



Cluster model DFT study of acetylene adsorption on the Cu (100) surface

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Abstract

The density functional theory and the cluster model approach have been used to study the adsorption of the acetylene molecule on the (100) surface of copper. Five possible adsorption sites have been considered: parallel twofold bridge, perpendicular twofold bridge, threefold hollow, diagonal fourfold hollow and aligned fourfold hollow sites. For each case, optimized geometries have been calculated. Vibrational frequencies have been calculated for the two energetically most favored adsorption sites. The results show clearly that on the (100) surface of copper the acetylene molecule adsorbs preferably on a fourfold hollow site. These theoretical results are in good agreement with recent Scanning Tunneling Microscopy results. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The study of the interaction of acetylene with transition metal surfaces is of considerable scientific interest because it provides insight into the chemistry of triple C–C bonds on metal surfaces and also due to the involvement of this molecule in some elementary catalytic reactions, such as the acetylene cyclotrimerization to form benzene. Therefore, in recent years, many papers have been published dealing with the interaction of acetylene with catalytically active transition metal surfaces such as the low index single crystal copper (111) [1–6], (110) [7–9] and (100) [9–21] surfaces.

The adsorption mode of acetylene on the (111) surfaces of copper has already been unequivocally determined both by experimental [1–3] and theoretical techniques [4–6]. In an earlier study using EELS, Bandy et al. [1] showed that at low temperatures, the acetylene adsorbs molecularly on a Cu(111) surface and the molecule undergoes significant rehybridisation on adsorption. In this study, the authors suggested that the molecule was adsorbed with its two C centers above adjacent fcc and hcp hollow sites. These results were unequivocally confirmed by subsequent NEXAFS [2] and PED [3] studies. Ab initio cluster studies [4–6] using a small $\text{Cu}_7\text{-C}_2\text{H}_2$ system, also confirmed that C_2H_2 stabilizes with its C–C axis parallel to the Cu(111) surface over a bridge site where the two C centers point towards adjacent fcc and hcp threefold hollow sites. In these calculations the optimized C–C distance of adsorbed C_2H_2 is

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increased by 0.16 Å with respect to that of the free molecule which is close to the experimental increase (0.27 ± 0.10 Å) [3]. Further, in the cluster model the C–H axes were found to tilt by 60° with respect to the C–C axis, pointing away from the surface.

The adsorption mode of acetylene on a Cu(110) surface seems to be more complex and the available experimental information concerning this system, is scarce. Outka et al. [7], using several spectroscopic techniques, concluded that at low temperatures (170 K) the acetylene molecule adsorbs molecularly on the Cu(110) surface, but is strongly distorted upon adsorption. In a recent paper [8], an experimental and a theoretical study of this adsorption system was presented. Using HREELS and ARUPS the authors concluded that acetylene adopts a low symmetry (most likely C_1) adsorption geometry on Cu(110). Then, using *Ab initio* Hartree–Fock cluster calculations the authors tested and confirmed this result. These calculations also showed that the C_2H_2 molecule was essentially sp^2 hybridised and the internal structure of the molecule was relatively insensitive to the adsorption site.

The adsorption of acetylene on the Cu(100) surface has also been the subject of several investigations during the last decades. However, the conclusions obtained have been in general very contradictory. Avery [9] based on his HREELS results, concluded that, when adsorbed on the Cu(100) surface, the acetylene molecule was highly distorted having a bond order of ~ 1.5 . He suggested that the most probable adsorption site was a twofold bridge site with the C–C bond parallel to or perpendicular to a Cu–Cu bond. A similar conclusion has been obtained by Hu et al. [10]. These authors used the multiple-scattering cluster method to calculate the NEXAFS spectra of acetylene adsorbed on a Cu(100) surface. By comparison between their theoretical results and the available experimental results, the authors concluded that the acetylene molecule adsorbs in a bridge site with the C–C bond parallel to the [100] or [010] direction. Arvanitis et al. [11–13] utilizing SEXAFS and NEXAFS found that at 60 K, the acetylene molecule was coordinated to three Cu surface atoms in a threefold hollow site, with the C–C bond lying parallel to the surface at 1.5 Å above the surface. They determined a CC bond length of 1.42 Å, indicating a significant stretching of the gas-phase CC bond length

