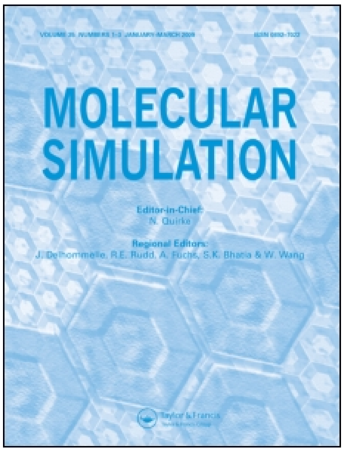

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Michelle J. S. Spencer[a]; Graeme L. Nyberg[a]
[a] Department of Chemistry, La Trobe University, Victoria, Australia

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DFT MODELLING OF HYDROGEN ON CU(110)- AND (111)-TYPE CLUSTERS

MICHELLE J.S. SPENCER and GRAEME L. NYBERG*

Department of Chemistry, La Trobe University, Victoria 3086, Australia

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Density Functional Theory (DFT) calculations using GAUSSIAN 98 have been performed on hydrogen adsorbed on clusters representing the (110) and (111) surfaces of Cu. Clusters were constructed to model different adsorption sites, and at least two different size clusters were used for each site. On the (111) surface, hydrogen prefers to adsorb in a hollow site, though with the hcp variant being favoured by the adsorption energy, and the fcc alternative by the vibrational frequencies. On the (110) surface, the "fcc" site on a (1 × 2) reconstructed surface is preferred.

Keywords: Chemisorption; Cluster; Copper; Density functional theory calculations; Hydrogen

INTRODUCTION

Since early discussions on the use and applicability of the cluster model approach [1], such calculations have been used to examine numerous species adsorbed onto different surfaces. The question that arises when choosing a cluster to model the surface is just what size is needed to represent the surface and what effect the edges of the cluster will have on the properties being examined. For some systems that have been studied, various properties of the adsorbate–substrate system (such as adsorption energy values) have been shown to be markedly affected by the size of the clusters employed. Of particular concern are those instances where

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*Corresponding author. E-mail: nyberg@latrobe.edu.au

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the values of some properties oscillate as the cluster size increases [2], rather than converging towards a limiting value. Nevertheless, despite such effects, cluster calculations have been shown, in many instances, to successfully describe the different properties of the adsorbate–substrate system with excellent agreement with experimental observations [3–7].

Hydrogen adsorption on transition metal surfaces using this approach has concentrated mainly on nickel [8,9], Ag(111) and Pt(111) [10], Ag, Pd and Ni(111) surfaces [11], Be(0001) [12] and Cu(100) [13–15]. On the (111) and (110) surfaces of copper, other methods have been employed. On the (111) surface, hydrogen adsorption has been examined using calculations on two- or three-layer slabs. *Ab initio* band structure calculations within a density functional formalism [16] and *ab initio* pseudopotential calculations [17] both suggest that hydrogen adsorbs in a hollow site. Self-consistent linearised augmented plane wave calculations [18] also suggest a hollow site, with the fcc site being slightly preferred over the hcp site. There do not appear to be either any cluster- or other-type calculations of hydrogen adsorbed on the (110) surface of copper.

In the present study, the adsorption of hydrogen on both the (111) and (110) surfaces of copper is examined via the cluster model approach. Clusters representing both these surfaces are constructed and the adsorption of H on these clusters is examined. The calculations are used to determine the most likely adsorption site and the results are compared to the experimental observations for hydrogen adsorbed on these surfaces. They are also necessary prerequisites to subsequent calculations of silane decomposition on these surfaces [19].

COMPUTATIONAL METHODS

The calculations were performed using the GAUSSIAN 98 [20] program on a 500 MHz Digital Alpha Computer Workstation.

Earlier comparisons [21] with the experimental results for a series of noble-metal-containing molecules had determined that the most suitable method for copper clusters was BPW91, used in conjunction with the basis set LANL2DZ. Hence all the present calculations were performed using this combination, the details of which we will now briefly outline.

The BPW91 method combines Becke's 1988 exchange functional [22] with Perdew and Wang's 1991 gradient corrected correlation functional [23–25]. The Los Alamos National Laboratory (LANL2) [26–28] basis set describes the inner or core electrons by an effective core potential (ECP). For copper, some of the outer core orbitals are retained; hence the basis set comprises the ECP + {(3s, 3p) + (3d, 4s, 4p)} basis functions. Both Minimum Basis (MB) and Double Zeta (DZ) alternatives are available, with the latter being markedly superior [21].

Using this method and basis set combination, it was found that the calculations generally did not converge commencing from the normal starting point used by the GAUSSIAN 98 program, so some pre-calculations using other methods or basis sets had to be run first. The output of these files was then used as a checkpoint input file to run the BPW91/LANL2DZ calculation. The HF and B3LYP methods and LANL2MB minimum basis set were all employed. It was not unusual for two or even three pre-calculations to be required. These calculations also had problems with convergence failures due to low-lying virtual orbitals [29]. Hence, these orbitals had to be manually shifted, or the number of SCF cycles had to be increased from the default 65, often to over 120. This resulted in further increasing the time needed to run the calculations.

