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Adsorption geometry of glycine on Cu(001) determined with low-energy electron diffraction and scanning tunnelling microscopy*

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Using low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) it has been found that glycine molecules adsorbed on Cu(001) can form but only the (2×4) and c(2×4) superstructures. On the basis of the missing LEED spots of the surface, it has been concluded that: each (2×4) unit cell consists of two molecules, one being the mirror image of the other; the C–C axis of both molecules lies in the mirror plane of the Cu substrate without a significant shift and twist from the plane; and the two O atoms of the carboxylate group of both molecules locate at the same height level without significant buckling. According to these conclusions, a structural model has been proposed for the (2×4) superstructure (a model for the c(2×4) superstructure already exists). We argue that the (2×4) and c(2×4) superstructures must have similar specific surface free energy, that their hydrogen bonds must be of N-H-O_{II} type, and that their local adsorption geometry must be similar or even the same. The advantage of combining STM with LEED to determine surface structures is clearly demonstrated.

Keywords: amino acids, surface adsorption, low-energy electron diffraction, scanning tunnelling microscopy (STM)
PACC: 8230, 8265, 7300, 0779

1. Introduction

The investigation of the adsorption of organic molecules on metal surfaces has become increasingly important. For instance, organic molecules, such as proteins, can alter inorganic microstructures, offering a very powerful tool for the design of novel materials.[1] Structural order over many length scales can be created by sophisticated use of self-organizing materials, and this may hold the key to developing new structures and devices.[2] Two-dimensional superlattices of molecularly linked metal clusters can now be prepared by self-assembly.[3] As amino acids are the building blocks of proteins and peptides, adsorption of these on metal surfaces has been used as a model system for investigation of protein–surface interactions.[4,5] Glycine, NH_2CH_2COOH, is the simplest among all 20 amino acids and thus its adsorption on metal surfaces has been studied most. Despite this, not many studies have been carried out on single-crystal surfaces in ultra-high vacuum (UHV) conditions,[6−12] because adsorption of glycine is much more complicated than that of flat and/or rigid molecules, even if the latter are much larger.[13] The difficulties are, at least, the following. (i) Glycine has several functional groups and a low symmetry. (ii) It may adsorb on surfaces in different forms (such as anionic and zwitterionic) as well as in different configurations. (iii) The configurations may vary with coverage. These difficulties make any experimental technique alone unable to disclose all the details of the adsorption geometry.[6−12] Again, because of these difficulties even in very recent calculations only adsorption of individual glycine molecules on metal surfaces, rather than their assembly, has been treated.[11,12,14] Consequently, even a small piece of information about the adsorption geometry is valuable.

Thanks to the joint effort of many research groups using many different techniques, including photoelectron diffraction (PhD), reflection absorption infrared spectroscopy (RAIRS), x-ray photoelectron spectroscopy (XPS), near edge x-ray absorption fine structure (NEXAFS), low-energy electron diffraction (LEED) and theoretical calculations, the following points are generally accepted.[7−9] (i) Glycine adsorbs on Cu(110) in its anionic form ($NH_2CH_2COO^-$). (ii) The (3×2) superstructure of the glycine/Cu(110) sys-

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tem has two molecules in each unit cell. (iii) One of the two molecules is the mirror image of the other so that the superstructure has a glide symmetry line perpendicular to the closely packed Cu rows. (iv) The O_2–C–C–N backbone of the molecules lies approximately parallel to the surface with the two oxygen atoms aligned approximately along the closely packed Cu rows, whereas the C–C axis and the C–N bond lie approximately perpendicular and parallel to the rows, respectively,[7–9] as shown in Fig.1. What is still left open is the adjustment to this molecular geometry that is necessary for optimization of the intra-layer hydrogen bonding: is it a shift and/or twist parallel to the surface and/or a buckling off the surface? On the other hand, the glycine/Cu(001) system has received much less attention,[10] although the first investigation of it was conducted two decades ago.[6] As a result, only a qualitative model has been proposed recently on the basis of scanning tunnelling microscopy (STM) for the Cu(001)c(2×4)–glycine superstructure and there is still a lack of knowledge about the details of the adsorption geometry.[10] Moreover, even on the superstructures that really exist on the surface there are still some discrepancies.[6]

