Theoretical Study of Chemisorption of Acetylene on the Cu(100) Surface

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The chemisorption of acetylene on the Cu(100) surface has been studied by molecular orbital calculations of the extended Hückel type. Separating the adsorbate–surface interaction into different components, it was found that the overlaps of the π orbitals of acetylene with the s and p_z orbitals of copper at the surface are the main sources of this interaction. Electron transfer from metal to adsorbate leads to significant weakening of the C—C bond. However, it is the covalent interaction which accounts for most of the adsorbate–surface stabilization.

The chemisorption of hydrocarbons on metal surfaces is an important and challenging aspect of surface science. One obstacle to a theoretical treatment of chemisorption is that the geometry of the adsorbate and the nature of the adsorption site are often uncertain. The uncertainty is both theoretical and experimental. While *ab initio* calculations with geometrical optimization of the adsorbate for all possible adsorption sites remain still mostly out of reach, neither are the experimental results always definitive. According to Zangwill, 'no adsorbate structure determination should be trusted until it is shown to be consistent with a battery of surface structural probes.'[1]
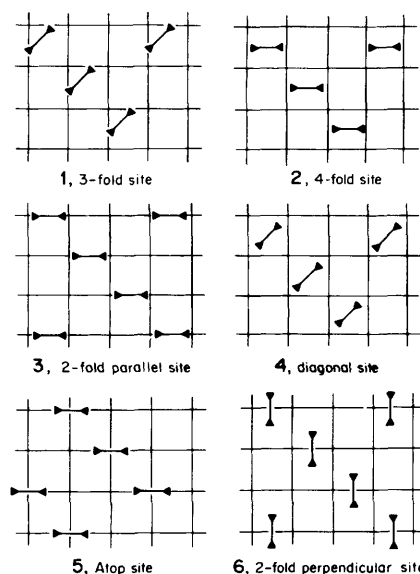
It was thought that acetylene was only slightly distorted on the Cu(100) surface.[2] A recent study by high-resolution electron energy loss scattering (HREELS) revealed, however, a strongly perturbed adsorbate with a C—C bond order of *ca.* 1.5. The vibrational spectra of acetylene obtained by this method for the three surfaces Cu(111), Cu(110) and Cu(100) are similar, implying a common adsorption site. This is probably the two-fold bridging site with the C—C bond either parallel or perpendicular to the Cu—Cu bond on the surface.[3] Results from near-edge extended X-ray absorption fine structure (NEXAFS) indicated a C—C bond parallel to the Cu(100) surface. The bond length determined by this method was found to be 1.41 Å.[4] Surface-extended X-ray absorption fine structure (SEXAFS) data gives a similar bond length (1.42 Å), suggesting the shortest Cu—C distance to be 1.86 Å, and a three-fold adsorption site.[5] Finally decomposition of acetylene on Cu(100) was reported.[6] Although the preferred adsorption site may still not be totally certain, the interaction between acetylene and the Cu(100) surface seems to be quite strong. There was a Hartree–Fock study on this issue,[7] but it did not resolve completely the problem of alternative adsorption sites.

In order to gain further insight into acetylene–copper binding, we have carried out some molecular orbital calculations based on the tight-binding approach within the extended Hückel formalism.[8,9] Since optimizations of bond length are generally unreliable for our method, the C—C and C—Cu bond length are taken from SEXAFS data[5] and are kept fixed for all calculations. The hydrogen positions, which are not reported experimentally, may be determined by optimization of the C—C—H bond angle, assuming a C—H bond length of 1.09 Å. The Cu(100) surface is an f.c.c. structure with C_{4v} symmetry. The nearest Cu—Cu distances are set to be 2.55 Å. For reasons of economy, the calculations were done on a three-layer metal slab with a coverage of $\frac{1}{2}$ on one side of the slab only. We will refer to this covered layer hereafter as the surface layer. For other computational

details, please refer to the Appendix. A description of the theoretical and analytical tools used in this paper may be found in a recent book.[10]

General Features of the Bonding

Altogether six adsorption sites were studied. Their top views are shown in **1** to **6**.

1, 3-fold site

2, 4-fold site

3, 2-fold parallel site

4, diagonal site

5, Atop site

6, 2-fold perpendicular site

In table 1 we present some of the computed bonding characteristics of various adsorption sites. The energies in these calculations are computed as a simple one-electron sum of the energies of the occupied orbitals. Studies of many organic, inorganic discrete molecules and extended systems have shown that extended Hückel method is moderately reliable; it tends to give trends in bonding preferences and electron shifts approximately correctly, but the actual magnitudes may be far astray.[11] The binding energy per unit cell is defined so that a positive binding energy means attraction.

