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ADSORPTION BEHAVIOR OF AMINO ACIDS ON COPPER SURFACES*

Zhao Xue-ying(赵学应), Wang Hao(王 浩), Yan Hao(晏 浩),
Gai Zheng(盖 铮), Zhao Ru-guang(赵汝光), and Yang Wei-sheng(杨威生)
The Mesoscopic Physics Laboratory and Department of Physics, Peking University, Beijing 100871, *China*

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The major results of a series of our recent investigations on the adsorption of eight amino acids on Cu(001) and (111) surfaces are reviewed in the present paper. In all studied cases the molecules adsorb onto the surface in their anionic form. With the increase of the coverage three different 2D phases of the adsorbates, that is, the 2D lattice gas, intermediate, and solid phases, appear sequentially, although for few systems one or two of them do not appear. In both the 2D lattice gas and intermediate phases the molecules "stand" with their two oxygen "feet" on the surface and the intermolecular interactions are repulsive, although in the former they can diffuse frequently whereas in the latter they are discommensurate in one direction with the substrate. In the solid phase the molecules "lie" down on the surface to form commensurate superstructures. Adsorption of amino acids may often induce step faceting as well as bunching to form facets. Adsorption of L-lysine on Cu(001) may cause steps bunching to form facets with all the same chirality. Our preliminary results show that it is possible to manipulate individual molecules with the STM tip even at room temperature. These results may have applications in nano-materials, nano-technology, and very likely also in chiral separations or enantioselective heterogeneous catalysis.

Keywords: amino acids, single crystal metal surfaces, adsorption, organic molecules, hydrogen bonds, step faceting, chirality, scanning tunneling microscopy (STM)
PACC: 8230, 8265, 7300, 0779

I. INTRODUCTION

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] Obviously, in all these cases, a knowledge of the adsorption or self-assembly of the organic molecules on the inorganic substrate surface as well as of the relevant molecule-molecule and molecule-substrate interactions is very important. Proteins consist of twenty naturally occurring amino acids, which (except proline) can be expressed with one general formula, NH_2-CHR-COOH, where R represents the side-chains of amino acids, and all these natural amino acids (except glycine) are of L-chirality (or of S-form in the absolute configuration). To take advantage of the lessons learned from nature to develop new materials it is natural to start from investigation of adsorption of amino acids to inorganic single crystal surfaces.

Although investigations of adsorption of amino acids on single crystal surfaces can date back to the seventies,[4,5] not many papers have been published until now,[6−10] probably because of the intrinsic complexity of adsorption of amino acids on even single crystal surfaces. We then have been carrying out a systematic study on adsorption of amino acids on the Cu(001)[11−19] and (111) surfaces,[20,21] very recently. Different from most organic molecules studied so far, which are either planar or rigid,[22] amino acids have chirality (except glycine) and several active functional groups with very different acidities and thus could exhibit complex adsorption behavior on the surface. These characters allow us to explore the influence of different intermolecular interactions, including van der Waals forces, hydrogen bonding, and Coulombic interactions, as well as the influence of different molecule-substrate interactions. So far we have studied adsorption on the Cu(001) surface of glycine (R=H),[11,12] *L-alanine* (R=CH_3),[13] *L-aspartic acid* (R=HO_2CCH_2),[14]

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L-lysine (R=H_2N-$(CH_2)_4$),[15] *L-phenylalanine* (R=C_6H_5-CH_2),[16] *L-tryptophan* (R=indole-CH_2),[17–19] *L-asparagine* (R=H_2NCOCH_2),[17,18] and *L-cysteine* (R=$HSCH_2$),[17,18] along with *DL-alanine* (R=CH_3).[19] These amino acids cover all four groups of amino acids (i.e., basic, acidic, neutral polar, and neutral nonpolar amino acids) and include the lightest one (glycine) and heaviest one (tryptophan), and hence their adsorption behaviors are expected to be quite representative. Besides, we have also studied the adsorption[20] and tried the manipulation[21] of glycine molecules on the Cu(111) surface.

In the present paper we review the results we have obtained, including the form of the adsorbed molecules, their binding energies and diffusion activation energies, self-assembly of the molecules into different two dimensional (2D) phases, adsorption-induced surface morphology changes and chirality, and room temperature manipulation of individual molecules on the surface.

II. EXPERIMENTAL

Two UHV systems were used in the experiment of the papers reviewed here.[11–21] The home-made scanning tunneling microscopy (STM) system[23,24] used in these papers is equipped with argon ion bombardment and annealing facilities along with the source for amino acid deposition. The Riber low-energy electron diffraction (LEED) system used in the glycine/Cu(001) paper[12] is equipped with Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), argon ion bombardment and annealing facilities, as well as the source for amino acid deposition. This system has also been reported previously.[25] In the STM experiment the bias voltage is applied to the sample and the tip is grounded. The constant-current mode of the STM was used throughout the work and the scanning rate was from 200 to 2000Å/s. Images can be acquired either with the AC mode (same as the AC input mode of oscilloscopes, sometimes also called differential or local-contrast-enhanced mode) or the DC mode (same as the DC input mode of oscilloscopes, with which normal gray scale images can be obtained). The STM images given in the present paper were acquired with the AC mode, unless otherwise mentioned. In the local work function mode a modulation voltage was applied to the z-piezo with the frequency and amplitude being 2.0×10^4Hz and V_{pp}=20mV, respectively. The tip was made out of W wire by electrochemical etching.

Amino acids were deposited onto the clean and well annealed Cu(001) and (111) surface, which were obtained by cycles of "argon-ion sputtering followed by annealing at 650K for about 10 minutes." After such preparations, LEED patterns with sharp spots on a low background and atomically resolved STM images could be obtained from the surface and were used to determine the crystallographic orientations of the surface and to calibrate the constant of the x- and y-piezo. The z-piezo constant was calibrated from the mono-step height (1.8Å) on the Cu (001) surface. The amino acids (in powder form) were commercially available with a purity higher than 99.0% and were used without further purification. The evaporation source was a small Ta foil bag filled with the amino acid and was kept at about 400K to 450K during deposition, depending on the amino acid. The Cu(001) sample was facing the source in a distance of 10cm and thereby was essentially at room temperature. This resulted in a deposition rate of about 2L/min (1L=1.33×10^{-4} Pa·s). For a slow deposition rate of about 2L/h the sample was left at the STM position and was not directly facing the evaporation source, and the result of the deposition could be monitored with the STM. The temperatures of the sample and the evaporation source were monitored with a PtRh-Pt and a copper-constantan thermocouple, respectively.

