Ab initio study of benzene adsorption on the Cu(1 1 0) surface and simulation of STM images

B.L. Rogers [a], J.G. Shapter [a], M.J. Ford [b,*]

[a] *School of Chemistry, Physics and Earth Sciences, Flinders University, G.P.O. Box 2100, Adelaide 5001, Australia*
[b] *Institute for Nanoscale Technology, University of Technology Sydney, P.O. Box 123, Broadway, NSW 2007, Australia*

Abstract

The adsorption of benzene molecules onto the Cu(1 1 0) surface has been studied using a crystalline linear combination of atomic orbitals approximation (LCAO). Adsorption energetics have been modelled at both the Hartree–Fock (HF) and density functional theory (DFT) level, and scanning tunneling microscope (STM) images generated for the preferred adsorption geometry. The calculated binding energies are strongly dependent upon basis set superposition errors (BSSE). As expected HF provides a relatively poor description of this loosely bound system, and is found to be unbound when BSSE is taken into account. Inclusion of electron correlation through DFT methods gives an optimised binding energy of 106 kJ mol^{-1} with the benzene molecule occupying a bridging site between the rows of surface copper atoms and an adsorption height of approximately 2 Å. This figure takes account of relaxation of benzene upon adsorption with the hydrogen atoms tilting away from the surface. Our predicted energetics compare favourably with previous theoretical studies using cluster methods and experimental binding energies determined from temperature programmed desorption (TPD). We have also simulated scanning tunneling microscope (STM) images using the Tersoff and Hamann method and compare our results with recent experimental measurements. Our simulation suggests the experimental image results from a benzene dimer rather than an isolated molecule.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Ab initio quantum chemical methods and calculations; Density functional calculations; Scanning tunneling microscopy; Physical adsorption; Copper; Aromatics

1. Introduction

Experimental STM images provide a powerful method for studying the adsorption and energetics of molecules on surfaces. The current observed in this technique reflects the local densities of states of tip and surface and tunnel conductance between the two. Interpretation of these images is, however, often far from trivial particularly in the case of adsorption of complex molecules. Theoretical simulation of STM images can aid the interpretation of these images [1,2] as well as providing an efficient method for identifying the appropriate regimes for undertaking the more time-consuming experiments. In particular, the prediction of variations in STM images of adsorbed molecules due to the presence of various functional groups in a

* Corresponding author. Tel.: +61-2-9514-7956; fax: +61-2-9514-7553.
E-mail address: mike.ford@uts.edu.au (M.J. Ford).

molecular framework may prove to be essential for the successful identification of imaged molecules, including biological macromolecules.

Previously, attempts have been made to model surface-adsorbate systems using cluster models, in which the bulk substrate is approximated through the use of a relatively small number of atoms arranged to simulate a small section of the surface. Hidaka et al. have modelled benzene adsorbed on a small 4-atom silver cluster in order to ascertain the effect of the surface-sample interaction on STM images [3]. In this study, the STM tip was simulated through the use of two palladium atoms positioned above the surface. Orlandi et al. used 6-atom and 11-atom clusters to model STM images of benzene and naphthalene rhodium and platinum surfaces respectively [4]. A single tungsten and palladium atom was used to model the tip in each of these calculations. Edelwirth et al. incorporated a much larger carbon cluster of 30 atoms in a square lattice three layers thick in order to model STM images of self-assembled adenine monolayers on graphite [5]. All of these calculations seek to accurately model interaction between sample and tip, at the expense of reducing the semi-infinite surface to a small cluster. These calculations scale rapidly with the number of atoms in the surface cluster.

An alternative approach is provided by the use of crystalline calculations. The substrate is modelled by a thin slab where translational symmetry is exploited to generate a solution as a sum of Bloch wavefunctions [6]. The use of periodicity in this manner results in substantial gains in computational efficiency and may result in an improved representation of the surface. A suitable comparison needs to be found in these calculations between slab thickness, and hence computational size, and convergence of calculated quantities. Several studies shed light upon this issue although the optimum conditions are still unclear. The pseudopotential calculations of Ke on the Si(1 1 1)-7×7 surface reconstruction show that a converged surface topography is achieved for slabs of five atomic layers [7]. Causá et al. found that although a two-layered slab was sufficient to model the surface energy and relaxation energy of LiH(0 0 1) using Hartree–Fock techniques, three atomic lay-

ers were necessary to model the quadrupole moment [8]. Similarly, Birkenheuer et al. found that the charge distribution and cohesive energy of the MgO(0 0 1) surface studied using local density functional techniques required three atomic layers to converge [9]. However, Kiejna et al., in density functional calculations of Al(1 1 0) have reported the persistence of quantum size effects, causing oscillations in the work function and surface energy, even in slabs up to 16 atomic layers thick [10]. Furthermore, Boettger suggests that slow oscillations in calculated values as a function of slab thickness may result in unrealistic values of optimum thicknesses [11]. Several authors report that other factors are of greater importance in the accuracy of slab-adsorbate calculations, including basis set selection [12] and prevention of through-slab adsorbate–adsorbate interactions [13].

The aim of the present work is to investigate the adsorption process of benzene on the Cu(1 1 0) surface using a first principles quantum chemical method where the surface is modelled by a crystalline slab infinite in two dimensions. One would expect such techniques to be appropriate to a metallic substrate where the electrons are obviously delocalised. We can test our calculations by comparison with experimental binding energies and can reveal further details of the adsorption process, such as preferred binding site. We also aim to demonstrate the utility of using the commercially available code CRYSTAL98 [14] with modest computing resources to simulate STM images of absorbed molecules. This is achieved from a fully self-consistent density of states calculation of the full substrate–adsorbate system and recourse to the Tersoff–Hamann approximation. Considerable interest in the Cu-benzene system has developed as a result of the Cu(1 1 0) catalysed coupling reaction of acetylene [15].