The C—C overlap population for acetylene, ethene and ethane at their equilibrium geometries are 1.928, 1.300 and 0.737, respectively. First let us mention some general trends. There is a large difference in binding energy between the first four adsorption sites and the last two, **5** and **6**, which are strongly disfavoured. The computed overlap populations point to a C—C bond order between 1.5 and 2. The optimum C—C—H bond angles for various adsorption sites corre-

Table 1. Optimized C—C—H angles, binding energies and C—C overlap populations for various adsorption sites

adsorption site	optimum C—C—H bond angle/°	binding energy/eV	C—C overlap population
3-fold, 1	120	0.36	1.054
4-fold, 2	120	0.28	1.034
2-fold parallel, 3	125	0.13	1.215
diagonal, 4	120	−0.01	1.115
atop, 5	140	−2.13	1.266
2-fold perpendicular, 6	130	−2.43	1.066

spond to a strongly rehybridized adsorbate. These two features are in agreement with the HREELS data.[6]

We next proceed to detailed analysis of the bonding sites, but before we do so, it is necessary to define some of the theoretical tools. The density of states (DOS) in our calculations is the number of a given type of orbital (molecular orbital, MO, atomic orbital, AO or fragment molecular orbital, FMO) per unit volume per unit energy. The DOS curve is a plot of energy as ordinate *versus* DOS as abscissa. Integration of the DOS curve with respect to energy up to a level E gives the number $N(E)$ of a particular type of orbital per unit volume below and up to E. The integral over the entire energy range gives the total number of orbitals per unit volume, N. One can graph $N(E)/N$, converted to percentage, *versus* energy. This we call 'the integration curve'. It indicates the percentage occupation of a given group of orbitals at any E. In all cases, the large dispersion of the total DOS of acetylene near the Fermi level indicates strong adsorbate–surface interaction.

Another indicator of interaction is the bond index, called the overlap population.[10] This is displayed either in differential form, as an overlap-population-weighted density of states called the COOP curve, or as an integrated sum up to Fermi level, the total overlap population. For the bare copper surface, the overlap populations between surface Cu–surface Cu, surface Cu–bulk Cu and bulk Cu–bulk Cu are 0.131, 0.102 and 0.084, respectively. The detailed calculations show, although this is not reported in table 1, that after adsorption there is little decrease in the overlap population for the last two types of bond but drastic reduction for the first type.

Three-fold Site, 1

This is the preferred adsorption site according to SEXAFS.

The optimum geometry is calculated with the molecular plane of the bent acetylene making an angle of 60° with the surface, 7.

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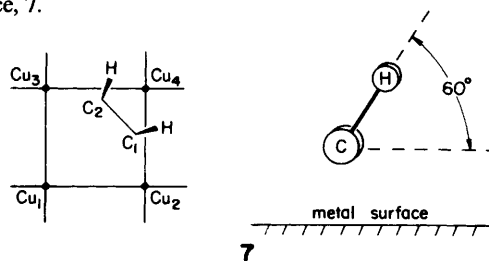
Fig. 1(a) shows the density of states (DOS) of a monolayer of acetylene arranged in the same geometry as the overlayer on the Cu(100) surface. The narrow bands of the monolayer indicate little adsorbate–adsorbate interaction. The band near −16 eV, belonging to a σ orbital, is only weakly perturbed for all adsorption sites and will be ignored hereafter. The four bands between −14 and −8 eV are due to the four π type frontier orbitals of acetylene,[12] sketched as **8**. Two of these π_σ and π_σ^*, mix in carbon s character as a result of HCC bending. They are expected to engage in σ bonding with the surface.
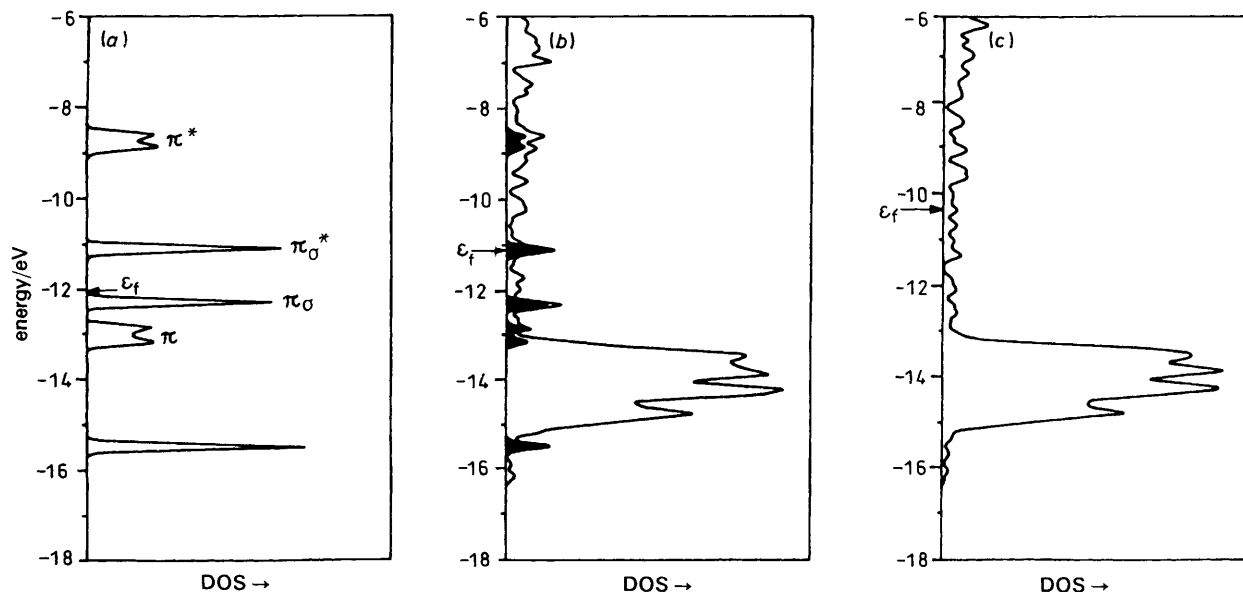

