A density functional theory investigation of the molecular and dissociative adsorption of hydrazine on defective copper surfaces

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This document contains additional information that has been omitted from the main manuscript for brevity. The bulk of this is extra details of molecular adsorption geometries that may give a more detailed insight into the adsorption behaviours but are summarised in the main manuscript. The three sections are: The electronic structure of the bare copper surfaces with adatoms; the geometries of the molecularly adsorbed hydrazine; and features of the electronic structure of adsorbed hydrazine.

S.1 Electronic structure of adatoms

The site-projected electronic Density of States (DOS) of the adatom and the surface atoms, shown in Figure S1, indicates the difference between the atomic environments of the copper atoms. On the (111) surface there is a much greater density of lower energy states for atoms with bulk coordination, and the distribution of states is pushed to higher energies for the surface atoms, although both show a similar range of energies down to more than -5 eV below the Fermi level. For the adatom the density is much lower in the -3 eV to -5 eV range and instead the higher energy states around -1.5 eV contain the majority of the density.

The DOS for the (100) surface again shows differences between the atomic environments, although they are not as marked as on the (111) surface. There is a greater density of lower energy

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Figure S1: The DOS of bulk, surface and a datom environments on the $(111),\ (100)$ and (110) surface.



Figure S2: Trans **111: b** and gauche **111: c** conformers adsorbed at the (111) adatom atop site have almost the same adsorption energies; an intermediate rotation **111: d** has a similar adsorption energy.

(<-3 eV) states for the bulk atoms, whereas the states above -2 eV have a higher density for the surface atoms, and are greatest for the adatom.

As with the other surfaces, the DOS for the (110) surface shows the greatest density of lower energy states for the bulk-like atoms. On this surface, however, there is a much greater similarity between the surface atoms and the adatoms. The DOS for both shows almost the same shape, with only a slightly higher density of the lower energy states around -3.5 eV visible for the surface atoms. In the range above -2 eV the adatom does not show the much greater density over the surface atoms that is seen on the (111) and (110) surfaces.

S.2 Molecular adsorption

S.2.1 The (111) surface

The different conformations of hydrazine derived from the position of the strongest adsorption configuration on the adatom are shown in Fig. S2.

With the molecule adsorbed away from the adatom the adsorption energy is significantly lower. In these geometries, Fig. S3 111: f and 111: g, there is minimal interaction with the adatom, and they are similar to isolated adsorption on the flat surface. The preferred geometry is one where a single nitrogen atom interacts with the surface copper atom and the molecule is pointing up at an angle of 27° to the surface. The calculated adsorption energy, at -0.52 eV, is about half that of the molecule adsorbed on the adatom. Again, the adsorption energy is found to remain



Figure S3: Gauche 111:g and trans 111:f conformers adsorbed on the flat (111) surface with minimal interaction with the adatom.

almost unchanged between the gauche and trans conformers, with the adsorbed molecules having very similar overall orientations; the trans conformer is only 2° more inclined to the surface with a 0.02 Å larger Cu–N distance. The Cu–N bond distance is longer than when the nitrogen is bound to the adatom, at 2.12 Å for **111:f** in the shortest case.

Bridging configurations, with both the nitrogen atoms of the hydrazine interacting strongly with two nearest neighbouring surface copper atoms, are found to be less favourable than adsorption at the same position, but with the molecule adsorbed on only a single surface copper atom. For the most stable bridging geometry on the flat surface, Fig. S4 111: h, the adsorption energy is 0.04 eV less than the singly bound molecule at the same position 111: f. The torsional angle of the molecule has changed significantly to reduce the interaction of the hydrogen atoms with the surface and to allow the nitrogen atoms to bond closer to the surface. The rotation of 32° from the relaxed gauche conformer towards an unfavoured eclipsed conformer results in the nearest hydrogen atoms lying at the same height above the surface as the nitrogen atoms, in an almost planar arrangement. The Cu–N distances, at 2.18 Å and 2.22 Å, are both longer than where there is only a single interaction.

Where the adsorbed molecule is bridging the adatom with the surface atom, Fig. S4 111: e, the adsorption is stronger than adsorption on the flat surface, although it is still 0.16 eV weaker than



Figure S4: Hydrazine bridging (111) flat surface atoms 111:h and bridging the surface with the adatom 111:e showing weaker adsorption than non bridging geometries.

when the molecule is adsorbed to the adatom only. The Cu–N distances are 2.08 Å to the adatom, and 2.28 Å to the surface, indicating that a stronger interaction is formed with the adatom. The N–N bond has also rotated 13° from the ideal gauche conformer towards the eclipsed conformation to accommodate this geometry.