The clusters that were constructed contained 2, 3 or 4 layers and are described as CuX–Y–Z..., where X, Y, Z... are the number of atoms in the 1st, 2nd, 3rd... layers, respectively.

CU(111)

Choice of Clusters

A set of different size clusters, comprising two or three layers, were constructed to represent the (111) surface. The maximum size cluster that could normally be handled using BPW91/LANL2DZ had about 13 atoms. Hence, the clusters used to model the adsorbed species on the surface had to be no larger than this.

It was found that the success of a calculation depended not only on the size of the cluster but also on its symmetry. Clusters with a lower symmetry were less likely to converge. Hence, smaller clusters than originally chosen had to be used.

Relaxation of Surface Layer

The termination of the atoms at the surface of a crystal can lead to surface relaxations or even reconstructions. These effects need to be considered when constructing clusters that represent different surfaces.

Surface relaxations involve changes in the positions of the atoms perpendicular to the surface. Generally, the interlayer spacing between the first and second layers contracts in order to increase the bonding of the surface atoms. This contraction can then lead to further changes in the subsequent layers; however, this effect is reduced as one extends into the bulk.

Reconstructions, on the other hand, result from more dramatic changes in the arrangement of the atoms near the surface, and involve parallel motions. Again, the rearrangement leads to a structure that is more stable, i.e. of lower energy.

For the (111) and (110) surfaces of copper, relaxation of the surface atoms occurs but the surfaces do not reconstruct. Several articles have studied the change in interlayer spacings resulting from surface relaxation.

In particular, the first interlayer spacing of Cu(111) has been determined by LEED. The earliest study [30] suggested that the interlayer distance remains the same to within 5% of the bulk value; the next [31] that it contracted by 4.1%; while the three most recent ones [32–34] indicate only a small contraction of 0.3–0.7%.

To model the change in the first interlayer spacing of Cu (111), five different clusters were constructed, each comprising three or four layers. The clusters chosen had less than 13 atoms, except one, which had 16 (Fig. 1).

During the calculation, the interlayer spacing between the first two layers of these clusters was allowed to vary and the optimised distance was determined. The change in the first interlayer spacing, $\Delta d_{1,2}$, relative to the bulk interlayer spacing of 2.09 Å is shown in Table I using the LANL2DZ basis set. A positive $\Delta d_{1,2}$ value indicates an expansion and a negative value a contraction. The 16 atom cluster (Cu3-6-7), not surprisingly, failed to converge under tight convergence conditions ($\times 10^{-8}$). Using a single-point calculation, though, the calculation did converge at each interlayer separation. As a result, a potential energy scan was performed (via a sequence of single-point calculations). The energies for eleven interlayer spacings, between 1.93 and 2.03 Å (with intervals

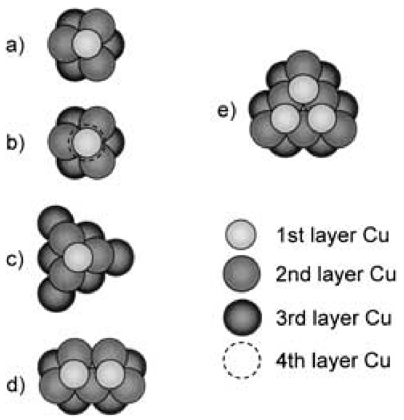

FIGURE 1 Clusters used to model the surface relaxation of Cu(111): (a) Cu1-3-3, (b) Cu1-3-3-1, (c) Cu1-3-6, (d) Cu2-5-5 and (e) Cu3-6-7.

TABLE I Change in the first interlayer spacing, $\Delta d_{1,2}$, of a series of different size clusters. The bulk interlayer spacing is 2.09 Å

Cluster	# Cu atoms	Change in interlayer spacing $\Delta d_{1,2}$, (Å)	
Cu1-3-3	7	-0.1398	(-6.7%)
Cu1-3-3-1	8	-0.1814	(-8.7%)
Cu1-3-6	10	-0.0526	(-2.5%)
Cu2-5-5	12	-0.1212	(-5.8%)
Cu3-6-7	16	*	

* Convergence failure.

of 0.01 Å) were calculated. The lowest energies were obtained for an interlayer distance of between 1.96 and 2.03 Å, suggesting the most likely relaxed value lies somewhere in between. The energy, however, was found to oscillate in this region (thus explaining the optimisation failure). This cluster was not included, as the results seemed unreliable.

For the remaining clusters, only a contraction occurs, consistent with the experimental observations. These contractions ranged from 2.5 to 8.7%, which are generally larger than observed experimentally. These distances might be reduced if extra atoms and/or layers could be added to the cluster. To the extent that these extra atoms interacted with those of the first and/or second layers, the interaction between these two layers tends to be reduced, and hence also the decrease in the interlayer distance. This effect is seen when going from the Cu1-3-3 to the Cu1-3-6 cluster, where the relaxation distance decreased from -6.7 to -2.5%. Due to this trend, and the conformity with the experimental results, no relaxed interlayer distances were used when modelling the H (and subsequently SiH_x intermediates) on the clusters.