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Fig. 1. (a) DOS of a monolayer of acetylene in the absence of a metal surface. (b) Contribution of acetylene to the total DOS of the overall system where all covalent interactions have been turned off. (c) DOS of the three-layer slab of copper.
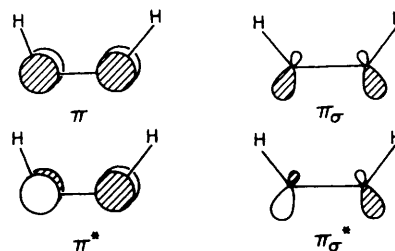
Table 2. Effect of the various contributions to acetylene bonding at the 3-fold site

	ionic	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.391	−0.005	0.141	0.453
C_1-Cu_2, C_2-Cu_3 overlap population	0	0.582	0.019	0.601
C_1-Cu_4, C_2-Cu_4 overlap population	0	0.046	0.239	0.285
stabilization of monolayer/eV	0.98	2.97	1.34	5.26
depopulation of π	0	0	0.501	0.367
depopulation of π_σ	0	0.533	0.004	0.531
population of π_σ^*	1.561	−0.345	0.056	1.251
population of π^*	0.004	0.097	0.175	0.207

The C—C overlap population (OP) for the monolayer is 1.507. In a free undistorted acetylene molecule with a C—C bond of 1.42 Å, it is 1.575. The difference is mainly due to bending of the hydrogens. It costs ca. 4.90 eV to form the monolayer from the free unstretched linear molecule (2.24 eV for stretching of C—C bond, 2.62 eV for bending and 0.04 eV because of small steric interactions of the acetylene molecules with each other).

When the monolayer is brought onto the surface, two things happen simultaneously:[13] (1) Electrons flow from the metal to fill any empty states of the adsorbate, should there be any such states below the Fermi level. We call this the ionic interaction or electron transfer. One way to estimate it computationally is by deleting all the overlaps between surface and adsorbate. Then electron transfer is allowed until the Fermi levels of the two components are the same. Fig. 1 shows the relevant density of states. In the present case, the π_σ^* band of the monolayer falls below the Fermi level of the free surface. Hence, the ionic interaction partially fills π_σ^*. It should be kept in mind, however, that the extended Hückel method generally exaggerates the electron flow.

(2) The orbitals of surface and the acetylene monolayer overlap and interact. The extent of dispersion of the bands of acetylene is then a rough measure of the degree of the interaction. This covalent bonding may be separated into σ and π contributions. The π part is due to π and π^* acetylene fragment orbitals. The σ part, defined as the complement of π, derives from all other remaining orbitals of acetylene. The main contributions to the σ part, however, come from π_σ and π_σ^* orbitals. The motive for this separation is that π and π^* are orthogonal to all other orbitals of the bent acetylene and surface induced mixing of these fragment MOs may be small. The σ part can be estimated by deleting only the overlaps between the acetylene π and π^* orbitals with the surface, and then subtracting out the ionic contribution. In a similar way, the π interaction may be estimated.

