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Temperature dependent stability of self-assembled molecular rows

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Monte Carlo simulations on the basis of first-principles total-energy calculations are used to rationalize the formation of well-separated (∼11 Å) molecular rows of phenylglycine upon co-adsorption of adenine and phenylglycine on Cu(110) [Chen and Richardson, Nature Materials 2, 324 (2003)]. Adsorption-induced Friedel oscillations of the substrate charge density give rise a lateral modulation of the adsorption energy sufficiently large to explain the experimental observation of well separated molecular rows at room temperature.

The engineering of highly organized systems from molecular building blocks opens up new avenues for realizing and exploring nanodevice concepts. Well-defined surfaces – in particular metal substrates – provide versatile platforms for the self-assembly of supramolecular structures, see, e.g. Ref. [1]. For the handling of complex molecules on metals, we need to understand adsorption, mobility, and lateral interaction in their dependence on the substrate and possibly co-adsorbed species. First-principles calculations have proven extremely valuable in rationalizing and predicting the adsorption behaviour of single [2–4] as well as directly interacting surface adsorbed molecules [5,6]. In addition to direct interactions, such as, e.g., H bonds between molecular functional groups, however, indirect substrate-mediated interactions may occur. Although typically smaller than 0.1 eV, they often decisively influence molecular self-assembly [1]. Scanning tunneling microscopy (STM) studies on adenine and phenylglycine adsorbed on Cu(110) [7] revealed a fascinating example of indirect, substrate mediated molecular recognition.

Chen and Richardson [7] observed that adenine deposited on Cu(110) at room temperature forms ordered one-dimensional molecular dimer chains that grow along the lateral [±1,2] directions (given with respect to the [$\bar{1}$10] and [001] Cu crystal orientations, see Fig. 1). Co-adsorbed phenylglycine forms double rows that run parallel to the adenine dimer chains. The microscopic interpretation of

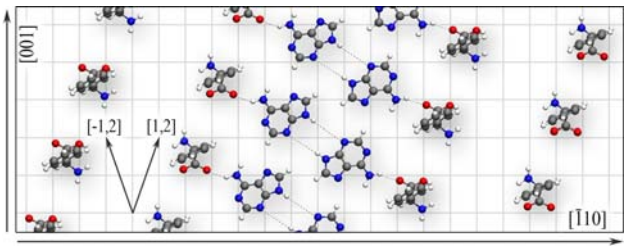

Figure 1 (color online) Molecular model derived in Ref. [7] for phenylglycine co-adsorbed with adenine forming dimer rows along the [1,2] direction on Cu(110). Hydrogen bonds are indicated with dashed lines.

the [1,2] oriented chain structure is shown in Fig. 1. The interaction between the adenine dimer row and the neighboring first phenylglycine row is characterized by hydrogen bonds, substrate locking and Coulomb repulsion [8]. The adsorption of the second row of phenylglycine molecules occurs, depending on the interpetation of the STM images [7], separated from the first row by at least 8 but not more than 12.8 Å(refering to the molecular centres). Density functional theory (DFT) total-energy calculations rationalized the formation of the second molecular row by charge-density oscillation-induced lateral variations of the adsorption energy [9]. The electronic origin of the indirect interaction in this case was confirmed by (i) tight-binding model calculations to the bond strength modification due to

the adsorbate induced charge density fluctuations (Friedel oscillations) and (ii) calculations with and without structural relaxations that allow for quantifying the influence of long-range strain fields. However, the modulation of the calculated adsorption energy is rather small, less than 0.1 eV, and therefore it is not clear if it is indeed sufficient to explain the formation of molecular rows at room temperature. It is the focus of the present work to explore the temperature influence on the molecular row formation with the help of Metropolis Monte Carlo simulations based on the total-energy data obtained from DFT calculations [9].

The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [10] and the PW91 functional [11]. Numerical details are given in Refs. [6,9]. Based on the potential energy surface (PES) obtained from first-principles for the adsorption of phenylglycine molecules in the presence of pre-adsorbed phenylglycine bonded to adenine, cf. Fig. 2, Monte Carlo (MC) Simulations [12] were performed using the Metropolis algorithm and the MersenneTwister [13] random-number generator. At each iteration, the second phenylglycine molecule may randomly walk to any neighboring surface position directly, cf. Fig. 3. If the adsorption energy is lower than in the previous state, the position will be accepted directly. Otherwise, it will be accepted only provided a random number between zero and one is smaller than the Boltzmann distribution function $\exp(-\frac{\Delta E}{k_B T})$. Here k_B denotes the Boltzmann constant, T the temperature, and ΔE the adsorption energy difference resulting from the corrugation of the PES. Here not only the minimum energy data obtained within the surface unit cell, i.e., the data shown in Fig. 2 enter, but also the fine structure of the PES shown in Fig. 4. The latter is decisive for the anisotropy of the diffusion, because it determines the translational barrieres. $2 \cdot 10^7$ steps were found to be sufficient to equilibrate the system. The MC simulations were performed using DFT data obtained for ideal substrates as well as using data sets were structural relaxation was allowed for. This enables us to determine the influence of long-range strain fields vs. long-range electronic effects on the molecular row formation.