Adsorption Sites

The hydrogen may adsorb in different sites on the surface, including atop, two hollow sites (fcc and hcp), bridge and substitutional sites. These five sites are

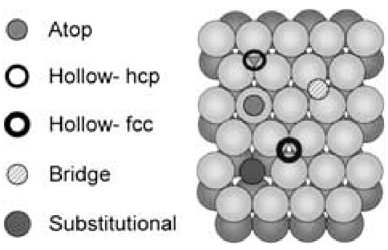

FIGURE 2 Different adsorption sites on a Cu(111) surface: atop, hollow- hcp and fcc, bridge and substitutional.

shown in Fig. 2. The difference between the two hollow sites is that there is an atom in the second layer directly below an hcp site, whereas it is absent for an fcc site.

In choosing clusters to best represent these different adsorption sites, enough atoms must be included to define the site. The simplest cluster for an fcc site would contain three atoms (Cu3). An extra atom in the second layer would define an hcp site (Cu3-1). A better choice would also contain the next nearest neighbours. A cluster that contains all the different adsorption sites is computationally too large; therefore, several different clusters were chosen to model the different sites.

Again, the choice of cluster was dependent not just on size but also on symmetry. Even if a cluster by itself converges, it may not do so with an adsorbed species. Also a particular problem with the GAUSSIAN program was encountered. After the first geometry optimisation step of some of the calculations for higher-symmetry clusters, the symmetry as-determined reduced to C_s or C_1, even though the co-ordinates did not reflect such a change in symmetry. This resulted in longer computational times, as well as incorrect symmetry labelling of the molecular orbitals. As a result of this change in symmetry, the use of symmetry was turned off to allow the geometry optimisations to continue. To obtain the molecular orbital symmetry assignments, the calculation was first run with the symmetry turned off and then re-run using the optimised parameters. This process, however, did not work for the bare clusters.

Adsorption Energy

As it is not possible to model the adsorbed species in all the different adsorption sites on a single cluster, the total electronic energy values cannot be compared directly. Hence, adsorption energy values were determined. For hydrogen adsorbed on a cluster, Cu_x, the reaction would be:

$$H_2 + 2Cu_x \rightarrow 2H{\cdot}Cu_x \qquad (1)$$

The adsorption energy is the difference between the energy of the products and the reactants.

A negative adsorption energy indicates the products are more stable and hence hydrogen is likely to adsorb on the surface. The most negative energy indicates the most favoured species or adsorption site. A positive energy suggests that adsorption on the surface is unlikely.

H/“Cu(111)”

To examine the adsorption of hydrogen on the Cu(111) surface, a Cu4-1 and two Cu6-1 clusters were chosen as shown in Fig. 3.

For the Cu6-1 clusters, the two extra atoms in the top layer can be placed either side of the Cu4-1 cluster, as indicated in (b) and (c). Three adsorption sites can be modelled on these clusters: bridge, fcc and hcp. The presence of the atom in the second layer of the clusters allows the two hollow sites to be distinguished. The atop and substitutional sites were not modelled as the experimental results do not suggest hydrogen adsorbs in either of these sites.

McCash *et al.* [35,36] interpreted their RAIRS (and VEELS) spectra as indicating that hydrogen adsorbs in a bridge site. The experimental results,

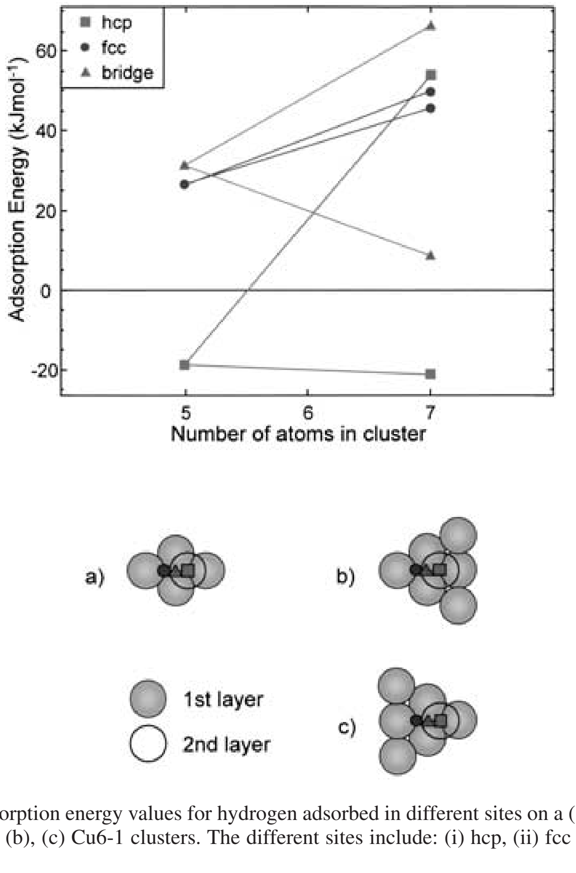

FIGURE 3 Adsorption energy values for hydrogen adsorbed in different sites on a (a) Cu4-1 cluster and two different (b), (c) Cu6-1 clusters. The different sites include: (i) hcp, (ii) fcc and (iii) bridge.

however, are contradicted by several calculations that suggest hydrogen prefers a hollow site [16,17], or more specifically an fcc site [18].