S.2.2 The (100) surface

On the (100) surface, molecular adsorption is again strongest onto the adatom. Different conformations of the hydrazine on the strongest adsorption site are shown in Fig. S5.

In contrast to previous work¹, a bridging geometry is found to be the most stable adsorption configuration on the planar surface, where the presence of the adatom and the larger cell size used in the present calculations are likely to be important factors in stabilising the adsorption geometry found here. The configuration for the most strongly bound bridging molecule is shown in Fig. S6 100: d, where the molecule lies flat on the surface with a torsion of 30° from gauche towards the eclipsed conformer. In this position the nitrogen atoms are at a distance of 2.13 Å and 2.14 Å from the surface copper, which is longer than the Cu–N distance for a single Cu–N interaction, but shorter than the bridging mode on the (111) surface. To account for the high adsorption energy



Figure S5: Gauche **100**: **b** and trans **100**: **c** conformers adsorbed at the (100) adatom atop site have similar adsorption energies; the eclipsed conformer, **100**: **j** has a significantly weaker adsorption energy.

other factors must be considered; for example, although the molecule is not directly bound to the adatom there will be other interactions through its hydrogen atoms that are only 2.7 Å away from the adatom. The effect of the adatom can be noted from the decrease in adsorption energy, when hydrazine is bridging surface atoms in the same geometry but at a different offset from the adatom, shown in Fig. S6 100: e. Another effect, which would not be seen in a smaller cell, is lateral relaxation of the surface atoms to accommodate the adsorbed molecule. In this case the Cu–Cu distance has widened by 0.05 Å (nearly 2% of their equilibrium separation) between neighbours where the hydrogen atoms are nearest the surface. This extra relaxation would allow for a closer, stronger binding, with the molecule able to relax further towards the gauche conformation; it will, however, not have been seen in the earlier work due to the periodic constraints of a smaller cell.

Unlike the (111) surface, where the molecule is bridging between the adatom and a surface atom, it is less strongly bound than when it bridges only between surface atoms. Figure S7 shows the configurations where hydrazine is bridging to the copper closest to the adatom 100: g and to a surface atom further away 100: f, where the latter configuration is more favourable. Whilst hydrazine in 100: g is bound more closely to the copper atoms, at 2.10 Å to the adatom and 2.25 Å to the surface, compared to 2.18 Å and 2.32 Å in 100: f, it is torsionally rotated 23° towards the eclipsed conformer which is energetically less favourable than 100: f, which is only rotated 6° from a gauche conformation.

On the (100) surface, molecular adsorption by a single nitrogen atom, without bridging, leads to the weakest binding to the surface, although the differences in adsorption energies are quite small.



Figure S6: Hydrazine bridging copper atoms on the flat (100) surface. The decrease in adsorption strength from the position in 100: d to 100: e indicates that the molecule is not completely isolated from the adatom.



Figure S7: Hydrazine bridging copper atoms on the (100) surface with the adatom. A molecule held more closely to the copper **100**: **g** is more weakly bound than the molecule that is able to remain torsionally closer to the gauche conformation by bridging with an atom further away **100**: **f**.



Figure S8: With the hydrazine only interacting strongly with a single surface copper atom on the (100) surface, the trans conformer **100: h** is very slightly more strongly adsorbed than the gauche conformer **100: i**.

Figure S8 depicts the trans 100: h and gauche 100: i conformers in their low energy geometries. The adsorption energies are similar and, in this case, the trans conformer is bound only slightly more strongly as demonstrated by the marginally shorter Cu–N distance of 2.09 Å compared to 2.11 Å for the gauche conformer. Whilst care has been taken to minimise the interaction of the molecule with the adatom in these configurations there will still be a weak interaction affecting the different geometries.

S.2.3 The (110) surface

As noted in previous work¹, the bridging configuration does not lead to as strong an adsorption, when the molecule is aligned with the long axis Fig. S9 110: f. The required torsion in the minimum energy structure is only 14° from the gauche conformer, but the wide bridging geometry results in other effects that make the structure non-ideal. The equilibrium spacing of the rows of atoms on the (110) surface is 3.63 Å, but where the rows are bridged by the hydrazine they have contracted to a separation of 3.56 Å. Even with these displacements the Cu–N distances are still lengthened to 2.15 Å and 2.22 Å. The orientation of the molecule is also rotated significantly from the line joining the bonded atoms, with the Cu–N bonds offset from the atop sites of the surface atoms. The combination of these geometric effects results in an adsorption that is less favourable than having the molecule aligned along the short edge of the cell.