The result of the MC simulations is shown in Fig. 5. Here we plot the equilibrium occupation of lattice sites according to the notation of Fig. 3 for temperatures ranging from 270 to 380 K. At room temperature the by far most likely position of the co-adsorbed phenylglycine is six to seven surface unit cells away from the pre-adsorbed phenylglycine row, in agreement with the experimental findings. This holds both for simulations based on a fully relaxed substrate and and for the surface where the relaxations are suppressed (ideal surface). The molecular rows get destabilized for temperatures higher than about 310 K. If the structural relaxation of the substrate is neglected, the amino acids get partially trapped in a hydrogen-bonded configuration (position 3 in Fig. 3). A mixture of bonding sites is predicted for full substrate relaxation.

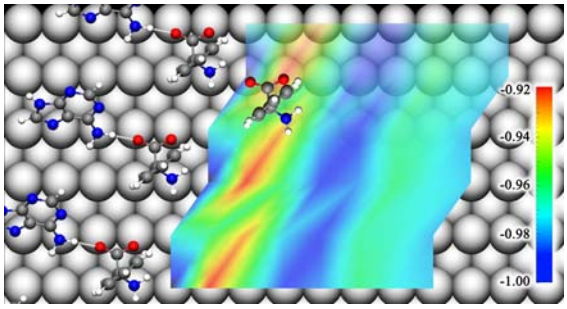

Figure 2 (color online) Calculated adsorption energies (in eV, in minimum energy position with respect to the Cu surface (1×1) unit cell, from Ref. [9]) of the 2nd row phenylglycine molecules for parallel molecular orientation without relaxation.

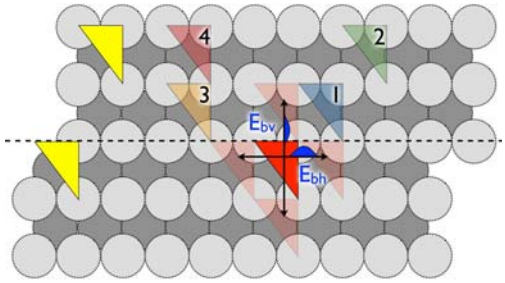

Figure 3 (color online) Illustration of the random walker phenylglycine molecule in the MC simulation. The most often occupied positions (1-4) are indicated. The two left-most triangles represent the pre-adsorbed phenylglycine molecules that are fixed during the simulations.

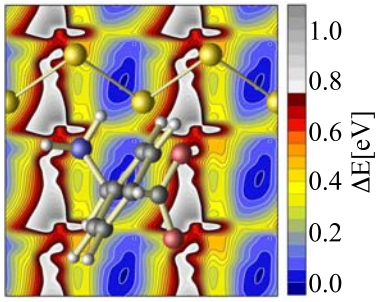

Figure 4 (color online) Potential-energy surface seen by phenyglycine in bonding position above Cu(110). The legend shows the energy difference with respect to the minimum. The positions of the uppermost copper atoms are indicated in the upper part of the figure. Data from Ref. [6].

While the calculations are in agreement with the available measurements [7] and demonstrate that energy differences as small as $\sim$ 100 meV [8,9] may indeed decisively determine adsorption phenomena even at room temperature, a word of caution is in order. The MC simulations presented here suffer from several shortcomings. On the

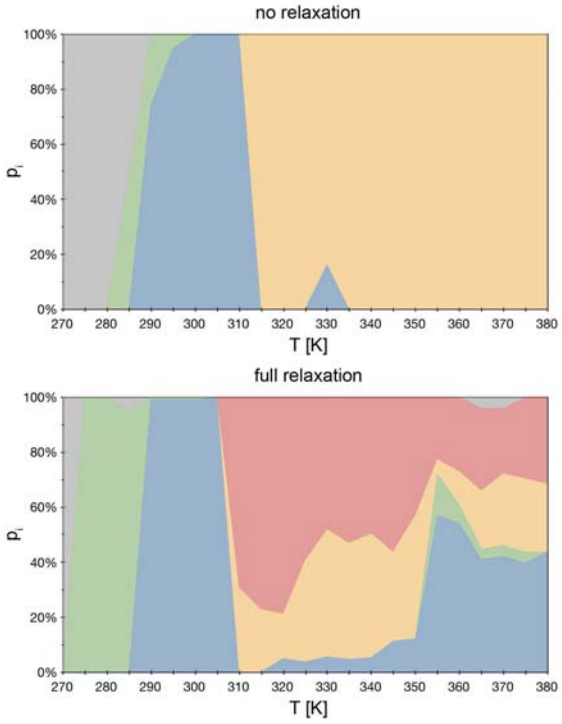

Figure 5 (color online) Temperature-dependent distribution of the adsorption positions (cf. Fig. 3) for the case of frozen and fully relaxed substrates as obtained from the MC simulations at various temperatures.

one hand, the random walker (phenylglycine molecule) in the simulations does not represent a single molecule but an infinite molecular row. This is related to the numerical expense of DFT calculations for large surface unit cells that prevented us from obtaining more realistic PES data. On the other hand, the lateral and rotational degrees of freedom of the adenine and first phenylglycine molecule are totally neglected.

In summary, we performed Metropolis Monte Carlo Simulation based on DFT data in order to reveal the temperature influence on the self-assembling process. The simulations show that the experimental results can be reproduced for room temperature. The present work underlines the importance of long-range Friedel oscillation-related indirect interactions for the understanding of molecular self-assembly processes on metal substrates.

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