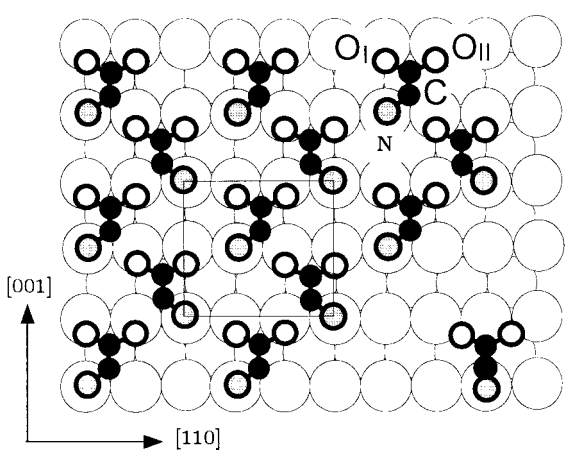


Fig.1. Schematic diagram of the adsorption geometry in Cu(110)(3×2)–glycine, as determined in Refs.[7]–[9]. the open, filled and shaded circles represent the oxygen, carbon and nitrogen atoms, respectively. The hydrogen atoms are not shown for simplicity. For comparison, a tested but wrong adsorption geometry is shown with the molecule at the lower-right corner.[7]

LEED crystallography[15] has been demonstrated to be a powerful technique for determining the adsorption details of organic molecules.[16] However, our observation shows that the glycine/Cu(001) LEED pattern becomes markedly degraded after an exposure of 30 min to the incident electron beam of our LEED optics (for those using a very small beam current[17] this may not happen), which is too short to allow some LEED I–V curves to be acquired. Fortunately, our observation also finds that the pattern has some 'absolute' missing spots, that is, missing at all incident-electron energies and all incident angles. Thus, some useful information about the adsorption geometry may be deduced from these.[18] Therefore, we study further the glycine/Cu(001) system via analysis of the missing LEED spots in conjunction with STM. We are indeed able to deduce many structural details of the adsorption geometry that would not be feasible if either LEED patterns or STM images were used alone.

2. Experimental details

The LEED and STM parts of the experiment were conducted in the UHV-LEED system and the UHV-STM systems, respectively. The former has been reported on previously.[19] The latter is essentially the same as the UHV-STM system reported before[20] but without the LEED facility, and was used in recent amino acid/Cu works.[10,21–26] In the STM experiment, the bias voltage is applied to the sample and the tip is grounded. A constant-current mode of the STM was used throughout the work and the scanning rate was from 200 to 2000Å/s. Images given here were acquired with the ac mode (the same as the ac input mode of oscilloscopes, sometimes also called differential or local-contrast-enhanced mode). The tip was made from W wire with electrochemical etching. The Cu(001) sample was cleaned by cycles of argon-ion sputtering followed by annealing at 750K for about 10 min. Glycine was evaporated from a Ta oven kept at about 400K on to the Cu(001) substrate, which was kept at room temperature and facing the opening of the oven. The deposition rate was set to about 2L/min (1L=1.33×10^{-4}Pa·s).