Benzene adsorption Cu(1 1 0) has been studied by variety of spectroscopic [13,16–20], thermodynamic [15,21], and scanned probe techniques [22,23]. Although several of these studies have focussed on investigating the bonding mechanism and electronic structure, few studies have targeted the determination of the actual adsorption site. The TPD studies of Lomas et al. [15] show benzene does not decompose on adsorption and sub-

sequent desorption from the Cu(1 1 0) surface. The authors find a desorption temperature of approximately 290 K at a surface coverage of 1 Langmuir, decreasing as coverages increases. Benzene reactively formed on the surface was found to desorb at higher temperatures. Kash et al. [21] report a desorption temperature of 242 K at the same coverage.

X-ray [18,24] and infrared [20] studies show that benzene adsorbs with its molecular plane parallel to the Cu(1 1 0) surface at low coverages, with bonding to the surface occurring through the delocalised π-orbitals of the carbon ring. These results have been confirmed by Doering et al. [22,23] using low-temperature STM. The latter authors also propose the preferred adsorption site. However, the Cu(1 1 0) substrate and the adsorbed benzene molecule require quite different imaging conditions and the adsorption site is extrapolated from the two images. Subsequent analysis of the results of these studies do suggest that no significant reconstruction of the (1 1 0) structure occurs. This observation is confirmed by the X-ray diffraction studies of Schuster and Robinson [25].

Further investigation into the adsorption site has been undertaken through ab initio cluster calculations performed by Pettersson and co-workers [26,27]. An all-electron density functional method was used to optimise the geometry of benzene adsorbed at a fourfold hollow bridging site on a 13-atom cluster of Cu atoms in the (1 1 0) structure. Ab initio cluster calculations of various unsaturated hydrocarbons on the Cu(1 1 0) surface performed by Lomas and Pacchioni [28] support these findings by suggesting that bridging sites are consistently favoured over atop sites. Geometry optimisation revealed two favourable structures of the adsorbed molecule: the gas-phase triplet quinoid inverse boat conformation, and the singlet planar carbon ring with elongation of the carbon–carbon bonds and a bending of the hydrogen atoms away from the surface. This latter form is referred to as the ''H-flip'' conformation. The authors find the quinoid structure to be marginally favourable. However, this would require a strong absorbate–substrate interaction in order to counter the energy required to excite the triplet state. Pettersson et al. suggest that although evidence exists that this may

occur, this evidence is statistically insignificant. The H-flip conformation is therefore proposed to represent the actual conformation of the adsorbed molecule [27]. An adsorption energy of 58 kJ mol^{-1} is calculated. X-ray adsorption spectroscopy experiments performed by Weinelt et al. [18] confirm this bending of the hydrogen atoms away from the surface. However, X-ray photoelectron spectroscopy (XPS) experiments performed in the same study revealed little evidence of carbon frame distortion. Benzene largely retains its gas-phase structure due to weak interaction with the Cu(1 1 0) surface [18].

In a cluster calculation performed by Lomas and Pacchioni [28] the gas-phase structure of benzene was used to determine the binding energy with the adsorption site fixed at a bridging position. An adsorption energy of approximately 13 kJ mol^{-1} and an adsorption height of 3.41 Å was calculated using a cluster of 28 Cu atoms. This adsorption energy is significantly less than that proposed by Pettersson and co-workers, suggesting that the H-flip form is energetically favourable. However, in both this calculation and that of Pettersson and co-workers the use of 28 and 13 atom clusters to represent the surface may be the limiting factor. Relatively small clusters may be insufficient to describe the delocalised nature of conduction band electrons in the metal [28]. It follows that such a cluster is not of sufficient size to accurately model the electron donation and back-donation bonding scheme suggested by the DCD model [17,27]. The adsorption orientation is of vital importance in the simulation of STM images. The densities of states of any adsorbed molecule are perturbed by the electronic states of the substrate. As STM images are sensitive to the densities of states as well as tunnel conductance, this perturbation influences the STM image. The local density of states of the substrate varies at different adsorption sites, and STM images typically mirror this dependence. Weiss and Eigler [29] have published STM images of benzene adsorbed on a Pt(1 1 1) surface which exhibit a strong dependence on the adsorption site. A self-consistent calculation of the preferred adsorption configuration is then an important aspect to calculating STM images.

One of the earliest methods of calculating theoretical STM images was developed by Tersoff and Hamann [30]. This method essentially assumes that the tunneling current is proportional to the local density of states of the sample at the position of the tip. The tunneling current is therefore independent of the tip structure and orientation. Although simplistic, the Tersoff–Hamann method is still popular, and several authors have recently reported success in simulating STM images of molecular and atomic adsorbates using the method [31–34] where the DOS for the substrate–absorbate system is calculated from first principles. More recently, several other methods of modelling STM images have been developed. Of particular importance is the ESQC method developed by Sautet and Joachim [35,36]. Here the effect of molecular orbitals on the tunnel conductance between a tip and surface is modelled in a very complete way. This method has the advantage of enabling STM images of large or complex systems to be calculated, and has very successfully reproduced the site dependence for benzene-Pt(1 1 1) observed by Weiss and Eigler [29]. In the ESQC method site dependence can be understood in terms of interference effects between tunnelling contributions through the various molecular orbitals.

In the present paper we describe ab initio calculations of benzene adsorbed on a Cu(1 1 0) surface, resulting in the description of adsorption energetics, elucidation of the adsorption site and development of theoretical STM images.

2. Calculation method

Calculations were carried out using the CRYSTAL98 suite of programs [14]. The package approximates true wavefunctions through an expansion of crystalline orbitals as a linear combination of atomic orbitals. Both Hartree–Fock (HF) and density functional (DFT) hamiltonians were employed. Dirac–Slater exchange [37] and Vosko–Wilk–Nusair [38] correlation were employed in the DFT calculations. The default conversion tolerances for the program were used throughout. Numerical integration was performed

using 25 symmetry irreducible k points. For the denser k point net used in evaluating the density matrix 81 symmetry irreducible k points were used. This k-space sampling is sufficient to ensure convergence of the calculated properties. The calculations were performed on the Linux Beowulf cluster maintained by the South Australian Partnership for Advanced Computing. All the calculations reported here were performed using a serial compilation of the CRYSTAL98 code [14]. Hence these calculations are well within the realm of desktop computing.