(1.21 Å). The threefold hollow site was also shown to be favored by Hartree–Fock cluster calculations [14] and by molecular orbital calculations based on the tight-binding approach within the extended Hückel formalism [15]. Marinova et al. [16] using HREELS also observed that at low temperatures (140 K) acetylene adsorbs molecularly on a Cu(100) surface, but is strongly distorted with CC and CH stretching frequencies indicating a bond order of 1.5 and a rehybridisation close to sp^3 . On this study [16], Marinova et al. suggested the threefold hollow and the diagonal fourfold hollow adsorption modes as being the most favorable ones. In a very recent STM study, Stipe et al. [17,18] found acetylene to be centered above the fourfold hollow site with the molecular plane aligned across the diagonal of the square formed by four Cu atoms. The molecular plane is parallel to either the copper [100] or [010] axis and is perpendicular to the surface. In this configuration, acetylene is expected to be coordinated to four Cu atoms. In subsequent studies, Stipe et al. [19] and Lauhon et al. [20] studied the thermally induced rotation of acetylene above the fourfold hollow site and were able to determine the rotational activation barrier.

The contradictory experimental and theoretical results, available in the literature, concerning the study of the adsorption of C_2H_2 on a Cu(100) surface were the motivation for our theoretical study of this system. In a previous paper [22] we have reported our first study of this system in which we have used a Cu_9 cluster to model the surface. On that study we have considered four possible adsorption sites, and based on energetic and vibrational frequency considerations we have concluded that the C_2H_2 molecule adsorbs preferably on the diagonal fourfold hollow site. However, the Cu_9 cluster used in that study cannot give a very reliable description of the corresponding metallic surface due to its small size and due to the problem of the dangling bonds (inherent to the cluster model approach). For these reasons in the present paper we present another study of the adsorption of C_2H_2 on a Cu(100) surface, but using a much larger Cu_{17} cluster to model the surface.

During the last few years [23–26], several different theoretical models have been used, to study catalytic reactions at solid surfaces. These models may be finite (clusters, finite cube) or infinite (periodic systems).

Metal clusters have long since been one of the most common approaches used, to model metal surfaces. This approach is a straightforward consequence of the idea that adsorption is a local phenomenon. Quantum chemical research on clusters has become very fruitful especially due to advances in the development of density functional theory techniques and the incorporation of gradient correction terms to the exchange-correlation energy. The cluster model approach will be used along this work.

The aim of the present study is to compile theoretical results for the adsorption of acetylene on five different adsorption sites on the (100) surface of copper in order to determine the preferred adsorption site and to compare our results with the available experimental results.

This paper is organized as follows. In Section 2 we describe the details of the computational method used and of the metal clusters used to describe the metal surface. In Section 3, we report and discuss the results obtained. Some general conclusions are summarized in Section 4.

2. Theoretical details

In the present work, the interaction of the acetylene molecule with the (100) surface of copper was studied using the cluster model approach. All the calculations have been performed using the Density Functional Theory. The BLYP method included in the GAUSSIAN 98 [27] package was used. This method combines the gradient corrected exchange functional of Becke [28] with the gradient corrected correlation functional of Lee et al. [29].

To model the copper (100) surface a two-layer cluster of C_{4v} symmetry, with 12 copper atoms in the first layer and five copper atoms in the second layer, has been used. In this cluster, all the 12 metal atoms of the first layer were described by the large LANL2DZ basis set and the five metal atoms of the second layer were described by the LANL2MB basis set. The LANL2DZ basis set treats the $3s^2 3p^6 3d^{10} 4s^1$ Cu valence shell with a double zeta basis set and treats all the remainder inner shell electrons with the effective core potential of Hay and Wadt [30]. The LANL2MB basis set treats the $3s^2 3p^6 3d^{10} 4s^1$ Cu valence shell with a minimal basis set and treats all the remainder

inner shell electrons with the effective core potential of Hay and Wadt [30]. The non-metallic atoms (C and H) were described by the 6-31G** basis set of double zeta quality with p polarization functions in hydrogen atoms and d polarization functions in carbon atoms.

In order to obtain a closed shell system and to make the calculations computationally less expensive, in all these calculations we considered a charge of (-1) for the overall $C_2H_2-Cu_{17}(12,5)$ system. It is known that calculations involving open-shell systems are computationally much more demanding than calculations involving closed-shell systems of similar size. Considering the very large size of the cluster and the high quality of the basis sets used in this study, the use of an open shell system would not be feasible.

In all the calculations, no surface reconstruction nor surface relaxation have been considered, that is, the metal cluster geometry was kept frozen. The nearest-neighbour distance was taken from the bulk and is 2.556 Å. This cluster forms a compact section of the corresponding ideal Cu(100) surface.

In this study five different adsorption sites have been considered, namely the aligned fourfold hollow site, the parallel twofold bridge site, the diagonal fourfold hollow site, the threefold hollow site and the perpendicular twofold bridge site, see Figs. 1 and 2.