Figure S9: Adsorption to the (110) surface is strongest on the flat surface in a geometry where the molecule is aligned with the short axis of the cell **110: b**. Having the molecule aligned with the long axis gives a lower strength adsorption **110: f**

Similar to the other surfaces, the strongest adsorption of the hydrazine to the adatom is found with the molecule adsorbed by a single nitrogen atom on the adatom atop site, shown in Fig. S10, with the molecule in either the gauche **110**: **c** or the trans **110**: **d** conformer. Again the N–H bonds tend to direct either or both of the hydrogen atoms towards the surface. For the gauche conformer there is a small torsion of 7°, which leaves the molecule with a hydrogen atom directed towards a surface copper atom at a distance of about 3 Å, a similar separation to that seen on the other surfaces. The trans conformer has both hydrogen atoms pointing down at a similar distance from the surface atoms, although the molecule has a different orientation in the cell to achieve this geometry. In both cases the Cu–N distance is 2.04 Å.

The hydrazine bridging the adatom with a surface atom gives an adsorption that is slightly weaker than a molecule bridging only the surface atoms. When bridging to the nearest and second nearest neighbours the copper atoms undergo displacements that bring the optimum structures geometrically closer to each other than they would be with rigid surface structures. These extensive displacements will be large factors in the lessening of the adsorption energy in these geometries.

The more favourable of the two adsorbed configurations has the molecule bridging to the nearest atom, shown in Fig. S11 110: g. To accommodate the molecule, the copper atoms have moved



Figure S10: Adsorption to the adatom on the (110) surface gives similar adsorption for the gauche 110: c and trans 110: d conformations of the hydrazine.

significantly to increase their separation from 2.50 Å to 2.75 Å. The hydrazine molecule is also torsionally rotated by 25°, but in this geometry the Cu–N distances are 2.18 Å and 2.10 Å, which is very close to the other configurations.

Bridging to the second nearest neighbour, as shown in Fig. S11 110: h, also causes significant displacement of the surface atoms. In this case the bridged atoms move to reduce their separations from 4.42 Å to 3.97 Å. The Cu–N distances, however, still remain slightly larger than in other configurations at 2.20 Å and 2.24 Å. The molecule in this case is less distorted and is only rotated 5° from the gauche conformer.

Adsorption to a single surface copper atom for the gauche conformer, shown in Fig. S12 110: e, is found to release about as much energy as adsorption to the adatom on the (110) surface. The molecule remains very close to the gauche conformation and the Cu–N distance is similar to that with the molecule bound to the adatom at 2.07 Å. Conversely the trans conformer has a relatively low adsorption strength (Fig. S12 110: i). In this geometry, the molecule is pointing up by 23° (compared to 5° when it is attached to the adatom), although the hydrogen atoms are still only about 2.7 Å from the surface copper atoms, and the steric repulsion forces with the surface will weaken the adsorption.



Figure S11: Bridging the adatom to the nearest neighbour 110: g and second nearest neighbour 110: h causes significant displacements of the surface atoms to accommodate the molecules resulting in slightly weaker adsorption than when bridging the flat surface.



Figure S12: The gauche conformer adsorbed on the surface gives a similar strength adsorption at to when it is adsorbed on the adatom **110**: **e**. The trans conformer is more weakly bound on this surface **110**: **i**.

	Geometry	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	$\rm Cu_{ads}$ / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e
111: a				0.12		
111: b	trans	-1.09	-0.14	-0.02	-0.11	
111: c	gauche	-1.09	-0.41	0.20	-0.02	
111: d	twisted	-1.06	-0.22	0.21	-0.35	
111: f	trans	-0.52	-0.34	0.15	-0.28	
$111: \mathbf{g}$	gauche	-0.52	-0.03	0.06	-0.43	
111: h	bridge	-0.49	-0.21	-0.07	-0.19	0.13
111: e	bridge	-0.93	-0.34	0.08	-0.24	0.18

Table 1: Bader charges of atoms for molecularly adsorbed hydrazine on the (111) surface with an adatom present. Columns are ordered with the closest copper atom following the nitrogen atom. Where the copper is the adatom the charge is **emphasised**.