Table 2 shows the results of four calculations. The last column corresponds to allowing all the orbitals of acetylene to interact with the surface simultaneously. We want to stress that the three contributions defined above, while appearing separately as entries in table 2, are not strictly additive because of couplings between them. Thus, the sum of the ionic, σ and π contribution is not exactly equal to the last column, only roughly so. The π contribution particularly affects the electron occupation of the π_σ^* orbital by changing the Fermi level, and vice versa. There is, however, one important exception, namely the C—Cu OP. A technique has been developed which allows us to project out the individual contribution of each orbital to the overlap population. In this way, the errors due to mixing of orbitals are completely eliminated. All the C—Cu OP have been calculated by this method and their partitionings are accurate.

A small point worth noting in table 2, and one that will recur later with greater impact, is that even in the ionic interaction there is some filling of π^*. At first sight this seems strange because the π^* band is above the Fermi level of the

free surface (see fig. 1). So how can this level be occupied? Well, even in the isolated acetylene monolayer the site symmetry differs from that of a single C_2H_2 molecule. Therefore, π^* and π_σ^* can mix and they do, even if only a little. Thus, a small part of the π^* band comes below the Fermi level of the free metal surface and becomes occupied.

The population of π_σ^* by electron transfer (the ionic contribution) may be the main source of C—C bond weakening. From the C—Cu OP and the stabilization energy, it seems that σ interaction with Cu_2 and Cu_3 is the major contribution to the adsorbate–surface stabilization (see 7 for numbering of Cu atoms), but which orbitals of Cu_2 and Cu_3 are important in this context? If we turn off all the interactions between acetylene and the surface s and p orbitals, leaving just d overlaps, the maximum C—Cu OP among the six adsorption sites is only 0.056. The contribution of d orbitals to C—Cu bonding should therefore be small. There will be a lot of mixing between surface s and surface p_z, because even in the absence of adsorbate they have the same symmetry throughout the whole two-dimensional Brillouin zone. Hence, we apply our method of projection. Table 3 lists the projected OP for the nine orbitals of copper. In all cases, the s orbitals account for more than 55% of the total C—Cu OP. The second most important orbital is p_z. It contributes ca. 23% for the C_1—Cu_2 and C_2—Cu_3 OP; 15% for the C_1—Cu_4 and C_2—Cu_4 OP. In fact, after adsorption, the electron occupation of the surface s band decreases by ca. 10% and the median filling energy for that band is pushed up by 3 eV. The change in the surface p_z band, however, is less obvious.

In summary, the adsorbate–surface interaction can be represented schematically by fig. 2. Notice that because of couplings between the ionic, σ and π interaction, there is an inconsistency of 0.03 eV in the decomposition of the stabilization energy.

Fig. 3 shows the density of states of the four acetylene FMOs in the composite surface–acetylene adsorption complex. The stickers indicate the energies of the corresponding orbitals in the free distorted molecule. For easy comparison, all the DOS of the FMOs in the rest of this paper are magnified by the same factor, namely 30. π, π_σ and π_σ^* develop substantial dispersion, indicative of strong inter-

Table 3. Contributions of the metal orbitals to the C—Cu overlap populations at the 3-fold site

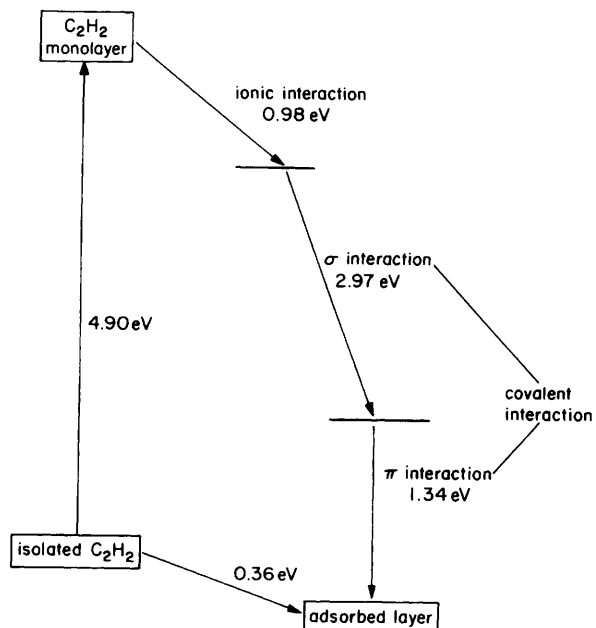| orbital	C_1—Cu_2	C_2—Cu_3	C_1—Cu_4	C_2—Cu_4
s	0.343	0.343	0.171	0.171
p_x	0.013	0.076	−0.002	0.042
p_y	0.076	0.013	0.042	−0.002
p_z	0.138	0.138	0.043	0.043
$d_{x^2-y^2}$	0.003	0.003	0.010	0.010
d_{z^2}	0.005	0.005	−0.007	−0.007
d_{xy}	0.002	0.002	−0.004	−0.004
d_{xz}	0.003	0.018	−0.006	0.038
d_{yz}	0.018	0.003	0.038	−0.006