An 86-4111(41D)G all-electron basis set developed by Doll and Harrison [39] was used to describe the copper in the HF calculations. For the DFT calculations, this basis set was modified to incorporate a Hay and Wadt small core (HAYWSC) pseudopotential in order to improve the computational time. The use of small core pseudopotentials is supported by previous studies in which similar pseudopotentials were found not to significantly affect the predicted surface geometry of rutile [40].

In order to confirm these results, the lattice parameters for bulk crystalline copper were optimised with respect to energy under DFT conditions using both HAYWSC and all-electron basis sets. The lattice parameter was also optimised under HF conditions using the all-electron basis set. The results are shown in Table 1 and compared with the experimental value determined by Straumanis and Yu [41]. The HF results show poor agreement with experimental values, grossly overestimating the lattice parameter. The DFT results agree well with experimental values, although the known trend of LDA to "overbind" the system and underestimate lattice parameters is exhibited [42]. More importantly, no significant loss of accuracy is observed with the use of Hay and Wadt small core pseudopotentials. These results agree with the observations of Doll and Harrison, who reported accurate simulation of the band structure, structural and cohesive properties of copper using LDA, but poor accuracy at the HF level of theory [39]. It is well known that the d-bands are not well reproduced in HF calculations of Cu, where the bands are predicted to lie well below the fermi level.

Table 1
Comparison of all-electron and HAYWSC optimised lattice parameters for bulk crystalline copper with the experimental value

	Lattice parameter (Å)
HF all-electron basis set	4.015 (11.07)
DFT all-electron basis set	3.531 (2.33)
DFT HAYWSC basis set	3.514 (2.79)
Experimental value	3.615

Numbers in parentheses indicate percent error with respect to the experimental bulk lattice parameter.

To simulate the Cu(1 1 0) surface the appropriate slab was cut from bulk Cu. Slabs of two, three and four atomic layers were used in order to investigate thickness effects; this is discussed in more detail below.

Previous studies suggest that benzene adsorbs parallel to the Cu(1 1 0) surface. In addition, we may assume that adsorption of benzene occurs at sites of maximum symmetry. Four possible adsorption sites for benzene on the Cu(1 1 0) surface have therefore been investigated. At each of these sites, benzene may adsorb to the surface in two different orientations, each at an angle of 90° to the other. A total of eight possible adsorption orientations are therefore used, as presented in Fig. 1.

The benzene molecule was described using 6-21G* all-electron basis sets. At both the HF and DFT level this basis set predicts bond lengths to better than 2%. Prior to all adsorption calculations, the bond lengths of gas-phase benzene were optimised with respect to the total energy. A supercell of the Cu(1 1 0) slab was employed in order to allow sufficient separation of adsorbed benzene molecules such that intermolecular effects are negligible. Separation between adjacent absorbed molecules was maintained in the order of 5 Å in order to prevent intermolecular interactions. Calculations were performed in which benzene was positioned above the Cu(1 1 0) three-layered slab in each of the proposed orientations, and the optimum adsorption height was determined in terms of total system energy. Subsequent calculations of the binding energy of adsorbed benzene in each of the orientations at the optimum adsorption heights revealed the preferred adsorption
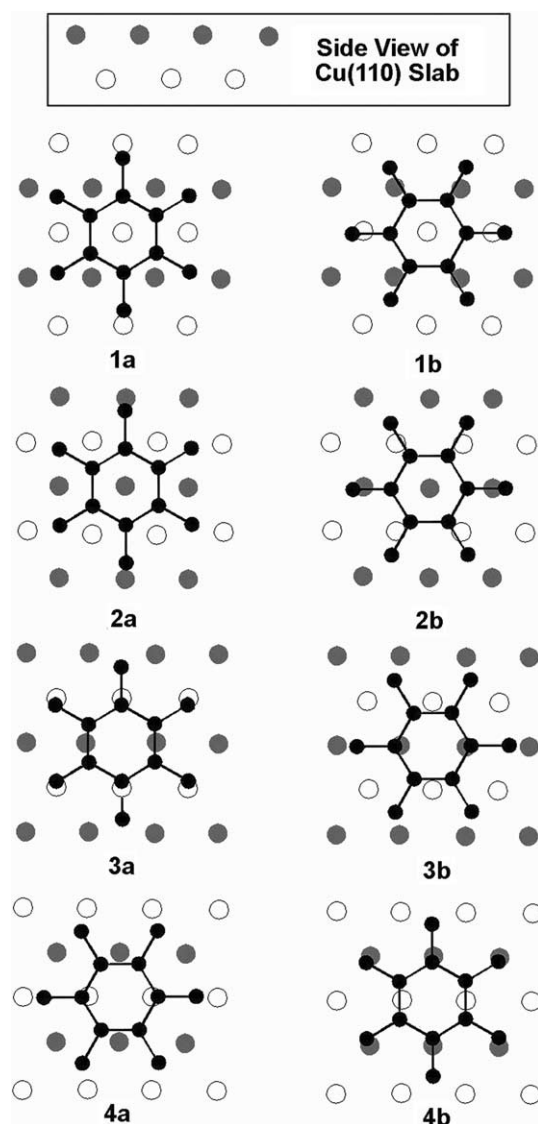

Fig. 1. Positions of the eight proposed possible adsorption orientations of benzene on the Cu(1 1 0) surface. Grey disks represent upper layer Cu atoms, while open circles represent second layer Cu atoms.

orientation of benzene on the Cu(1 1 0) surface. Calculations of the binding energy of adsorbed benzene in the preferred orientations were then performed using two- and four-layer Cu(1 1 0) slabs in order to investigate the effects of slab thickness on adsorption energies. Similar calculations were subsequently performed in which benzene in the H-flip conformation proposed by

Pettersson and co-workers [26,27] was positioned above the Cu(1 1 0) four-layered slab in each of the proposed orientations, and the optimum adsorption height was determined in terms of total system energy.