In order to reduce the size of the calculations, in the study of all the adsorption modes the CC bond of acetylene was forced to be parallel to the surface. This approach is fully supported by the available experimental information. Also in all the calculations we forced the four atoms of the C_2H_2 molecule to be coplanar and to stay in a plane perpendicular to the surface. In the study of the adsorption on the aligned fourfold hollow and diagonal fourfold hollow sites the symmetry of the overall system $Cu_{17}-C_2H_2$ was C_{2v} . In the study of the adsorption on the parallel and perpendicular twofold bridge sites and on the threefold hollow site the symmetry of the overall system $Cu_{17}-C_2H_2$ was C_s . In the study of the adsorption on the threefold hollow site the plane of the molecule is perpendicular to the surface and contains the point of interception of the bisecting lines of the angles of the triangle formed by the three copper atoms directly involved in the bonding to the C_2H_2 molecule. In this adsorption mode, the CC bond of acetylene is parallel to the line joining the nucleus of the two non-nearest-neighbour copper atoms of the triangle, see Fig. 1.

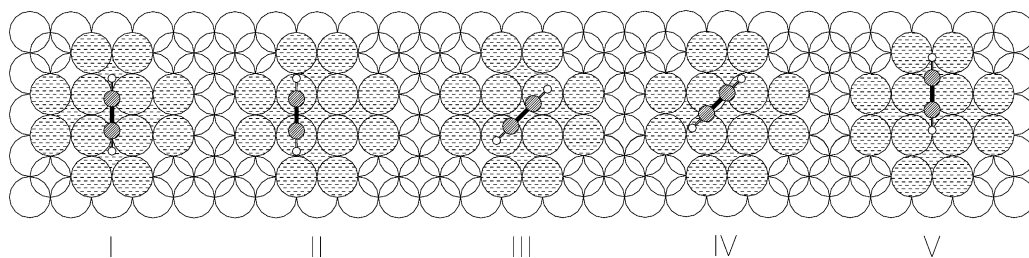


Fig. 1. Schematic view of the several systems considered in the present study: (I) Aligned fourfold hollow- $C_2H_2/Cu_{17}(12,5)$; (II) Parallel twofold bridge- $C_2H_2/Cu_{17}(12,5)$; (III) Diagonal fourfold hollow- $C_2H_2/Cu_{17}(12,5)$; (IV) Threefold hollow- $C_2H_2/Cu_{17}(12,5)$; (V) Perpendicular twofold bridge- $C_2H_2/Cu_{17}(12,5)$.

It is well known that the determination of the adsorption energies is one of the most critical aspects of the cluster modeling of surfaces [31]. For small clusters, usually the adsorption energies oscillate with the cluster size even if the bonding nature remains the same [32]. Another related problem already reported on the literature is that for some systems the optimized geometric parameters of the system show that there is a bond between the adsorbate and the metal cluster, but energetic considerations show that the overall system ‘cluster + adsorbate’ is unbound with respect to the dissociation limit but with local minima on the energy surface. This phenomenon has already been reported on several papers [8,33,34] and has been investigated in detail by Clotet

et al. [33] for the Cu(111) surface and is known to involve a crossing or avoided crossing of electronic states. It has been suggested that the use of naked metal clusters in calculating good chemisorption energies of adsorbates requires the cluster to be in a prepared bonding state. The argument used is that the excitations to higher states are involved in the preparation. For the infinite surface, this value is close to zero, but for a small cluster, the required excitation energy should be added to the calculated chemisorption energy of the ground state of the cluster. This idea has been recently used by Triguero et al. [34] to calculate the surface chemisorption energy of acetylene and ethylene to cluster models of the copper (100), (110) and (111) surfaces. According to these authors, in these

