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# Interplay between Fast Diffusion and Molecular Interaction in the Formation of Self-Assembled Nanostructures of S-Cysteine on Au(111)

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We have studied the first stages leading to the formation of self-assembled monolayers of S-cysteine molecules adsorbed on a Au(111) surface. Density functional theory (DFT) calculations for the adsorption of individual cysteine molecules on Au(111) at room temperature show low-energy barriers all over the 2D Au(111) unit cell. As a consequence, cysteine molecules diffuse freely on the Au(111) surface and they can be regarded as a 2D molecular gas. The balance between molecule–molecule and molecule–substrate interactions induces molecular condensation and evaporation from the morphological surface structures (steps, reconstruction edges, etc.) as revealed by scanning tunnelling microscopy (STM) images. These processes lead progressively to the formation of a number of stable arrangements, not previously reported, such as single-molecular rows, trimers, and 2D islands. The condensation of these structures is driven by the aggregation of new molecules, stabilized by the formation of electrostatic interactions between adjacent  $NH_3^+$  and  $COO^-$  groups, together with adsorption at a slightly more favorable quasi-top site of the herringbone Au reconstruction.

### 1. Introduction

Understanding the adsorption, bonding, and interaction of the simplest constituents of proteins (i.e., amino acids) on surfaces is a necessary step toward broad applications in the interdisciplinary emerging field of nanobiotechnology. For example, self-assembled monolayers of different amino acids on well-controlled surfaces provide convenient models for understanding chiral selection mechanisms in the formation of highly ordered molecular structures,<sup>1,2</sup> strategies to functionalize large molecularbased nanostructures for solid-state advanced biosensors,<sup>3,4</sup> and organic-inorganic platforms for new devices. The formation of highly ordered molecular self-assembled networks of amino acids on well-controlled metal surfaces has been previously studied.<sup>2,5</sup> These molecular layers have been structurally analyzed, and their chemical adsorption forms have been derived from these studies.<sup>6–8</sup> However, very little is known about the mechanisms underlining the formation of these layers. A description of these mechanisms at the atomic level is currently lacking and deserves special attention. It requires a complete understanding of the energy balance between substrate-molecule and moleculemolecule interactions, which are better addressed in the submonolayer coverage regime. Thus, the submonolayer deposition of amino acids, as cysteine, is an excellent framework in which to understand the self-assembly mechanisms leading to the

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formation of more highly ordered structures out of their constituents. This is particularly interesting for the Au(111)-( $22 \times \sqrt{3}$ ) herringbone reconstruction, which includes both hcp and fcc domain terminations with different adsorption energies.<sup>9</sup> It is known that the zwitterionic form is preferred for cysteine on different noble metal surfaces as Cu(110),<sup>7</sup> Au(111),<sup>10,12,13</sup> and Au(110).<sup>6,11,12</sup> However, the coexistence of other minor chemical adsorption forms (neutral, anionic, or cationic) has been reported for other surface terminations and coverages,<sup>6,10,12,13</sup> being that their presence is an unsolved puzzle.

Moreover, the study of submonolayer coverage makes it feasible to address the role of diffusion processes. Molecular diffusion mechanisms on surfaces are a key point in nanoscale engineering to control the assembly of molecular rotors<sup>14</sup> or other bio-objects. However, S–Au bonding is technologically relevant because it is an important reference to understanding the formation of different types of self-assembled monolayers (SAMs). Thus, different proteins, nucleic acids, or artificial peptides for technological applications are covalently bound to gold surfaces by sulfur atoms from cysteine moieties.<sup>4,15</sup>

We shall show that in the case of cysteine on Au(111) the substrate plays an important role in defining the diffusion directions, the molecular orientations, and, as a consequence, the

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#### Article

different metastable molecular arrangements that are developed. We demonstrate that the diffusion barriers of the molecule are very small and therefore fast directional molecular diffusion mechanisms are activated. These fast diffusion processes lead to the formation of new structures not previously reported, such as cysteine trimers, molecular rows, or ordered networks that evolve through time toward 2D self-assembled molecular structures. We use a combination of scanning tunnelling microscopy (STM) and density functional theory (DFT) calculations to support our interpretation of experimental data. This combination of theoretical calculations with experimental techniques allows us to describe an unreported diffusion process of these molecules on the surface, which is the basis of the understanding of the formation of self-assembled layers of amino acids on noble metal surfaces.