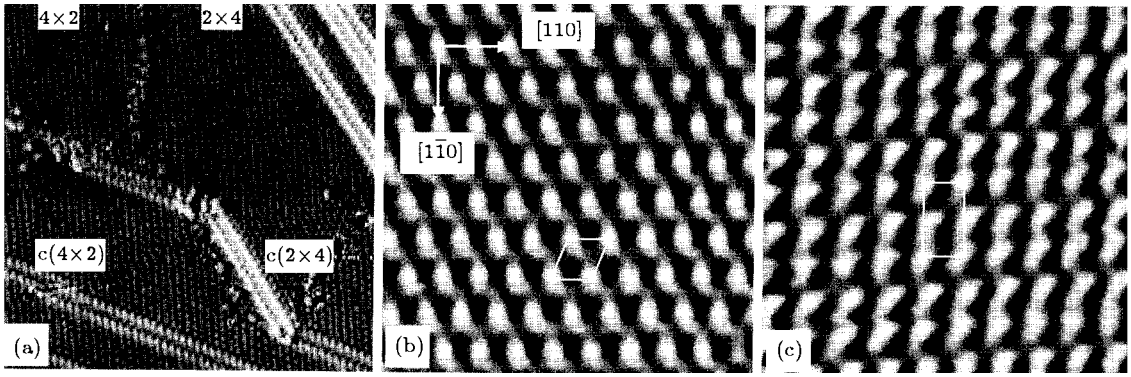


Fig.2. STM images of the superstructures of glycine adsorbed on Cu(001) at room temperature. (a) A large-scale image (25.6nm× 25.6nm, –1000mV, 0.6nA), showing the surface morphology. As the image was acquired with the ac mode, the features in the (4×2) and c(4×2) regions do not seem to be related by 90° rotation with those in the (2×4) and c(2×4) regions, respectively. However, zoom-in images show that they are. (b) A zoom-in image obtained from the c(2×4) region in (a), showing the Cu(001)c(2×4)–glycine superstructure (4.9nm×4.9nm, –500mV, 1.0nA), with a c(2×4) unit cell outlined. (c) A zoom-in image obtained from the (2×4) region in (a), showing the Cu(001)(2×4)–glycine superstructure (4.9nm×4.9nm, –1200mV, 0.5nA), with a (2×4) unit cell outlined.