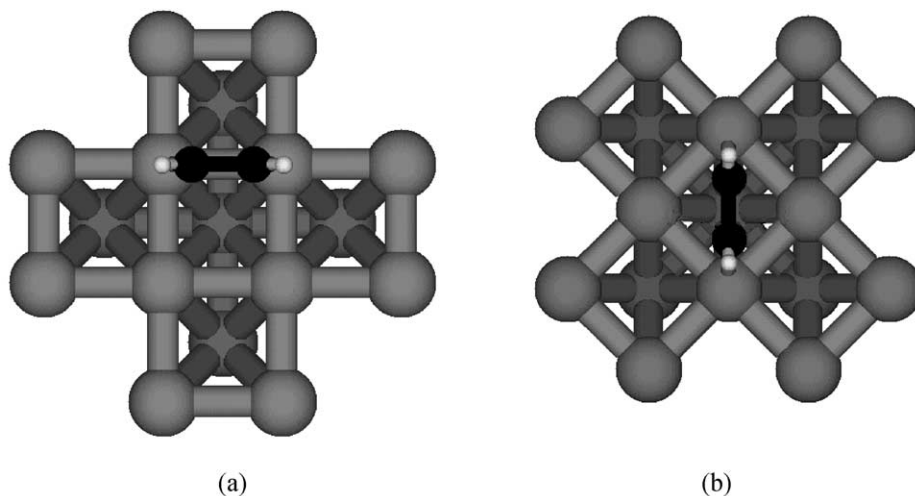


Fig. 2. Top view of two of the $C_2H_2/Cu_{17}(12,5)$ adsorption systems considered in the present study: (a) the parallel twofold bridge- $C_2H_2/Cu_{17}(12,5)$ system and (b) the diagonal fourfold hollow- $C_2H_2/Cu_{17}(12,5)$ system. The 12 metal atoms of the first layer are treated with the LANL2DZ basis set and the five metal atoms of the second layer are treated with the LANL2MB basis set.

systems there are two triplet states: a triplet surface state and a triplet adsorbate state, which are coupled to produce a net singlet state for the two metal-carbon bonds.

It must however, be noted that, for the C_2H_2 –Cu(100) adsorption system these authors have only considered the adsorption on the parallel twofold bridge site which, according to the theoretical evidence to be presented in the present paper and also according with the experimental information available in the literature, is not the most favored adsorption site.

A similar situation has been found in the present work for some of the C_2H_2 –Cu₁₇(12,5) adsorption systems considered. This presents a major difficulty in interpreting the adsorbate binding energies obtained for these systems. Given these difficulties, in this study we have decided to express all the adsorbate binding energies in a relative way, taking the lowest energy system as a reference system with zero energy.

3. Results

3.1. Free C_2H_2 molecule

The free acetylene molecule was optimized at the BLYP/6-31G** level. Then, vibrational frequencies for the optimized free C_2H_2 molecule have been calculated. The computed geometry and vibrational frequencies are listed in Table 1 along with the corresponding experimental values [35,36]. There is

Table 1
Optimized geometry and vibrational frequencies (cm^{-1}) for the free C_2H_2 molecule

C_2H_2	Theoretical values	Experimental values
Distance (CC) (Å)	1.215	1.204 ^a
Distance (CH) (Å)	1.071	1.058 ^a
Angle (HCC) (°)	180.00	180.0 ^a
ρ_{as} (CH)	472	612 ^b
δ_{as} (CH)	472	612 ^b
ρ_s (CH)	744	729 ^b
δ_s (CH)	744	729 ^b
ν (CC)	2019	1974 ^b
ν_{as} (CH)	3370	3287 ^b
ν_s (CH)	3463	3374 ^b

^a Ref. [35]

^b Ref. [36]

a good agreement between the theoretical results and the corresponding experimental results. Both of these results show that the acetylene molecule in its ground state is linear with a $D_{\infty h}$ symmetry.

3.2. The C_2H_2 –Cu₁₇(12,5) adsorption systems

We began by performing geometry optimizations (only subject to the symmetry constraints mentioned in Section 2) of the C_2H_2 molecule adsorbed in five different adsorption sites in the Cu₁₇(12,5) cluster.

Table 2 summarizes the computed optimized geometries and relative adsorption energies for the five studied adsorption modes. The relative adsorption energies are expressed taking the most stable system (aligned fourfold hollow) as the zero energy, and therefore all the adsorption modes with positive adsorption energies are less stable than the aligned fourfold hollow adsorption mode. In this table the CC–surface distance is defined as being the perpendicular distance between the CC bond and a plane containing the nucleus of the metal atoms of the upper layer. Similarly to previous *Ab initio* cluster studies on Cu(111) [4] and Cu(110) [8] surfaces, the results in Table 2 clearly show that on a Cu(100) surface the geometric structure of the acetylene molecule is highly perturbed upon adsorption. A comparison with the calculated geometrical parameters of the free acetylene molecule shows that for example the CC bond is elongated by 0.166 Å (diagonal fourfold-hollow) and by 0.181 Å (aligned fourfold-hollow) and the CH bonds are bent upward by 61.6° (diagonal fourfold-hollow) and by 60.7° (aligned fourfold-hollow). The length of the CC bond in chemisorbed acetylene is between the values of 1.33 Å for gas phase ethylene (sp^2 hybridisation) and 1.54 Å for gas phase ethane (sp^3 hybridisation). This shows that upon adsorption the hybridisation of the acetylene molecule changes from sp (in the gas phase) to somewhere between sp^2 and sp^3 .