Fig. 2. A schematic energy decomposition for the interaction of acetylene with the copper surface at the three-fold site.

action. π^* does not. While this interaction is not significant energetically here, this will be different in other adsorption sites. So it is interesting to trace the reasons for small interaction of π^*.

Consider the local environment of the adsorbate, as indicated in 9. The s and p_z orbitals of Cu_1 and Cu_4 are orthog-


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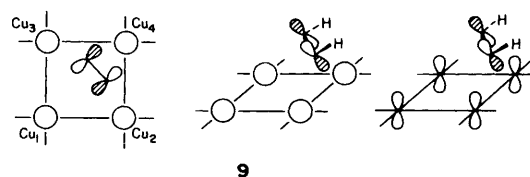
onal to π^*, while those of Cu_2 and Cu_3 are close to its nodal plane. Since these two types of orbitals are important in Cu—acetylene bonding, a smaller dispersion is expected. Note that, in principle, all orbitals of acetylene can mix with any orbitals of the surface at a general point of the Brillouin zone, so the conclusion drawn from local symmetry is not exact. The other three frontier orbitals of acetylene interact substantially, as may be seen from their dispersions. They probably account for most of the adsorbate–surface bonding. As a final comment, we would like to draw the readers' attention to the positions of the Fermi level. Strictly speaking, the Fermi level of a metal surface should remain unchanged after chemisorption. It does move in our calculations, from -10.34 eV in fig. 1(c) to -10.51 eV in fig. 3, owing to the finite thickness of the metal slab.

Four-fold Site, 2

The geometry and labelling of atoms is indicated in 10. The
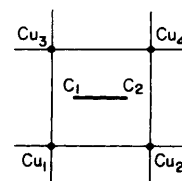
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symmetry constraint we noted above for the π^* in the three-fold site is now removed. Thus, π^* can overlap better with the s and p_z orbitals and takes a more important part in the C—Cu bonding. It should be more populated and show greater dispersion, as confirmed by fig. 4 and the electron occupation in table 4. The dispersions of the other three frontier orbitals are comparable to that of π^*. Therefore, unlike
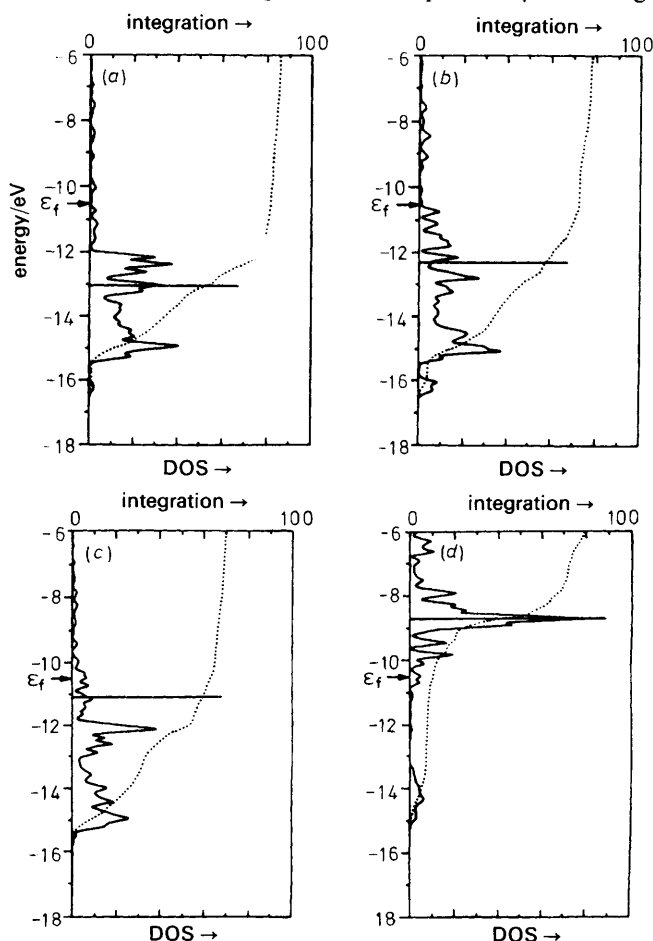