III. RESULTS AND DISCUSSIONS

A. Molecular form and binding energy

It has been known that amino acids may, depending on the concrete environment, appear in different molecular forms, that is, the neutral form (NH_2-CHR-COOH), anionic form (NH_2-CHR-COO^-), cationic form (NH_3^+-CHR-COOH), and zwitterionic form (NH_3^+-CHR-COO^-). It has also been known that in the case of glycine/Cu(110)[8–10] the amino acids appear in their anionic form and that in the case of glycine/Cu(001) the calculated binding energy of the anionic form is about 1.5eV, markedly higher than that of the other forms.[7] Because all eight amino acids that we have studied so far can adsorb on the Cu(001) surface, we were able to do desorption experiments for these systems, that is, we annealed the sample step by step and looked at the surface with the STM after each step up to a temperature where no adsorbates were left on the surface. It turned out that on the Cu(001) surface the desorption tempera-

ture of glycine is 465K,[11] which is the lowest among all studied, while that of tryptophan is higher than 620K,[19] which is the highest among all studied and is even higher than the dissociation temperature of crystalline tryptophan. From the desorption temperatures we were able to get an estimation of the binding energies of these systems: not lower than 1.6eV to 1.8eV.[11−19] From this binding energy range, according to the experiments and calculations that we have just mentioned, it has been conclude that amino acids adsorb on the Cu(001) surface in their anionic form.

B. Self-assembly of the adsorbates

Adsorbates of most of the studied amino acids on the Cu(001) surface may, with an increasing coverage, proceed through three distinctly different phases, that is, the 2D lattice gas, 2D intermediate, and 2D solid phase. For some amino acids one or even two of these phases, somehow, can not form. As to be discussed below, in the gas phase the molecules are "standing" with their two oxygen "feet" on the substrate surface and can diffuse frequently; in the intermediate phase the "standing" molecules align into short rows; while in the solid phase they "lie" down on the surface with not only the two oxygen atoms but also the nitrogen atom bound to the surface, forming superstructures.

1. *The 2D lattice gas phase*

All the studied amino acids, except tryptophan, form the 2D gas phase on the Cu(001) surface at low coverages, rather than molecular islands, indicating that the intermolecular interactions are repulsive. If the molecules are "standing" on the surface then the intermolecular interactions ought to be dominated by the coulombic repulsive forces. When the coverage is very low the molecules can be imaged as individual protrusions (see Figs.1(a) and (b)). Consecutive images of a same area can tell that the molecules diffuse frequently on the surface even at room temperature. From such images the diffusion activation energy can be estimated. Although it varies a bit from one amino acid to another but is always around 0.85eV.[13−19] As this value is about half of the binding energy we believe that the diffusion process is a one-bond-breaking or walking process, rather than "jumping" with the two oxygen "feet." At higher coverage, molecules are so close that images of individual molecules coalesce, and thus all terraces on the entire surface are covered by the carpet-like 2D gas phase. At even higher coverage, small islands of the 2D solid phase start to nucleate and grow either inside terraces or along steps, with the rest areas remaining to be carpet-like (see Figs.1(c) and (d)). From the DC-mode images (see Fig.1d) one can find that the top of the gas phase is higher than that of the solid phase, indicating that the molecules are "standing" in the former whereas "lying" in the latter. Although it was not possible to image simultaneously the molecules and the substrate atoms, on the basis of previous calculations,[7,10] we believe that in the gas phase the molecules are in registry with the substrate atoms and thus form a 2D lattice gas.

It is very interesting to point out that the gas phase of the aspartic acid/Cu(001) system is unique among those of the other systems in the sense that some of its molecules (the bars in Fig.1(b)) diffuse more frequently than the others (the round protrusions in Fig.1(b)), thus corresponding to a slightly lower diffusion activation energy (0.79eV) compared to that of the others (0.88eV),[14] while for the other studied systems there is only one diffusion activation energy. The fact that an aspartic acid molecule has two carboxyl groups and either of them may bind to the surface has been suggested to be responsible for this.[14] However, at this stage it is hard to tell which activation energy corresponds to which carboxyl group. Moreover, the fact that adsorbates of tryptophan on the Cu(001) surface could not form the gas phase seems to indicate that the big indole group of the molecules, apart from the carboxylate group, is also bound to the surface, thus making the molecules immobile.[17−19]