Fig. 3 and Table 3 show, for the two lowest energy adsorption modes (aligned and diagonal fourfold hollow), the distribution of atomic charges in the optimized systems. The results show that in both adsorption modes the added charge is located mainly on the five copper atoms of the second layer.

Considering as reference the energy of the lowest spin multiplicity bare cluster and the energy of

Table 2

Relative energies of the system C_2H_2/Cu_{17} and optimized geometries for C_2H_2 adsorbed on the diagonal fourfold hollow, aligned fourfold hollow, threefold hollow, perpendicular twofold bridge and parallel twofold bridge sites. The distances are given in Å, the angles in degrees and the relative energies in kJ mol^{-1} . The CC–surface distance is defined as being the perpendicular distance between the CC bond and a plane containing the nucleus of the metal atoms of the upper layer

Adsorption mode	Relative energy ^a (kJ mol^{-1})	$r(\text{CC-surface})$ (Å)	$r(\text{C-C})$ (Å)	$r(\text{C-H})$ (Å)	$\alpha(\text{CCH})$ (°)
Aligned fourfold hollow	0.0	1.545	1.396	1.108	119.25
Diagonal fourfold hollow	+13.8	1.627	1.381	1.108	118.37
Threefold hollow	+67.5	1.654	1.388	1.106	120.75
Parallel twofold bridge	+92.1	1.896	1.345	1.102	125.70
Perpendicular twofold bridge	+140.2	1.716	1.333	1.095	129.95

^a Taking the energy of the lowest energy system as the zero energy.

the lowest spin multiplicity gas phase acetylene molecule, it is observed that in some of the studied adsorption systems, namely on the parallel and perpendicular twofold-bridge adsorption modes, after full geometry optimizations the energy of the overall system is higher than the sum of the energies of the separated fragments, that is the acetylene molecule is energetically unbound with respect to the separated fragments but with a local minimum in the potential energy surface. This phenomenon was mentioned in Section 2 and has already been extensively studied and documented in the literature [8,33,34].

This observation motivated the study of the relative energy curves $E(z)$ that characterize the

acetylene–metal interaction for some of the studied adsorption modes. In the study of these relative energy curves, we performed restricted optimizations in which we forced the acetylene molecule to move horizontally, using steps of constant length, from the aligned fourfold hollow site to the parallel twofold bridge site (scan 1, see Fig. 4(i)) and from the diagonal fourfold hollow site to the threefold hollow site (scan 2, see Fig. 4(ii)). In all these optimizations the internal geometric parameters of the acetylene molecule (with its CC bond parallel to the surface) as well as the distance between the acetylene molecule and the metal surface were fully optimized. The relative adsorption energy curves obtained are presented on Figs. 5 and 6.

In scan 1, the optimized geometry and the relative energy of the system corresponding to the last point of

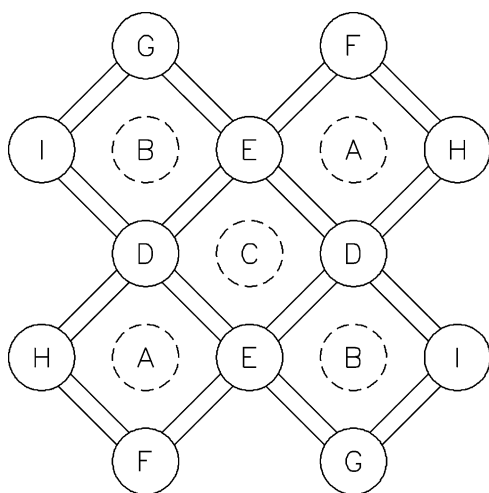


Fig. 3. Copper atoms in the Cu_{17} cluster. In the two lowest energy adsorption modes (diagonal and aligned fourfold hollow), atoms labelled in this figure with the same letter have the same atomic charges.

Table 3

Distribution of atomic charges in the optimized systems corresponding to adsorption on the diagonal and aligned fourfold hollow sites

Atoms	Adsorption mode	
	Diagonal fourfold hollow	Aligned fourfold hollow
Cu (A)	−0.966	−0.946
Cu (B)	−0.966	−0.963
Cu (C)	−1.257	−1.233
Cu (D)	1.267	1.194
Cu (E)	1.153	1.194
Cu (F)	−0.079	−0.048
Cu (G)	−0.079	−0.105
Cu (H)	−0.075	−0.048
Cu (I)	−0.075	−0.105
C	−0.139	−0.148
H	0.088	0.092