Moreover, the enhanced diffusion of cysteine on the Au(111) surface makes it behave as a 2D molecular gas.<sup>16</sup> Adsorption and desorption from the different topographic features can be analyzed by recording real-time sequences of STM images.

### 2. Experimental and Theoretical Methods

In-situ multitechnique experiments have been performed: X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), low-energy electron diffraction (LEED), and STM under ultrahigh vacuum conditions (base pressure of  $1 \times 10^{-10}$  mbar). The Au(111) crystal has been cleaned by cycles of Ar<sup>+</sup> ion sputtering, flashing, and annealing to ~700 K, and the surface structure and cleanliness were monitored by LEED and STM before and after adsorption experiments. Before sublimation, *S*-cysteine was outgassed and then heated to 373 K and exposed to the gold crystal. During sublimation, the main chamber pressure typically rose to 2 ×  $10^{-9}$  mbar. STM images were taken at room temperature using a commercial Omicron microscope combined with Dulcinea electronics from Nanotec Electronics.<sup>17</sup> Images were measured in constant-current mode (topographic mode) using a W tip with a typical bias voltage of -1.5 V (filled states of the sample) and tunnel currents of 0.3–0.4 nA. STM images were analyzed using WSxM software.<sup>17</sup>

Calculations have been performed using three complementary techniques: (i) a fast, order-*N* real-space approach,<sup>18</sup> (ii) a thorough quantum chemistry method based on a finite-cluster model and a localized basis,<sup>19</sup> and (iii) an accurate periodic supercell model based on an extended plane-wave basis.<sup>20</sup> The first method allows us to explore large models made of many atoms and get quick estimates for expensive calculations such as diffusion barriers of cysteine molecules adsorbed on the Au(111) surface. The second method captures the essence of the local chemistry. It is, however, based on finite clusters with a limited number of atoms and cannot model the metallic surface in its full complexity. Nonetheless, it has helped us to build approximate geometrical models that yield reasonable input for more accurate formalisms based on periodic systems and plane waves. Our order-*N* efficient DFT local density approach (LDA)<sup>21</sup> employs a basis formed by quasi-atomic orbitals that vanish



**Figure 1.** Energy landscape for a cysteine molecule on different sites of the Au(111) unit cell. Calculations have been performed by considering a cysteine molecule on a three-layer slab with  $4 \times 4$  periodicity. At each site, we show the best energy value obtained when the molecule has been rotated in several azimuthal orientations and in the *z* direction. (Inset) Schematic representation of cysteine S-CH<sub>2</sub>-CH-NH<sub>3</sub><sup>+</sup>-COO<sup>-</sup> (zwitterion) on the most favorable adsorption site on (4 × 4)-Au(111). Only one layer is shown for clarity.

beyond a cutoff radius<sup>18</sup> (the basis used here has been tested in previous publications).<sup>22–24</sup> We have considered different adsorption sites, molecular geometries, and orientations with respect to the Au(111) surface. The computational effort necessary to perform these calculations with enough accuracy is very large, in particular, if ab initio methods based on properly converged plane waves or a linear combination of atomic orbitals (LCAO) basis are used (e.g., our calculations with CASTEP<sup>20</sup> or Gaussian<sup>19</sup>). This computational effort limits the parameter space of configurations that can be explored. Therefore, we have used the Fireball<sup>18</sup> method to explore a larger portion of configurations with a good balance between the computational time consumed and the validity of the results. For the sake of internal consistency, we shall derive our conclusions from Fireball values only.

In our calculations, the supercell consists of a three-layer slab with fcc stacking and a  $4 \times 4$  periodicity parallel to the surface. Under these conditions, we can assume that molecule–molecule interactions are not important. We estimate the diffusion barriers by comparing the final energies after the system relaxation for different adsorbed sites and molecular orientations. In each case, the last Au layer and the (*x*, *y*) coordinates of the S in the molecule are fixed (constrained minimization).