The binding energy calculations were performed using the counterpoise method to account for basis set superposition errors. This was found to have a dramatic effect on calculated binding energies and is clearly required in order to generate reliable values. The imbalance between basis set size describing the substrate compared with the benzene molecule could be responsible for this. A large basis set on the Cu slab is required in order to generate a reasonable electronic structure [39]. The relatively small basis set used to describe the benzene represents a compromise between computational time and accuracy. No account is taken of surface relaxation of the Cu either before or after adsorption. We would expect such effects to be relatively small, and experimental STM images support the view that there is little surface reconstruction, although relaxation of the interlayer spacing near the surface may still play a small role.

Adsorption chemistry was investigated by generating electron density difference plots for the optimised geometries by subtracting electron density maps of isolated benzene and copper from an electron density plot of the combine surface-adsorbate system. Simulated STM images of preferred orientations were calculated using CRYSTAL98 [14] through the method described by Tersoff and Hamann [30], and comparisons made with published experimental results.

3. Results and discussion

3.1. Cu(1 1 0) surface

As a first test of the effects of slab thickness optimised lattice parameters for Cu(1 1 0) slabs of various thicknesses are shown in Table 2. In these calculations the slab is built from a single unit cell and hence one parameter, the lattice constant of the FCC cell from which the slab is built, is optimised. Although in some senses this is unrealistic given that this is not a bulk crystal, one might

Table 2
Comparison of optimised lattice parameters for Cu(1 1 0) slabs

Slab thickness	HF/all-electron basis set (Å)	DFT/HAYWSC basis set (Å)
2	3.720 (2.90)	3.304 (8.61)
3	3.804 (5.24)	3.384 (6.38)
4	3.906 (8.05)	3.420 (5.38)
5	3.893 (7.70)	3.443 (4.76)

Slab thickness is given as the number of atomic layers. Numbers in parentheses represent the percent error with respect to the experimental bulk value.

nevertheless expect the optimised lattice constant to approach the bulk value as the slab becomes thicker. Examination of Table 2 reveals that the DFT results generally give values below the bulk lattice parameter, however the value appears to converge towards the bulk value with increasing slab thickness. This trend is not observed in the HF calculations, with the lattice parameter being both under- and overestimated. The lack of a consistent trend might suggest oscillations in the properties of the slabs calculated at the HF level, while the observed trend in the DFT calculations suggest a degree of confidence in this method.

As a further test of thickness effects we have calculated STM images of the Cu(1 1 0) surface calculated with DFT and the HAYWSC basis set and compared these with experimental images from Doering et al. [22,23]. Experiment and theory were normalized by fixing the ratio of peak height to trough *across* the rows of surface atoms for all images to same value. We can then compare electron densities *along* the rows of surface atoms, as shown in Fig. 2. Results for only the two and three layer slabs are shown in Figs. 2, 4 and 5 layer slabs give very similar results. Agreement in the intensity variation between experiment and theory for the two slabs is reasonable, the pitch of electron density variation does, however, vary between the different slab thickness because of the different values for the optimised lattice parameter. These observations again give us confidence that the DFT/HAYWSC calculation is performing well and that two or three layer slabs represent a suitable compromise between computational efficiency and accuracy.

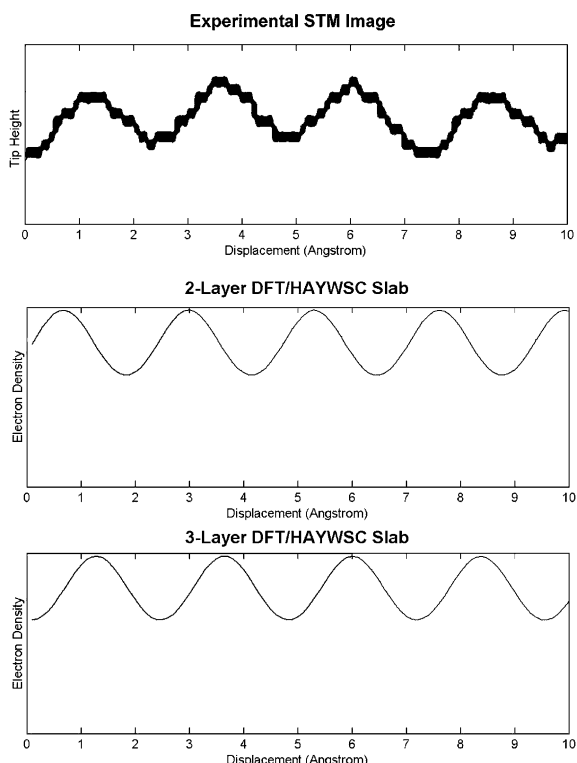From the experimental image [22,23] the separation between surface layer copper atoms within

Experimental STM Image

2-Layer DFT/HAYWSC Slab

3-Layer DFT/HAYWSC Slab

Fig. 2. Comparison of a cross-section derived from an experimental STM image of the Cu(1 1 0) surface from the work of Doering et al. [22,23] and cross-sections showing the electron density along a row of surface atoms for the two and three layer Cu(1 1 0) slabs calculated using DFT and an HAYWSC basis set. The y-axes of all plots have been internally standardised to enable direct comparison.

the (1 1 0) rows is approximately 2.5 Å, giving a lattice parameter of approximately 3.5 Å. This value compares well with the bulk lattice parameter of 3.615 Å and suggests that no significant relaxation of the Cu(1 1 0) surface in the plane of the surface occurs. This provides evidence that using the bulk crystal structure in constructing our slabs is appropriate.