The adsorption energies of hydrogen in the bridge and two hollow sites on the two clusters were calculated (Table AI in Appendix) and are shown in Fig. 3. Only the hcp site yields a negative energy, and so is favourable to adsorption. For the bridge and hcp hollow sites there is, surprisingly, a considerable difference between the adsorption energies of the two 6-1 clusters. To balance any effect from adding two atoms to only one side of the Cu4-1 cluster, a Cu8-1 cluster was attempted, where two atoms were added to both sides. This calculation, however, would not converge for any of the adsorption sites.

The two Cu6-1 clusters were examined in more detail in order to try and explain the large energy differences observed. The energies for the two metal clusters themselves differed by only ~ 0.057 eV, the major difference coming from the pairs of H·Cu6-1 clusters, where the difference was ~ 0.33 eV. This indicated that the difference did indeed involve the hydrogen. The molecular orbitals with the greatest hydrogen contribution were examined, but both clusters were similar in that both showed the inner atoms of the cluster (or those defining the site) to have the largest bonding contribution to these molecular orbitals, with the outer atoms bonding less, as would be expected. The actual energies of these orbitals for both clusters were also virtually identical. Just what is responsible for the energy differences between these two clusters is thus not evident.

The dependence of adsorption energy on cluster size has also been observed for other systems studied previously, including CO/Cu(100) [2,37–39] and CO/Cu(111) [37], formate/Cu(100), (110), (111) [40], Na, Li, K/Cu(111) [41], H, C, N, CH_x/Cu(100) [13], H, O, OH/Ag(111), Pt(111) [10], O/Ni(100) [42], H/Ni(l00),(111) [8], H/Ni(100) [43], O/Ni(100), (111) [44] and H/Be(0001) [12]. In a number of these cases [10,12,42–44], the problem was solved by using what was called "bond-preparation", which has also been applied to other systems [45–49]. For this process, the electronic structure of the cluster must fit that of the adsorbate. As was illustrated for hydrogen adsorption [8], the cluster must have a singly occupied orbital of a_1 (or totally symmetric) symmetry, which matches the hydrogen 1s orbital of a_1 symmetry. Furthermore, this cluster orbital must be localised in the region of the adsorption site. If either of these criteria are not met, then an excited state of the cluster, which does have such an orbital, must be used instead.

These criteria do not, however, account for the differences found for the two Cu6-1 clusters, where the cluster orbital forming the bond with the hydrogen does have a' or a_1 symmetry for both clusters and, as indicated above, is appropriately localised. Hence, there seems to be no ready explanation as to the differences, and it is not clear as to which is the better value or cluster to use.

If the average value for the two different Cu6-1 clusters is taken as the "actual" value then all three sites indicate adsorption is unfavourable. The hcp site has the lowest energy, followed by the bridge and then fcc sites. For the Cu4-1 cluster, the hcp site is also most favourable and furthermore, has a negative energy. The fcc site, followed by the bridge site, again have positive values. Hence, the hcp site is favoured for both sized clusters, in agreement with two previous calculations that suggest the hollow site is preferred [16,17], even though it is the hcp rather than the previously favoured fcc site [18].

The corresponding vibrational frequencies for hydrogen adsorbed in the three different sites on the Cu4-1 cluster were also calculated. The experimental H–Cu symmetric stretch frequency has been shown to occur at 1040 cm^{-1}, with the first overtone of the deformation mode occurring at 1150–1170 cm^{-1} [35]. Our calculated values were 1013, 1023 and 1067 cm^{-1} for the hcp, fcc and bridge sites, respectively, which all compare well with the experimental value, with the fcc site closest.

The frequencies were also calculated in the three theoretical studies previously mentioned, and showed the hollow site to have a lower frequency than that of the bridge site (which was also lower than the atop site [16]). The previously calculated values for the hollow sites were larger than ours with the closest being 1078 cm^{-1} [16]. The bridge sites were substantially larger with values of more than 1230 cm^{-1}.

Our calculations for the bridge site determined two imaginary frequencies for the two "wagging" modes of hydrogen, further suggesting this is not the favoured site. For the hcp site, there was one imaginary frequency, while there were none for the fcc site. Furthermore, one of the "wagging" modes for the fcc site was calculated to occur at 578 cm^{-1} which correlates well with the experimental value observed for the first overtone of this mode. Hence, the frequency values suggest that the adsorption site is fcc, in contrast to the adsorption energy values, but in agreement with the previous calculation [18].