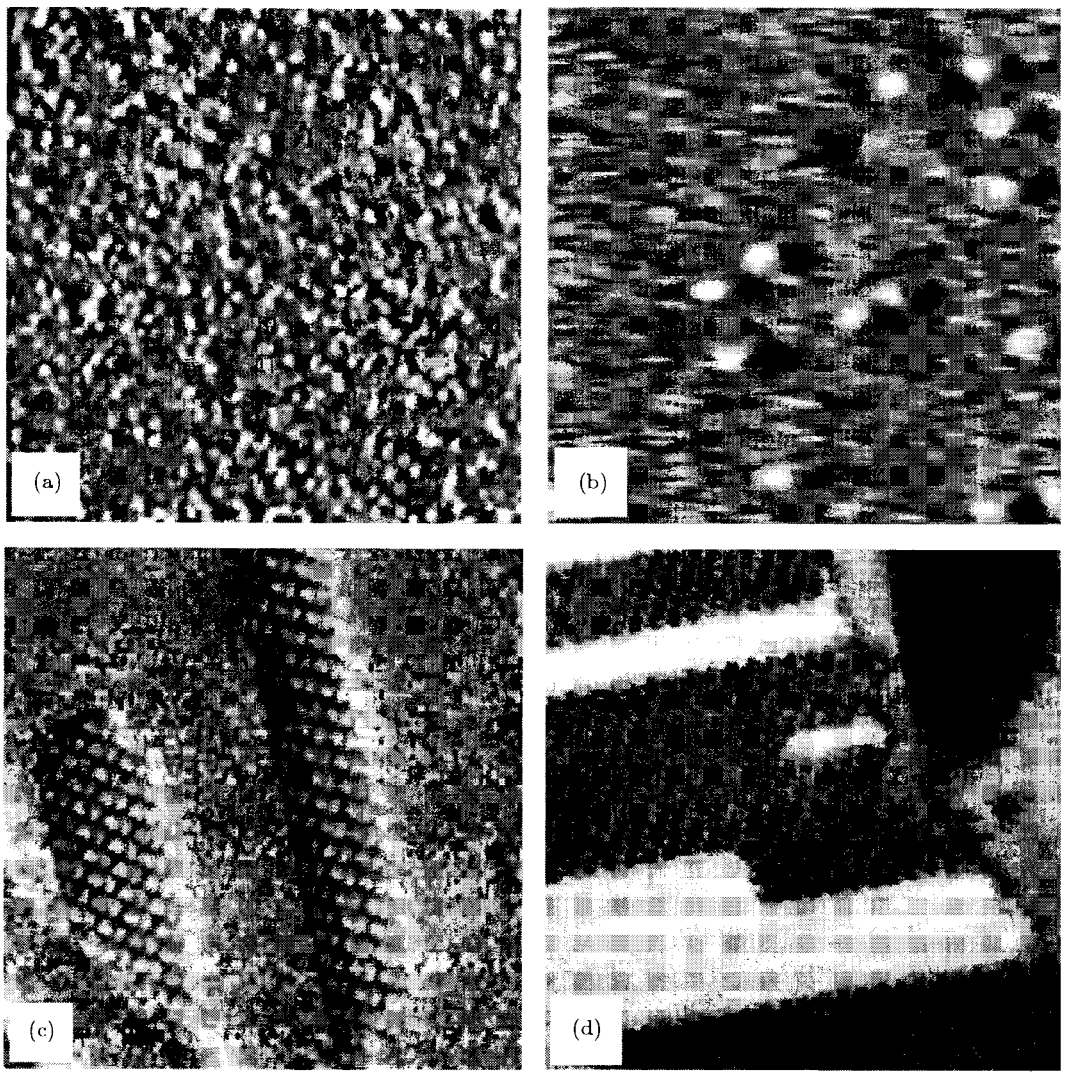


Fig.1. (a) STM image (300Å× 300Å, -2.0V, 0.4nA) of the L-lysine/Cu(001) surface with low coverage. Protrusions are image of individual molecules. (b) STM image (80Å×80Å, -0.5V, 1.0nA) of the 2D gas phase of aspartic acid adsorbed on the Cu(001) surface. Note that the bars and mounds are all images of individual molecules but with a higher and lower diffusion frequency, respectively. (c) STM image (200Å× 200Å, 1.0V, 0.6nA) of the lysine/Cu(001) surface with a higher coverage so that the 2D solid phase (areas with ordered features) coexists with the 2D gas phase. (d) STM image (DC-mode, 265Å×265Å, 1.0V, 0.6nA) of the lysine/Cu(001) surface with an even higher coverage, showing that the top of the 2D solid phase is lower (darker) than that of the 2D gas phase.

2. *The 2D solid phase*

Among the eight studied amino acids, glycine,[11,12] alanine,[13] lysine,[15] phenylalanine,[16] and tryptophan[18,19] can form one or more well ordered superstructures on the Cu(001) surface, depending on the coverage or annealing temperature, while cysteine can form small domains of the c(4×2) superstructure.[18] As examples, some images are shown in Fig.2. The following considerations let us believe that molecules in the solid phase could not "stand" up but must, instead, "lie" down on the surface. (i) The coverage of the 2D solid phase is higher than that of the gas and intermediate phase. (ii) The molecules do not only have a net negative charge but also a dipole moment, and thus further squeezing the dipole moments while they are parallel to each other would be energetically too costly. (iii) When molecules are dense enough hydrogen bonds may form but only if the molecules "lie" down on the surface, that is, if not only the carboxylate group but also the amino group are close to the surface. (iv) Moreover, as mentioned above and to be shown later, the top of the solid phase, is lower than of both the gas and intermediate phases.

It should be pointed out that for all superstructures we have studied so far each molecule, somehow, can be imaged as only one protrusion. Nevertheless, on the basis of the STM images some models have still been proposed for further investigation.[11−13,15,16,18,19] Note that these models were proposed under the following considerations: (i) the number of molecules per unit cell; (ii) all possible molecular configurations; (iii) van der Waals radii of all involved atoms; and (iv) conditions for H bond formation, including bond lengths and angles.

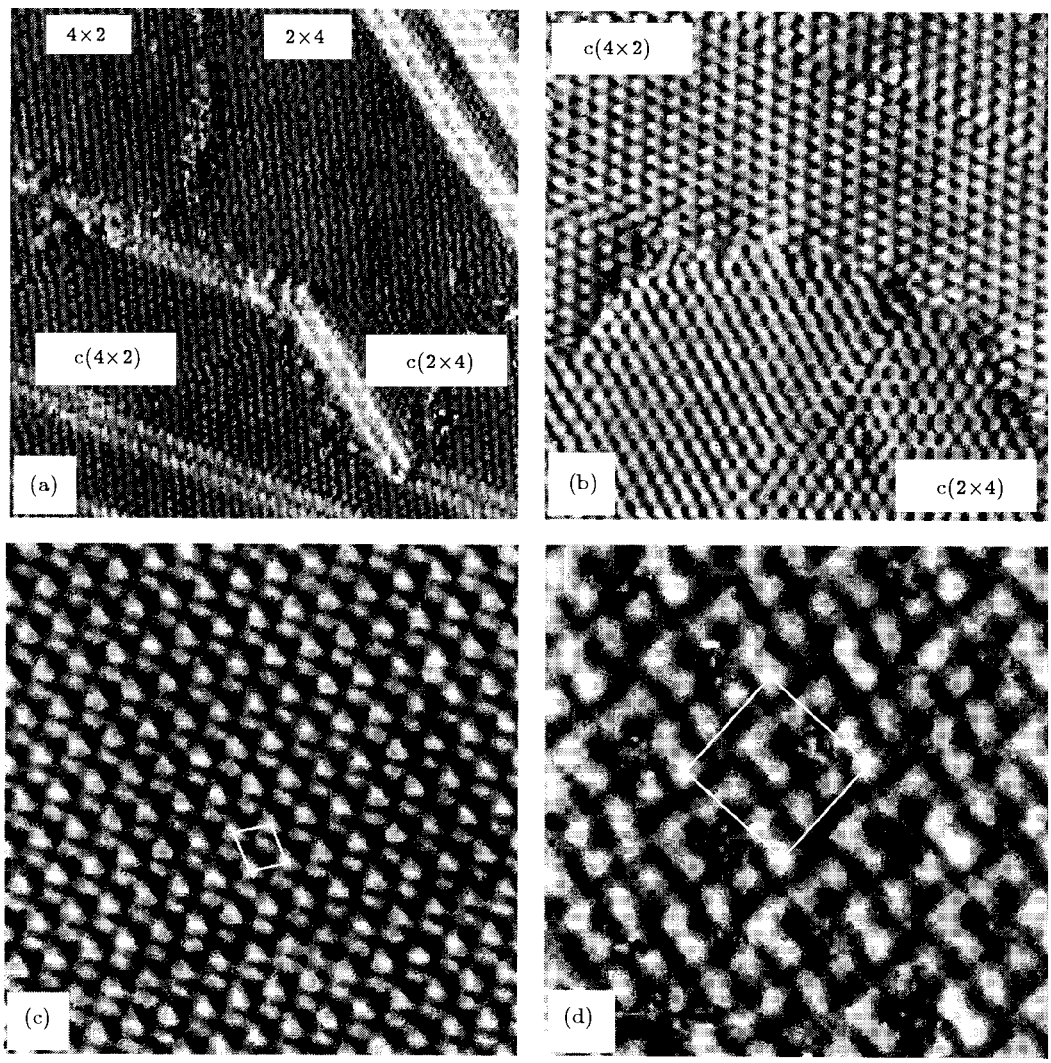


Fig.2. STM images of the superstructure appearing on four different surfaces. (a) Glycine/Cu(001), 256Å×256Å, -1.0V, 0.6nA. (b) Phenylalanine/Cu(001), 140Å×140Å, 1.0V, 0.6nA. (c) Lysine/Cu(001), 133Å×133Å, 1.0V, 0.6nA. (d) Tryptophan/Cu(001), 105Å×105Å, 1.0V, 0.6nA.

