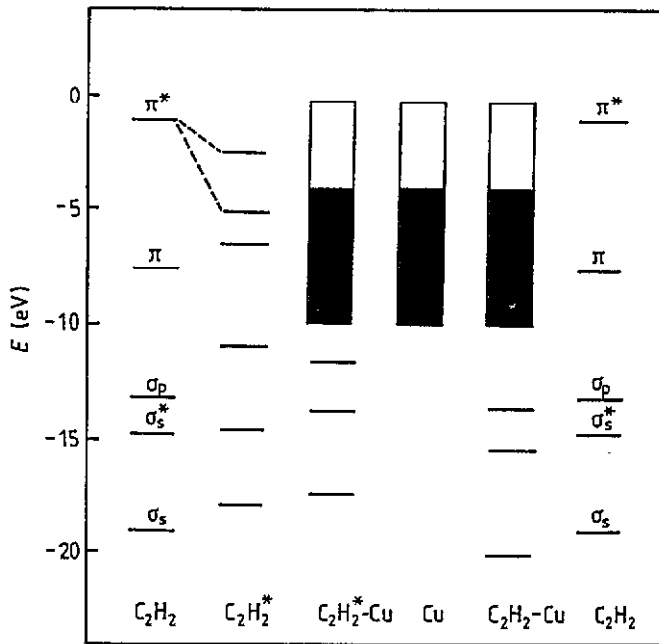
Figure 3. Ground-state energy levels of free C_2H_2, distorted $C_2H_2^*$, substrate Cu_{24} and adsorbed systems C_2H_2–Cu and $C_2H_2^*$–Cu for C_2H_2 adsorption on the long-bridge site.
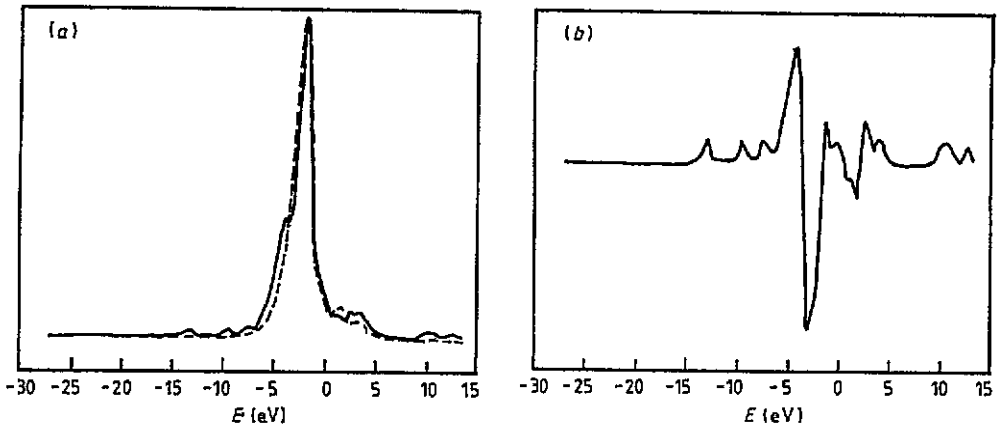

Figure 4. TDOS curves of $C_2H_2^*$ on the long-bridge site of ideal Cu(111); (*a*) TDOS curve, (– – –, TDOS of clean Cu); (*b*) the differential spectrum.

3.2. C_2H_2 adsorption on stepped Cu(111)

Firstly, in order to simulate the step, we studied a cluster of Cu_{33}–C_2H_2 (see figure 1(*b*)) using the ASED MO method. Two kinds of adsorption site on stepped Cu(111) are considered in our calculations: one is when the $C_2H_2^*$ molecular axis is parallel to the step direction; the other is when $C_2H_2^*$ tilts to the surface normal and its molecular axis is vertical to the step direction.