Fig. 3. (a)–(d): DOS and integration curves of the four FMOs, π, π_σ, π_σ^* and π^* at the three fold site. ε_f mark the positions of the respective energy levels in the free acetylene.
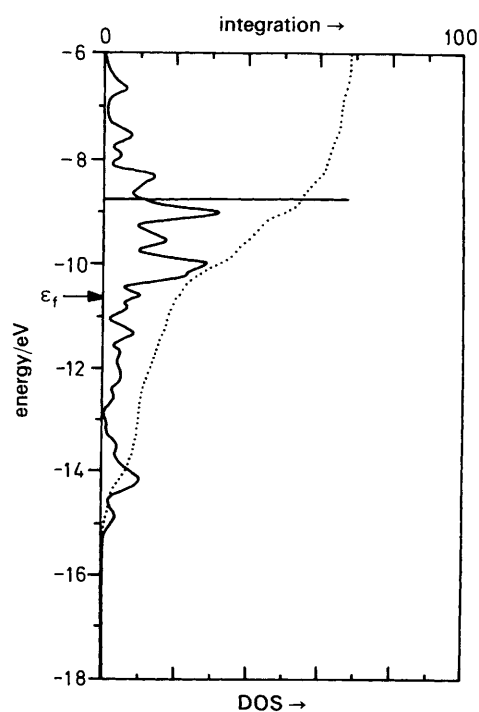

Fig. 4. DOS and integration curve for the π^* at the fourfold site.

Table 4. Effect of the various contributions to acetylene bonding at the 4-fold site

|	ionic	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.255	0.026	0.223	0.492
C_1—Cu_1, C_2—Cu_4 overlap population	0	0.341	0.179	0.520
C_1—Cu_3, C_2—Cu_2 overlap population	0	0.301	0.154	0.455
stabilization of monolayer/eV	0.99	2.91	1.91	5.29
depopulation of π	0	0	0.558	0.498
depopulation of π_σ	0	0.483	−0.012	0.542
population of π_σ^*	1.492	−0.250	−0.093	1.220
population of π^*	0.043	−0.017	0.309	0.418

the three-fold site, all four frontier orbitals interact strongly with the surface. The C_1—Cu_3 and C_2—Cu_2 overlap populations are less than those between C_1—Cu_1 and C_2—Cu_4 because of through-metal adsorbate–adsorbate interaction.

Two-fold Parallel Site, 3 and Diagonal Site, 4

In 11, we give the numbering of the atoms in the two-fold
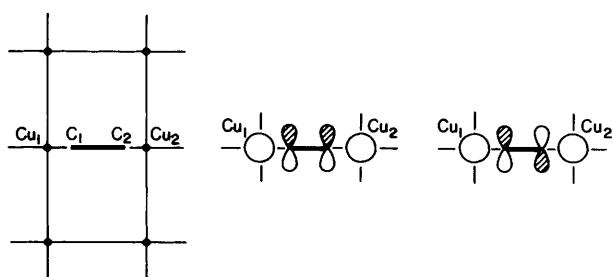
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parallel site 3. 4 is related to 1, for it can be obtained by moving the acetylene on the three-fold site, just a little bit along the diagonal, to the final position shown in 12.
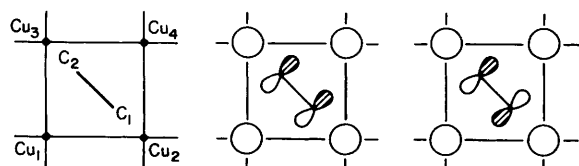

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As shown in 11 and 12, in these two adsorption sites both π and π^* are orthogonal to the nearest s and p_z orbitals of copper. The σ contribution is thus much greater than the π.

For example, the DOS of the π and π^* orbitals are less dispersed than those of π_σ and π_σ^*, respectively, and π_σ is more depopulated than π. These are well illustrated by table 5 and 6. (To save space, the DOS curves are not shown here.)

For all the binding sites we have considered so far, the stabilization due to adsorbate–surface bonding essentially balances the destabilization due to weakening of bonding within the acetylene and copper surface layers. For 5 and 6, the latter destabilization outweighs the former. So far we have focused on the adsorbate. Now we are going to pay more attention to the surface. We separate the surface orbitals into two groups. Group 1 consists of s and p_z and group 2 contains the other surface orbitals. By deleting the overlaps between acetylene and group 1 or group 2 orbitals together with the projection technique, their respective contributions to the bonding can then be estimated.