Cluster Size Effect on Adsorption Energy

To examine more widely the effect of cluster size on the adsorption energy of hydrogen on Cu(111), a set of eight different clusters were chosen. These clusters comprised 3–13 copper atoms, each containing an fcc site. An hcp site was not chosen, as there are not as many clusters that can be constructed, which have less than 13 atoms. For a bridge site, most of the clusters that could be chosen would have only C_s symmetry, and hence might not converge or would take longer to do so.

The adsorption energies (Table AII in Appendix) for the eight clusters are shown in Fig. 4. Surprisingly, a Cu6-3-1 and a Cu3-6-1 cluster both failed to converge.

The difference between the Cu4-1 and Cu6-l clusters seen previously was $\sim 27\,\mathrm{kJ\,mol^{-1}}$. Now with the other clusters, differences of up to $240\,\mathrm{kJ\,mol^{-1}}$ are seen. There does not appear to be an obvious trend in the energy values as the size of the cluster is increased. Experimentally, the adsorption energy has been determined to be $\sim -80\,\mathrm{kJ\,mol^{-1}}$ [50] and it is the largest cluster that most closely coincides with this value, even though the experimental value may relate to a different adsorption site, which is yet to be clarified. As the cluster size has increased, however, the adsorption energies do not appear to have converged towards this value, or to have followed a trend. Clusters with either the same number of atoms or very similar structures do not necessarily even have close

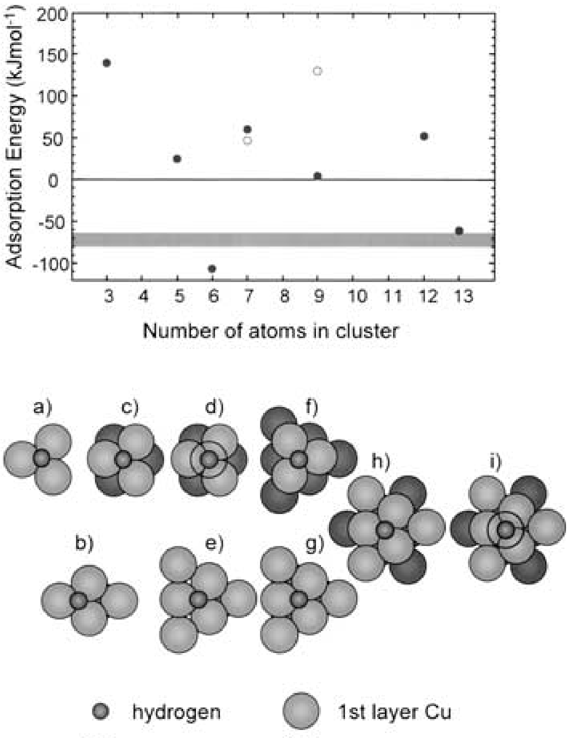

FIGURE 4 Adsorption energy values for hydrogen adsorbed in an fcc site on different size (111)-type clusters: (a) Cu3(3), (b) Cu4-1(5), (c) Cu3-3(6), (d) Cu3-3-1(7), (e) Cu6-1(7), (f) Cu3-6(9), (g) Cu6-3(9), (h) Cu6-6(12), (i) Cu6-6-1(13). Open symbol corresponds to clusters (e) and (g). Experimental adsorption energy value [49] indicated by horizontal bar.

values. In particular, the Cu6-3 and Cu3-6 clusters, both having nine atoms, have an energy difference of $\sim 130\,\mathrm{kJ\,mol^{-1}}$. Also there is a difference of $\sim 160\,\mathrm{kJ\,mol^{-1}}$ between the Cu3-3 and Cu3-3-1 clusters where the only difference is the addition of a single atom in the third layer. A similar difference is also seen between the Cu6-6 and Cu6-6-1 clusters, but there the energies are in the opposite order.

Similar to previous studies, the present set of calculations also shows the adsorption energy values to be dependent on the cluster size and structure. In particular, there appears to be an inordinate effect on the energy value with the addition of just one atom in the third layer. It is not possible, though, to determine whether the convergence limit has been reached as larger clusters cannot be calculated. For formate adsorbed in a short-bridge site on Cu(111)-type clusters [40], the adsorption energy values did not converge until the cluster had more than 18 atoms, which is more than can be calculated here. Even though the bond-preparation method did not explain the different energies found for the two H·Cu6-1 clusters, it was reconsidered for the present calculations. However, it could not be applied due to the problem with the loss of symmetry mentioned earlier, which meant the symmetry of the interacting cluster orbital could not be determined. Therefore, the best approximation of the adsorption energy from the present results is $\sim 0\,\mathrm{kJ\,mol^{-1}}$.