In the first case, we optimized the angle α of the $C_2H_2^*$ molecular plane to the surface normal, the C–C–H bond angle β, the C–C bond length a, the C–H bond length b and the distance c between the $C_2H_2^*$ molecular axis and the step. A stable complex (figure 5; only part of the cluster is drawn) with $\alpha = 42°$, $\beta = 130°$, $a - 1.534$ Å, $b = 1.169$ Å and $c = 1.936$ Å has been found in our calculations, with a binding energy of 2.297 eV. In the second case, we have obtained an optimized structure as shown in figure 6 (only part of the cluster is drawn) with a binding energy of 1.79 eV. Our results show that the binding energies of C_2H_2 near the step are much larger than those on ideal Cu(111) plane. However, the C–C bond lengths of C_2H_2 on stepped Cu(111) are only slightly larger than those on ideal Cu(111) and the C–H bond lengths are almost invariant. The calculated MO occupation numbers of C_2H_2 (a) on stepped Cu(111) are shown in table 4. From table 4, we find that the π and π^* orbital occupation numbers of C_2H_2 adsorbed on the stepped surface are only slightly different from those of $C_2H_2^*$ on the ideal surface. These results mean that the activation of C_2H_2 molecules on stepped Cu(111) does not change obviously compared with that on ideal Cu(111). In order to verify this, we have calculated the bond orders of C–C and C–H for adsorbed C_2H_2 in both cases. Our results are listed in table 2 which shows that the bond order of C–C for C_2H_2 on the stepped surface is slightly smaller than that on the ideal surface and the bond order of C–H is nearly constant for the ideal surface and the stepped surface. Therefore, we think that the monatomic step of Cu(111) hardly influences the activation of adsorbed C_2H_2.
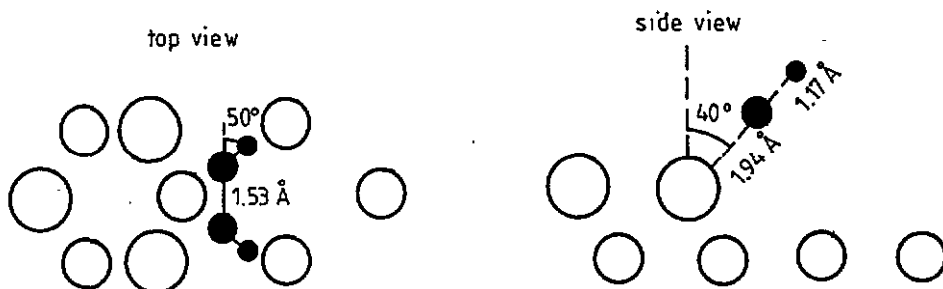

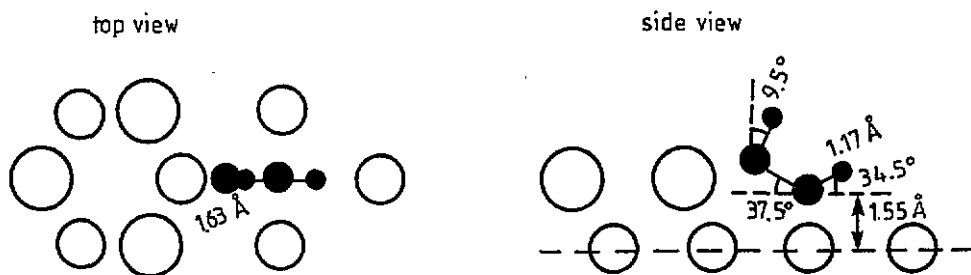Figure 5. Schematic adsorption geometry for C_2H_2 on stepped Cu(111): first case.

Figure 6. Schematic adsorption geometry for C_2H_2 on stepped Cu(111): second case.

Additionally, we studied the adsorption of C_2H_2 in the vicinity of the step. We found that C_2H_2 adsorbed on the short-bridge site in the vicinity of the step will be as in the

first case (figure 5) mentioned above with no barrier. However, $C_2H_2^*$ adsorbed on the long-bridge site near the step cannot be considered as in the second case (figure 6).