3.2. Adsorption energetics

Calculated adsorption energetics, including adsorption energy and geometry will be effected by basis set superposition errors (BSSE), slab thickness, through slab interactions and relaxation of

the surface/molecule upon adsorption. We have investigated the relative contribution each of these makes to our predicted values. Without counterpoise corrections, both the HF and DFT calculations lead to bound systems (for most adsorption geometries), with HF giving values of the order of 10 kJ mol^{-1} and DFT around 250 kJ mol^{-1}. The HF values seem reasonable, but it is difficult to explain why HF and DFT give such different binding energies and DFT gives bond strength more typical of covalent systems. Inclusion of BSSE leads unbound systems at HF and bound systems (for some geometries) at DFT with values up to 100 kJ mol^{-1}. BSSE corrections are probably the most important factor in obtaining reasonable adsorption energetics, particularly in cases such as ours in which we are forced to use very imbalanced basis sets. It is also clear that the inclusion of electron correlation (in our case through DFT methods) is important to describe this system reasonably well.

Adsorption energies and heights for one of the proposed adsorption sites, site 1b in Fig. 1, as a function of slab thickness at the DFT level are presented in Table 3. The adsorption site chosen is one of the more stable configurations. Adsorption heights are relatively insensitive while energies oscillate with slab thickness showing no obvious convergence even up to four layers. This may well be the limiting factor in our predicted binding energies, and clearly we need to use a slab that is as thick as possible, that is four layers in the present case. We have also performed calculations in which molecules are adsorbed onto both sides or one side of the slab. For three or four layer slab there is little difference indicating through slab interactions are relatively small. We therefore perform our calculations with adsorption on both sides as this leads to increased symmetry and consequently an improvement in computation time.

Finally we have investigated the effects of relaxation of the molecule upon adsorption as suggested by Pettersson et al. [26] Here the H atoms are pushed away from the Cu surface and there is slight distortion of the C–C bond lengths; the so-called H-flip geometry. Using the optimised benzene geometry from Pettersson et al. [26] we

obtain, for the 1b site and a four layer slab, an adsorption height of 2.053 Å and energy of −100.7 kJ mol^{-1}. Comparing this with the value in Table 3 in which the benzene has not been relaxed upon adsorption, we see that height decreases slightly, while adsorption energy more than doubles. This is expected, as the tilting of the hydrogen atoms away from the surface allows the carbon atoms to get closer to surface copper atoms and form a stronger bond.

Table 4 presents predicted values for the adsorption height and binding energy for each of our proposed adsorption sites. These are all DFT calculations using a four layer slab and the H-flip benzene geometry with BSSE corrections. The results fall into two groups: sites 2a, 2b, 3a and 3b are either unbound or only weakly bound, and 1a, 1b, 4a and 4b are relatively strongly bound. The first four adsorption sites position the benzene molecule directly on top of the row of surface Cu atoms, whereas in the latter four it is positioned between the rows. One would expect these latter bridging sites to be more stable. Even though we calculate an overall positive binding energy for the 2b site there still appears an energy minimum around an adsorption height of approximately 2 Å. Either there is a small energy barrier to desorption from this site or the positive overall binding energy is an artefact of the calculation. The latter might indicate that we cannot determine binding energies to a reliability better than about 11 kJ mol^{-1}. Adsorption energies for the four favoured sites are similar at approximately 100 kJ mol^{-1} and agree well with the value of 99 kJ mol^{-1} derived from the TPD data of Lomas et al. [15]. The calculated value from Petersson et al. [26] is 58 kJ mol^{-1}. The largest adsorption energy was calculated for orientation 4a, in which the benzene ring adopts a bridging position between surface layer rows centred on the surface layer atoms. Experimental STM studies by Doering et al. [23] have also proposed that this is the adsorption orientation, although as we have discussed earlier imaging of benzene on Cu is not trivial. In addition the accuracy of our calculation may not be sufficient to distinguish this site from the other three favoured sites, namely 1a, 1b and 4b. Certainly these results indicate that adsorption

of benzene between the rows of copper surface atoms is preferred over adsorption on top of the surface rows.

3.3. Adsorption chemistry

In order to investigate the bond formed between benzene and the Cu(110) surface, electron density difference maps have been calculated for the preferred adsorption geometry. The maps were prepared using the four-layer Cu(110) slab calculated at the DFT level of theory. Looking at Fig. 3(a) we see that electron density increases between
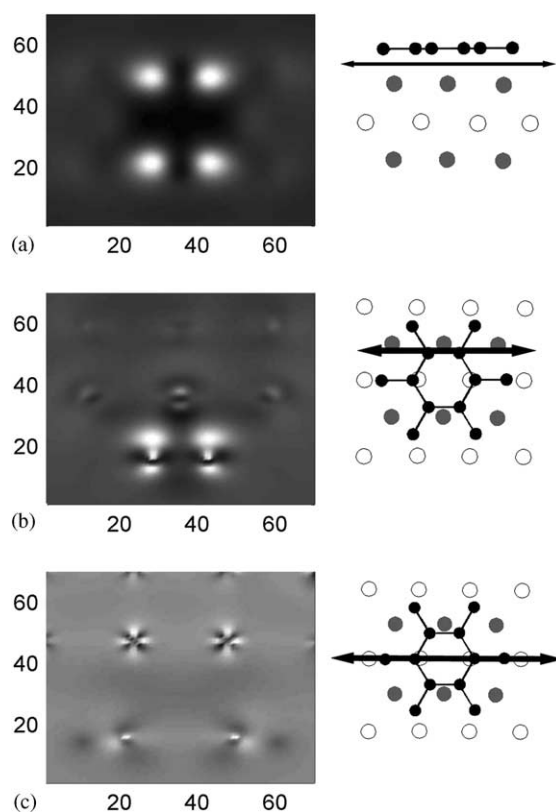

Fig. 3. Density difference plots of benzene adsorbed in orientation 4a on a four-layer Cu(110) surface calculated using the DFT level of theory: (a) in a plane midway between the benzene ring and surface Cu atoms parallel to the surface, (b) perpendicular to the surface through C atom positioned above a row of surface Cu atoms, and (c) perpendicular to the surface through the two C atoms positioned between the rows of surface Cu atoms. Arrows on diagrams indicate the orientation of the plane.

the benzene ring and copper surface around the four carbon atoms in close proximity to the surface copper atoms. The other two carbon atoms which lie between the surface Cu rows show a small decrease in electron density.