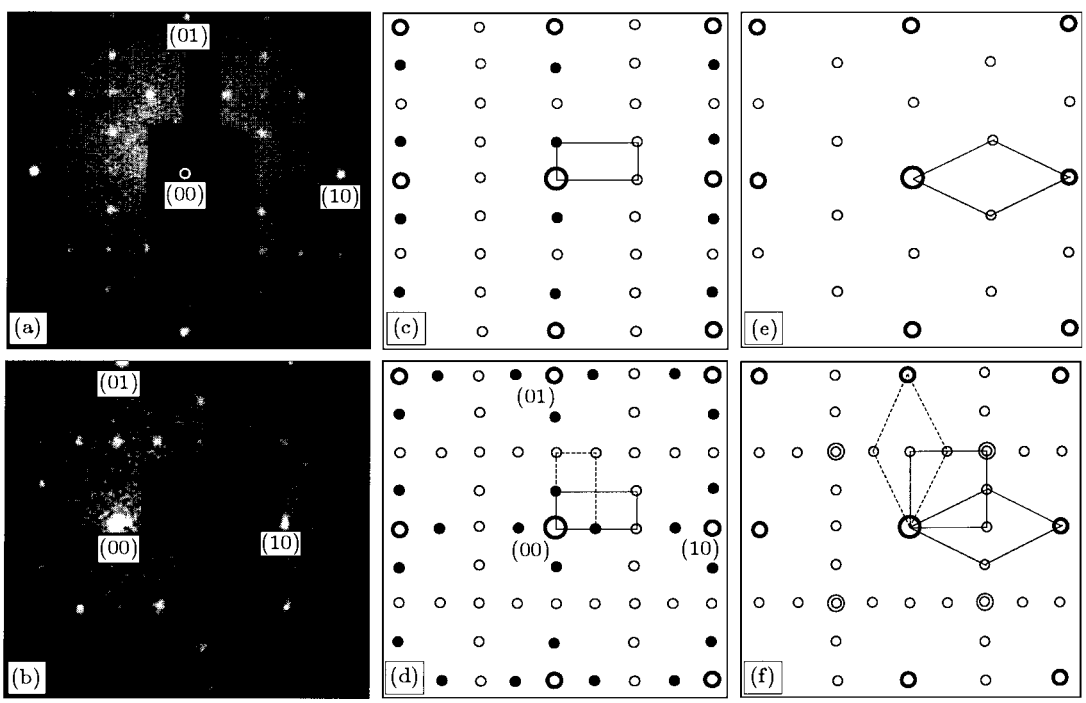


Fig.3. (a) Real LEED pattern (60 eV, normal incidence) of the saturated glycine/Cu(001) surface. (b) Real LEED pattern (56 eV, off-normal incidence, θ=10°) of the same surface. (c) Schematic LEED pattern of the (2×4) superstructure, with open and filled circles representing the visible and missing spots, respectively. A unit cell is outlined. (d) Interpretation of the real LEED pattern, suggested in Ref.[6]: the surface consists of domains of the (4×2) and (2×4) superstructures. (e) Schematic LEED pattern of the c(2×4) superstructure. All spots are visible in the real pattern. (f) Schematic LEED pattern of the surface consisting of domains of c(2×4), c(4×2) and (2×2) superstructures. Double circles represent the spots belonging only to (2×2), and all spots are visible in the real pattern.

3. Observation

Typical STM images and LEED patterns of the Cu(001) surface with 10L or more glycine deposited are given in Figs.2 and 3, respectively.

STM shows that the surface consists of domains of the c(2×4), c(4×2), (2×4) and (4×2) superstructures, or simply c(2×4) and (2×4), with the former mainly on smaller terraces or being adjacent to steps. Note that in an earlier paper only the c(2×4) superstructure was reported;[10] this was because the Ar^+-bombarded clean Cu(001) surface was annealed at 650K and thereby the terraces were much smaller.

The LEED patterns given in Figs.3(a) and (b) ac-

tually are very similar to that given in Fig.8 of Ref.[6] (although the beam energies are different), where the pattern, on the basis of LEED alone, was interpreted as the superposition of (2×4) and (4×2) spots,[6] or simply (2×4), as schematically shown by Figs.3(c) and (d). As one can see from Fig.3(d), this interpretation expects more spots than those seen in the real LEED patterns (see Figs.3(a) and (b)) or, in other words, the (2×4) superstructure gives rise to many 'absolute' missing spots, i.e. invisible whatever the beam energy or incidence angle is. Now, as we have just seen from the STM images, the real surface consists of not only (2×4) but also c(2×4) domains. Because all c(2×4) spots (see Fig.3(e)) are visible in the real patterns, we come to the same conclusion that the (2×4) superstructure of the surface gives rise to many 'absolute' missing spots.

It has been demonstrated that useful information of the unit cell structure may be deduced from the regular distribution of the 'absolute' missing LEED spots.[18] However, first we must consider other possibilities that might also give rise to missing spots. The first is the coexistence of anti-phase (2×4) domains. However, this possibility can be ruled out easily, because a simple calculation of the phase differences shows that among all seven possible (2×4) anti-phase domains only that shifted by a lattice vector of ($0\boldsymbol{a}+2\boldsymbol{b}$) can give rise to the right missing spots, while such anti-phase domains have never been seen in the STM images. Instead, only those shifted by a vector of ($1\boldsymbol{a}+2\boldsymbol{b}$) have been seen occasionally. Another possibility is if the (2×4) superstructure itself has the glide line symmetry. However, this possibility can also be ruled out easily, because the missing spots connected to a glide line are missing only at normal incidence,[27−29] while the missing spots of the surface are missing whatever the incidence angle is, as shown in Figs.3(a) and (b). Moreover, there are many more missing spots in the real patterns than glide-line missing spots, i.e. [0,±(2n+1)/4] spots for the p(2×4)g symmetry.[27−29] We thus conclude that the structure of the (2×4) unit cell itself must be responsible for the missing spots.

4. Discussion

Now, we try to deduce from the regularly distributed missing spots some structural information about the (2×4) unit cell, because it has been shown that the existence of such spots implies that in each unit cell there must be two or more identical atoms or groups of atoms (or molecules).[18] Considering the sizes of the unit cell and the molecules, we know immediately that in the (2×4) unit cell there must be two glycine molecules and that the two must have the same local adsorption geometry. Following the process described in Ref.[18], one can find that if a (2×4) superstructure can give rise to the missing spots shown in Fig.3(d) then the superstructure must be able to give rise to more missing spots, so that its LEED pattern becomes (2×2) or, more precisely, (2×2)-like, as Fig.3(f) shows. Note that, in the real pattern, the '1/2 1/4' and '1/4 1/2' type spots are visible (see Figs.3(a) and (b)), instead of missing, only because they are also spots of the c(2×4) superstructure (see Fig.3(e)).