Like the case of ideal Cu(111), the TDOS of C_2H_2 adsorbed on the stepped surface is given in figure 7. On comparison with the TDOS of C_2H_2 adsorbed on an ideal surface, there are no obvious differences.
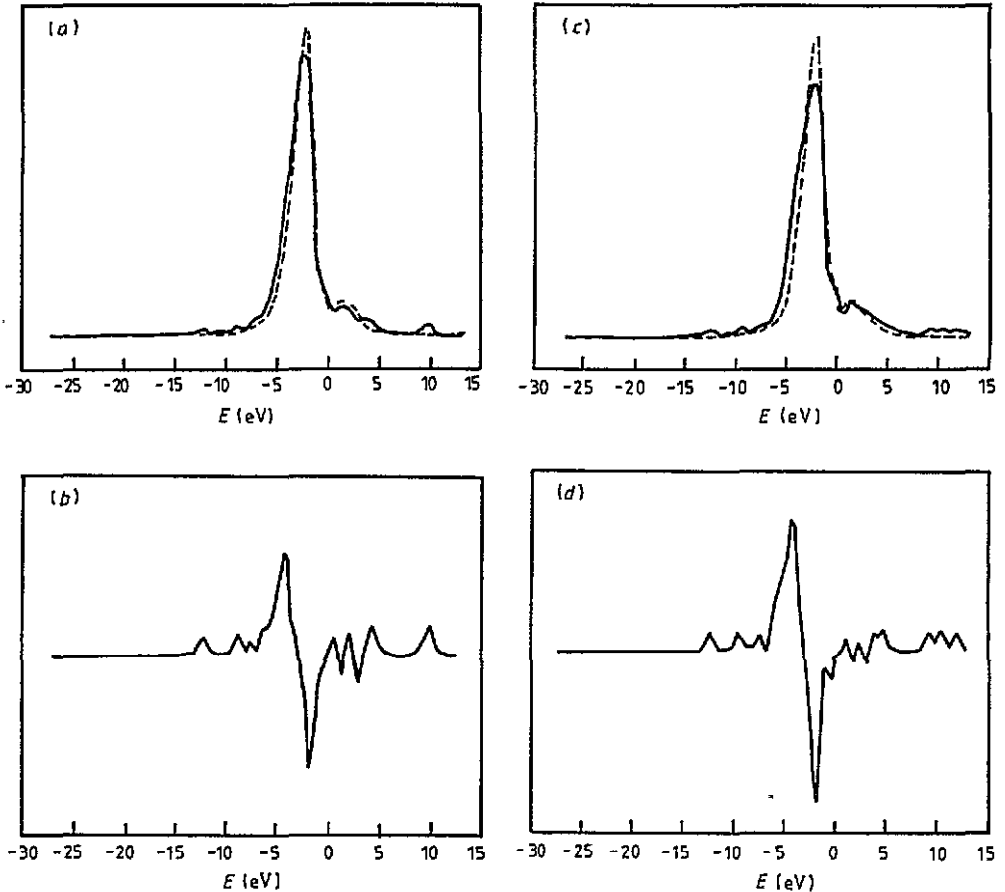

Figure 7. TDOS curves of C_2H_2 on stepped Cu(111): (*a*) TDOS of the first case (----, TDOS of clean Cu); (*b*) the differential spectrum of the first case; (*c*) TDOS of the second case (----, TDOS of clean Cu); (*d*) the differential spectrum of the second case.

4. Summary

The adsorption of C_2H_2 on the Cu(111) and stepped Cu(111) surface as well as the influence and mechanism of a monatomic steps have been studied by theoretical calculations. A summary of the important results is as follows.

(1) On the ideal Cu(111) surface, two stable configurations are found. One is on the bridge site with the C–C axis parallel to the surface; the other is two C atoms on the two

symmetrically distinct threefold-coordinated hollow sites on the surface. The latter is the favourable structure, in agreement with the results of photoelectron diffraction.

(2) All adsorbed C_2H_2 molecules are distorted because both the acetylene π donation to surface and substrate back-donation to the acetylene π^* orbital result in the equilibrium bonding geometry.

(3) The large increase in C–C bond length and the large decrease in the C–C bond-stretching vibrational frequency and bond order to values between those of the double and single bonds are in good agreement with the results of photoelectron diffraction and the HREELS study.

(4) On the stepped Cu(111) surface, two new types of chemisorption complex can be formed with the binding energies largely increased.

(5) It is clear that π donations are enhanced and π^* orbitals are back-donated when distortion occurs. The peaks at 13.3 eV, 9.66 eV and 7.62 eV below the Fermi energy in the TDOS of adsorbed C_2H_2 on ideal Cu(111) are from the σ_s, σ_s^* and σ_p C_2H_2 MOs.

(6) For C_2H_2 adsorbed on the stepped surface, the bond length and bond order of C–C and C–H are almost equal to those on the ideal surface. The π and π^* orbital occupation numbers of C_2H_2 adsorbed on the stepped surface are only slightly different from those on the ideal surface. The monatomic step of Cu(111) strengthens the bonding between the C_2H_2 and the substrate but hardly influences the activation of the adsorbed C_2H_2.

Acknowledgments

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