Charge redistribution due to bonding between the benzene ring and surface is also evident in Fig. 3(b). Here the density difference is plotted in a plane perpendicular to the surface through the two carbon atoms closest to the surface Cu rows. Electron density about the positions of the two carbon atoms appears to have been pulled into the region between these atoms and the copper surface, while smaller yet similar variations may be observed at the positions of the surface layer copper atoms.

For a perpendicular plane through the other two carbon atoms (Fig. 3(c)), those sitting between the copper surface rows, the redistribution of density is smaller and occurs between the carbon atoms themselves rather than toward the copper substrate. Change of electron density in the sub-surface layer of Cu atoms is also evident in these plots. Two layers of atoms from the substrate participate in the bonding process when benzene adsorbs. This is perhaps not surprising given the delocalised nature of the electrons in the metallic copper substrate, and demonstrates why (at least) four layer slabs are necessary to describe the adsorption process.

These density difference diagrams suggest that adsorption occurs primarily through those carbon atoms which are in close proximity to surface layer copper atoms. Bonding in this system is conventionally described in terms of the DCD model of adsorption proposed by Dewar [43], Chatt and Duncanson [44] where electrons are donated from the molecular π-orbitals into the metal and back-donated from the metal to the anti-bonding orbitals of benzene. The noticeable increase in density between the benzene ring and copper surface observed in Fig. 3(a) and (b) can be interpreted in terms of donation from the π-orbitals into the metal while the smaller redistribution between the carbon atoms themselves in Fig. 3(c) results from back-donation into the anti-bonding orbitals of benzene. Electronic bands derived from the 3d as well as 4s orbitals on the copper atoms of the

substrate can contribute to the adsorption chemistry provided they lie reasonably close to the fermi energy and therefore overlap with orbitals on the adsorbate. This is one of the reasons why the DFT method gives a better description of the adsorption energetics compared with HF: it is well known that HF predicts 3d bands in copper which lie too far below the fermi level [39].

The dominant bonding interaction takes place between carbon atoms of benzene and surface layer copper atoms that are arranged in close proximity. Examination of the orientations proposed in Fig. 1 reveals that all but the 2a and 2b orientations optimise the distance between C atoms and surface Cu atoms. With this rationale, however, it is difficult to explain why orientations 3a and 3b are significantly less energetically favourable than the similar orientations 4a and 4b.

3.4. Simulated STM images

A theoretical STM image of benzene in the H-flip geometry adsorbed on the Cu-1 1 0 surface in orientation 4a is presented in Fig. 4. This image simulates a 40 mV bias between surface and tip and a tip height of 2.5 Å, representing conditions consistent with the experimental images of
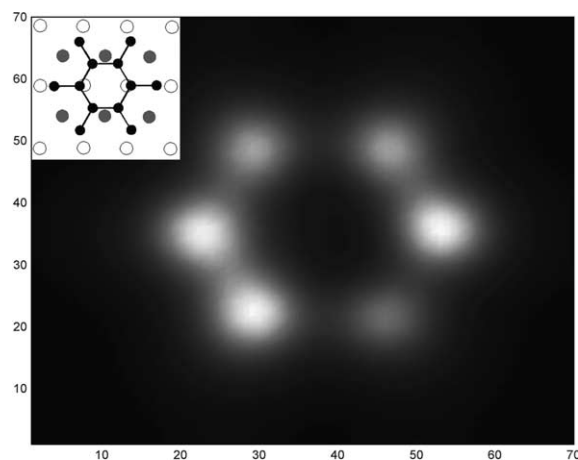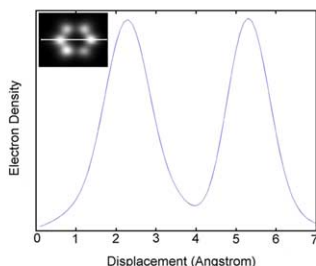

Fig. 4. Theoretical STM image of H-flip benzene adsorbed on the Cu-1 1 0 surface in orientation 4a. The image was obtained using conditions designed to simulate a 40 mV negative bias on the sample, as in the work of Doering et al. [22,23]. A tip height of 2.5 Å and a scanning area of 7 Å×7 Å was simulated.

Doering et al. [22,23]. Examination of this image in conjunction with Fig. 1 reveals a slightly lower intensity, corresponding to a lower electron density, at the positions of those carbon atoms which lie in close proximity to surface layer copper atoms. Distortion of the benzene ring upon adsorption modelled in our calculation is also evident as a slight elongation of the ring along one axis.

A cross-section of the theoretical STM image showing the variation in electron density across the middle of benzene molecule is shown in Fig. 5(a). The benzene ring is clearly resolved in this cross-section with high intensity centred on the carbon frame and a significant drop in the region inside the ring. Under these imaging conditions Fig. 5(a) indicates that the width of the STM image of the molecule will be approximately 5 Å.
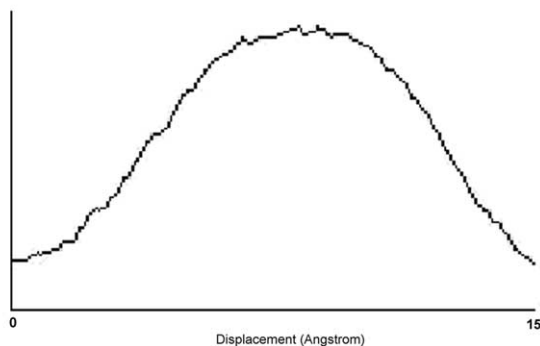

Fig. 5. (a) Cross-section derived from the image presented in Fig. 4 showing the electron density across the benzene molecule. Inset shows the position of the cross-section. (b) Cross-section derived from an experimental STM image of benzene adsorbed on a Cu-1 1 0 surface from the work of Doering et al. [22,23].