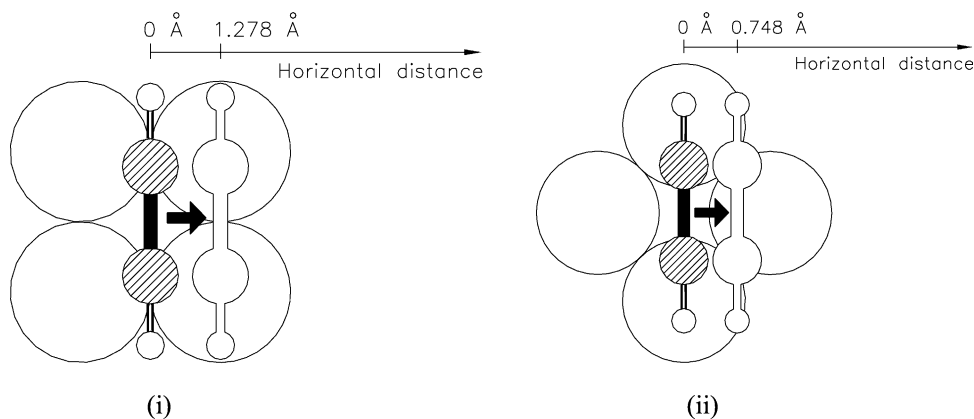


Fig. 4. (i) Scan from aligned fourfold hollow to parallel twofold bridge, (ii) Scan from diagonal fourfold hollow to threefold hollow. For simplicity, in this figure only the four copper atoms directly involved in the bonding have been represented. However, in the calculation of all the points in the relative energy curves, the $\text{Cu}_{17}(12,5)$ cluster described in Section 2 has been used.

the relative energy curve is exactly the same that has been previously obtained for the adsorption on the parallel twofold bridge site. In scan 2, the optimized geometry and the relative energy of the system corresponding to the last point of the relative energy curve is exactly the same that has been previously obtained for the adsorption on the threefold hollow site.

The results in Table 2 and in Figs. 5 and 6 show that the adsorption of the acetylene molecule on the cavity formed by four copper atoms (namely the adsorption on the aligned and diagonal fourfold hollow sites) is energetically much more favored

than the adsorption on the other three sites considered.

Based only on energetic arguments, and considering the large energetic difference obtained between the adsorption on the fourfold hollow sites (aligned and diagonal) and the adsorption on the other three adsorption sites studied, the threefold hollow, the parallel twofold hollow and the perpendicular twofold hollow sites were excluded from the list of possible adsorption sites. It must be noted that the difference in stability between the diagonal fourfold hollow site and the next more stable adsorption site (the threefold hollow site) is greater than $50 \text{ kJ}\cdot\text{mol}^{-1}$. Furthermore this decision is also fully supported by the results

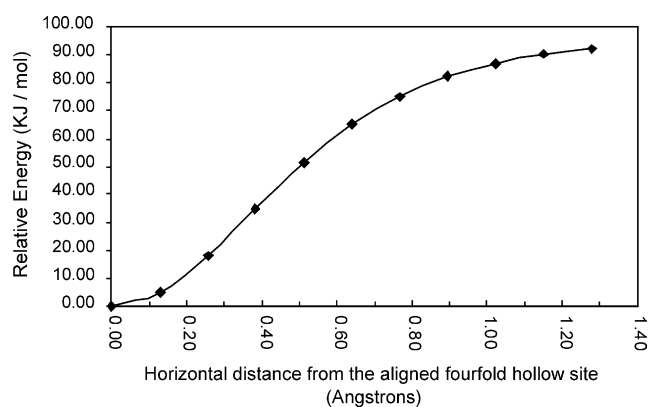


Fig. 5. Relative energy curve (Taking the energy of the aligned fourfold adsorption mode as the zero energy) corresponding to the horizontal displacement of the acetylene molecule adsorbed on a $\text{Cu}_{17}(12,5)$ cluster, moving between the aligned fourfold hollow site and the parallel twofold bridge site. The first point on the curve (distance = 0,00) corresponds to the aligned fourfold hollow adsorption mode. The last point on the curve (distance = 1,278 Å, i.e. one-half of the Cu–Cu nearest neighbour distance) corresponds to the parallel twofold bridge adsorption mode.