S.3 Electronic structure of adsorption

S.3.1 The (111) surface

Although the energy of adsorption is similar for different rotational conformers adsorbed on the adatom, the electronic configuration of the molecule differs in each case. The nitrogen atom is donating charge onto the surface through its lone pair of electrons. The way in which this charge is partitioned can give an idea of the strength of the bond. The Bader charges in Table S1 show that the charge difference between the nitrogen and the adatom for the gauche configuration, **111:c**, is greater than in the trans case, **111:b**, although the converse is true when the molecule is bound to the surface in **111:f** and **111:g**. The gauche conformer shows the greatest charge difference between the two nitrogen atoms within the molecule in both cases.

The DOS shows how the electronic structure is affected by the interactions with the surface. Plotting only the p-band states on the nitrogen atoms shows an asymmetry for the gauche conformation, where the nitrogen bound to the copper atom has the higher density of lower energy states. In comparison, the states for the trans conformer show a greater symmetry. Whilst Fig. S13 shows the DOS for the molecule attached to the surface, the same effect is seen for the configurations where the molecule forms a single Cu–N bond, except that in the case of binding to the adatom the distribution of states is shifted to lower energies.

Exploring the charge density involved in the Cu-N interaction shows the differences in the



Figure S13: The DOS for the p-band states projected onto the nitrogen atoms with the hydrazine molecule adsorbed on the (111) surface. The density is shown for the gauche 111:g and the trans 111:f conformations.



Figure S14: Charge density (left) and ELF (right) showing the slice through the Cu–N bond and the molecule for the gauche conformer on the adatom 111: c and on a surface atom 111: g on the (111) surface.

strength of the bonding. Figure S14 shows slices through the C–N bond of both the charge densities and Electron Localisation Function (ELF) of the gauche molecule on the adatom and surface atom. The charge density in the bond is clearly greater when hydrazine is bonded to the adatom, which is also apparent from the more extensive region of localisation. The slices also cut partially through the region of N–H bond localisation and show the extent of the influence of the localised electrons, which is closer to the surface than the charge density alone might suggest. For the hydrogen facing the surface the outer edge of the region of localisation is compressed slightly compared to that of the hydrogen facing outward into the vacuum.

The electronic structures of the bridging configurations are shown in Fig. S15. The charge densities show that there is symmetry in the bonding to the surface atoms in 111: h, which contrasts with 111: e where the stronger bonding to the adatom is shown by the greater charge density involved in the Cu–N bonding. In the DOS, in the same figure, the electronic structure is identical for both of the nitrogen atoms and for both of the copper atoms to which they are bonded, when bridging the planar surface atoms. When bridging to the adatom the distribution of states is different for the two nitrogen atoms; the peak at $\sim 6 \text{ eV}$ is particularly strong for the nitrogen bonded to the adatom, which is also shown in a resonant peak on the adatom, whereas there is more density for the states at a slightly higher energy on the nitrogen bonded to the surface. The Bader charges in both bridging cases are similar, although the stronger adsorption to the adatom

	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e
111: i	-2.37	-0.12	0.42	0.01	-0.66	0.42	0.10
111: j	-2.10	-0.35	0.34	-0.17	-0.20	0.34	-0.18
111: k	-1.51	-0.61	0.35	0.13	-0.39	0.30	0.15
111: l	-1.26	-0.71	0.32		-0.50	0.07	0.28
111: m	-1.20	-0.39	0.11	0.13	-0.60	0.08	0.27

Table 2: Bader charges on atoms for dissociated adsorption on the (111) surface with an adatom present. The columns are ordered with each nitrogen atom followed by the two copper atoms to which it is bound. Where the copper atom is the adatom the charge is **emphasised**.

Table 3: Bader charges of atoms for molecularly adsorbed hydrazine on the (100) surface with an adatom present. Columns are ordered with the closest copper atom following the nitrogen atom. Where the copper is the adatom the charge is **emphasised**.

	Geometry	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	$\rm Cu_{ads}$ / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e
100: a				-0.35		
100: b	gauche	-0.97	-0.24	0.14	-0.29	
100: c	trans	-0.96	-0.36	0.36	-0.24	
100: j	eclipsed	-0.49	-0.47	0.15	-0.22	
100: d	bridge	-0.86	-0.09	0.03	0.12	-0.44
100: e	bridge	-0.80	0.15	0.04	-0.25	0.04
100: f	bridge	-0.72	-0.24	0.08	-0.41	0.30
100: g	bridge	-0.76	-0.25	-0.07	-0.11	0.23
100: h	trans	-0.71	-0.44		-0.32	-0.09
100: i	gauche	-0.71	-0.19		-0.31	-0.01

leads to a greater difference between the nitrogen and the copper.