Table 3
Comparison of adsorption energies and adsorption heights of benzene on the Cu(1 1 0) surface in orientation 1b calculated at the DFT level of theory using slabs of varying thickness

Slab thickness (layers)	Adsorption energy (kJ mol^{-1})	Adsorption height (Å)
2	−49.1	2.146
3	−25.6	2.154
4	−40.7	2.150

Adsorption height refers to the height of the benzene ring above the surface layer Cu atoms.

Table 4
Comparison of adsorption energies and adsorption heights of benzene in the H-flip conformation proposed by Pettersson et al. [26] on the Cu(1 1 0) surface in each of the eight proposed orientations calculated at the DFT level of theory

Orientation	Adsorption energy (kJ mol^{-1})	Adsorption height (Å)
1a	−106.5	2.016
1b	−100.7	2.053
2a	−7.6	2.015
2b	11.8	2.119
3a	−28.0	2.085
3b	−26.0	2.094
4a	−109.1	2.003
4b	−98.7	2.082

A four layer slab is implemented. Adsorption height refers to the height of the benzene ring above the surface layer Cu atoms.

Although the experimental STM image of Doering et al. [22,23] also shows distortion of the benzene ring along one axis it is more pronounced than in our simulated image. We have also derived cross-sections through the benzene ring from this experimental data to compare with our simulation in Fig. 5(a). This cross-section was determined by bisecting the oval-shaped feature of the experimental image along its longest axis and is shown in Fig. 5(b). No decrease in electron density is observed in the centre of the cross-section corresponding to the centre of the benzene adsorbate. In addition, the width of the cross-section is approximately 11 Å. This value is comparable to the dimensions of two complete benzene molecules. This result might suggest that the experimental image is the result of a benzene dimer.

The experimental image of benzene on the Cu(1 1 0) surface presented by Doering et al.

[22,23] is extremely demanding to obtain, requiring careful control of the imaging conditions and is consequently not trivial to interpret. It does suggest that benzene adopts a bridging adsorption site between two surface layer copper rows. It does not, however, provide a clear indication of the lateral position of the benzene ring along these rows. Our simulated images are consistent with these findings.

4. Conclusion

We have reported ab initio calculations of the adsorption of benzene molecules onto the Cu(1 1 0) surface using a periodic linear combination of atomic orbitals approximation using HF and DFT methods. Benzene coverage is well below single monolayer so that adsorbate–adsorbate interactions are negligible. This approach attempts to describe the substrate surface reliably by modelling it as an essentially infinite slab in two dimensions, compared with cluster calculations where a small section of the surface is modelled. It has the attraction of requiring modest computing facilities. We have attempted to identify the preferred adsorption site, calculate the adsorption energy and ultimately simulate an STM image of this system under imaging conditions consistent with experiment. However, it must be noted that our method does not take account of tip–surface interactions in simulation of the STM images.

Overall, our predicted energetics and preferred adsorption site compare well with the available experimental evidence and give us confidence in our simulated STM images. We find that basis set superposition errors (BSSE) have a profound effect upon the calculated adsorption energies. Without the inclusion of BSSE corrections the system is bound at both the HF and DFT levels with DFT binding energies more consistent with formation of a covalent bond. Inclusion of BSSE leads to generally positive HF binding energies at the HF level and DFT values consistent with values derived from temperature programmed desorption (TPD) measurements.

Copper slabs of two to four atomic layers have been used and indicate that at least four layers are required for reasonable representation of the substrate. Relaxation of the benzene molecule upon adsorption has also been investigated and show that rotation of the hydrogen atoms away from the surface are an important consideration and increase the calculated binding energy by about a factor of 2. We have not attempted to model relaxation of the copper surface and expect this to play a less significant role. This conclusion is supported by experimental evidence.

Taking all of these factors into account we predict a binding energy of 106 kJ mol^{-1}. Previous cluster calculations give a value of 58 kJ mol^{-1} [26], while a value of 99 kJ mol^{-1} is reported from experimental TPD value [15]. We find that the preferred adsorption site is where the benzene adsorbs at a bridging position between the rows of copper surface atoms rather than in the atop position on top of the copper rows. Although it is difficult for us to unambiguously identify the exact adsorption orientation, we find the largest binding energy for the a bridging position with the benzene ring centred with respect to the surface layer atoms. In their experimental STM images Doering et al. [23] reach the same conclusion.

Comparing our simulated STM images with the experiments of Doering et al. [23] we find that the calculations give images which are smaller in lateral spread by about a factor of 2. This result may be explained by the experiment imaging more than a single benzene molecule, possibly a benzene dimer.

Overall the results presented in this paper demonstrate the utility of the CRYSTAL98 software package and modest computing resources as providing an effective method for predicting STM images. Attention, however, must be paid to a number of aspects of the calculation, particularly the effects of BSSE and the use of Hamiltonians which attempt to describe electron correlation, i.e. density functional methods as opposed to Hartree–Fock. Consideration of molecular relaxation upon adsorption and slab thickness are also required to generate reliable binding energies. The latter point deserves further attention as our results still do not show that four layers is sufficient to have reached convergence of calculated properties. Our STM images have been simulated

within the Tersoff–Hamann approximation [30] from a fully self-consistent calculation of the density of states of benzene absorbed on the Cu(1 1 0) surface using CRYSTAL98. This is a relatively straightforward approach which we have implemented on extremely modest hardware, and the present work demonstrates the utility of this approach. However this method does not treat tunnel conductance explicitly. The severity of this limitation in the present case is yet to be determined.