It is noteworthy that in some cases LEED patterns may be very helpful in providing detailed structural information, especially when used in conjunction with STM images.[12] For instance, on the glycine/Cu(001) surface there coexist two superstructures, that is, c(2×4) and (2×4) (see Fig.2(a)). On the basis of STM images alone a plausible model (see Fig.3(a)) was proposed for the former under the considerations mentioned above,[11] but none for the latter because it consists of two molecules in each unit cell and thus is more difficult. However, if the LEED pattern of the surface is considered together with the STM images, then one can find not only that the (2×4) superstructure has some systematically missing spots,[26] but also many structural details of its unit cell. These details have not only led us naturally to the (2×4) model shown in Fig.3(b), but also given further support to the c(2×4) model (see Fig.3(a)).[12]

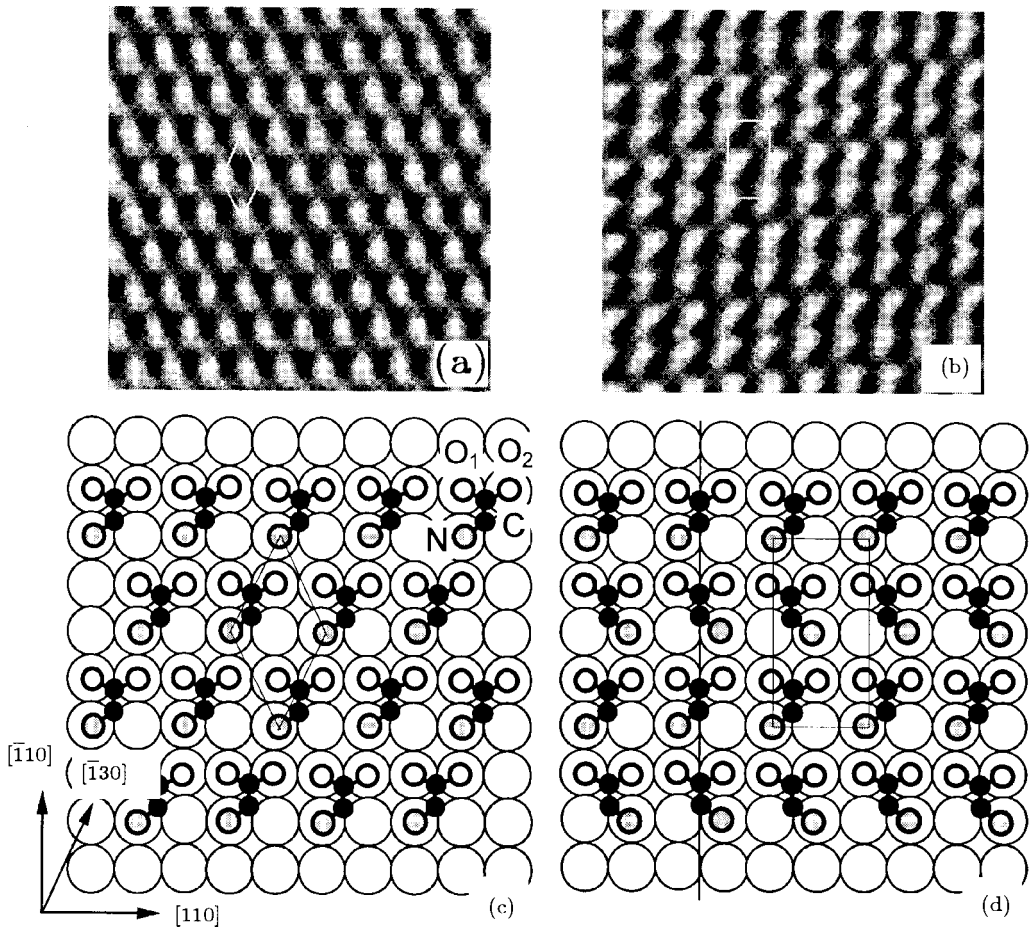


Fig.3. (a) STM image (50Å×50Å, -1.0V, 0.6nA) of the Cu(001)c(2×4)-glycine superstructure, with a c(2×4) unit cell outlined. (b) STM image (50Å×50Å, -1.0V, 0.6nA) of the Cu(001)(2×4)-glycine superstructure, with a (2×4) unit cell outlined. (c) Schematic drawing of the Cu(001)c(2×4)-glycine model, with the large open circles representing the top layer Cu atoms, and the small open, filled, and shaded circles representing the oxygen, carbon, and nitrogen atoms of the molecules, respectively. (d) Schematic drawing of the Cu(001)(2×4)-glycine model.

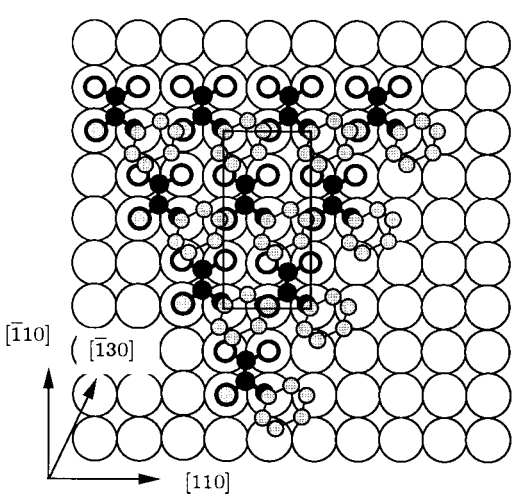


Fig.4. Schematic drawing of the model proposed for the Cu(001)c(2×4)-phenylalanine superstructure, with the smallest shaded circles representing the phenyl rings of the molecules. The rest are the same as those in Fig.3.