S.3.2 The (100) surface

As on the (111) surface, the adsorption on (100) is characterised by the copper atom to which the nitrogen is bound taking a positive charge and the bonded nitrogen having a negative charge. Table S3 shows the Bader charges on the atoms for the molecularly adsorbed hydrazine.

There is a clear difference in the DOS for the different conformers when they are bonded to the adatom. From Fig. S16 the trans conformer 100: c shows the greatest symmetry in the p-band states for the nitrogen atoms, with only a slight bias towards the higher energy states seen for the



Figure S15: Slice through the charge density (left) showing both Cu–N bonds for the molecule bridging surface atoms **111: h** and bridging the surface with the adatom **111: e**. Also shown are the DOS for interacting Cu d-band and N p-band states in each configuration (right).



Figure S16: The electronic DOS for the trans **100**: **c** and gauche **100**: **j** and gauche **100**: **b** conformations of the molecule when bonded to the adatom on the (100) surface. States in the p-band are shown for the nitrogen bonded to the adatom and the unbound nitrogen, with the d-band states shown for the copper adatom.

outer nitrogen atom. The eclipsed conformer 100: j has less symmetry in the states; there is a greater bias towards the higher energy states on the outer nitrogen. The gauche conformer 100: b, on the other hand, has distinct states for each nitrogen atom, but also shows significantly more resonance in the copper d-band states.

The ELF demonstrates, in Fig. S17, the effect of the torsional rotation of the molecule on the lone electron pair on the outer nitrogen atom. The eclipsed conformer 100:j has the lone electron pair pointing down at the surface and the slice through this region indicates that it is fairly constrained in this position. The outer region of localisation is particularly compressed near the surface. In comparison the localisation of the lone pair on the trans conformer 100:c, which has the lone electron pair pointing directly up and away from the surface, extends much further into the vacuum as the outer edge is not constrained.



Figure S17: Slices through the ELF of hydrazine bonding to the adatom on the (100) surface. Lone pair localisation is shown for the eclipsed **100: j** and trans **100: c** conformations of the molecule.

Bridging configurations show the difference between the bonding to the adatom and to the surface atom. The details of the electronic structure are summarised in Fig. S18. Bridging the two surface atoms, 100: d, gives identical electronic configurations for both the nitrogen atoms. The strength of the bonding interaction, indicated by the charge density in the bonding, is also equal for both the Cu-N interactions. The two configurations with bridging from the surface to the adatom give different results. The charge density slices show that geometry of the Cu–N–N–Cu bridge is being pushed closer or pulled apart compared to bonding with the surface atoms only. In both of these cases the charge density involved in the bonding with the adatom is greater than with the surface, although the difference is not as large as on the (111) surface. Both structures also show asymmetry in their DOS. The wide bridge 100: f has states at ~ -5 eV, with the nitrogen bonded to the surface having states at slightly higher energies and the nitrogen bonded to the adatom having states at lower energies. For the short bridge, **100**: **g** the split is even more pronounced. The lower energy states are pushed down to $-6 \,\mathrm{eV}$, although the density of these states is similar for both nitrogen atoms, with the one bonded to the adatom having only marginally greater density in the lower energy states. In both structures the greatest resonance of copper states with the bonding nitrogen states is shown for the adatom.



Figure S18: Slice through the charge density (top) showing both Cu–N bonds where the hydrazine is bridging surface atoms **100**: **d**, bridging the adatom with the nearest surface atom **100**: **f** and bridging the adatom with the second nearest surface atom **100**: **g**. Also shown are the DOS for interacting Cu d-band and N p-band states in each configuration (bottom).

Table 4:	Bader ch	arges on	atoms fo	or dissocia	ated ads	sorption	on the	(100)	surface	with a	in adat	tom
present.	The colu	mns are	ordered v	with each	nitroge	en atom	followe	d by t	he two	copper	atom	s to
which it	is bound.	Where t	he coppe	r atom is	the ada	atom the	e charge	e is en	iphasis	ed.		