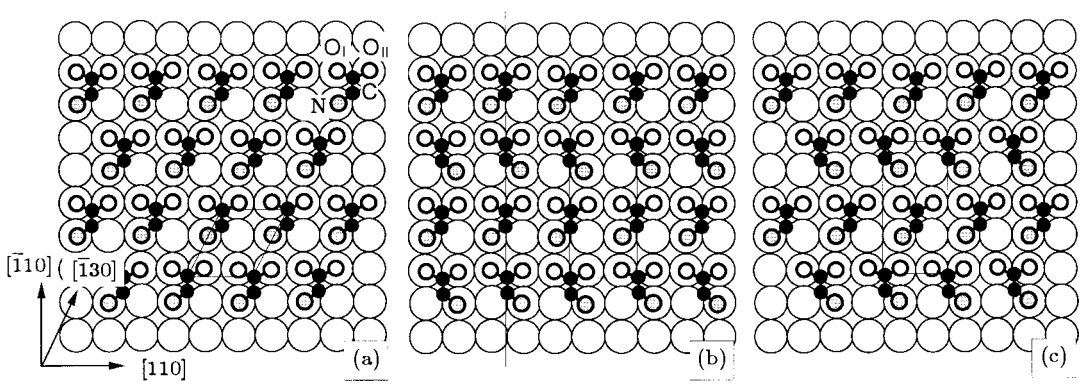


Fig.4. Models proposed for the superstructures on the glycine/Cu(001) surface, with the large open circles, five-circle groups, as well as small open, shaded and filled circles representing the Cu atoms, glycine molecules, as well as O, N and C atoms, respectively. Note that the hydrogen atoms are not shown for simplicity. (a) The Cu(001)c(2×4)–glycine model,[10] with a unit cell outlined and the O_I, O_{II}, N and C atoms of the glycine molecule marked at the upper-right corner. (b) The Cu(001)(2×4)–glycine model, with a unit cell outlined and the mirror plane marked with thin lines. (c) The wrong model of the Cu(001)(2×4)–glycine superstructure.

The question then is what kind of arrangement of the two molecules in a (2×4) unit cell can give rise to very weak '1/4'-order LEED spots meanwhile giving rise to strong '1/2'-order spots so that the pattern looks like (2×2)? As mentioned above, for the glycine/Cu(110) system two different adsorption geometries have been tested, and the one schematically shown at the lower-right corner of Fig.1 is wrong.[7–9] For the present (2×4) superstructure, that geometry can also be ruled out because with two such molecules in a(2×4) unit cell the superstructure could only be either (2×2) or c(2×4). With the geometry shown in the remaining part of Fig.1, which is the correct geometry in the case of glycine/Cu(110), molecules are able to form the (2×4) structure, because glycine is achiral and thus may adsorb on the surface in two equivalent geometries of this type. With this in mind, a model has been proposed for the (2×4) superstructure and this is shown in Fig.4(b). Note that this structure can indeed give rise to very weak (or practically invisible) '1/4' order spots meanwhile giving rise to strong '1/2' order spots so that the pattern looks like (2×2), provided that the O–O axis is parallel to the [110] direction and the C–C axis lies in the mirror plane of the Cu substrate. To believe this, note that hydrogen can only make negligibly small contributions to LEED[15] and thus, as far as LEED intensities are concerned, we have to consider only the contributions from the ten atoms of the two O_2–C–C–N backbones in the (2×4) unit cell. To estimate the relative intensities of the fractional order spots, we may neglect multiple scattering contributions (i.e. using kinematic approximation of LEED[15]) and ignore the adsorbate induced reconstruction of the Cu surface.[1] Moreover, because we just want to have an estimation of the overall intensity of the '1/4'-order spots relative to that of the '1/2'-order spots it is good enough to neglect the phase angle differences among the electron waves scattered from different atoms. It is also good enough to assume that C, N and O atoms have the same scattering factor, or simply taking 1. Under these approximations, all of the ten atoms in a unit cell contribute to the '1/2'-order spots, while only two N atoms contribute to the '1/4'-order spots because O_2–C–C forms a (2×2) lattice rather than (2×4). Consequently, the overall intensity of the '1/4'-order spots relative to that of the '1/2'-order spots is $2^2/10^2$=4%, or the '1/4'-order spots are almost two orders of magnitude weaker than the '1/2'-order spots and hence are practically invisible or missing. It is interesting to point out that, on the basis of LEED, the slightly different (2×4) model shown in Fig.4(c) can be ruled out with confidence. This is because, in this structure, O_2–C–C forms a c(2×4) lattice and thus does not give rise to '1/2 1/2' spots (the double circles in Fig.3(f)), while these are clearly visible in the real LEED pattern (see Figs.3(a) and (b)). On the other hand, the N atoms in this structure, though forming a (2×2) lattice, only give rise to the practically invisible '1/2 1/2' spots, as discussed above.