Atop Site, 5

The C—Cu overlap populations and stabilization energies in table 7 suggest that group 1 orbitals are more important. The change in electron occupation of π and π^* after turning on their interaction with group 1 orbitals are small. These acetylene MOs cannot overlap effectively with the s and p_z orbitals of the copper surface owing to local symmetry constraints, 13.
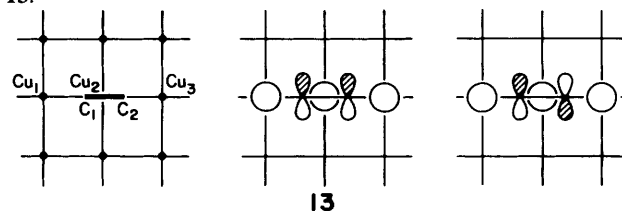
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Table 5. Effect of the various contributions to acetylene bonding at the 2-fold parallel site

	ionic	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.167	0.103	0.043	0.283
C_1—Cu_1 overlap population	0	0.600	0.022	0.622
C_2—Cu_2 overlap population	0	0.600	0.022	0.622
stabilization of monolayer/eV	0.65	4.22	0.03	4.75
depopulation of π	0	0	0.049	0.023
depopulation of π_σ	0	0.480	0.000	0.481
population of π_σ^*	1.283	−0.056	−0.063	1.226
population of π^*	0.040	−0.013	0.054	0.078

**Table 6.** Effect of the various contributions to acetylene bonding at the diagonal site

	ionic	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.319	−0.040	0.049	0.360
C_1—Cu_2, C_2—Cu_3 overlap population	0	0.585	0.022	0.607
C_1—Cu_1, C_2—Cu_4 overlap population	0	0.010	0.052	0.063
stabilization of monolayer/eV	0.95	3.77	0.45	4.91
depopulation of π	0	0	0.049	0.236
depopulation of π_σ	0	0.556	0	0.548
population of π_σ^*	1.313	−0.070	−0.063	1.258
population of π^*	0.001	0.000	0.078	0.090

Table 7. Effect of the various contributions to acetylene bonding at the atop site

	ionic	s and p_z	group 2	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.029	0.255	0.079	0.203	0.100	0.246
C_1—Cu_2, C_2—Cu_3 overlap population	0.000	0.200	0.124	0.310	0.014	0.324
C_1—Cu_1, C_2—Cu_4 overlap population	0.000	0.086	0.022	0.107	0.001	0.107
stabilization of monolayer/eV	0.52	1.24	0.30	1.64	−0.12	1.89
depopulation of π	0.000	0.006	0.054	0.000	0.006	0.046
depopulation of π_σ	0.000	0.339	0.036	0.358	−0.001	0.356
population of π_σ^*	0.505	0.449	0.143	0.269	−0.033	0.771
population of π^*	0.020	0.001	0.018	−0.003	0.021	0.047

The sixth column in table 7 confirms the small π contribution. Having taken care of the π interaction, we now concentrate on the σ part. π_σ^* is orthogonal to the nearest group 1 orbitals. However, as indicated by the overlap populations, π_σ and π_σ^* interact to certain extent with the s and p_z orbitals of Cu_1 and Cu_3. The dispersion of π_σ^* is therefore quite large. Nevertheless, π_σ is the only orbital of acetylene that can overlap effectively with the group 1 orbitals. We think it may be the major source of adsorbate–surface interaction. It is the weak π contribution and insufficiently strong σ interaction (compared to 3 and 4) that make 5 such a poor adsorption site.

Two-fold Perpendicular Site, 6

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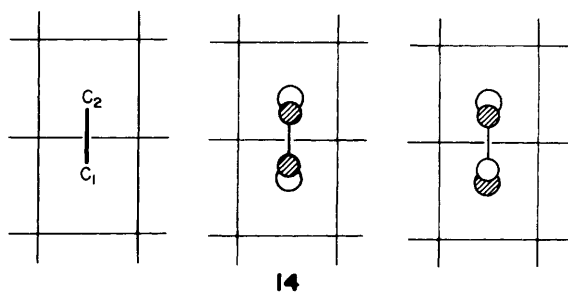
In 6, the orientations of π_σ and π_σ^* prevent any good overlap with the surface orbitals, 14. The C—C overlap populations in table 8 show that 6 is the only binding site in which the σ interaction is so weak that π part becomes more important. In fact, it is also the only site in which the π orbital is more depopulated than π_σ, although initially the former is further below the Fermi level. The small sigma contribution together with the fact that π^* is orthogonal to the nearest group 1 orbitals seem to explain the poor bonding as well. Note the small change in electron occupation of π^* in table 8 as its interaction with the s and p_z orbitals is turned on.