CU(110)

Choice of Clusters

Similar to the (111) surface, a set of clusters had to be chosen to model the adsorbed H on the (110) surface. The main difference between the (111) and the (110)-type clusters was, surprisingly, the superior success rate of the latter calculations. The program had less difficulty with these clusters of C_{2v} symmetry than the C_{3v} ones of the (111) surface. Also, during geometry optimisation steps the symmetry of the cluster was retained, unlike many of the (111) clusters that reduced to C_s or C_1 symmetry. Larger clusters could also be computed, which allowed a more complete set of results to be obtained.

Adsorption Sites

Again, the different adsorption sites of this surface had to be modelled. The six sites shown in Fig. 5 include short-bridge, long-bridge, hollow, atop, substitutional and "fcc" sites. The atop and short-bridge sites are similar to those seen on the (111) surface. There is also a long-bridge site, a hollow site and an "fcc" site. This latter site obtains its name from its origin on the (111) surface.

The set of clusters chosen to represent these six adsorption sites is shown in Fig. 6. The position of the adsorbed species is indicated with a cross. At least two different size clusters were chosen to represent each of the six possible adsorption sites. For each site a "small" cluster was constructed, which usually comprised the immediate atoms surrounding the adsorption site. Additional atoms were added for the larger clusters.

As clusters with up to 17 atoms could be calculated for this surface, the calculation time became an important factor. The smallest cluster, Cu2-2, required only $\sim$3 min CPU time to run under tight convergence conditions. For the Cu9-8 cluster, 6.6 hr were needed. For most of the clusters, however, the BPW91/LANL2MB calculation needed to be run first in order to provide an initial estimate of parameters. Hence, the calculation time, even though not doubled, was increased each time by this pre-calculation. For the adsorbed hydrogen calculations, the time was increased significantly, particularly as they often required extra pre-calculations, using various combinations of HF or B3LYP and LANL2DZ or LANL2MB. For example, the H·Cu8-9 calculation, using BPW91/LANL2DZ, required 24.5 h to compute and $\sim$50.5 h including pre-calculation times. Frequency calculations or population analyses only added to these times.

H/"Cu(110)"

The adsorption of hydrogen was modelled on the clusters shown in Fig. 6. The dissociative adsorption energy values were calculated the same as for the (111)-type clusters and are displayed in kJ mol^{-1} in Fig. 7 and listed in Table AIII in Appendix. The experimental value is also indicated [50].

Many studies have examined the adsorption of hydrogen on Cu(110) in order to investigate the adsorption site and surface arrangement, including [51–56]. At

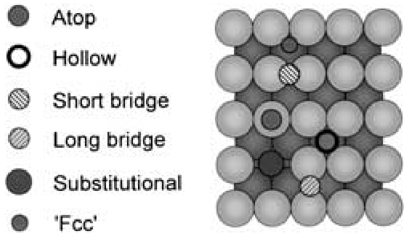

FIGURE 5 Different adsorption sites on a Cu(110) surface: atop, hollow, short-bridge, long-bridge, substitutional and "fcc".

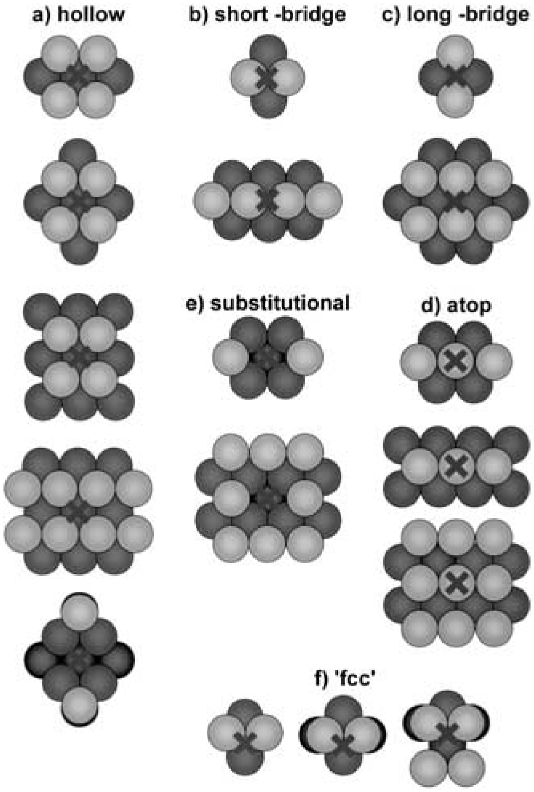

FIGURE 6 The set of clusters used to model the adsorption of H in the different adsorption sites on Cu(110): (a) hollow: Cu4-3, Cu4-5, Cu4-9, Cu8-9, Cu2-4-5, (b) short-bridge: Cu2-2, Cu4-6, (c) long-bridge: Cu2-2, Cu6-8, (d) atop: Cu3-4, Cu3-8, Cu9-8, (e) substitutional: Cu2-4-1, Cu8-8-1 and (f) “fcc”: Cu2-2, Cu2-2-2, Cu4-2-2. X indicates the adsorption site.

low exposures and temperatures (100 K), hydrogen induces a (1 × 3) reconstruction. At higher exposures and temperatures a (1 × 2) missing-row reconstruction forms, and H adsorbs in an fcc-type site [52,55,56]. This arrangement is shown in Fig. 8.