It is very interesting that glycine,[11] alanine,[13] phenylalanine,[16] and cysteine,[18] though having very different side chains, can all form a c(2×4) superstructure on the Cu(001) surface. This supports strongly that H bond formation is the common driving force of the superstructures and that the side chains are not lying on the surface in such cases. For comparison with the Cu(001)c(2×4)-glycine model shown in Fig.3(a), the Cu(001)c(2×4)-phenylalanine model is given in Fig.4.[16] It has been pointed out that, in addition to formation of H bonds, π-stacking interactions between phenyl rings of neighboring molecules is also responsible for stabilization of this superstructure.[16]

3. *The intermediate phase*

Among the eight tested amino acids, glycine, alanine, and phenylalanine can form the intermediate phase in a coverage range between those of the gas and solid phases, and the STM images of the intermediate

phase of the three are nearly identical. Lysine can also form something similar to the intermediate phase but not that typical. Typical images of this phase are given in Fig.5. even when the deposition rate is very low, the transition from the 2D gas to the intermediate phase proceeds very fast and continuously, that is, not via nucleation and growth. Further deposition onto the intermediate phase results in nucleation and growth of islands of the 2D solid phase (see the island at the center of Fig.5(a)), and thus the transition is of first order. The top of the intermediate phase is above that of the 2D solid phase (this can be seen even from the AC-mode image in Fig.5(a)). The intermediate phase consists of narrow domains with a width of about 46Å, and the domain walls on a terrace are often parallel to the edge of the terrace (see Fig.5(a)). From enlarged images one can find that the domains consist of parallel stripes. The stripes are, in most cases, along a $< 110 >$ direction and nearly perpendicular to the domain walls, and have a width twice of the Cu-Cu spacing (about 5.1Å, see Fig.5(b)). If a local work function image (see Fig.5(c)) is acquired simultaneously with a STM image then the stripes can often be seen more clearly in the local work function image.

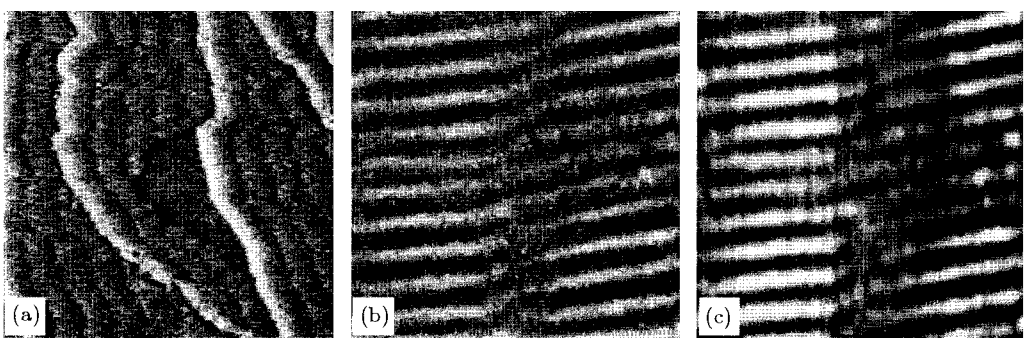


Fig.5. (a) STM image of the intermediate phase of L-alanine adsorbed on Cu(001) formed with a low deposition rate (500Å×500Å, 1.0V, 0.4nA). Note that this phase consists of quasi-periodic narrow domains with a width of about 46Å. Note also that the 2D solid island at the center of the image is lower than the intermediate domains, because the fast scanning direction of this AC mode image was from left to right whereas the left and right borders of the island are dark and bright, respectively. (b) STM image of the intermediate phase (75Å×50Å, -1.0V, 0.3nA), showing two domains separated by the vertical domain wall at the center. The width of the stripes is about 5.1Å. (c) Local work function image (75Å×50Å) acquired simultaneously with (b).

It has been suggested that in the intermediate phase the molecules are not only standing on the surface but also aligned into rows with a width of about 5.1Åand a length of about 46Å, whereas the domain walls seem to be an indication that the molecular spacing along the row is discommensurate with the underneath Cu-Cu spacing.[17,15] Discommensuration is considered to originate from the adsorbate-adsorbate and adsorbate-substrate interaction of the same order of magnitude and often results in quasi-periodically ordered domains separated by domain walls.[27] Considering that in the solid phase the molecular spacing in the $< 110 >$ direction is exactly twice of the Cu-Cu spacing and that the coverage of the intermediate phase is a bit lower than that of the solid phase, one should not be surprised to see the intermediate phase having a molecular spacing in the row direction to be slightly larger than twice of the Cu-Cu spacing, that is, to be discommensurate with the Cu-Cu spacing.

4. *The Glycine/Cu*(111) *system*

Our preliminary results show that glycine adsorbed on the Cu(111) surface can also form three different 2D phases,[20] and some typical images are given in Fig.6. As one can see from the DC-image in Fig.6(d), the top of the 2D solid islands is obviously below than that of the 2D gas. These characters are essentially the same as those of the glycine adsorbates on the Cu(001) surface, indicating that the driving forces of the 2D phases mentioned above are also valid in this case. Interestingly, from Fig.6(d) one can also see many eye-catching white round features arranged in a hexagonal order. According to their size, each such feature must consist of many molecules; although in no tunneling condition could their interior structure be imaged. These features are similar to but different from the 2D gas phase and seem to appear only on the (111) substrate.

