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COMMUNICATION

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Atoms or molecules adsorbed on crystalline substrates often form regular patterns in a well-defined epitaxial relationship with the substrate surface. Such superstructures are the result of the intricate interplay between adsorbate-substrate and adsorbate-adsorbate interactions.¹ A strong lateral corrugation of the substrate-adsorbate potential often results in commensurate structures, where the adsorbates are located on identical, energetically preferred adsorption sites in complete registry with the substrate. On the other hand, the lateral interactions between neighbouring adsorbates tend to favour structures in which the mutual distance between the adsorbates is close to their natural one, which is generally incommensurate with the substrate lattice. Besides the fundamental commensurate (C) and fully incommensurate (IC) structures more complex structural coincidences such as domain wall phases, rotational epitaxy and moiré structures can occur, depending on the relative size of the competing interactions and the natural lattice misfit.^{2,3} The relative stability of these different phases also depends on external

parameters like the surface coverage and temperature, which can give rise to complex phase diagrams with a variety of solid phases with different superstructures.^{4,5} The simplest case is that of a (quasi) one-dimensional (1D) arrangement of atoms or molecules with natural spacing b on a corrugated surface with periodicity a , corresponding to a nominal lattice mismatch $\delta = (b-a)/a$. Such systems can be treated analytically within the Frenkel-Kontorova model, which assumes a sinusoidal substrate corrugation potential $V(x) = V_0 \sin(2\pi x/a)$ and a harmonic coupling (with force constant k) between neighbouring adsorbates.⁶ The energetically stable solutions to this model depend on the three parameters δ , V_0 and k and include fundamental C, IC and domain wall phases as well as high-order commensurate (HOC) phases. The latter are characterized by a commensurate coincidence lattice, in which $m > 1$ adsorbates cover a commensurate distance $n \times a$ of the substrate lattice. HOC phases tend to minimize the average lattice mismatch of the coincidence unit cell, i.e., $m \times b \approx n \times a$. However, an $(m : n)$ HOC commensurate phase in which the m adsorbate particles are equally spaced within the $n \times a$ HOC unit cell is energetically not preferred against an incommensurate phase in the case of a purely sinusoidal substrate corrugation potential.² Instead, a HOC phase gains its stability by either (1) local lateral relaxations of the adsorbates within the HOC unit cell towards the nearest minima of the corrugation potential, (2) a finite domain size, where the adsorbates at the border are located in energetically preferred adsorption sites, or (3) a deviation of the corrugation potential from a simple sinusoidal shape.

In fact, quasi 1D structures can be realized experimentally using anisotropic substrates such as fcc(110) surfaces. For instance, a combined experimental and theoretical study has demonstrated the existence and the range of stability of various uniaxial $(m : n)$ HOC phases of Xe on Cu(110) as well as the transition between these HOC phases as a function of coverage and temperature.⁷ While there is plenty of evidence for HOC structures in simple atomic adsorbate systems, there are only few documented examples of (2D) HOC structures of inorganic or organic molecules.^{8,9,10} Yet the structures of molecular

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adsorption height varies by about 0.3 \AA with the lateral position x .