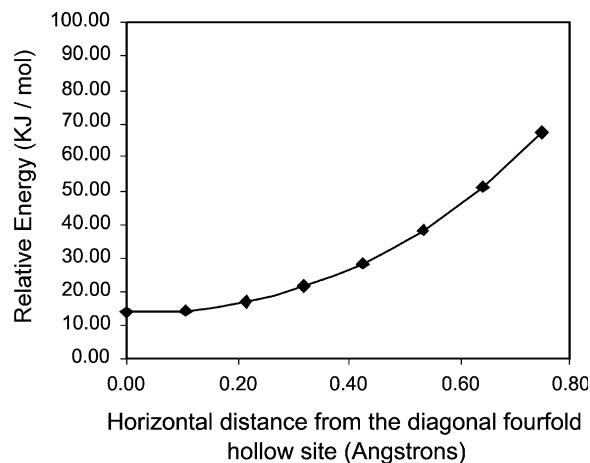


Fig. 6. Relative energy curve (Taking the energy of the aligned fourfold adsorption mode as the zero energy) corresponding to the horizontal displacement of the acetylene molecule adsorbed on a $\text{Cu}_{17}(12,5)$ cluster, moving between the diagonal fourfold hollow site and the threefold hollow site. The first point on the curve (distance = 0,00) corresponds to the diagonal fourfold hollow adsorption mode. The last point on the curve (distance = 0.748 Å) corresponds to the threefold hollow adsorption mode.

presented in Figs. 5 and 6 which show clearly that the parallel twofold bridge and the threefold hollow adsorption modes do not correspond to minima on the potential energy surface and so are unstable.

The difference in stability between the aligned fourfold hollow site and the diagonal fourfold hollow site is only 13.8 kJ.mol^{-1} . This difference is too small to allow us to conclude unambiguously which is the most stable adsorption mode. In order to obtain a more clear picture of the adsorption on the fourfold hollow site and

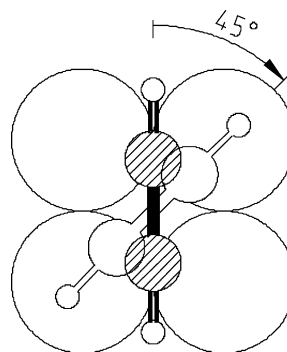


Fig. 7. Scan from the aligned to the diagonal fourfold hollow adsorption mode. For simplicity, in this figure only the four copper atoms directly involved in the bonding have been represented. However, in the calculation of all the points in the relative energy curve, the $\text{Cu}_{17}(12,5)$ cluster described in Section 2 has been used.

of the relation between the aligned and the diagonal adsorption modes we have studied the relative energy curve that characterizes the rotation of the acetylene molecule around the fourfold hollow site. For this purpose we have performed a restricted optimization in which we have forced the acetylene molecule to rotate around an axis (perpendicular to the metal surface and passing through the center of the CC bond), using rotation steps of constant amplitude (5°), from the aligned fourfold hollow site to the diagonal fourfold hollow site (see Fig. 7). Similarly to the previous scans, in all these optimizations the internal geometric parameters of the acetylene molecule (with its CC bond parallel to the surface) as well as the distance between the acetylene molecule and the metal surface

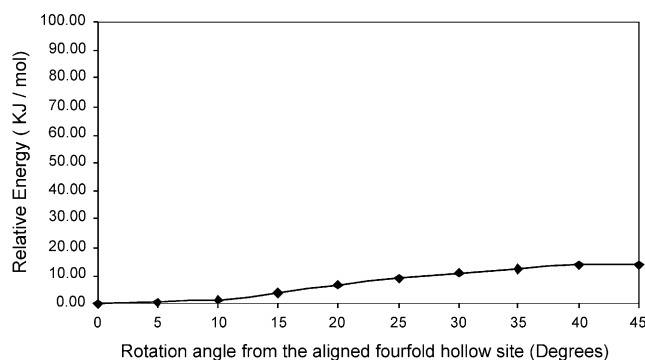


Fig. 8. Relative energy curve (Taking the energy of the aligned fourfold adsorption mode as the zero energy) corresponding to the rotation of the acetylene molecule (around a vertical axis and passing through the center of the CC bond) moving between the aligned (0°) and the diagonal (45°) fourfold hollow site. In order to facilitate the comparison, in this graphic we have used the same energy scale as in Figs. 5 and 6.

Table 4
Calculated vibrational frequencies (cm^{-1}) of acetylene adsorbed on the diagonal fourfold hollow and aligned fourfold hollow sites

Adsorption mode	Experimental ^a	Diagonal fourfold hollow	Aligned fourfold hollow
Rotation ^b	–	–136	169
$\nu(\text{C}-\text{Cu})$	420	383	368
$\rho_s(\text{CH})$	630	618	581
$\rho_{as}(\text{CH})$	–	962	948
$\delta_s(\text{CH})$	950	1045	1010
$\delta_{as}(\text{CH})$	1140	1187	1159
$\nu(\text{CC})$	1320	1377	1293
$\nu_{as}(\text{CH})$	–	2890	2898
$\nu_s(\text{CH})$	2880	2925	2932

^a Ref. [16]

^b This is the frequency of rotation around the vertical axis. In the diagonal-fourfold-hollow adsorption mode it has an imaginary value indicating a maximum

were optimized. The relative adsorption energy curve obtained is presented in Fig. 8. In order to facilitate the comparison, in Fig. 8 we have used the same energy scale as in Figs. 5 and 6.