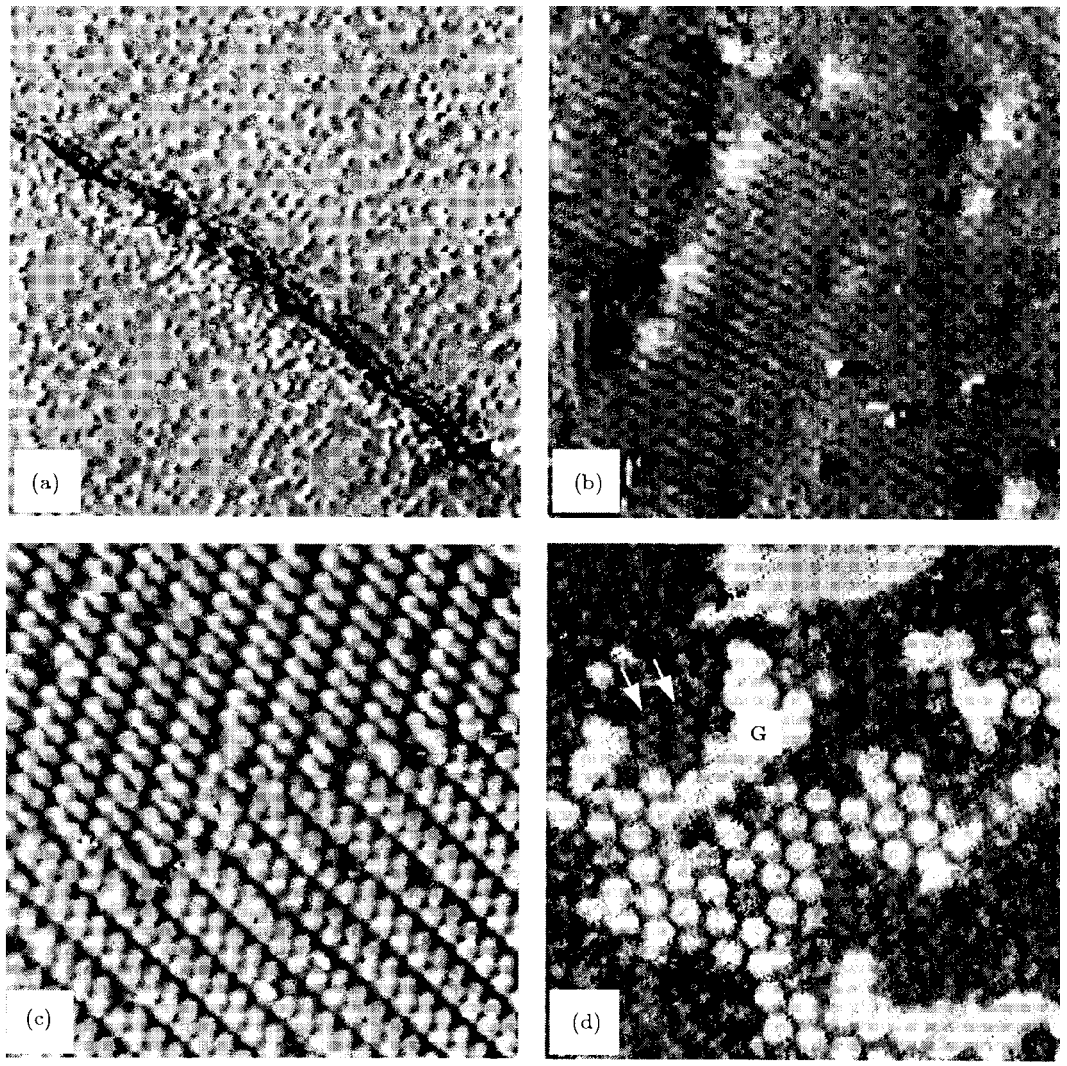


Fig.6. STM images obtained from the glycine/Cu(111) surface. (a) The 2D gas phase (270Å×270Å, 2.0V, 0.6nA), showing individual molecules adsorbed on two terraces separated by a step running from lower-right to upper-left. (b) The 2D intermediate phase (155Å×155Å, 1.0V, 0.6nA), showing the parallel stripes with a width of about 5Å. (c) The 2D solid phase (270Å×270Å, -1.5V, 0.6nA), showing two rotationally equivalent domains of the (4×8) superstructure. (d) Coexistence of the different 2D phases (DC-mode, 285Å×285Å, 1.0V, 0.6nA), with the arrows pointing to the small domains of the (4×8) superstructure and the character G marking the gas phase. The eye-catching white round features arranged in a hexagonal order seem to be closely related with the 2D gas phase and are currently under investigation.

C. Adsorption-induced surface morphology change

Adsorption of glycine,[11] alanine,[13] phenylalanine,[16] and tryptophan[19] on the Cu(001) surface can make steps faceting to eight < 310 > directions and then bunching into eight {3 1 17} facets, especially if the surface is annealed. Typical images are given in Fig.7. It becomes clear now that step faceting is a general feature of adsorption of reactive species on metal surfaces and that it is the reconstruction on the terraces that stabilize the step faceting because faceted steps always align parallel to the close-packed directions of the reconstruction on the terraces.[28] In our case, we believe that the same driving force is responsible for step faceting to < 310 > directions, because < 310 > steps connected mostly to the Cu(001)c(2×4)-glycine superstructure,[19] and only to the Cu(001)(4×4)-L-tryptophan reconstruction but never to $\begin{pmatrix} 7 & 7 \\ -7 & 7 \end{pmatrix}$- and $\begin{pmatrix} 6 & 4 \\ -5 & 4 \end{pmatrix}$-L-tryptophan.[19] As Fig.7(b) shows, adsorption of amino acids on the Cu(001) surface may modify dramatically the surface morphology, and this may have applications in nanostructure formation or template preparation.

