

Self assembling of (S)-Glutamic Acid on Ag(100): a combined LT- STM and ab initio investigation.

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Amino acids adsorption at metal and oxide surfaces is a model system for chemisorption of biofunctional molecules. To date most investigations concentrated on the simplest species (cysteine, glycine, alanine, lysine, aspartic acid) on Cu [1], but also on Ni [2], Ag [3] and non-metallic substrates. In general, these systems form ordered adlayers with chemisorbed molecules in the anionic ($\text{H}_2\text{N.CR'R''}. \text{COO}^-$) or in the zwitterionic ($\text{NH}_3^+.\text{RCH.COO}^-$) form. On roughened Ag surfaces at $T=300$ K [4] amino acids adsorption as zwitterions was suggested. In contrast, (S)-glutamic acid (GA) [3] is found to bind on Ag(110) mainly in the anionic form. Due to the weak molecule-metal interaction, it organises in extended islands with geometry depending on evaporation parameters.

We extended the investigation to GA ($\text{C}_5\text{H}_9\text{NO}_4$) adsorption on Ag(100) using a combined low temperature STM and periodic ab initio molecular dynamics (MD) approach followed by complete geometry optimisation. Experimentally we found that GA molecules self-assemble in ordered structures depending on the preparation conditions: high density, extended monolayer islands are observed for exposures at $250 \text{ K} < T < 325 \text{ K}$ while less dense islands with two different geometries form at $325 \text{ K} < T < 360 \text{ K}$. The former structures are unstable for bias voltages $V > 500 \text{ mV}$ while the latter ones show a dependence on bias for $V > 1.2 \text{ V}$, suggesting a strong modulation of the density of states.

We employed the calculation facility at GENCI to simulate one of the observed self-assembled structures, namely, the squared structure forming at 350 K (see Fig. 1).

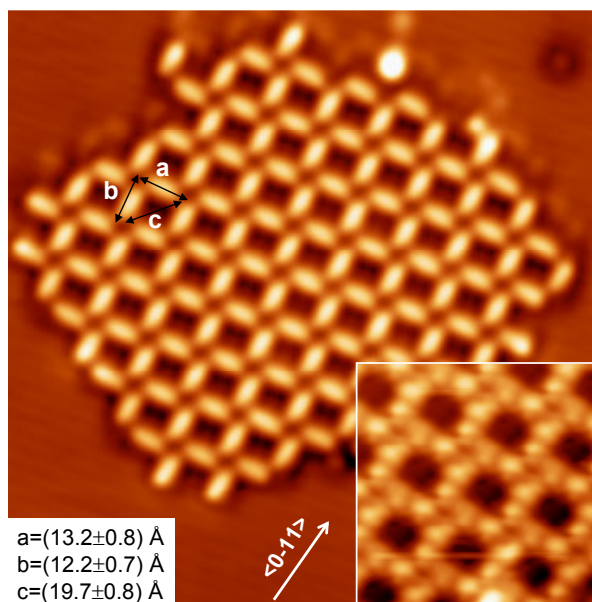


Fig. 1: STM image of a (S)-GA island produced upon GA evaporation on Ag(100) at $T=350$ K. Characteristic dimensions are reported on the figure. Image size $157 \text{ \AA} \times 157 \text{ \AA}$, $V=0.10 \text{ V}$, $I=3.3 \cdot 10^{-10} \text{ A}$. Inset: High resolution image of a portion of the same layer, showing the submolecular units of GA molecules. Image size $50 \text{ \AA} \times 50 \text{ \AA}$, $V=0.10 \text{ V}$, $I=3.3 \cdot 10^{-10} \text{ A}$.

To reproduce the pattern deduced from STM images we chose an Ag unit cell of 68 atoms distributed on 4 layers, the upper two of which were let free to relax. Two GA molecules were placed in the unit cell, parallel to the Ag surface and at 90° with respect to each other. We performed a systematic search on the possible GA adsorbed conformers (neutral molecule (N), zwitterion (Z), radical (R) and biradical (Bi)) and on the mixture of two of them at the silver surface (N-N, Z-Z, R-R, N-Z, N-R and Z-R). In addition, different orientations of the NH_2 end of the GA molecules with respect to each other were investigated.