Having shown the compatibility of the (2×4) model in Fig.4(b) with both the LEED and STM results, we now address the justifications of the model. In this context, note that a structural model has been proposed for the Cu(001)c(2×4)–glycine structure,[10] which is given in Fig.4(a). The driving force behind the model structure apparently is hydrogen bond formation, which is also the key to the crystalline bulk of glycine. Now, in the (2×4) model N–H–O_{II} hydrogen bonds can also form but with a small difference. In the c(2×4) structure the N–H–O_{II} hydrogen bonds form chains lying along the ⟨103⟩ direction[10] whereas in the (2×4) structure the chains are aligned in the ⟨110⟩ direction. As either of the two covers approximately half of the surface, this difference seems to have no significant influence on the specific surface free energy. However, this difference explains why the c(2×4) structure prefers places neighbouring to ⟨103⟩ steps or {3 1 17} facets (see Fig.2(a)), where the hydrogen bond chains are also aligned in the ⟨103⟩ direction.[10] Knowing that in both c(2×4) and (2×4) structures there are only N–H–O_{II} rather than N–H–O_I hydrogen bonds, it is not difficult to understand why the surface does not like the (2×4) structure shown in Fig.4(c), where only N–H–O_I hydrogen bonds can form. It does not seem to be a coincidence that, in the case of alanine/Cu(001) and lysine/Cu(001), the superstructures consist of only or mainly the N–H–O_{II} hydrogen bonds.[21,22] Moreover, knowing that in the Cu(001)(2×4)–glycine structure the two molecules are mirror images of each other, we understand why alanine and phenylalanine form only the c(2×4) structure on the Cu(001) surface but never the (2×4). It is because they are chiral and thus the

Note that both multiple scattering and adsorbate induced reconstruction of the Cu surface can only make the '1/4'-order spots brighter, rather than dimmer, if without the two effects these spots are dim or invisible. Consequently, the fact that these spots are indeed missing in the real pattern is a strong indication that both effects are negligible.

adsorption energy of their two sides must be markedly different; no wonder, only one side of them is able to adsorb on the surface.[21,23]

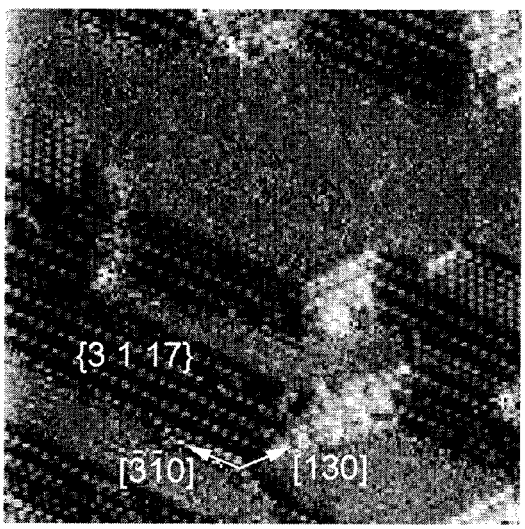


Fig.5. STM image acquired from the glycine/Cu(001) surface with a low coverage of glycine (27.0nm× 27.0nm, –1000mV, 1.0nA), showing steps faceting to the ⟨103⟩ direction and bunching to form {3 1 17}1×1 facets while no ordered structures developed on the (001) terraces.