References

[1] M.L. Bocquet, P. Sautet, Surf. Sci. 360 (1996) 128.
[2] S. Corbel, J. Cerdá, P. Sautet, Phys. Rev. B 60 (1999) 1989.
[3] M. Hidaka, T. Fujita, H. Nakai, H. Nakatsuji, Chem. Phys. Lett. 264 (1997) 371.
[4] G. Orlandi, A. Troisi, F. Zerbetto, J. Am. Chem. Soc. 121 (1999) 5392.
[5] M. Edelwirth, J. Freund, S.J. Sowerby, W.M. Heckl, Surf. Sci. 417 (1998) 201.
[6] F. Bloch, Z. Physik. 52 (1928) 555.
[7] S.H. Ke, T. Uda, K. Terakura, Phys. Rev. B 62 (2000) 15319.
[8] M. Causá, R. Dovesi, F. Ricca, Surf. Sci. 237 (1990) 312.
[9] U. Birkenheuer, J.C. Boettger, N. Rosch, J. Chem. Phys. 100 (1994) 6826.
[10] A. Kiejna, J. Peisert, P. Scharoch, Surf. Sci. 432 (1999) 54.
[11] J.C. Boettger, Mater. Res. Soc. Symp. Proc. 492 (1998) 157.
[12] J.C. Boettger, U. Birkenheuer, S. Kruger, N. Rosch, S.B. Trickey, Phys. Rev. B 52 (1995) 2025.
[13] J. Neugebauer, M. Scheffler, Phys. Rev. B 46 (1992) 16067.
[14] V.R. Saunders, R. Dovesi, C. Roetti, M. Causá, N.M. Harrison, R. Orlando, C.M. Zicovich-Wilson, CRYSTAL98 User's Manual, University of Torino, Torino, 1998.
[15] J.R. Lomas, C.J. Baddeley, M.S. Tikhov, R.M. Lambert, Langmuir 11 (1995) 3048.
[16] L. Triguero, Y. Luo, L.G.M. Pettersson, H. Ågren, P. Väterlein, M. Weinelt, A. Föhlisch, J. Hasselström, O. Karis, A. Nilsson, Phys. Rev. B 59 (1999) 5189.
[17] L. Triguero, A. Föhlisch, P. Väterlein, J. Hasselström, M. Weinelt, L.G.M. Pettersson, Y. Luo, H. Ågren, A. Nilsson, J. Am. Chem. Soc. 122 (2000) 12310.
[18] M. Weinelt, N. Wassdahl, T. Wiell, O. Karis, J. Hasselström, P. Bennich, A. Nilsson, J. Stöhr, M. Samant, Phys. Rev. B 58 (1998) 7351.
[19] J.R. Lomas, C.J. Baddeley, M.S. Tikhov, R.M. Lambert, Chem. Phys. Lett. 263 (1996) 591.
[20] S. Haq, D.A. Kind, J. Phys. Chem. 100 (1996) 16957.
[21] P.W. Kash, M.X. Yang, A.V. Teplyakov, G.W. Flynn, B.E. Bent, J. Phys. Chem. B 101 (1997) 7908.
[22] M. Doering, J. Buisset, H.-P. Rust, B.G. Briner, A.M. Bradshaw, Faraday Discuss. 105 (1996) 163.
[23] M. Doering, H.-P. Rust, B.G. Briner, A.M. Bradshaw, Surf. Sci. 410 (1998) L736.
[24] M. Bader, J. Haase, K.-H. Frank, C. Ocal, A. Puschmann, J. Phys. Coll. C 8 (1986) 491.
[25] R. Schuster, I.K. Robinson, Phys. Rev. Lett. 76 (1996) 1671.
[26] L.G.M. Pettersson, H. Ågren, Y. Luo, L. Triguero, Surf. Sci. 408 (1998) 1.
[27] L. Triguero, L.G.M. Pettersson, B. Minaev, H. Ågren, J. Chem. Phys. 108 (1998) 1193.
[28] J.R. Lomas, G. Pacchioni, Surf. Sci. 365 (1996) 297.
[29] P.S. Weiss, D.M. Eigler, Phys. Rev. Lett. 71 (1993) 3139.
[30] J. Tersoff, D.R. Hamann, Phys. Rev. B 31 (1985) 805.
[31] D. Vogtenhuber, R. Podloucky, J. Redinger, E.L.D. Hebenstreit, W. Hebenstreit, U. Diebold, Phys. Rev. B. 65 (2002) 125411.
[32] F.E. Olsson, M. Persson, N. Lorente, L.J. Lauhon, W. Ho, J. Phys. Chem. B 106 (2002) 8161.
[33] F. Máca, Surf. Interface Anal. 27 (1999) 555.
[34] P. Mutombo, V. Cháb, Surf. Sci. 532–535 (2003) 645.
[35] P. Sautet, C. Joachim, Chem. Phys. Lett. 185 (1991) 23.
[36] P. Sautet, M.-L. Bocquet, Phys. Rev. B 53 (1996) 4910.
[37] P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26 (1930) 376.
[38] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[39] K. Doll, N.M. Harrison, Chem. Phys. Lett. 317 (2000) 282.
[40] J. Muscat, N.M. Harrison, G. Thornton, Phys. Rev. B 59 (1999) 2320.
[41] M.E. Straumanis, L.S. Yu, Acta Crystallogr. A 25 (1969) 676.
[42] S. Narasimhan, S. de Gironcoli, Phys. Rev. B 65 (2002) 64302.
[43] M.J.S. Dewar, Bull. Soc. Chim. France 18 (1951) C71.
[44] J. Chatt, L.A. Duncanson, J. Chem. Soc. (1953) 2939.