	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e
100: k	-2.46	-0.50	0.35	-0.16	-0.38	0.35	0.10
100:l	-2.10	-0.85	0.39	0.04	-0.73	0.39	0.10
100: m	-1.95	-0.50	0.14	0.12	-0.76	0.27	-0.03
100: n	-1.89	-0.86	0.19	0.25	-0.83	-0.04	0.19
100: o	-1.71	-0.75	0.32		-0.88	0.07	0.08

	Geometry	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	Cu_{ads} / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e
110: a				-0.03		
110: b	bridge	-1.11	-0.47	0.09	-0.45	0.0582
110: f	bridge	-0.83	-0.29	-0.16	-0.34	-0.1129
110: c	gauche	-0.87	-0.23		-0.09	-0.81
110: d	trans	-0.87	-0.38		-0.24	-0.14
110: h	bridge	-0.82	-0.23	0.17	-0.21	0.16
$110: \mathbf{g}$	bridge	-0.80	-0.64	-0.69	-0.05	0.16
110: e	gauche	-0.86	-0.46	0.35	-0.32	
110: i	trans	-0.79	-0.55	0.38	-0.34	

Table 5: Bader charges of atoms for molecularly adsorbed hydrazine on the (110) surface with an adatom present. Columns are ordered with the closest copper atom following the nitrogen atom. Where the copper is the adatom the charge is **emphasised**.

S.3.3 The (110) surface

The charges in each system are collected in Table S5 for the molecularly adsorbed species and in Table S6 for the dissociated adsorption.

A comparison of the bridging molecular structures in Fig. S19 shows that the charge density involved in the Cu–N interactions is almost identical for bonding to the surface and to the adatom. The molecule bridging with the nearest 110: g and the second nearest 110: h surface copper atoms from the adatom both show that the distribution of charge density is indistinguishable for the two bonds. These can be compared to the structures bridging the surface atoms, which shows that the most distinguishing feature between these structures is the overall geometry and not different strengths of Cu–N bonding. The most stable configuration 110: b shows a small displacement of the surface atoms, showing that although the (110) surface provides the most ideal arrangement for adsorbing the molecule in this study, it still does not obtain perfect registry between the surface and the molecule. The wide reach of the molecule over the rows of copper atoms on the (110) surface is shown for the other bridging structure 110: f. The configuration in 110: h also shows a wide bridging arrangement with displacement of the adatom and the bonded surface atom as they are pulled together. In comparison 110: g shows a much shorter bridge where the adsorption is pushing the copper atoms apart.

The DOS also confirms that the bonding environments for surface atoms and the adatom are similar, though not completely identical. Figure S20 shows the states for several different configura-



Figure S19: Slices through the charge density of the bonding interaction of hydrazine with the (110) surface for bridging configurations. Bridging the adatom to the nearest surface atom 110: g and to the second nearest surface atom 110: h compared with the strongest adsorbed short bridging geometry between surface atoms 110: b and the weaker long bridge 110: f.



Figure S20: The DOS for nitrogen p-band states and copper d-band states where the hydrazine molecule is bridging surface atoms **110**: **b**, and bridging the adatom with a surface atom in a short **110**: **g** and a long **110**: **h** geometry.

tions of adsorption. Bridging of the surface atoms in **110**: **b** gives an identical DOS for both nitrogen and copper pairs. Very slight differences are, however, visible where bridging to the adatom occurs. In the short bridge arrangement, **110**: **g**, the distribution of the states on both the nitrogen atoms shows the same shape, but the density is pushed slightly to the higher energies on the nitrogen bonding to the surface. Conversely, in the long bridging configuration, **110**: **h**, it is the distribution of states on the nitrogen bonded to the adatom that is pushed to the higher energies.

The full set of Bader charges for the adsorption of the dissociated molecule on the (110) surface is given in Table S6.

References

[1] T. D. Daff, D. Costa, I. Lisiecki, and N. H. de Leeuw, J. Phys. Chem. C 113, 15714 (2009).

Table 6: Bader charges on atoms for dissociated adsorption on the (110) surface with an adatom present. The columns are ordered with each nitrogen atom followed by the two copper atoms to which it is bound. Where the copper atom is the adatom the charge is **emphasised**.

	$\rm E_{ads}$ / eV	${\rm N}_1$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e	$\rm N_2$ / e	$\rm Cu_{ads}$ / e	$\rm Cu_{ads}$ / e
110: j	-2.66	-0.46	0.28	0.32	-0.77	-0.14	0.13
110: k	-2.61	-0.65	-0.92	0.51	-0.81	0.33	0.36
110:l	-2.54	-0.61	0.58	0.18	-0.97	0.58	0.27
110: m	-2.27	-0.50	0.03	0.63	-0.36	-0.66	0.63
110: n	-2.25	-1.04	0.49	0.32	-0.96	0.49	0.37