Now we show that more details about the adsorption geometry can be deduced from the regular distribution of the missing LEED spots of the (2×4) structure. In this context, note that in the case of Cu(110)(3×2)–glycine, in order to optimize the hydrogen bonds, the C–C axis of the molecules has to make a shift[8] or twist[7] away from the mirror plane of the Cu substrate. In the present case, however, a significant shift and/or twist of the C–C axis would distort the (2×2) order of O_2–C–C towards (2×4) and thus would eliminate the missing spots. Therefore it should be ruled out. Moreover, the two O atoms of the carboxylate group must not be buckled significantly away from the (001) plane for the same reason. According to the sensitivity of LEED, a vertical shift of 0.05Å or a lateral shift of 0.1Å should certainly be considered as significant.[15] These detailed features are expected to hold for the c(2×4) superstructure as well because the N–H–O_{II} hydrogen bonds, as mentioned, also play a key role. On the other hand, we would like to point out that, although the C-C axis is expected to be approximately parallel to the [–1 1 0] direction in order to form hydrogen bonds and to make the N atom of the amino group able to bind to the Cu substrate,[7–9] a rotation of it in the mirror plane can still not be ruled out. Besides, although the two O atoms of the carboxylate group are expected to be at atop sites[14] a shift along the [–1 1 0] direction would not eliminate the missing spots and thus also cannot be ruled out either. Unfortunately, our STM and LEED data can only leave these questions open.

Finally, we point out that, although a LEED pattern different from that in Fig.3(a) was reported as seen from the low-coverage glycine/Cu (001) surface,[6] the ordered structure that gave rise to that pattern was not a superstructure existing on (001) terraces but on the {3 1 17} facets of the surface. To show this, a typical STM image obtained from the glycine/Cu(001) surface with a low coverage is shown in Fig.5. From this image, one can see that steps on the surface are not only faceted to the ⟨103⟩ direction but also bunched together to form {3 1 17}(1×1)–glycine facets while on the (001) terraces only small patches of the c(2×4) superstructure start to grow along step edges. Obviously, the coexistence of the eight equivalent {3 1 17} facets can give rise to a complicated LEED pattern and their unit vectors are along the ⟨103⟩ direction.[10] Since the unit vectors of that reported pattern were indeed in the ⟨103⟩ direction[6] we suggest that the pattern was from the {3 1 17} facets. Consequently, we conclude that glycine adsorbed on the Cu(001) surface can form only two superstructures: c(2×4) and (2×4).

5. Summary

In summary, it has been found that glycine molecules adsorbed on Cu(001) can form (2×4) and c(2×4) structures coexisting on the surface, although at low coverage they do not form any ordered structure on (001) terraces but can only make steps faceting to ⟨103⟩ and bunching to form {3 1 17} facets. It has also been found that in each (2×4) unit cell there are two molecules, with one being the mirror image of the other, that the C–C axis of the two molecules lie in the mirror plane of the Cu substrate without significant shift and twist from the plane, and that the two O atoms of the carboxylate group of the two molecules remain at the same height level without significant buckling. A model has thus been proposed for the Cu(001)(2×4)–glycine structure with confidence, only with the possible tilt angle of the C–C axis in the mirror plane and the possible [–1 1 0] shift of the O atoms from atop sites remaining to be determined. Moreover, we conclude that the two superstructures must

have similar specific surface free energy, that their hydrogen bonds must be of N–H–O_{II} type, and that the local adsorption geometry in the c(2×4) structure must be the same as that in the (2×4) structure, although the former has only one molecule in each unit cell.

We believe that the models, along with all these important structural details, have provided a very important starting point for further LEED crystallography investigations of the superstructures of the glycine/Cu(001) system, if experimental LEED I–V curves could eventually be acquired. Moreover, if the STM images were considered alone, it would be possible only to find the (2×4) and c(2×4) structures, while with the LEED patterns alone even this would not be possible. Thus, we believe what has also been demonstrated here is the great advantage of combining the real space technique STM with the reciprocal space technique LEED in determining complex surface structures.

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