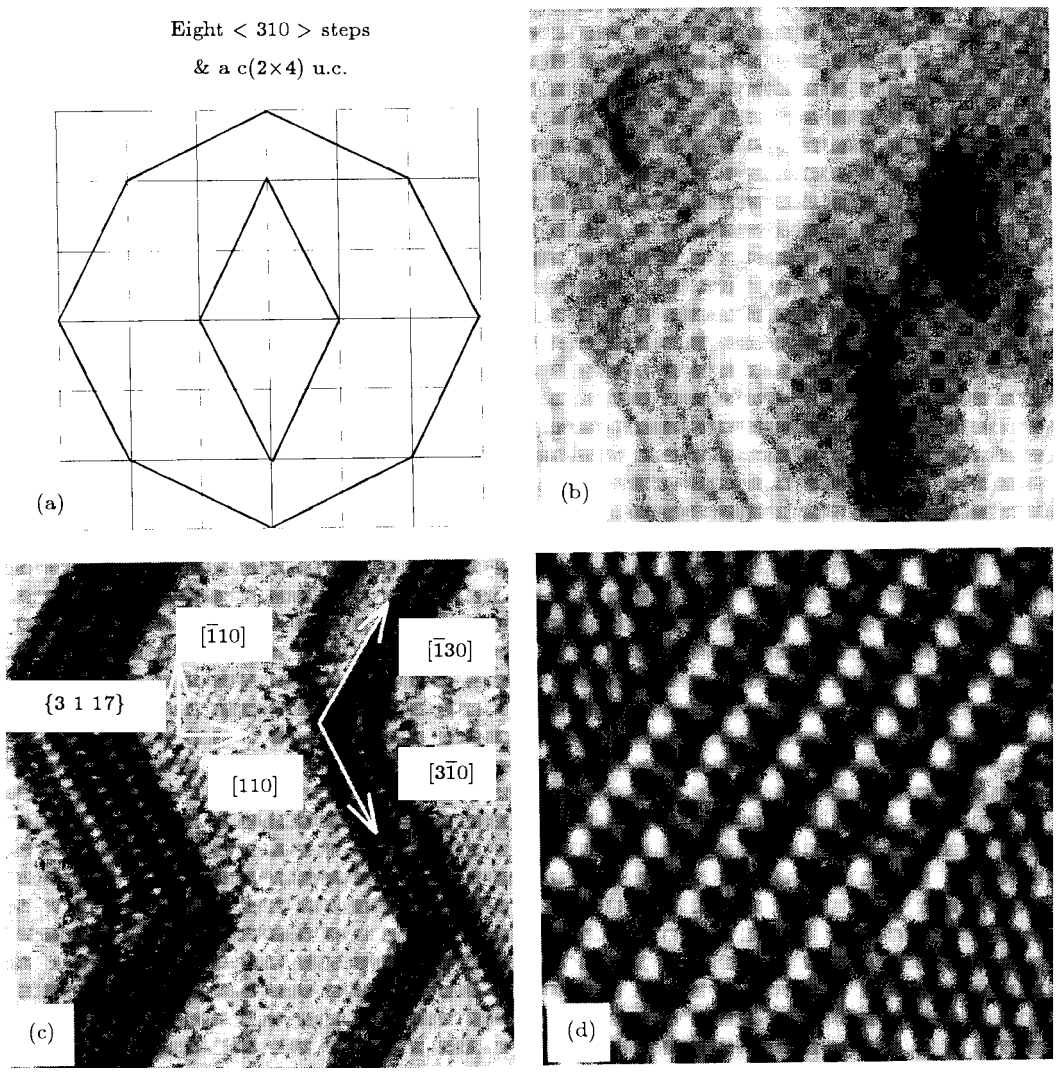


Fig.7. (a) Schematic diagram, showing the relative orientations of the Cu(001) surface, a c(2×4) unit cell and all eight possible < 310 > steps. (b)-(d) STM images obtained from the annealed Cu(001) surface saturated with glycine. (b) Low magnification image (2650Å×2650Å, 1.0V, 1.0nA), showing the general surface morphology. (c) Medium magnification image (175Å×175Å, -1.2V, 0.5nA), showing the < 310 > steps and bunching of such steps into {3 1 17} facets. (d) Zoom-in image (75Å×75Å, -1.2V, 1.0nA), showing a (3 1 17) facets at the center.

D. Adsorption-induced surface chirality

Although L-lysine molecules can only randomly adsorb along originally curved steps on the Cu(001) surface and do not cause any step faceting at room temperature, annealing can make all steps restructured into {3 1 17} facets (see Figs.8(b) and (c)),[15] which is (4×1) reconstructed (see Fig.8(d)). Despite that the facets are also {3 1 17}, there are some differences between this and the step-faceting-and-bunching case mentioned in the preceding section. The most significant difference is that in the present case only four out of eight {3 1 17} facets appear on the well-annealed surface, i.e., (-1 -3 17), (3 -1 17), (1 3 17) and (-3 1 17). In contrast, in the case of glycine, L-alanine, and L-phenylalanine all eight {3 1 17} facets can be found on the surface, as mentioned in the last section. It has been pointed out that in the present case the four {3 1 17} facets that appear on the surface all have the R chirality (according to the nomenclature proposed by McFadden *et al.*[29]), while the rest four {3 1 17} facets, that is, (3 1 17), (-1 3 17), (-3 -1 17) and (1 -3 17), which have never been seen on the surface, all have the S chirality.[15] This indicates that the adsorption energy of an L-lysine molecule on R-{3 1 17} facets must be higher than that on S-{3 1 17}. In other words, it is the higher adsorption energy of L-lysine on R-{3 1 17}, rather than the superstructure

on the (001) terraces, that drives the steps to become R-{3117} facets. At this stage we do not know the precise adsorption energy difference between the R- and S-{3 1 17} facets but because the surface was annealed at 430K, the difference must be larger than kT of this temperature, that is, 37meV. Nevertheless, the difference ought to be high enough to provide some enantioselectivity if, say, a Cu(3 1 17) surface is used in adsorption of DL-lysine.

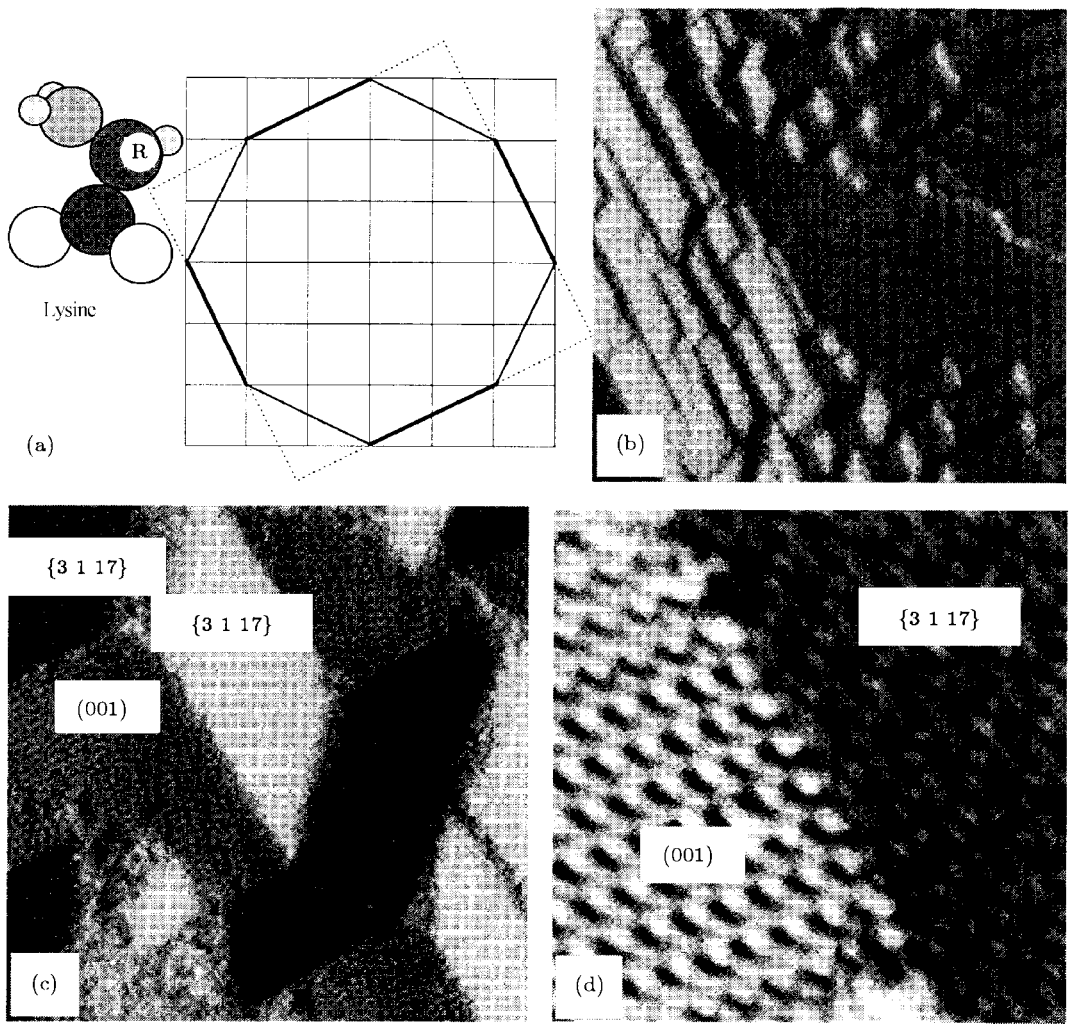


Fig.8. (a) Schematic diagram of a L-lysine molecule (R: the side chain) and the intersection lines of all eight possible {3 1 17} facets with the Cu(001) surface. Note that the four thick lines are rotationally equivalent with each other whereas the four thin ones are also. (b)-(d) STM images obtained from the annealed Cu(001) surface saturated with L-lysine. (b) Low magnification image (2200Å×2200Å, 1.0V, 0.6nA), showing the general surface morphology. (c) Medium magnification image (540Å×540Å, 1.0V, 0.6nA). (d) High resolution image (130Å×130Å, 1.0V, 0.6nA).