## 3. Results and Discussion

We have confirmed by XPS spectra (data not shown) that at least 95% of the cysteine molecules adsorb on the Au(111) surface as zwitterionic species, in good agreement with previous work<sup>10,12,13</sup> and as also reported for Au(110).<sup>6,11,12</sup> Furthermore, XPS data corroborate that the thiol group is deprotonated after adsorption. This information has been input into our DFT calculations, where we have assumed adsorption of the chemical form Au(111)---S-CH<sub>2</sub>-CH-NH<sub>3</sub><sup>+</sup>-COO<sup>-</sup> (Figure 1 inset). This configuration has been calculated on different adsorption sites and with different orientations with respect to the Au(111) surface. As expected on chemical intuition grounds, our calculations for an isolated *S*-cysteine molecule on the Au(111) surface show that the

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bonding between the molecule and the surface takes place through the S atom. The optimized S-Au distance is about 0.255 nm, and the most favorable adsorption position is on a pseudotop site along the line joining the hollow-hcp and top sites (Figure 1 inset) in a configuration in which the oxygen atoms approach the surface up to 0.26 nm, whereas the N atom is slightly detached from it. The two oxygen atoms of the carboxylate group are close to the top position of the Au atoms, and the oxygen-gold interaction cannot be neglected. Therefore, the molecule acquires a quasi-planar conformation that resembles the one experimentally determined by Cossaro et al. on Au(110).<sup>6</sup> This double interaction of the molecule with the surface, through S and O, is a key point in determining the molecular azimuthal orientation. It has been reported by DFT that the preferential site for the S headgroup in the cys/Au(111) system is the bridge-fcc site.<sup>25,26</sup> Di Felice et al., using an accurate DFT formalism based on pseudopotentials and plane waves, found an S-Au distance of 0.251 nm, in good agreement with our calculations.<sup>25</sup> Using a similar approach (CASTEP), we reproduce the key results presented in that work. However, in this work we are interested in models including many atoms in order to explain dimers or even trimers of molecules; therefore, we want to explore a large number of configurations. Thus, we have favored the use of a faster, even if possibly less accurate. DFT method that allows us to consider an order of magnitude more configurations than using plane waves. Results from Fireball have been critically compared with values deduced from either CASTEP<sup>25</sup> or Gaussian,<sup>26</sup> but to maintain internal consistency, our conclusions are exclusively based on calculations obtained with Fireball. Although the ordering of the two sites studied by Di Felice et al. (bridge and hollow fcc) is reproduced by our calculations, we find a different optimum geometry located between the hollow hcp and the top sites and a different orientation for the molecule that lies more planar than previously reported. This last effect agrees well with previous experimental work,<sup>6</sup> with our STM images, and with the single core-level O 1s component distinguished by XPS spectra. Moreover, whereas the particular values for adsorption energies might be affected by our use of the LDA approximation, the ordering of the different configurations is not prone to depend on these calculation details.

By constrained optimization on different symmetry positions in the unit cell, we have determined an upper value for the diffusion barrier of a single molecule. The result is shown in Figure 1 together with the relative positions in the unit cell. The Figure shows that the pseudotop site is the preferred one with adsorption energy slightly lower than that of the others, particularly that of the previous best candidate, the hollow-fcc site. However, the energy difference between all sites in the unit cell is small, and the molecule is expected to diffuse quickly at room temperature following a path that goes from hollow hcp to hollow fcc through the top site with activation energy barriers of about 100 meV. We notice that diffusion barriers along the [110] surface direction are even smaller (lower than 60 meV). These calculated values are accurate to within 20%. The anisotropy in the energy barrier height induces a fast diffusion channel along this crystallographic direction at room temperature. Along the [112] direction, higher barriers will make the molecules reside longer on the hollow-top region of the unit cell, slowing their diffusion.

We should comment that the low values found for the diffusion of a single molecule do not necessarily imply a weak interaction between the deprotonated mercapto group and the gold atoms. Plane-wave calculations in  $p(4 \times 4)$  (3 layers, 48 Au atoms in the supercell) show that a molecule sitting near the top site (Figure 1) makes the Au atom underneath move outward by about 0.14 Å because of the interaction with the S atom. Besides, the nearest gold neighbor, located directly below the carboxylate group, relaxes inward by about the same distance. We have not tried to separate the different contributions to the total energy, but it is reasonable to assume that these elastic deformations on the gold substrate for configurations that favor the chemical interaction between S and Au carry energy penalties that tend to smooth the diffusion barriers. However, the diffusion of such a complex molecule is influenced by other interactions, in particular, oxygen-gold. The surprising low values for diffusion barriers are therefore related to an energy balance where some energy is paid to weaken S-Au interactions whereas energy is gained elsewhere by improving conditions for other interactions. Whereas these low diffusion barriers agree well with our qualitative STM observations, a word of caution is in order because they have been obtained within the LDA approximation, which is known to be prone to underestimate diffusion barriers. However, GGA-like calculations are believed to overestimate these values, and indeed our own calculations using this approximation result in larger values. Finally, we remark that to obtain proper values for barriers it would be necessary to obtain the Hessian matrix to locate a transition state, a computational task that is too expensive for the present problem.