For the Cu3-4 atop cluster two of the atoms in the top layer have only two atoms to bond to in the second layer, instead of four. Hence, the “intermediate” Cu3-8 cluster was included to see what difference the addition of these atoms made. It was found the energy was lower for the larger cluster and lower still for the Cu9-8 cluster. Indeed, in all cases except for the hollow and fcc sites, the largest cluster gives the lowest energy. The Cu4-5 and Cu4-9 hollow clusters also have a similar relationship, with the four top-layer atoms of the Cu4-5 cluster bonding to only three-second layer atoms. Here, though, the larger cluster actually has a more positive energy value. Hence some other effect may be causing the relative difference in the energies.

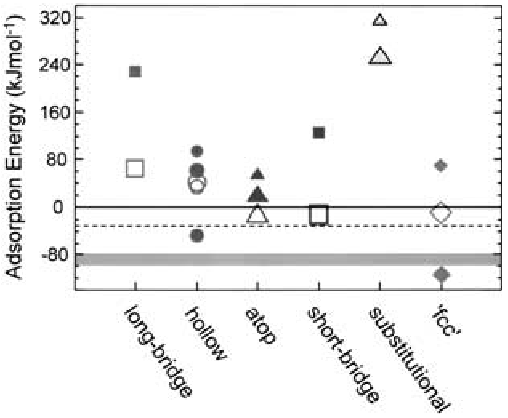

FIGURE 7 Adsorption energy values for hydrogen bonded onto the (110)-type clusters in the different adsorption sites using LANL2DZ. Large clusters are indicated with a larger open symbol, small clusters with a closed or smaller symbol. The experimental adsorption energy [49] indicated by horizontal bar.

Hydrogen adsorption is unfavourable on most of the clusters, particularly in a long-bridge or substitutional site. The hollow, atop or particularly the "fcc" sites appear to be the most likely.

An "fcc" cluster gave an adsorption energy which was closest to the experimental value, but the three different fcc-type clusters each gave a fairly different energy. Similar to the other sites, the smallest cluster has the highest value, with the two larger clusters giving the lower energies, but the Cu2-2-2 is lower than the Cu4-2-2. The former cluster also represents a (1 × 2) reconstructed surface whereas the latter does not. This result, therefore, corresponds to the experimental observation that adsorbed hydrogen induces a (1 × 2) reconstruction.

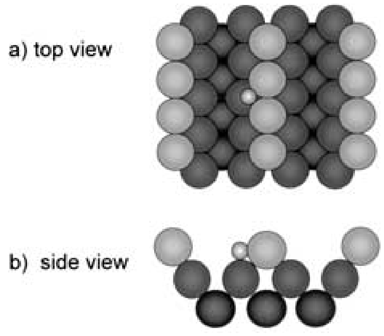

FIGURE 8 The missing-row reconstruction of Cu(110) induced by hydrogen which adsorbed in an "fcc" site [51,55]: (a) top view, (b) side view.

Most of the smaller clusters for the other sites can also represent a reconstructed surface, but these all have higher energies. As the adsorption energy value for the hollow site is the next closest to the experimental value, a "larger" reconstructed "quasi-hollow" cluster was calculated. This Cu2-4-5 cluster results in a positive energy, indicating adsorption is unfavourable.

The calculations that represent a reconstructed cluster do not take into account, however, the energy required for the reconstruction. Hence the calculated adsorption energy values would need to be lower than the experimental value in order to allow for this. It is thus encouraging that the reconstructed "fcc" cluster has an energy below the experimental value, though the agreement may not be so close when raised by the reconstruction energy.

The hydrogen was calculated to lie ~ 1 Å from the three copper atoms defining the "fcc" adsorption site (Table A III). For the other adsorption sites, the H–Cu distance varied with the site, as one might expect. The distance was shown to decrease as the hydrogen moved from an atop site to a short-bridge, long-bridge, hollow and then substitutional site, where it sits below the level of the top layer of copper atoms for this latter site. There were no major variations in bond distances for the different size clusters of the particular sites, where the variations were less than 0.2 Å. The exception was the long-bridge site, where the distance was ~ 0.6 Å shorter for the larger cluster.

CONCLUSION

The adsorption of hydrogen onto the (111) and (110) surfaces of copper has been modelled using DFT calculations. Even though the calculations were limited by cluster size and the resulting energy values were dependent on their size and shape, the calculations generally supported the available experimental observations.

On Cu(111), hydrogen prefers to adsorb in a hollow site. The adsorption energy values favoured the hcp site, whereas the frequency values showed the fcc site to be preferred. The adsorption energies for hydrogen adsorbed in an fcc site examined over a wider range of clusters, however, showed a large variation with cluster size.

On Cu(110), hydrogen prefers to adsorb in an fcc site on a (1×2) reconstructed surface. This supports the experimental observation.