The configurations which consider H abstraction, leading to a carboxylate moiety, systematically resulted in a strong interaction of the carboxylate with the Ag surface, with extraction of a Ag atom from the surface and important disordering of the Ag surface. In this case, the calculated energies of reaction are positive (values between 0.3 and 1.8 eV, depending on the configurations), indicating endothermic processes. This trend was confirmed by the very high energy value, again indicative of an endothermic process, calculated for the Bi-Bi radical adsorption (5.79 eV). Therefore, we deduced from these results that GA adsorbs in the intact form on the surface, i.e. without H abstraction. For the conformations considering Z-Z and N-Z combinations we observed that the Z moiety is spontaneously neutralized during the optimization, so finally we retained only the exothermic N-N configurations and we considered only the neutral form of GA in those configurations suitable to reproduce the experimental pattern. The most stable structure found is shown in Fig. 2: a square structure is achieved by the GA molecules which form no chemical bond with the silver surface (Fig. 2b). Furthermore a H-bond cycle is seen at the square formed by four GA molecules (Fig. 2c), with two short H—O distances of ~ 1.85 Å and two longer ones of ~ 2.3 Å. This structure, which maximizes the H-bond network at the cross section between individual GA molecules, is also the most stable of all investigated configurations (including radical, zwitterions and N conformations). The calculated total adsorption energy, including dispersion forces, is $\Delta E_{\text{ads}} = -0.86$ eV, of which -0.30 eV is the cohesion energy among GA molecules. The value of ΔE_{ads} represents a weak energy of interaction, which is typical of a physisorption. This allows on the one hand the GA layer to form, on the other hand the structure of the GA layer to be unperturbed by the Ag substrate. It is noticeable that this situation allows self-assembling of neutral amino-acids, a situation which is not found in “real life”.

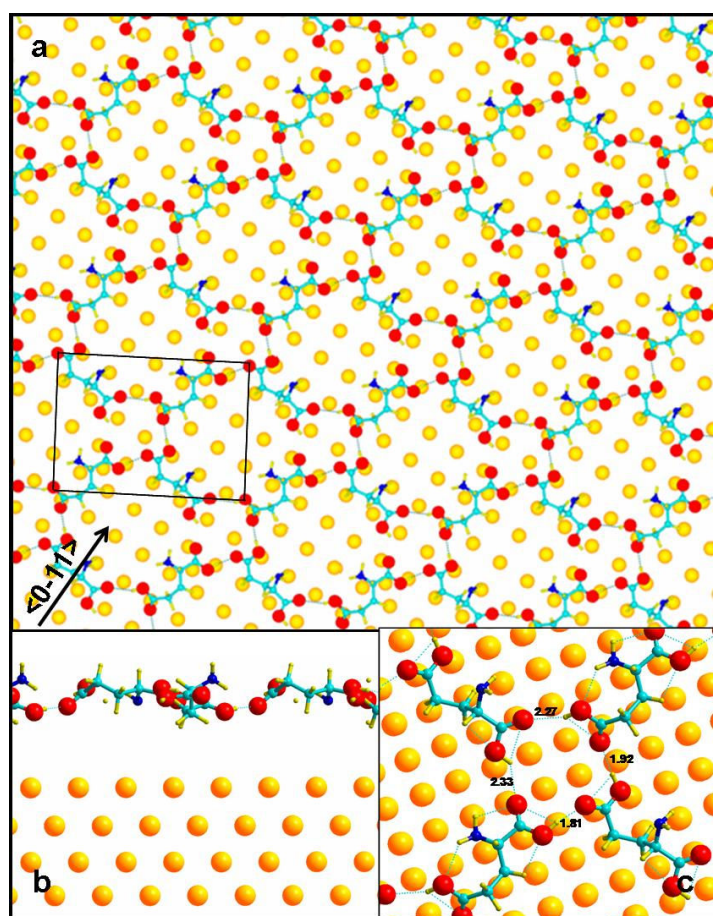


Fig. 2: Optimised configuration for the squared GA structure.

a) Top view; b) Side view; c) Enlargement showing the OH ring at the vertex of the squares.

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