Nonetheless, the average values for the diffusion barriers suggest that the cysteine molecules diffuse extremely fast at room temperature throughout the Au surface. Indeed, assuming typical vibrations in the THz range, a barrier of around 0.1-0.2 eV results in random hops of the molecule on the order of a few nanoseconds. We remark, however, that even for such a fast diffusing molecule the anisotropy in the barriers plays a significant role at room temperature (e.g., a relative difference of 50 meV between two diffusing directions would make the most favorable one 7 times more likely than the other one). We will show next that many structural properties of the submonolayer coverage arrangements are related to these results.

STM images recorded right after depositing a submonolayer coverage of S-cysteine molecules do not show any morphological features on the surface related to the molecules. We exclusively observe spikes on the substrate terraces that correspond to molecules diffusing faster than the scan speed. A spike appears in the STM current every time a molecule moves underneath the STM tip. These fast-diffusing molecules could be imaged, however, at the step edges because the larger coordination produces a longer permanence time. We have to wait a few hours after dosing the molecule in order to obtain STM images exhibiting molecular features. Interestingly, if we acquire successive images on the same area, video movies showing the time evolution of the different structures can be recorded. (A video movie showing cysteine diffusion is available in Supporting Information). Images in Figures 2 and 3 are snapshots extracted from these videos and correspond to a general overview of the Au(111) surface after the adsorption of about 0.4 ML of S-cysteine at ~20 °C. Many different molecular arrangements and disordered and ordered molecular structures are seen on the surface.<sup>5</sup> The images shown in Figure 2 are spaced by about 8 h, and those in Figure 3, by 30 min. In the central part of the images of Figure 2, anchored to the step edges, an area lacking any order can be distinguished. The height of the features (about 0.2 nm) suggests that they are in the lower part of the steps. The shape and size of these areas evolve with time. Indeed, we can consider these diffusing molecules throughout the surface as a 2D molecular gas in which the

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Figure 2. Series of STM images extracted from a video (image size 116 nm  $\times$  116 nm). In the blue square, one of the diffusing cysteine molecules at the elbows of the Au(111) reconstruction is marked, and in the two green circles, the formation of trimer molecular structures can be distinguished.



Figure 3. Series of STM images (image size  $66 \text{ nm} \times 66 \text{ nm}$ ) extracted from a video showing the formation of stable, extended 2D islands formed by cysteine wires after a long diffusing time.

surface plays the role of a solid support providing a reduced dimensionality to the system.<sup>16</sup> In Figures 2 and 3, it is shown how the molecules "evaporate" and "condense" progressively on the different morphological structures (reconstruction corners and step edges). Interestingly, these morphological defects are not the final nucleation points but just structures with a larger dwelling time where evaporation and condensation rates are similar. The nucleation points are on the terraces, where after some time the molecules meet each other, making groups of steady structures stabilized by H bonds or electrostatic interactions. These are the true nucleation sites where the molecules from the 2D gas condense. We see in the STM movies that after a few hours the molecules imaged at the step edges disappear in favor of the ordered structures. We have identified three stable types of morphological molecular assemblies that increase with time. Molecular wires and islands enlarge their length whereas trimers increase their number. In all of these cases, the sulfur atom and the oxygen atoms of the carboxylate group from the cysteine interact with the Au surface.

Among all of the stable structures that we have identified, we describe first ordered single molecular rows that can be observed between the channels of the characteristic Au(111)-(22× $\sqrt{3}$ ) herringbone reconstruction, as shown in Figure 4. We observe preferential binding of the molecules on the fcc domains of the Au(111) surface reconstruction.<sup>9</sup> The wires are formed along the [110] surface direction. This can be understood from our DFT calculations, as illustrated in Figure 5. The [110] direction is the faster diffusing molecular channel; therefore, the molecules are likely to meet each other preferentially along this direction. The blue arrow in Figure 5 indicates this direction. During the diffusion, they reside longer in the region between hollow-hcp and top sites. When a diffusing molecule meets another, they establish electrostatic interactions between the carboxylate group of a molecule (negatively charged) and the amino group of the other (positively charged). We estimate the distance between these chemical groups to be 0.28 nm, which is in good agreement with