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APPENDIX

TABLE AI Total electronic energy values and H–Cu bond distances relative to the top copper layer for H adsorbed on a Cu4-1 and two Cu6-1 clusters, using BPW91/LANL2DZ

Cluster/species	Energy (au)	H. Cluster		
		hcp	fcc	bridge
Cu4-1	− 981.271190662	− 981.860670943	− 981.85203276	− 981.851139878
H–Cu (Å)	–	1.2144	1.0294	1.2949
Cu6-1 (i)	− 1373.84854134	− 1374.42411499	− 1374.42491679	− 1374.42179223
H–Cu (Å)	–	1.2034	1.1416	1.2752
Cu6-1 (ii)	− 1373.84644211	− 1374.43637131	− 1374.42361325	− 1374.43071195
H–Cu (Å)	–	1.2000	1.1640	1.2526
H_2	− 1.171743350			

TABLE AII Total electronic energy values and H–Cu bond distances for H·Cu_x (fcc) using BPW91/LANL2DZ

Cluster	Energy (au)	Cluster	Energy (au)	Adsorption Energy (kJ mol^{-1})	H–Cu (Å)
Cu3	− 588.720287368	H·Cu3	− 589.279185876	141.52	0.8270
Cu4-1	− 981.271190662	H·Cu4-1	− 981.85203276	26.39	1.0294
Cu3-3	− 1177.56524858	H·Cu3-3	− 1178.17117333	− 105.22	1.0433
Cu3-3-1	− 1373.8736369	H·Cu3-3-1	− 1374.44775279	61.68	0.8874
Cu6-1	− 1373.84837971	H·Cu6-1	− 1374.42491679	48.98	1.1416
Cu3-6	− 1766.44993534	H·Cu3-6	− 1767.01069996	131.73	1.0000
Cu6-3	− 1766.44993526	H·Cu6-3	− 1767.03467537	5.94	1.0522
Cu3-6-1	− 1962.72375975	H·Cu3-6-1	–*	–	–
Cu6-3-1	− 1962.71377183	H·Cu6-3-1	–*	–	–
Cu6-6	− 2355.31768116	H·Cu6-6	− 2355.89328003	53.9	1.0039
Cu6-6-1	− 2551.59639627	H·Cu6-6-1	− 2552.19365874	− 59.77	1.0597

* Convergence failure.

TABLE AIII Calculated total electronic energy values, adsorption energy values and H−Cu distances for H adsorbed in the different sites on the Cu(110)-type clusters: hol = hollow, sbr = short-bridge, lbr = long-bridge, top = atop, sub = substitutional, fcc = "fcc", using BPW91/LANL2DZ

Cluster	Energy (au)	H. Cluster	Energy (au)	Adsorption Energy (kJ mol^{-1})	H−Cu (Å)
Cu4-3.hol	− 1373.85047452	H·Cu4-3.hol	− 1374.41824879	94.95	0.6187
Cu4-5.hol	− 1766.37834327	H·Cu4-5.hol	− 1766.97287076	− 45.42	0.5989
Cu4-9.hol	− 2551.48549729	H·Cu4-9.hol	− 2552.03745117	38.29	0.5288
Cu8-9.hol	− 3336.64217405	H·Cu8-9.hol	− 3337.21914178	46.72	0.6178
Cu2-4-5.hol	− 2158.93497481	H·Cu2-4-5.hol	− 2159.50964718	58.76	0.5533
Cu2-2.sbr	− 784.990130987	H·Cu2-2.sbr	− 785.552049484	125.68	1.3046
Cu4-6.sbr	− 1962.689931319	H·Cu4-6.sbr	− 1963.27722352	− 7.45	1.1578
Cu2-2.lbr	− 784.990130987	H·Cu2-2.lbr	− 785.532270502	229.46	0.9614
Cu6-8.lbr	− 2747.80271545	H·Cu6-8.lbr	− 2748.37538326	69.28	0.3603
Cu3-4.top	− 1373.85047452	H·Cu3-4.top	− 1374.42551283	56.84	1.5863
Cu3-8.top	− 2158.94261099	H·Cu3-8.top	− 2159.52321809	27.62	1.5481
Cu9-8.top	− 3336.64217405	H·Cu9-8.top	− 3337.19426753	− 4.68	1.5875
Cu2-4-1.sub	− 1373.85047452	H·Cu2-4-1.sub	− 1374.37589103	317.2	− 1.0041
Cu8-8-1.sub	− 3336.64217405	H·Cu8-8-1.sub	− 3337.15148935	261.25	− 0.9715
Cu2-2.fcc	− 784.990130987	H·Cu2-2.fcc	− 785.531471012	70.34	0.8539*
Cu2-2-2.fcc	− 1177.56524858	H·Cu2-2-2.fcc	− 1178.17117333	− 105.22	1.0433*
Cu4-2-2.fcc	− 1570.1153243	H·Cu4-2-2.fcc	− 1570.70182716	− 3.11	1.0072*

* Distance from the three Cu atoms defining the site.