We have also performed the calculation of the vibrational frequencies for acetylene adsorbed on these two lowest energy adsorption sites. The results obtained, along with the available experimental results, are presented in Table 4.

According to the results shown in Fig. 8, the diagonal adsorption mode corresponds to a maximum on the energy profile for the rotation of C_2H_2 around the fourfold hollow site. This result is supported by the results shown in Table 4: in the case of adsorption on the diagonal fourfold hollow site, the frequency of rotation around the vertical axis has an imaginary value. This is, however, the only imaginary frequency of the diagonal adsorption mode and therefore this adsorption mode corresponds to a first order saddle point on the potential energy surface. The results obtained also show that for both adsorption modes

there is a fairly good agreement between the calculated results and the available experimental results.

According to our calculations, the aligned adsorption mode has zero-point vibrational energy $\text{ZPE} = 73.556 \text{ kJ.mol}^{-1}$ and has at 298K a vibrational entropy $S = 0.037 \text{ kJ.mol}^{-1}.\text{K}^{-1}$.

As we mentioned in Section 2, in all these calculations we used an added charge of (-1) in order to obtain a closed shell system. However, we could have chosen instead an added charge of $(+1)$ which would have the same technical role. In order to test whether the results would be identical or not, we have performed, for the aligned and diagonal fourfold hollow adsorption modes, geometry optimizations using an added charge of $(+1)$ instead of (-1) . The results are shown in Table 5. The results show that using an added charge of $(+1)$ we obtained the same relative order of stability (the aligned mode is again more stable than the diagonal mode) and the difference in stability is very similar to that obtained using an added charge of (-1) (11.5 vs 13.8 kJ mol^{-1}). Furthermore, a comparison of the results in Table 5 with those in Table 2 shows that the optimized geometries with charge $(+1)$ are very similar to the optimized geometries with charge (-1) . Therefore, it is our belief that for the other adsorption modes the results obtained with a $(+1)$ charge would also be almost identical to the results obtained with a (-1) charge and our final conclusions would be the same.

4. Conclusions

The results presented in this paper clearly show that on a Cu(100) surface the acetylene molecule adsorbs on a fourfold hollow site. From a list of five possible adsorption modes referred in the

Table 5
Relative energies of the system $\text{C}_2\text{H}_2/\text{Cu}_{17}$ and optimized geometries for C_2H_2 adsorbed on the diagonal fourfold hollow and aligned fourfold hollow sites, using an added charge of $(+1)$

Adsorption mode	Relative energy ^a (kJ mol^{-1})	$r(\text{CC}-\text{Surface})$ (\AA)	$r(\text{C}-\text{C})$ (\AA)	$r(\text{C}-\text{H})$ (\AA)	$\alpha(\text{CCH})$ ($^\circ$)
Aligned fourfold hollow	0.0	1.537	1.382	1.106	121.17
Diagonal fourfold hollow	+11.5	1.623	1.375	1.106	119.20

^a Taking the energy of the lowest energy system as the zero energy.

experimental literature, our calculations clearly allowed us to exclude unambiguously three of those five initial possibilities.

Recent Scanning Tunneling Microscopy results have shown that the adsorption of an acetylene molecule on the Cu(100) surface occurs on a fourfold hollow site, the diagonal adsorption mode being the most favored one. Our theoretical results are in good agreement with these Scanning Tunneling Microscopy results in that our results also show clearly and unambiguously that the acetylene molecule adsorbs on a fourfold hollow site. However, when it comes to determine which of the two adsorption modes, aligned or diagonal fourfold hollow, is the most favored one, our results contradict the STM results. It is our belief that this contradiction most likely results from the problems inherent to the cluster modeling of metal surfaces. It is not unquestionable that the relatively small Cu₁₇ cluster (without embedding) used in the present work can give a very good description of the corresponding metallic surface and an unbiased description of the different adsorption modes. These problems become particularly important when comparing two adsorption modes that differ only slightly on their adsorption energies, as happens in the present work with the aligned and the diagonal fourfold hollow adsorption modes. However, despite this small disagreement with the experimental results it is our belief that the results presented in this work give some new insights in the chemisorption of acetylene on (100) copper surfaces and support the usefulness of the cluster model approach in the study of chemical processes on solid surfaces.

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