**Figure 4.** STM images of cysteine molecules on Au(111)-reconstructed surface for submonolayer coverage, showing on the left side cysteine single-molecule wires. Preferential adsorption at fcc domains (indicated by a dashed arrow) of the Au reconstruction is clearly observed ( $35 \text{ nm} \times 22 \text{ nm}$ , upper-left panel,  $71 \text{ nm} \times 36 \text{ nm}$ , lower-left panel). On the right side ( $35 \text{ nm} \times 27 \text{ nm}$ , upper-right panel), cysteine 2D islands with intermolecular resolution are shown.

the reported value 0.25-0.29 nm for the NH···O hydrogen bond (donor-aceptor).<sup>27,28</sup> In some STM images of the molecular wires, internal structure is shown (not shown for conciseness). The molecule-molecule distance is about 0.6 nm, in agreement with the theoretically derived value of 0.58 nm. Figure 5 shows the optimized DFT structure of this configuration in which hydrogen bonds and electrostatic forces between carboxylate and amino groups stabilize the structure. We have circled on the Figure

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**Figure 5.** (Upper) Schematic model of the cysteine adsorption DFT. The arrow indicates the diffusion direction, and the circle indicates the interaction established to form the molecular wires along the [110] direction. (Lower) STM image (image size  $26 \text{ nm} \times 21 \text{ nm}$ ) showing a step edge and in the lower terrace single-molecule cysteine wires running along this [110] direction with preferential adsorption at the fcc part of the reconstruction.

the interaction between adjacent molecules. Furthermore, this configuration presents another interesting point: the O atoms of the carboxylate groups stay near the top position with respect to the Au surface, which helps further to stabilize the structure. Therefore, molecules diffusing along [110] directions bind to each other and stay on this favorable site. These clusters are seeds for additional molecules to be aggregated. The wire grows in the [110] direction, as has been suggested by our calculations and is now corroborated experimentally. This is schematically represented in Figure 5. Thus, we can conclude that the mechanism of formation of these wires is aggregation by diffusion.

Remarkably, on the Au(110) face the formation of paired rows of cysteine molecules through O-H···O bonding has being observed.<sup>29</sup> The authors also described a mechanism of fast diffusion and the formation of different dimers oriented along crystallographic directions. Unlike the results on the (110) face, in our case the NH···O bond is preferred because of the role played by the substrate. On the (111) face, the molecule has an optimum size to coordinate with the Au substrate atoms with both the sulfur and the carboxylate group; correspondingly, one of the oxygen atoms can establish interactions with the NH group of an adjacent molecule (Figure 5). In any case, we have calculated the formation of a dimer stabilized by two  $OH \cdots O$  bridges. In the dimer, the molecules share two  $OH \cdots O$  bonds whereas in the trimer NH $\cdots$ O interactions are involved. Unlike the (110) face and similar to our previous discussion of the rows, the three-fold symmetry of the substrate induces trimer instead of dimer formation. Our calculations indicate that no stable bridging structures can be formed. Therefore, we conclude that on the Au(111) face the interaction with the surface induces the formation of single molecular rows instead of the dimers reported for the (110) face.

The morphology and length of these wires are small, and they appear to be broken in a zigzag conformation (Figure 4). We have experimentally verified that these wires do not traverse toward the hcp domain of the herringbone reconstruction but they remain in the fcc part of the reconstruction.<sup>9</sup> Indeed, the molecular wires

increase their length by aggregation, as discussed above, until they approach the change in atomic registry at the border of the domain. Here, the molecule modifies its adsorption site by shifting about two atomic rows toward the fcc side of the reconstruction. This rectification mechanism confers to the molecular rows the zigzag appearance observed by STM (Figure 4). Thus, cysteineassembled unimolecular wires slightly reorientate their position to accommodate the main chain direction along the [112] surface direction. This reorientation is made possible by the low diffusion barriers depicted in Figure 1. The meandering conformation of the wires is therefore related to the delicate balance between the molecule-substrate interaction, which favors adsorption on the fcc sites of the reconstruction, and the molecule-molecule interaction that favors molecular row packing along the [110] surface direction, establishing H-bonding networks between adjacent molecules. Molecular preferential adsorption on fcc domains has been reported for many different molecular systems (as  $C_{60}$ or PCBM molecular layers). The reason for this preferential nucleation may be both steric (the fcc areas are wider than the hcp ones) and/or electronic (the charge density of the surface-state electrons is different in fcc/hcp regions and in the dislocation lines of the reconstruction). $^{30-36}$ 