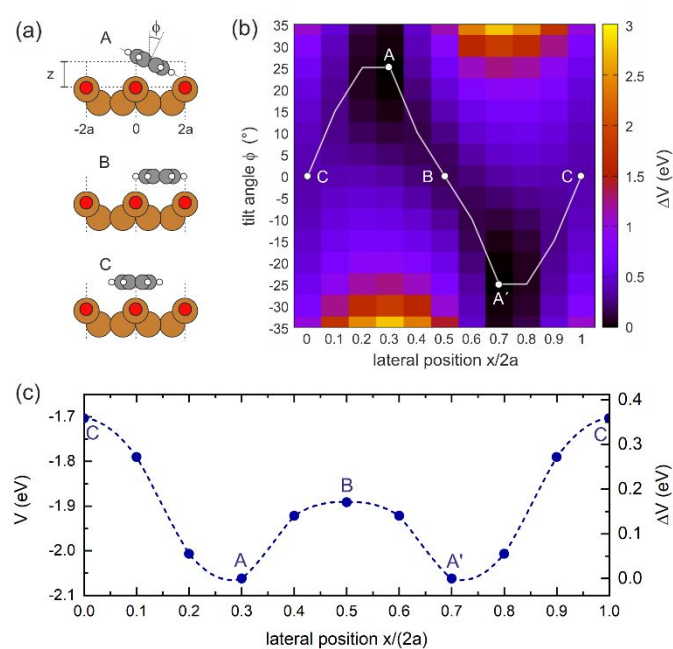


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Yet, according to the DFT results, the molecules are not bent or distorted, such that the azimuthal tilt angle ϕ is the only but central additional parameter that affects the minimum adsorption energy. For a direct comparison of the theoretical findings with the experimental data, STM images were simulated for the most prominent configurations of the DHTAP molecule on the Cu(110)-(2×1)O surface, namely the energetically most favourable site (A), where the molecule is in the tilted position, a molecule centred between two Cu-O rows (B) and the adsorption site right above a Cu-O row (C). Using the Tersoff-Hamann approximation,¹⁷ which assumes tunnelling from/into an atomic s-orbital at the tip, we have evaluated the local density of states in energy windows of $\pm 0.5 \text{ eV}$ with respect to the Fermi level. The results for negative energies (occupied states) are compared in Fig. 3 with the experimental STM images recorded for the same sample bias $V_s = 0.5 \text{ V}$. There is a good agreement of the apparent shapes of the measured (2, 1, 3) and the simulated STM images (B, A, C), respectively, whose nodal structure essentially resembles the shape of the highest occupied molecular orbital of DHTAP.¹² This allows an unequivocal identification of the adsorption sites and tilt of the molecules.⁵ In particular, the croissant-like shape of the species of type (1) in Fig. 1 can now be interpreted to arise from a significant tilt of the DHTAP molecule towards the nearest Cu-O row and the asymmetric bonding configuration of the molecules, rather than to an actual bending or deformation of the molecule. Moreover, the DFT calculations (Fig. 2) reveal that the molecules of type (1) and the mirror symmetric

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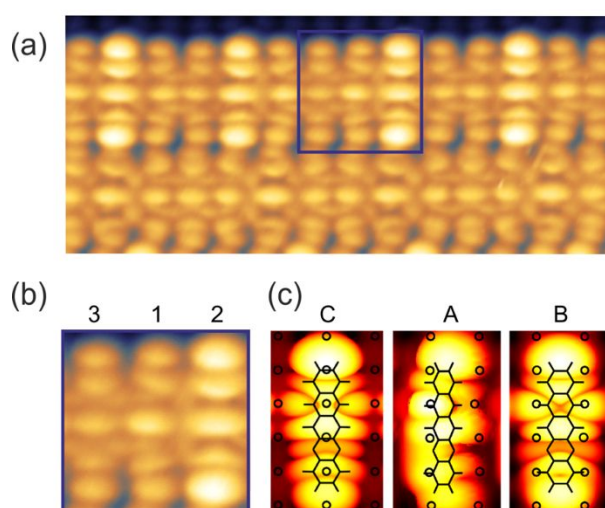


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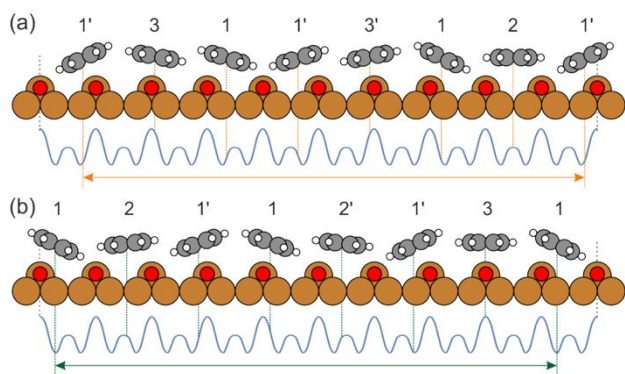


Fig. 4 Schematic of the energetically preferred arrangements of the DHTAP molecules in the (7:9) HOC phase, assuming a constant separation of the molecules and local configurations (ϕ , z) interpolated from the DFT results for individual DHTAP molecules. (a) $x_0 = 0$ and (b) $x_0 = a$ (see text).

This additional relaxation energy is counteracted by the loss of the intermolecular binding energy for larger displacements due to the stiffness (force constant k) of the molecule interaction potential. However, we expect that k could be rather weak since the molecules can compensate changes in the intermolecular spacing by adapting their azimuthal tilt angle. In fact, a similar stress release mechanism has been observed for the adsorption of para-sexiphenyl molecules on the Cu(110)-(2 \times 1)O surface, where the flexibility of tilting the molecules stabilizes a (simple) commensurate arrangement along the $[\bar{1}10]$ direction.¹⁸

We believe that our results are also relevant for other molecular adsorption systems. Indeed, HOC phases have been observed in previous studies.^{8,9,10} For instance, pentacene on Cu(110)-(2 \times 1)O forms a HOC-phase with an epitaxial matrix $\begin{pmatrix} 1 & 4 \\ -3 & 2 \end{pmatrix}$ (see Figs. 1(d) and (e) in Ref. 9) containing three molecules per unit cell. Although the structure is clearly “2D”, a closer inspection reveals that it is actually composed of staggered chains in which the molecules show an alternating image contrast. However, due to the lower quality of the STM image in Fig. 1(d) of Ref. 9, it is unclear to what extent the different adsorption sites and/or the molecular conformation (bending, tilt, ...) are responsible for the stabilization of this superstructure.