As for why this happens only to L-lysine/Cu(001) system, but not to the L-alanine/ and L-phenylalanine/Cu(001) systems, the "three-point interaction model"[30] can give the answer, which says that for chiral recognition to happen the independent chiral stationary phase (CSP) must have a minimum of three simultaneous interactions with one of the enantiomers.[30] When using a clean Cu{3 1 17} surface, which is chiral,[29] as the CSP, the amino group and the carboxylate group of an amino acid molecule can form strong chemical adsorption bonds with the surface, in other words, providing two interactions with the CSP.[31,10] For an alanine molecule, only this two active functional groups are connected to its asymmetric α-carbon. However, the side chain of a L-lysine molecule, i.e., the -$(CH_2)_4NH_2$ group, provides the third simultaneous interaction and thus makes chiral recognition possible.

E. Manipulation of individual molecules

As we have seen from Figs.6(a) and 1(a), individual glycine molecules can be imaged without being disturbed if the tunneling resistance is high. However, if the tunneling resistance is low enough then the STM tip is able to push individual glycine molecules moving forward step by step on the Cu(111) surface,[19,21] as Fig.9 demonstrates. As one can easily see from this figure, the zigzag trace of such a moving molecule consists of many similar half-mounds aligned in the close-packed directions of the surface. Therefore, it is not difficult to think of the concrete moving process of a molecule. At the beginning the tip was able to image the molecule although the tunneling resistance was set to very low. However, before the tip could scan over the entire molecule the tip-molecule interaction became so intense that the molecule was pushed away from its original position. Moreover, the moving process must consist of consecutive one-bond-breaking steps or, in other words, the molecule "walks" rather than "jumps", because at low coverage the molecules are "standing" on the surface with their two oxygen "feet" and the traces are continuous, albeit zigzag.

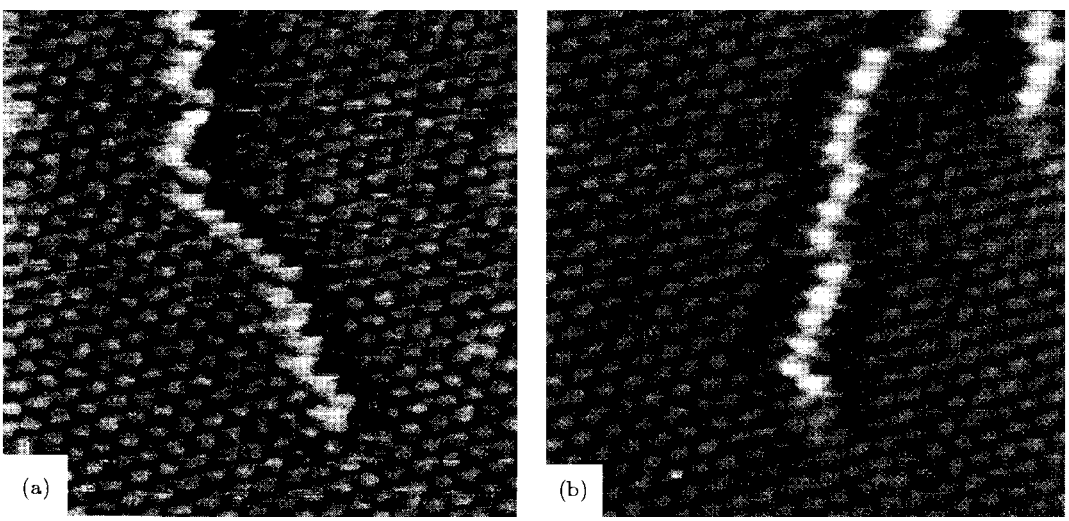


Fig.9. STM images (46Å×46Å, 85mV, 10nA) acquired from the glycine/Cu(111) surface. Each zigzag feature consisting of many similar half-mounds is the moving trace of one molecule pushed forward by the tip along the close-packed directions of the surface. (a) Containing a long trace. (b) Containing a long and a short trace.

Although 10 years have already passed since the first successful positioning of single Xe atoms adsorbed on the Ni(110) surface at liquid helium temperature with a STM tip was demonstrated,[31] and now it has been shown that controlled positioning of individual large rigid molecules with four bulky hydrocarbon groups attached as the "feet" can be achieved even at room temperature,[32] demonstrated by Fig.9 is the possibility of room temperature positioning of small natural molecules consisting of only ten atoms.

IV. SUMMARY

Adsorption of glycine, L-alanine, L-phenylalanine, L-lysine, L-cysteine, L-aspartic acid, L- tryptophan, and L-asparagine on the Cu(001) surface and glycine on the Cu(111) surface has been studied with STM and, in some cases, LEED. The major results are summarized as follows. (i) In all these systems the molecules adsorb on the surface in their anionic form. (ii) With the increase of the coverage three different 2D phases of the adsorbates, that is, the 2D lattice gas, intermediate, and solid phases, appear sequentially, although for some systems one or two of these could not form. (iii) In the 2D lattice gas phase the molecules "stand" with two oxygen "feet" on top of two neighboring surface Cu atoms and the intermolecular interactions are Columbic and repulsive. The molecules can diffuse frequently even at room temperature, and the diffusion process consists of "one-bond-breaking" steps. (iv) In the intermediate phase the molecules also "stand" on the surface and the intermolecular interactions are also repulsive, however, the molecules align into short rows and are discommensurate with the substrate in each row. (v) In the solid phase the molecules are bound to the surface not only with two oxygen atoms but also the nitrogen atom or, in other

words, they "lie" down on the surface to form commensurate superstructures, which is motivated by formation of H bonds. (vi) Adsorption of amino acids may often induce step faceting to the close-packed directions of the superstructures, as well as bunching to form some facets. (vii) Most amino acids are chiral and thus adsorption of, at least, L-lysine on Cu(001) may cause steps bunching to form facets with only the R but never the S chirality. (viii) Preliminary results obtained from the glycine/Cu(111) system indicate that it is possible to manipulate small natural molecules consisting of only ten atoms even at room temperature. These results may have applications in nano-materials, nano-technology, and very likely also in chiral separations or enantioselective heterogeneous catalysis.

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