We also observe islands of molecules (i.e., a 2D-ordered molecular structure) appearing on the surface after a certain time. They can be seen in Figure 4 (right side). They are formed by molecular parallel rows in which we observe intermolecular resolution. They are separated by 1.25 nm (0.6 nm between adjacent molecules, the same as for the molecular wires) and run along the [110] direction. Here we report for the first time the formation of this particular ordered structure. Previously, the existence of ordered phases of cysteine molecules exhibiting a 4-fold symmetry configuration was reported.<sup>5</sup> Indeed, we have found this surface crystallographic phase for slightly higher substrate temperatures (35-40 °C). Our 2D islands, however, are the final condensed form of the 2D molecular gas. As shown in the series of consecutive images in Figure 3, 2D islands are the sole structures to increase their size with time, becoming the most stable structure 24 h after deposition.

Finally, of particular interest are the features imaged at the reconstruction elbows. We can distinguish two types of features: blurred and defined. The fuzzy features consist of spikes along the scanning direction and are imaged on top of the reconstruction elbows. They could correspond to diffusing molecules of the 2D molecular gas that are observed in the STM images because of a longer dwelling time on this favorable position of the surface.<sup>14,27</sup> Some of them can be observed in the area marked with a square in Figure 2. Moreover, we also observe groups of well-defined molecular features with triangular shapes (marked with circles). The detail of these structures is shown in Figure 6. We observe three molecular features imaged between the elbows of the Au herringbone reconstruction and inside the fcc side of the surface reconstruction. The separation between bumps is about 1.7 nm, and they have a triangular shape with a depression in the middle. They are always imaged with the same orientation with respect to

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**Figure 6.** Detail of the trimer structures and DFT-calculated configurations. The structural position over the STM image (image size  $16 \text{ nm} \times 7 \text{ nm}$ ) is only a guide.

the surface, and their number increases with time as shown in Figure 2 (circled features). They also correspond to stable structures. Their formation must be related to a longer dwelling time when approaching the reconstruction corner, which could promote H-bond interactions, leading to the stabilization of these structures.

However, the size and separation between bumps is too large to be formed by a single molecule; therefore, they have to be constituted of molecular aggregation. Indeed, in some images they also seem to be formed by three other bumps. As shown in Figure 6, we propose a tentative model based on distances derived from our STM images and the likely interactions to be found on such large objects as the trimers. The terminating strong polar carboxylate group interacts with the  $NH_3^+$  groups to stabilize three cysteine molecules. Thus, each of the three bumps observed corresponds to three molecules, as can be inferred from the balland-stick model superimposed on the STM image of a trimer structure. The hydrogen bond distance in these structures is 0.28 nm, similar to the one found in the molecular rows. In our simulations, these structures cannot be formed by just a pair of cysteine molecules because we have observed the formation of H bonds where hydrogen is almost resonating between two molecules.<sup>30</sup> In the dimer, the molecule shares two  $OH \cdots O$  hydrogen bonds whereas in the trimer three  $NH \cdots O$  bonds are involved. Unlike the (110) face, the 3-fold symmetry of the substrate induces trimer instead of dimer formation, as we have discussed above.

It is important to remark that the distance between molecular trimers is 1.7 nm. This distance is far too large to promote the formation of S-S dimers connecting them. These molecular trimers separate from each other and cluster in a trimeric structure, occupying the whole length of the fcc domain of the Au reconstruction. Thus, the interaction stabilizing the large trimeric structure is driven by long-range van der Waals forces combined with a chemical interaction with the substrate. At present, we do not have a satisfactory explanation for the assembly in three molecular groups. Similar molecular structures formed by related mechanisms have recently been reported to lead to arrays of single-molecule rotors on the Au surface.<sup>14</sup>

### 4. Conclusions

Fast-diffusing cysteine molecules on the Au surface can be regarded as a 2D molecular gas. Continued molecular condensation and evaporation from the morphological surface defects, as reconstruction kinks or steps edges, lead progressively to the formation of stable arrangements such as unimolecular rows, trimers, and 2D islands where the molecules condense in stable structures. The condensation process is driven by the formation of stable NH···O electrostatic interactions between adjacent molecules together with both adsorption of the sulfur atom in the slightly more favorable pseudotop site of the Au reconstruction and one of the oxygen atoms of the carboxylate group sitting near another top site.

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**Supporting Information Available:** Video showing cysteine diffusion. This material is available free of charge via the Internet at http://pubs.acs.org.