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We have shown that high-order commensurate (HOC) phases can be stabilized through internal degrees of freedoms - in the present case the azimuthal tilt of DHTAP molecules adsorbed on a Cu(110)-(2 \times 1)O surface. This stabilization can occur through a combination of several mechanisms: (i) different adsorption configurations of a molecular adsorbate can result in multiple energy minima within the substrate unit cell, thus leading to a strong deviation of the effective corrugation potential from a purely sinusoidal shape. (ii) The configurational flexibility can lead to a significant softening of the intermolecular binding potential and thus facilitate the local relaxation within the HOC unit cell. (iii) Finite domains gain energy if they are terminated by molecules in the energetically preferred adsorption configuration.

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Notes and references

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COMMUNICATION

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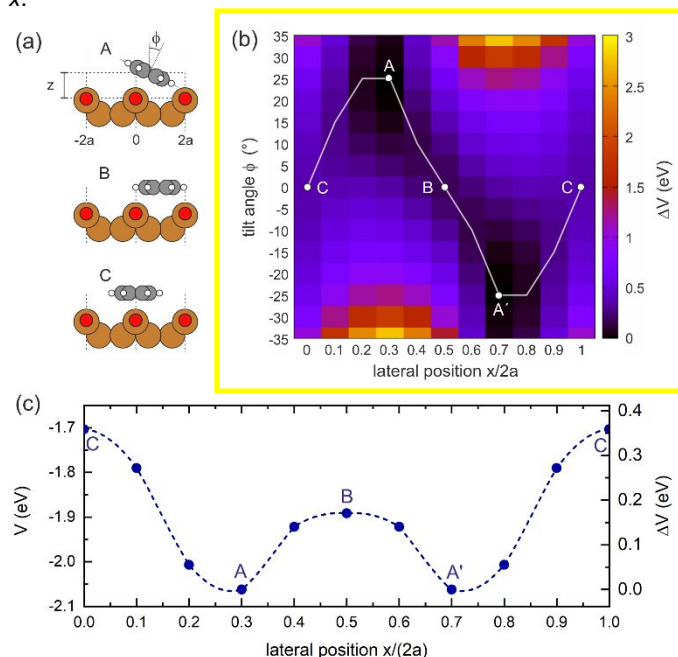


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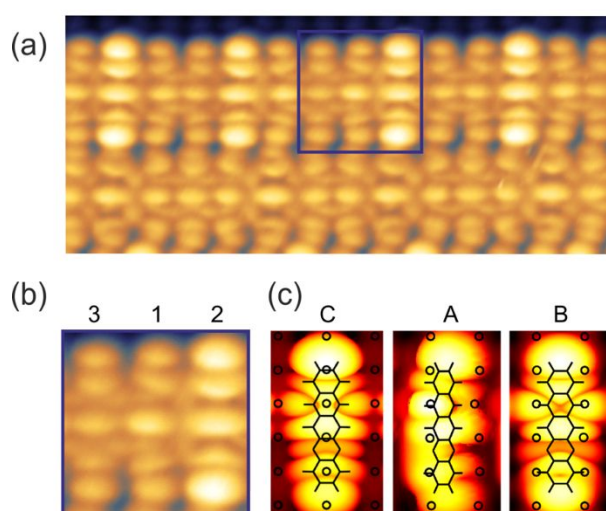


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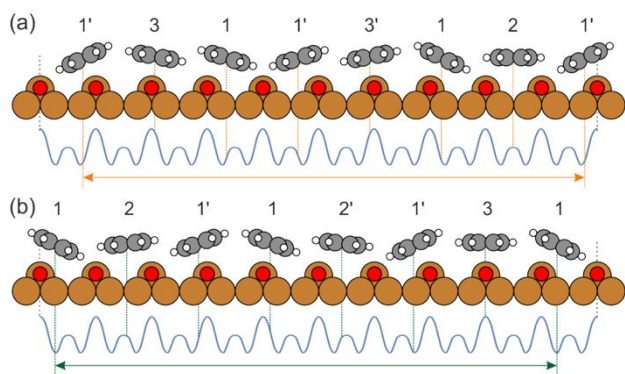


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‡ Here we define the monolayer as the dense packing of DHTAP molecules arranged into a (9 \times 9) coincidence lattice with 2 \times 7=14 molecules per unit cell, see Figure 2(b).

§ Note that the experimental STM images appear rather symmetric while the calculated ones show a clear difference between the NH and the N positions of the DHTAP molecule. This is because the STM calculations were performed for individual molecules. Indeed, DFT calculations for pairs of DHTAP molecules reveal that two parallel molecules arrange in a head-to-tail fashion, where the NH and N groups of neighbouring molecules form N - H-N bonds at both ends of the molecules, thus yielding a more symmetric electron density distribution.

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