Conclusion

The interaction between acetylene and the Cu(100) surface occurs mainly through the π system of the adsorbate and the group 1 (s and p_z) orbitals on the metal. Whenever a sym-

metry constraint prevents effective overlap of any π orbitals of the acetylene with these surface orbitals, the covalent interaction of the particular π orbital becomes smaller.

2 is the only adsorption site at which all four π orbitals of acetylene can overlap effectively with group 1 orbitals. It might have been expected to have the strongest adsorbate–surface stabilization. Unfortunately, it is also the site with greatest weakening of Cu—Cu bonds at the surface and strongest through-metal adsorbate–adsorbate destabilization. The resulting compromise then leads to a binding energy for 2 that is roughly equal to that of 1 and 3.

The surface s band, being half filled, can accept electrons from or donate electrons to the π system (Dewar–Chatt–Duncanson model). The surface p_z orbitals are essentially empty. They cannot participate much in back-donation of electrons to the adsorbate. Their orientations, however, allow effective overlap with the orbitals of acetylene. These two types of surface orbitals have the same symmetry throughout the whole Brillouin zone, so it does not make much sense to treat them separately. Judging from the change in DOS after adsorption and the projected overlap populations, the s orbitals may be more important. On the other hand, the d orbitals of copper seems to contribute little to the bonding between acetylene and the metal surface. Indeed a recent theoretical study of oxygen on the Cu(100) surface suggests that they only account for ca. 2% of the total chemisorption energy.[14] The charge on the adsorbed acetylene is negative, indicating a net flow of electrons from the surface to the adsorbate.

The covalent interaction between acetylene and the copper surface is the main source of stabilization, but the ionic interaction (electron transfer) accounts for most of the occupation of π_σ^*. The ionic interaction is also the major contribution to the C—C bond weakening, except in the last two sites, which are anyway highly destabilized.

Analogies with known molecular complexes are often useful in surface science. For all the discrete copper–acetylene complexes and related compounds that have been isolated, the formal oxidation state of copper is +1. In addition, there is practically no change in the C—C bond length of the coordinated acetylene and the C—Cu bond distances are usually near 2.0 Å.[15,16] This is quite different from what we know experimentally about acetylene on the Cu(100) surface. It

Table 8. Effect of the various contributions to acetylene bonding at the 2-fold perpendicular site

	ionic	s and p_z	group 2	σ	π	all orbitals of acetylene
decrease in C—C overlap population	0.184	0.286	0.035	0.092	0.216	0.447
C_1—Cu_2, C_2—Cu_3 overlap population	0.000	0.204	0.111	0.151	0.165	0.315
C_1—Cu_1, C_2—Cu_4 overlap population	0.000	0.188	0.111	0.142	0.157	0.299
stabilization of monolayer/eV	0.66	0.74	0.62	−0.29	1.96	1.83
depopulation of π	0.000	0.441	0.062	0.003	0.528	0.490
depopulation of π_σ	0.000	0.218	0.135	0.279	−0.019	0.253
population of π_σ^*	0.739	0.498	0.069	0.177	0.512	0.905
population of π^*	0.032	0.041	0.183	−0.004	0.235	0.273

appears that the complex–surface analogy is not of direct use here. However, we can still use similar theoretical concepts to analyse both cases.

As we mentioned in the introduction, it seems that the chemistry of the Cu(100) surface presents some trouble for theorists and experimentalists alike.[17] Our rough computations neglect optimization of bond length, surface reconstruction and surface relaxation. So we do not claim high reliability. Nevertheless, we think we have gained some insight into the bonding of acetylene to a copper surface.

Appendix

The bond lengths and parameters used in all calculations are given in table 9. A double zeta expansion of the d orbitals is employed. The k points are chosen according to the method of Böhm and Ramirez.[18]

Table 9. Bond lengths and extended Hückel parameters

bond	bond length/Å
C—C	1.42
C—H	1.09
C—Cu	1.86
Cu—Cu	2.55

atom	orbital	H_{ii}/eV	$\zeta_1{}^a$	ζ_2	$c_1{}^a$	c_2
C	2 s	−21.4	1.62			
	2 p	−11.4	1.62			
H	1 s	−13.6	1.30			
Cu	4 s	−11.4	2.20			
	4 p	−6.06	2.20			
	3 d	−14.00	5.95	2.3	0.59	0.57

^{a} Exponents and coefficients in a double-zeta expansion of the Cu orbitals.

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